Programme & Book of Abstracts

Aug 4-8, 2019 Xining, China

NSFC

CCS
中国化学会

CHINESE
CHEMICAL
SOCIETY

Aug. 4, 2019
Registration 8:30~21:00
Buffet

Aug. 5, 2019
Open Ceremony and Photography 8:30-9:00
🟥 **PL1: Glenn Hefter** 9:00-9:45
🟥 **KL1: Jianji Wang** 9:45-10:20
Coffee break (20 min)
🟥 **PL2: Buxing Han** 10:40-11:25
🟥 **KL2: M.C. Bellissent-Funel** 11:25-12:00

Aug. 6, 2019
🟥 **PL3: Yoshifumi Kimura** 8:30-9:15
🟥 **PL4: PÁL M. Sipos** 9:15-10:00

Aug. 7, 2019
🟥 **KL3: Susumu Okazaki** 8:30-9:05
🟥 **KL4: Paola D'Angelo** 9:05-9:40

Coffee break (20 min)

Aug. 6, 2019 🟥	Aug. 6, 2019 🟨	Aug. 6, 2019 🟩
K. Thomsen 10:20-10:45	**M.S. Gruszkiewicz** 10:20-10:45	**M. Corea** 10:20-10:45
T. L. Deng 10:45-11:10	**Z. B. Bao** 10:45-11:10	**J. L. Zhang** 10:45-11:10
X. L. Huang 11:10-11:30	W. Li 11:10-11:30	X.R. Huang 11:10-11:30
Y.J. Xu 11:30-:11:50	R. S. Alwi 11:30-:11:50	J. Mhalla 11:30-:11:50
X. M. Cui 11:50-12:10	X. Ge 11:50-12:10	Y.H Dong 11:50-12:10

Aug. 7, 2019 🟥	Aug. 7, 2019 🟨	Aug. 7, 2019 🟩
W. Waghorne 10:00-10:25	**I. Persson** 8:30-8:55	**Cory Pye** 10:00-10:25
J. T. Wu 10:25-10:50	**Z.W. Yu** 8:55-9:20	**Y.X. Yu** 10:25-10:50
B. Hu 10:50-11:10	K. Yoshida 10:50-11:10	T. Nagai 10:50-11:10
Q. Tian 11:10-11:30	L. Almásy 11:10-:11:30	W.Y. Su 11:10-11:30
L. Sun 11:30-11:50	W. J Cui 11:30-11:50	Y.L Zhao 11:30-11:50
K.Y. Zhao 11:50-12:10	P. Tan 11:50-12:10	F. Li 11:50-12:10

Aug. 8, 2019
🟥 **E. Okamura** 10:00-10:25
🟥 **L. Hong** 10:25-10:50
🟥 **T. Yamaguchi** 9:20-9:45
🟥 **M. V. Fedotova** 9:45-10:10
Coffee break (20 min)
🟥 **PL5: Zhijian Wu** 10:30-11:15
🟥 **KL5: Edgar Vargas** 11:15-11:50
Closing Ceremony 11:50-12:00

Lunch break (Buffet)

Aug. 5, 2019 🟥	Aug. 5, 2019 🟨	Aug. 5, 2019 🟩
C. Magalhâes 14:30-14:55	**A. Kumar** 14:30-14:55	**Kh. Kh. Turaev** 14:30-14:55
X.H. Lu 14:55-15:20	**H. R. Li** 14:55-15:20	**L. J. Li** 14:55-15:20
H. Zhou 15:20~15:40	M. Bešter-Rogač 15:20~15:40	Y. Zhao 15:20~15:40
J.Q. Liu 15:40~16:00	A.L. Zhu 15:40~16:00	Y. F. Chen 15:40~16:00
L.Z Meng 16:00~16:20	X. M. Lu 16:00~16:20	K.H Shah 16:00~16:20

Aug. 6, 2019 🟥	Aug. 6, 2019 🟨
S. Brudar 14:30-14:50	B. Kutus 14:30-14:50
Z.Y. Li 14:50-15:10	W. Cao 14:50-15:10
S.Q Chen 15:10-15:30	Y.J Chen 15:10-15:30
É. Bajnóczi 15:30-15:50	K. Fujii 15:30-15:50
J.Y. Peng 15:50-16:10	N. Zhang 15:50-16:10

Coffee break (20 min)

Aug. 5, 2019	Aug. 6, 2019	Aug. 7, 2019	Aug. 8, 2019
🟧 **Poster Session (odd number) 16:40~18:00**	🟧 **Poster Session (even number) 16:30~18:00**	**Culture Tour** (Exhibition Room of QISLCAS, Herbarium of NIPBCAS, and Tibetan Medicine Museum of China)	36ICSC **End of Sessions**
Buffet	Buffet	Banquet and Award Ceremony	

🟥	**1st floor**
🟩	**5th floor**
🟨	**6th floor**
🟧	**Lobby**

36th International Conference on Solution Chemistry

ICSC2019

August 4-8, 2019

Xining, China

Qinghai Institute of Salt Lakes, Chinese Academy of Sciences

***The 36ICSC logo incorporates elements from the logo of IUPAC (This year celebrating its 100th anniversary) and previous Solution Chemistry Conferences.**

Welcome Letter

Ladies and gentlemen:

We would like to fervently welcome every colleague in the world to the **36th International Conference on Solution Chemistry** (36ICSC or ICSC2019). The 36ICSC will be organized by **Qinghai Institute of Salt Lakes, Chinese Academy of Sciences (QISLCAS), in Xining, China, on 4-8th, Aug., 2019**.

It's the first time for this time-honored conference to be held in China. As a developing country with the largest population in the world, China possesses diverse advantages, including stable economic growth, rapid development of science and technology, multicultural harmony, and a safe social environment in recent decades, with the help of many countries, to host this conference. As an important base for salt lake resource exploration, QISLCAS has performed various studies on solubility and heterogeneous equilibria, thermodynamics, and time-space-averaged structures of aqueous multicomponent electrolyte solutions for more than thirty years with the help of many foreign friends.

Solution chemistry is essential to improving public health and welfare and to inform sustainability. Humans are confronting many challenges and opportunities, such as resource depletion, environmental degradation, and global governance, *etc*. The fairyland of solution chemistry is an exciting area, in which the aspirants work assiduously, and we'll continue to meet and bring inspired people together in forums like this, to ensure this field remains at the cutting edge.

We would like to invite colleagues from all over the world to attend this conference and to bring new discoveries, new methods, and new theories in the field to this gathering. Let us get together to share academic thoughts, to pioneer the frontiers of science and to shape the future in the field. We respect, welcome and thank all the participants in advance.

Yours sincerely,

Chun-hui Fang

The Local Chairman of 36ICSC

August 1, 2019

Invited Speakers


Glenn Hefter (Australia)


Buxing Han (China)

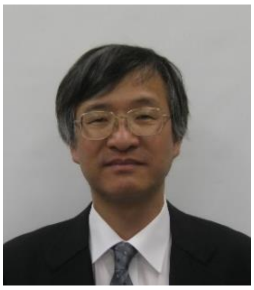

Yoshifumi Kimura (Japan)


PÁL M. Sipos (Hungary)


Zhijian Wu (China)


Jianji Wang (China)


M-C Bellissent-Funel (France)


Susumu Okazaki (Japan)


Paola D'Angelo (Italy)


Edgar F. Vargas (Colombia)


C. Magalhâes (Portugal)


Xiaohua Lu (China)


Anil Kumar (India)


Haoran Li (China)

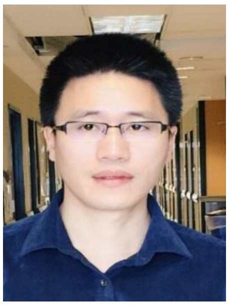

Kh. Kh. Turaev (Uzbekistan)


Lijuan Li (China)

Kaj Thomsen (Denmark)

Tianlong Deng (China)

M. S. Gruszkiewicz (USA)



Zongbi Bao (China)

Mónica Corea (Mexico)

Jianling Zhang (China)

W. Waghorne (Ireland)

Jiangtao Wu (China)

Ingmar Persson (Sweden)

Zhiwu Yu (China)

Cory Pye (Canada)

Yangxin Yu (China)

Emiko Okamura (Japan)

Hong Liang (China)

Toshio Yamaguchi (Japan)

M. V. Fedotova (Russia)

Scientific Programme

Open Ceremony and Plenary

Time: Aug. 5, 2019 (Monday) **Place: The Auditorium (1st floor)**

Open Ceremony			**Host: Yongquan Zhou**	
8:30-9:00	Open Ceremony + Photography			
Plenary Lecture			**Chair: Buxing Han**	
Time	Speakers	Institute/University	Lecture Title	S.N.
9:00-9:45	Glenn Hefter	Murdoch University, Australia	Dielectric Relaxation Spectroscopy: An Old but New Technique for the Investigation of Solutions	**PL-1**
9:45-10:20	Jianji Wang	Henan Normal University, China	Solvation and Phase Transfer of Functional Ionic Liquids	**KN-1**
10:20-10:40	**Coffee Break**			
Plenary Lecture			**Chair: Yoshifumi Kimura**	
10:40-11:25	Buxing Han	Institute of Chemistry, CAS, China	Properties of Green Solvents and Their Application in Green Chemistry	**PL-2**
11:25-12:00	M.C. Bellissent-Funel	Université Paris-Saclay, CEA Saclay, France	Water Confined in Solutions of Biological Relevance	**KN-2**
12:00-14:30	**Lunch Break**			

Topic A. Solubility Phenomena and Phase Equilibria (1)

Time: Aug. 5, 2019(Monday) **Place: The Auditorium (1st floor)**

Sessional Lectures			**Chairs: Tianlong Deng + Kaji Thomsen**	
Time	Speakers	Institute/University	Lecture Title	S.N.
14:30-14:55	M. C. F. Magalhães	University of Aveiro, Portugal	New Paradigms for Green Chemistry	**I-1**
14:55-15:20	Xiaohua Lu	Nanjing Tech University, China	Generalized Gibbs Free Energy of Confined Nanoparticles	**I-2**
15:20-15:40	Huang Zhou	Tianjin University of Science and Technology, China	Comprehensive Thermodynamic Models and Phase Diagram Prediction for Typical Salt-lake Brine	**O-1**
15:40-16:00	Jin Qiang Liu	Luoyang Normal University , China	Experimental Measurement of the Solubility of Gramine in Five Low Alcohols from (291.25 to 323.15) K	**O-2**
16:00-16:20	Lingzong Meng	Linyi University, China	Chemical Engineering Simulation of Brine Processing with Phase Diagrams and Pitzer Models of the Salt-Water Systems	**O-3**
16:20-16:40	**Coffee Break (20 min)**			

Topic B. Ionic Liquids

Time: Aug. 5, 2019 (Monday) **Place: The Lecture Hall (6th floor)**

Sessional Lectures			**Chairs: Susumu Okazaki + Kelei Zhuo**	
Time	Speakers	Institute/University	Lecture Title	S.N.
14:30-14:55	Anil Kumar	CSIR-National Chemical Laboratory, India	Polarity of Ionic Liquids	**I-3**
14:55-15:20	Haoran Li	Zhejiang University, China	Empirical Study on the Structure, Physicochemical Property and Application of Chelate-based Ionic Liquids	**I-4**
15:20-15:40	M. Bešter-Rogač	University of Ljubljana, Slovenia	Ionic Liquids in Solutions: from Simple Electrolytes to Surfactants	**O-4**
15:40-16:00	Anlian Zhu	Henan Normal University, China	A High-throughput Strategy for the Discovery of Multifunctional Ionic Liquids Reaction System	**O-5**
16:00-16:20	Xingmei Lu	Institute of Process Engineering, Chinese Academy of Sciences, China	Utilization of Shrimp Shells with Ionic Liquids and Deep Eutectic Solvents	**O-6**
16:20-16:40	**Coffee Break (20 min)**			

Topic C. General Solution Chemistry and Industrial Applications

Time: Aug. 5, 2019 (Monday) **Place: The Meeting Room (5th floor)**

Sessional Lectures			**Chairs: Jalel Mhalla + Yangxin Yu**	
Time	Speakers	Institute/University	Lecture Title	S.N.
14:30-14:55	Kh. Kh. Turaev	Termez State University, Uzbekistan	Extraction of Platinum Metals From Strongly Acid Solutions	**I-5**
14:55-15:20	Lijuan Li	Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, China	Eco-friendly Separation and Effective Applications of Lithium Resources from Salt Lake Brine with High Magnesium-to-lithium Ratio: Their Science and Technology	**I-6**
15:20-15:40	Yang Zhao	Henan Normal University, Henan China	A Mechanism Study on Absorption of Humid CO_2 by [Emim][Gly] Ionic Liquid	**O-7**
15:40-16:00	Yifeng Chen	Nanjing Tech University, China	CO_2 Separation Using a Hybrid Choline-2-Pyrrolidine-carboxylic Acid/Polyethylene Glycol/Water Absorbent	**O-8**
16:00-16:20	Khizar Hussain Shah	COMSATS University Islamabad, Abbottabad Campus, Pakistan	Adsorption of Bacteria by Highly Efficient, Economic and Biodegradable Magnetic Coated Chitosan	**O-9**
16:20-16:40	**Coffee Break (20 min)**			
16:40-18:00	**Poster Session (Odd number)** **Chairs: PÁL M. Sipos + Susumu Okazaki + Paola D'Angelo + Jianling Zhang +Dewen Zeng**			
18:00-20:00	**Buffet**			

Plenary Lectures

Time: Aug. 6, 2019 (Tuesday) **Place: The Auditorium (1st floor)**

Plenary Lectures **Chair: Zhiwu Yu**

Time	Speakers	Institute/University	Lecture Title	S.N.
8:30-9:15	Yoshifumi Kimura	Doshisha University, Japan	Molecular Dynamics and Chemical Reactions in Ionic Liquids Reflecting the Heterogeneous Structure	**PL-3**
9:15-10:00	Pál Sipos	University of Szeged, Hungary	Equilibria and Structure of Complexes Forming in Hyperalkaline Aqueous Solutions	**PL-4**
10:00-10:20	**Coffee Break (20 min)**			

Topic D. Solubility Phenomena and Phase Equilibria (2)

Time: Aug. 6, 2019 (Tuesday) **Place: The Auditorium (1st floor)**

Sessional Lectures **Chairs: M. C. F. Magalhães + Xiaohua Lu**

Time	Speakers	Institute/University	Lecture Title	S.N.
10:20-10:45	Kaj Thomsen	Technical University of Denmark, Denmark	Modeling Phase Equilibria of Acetone – Water – Salt Mixtures	**I-7**
10:45-11:10	Tianlong Deng	Tianjin University of Science and Technology, China.	Thermodynamics, Phase Equilibria and Phase Diagram on the Salt Lake Brine Systems	**I-8**
11.10-11:30	Xueli Huang	Xinjiang University, China	Research Progress in Phase Equilibria of Salt-Water System at Low Temperature	**O-10**
11:30-11:50	Yingjie Xu	Shaoxing University, Shaoxing, China	Prediction of Vapor–Liquid Equilibria of Alcohol + Hydrocarbon Systems by 1H NMR Spectroscopy	**O-11**
11:50-12:10	Xiangmei Cui	Qinghai University, China	Vapor-Liquid Equilibrium of HCl-H_2O System at Low Pressure	**O-12**
12:10-14:30	**Lunch Break** International Steering Committee Meeting of ICSC			

Topic E. Supercritical Fluids and Solutions under Extreme Conditions

Time: Aug. 6, 2019 (Tuesday) **Place: The Lecture Hall (6th floor)**

Sessional Lectures			**Chairs: Jianling Zhang + W. Waghore**	
Time	Speakers	Institute/University	Lecture Title	S.N.
10:20-10:45	Miroslaw S. Gruszkiewicz	Oak Ridge National Laboratory, USA	Pore-confined Supercritical Fluids: the Universal Origin of the High Pressure Excess Sorption Maxima	**I-9**
10:45-11:10	Zongbi Bao	Zhejiang University, China	Carbon Dioxide-philic Open-chain Crown Ether Bridged Diphosphate for Metal Ions Extraction in scCO2	**I-10**
11.10-11:30	Wei Li	Capital Normal University, China	Fabrication of Hierarchically Porous Materials by Using Supercritical CO_2	**O-13**
11:30-11:50	Ratna Surya Alwi	Fajar University, Indonesia	Solubilities of 4-Aminoazobenzene and 4-Diethylaminoazobenzene in Supercritical Carbon Dioxide	**O-14**
11:50-12:10	Xuan Ge	Shanghai Jiao Tong University, China	The Structural Origins of Titanium Dioxide (TiO_2) Polymorphic Nucleation in Undercooling Melt	**O-15**
12:10-14:30	**Lunch Break**			

Topic F. Colloids and Interfaces

Time: Aug. 6, 2019 (Tuesday) **Place: The Meeting Room (5th floor)**

Sessional Lectures			**Chairs: Jiangtao Wu +M. S. Gruszkiewicz**	
Time	Speakers	Institute/University	Lecture Title	S.N.
10:20-10:45	Mónica Corea	Instituto Politécnico Nacional, México	Thermodynamic Behavior of Polymers Sensitive to pH	**I-11**
10:45-11:10	Jianling Zhang	Institute of Chemistry, Chinese Academy of Sciences, China	Self-Assemblies in Green Solvents	**I-12**
11.10-11:30	Xirong Huang	Shandong University, China	Novel Hydrophobic Ionic Liquid Based Microemulsion for Laccase Catalysed Reaction	**O-16**
11:30-11:50	Jalel Mhalla	University of Monastir, Tunisia	High Coupling Effect Between the Micellization, Ionic Condensation and Hydrophobic Absorption.Interpretation of the Co Catalytic Effect of $NaBPh_4$ over the Nano Polymerization of Styrene by the Zirconocene Dichloride in SDS Micelles.	**O-17**
11:50-12:10	Yihui Dong	Nanjing Tech University, China	AFM Study of pH-Dependent Adhesion of Single Protein to TiO_2 Surface	**O-18**
12:10-14:30	**Lunch Break**			

Youth Forum (1)

Time: Aug. 6, 2019 (Tuesday) **Place: The Auditorium (1st floor)**

Sessional Lectures **Chairs: Toshio Yamaguchi + Tianlong Deng**

Time	Speakers	Institute/University	Lecture Title	S.N.
14.30-14:50	Sandi Brudar	University of Ljubljana, Slovenia	Studying Phase Stability of Hen Egg-white Lysozyme Solutions with Molecular Dynamics	**Y-1**
14.50-15:10	Zhiyong Li	Henan Normal University, China	Reversible Phase Behavior Modulation of azobenzene Ionic Liquid-based Emulsions by UV/vis Irradiation	**Y-2**
15:10-15:30	Shangqing Chen	Tianjin University of Science and Technology, China	Salt Lake Brines: Green and Abundant Catalyst for the Transformation of CO_2	**Y-3**
15:30-15:50	Éva G. Bajnóczi	Swedish University of Agricultural Sciences, Sweden	Hydration in Concentrated Alkali Metal Chloride Aqueous Solutions – The Winner Takes It All?!	**Y-4**
15:50-16:10	Jiaoyu Peng	Qinghai Institute of Salt Lakes, Chinese Academy of Sciences , China	Chemistry of Mg-borates in Sulfate-type Saline Lake and its Application in Boron Recovery From Brine	**Y-5**
16:10-16:30	**Coffee Break (20 min)**			
16:40-18:00	**Poster Session (Even number)**			
18:00-20:00	**Buffet**			

Youth Forum (2)

Time: Aug. 6, 2019 (Tuesday) **Place: The Lecture Hall (6th floor)**

Sessional Lectures **Chairs: Glenn Hefter + Lijuan Li**

Time	Speakers	Institute/University	Lecture Title	S.N.
14.30-14:50	Bence Kutus	Max Planck Institute for Polymer Research, Germany	The Effect of Isotopic Composition on the Dielectric Relaxation of Water	**Y-6**
14.50-15:10	Wei Cao	Tsinghua University, China	Exfoliation of Two-Dimensional Materials: The Role of Entropy	**Y-7**
15:10-15:30	Yujuan Chen	Henan Normal University, China	Interaction and Synergistic Effect of Heteroatoms in Co-Doped Graphene in Ionic liquid-based Supercapacitor	**Y-8**
15:30-15:50	Kaori Fujii	Doshisha University, Japan	Excited State Proton Transfer of Cyanonaphtholin High-temperature and High-pressure Alcohol: Effect of Solvent Polarity and Hydrogen Bonding Ability	**Y-9**
15:50-16:10	Ning Zhang	Central South University of Forestry and Technology, China	Solution Structure of Sparingly Soluble Fluoride: Insights from Molecular Dynamics and Density Functional Theory Calculations	**Y-10**
16:10-16:30	**Coffee Break (20 min)**			
16:30-18:00	**Poster Session (Even Number)** **Chairs: Ingmar Persson + J. Mhalla + Xueli Huang + Lijuan Li + Jiangtao Wu**			

Keynote Lectures

Time: Aug. 7, 2019 (Wednesday) **Place: The Auditorium (1st floor)**

Plenary Lectures **Chair: M. C. Bellissent-Funel**

Time	Speakers	Institute/University	Lecture Title	S.N.
8:30-9:05	Susumu Okazaki	Nagoya University, Japan	All-Atomistic Molecular Dynamics Study of Viruses	**KN-3**
9:05-9:40	Paola D'Angelo	University "La Sapienza"of Rome, Italy.	Understanding Solvation Properties in Liquid Solutions by XAS and Molecular-Dynamics Simulations	**KN-4**
9:40-10:00	**Coffee Break (20 min)**			

Topic G. Solution Thermodynamics

Time: Aug. 7, 2019 (Wednesday) **Place: The Auditorium (1st floor)**

Sessional Lectures **Chairs: Liang Hong + Pal M. Sipos**

Time	Speakers	Institute/University	Lecture Title	S.N.
10.00-10:25	Waghorne Earle	University College Dublin, Ireland	Scales of Solvent Acidity, Basicity and Polarity – Experimental Basis and Relation to Molecular Properties	**I-13**
10.25-10:50	Jiangtao Wu	Xi'an Jiaotong University, China	Thermophysical Properties Research of Alterative Refrigerants	**I-14**
10:50-11:10	Qiang Tian	Southwest University of Science and Technology, China.	The Growth of Cage-like Uranyl Peroxide Nanoparticles: a Small-angle Scattering Study	**O-19**
11:10-11:30	Bin Hu	Qinghai Institute of Salt lakes, CAS, China	Density Prediction for Aqueous Lithium Containing Multicomponent Solutions	**O-20**
11:30-11:50	Li Sun	Technical University of Denmark, Denmark	Modeling of Gas Solubility in Aqueous Electrolyte Solutions Using the Electrolyte Cubic-Plus-Association Equation of State	**O-21**
11:50-12:10	Kaiyu Zhao	Tianjin University of Science and Technology, China	Isopiestic Measurements of Thermodynamic Properties for the Aqueous System ($LiBO_2$ + $Li_2B_4O_7$ + H_2O) at 288.15 K	**O-22**
12:10-14:30	**Lunch Break (2.5 hour)**			
14:30-18:00	**Culture Tour** (Exhibition Room of QISLCAS, Herbarium of NIPBCAS and Tibetan Medicine Museum of China) **Assembling:** At the gate of QISLCAS, 14:30			
18:30-21:00	**Banquet & Award Ceremony** **Location:** Wanda Realm *Block 1, 76 Xichuan South Road, Chengxi district, Xining, China*			

Topic G. Solution Structure and Dynamics

Time: Aug. 7, 2019 (Wednesday) **Place: The Lecture Hall (6th floor)**

Sessional Lectures **Chairs: Haoran Li +M. V. Feddotava**

Time	Speakers	Institute/University	Lecture Title	S.N.
10.00-10:25	Ingmar Persson	Swedish University of Agricultural Sciences, Sweden.	Hydration of Inorganic Anions in Aqueous Solution, Structure and Hydrogen Bonding	**I-15**
10.25-10:50	Zhiwu Yu	Tsinghua University, China	Unveiling the Structural Properties of Liquid Mixtures Using A Method Combining Excess Spectroscopy and Quantum Chemistry	**I-16**
10:50-11:10	Koji Yoshida	Fukuoka University, Japan	Inelastic X-ray Scattering Measurements of Copper/Ethylene Glycol and Alumina/Water Nanofluids	**O-23**
11:10-11:30	L. Almasy	Southwest University of Science and Technology, China.	Microheterogeneity in Aqueous Solutions by Radiation Scattering and Computer Simulations	**O-24**
11:30-11:50	Wanjing Cui	Tianjin University of Science and Technology, China	Solution Chemistry and Trace Iodine Removal of High Salt Brine System	**O-25**
11:50-12:10	Pan Tan	Shanghai Jiao Tong University, China	Many-Body Effect Induces Gradual Crossover from Sub-Diffusion to Normal Diffusion	**O-26**
12:10-14:30	**Lunch Break (2.5 hour)**			

Topic H. Computational Solution Chemistry

Time: Aug. 7, 2019 (Wednesday) **Place: The Meeting Room (5th floor)**

Sessional Lectures **Chairs: A. Kumar + Xiaohua Lu**

Time	Speakers	Institute/University	Lecture Title	S.N.
10.00-10:25	Cory Pye	Saint Mary's University, Canada	Computational Chemistry Applied to Solutions	**I-17**
10.25-10:50	Yangxin Yu	Tsinghua University, China	A Partially perturbative Density Functional Theory for Electrokinetic Properties	**I-18**
10:50-11:10	Weiyi Su	Hebei University of Technology, China.	Molecular simulation of D-mannitol Polymorphs in Solution	**O-27**
11:10-11:30	Tetsuro Nagai	Nagoya University, Japan	Novel Method to Evaluate Position-Dependent Diffusion Constant of Small Molecules in Heterogeneous Systems	**O-28**
11:30-11:50	Yuling Zhao	Henan Normal University, China.	Insight into Understanding the Microstructure and demulsification Mechanism of Temperature-Responsive Ionic Liquid Microemulsion	**O-29**
11:50-12:10	Fei Li	Hebei University of Technology, China	Study on the Structure of Sodium Chloride Aqueous Solution by Synchrotron X-ray Scattering and Molecular Dynamics Methods	**O-30**
12:10-14:30	**Lunch Break (2.5 hour)**			

Topic I. Biology Effects of Solutions

Time: Aug. 8, 2019 (Thursday) **Place: The Auditorium (1st floor)**

Invited Lectures			**Chairs: Paola D'Angelo + Cory Pye**	
Time	Speakers	Institute/University	Lecture Title	S. N.
8:30-8:55	Emiko Okamura	Himeji Dokkyo University, Japan	Real-Time in-Situ NMR of Biologically Relevant Reactions in Peptide Solution: Spontaneous Peptide Bond Cleavage of Aspartyl Isomers and Preaggregation of Amyloid-Fragments	**I-19**
8:55-9:20	Liang Hong	Shanghai Jiao Tong University, China	Abnormal Dynamics of Water Molecules on the Protein Surface	**I-20**
9:20-9:45	Toshio Yamaguchi	Fukuoka University, Japan	Ion Hydration and Association in Aqueous Electrolyte Solutions in the GPa Range	**I-22**
9:45-10:10	Marina V. Fedotova	G.A. Krestov Institute of Solution Chemistry of the Russian Academy of Sciences, Russia	Compatible Osmolytes -Bioprotectants: Is There a Common Link Between Their Hydration and Their Protective Action Under Abiotic Stresses?	**I-23**
10:10-10:30	**Coffee Break (20 min)**			

Plenary& Keynote & Closing Ceremony

Time: Aug. 8, 2019 (Thursday) **Place: The Auditorium (1st floor)**

Plenary& Keynote			**Chair: Toshio Yamaguchi**	
Time	Speakers	Institute/University	Lecture Title	S.N.
10:30-11.15	Zhijian Wu	Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, China	Absorption Mechanisms in Aqueous Solutions	**PL-5**
11:15-11:50	Edgar F. Vargas	Universidad de los Andes, Colombia	Physiochemical Properties of Resorcin[4]Arenes In Solution	**KN-5**
Closing Ceremony		**Chairs: Toshio Yamguchi + Yongquan Zhou + Edgar F. Vargas**		
11:50-12:00	**Close Ceremony**			
12:00-14:30	**Buffet**			

Poster Presentations

Odd number: Aug. 5, 2019 16:40 ~ 18: 00 **Place: The Lobby (1st floor)**

Even number: Aug. 6, 2019 16:30 ~ 18: 00 **Place: The Lobby (1st floor)**

P-1	**Kenzo Aki (**Himeji Dokkyo University, Japan**)**
	The Kinetics of Amino Acid Isomerization in Amyloid Beta Fragments Quantified by Real-Time 1H-NMR
P-2	**Umarbek Alimov** (Tianjin University of Science and Technology, China)
	Volumetric Properties of Sodium Hypophosphite Aqueous Solution from 283.15 to 363.15 K at 101.325 kPa
P-3	**Bobo Cao** (Tsinghua University, China)
	Regulation of $MgCl_2$ on the Self-Assembly of Ionic Liquid Surfactant ([C16mim]Cl) in Aqueous Solutions
P-4	**Gang Chen** (Institute of Chemistry, Chinese Academy of Sciences, China.)
	Metal Ionic Liquids for the Cycloaddition of CO_2 under Ambient Conditions
P-5	**Shangqing Chen** (Tianjin University of Science and Technology, China)
	Basic Salt Lake Brine: Efficient Catalyst for the Transformation of CO_2 into Quinazoline-2,4(1H,3H)-diones
P-6	**Wanjing Cui** (Tianjin University of Science and Technology, China)
	Speciation Analysis of Iodate and Iodide in High Salt Brine by High Performance Liquid Chromatography and Inductively Coupled Plasma Mass Spectrometry
P-7	**Xiaoyue Cao** (Shaanxi Normal University, China)
	Thermodynamic Properties of CsCl + Tetramethylurea + Water Ternary System at 298.15 K
P-8	**Weibiao Du** (Xi'an Jiaotong University, China)
	Improvement of Binary Interaction Coefficient in McAllister Three-body Viscosity Model
P-9	**D. Dragoescu** (Institute of Physical Chemistry Romanian Academy, Romania)
	Thermophysical Properties for Solutions of 1,2-hexanediol + Water Binary Mixtures at Different Temperatures and Atmospheric Pressure
P-10	**Yanfei Fan** (Central South University, China)
	Heat Capacity of Rb_2SO_4(aq) and Cs_2SO_4(aq) Solutions and Thermodynamics Modeling of $Rb_2SO_4 + H_2O$ and $Cs_2SO_4 + H_2O$ Systems
P-11	**Mingyuan Feng** (Hebei University of Technology, China)
	Molecular Dynamics Simulation of Temperature Influence on Ionic Hydration in $CaCl_2$ and $MgCl_2$ aqueous Solutions
P-12	**Haiwen Ge** (Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, China)
	Volumetric Properties and Ion-interaction Model for Aqueous Lithium Borate Solutions
P-13	**Qi Ge** (Chengdu University of Technology, China)
	Mean Activity Coefficients of KCl in KCl + $SrCl_2$ + H_2O Ternary System at 308 K by EMF Method

P-14	**Lijiang Guo** (Institute of Process Engineering, Chinese Academy of Science, China)
	Solubility and Model Simulation of Limited Solid Solution Containing System RbCl−CsCl−H_2O
P-15	**Yunyun Gao** (Chengdu University of Technology, China)
	Solubility Prediction of the Ternary System NaCl–$SrCl_2$–H_2O at 273 K and 308 K
P-16	**Xiaolei Hao** (Tsinghua University, China)
	The Effect of Imidazolium-based Ionic Liquids [C_4mim][OAc] and [C_6mim][OAc] on Phase Behavior of DPPC
P-17	**Tao Han** (Tianjin University of Science and Technology, China)
	Determination of Lithium in High Salinity Samples by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)
P-18	**Yucui Hou** (Taiyuan Normal University, China)
	Efficient Separation of Phenol from Oils Using Environmentally Zwitterions Via forming Deep Eutectic Solvents
P-19	**Hongfang Hou** (Tianjin University of Science and Technology, China)
	Apparent Molar Volumes of Sodium Arsenate Aqueous Solution from 283.15 K to 363.15 K at Atmospheric Pressure：An Experimental and Thermodynamic Modeling Study
P-20	**Qin Huang** (Chengdu University of Technology, China)
	Correlation of the Solubilities of KCl in Mixed Solvents at 298 K: PEG1000/4000 + H_2O and Ethanol + H_2O
P-21	**Xiucan Jia** (Xi'an Jiaotong University, China)
	Densities and Viscosities of Four Fatty Acid Esters at Temperatures from 303 K to 362 K and Pressures up to 30 MPa
P-22	**Peihuan Jiang** (Chengdu University of Technology, China)
	Study on the Stable Phase Equilibria of the Quaternary System Li^+, K^+//Cl^-, $B_4O_7^{2-}$–H_2O at 273 K
P-23	**Payam Kalhor** (Tsinghua University, China)
	Insights into the Microstructures of Three Alcohol–containing Binary Mixtures Using Excess Infrared Spectroscopy and DFT calculation
P-24	**Fujimoto Kazushi** (Nagoya University, Japan)
	Molecular Study of Hepatitis B Virus with PgRNA in the Solution by Molecular Dynamics Calculation
P-25	**Can Liu** (Tianjin University of Science and Technology, China)
	Synthesis and Property Characterization on the Thermal Energy Storage Phase Change Materials Based on Octadecanoic Acid and Octadecanol
P-26	**Dongdong Li** (Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, China)
	ISLEC: A CALPHAD-Type Aqueous Solution Thermodynamic Modeling Software Based on A Pitzer-Simonson-Clegg Approach
P-27	**Dongchan Li** (Hebei University of Technology, China)
	Phase Equilibria of the Quaternary System (KCl + $CaCl_2$ + $SrCl_2$ + H_2O) at 288.15 K

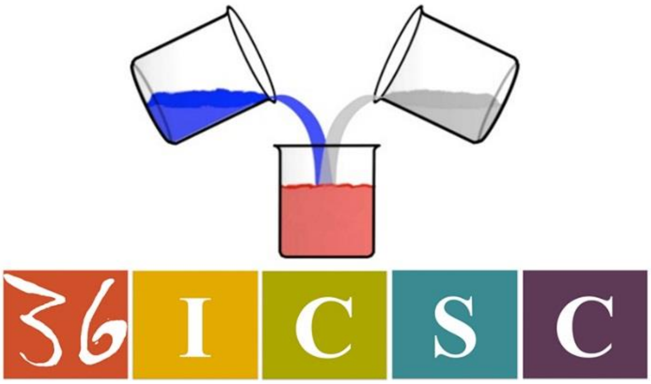
P-28	**Maolan Li** (Chengdu University of Technology, China)
	Correlation of Solubility of KCl/RbCl/CsCl-PEG1000-H_2O at 298 K
P-29	**Panpan Li** (Tianjin university of Science and Technology, China)
	Phase Equilibria and Phase Diagrams for the Ternary Aqueous System Containing Lithium, Sodium and Pentaborate Ions at 298.2 and 323.2 K and 101.325 kPa
P-30	**Hongxia Li** (Chemistry department/bao tou teachers' college, China)
	Solubility Phase Diagram of the Ternary System Li^+, $Mg^{2+}/Cl^-(SO_4^{2-})$–H_2O at 348.15 K
P-31	**Shuni Li** (Shaanxi Normal University, China)
	Phase Behavior of Tetramethylurea+ CsCl+H_2O Systems at 298.15 K and 308.15 K
P-32	**Jingfeng Liu** (Chengdu University of Technology, China)
	The Stable Phase Diagram of the Quaternary Water-Salt System Li^+, Na^+, Cs^+ // SO_4^{2-} - H_2O at T = 298.2 K
P-33	**Hongyan Liu** (Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, China)
	Micro Hydration Structure of Aqueous Li^+ by DFT and CPMD
P-34	**Lijiang Guo** (Baotou Teachers' College, China)
	Solubility and Mmodel Simulation of Limited Solid Solution Containing System RbCl−CsCl−H_2O
P-35	**Chenglong Liu** (Tianjin University of Science and Technology, China)
	Solvent Extraction of Magnesium from Salt Lake Brines and Thermodynamics Study
P-36	**Xing Liu** (Chengdu University of Technology, China)
	Studies on the Mean Activity Coefficients of NaBr in the Ternary System NaBr-$SrBr_2$-H_2O at 308 K
P-37	**Long Li** (Tianjin University of Science and Technology, China)
	Studies on the Thermodynamic Properties of Electrolyte Solutions Containing Lithium Borates
P-38	**Min Liu** (Chengdu University of Technology, China)
	Correlation of the Solubility of $SrCl_2$ + NH_4Cl + H_2O Ternary System at 298 K with Pitzer Mode
P-39	**Yaoyao Li** (Tianjin University of Science and Technology, China)
	(Solid+Liquid) Phase Equilibria of LiCl + $LiBO_2$ + H_2O Ternary Systems and Raman Spectrum
P-40	**Xiaofan Ma** (Henan normal university, China)
	Solvent-induced Assembly of Mn(II) Coordination Polymers Containing 3,3',5,5' - biphenyltetracarboxylic Acid
P-41	**Kazuhiko Ohashi** (Kyushu University, Japan)
	Vibrational Spectroscopic and Computational Studies on Formamide Solutions of Alkali-metal Ions
P-42	**Guoliang Nie** (Chengdu University of Technology, China)
	Phase Equilibria in Ternary System LiCl–Li_2SO_4–H_2O at 373 K
P-43	**Dengke Pang** (Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, China)
	Extraction of Cesium and Rubidium with Saponified 4-tert-butyl-2-(α-methylbenzyl) Phenol

P-44	**Xiaoyun Qi** (Chengdu University of Technology, China)
	Study on Metastable Phase Equilibrium of Ternary System Li_2SO_4-$Li_2B_4O_7$-H_2O 273 K
P-45	**Jingxuan Qiu** (Changchun University of Technology. China)
	Measurement and Correlation of Solubility of Myo-inositol in Water + Ethanol Binary Solvent System
P-46	**Hongwei Ren (**Hebei University of Science and Technology**)**
	Preparation of Nitrogen Doped Carbon Quantum Dots Based on A Natural Deep Eutectic Solvent As the Functional Monomer for Specific Recognition of Cu^{2+}
P-47	**Yunlei Shi** (Lanzhou University, China)
	Highly Efficient and Reversible Inversion of a Pickering Emulsion Triggered by CO_2/N_2 at Ambient Conditions
P-48	**Shi-Hua Sang** (Chengdu University of Technology, China)
	Study on Metastable Equilibria in the Quaternary System LiCl–$Li_2B_4O_7$–KCl–$K_2B_4O_7$–H_2O at 273 K
P-49	**Miaosen Shi** (Tianjin University of Science and Technology, China)
	Solid–liquid Phase Equilibria of the Reciprocal Quaternary System (Na^+, Cs^+// Cl^-, SO_4^{2-} - H_2O) at 298.15 K and 0.1 Mpa
P-50	**Sijie Song** (Zhejiang University, China)
	Synthesis, Characterization and Physicochemical Properties Determination of Chelate-based Ionic Liquids
P-51	**Kangrui Sun** (Tianjin University of Science and Technology, China)
	Apparent Molar Volumes for $Cs_2B_4O_7$ Aqueous Solution at Temperatures from (283.15 to 363.15) K and 101 kPa
P-52	**Yota Suzuki** (Waseda University, Japan)
	Sensing Mechanism of *O*-azo Phenylboronic Acid-based Chemosensors for Saccharide: Color Change Caused by Solute-solvent Interaction
P-53	**Ning Zhang** (Central South University of Forestry and Technology, China)
	Solvent Effect on the Association of Cu(II)-chloride Complexes: Insight from UV-Vis, XAS and Molecular Dynamics
P-54	**Hanlin Tong** (Chengdu University of Technology, China)
	The Stable Phase Diagram of the Ternary Water-Salt System K^+, Rb^+ // SO_4^{2-} - H_2O at $T = 298.2$ K
P-55	**Siye Tang** (Luoyang Normal University, China)
	Theta Temperature of Poly(L-lactide) and the Relationship Between Theta Temperature and Solubility Parameter, Interaction Parameter
P-56	**Guangguo Wang** (Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, China)
	Structure of Aqueous $CaCl_2$ Solutions by X-Ray Scattering and Density Functional Theory
P-57	**Huiyong Wang** (Henan Normal University, China)
	Scalable Exfoliation and Dispersion of Few-layer Hexagonal Boron Nitride Nanosheets in NMP-salt Solutions

P-58	**Lin Wang** (Chengdu University of Technology, China)
	Liquid-liquid Equilibria for Ternary System CsCl + PEG + H_2O at 298 K: Effect of Different Polymer Molecular Weight
P-59	**Peng Wu** (Tianjin University of Science and Technology, China)
	Sulfate Solution Physical Properties and Temperature-dependent Phase Diagram
P-60	**Shiqiang Wang** (Tianjin University of Science and Technology, China)
	Solid-Liquid Phase Equilibria in the Aqueous System Containing Potassium, Magnesium, and Borate at 308.15 K
P-61	**Xiaopo Wang** (Xi'an Jiaotong University, China)
	Thermophysical Properties of Decanoic Acid Methyl Ester with Different Alcohols
P-62	**Xuyang Wang** (Hebei University of Technology, China)
	Study on the Structure of Sodium Chloride Aqueous Solution by Synchrotron X-ray Scattering and Molecular Dynamics Methods
P-63	**Dazhen Xiong** (Henan Normal University, China)
	Tunable UCST-type Phase Behavior of Alkanolamine-based Deep Eutectic Solvents
P-64	**Pan Xu** (Chengdu University of Technology, China)
	Lithium Ionic Sieve and its Adsorption Performance for Lithium From Underground Brine
P-65	**Jiajia Yin** (Xi'an Jiaotong University, China)
	Liquid Densities for Mixtures of Methyl Decanoate with N-propanol and N-butanol from 293.15 K to 363.15 K at Pressures up to 60 MPa
P-66	**Bo Yan** (Tianjin Unversity of Science and Technology, China)
	Studies on the Association Equilibrium Characteristic of Mg^{2+} and SO_4^{2-} by Raman Spectroscopy
P-67	**Chao Ye** (Chengdu University of Technology, China)
	Phase Equilibria of Ternary System $LiCl–Li_2B_4O_7–H_2O$ at 273 K
P-68	**Liuying Ye** (Hubei University of Technology, China)
	Thermodynamic Modeling of $NaBO_2 + H_2O$ And $NaBO_2 + NaCl + H_2O$ Systems
P-69	**Wannian Ying** (Chengdu University of Technology, China)
	The Stable Phase Diagram of the Ternary Water-Salt System Mg^{2+}, Cs^+ // SO_4^{2-} - H_2O at T = 323.2 K
P-70	**Yan Yu** (Tianjin University of Science and Technology, China)
	Phase Equilibria of the Reciprocal Quaternary System (Li^+, K^+//Cl^-, $B_5O_8^-$ - H_2O) at 298.15 K and 101.325 kPa
P-71	**Fei Yuan** (Tianjin University of Science and Technology, China)
	Dilution Enthalpies of the Aqueous Solutions on Lithium Borates and the Application of Ion-interaction Model
P-72	**Junsheng Yuan** (Hebei University of Technology, China)
	Structure Study of Ammonium Chloride Solutions by Spectroscopic Method and Molecular Dynamics Simulation

P-73	**Shanshan Zhu** (Xi'an Jiaotong University, China)
	Viscosity of Mixtures of Dimenthyl Ether, Isobutene with Squalane in Saturated Liquid Phase
P-74	**Wenqian Zhang** (Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, China)
	Structure of Aqueous RbCl and CsCl Solutions in the GPa Range by Neutron Diffraction
P-75	**Fanyu Zhang** (Institute of Chemistry, Chinese Academy of Sciences, Beijing, China)
	Supercritical Fluid for the Synthesis of Perovskite Nanocrystals
P-76	**Min Zhang** (Tianjin University of Science and Technology, China)
	Study on Separation Technology of Manganese Sulfate and Magnesium Sulfate in Manganese Electrolyte
P-77	**Ziyu Zhuang** (Central South University, China)
	Thermodynamic Modeling of the Solubilities of Boric Acid in Chloride and Sulfate Aqueous System: A Preliminary Study
P-78	**Wenhua Zhang** (Qinghai Normal University, China)
	Structure of Alkaline Aqueous $NaBH_4$ Solutions by X-Ray Scattering
P-79	**Jiying Zhao** (Qinghai Normal University, China)
	Structure of Molten Nitrate (Hitec): X-ray Scattering Study
P-80	**Lei Zhao** (Beijing university of technology, China)
	In Situ Monitoring of the Adsorption Kinetics of Surfactants in Microchannel by Pulsed Streaming Potential Measurement
P-81	**Hong Zheng** (Chengdu University of Technology, China)
	Solubility of K_2SO_4 in (PEG1000+H_2O) Mixed Solvents at 298.15 and 308.15 K
P-82	**Shudong Zheng** (Qinghai University, China)
	Study on Lithium Enrichment and Potassium Extraction from Simulated Brine Solution
P-83	**Qiufeng Zheng** (Chengdu University of Technology, China)
	Thermodynamic Model Calculation of Solid-liquid Equilibrium in Ternary System $NH_4Cl+MgCl_2+H_2O$ at 298 K
P-84	**Yuan Zhong** (Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, China)
	Study on the Dehydration Process of Magnesium Nitrate Hexahydrate
P-85	**Guanglai Zhu** (Anhui Normal University, China)
	Local Microstructure Study on Pyridinium Ionic Liquids
P-86	**Yongquan Zhou** (Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, China)
	Dihydrogen Bonds in Aqueous $NaBD_4$ Solution by Neutron and X-Ray Scattering: Concentration and Temperature Effects
P-87	**Wenzhang Zuo** (Chengdu University of Technology, China)
	The Stable Phase Diagram of the Ternary Water-Salt System Na^+, Rb^+ // SO_4^{2-} - H_2O at 323.2 K

P-88	**Junfeng Wang** (Chinese Academy of Sciences, China)
	Structure Effect of Ionic Liquid to Enhance TBP Extraction for Effective Separation of Lithium and Magnesium
P-89	**Fayan Zhu** (Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, China)
	Mechanism for Hydrolysis of Double Six–Membered Ring Tetraborate Anion
P-90	**Chunhui Fang** (Qinghai Institute of Salt Lakes, Chinese Academy of Sciences, China)
	Recent Progress in Structure of Aqueous Polyborate Solutions
P-91	**Jiayin Hu** (Tianjin University of Science and Technology, China)
	Basic Ionic Liquids Promoted Chemical Transformation of CO_2 to Organic Carbonates
P-92	**Yan Li** (Tianjin University of Science and Technology, China)
	Solubilities, Densities, Refractive Indices and pH Values for the Aqueous Ternary Systems ($LiCl + LiB_5O_8 + H_2O$) and ($Li_2SO_4 + LiB_5O_8 + H_2O$) at 288.15 K and 101 kPa



Plenary & Keynote Lectures

Dielectric Relaxation Spectroscopy: An Old but New Technique for the Investigation of Solutions

Glenn Hefter

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Dielectric (Relaxation) Spectroscopy, DRS, measures the response of a sample to an imposed small-amplitude electric field oscillating at GHz (microwave) frequencies. As such, DRS probes the behaviour of dipolar species on the picosecond timescale. DRS is widely applicable to the study of electrolyte and non-electrolyte solutions in aqueous and nonaqueous solvents, ionic liquids, colloidal systems, etc. More importantly, DRS can provide fundamental information on solutions that is virtually unobtainable by any other technique. An overview will be given of the basic principles of this old but yet new technique. Some of the many insights that have been gained into the behaviour of a wide variety of solutions through a long-standing and on-going collaboration between my group at Murdoch University and that of Prof. Richard Buchner at the University of Regensburg in Germany will be presented. The topics covered will include the quantification of ion pairing in electrolyte solutions, the characterization of room temperature ionic liquids and their mixtures, hydrophilic and hydrophobic hydration of ions, Hofmeister effects, and so on.

Properties of Green Solvents and Their Application in Green Chemistry

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Solvent plays a key role in chemistry and chemical industry. Effective utilization of green solvents, such as water, supercritical fluids (SCFs), ionic liquids (ILs), liquid polymers, switchable solvents is an important area of green chemistry. The use of green solvents provides additional control factors for optimizing different chemical processes and developing new processes. In recent years, we are very interested in pyhsicochemical properties of green solvents and their applications in green chemistry, such as phase behavior and intermolecular molecular interaction in complex green solvent systems and catalytic conversion CO_2 and biomass in green solvents. In this presentation, I would like to discuss some recent results[1-11].

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Molecular Dynamics and Chemical Reactions in Ionic Liquids Reflecting the Heterogeneous Structure

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It has been well recognized that ionic liquids (ILs) with long alkyl-chain have a segregated structure due to the inhomogeneous distribution of polar parts and non-polar parts. This inhomogeneity of ILs brings about unique solvation phenomena of solute molecules dissolved in ILs. In our research group, various solvation-state selective phenomena have been investigated by using the laser spectroscopy such as the solvation state selective vibration spectra[1-3], translational and rotational dynamics of small molecules in ILs[4-6], and the solvation state selective fundamental chemical reactions[7-14]. In this lecture, I will present several examples of molecular dynamics and chemical reactions in ILs which reflects the heterogeneous structure of ILs.

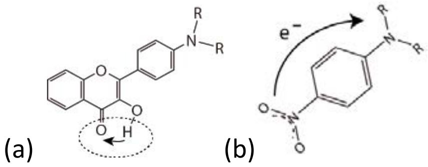

Fig 1. Probe molecules studied here
(a) IPT and (b) IET.

Keywords: *ionic liquid, proton transfer, electron transfer, heterogenous structure, selective solvation*

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Equilibria and Structure of Complexes Forming in Hyperalkaline Aqueous Solutions

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In aqueous solutions of $2 \leq \mathrm{pH} \leq 12$, the structure and equilibria of complexes comprising of organic ligands with –OH and/or –COO$^-$ donor groups (*e.g.,* sugar carboxylates, like gluconate, heptagluconate, gulonate, isosaccharinate, *etc.* or small molecular hydroxy-carboxylates, like tartrate, citrate, malate, lactate, *etc.*) and alkaline earth metal ions (in particular Ca^{2+} and Mg^{2+}) are relatively well characterized. The interactions involve weak binding of the metal ion to −OH and/or −COO$^-$ and the formation constant of these simple, mostly mononuclear complexes (or rather ion-pairs) is low.

The situation becomes much more complicated under hyperalkaline (pH > 13) conditions, where alkaline earth metal ions are capable of forming rather unusual complexes. In some cases, these complexes are of unexpectedly high stability and are often multinuclear (bi- or trinuclear). Another striking feature is, that the predominant multinuclear complexes are frequently charge-neutral.

Ca^{2+}- (and in some cases, Mg^{2+}-) complexes present in such high-pH solutions may serve as precursors or templates to form ternary (heteropolynuclear) species of the $M(II)_nL_mM(III)$ type (where M(III) = Fe(III), Al(III), trivalent radionuclides, *etc.*), which has clear practical implications (*e.g.,* in radioactive waste repositories, binding of Al(III) in the Bayer's alumina-trihydrate production or interactions with Fe(III) of vat dyes in various dyeing processes, *etc.*)

In the current contribution, examples will be shown on Ca- and Mg-complexes, that form in hyperalkaline aqueous solutions. The factors affecting the composition, stability and structure of such complexes will be analysed. Additionally, the challenges that a researcher faces, when such solutions are experimentally studied, will also be discussed and an attempt will be made to show, how the conventional solution chemical tools are made suitable to operate in extremely alkaline solutions. The formation of some heteropolynuclear complexes with the involvement of Al(III) and Nd(III) (latter is a generally accepted model for trivalent lanthanides and actinides) will also be discussed.

Keywords: *calcium, magnesium, high pH solutions, complex equilibria, structure*

Adsorption Mechanisms in Aqueous Solutions

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Adsorption in aqueous solutions is one of the most widely used processes in physicochemical operations, and is of particular importance for separation and purification. The interactions between adsorbents and adsorbates, including complexation, precipitation, electrostatic interactions, hydrophobic interactions, hydrogen bonding, *etc.* were discussed comprehensively. The adsorptions of Li^+, Rb^+, Cs^+, I^-, H_3BO_3, and organic dyes, were presented as examples to explain these interactions in detail. The effects of solution pH and ionic strength on the interactions between adsorbates and adsorbents were discussed emphatically to further understand the adsorption mechanisms.

Keyword: *Adsorption mechanism; Complexation; Precipitation; Electrostatic interaction; Hydrophobic interaction*

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Solvation and Phase Transfer of Functional Ionic Liquids

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Ionic liquids are liquid salts, and the most important features of them are ultra-low vapor pressure and structural designability. The former makes it possible to avoid air pollution by replacing traditional volatile organic compounds (VOCs) with ionic liquids, while the latter may help us to create huge kinds of functionalized ionic liquids for particular application in different fields. These two unique features drive the rapid development of ionic liquids in green chemistry and technology. In ionic liquid chemistry, these liquid materials are mostly applied as solvents and catalysts. Thus, solvation of chemical compounds in ionic liquids and that of ionic liquids in molecular solvents are very important, which often determines yield and selectivity of reactions, product separation and solvent recycling.

Here, recent progress in the solvation of functional ionic liquids is summarized with the main concerns: (i) The design of several class of the functionalized ionic liquids and the tune of their physical and chemical properties by structural modulation; (ii) Solvation of functional ionic liquids in water and in other molecular solvents, as well as in ionic liquids and ionic liquid mixtures; (iii) Solvation of CO_2 in functional ionic liquids; (iv) The applications of functionalized ionic liquids in low concentration CO_2 capture, phase transfer between water and organic compounds, emulsification and demulsification of ionic liquid based microemulsions, and high temperature microemulsions consisting solely of ionic liquids. Then, the challenges and future researches in the concerned fields are also addressed.

Keywords: *Functional ionic liquids; Solvation; Phase transfer; Interactions*

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Water Confined in Solutions of Biological Relevance

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In many relevant situations, water is not in its bulk form but instead attached to some substrates or filling some cavities. We shall call water in the latter environment as « confined water » as opposed to bulk water. It is known that the confined water is essential for the stability and the function of biological macromolecules[1,2]. In this paper, we provide a review of the experimental and computational advances over the past decades in understanding the structure and dynamics of water confined in aqueous solutions of biological relevance as well as the role of water in the dynamics and function of proteins.

Examples involving water in solution of organic solutes (cryoprotectants such as dimethylsulfoxide (DMSO)[3], sugars such as trehalose[4]) are presented. Finally, the influence of pressure on the structure and dynamics of lysozyme and water[5] is discussed.

Keywords: *Structure, Dynamics, Hydration water, Trehalose, DMSO, lysozyme*

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All-Atomistic Molecular Dynamics Study of Viruses

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For over a half century, supercomputers have been making progress very rapidly in their performance. For example, the K-computer constructed in 2013 in Kobe is composed of 82,944 compute nodes and has a performance of 10 PFlops. Using this supercomputer, we could enjoy 10 million-atom molecular dynamics(MD) calculations for the first time. The system is large enough to investigate very large bio systems and polymers. Further, the post-K computer will appear in public next year as one of the open science investigation facilities in Japan. This has a performance 100 times higher than the present K-computer. Thus, MD calculation is still extending its field to very large real molecular systems. In the present talk, we present our recent MD calculations of entire virus particles in solution.

A highly parallelized general purpose MD simulation program MODYLAS[1] has been developed for the K-computer. The MODYLAS may use 2^{16}(65,536) nodes simultaneously, i.e. totally 2^{19}(524,288) cores, or more. It is equipped by the fast multipole method (FMM) to evaluate long-ranged forces, avoiding FFT needed in the conventional PME. Our preliminary benchmark test using 2^{16}(65,536) nodes showed that the parallelization efficiency is excellent even in the case of this very highly parallelized MD calculation. It can complete one MD step for a system composed of ten million atoms in 5 ms. The MODYLAS is being developed further towards post K-computer. The MODYLAS on the post K-computer will finish one MD step calculation in 3 ms for one hundred million atom systems.

Polio virus and HBV capsids are both composed of 240 proteins. The diameter is about 30 nm. The systems may be constructed in computer by about 6.5-10 million atoms including solvent electrolyte solution. The MD calculations have been performed focusing our attention on physical chemistry of polio virus empty capsids[2] and pharmaceutics of HBV. The former is concerned with the stability of the capsids and the initial process of infection, i.e. recognition by a receptor (CD155), while the latter with the DDS of an antiviral reagent.

First, we show a sophisticated molecular setup of the polio virus capsid that stabilizes itself in solution together with the RNA, producing negative pressures inside the empty capsid. We also found equilibrium very rapid spontaneous exchanges of water molecules between the inside and outside of the capsid. Further, we show that attractive mean forces act between the virus capsid and the receptor in the aqueous electrolyte solution in spite of the like sign of the total net charge of each capsid and receptor. Electrolytes play a very important role in generating the attractive forces. In contrast, thermally fluctuating forces acting on the virus and receptors from the solvent molecules are very strong such that they are about one thousand times greater than the mean forces. This indicates that, at long distance, the viruses approach to the receptors by random walk.

Further, we also show our calculation of HBV containing pg-RNA inside the capsid. In addition to physical chemistry of the virus, molecular mechanism of the permeation of an antiviral reagent into the inside of the capsid has been investigated at a free energy level using a fragment of the capsid.

Keywords: *molecular dynamics calculation; virus, receptor; antiviral reagent*

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Understanding Solvation Properties in Liquid Solutions by XAS and Molecular-Dynamics Simulations

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In the last ten years a growing number of studies were devoted, both experimentally and theoretically, to understanding the structural properties of liquid systems and ionic solutions, and more clear pictures are emerging. This was possible by the improvements of the experimental techniques and the development of more sophisticated and reliable theoretical models. As we will detail in this work, experimentally in the last years X-ray absorption spectroscopy (XAS) played a major role in unraveling many structural aspects of liquid systems. This was possible by coupling experiments with theoretical simulations and by better exploiting the X-ray absorption near edge spectroscopy (XANES) that is very sensitive to three-dimensional structures. Here, we will show specific applications to several liquid systems. Aqueous solutions containing lanthanoid and actinoid ions are analysed with the aim of providing a unified description of the hydration properties of these series. A second field of application is the case of transition metals dissolved in organic media. Lastly, we will show how the combined approach using XAS and molecular dynamics simulations can be applied to the study of complex systems such as ionic liquids, that represent a new innovative research field.

Keywords: *Hydration; Solvation; Ionic Liquids; XAS spectroscopy; Molecular Dynamics*

Physiochemical Properties of Resorcin[4]Arenes in Solution

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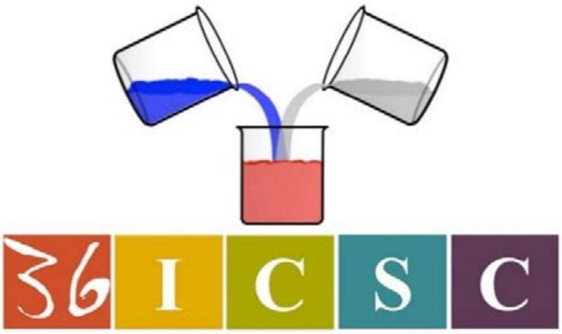
The resorcin[4]renes are macrocycles with interesting structural properties that permit their use in supramolecular chemistry. Although they offer a large spectrum of applications, their behavior in solution has not been sufficiently studied. Studies on physicochemical properties in solutions are of great importance to understand processes such as host – guest chemistry or biomolecule – macrocyclic interactions.

This contribution shows information about the behavior in solution of some ionic and non-ionic resorcinarenes in aqueous and non-aqueous solvents. Thermodynamic, acoustic and transport properties have been determined as a function of concentration and temperature. These studies permitted to analyze aggregation phenomena, especially in non-aqueous solutions. In addition, solvation processes of resorcinarenes have been studied taking as reference homologous series where the hydrocarbon chains have been modified systematically. The presence of the resorcinarenes on the properties of biomolecules, like enzymes, also has been studied too.



Invited Lectures

New Paradigms for Green Chemistry

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Demographic pressure and human activities mobilize chemical elements on the Earth’s surface, impacting the environment, both locally and globally, in terms of mass and energy.

Green chemistry principles have been focused on eliminating or at least reducing the use or generation of materials considered hazardous to humans and the environment [1]. Less hazardous and lower quantities of starting materials, reaction media and residues (waste/by-products), and lower energy requirements are the current aims of green processes.

The effects of the chemical constituents of materials on living entities depend upon the nature of the interactions between them. Already in 1992, Agenda 21 of Rio de Janeiro, Brazil [3], indicated that “toxic materials” demanded environmentally sound management. This requires agreement on the identification of toxic materials, and on their disposal and management. As chemical elements cannot be created or destroyed by chemical means this suggests that a better approach is either to find new applications for used materials (and their by-products and end-products) rather than just minimizing or replacing them, or to develop better ways of immobilizing them.

To exploit these ideas will require study of the physical and chemical properties of materials and their reaction products. As water is the ultimate environmentally benign substance, particular attention will need to be given on better understanding and developing processes in this medium or at least in water-rich variants of other reaction media. Special consideration is also required for the energetic problems that arise from limitations imposed by the Second Law of Thermodynamics [2].

Some examples using radioactive elements as well as arsenic, cadmium, lead and mercury will be used to illustrate the need for changes in mentality and procedures. New paradigms will be proposed to enlarge the scope and change our approach to the concept of hazardous elements. To build a more sustainable (greener) environment, much more scientific information will be needed to improve risk assessment and materials handling. Education will play a very important role in making these changes.

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Keywords: *green chemistry; solubility;*

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Generalized Gibbs Free Energy of Confined Nanoparticles

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The nanoparticles generally show abnormal properties compared to those in the bulk phase, and they exhibit significant potential in various applications such as catalysis and energy conversion. However, the theoretical work for describing the properties of nanoparticles is limited with poor prediction capacity. In this work, the Gibbs free energy was studied, from both marcoscope and microscope, predictive models were proposed to study the thermodynamic properties of nanoparticles with a generalized description of the Gibbs free energy considering the effects of surface-energy and the substrate contacted. The proposed model from the microscope was based on the corresponding states theory to describe the effect of the substrate on the Gibbs free energy of nanoparticles, in which the molecular parameter with a generalized parameter was obtained from the melting point of metals due to sufficient information. The comparison with the new measured experimental results proves the reliability of the model prediction.

Keywords: *Gibbs Free Energy; Confined Nanoparticles; Modeling*

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Polarity of Ionic Liquids

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It is of great importance to understand polarity of ionic liquids for their successful applications to a variety of chemical reactions, separation, extraction etc. An attempt will be made to critically review our own work on polarity of ionic liquids along with available important reports on polarity. The polarity data of ionic liquids will be quantitatively described in terms of interaction parameters. Some interesting results on polarity of mixed ionic liquids will be presented and discussed in terms of synergistic effects.

Empirical Study on the Structure, Physicochemical Property and Application of Chelate-based Ionic Liquids

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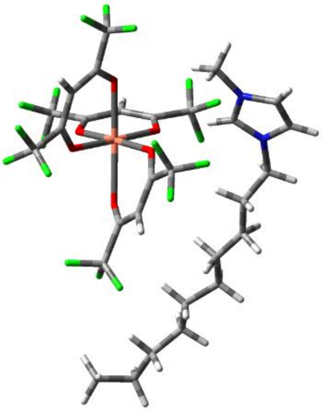

As a salt, chelating compound can also melt at nearly room temperature, which is so called chelate-based ionic liquid (ChIL).[1] The introducing of metal ions gives ChILs additional properties, such as special colour, magnetism and excellent catalysis ability, making ChILs into the functionalized-IL field.[2]

Alkanolamine-based ChILs composed of alkanolamine and Lithium-ion, with a multidentate cation were synthesized to capture CO_2.[3] To catalyze the oxidation reaction, β-diketonate anions as bidentate ligands were also used in the synthesis of ChILs, containing different monovalent transition metals.[4] The successful applications of ChILs made it important to study the physicochemical properties of ChILs and their binary mixtures with molecular solvents, whose systematic investigations are still scarce now. In this case, we carried out a series of researches, which can be divided into two parts: on one hand, we developed a series of single crystals of ChILs, and spectral calculations, EPR experiments *etc*. were used to study their microstructure. [5] On the other hand, the interaction between ChILs and molecular solvents were interpreted by measuring the density, viscosity, electrical conductivity and surface tension of ChILs and their binary mixtures with molecular solvents. The systematic researches on microstructure and macroscopic properties of ChILs will be meaningful to the design and practical application of many processes. [6]

Keywords: *metal-chelating; ionic liquids; physicochemical; application*

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Extraction of Platinum Metals from Strongly Acid Solutions

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According to experimental data, it is known that hydrometallurgical industrial products of the Republic of Uzbekistan have a high content of platinum group elements (Pt, Pd, Ru, Rh, Ir, Os). For a more in-depth study of the distribution of platinoids in industrial products, a method for determining Pt and Pd with preliminary concentration has been developed. The main sources of production of platinum metals (PM) are copper-nickel ores. The content of platinum and palladium in ores reaches 1.5-2.0 g/t. The ores are processed through pyrometallurgical operations, with the platinum metals being concentrated in the ferrous metal and fed to the electrolytic refining of nickel and copper anodes. Moreover, depending on the conditions, carrying out these operations more or less quantities of PM may turn into waste or recycled products, which ultimately leads to their irretrievable losses. One of the promising methods for extracting small amounts of PM from complex process solutions is the extraction method.

Phosphorus dithioacids, like all sulfur-containing ligands, interact in an aqueous medium with the formation of chelate complexes only with those cations which, in accordance with the hypothesis of Kuznetsov's analogy, form characteristic hardly soluble sulphides. Typical soft and intermediate Lewis acids: Cu^+, Ag^+, Au^+, Te^+, Hg^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Zn^{2+}, Pb^{2+}, Bi^{3+}, Cu^{2+}, Pd^{2+} interact with $(i\text{-}C_3H_7O)_2PSSH$ in aqueous solutions , in most cases, quantitatively at room temperature. Platinum metals that exist in aqueous solution in a stable anionic form, interact quantitatively with an excess of ligand and heating in a water bath for several minutes.

Compounds of O,O - diisopropyldithiophosphates (D-i-PDTP) of platinum metals are well extracted into chloroform. Metals, giving less strong complexes with anions of acids, are extracted mainly from acidic solutions (hydrochloric, nitric and sulfuric acid). We investigated the degree of extraction of platinum and palladium, depending on the concentration of acids in the aqueous phase. It is established that the extraction equilibrium occurs in the first 40 minutes. At the same time, the achievement of equilibrium was judged by the values of the distribution coefficients of noble metals. For further study of the laws of extraction of noble metals, the following conditions were chosen: organic solvent - chloroform; phase contact time - 60 minutes. Platinum (IV) is most extracted from nitric acid solutions. Therefore, with residues of nitric acid forms less stable complex compounds than with chlorine ions. Therefore, the less durable complexes of platinum with nitrate - ions give way to a large dithiophosphate anion and form extractable complexes. With a single extraction, platinum (IV) is extracted from sulfuric acid solutions by more than 80%, and from hydrochloric acid (1.5-3 M) - by no less than 75%. Below and above this concentration, the degree of its extraction is somewhat reduced. Palladium is extracted with a threefold extraction from hydrochloric acid (0.05-5 M) solutions. The degree of its extraction (95%) from nitric acid solutions of 8-11 M HNO_3 is relatively high. Apparently, the sulfate compounds of palladium are relatively stronger, which impairs its extraction from sulfate solutions.

Keywords: *extraction, O,O - diisopropyldithiophosphate platinum (IV), nitric acid solutions, sulfuric acid solutions, chloroform.*

Eco-friendly Separation and Effective Applications of Lithium Resources from Salt Lake Brine with High Magnesium-to-lithium Ratio: Their Science and Technology

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The methods to design, synthesize and select environment-friendly and atomic economic extractants for lithium recovery from brine and the evaluation system for their performance were developed, and the synthesis for 21 kinds of organic compounds of amides and phosphate esters were accomplished with the structure-function relationship discovered and the model of molecule design for novel high efficient extractants of amides and phosphate esters established. Many novel high efficient green extraction systems with great application prospect were developed and the co-extraction effect, salting out effect, extraction complex structures, kinetics and thermal dynamics for the lithium extraction from salt lake brine with high mass ratio of Mg to Li were systematically studied, obtaining the regulation of the interaction among the interfacial ions and molecules on molecule level and their mass transfer during the lithium separation process. The key technology of new extraction system applied in lithium recovery from different salt lakes were exploited, and green high efficient lithium products recovery from different kinds of feed liquids, like brines from different salt lakes, and the recovered liquid from used batteries, were realized, indicating that the extraction was obviously a better and more efficient method in the selective separation of lithium and magnesium and the high efficient resource utilization comparing with other existing technologies, which also breaks through the international technology difficulty of lithium recovery from the salt lake brines with high mass ratio of Mg to Li in Qinghai, and provides scientific foundation for the high efficient, clear and high valued utilization of salt lake lithium resource in our country.

Keywords: *lithium recovery; salt lake brine; extraction system; mechanism*

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Modeling Phase Equilibria of Acetone – Water – Salt Mixtures

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Liquid-Liquid, Solid-Liquid, and Vapor-Liquid Equilibria in acetone water solutions with NaCl, Na_2SO_4, KCl, and K_2SO_4 were modeled using the Extended UNIQUAC model. Previous papers on the thermodynamic modeling of phase equilibria in acetone-water-salt solutions were limited to the modeling of vapor-liquid equilibrium.

According to the experimental data available in the open literature, solutions with K_2SO_4 do not split into two liquid phases and the lower consolute temperature of acetone water mixtures with KCl is 40 °C. The corresponding temperature for Na_2SO_4 solutions is reported to be 29.8 °C. For solutions with NaCl, liquid-liquid equilibrium was reported at temperatures down to 4 °C.

Figure 1 shows the experimental and calculated solid-liquid equilibrium curve in the Acetone-water-Na_2SO_4 system at 12 °C. With increasing acetone content, the water activity is lowered, resulting in anhydrous Na_2SO_4 becoming the stable solid phase rather than glauber salt, $Na_2SO_4 \cdot 10H_2O$. The acetone concentration required for this transition differs widely between the experimental studies available.

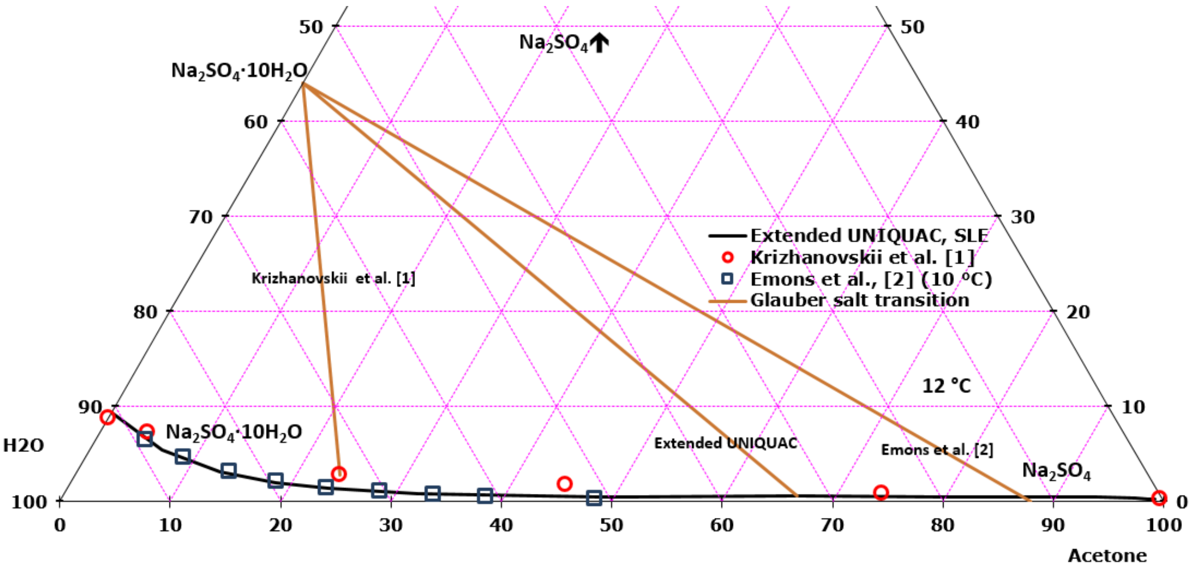

Figure 1. Experimental data and modeling result for solid-liquid equilibrium in the acetone-water-Na_2SO_4 system at 12 °C. The measured and calculated $Na_2SO_4 \cdot 10H_2O/Na_2SO_4$ transitions are marked.

The modeling was performed with the Extended UNIQUAC model which combines a Debye-Hückel term with the UNIQUAC local composition model.

Discrepancies between the reported experimental data for the system studied here is probably a contributing reason why the thermodynamic modeling of this system is more difficult than the modeling of similar systems containing alcohols instead of acetone.

Keywords: *Mixed solvent; Acetone; Liquid-Liquid Equilibrium; Solid-Liquid Equilibrium; Vapor – Liquid Equilibrium*

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Thermodynamics, Phase Equilibria and Phase Diagram on the Salt Lake Brine Systems

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Salt lakes in China are widely distributed in the area of the west of China, and there are a lot of valuable inorganic resources such as potassium salts, lithium salts, magnesium salts, sodium salts as well as the double salts of chlorides, sulphates and borates [1]. The following four aspects are concerned in this presentation:

Firstly, the online database of the salt-water systems established and the software of solubility prediction systems for the aqueous systems are introduced [2]. Secondly, studies on the phase equilibria on several types of salt lake brine systems are reported [3-6]. Thirdly, the thermodynamic properties on heat capacity, heat of dissolution, heats of dilution and mixing on the binary or ternary aqueous solution systems will be discussed. Finally, the industrial potassium fertilizer productions on potassium chloride and potassium sulfate are introduced.

Keywords: *Exploitation and Utilization; Phase Equilibrium; Database of salt-water system; Software of solubility prediction*

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Pore-confined Supercritical Fluids: the Universal Origin of the High Pressure Excess Sorption Maxima

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Adsorption of dense and compressible fluids is inherently more difficult to measure accurately than adsorption of gases, because accurate densities/volumes of the adsorbed phase become relevant for determination of excess sorption, but are generally not accessible to classical experimental adsorption methods. The density of the adsorbed (confined) supercritical fluid is relatively high, and at the same time susceptible to significant modification by the proximity of solid-fluid interface and by pressure.

Properties of light alkane hydrocarbons (C1-C3) and CO_2 confined in the pores of silica aerogel (nominal density 0.2 g/cm^3) were studied experimentally and by computer simulation. Five isotherms of ethane (25.0, 32.0, 32.3, 33.0, and 35.0) °C were measured over a temperature range including the critical temperature of the bulk fluid (T_c = 32.18 °C) to ~220 bar by the vibrating tube densitometry (VTD) method. The VTD approach, adapted to confined fluids, can yield unique information complementary to traditional excess sorption methods for microporous systems, while showing excellent agreement with gravimetric results for moderate pore sizes and moderate pressures. Two isotherms (35 °C and 50 °C) of methane adsorption in SiO_2 aerogel were measured far above its critical temperature, T_c = -82.59 °C, at 0 - 150 bar using the gravimetric method.

The experimental results for methane, ethane, propane and CO_2 show behavior conforming to the principle of corresponding states over the entire covered reduced temperature ranges from T_r = 0.976 to T_r = 1.696. The magnitudes of the excess adsorption maxima, and the reduced fluid densities where the maxima occur for C1-C3 hydrocarbons and CO_2, are similar functions of the reduced temperature. This similarity indicates that, under the conditions covered in this work, the differences in molecular size and shape have only minor impacts on the solid-fluid interactions underlying the adsorption behavior. The maxima of excess adsorption, observed experimentally at high fluid pressure and density, follow the extension of the vapor-liquid coexistence line into the supercritical region, approximated by the locus of maximum fluid compressibility or the Widom (pseudoboiling) line. The experimental results are supported by large-scale GCMC simulations of a lattice gas confined in the pores of a computer representation of the SiO_2 aerogel framework, yielding excess adsorption isotherms in good agreement with experiment, as well as the underlying microstructures of the adsorbed fluids.

Keywords: *confined fluids; high pressure adsorption; supercritical fluids; universal scaling laws; Widom line*

Carbon Dioxide-philic Open-Chain Crown Ether Bridged Diphosphate for Metal Ions Extraction in $scCO_2$

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The control of heavy metal pollution and the recycling of precious metals have increasingly become a hot issue in the world [1-4]. Traditional organic solvent extraction method is easy to cause secondary environmental pollution [5]. As a green technology, supercritical CO_2 chelating extraction (SCCE) of metal ions has obvious superiority to the traditional extraction methods. With its fast speed, high extraction efficiency and non-toxic properties, SCCE has great application prospects in the treatments of metals [6-7]. extraction of metal ions. Up to now, it has been acknowledged that the fluorinated chelating ligands are quite superior to the non-fluorinated ones. Unfortunately, the high cost and environmental toxicity hampered their large-scale application [8]. As a result, it is highly desirable to develop new efficient non-fluorinated chelating ligands for $scCO_2$, but it is still a challenge job in this field. It could afford CO_2-philic ligands by simply attaching CO_2-philic non-fluorinated groups to the chelating heads, however, which generally exhibited low $scCO_2$ extraction efficiency of metal ions, because of much more emphasis on the CO_2 affinity of the free ligands in the designing process. Therefore, the new design methodology is quite necessary.

A deeper insight into the interactions between metal chelates and CO_2 has been achieved by quantum chemistry and COSMO-RS calculations, and a new strategy for designing non-fluorinated ligands for $scCO_2$ was proposed by the combination of both concepts: (1) The positive charges on the central metal cation could be dispersed among the metal chelate system, avoiding highly-polar center; (2) The non-chelating donors could interact with CO_2 molecule, e.g. through the specific Lewis Acid (LA) - Lewis base (LB) interactions, energetically enhanced the CO_2-philicity of the metal chelate. Accordingly, series of open chain crown ether like diphosphate chelating agents were designed and exhibited considerable solubility in $scCO_2$. The ligands' structure effect on their solubility and their selectivity to the metals were studied through the extraction experiments and also the quantum chemical calculations. Satisfactory separation results were obtained in the extractions of lanthanides, heavy metals and alkaline earth metals and also the chelating mechanism was studied.

Keywords: *Supercritical CO_2; Chelating extraction; Molecule design; Open chain crown ether; COSMO-RS*

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Thermodynamic Behavior of Polymers Sensitive to pH

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Stimuli-response polymer particles are of the special interest for their unique phase-transition properties. Such transitions are usually accompanied by a reversible but discontinuous volume change due to large and abrupt physical and chemical changes in response to external variations in environmental conditions[1] such as pH[2], temperature[3], solvent composition[4], salt concentration[5], electrical field[6].

Polymers responsive to pH are polyelectrolytes or have hydrophilic functional groups that bear acid or base groups in their structure as carboxylic acid (-COOH), sulfonic acid (-SO_3H), alcohols (-OH) or primary, secondary or tertiary amines groups[7]. These groups allow to materials to either protonate or deprotonate in response to the changes in their environmental pH allowing them to shrink or swelling[8].

In this work, two series of polymeric particles functionalized with different concentrations of acrylic acid (10, 15, 20 and 25 wt.%) were synthesized by emulsion polymerization techniques and two morphologies of particles were prepared. The first consisted of particles with multilayer morphology which were synthesized by a semicontinuos process in four stages. The second was particles with a homogeneous morphology, which were synthesized in a power feed semicontinuos process. In both cases, a gradient of concentration of carboxylic groups was generated inside the polymeric particles. The materials were treated with NaOH solution and their sensitivity towards pH changes were evaluated by measuring their volumetric and calorimetric thermodynamics properties and SEM.

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Self-assemblies in Green Solvents

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Supercritical CO_2 and ionic liquids, which are usually regarded as green solvents, have some unique properties that are different from the common solvents (water and oil). To construct the self-assemblies in supercritical CO_2, ionic liquid and mixed solvent systems is very attractive owing to their unusual and tunable solvent properties. In this presentation, I will discuss our recent researches on self-assemblies in green solvents. Various new assemblies, including amphiphilic molecular assemblies and self-assemblies of functional materials (*e.g.* metal-organic framework, graphene oxide) have been constructed in green solvent systems. Their microstructures and properties can be easily adjusted by controlling the properties of solvents (*e.g.* CO_2/ionic liquid, CO_2/water, ionic liquid/water, CO_2/polyethylene glycol, *etc*). The as-constructed assemblies in green solvents have been utilized as promising "microreactors" for material synthesis and chemical reaction.

Keywords: *Self-assemblies; Green solvent; Supercritical CO_2; Ionic liquid; Microstructures and functions*

Scales of Solvent Acidity, Basicity and Polarity – Experimental Basis and Relation to Molecular Properties

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The use of linear free energy relationships to rationalize solvent effects on chemical processes makes use of a series of parameters, generally but not exclusively experimental, that capture specific qualities of a solvent, such as Lewis[1] or hydrogen bond basicity[2] and acidity[3][4] and the ability to stabilize charge by non-specific interactions, commonly called polarity{5][6]. While the operational descriptions of these parameters, basicity, acidity and stabilization of charge are immediately recognizable, their connection to the underlying properties of the solvent molecules are less clear.

Recently we have correlated a number of these solvent parameters with solvent descriptors reflecting different molecular properties estimated from computational chemistry of the optimized, gas phase, molecular structures. These have shown, for example, that the strong correlation between Gutmann's donor number, a measure of Lewis basicity and Kamlet and Taft's β, a measure of hydrogen bond basicity, results from both parameters being substantially determined by the partial charge on the most negative atom and the energy of the charge donating orbital (broadly the HOMO) of the solvent molecules[7].

This talk will concentrate on the Gutmann[1][3], Kamlet and Taft[2][4], and Reichardt parameters[6] and will review their experimental bases and the relationships among them.

The relationships between the experimental parameters and molecular properties, derived from gas phase quantum mechanical calculations will be presented and discussed.

Finally, a number of issues that arise from the limitations of computational chemistry will be discussed.

Keywords: *Solvent parameters; Acidity; Basicity; Solvent polarity; Computational chemistry*

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Thermophysical Properties Research of Alterative Refrigerants

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This presentation briefly reviews some representative works about alternative refrigerants over past 20 years in our thermodynamic research group at Xi'an Jiaotong University, for example the refrigerant mixture of R152a/R125 was proposed as working fluid in refrigerators. According to existing international agreements, refrigerant mixtures currently viewed as promising alternatives, especially HFO/HFC mixtures, should be studied thoroughly on their thermophysical properties. The apparatuses for measuring different thermophysical properties were established to obtain reference experimental data with high accuracy (such as PVTx, Vapor Liquid Equilibrium, thermal conductivity, viscosity, etc.). Based on these data, reference models for optimizing refrigeration equipment have been well developed.

Keywords: *Thermophysical properties; refrigeration; experimental apparatus; thermophysical models.*

Hydration of Inorganic Anions in Aqueous Solution, Structure and Hydrogen Bonding

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Structure determination of hydrated metal ions in aqueous solution has been subject for numerous studies.[1-3] However, for hydrated anions in aqueous solution only some have been studied thoroughly including the halide ions and some oxo-anions as sulfate, phosphate and perchlorate.[1,2] The structures and the strength of the hydrogen bonding of the most common oxo-anions in aqueous solution will be presented. The structures have been determined by means of large angle X-ray scattering (LAXS), and in some cases also by EXAFS. The hydrogen bond strength of the hydrating water molecules have been determined by means of double difference infrared spectroscopy (DDIR) using the O-D stretching in water containing ca. 8% HDO.[4] Monovalent oxo-anions are regarded as structure breakers as the hydrogen bonds between the hydrating water molecules and the anion oxygens are weaker than between water molecules in pure water,[5] while the opposite is found for the di- and trivalent metal oxo-anions. The DDIR measurements show also that the mono- and divalent oxo-anions have only one well-defined hydration shell, while trivalent oxo-anions have two such shells. Another interesting observation is that each oxo-anion oxygen atom hydrogen binds to three water molecules for anions with a central atom in the third series (e.g. P, S and Cl), while for heavier elements only two water molecules are hydrogen bound to each anion oxygen atom.

Keywords: *Hydration, Anions, Structure, Strength of hydrogen bonds*

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Unveiling the Structural Properties of Liquid Mixtures Using A Method Combining Excess Spectroscopy and Quantum Chemistry

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Liquids are much more complicated than gases and crystals. They do not like gases which are characterized by far separation of molecules and thus can be dealt with the perfect gas law or its modified forms, nor do they like crystals which have well defined structures and thus can be treated by the laws of solid-state physics. What’s more, liquids are not completely disordered. They are long-range disordered and short-range ordered. Specific molecular interactions including hydrogen-bonding and halogen-bonding would allow the occurrence of various associates/clusters/complexes. Although there have been discussions on these concepts for long, identification of them is very difficult, if not impossible.

In this contribution, a method for identifying the associates/clusters/complexes in liquid mixtures will be presented. It is based on excess spectroscopy, developed in our laboratory (see Figure 1 for some examples), and assisted with quantum chemical calculation. Here the special spectroscopic technique is used to work out more peaks, while quantum chemical technique is employed to assign the peaks to species in liquid samples. Various systems have been examined in our laboratory including ionic liquid-molecular solvent systems with focuses on both hydrogen bonding and halogen-bonding interactions.

A particularly case is that there are only two different existing forms of a molecule in a binary liquid solution. In this so-called two-state situation, the excess infrared spectra of a vibration mode of the respective molecule will show identical band shape if the other component is transparent in the region. More conveniently, the positions of the positive peak, negative peak, and zero-value will be seen to be fixed with varying compositions of the binary system. On the contrary, if these positions are concentration-dependent, it is a non-two-state situation, implying there are more than two existing forms of the examined component in the solution.

Keywords: *Excess spectroscopy, Solution chemistry, Molecular Interaction, Associate, FTIR*

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Computational Chemistry Applied to Solutions

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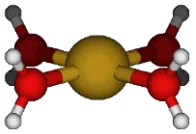
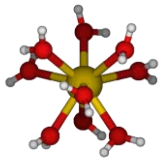
Ab initio computational chemistry has been employed in the past by the author to interpret the vibrational spectra of cations such as Li^{+}[1,2], Cd^{2+}[3], Mg^{2+}[4], Zn^{2+}[5], Sc^{3+}[6], Al^{3+}[7], Ga^{3+}[8], In^{3+}[9], Bi^{3+}[10], and Be^{2+}[11]; anions such as SO_4^{2-}[12], PO_4^{3-}[13], HPO_4^{2-}[14], $H_2PO_4^{-}$[15], ClO_4^{-}, BrO_4^{-}, SeO_4^{2-}, AsO_4^{3-}, VO_4^{3-}[16] and the borates[17]; and ion pairs such as LiX (X = F – I)[18], $ScCl_m^{(3-m)+}$ (m = 1 – 6)[19], $ZnCl_m^{(2-m)+}$ (m = 1 – 6)[20], $ZnBr_m^{(2-m)+}$ (m = 1 – 6)[21], and $CuCl_m^{(m-1)-}$ (m = 0 – 6)[22], in aqueous solution. Symmetry and group theory has been an invaluable aid in calculation and interpretation.

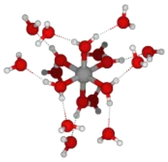
In this talk, the author will discuss the use of symmetry and group theory and its application to three cationic systems: $Cu(H_2O)_n^{+}$, n = 0-6; $M^{m+}(H_2O)_n$, n = 1-9, $M^{m+} = Hg^{2+}$, Tl^{3+}, Pb^{2+}, Sn^{2+}, Sb^{3+}; and $M^{m+}(H_2O)_{18}$, $M^{m+} = Mg^{2+}$, Zn^{2+}, Cd^{2+}, Al^{3+}, Sc^{3+}, Ga^{3+}, and In^{3+}.



$Cu(H_2O)_4^{+}$ D_{4h}



$Pb(H_2O)_9^{2+}$ C_3



$Mg(H_2O)_{18}^{2+}$ [6+12] T

Keywords: *ab initio, vibrational spectra, solutions, ions, symmetry*

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A Partially Perturbative Density Functional Theory for Electrokinetic Properties

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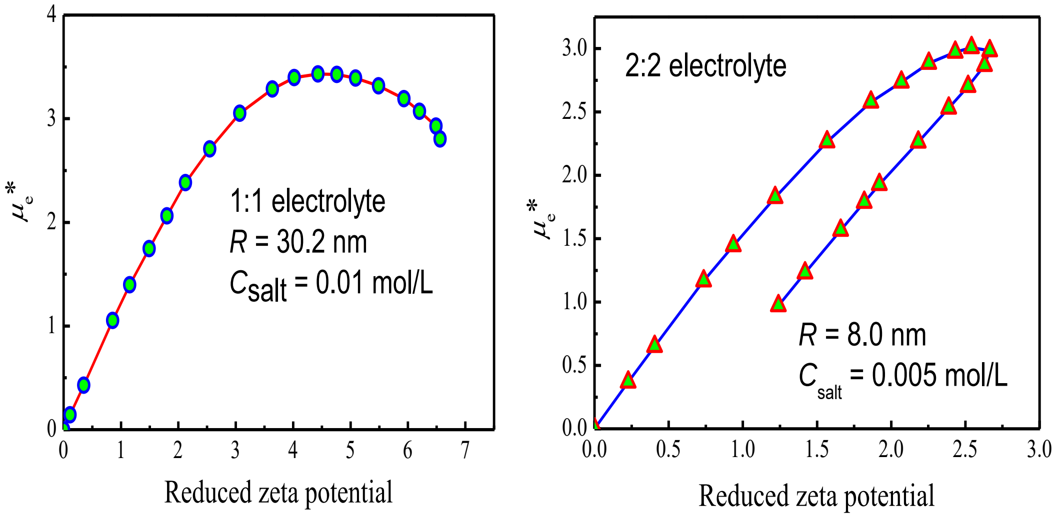
Electroosmotic flow (EOF) and electrophoretic mobility induced by an external electric field has a variety of practical applications. The Poisson-Boltzmann (PB) equation which is based on the continuum theory fails to describe the ion distribution accurately in the charged cylindrical nanopores, due to its neglect of the volume of the ion and the correlation between the ions. A partially perturbative density functional theory (PDFT) which takes these factors into account is applied to investigate the ion distributions in the pore. A variety of electrolyte solutions, both charge symmetric and asymmetric, can be correctly characterized by the theory. Based on ion distributions given by the DFT, the transient velocity profile of the EOF is studied with the Navier-Stokes (NS) equation, by assuming the viscosity of the solution in the pores is the same as the solvent. The characteristics of the EOF are discussed under the influences of the intensity of the external filed, the bulk density and the thickness of the electric double layer. Some special phenomena which can't be found in the traditional treatment, such as the fluctuation of the velocity and charge reversal can be captured by the theory. The abnormal distribution of the charge in nanoscale which is induced by the intensive interactions between ions and between ions and the charged wall is thought to be the main cause of the phenomena. Our results show that DFT combined with various hydrodynamic equations is successful in prediction of dynamic properties of electrolytic systems.



(a) 1:1 electrolyte (b) 2:2 electrolyte

Fig. 1. Comparison of calculated results from the PDFT with those from simulations.

Keywords: *electrolyte solution; electroosmotic flow; electrophoretic mobility; density functional theory*

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Real-Time in-Situ NMR of Biologically Relevant Reactions in Peptide Solution: Spontaneous Peptide Bond Cleavage of Aspartyl Isomers and Preaggregation of Amyloid-Fragments

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In-situ analytical methods are essential for the reliable observation of biologically relevant reactions in peptide solution without perturbation of the system. NMR is a versatile noninvasive technique that provides site-selective information about both static and dynamic properties of peptides in solution. The low-sensitivity problems have been nowadays overcome by the improvement of the computerized instrumentation and the stable, homogenous generation of the high magnetic field. Here we present an ability of NMR to quantify real time processes of biologically relevant reactions *in situ*, via intra- and intermolecular interactions of peptides in solution.

The first example is a spontaneous, non-enzymatic peptide bond cleavage at an aspartyl (Asp) residue. It has been reported that D-β-Asp is typically accumulated in aged eye lens αA- and αB-crystallins at Asp58 and Asp62, respectively [1]. High resistance of D-β-Asp to biomolecular reactions is predictable, that is, less reactivity of D-β-Asp is expected to the spontaneous peptide bond cleavage. We have compared bond cleavage reactions at L-α- and D-β-Asp residues, by applying real-time solution-state ^{1}H NMR to αA-crystallin 51–60 fragment, $\mathrm{S^{51}LFRTVLD^{58}SG^{60}}$, and αB-crystallin 61–67 analog, $\mathrm{F^{61}D^{62}TGLSG^{67}}$. Kinetic analysis showed how tough the uncommon D-β-Asp was against the peptide bond cleavage as compared to natural L-α-Asp [2]. Differences in pK_a and conformation between L-α- and D-β-Asp side chains were plausible factors to determine reactivity of Asp isomers via the formation of intramolecular cyclic anhydride intermediate [2]. The study, for the first time, provides a rationale to explain less reactivity of D-β-Asp to allow abnormal accumulation with time. Second is a real-time in-situ NMR observation of the aggregation of amyloid-beta (Aβ) 8–25 fragments, $\mathrm{S^{8}GY^{10}EVHHQKLVFF^{20}AEDVG^{25}}$ in solution prior to the fibril formation. Although the final structure of Aβ fibril has been determined at atomic resolution [3], the initial stage of its aggregation is still to be solved. The NMR chemical shift and the intensity changes in combination with the CD spectra revealed the presence of soluble, small oligomeric intermediates in addition to Aβ monomers in solution, followed by the appearance of insoluble, large aggregates in advance of the formation of β sheet structure. Molecular views of intermediates and aggregation mechanisms were proposed in comparison with NMR spectral changes in wild-type Aβ8–25 and its two mutants, A21G and E22G. It was found that the mutation of just one amino acid modified aggregation properties of Aβ8–25; it slowed or accelerated the fibril formation by controlling the progress of conversion from monomer to aggregate via a soluble, small oligomer

Keywords: *Real-time in-situ NMR; Peptide bond cleavage; Aspartyl isomer; Aggregation; Amyloid-beta*

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Abnormal Dynamics of Water Molecules on the Protein Surface

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Dynamics of hydration water is essential for the functionality of enclosed protein molecules. Diffusing water not only transports enzymatically essential ingredients, e.g., ions, substrates and protons, into the catalytic sites of proteins, but also renders internal flexibility necessary for the functioning of bio-macromolecule. It has been demonstrated that water molecules exhibit sub-diffusion on protein surfaces; yet the microscopic mechanism remains vague. Here, we combine neutron scattering experiments with molecular dynamics simulations and analytic modelling to study dynamics of hydration water in protein powders. We find that water molecules jump randomly between trapping sites on protein surfaces. The trapping times of these sites follow a broad, power-law distribution, which results in sub-diffusion. Moreover, the rotation and translational motion are gradually decoupled towards the surface of the bio macromolecules. This decoupling effect is particularly pronounced for water molecules which have a structural role to stabilize the protein molecule and facilitate the protein function.

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Ion Hydration and Association in Aqueous Electrolyte Solutions in the GPa Range

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The properties of aqueous electrolyte solutions and chemical reactions taking place in the solutions originate from the ion-water (ion hydration), ion-ion (ion association), and water-water (hydrogen bonds) interactions. Thus, it is essential to investigate the structure of aqueous electrolyte solutions at the atomic level. Hydrated ions are classified as structure making and structure breaking ions, depending on ionic size and charge. When pressure and temperature are applied to water, hydrogen bonding in water and the resulting structure and properties are perturbed substantially, which has provided us a hint to understand the nature of hydrogen bond and water [1]. Owing to the advent of high-temperature and high-pressure techniques in x-ray and neutron diffraction along with the intense synchrotron radiation and pulsed neutron facilities available worldwide, x-ray and neutron diffraction experiments in the GPa range and at a few thousand K are now possible [2]. In recent years, aqueous electrolyte solutions under extreme conditions have drawn much attention in both fundamental and applied sciences, such as hydrothermal vents at the 500~3000 meter depth of the ocean which is rich in precious minerals. Electrolyte solutions in the GPa range exist near the boundary of continental plates and above the mantle of the earth, which might be responsible for earthquake and eruption of the volcano.

In the present study, X-ray and neutron diffraction experiments are performed on aqueous chloride solutions of a series of monovalent and divalent metal ions at 300 to 523 K and several GPa by using a synchrotron radiation facility (SPring-8) and a pulsed neutron facility (J-PARC MLF). The experimental structure factors are subjected to empirical potential structure refinement modeling to reveal the details of ion hydration and association and solvent water in terms of the pair correlation function, coordination number distribution, and 3-dimensional spatial density function. The structural properties of aqueous electrolyte solutions are discussed at the molecular level concerning pressure, temperature, and ionic size [3].

Keywords: *Water; Electrolyte solution; X-ray and neutron diffraction; high-pressure*

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Compatible Osmolytes-Bioprotectants: Is There a Common Link Between Their Hydration and Their Protective Action under Abiotic Stresses?

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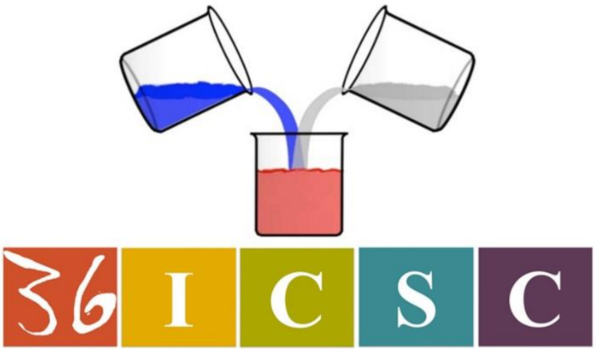
Compatible osmolytes accumulate in the cell cytoplasm to protect structure of proteins and enzymes under abiotic stresses. It is assumed that the osmolyte hydration is playing an important role in their protective mechanism. However, the details of osmolyte interactions with water surroundings are far from being fully understood. This contribution will summarize the recent own data on the hydration structure of a set of compatible osmolytes such as glycine, TMAO, proline, ectoine, glycine-betaine under effect of concentration, temperature, pressure, and salt addition as well as their ion-binding. A link of the hydration features as well as ion-binding of osmolytes with their biological role will be discussed.

Keywords: *Compatible osmolytes; Hydration; Ion-molecular binding; Abiotic stresses*



Oral Lectures

Comprehensive Thermodynamic Models and Phase Diagram Prediction for Typical Salt-lake Brine

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Phase diagrams are the basic tools for processes industry developments. Since the multitudinous species and complex structure of electrolyte aqueous solution, the expression of physical properties, phase equilibria and phase diagrams, are the difficulties and persistent hot spots in the research for more than 100 years.

In recent years, in order to meet the needs of salt-lakes resources development, the physical properties phase behaviors and phase diagrams in the whole temperature range for chloride type and sulfate type brine in Qinghai Salt Lake should be simulated. Thus one comprehensive thermodynamic models improved from the classical eNRTL models were proposed, which can deal with the complex brine containing ions species of Na^+, Mg^{2+}, Ca^{2+}, K^+, Li^+, Cl^-, SO_4^{2-},etc.

The comprehensive thermodynamic models account for an improved Symmetrical PDH term, one local composition term (NRTL part) and the chemical contribution term. The liquid phase non-ideality was expressed by two binary interactions of water-electrolyte and electrolyte-electrolyte interactions. The binary interaction energy parameters with the temperature dependence expressed in a Gibbs-Helmholtz type equation. The three temperature coefficients for the binary parameters are related to the excess Gibbs energy, the excess enthalpy, and the excess heat capacity contribution terms, respectively.

With the binary and ternary parameters, the model provides accurate representation and reliable predictions for various thermodynamic properties. The complete phase diagrams for 20 ternary systems from low temperature of eutectic point (even less than -84℃) to boiling temperature under normal pressure have been predicted. The model is expected to cover more ions simultaneously.

Keywords: *Electrolyte aqueous solution; Properties; Phase diagram; Symmetric eNRTL; Salt lake Brine*

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Acknowledgments

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Experimental Measurement of the Solubility of Gramine in Five Low Alcohols from (291.25 to 323.15) K

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Gramine is a kind of alkaloids and it has high sterilization performance.[1,2] It is a key intermediate in the synthesis of tryptophan and other chemicals, especially pesticides with high efficiency, low toxicity, low resistance and low residue. The purification of gramine was usually carried out through recrystallization with 95% ethanol. However, the solubility of gramine was scarcely reported in literature. In this article, the solubility of gramine was measured using synthetic method in five low carbon alcohols, including methanol, ethanol, 1-propanol, 2-propanol and 1-butanol from 291.25 to 323.15K.

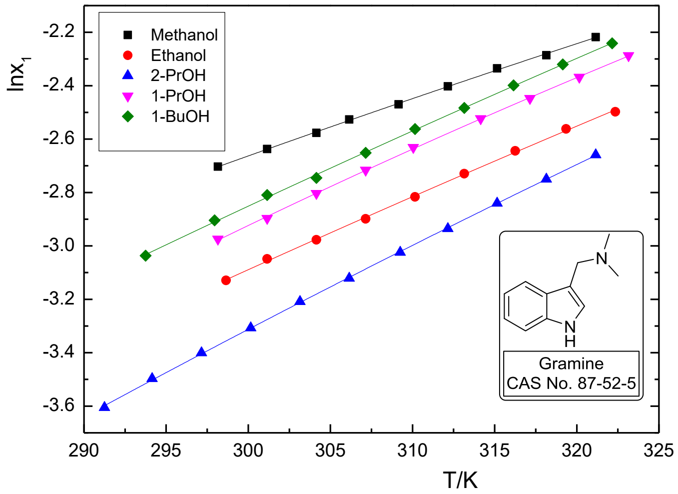

Fig 1. Solubility of gramine in different low carbon alcohols, scatter ■, methanol; ●, ethanol; ▼, 1-propanol; ▲, 2-propanol; ◆, 1-butanol. Solid line, computed data based on the modified Apelblat equation.

The solubility of gramine in different low carbon alcohols increases with the rise of temperature and follows the ladder of methanol > 1-butanol > 1-propanol > ethanol > 2-propanol, which is different from the polarity of the solvent [methanol (76.2) > ethanol (65.4) > 1-propanol (61.7) > 1-butanol (60.2) > 2-propanol (54.6)]. Polarity is not the sole factor affecting the solubility. As we have disclosed in other system[3], the solubility behavior is the net contribution of polarity, dipole moment, dielectric constant and Hildebrand solubility parameter. These data could be serve as fundamental data for its purification.

Keywords: *Gramine; Solubility; Modelling*

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Variable Temperature Chemical Model Study on Equilibrium Solubilities in the Ternary System $NaCl–NaBO_2–H_2O$

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Solubilities of the ternary system $NaCl–NaBO_2–H_2O$ at 323.15 K were investigated with the isothermal dissolution equilibrium method. The phase diagram consists of three single-salt crystallization regions for NaCl, $NaCl·NaBO_2·2H_2O$ and $NaBO_2·4H_2O$, three univariant solubility curves and two invariant points. A comparison of the diagrams of this system from 288.15 to 323.15 K shows that area of $NaBO_2·4H_2O$ region decreased whereas the areas of $NaCl·NaBO_2·2H_2O$ increased obviously [1,2]. The Pitzer binary parameters of $NaB(OH)_4$, Pitzer mixing parameters $\theta_{Cl,B(OH)4}$ and $\Psi_{Na,Cl,B(OH)4}$, and the solubility product constant (Ksp) of $NaCl·NaBO_2·2H_2O$ and $NaBO_2·4H_2O$ were fitted with the solubility data at 323.15 K (the present study) and 288.15 K, 298.15 K and 308.15 K in literatures on the basis of Pitzer model. The variable temperature chemical model for above parameters from 288.15 K to 323.15 K was built. The model was then used for predicting the solubilties of the ternary systems. The experimental solubilities agree with the theoretical results calculated with the Pitzer parameters and Ksp of the salts. The results show that the boron ions in the above systems can be considered as $B(OH)_4^-$, which is the same as those in the literature [3]. These results on phase diagrams and thermodynamic models of system $NaCl–NaBO_2–H_2O$ can supply theoretical reference for borate separation from chloride type brine.

Keywords: *Solid-liquid phase equilibrium; Pitzer thermodynamic model; Sodium metaborate; Solubility calculation; Phase diagram*

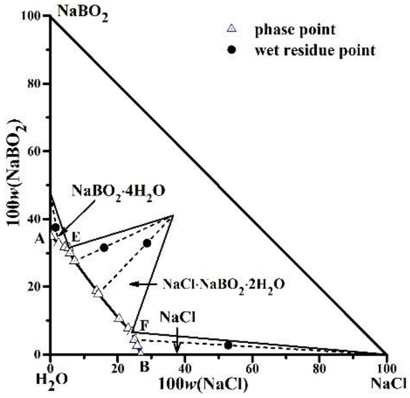

Fig 1. Phase diagrams of the ternary system $NaCl–NaBO_2–H_2O$ at 323.15 K

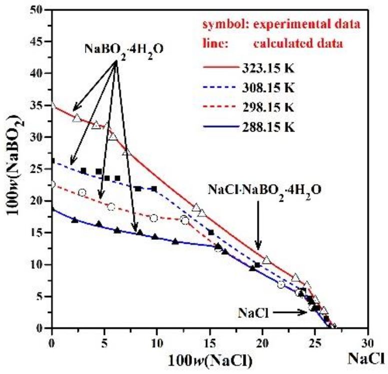

Fig 2. Experimental and calculated phase diagrams of system $NaCl–NaBO_2–H_2O$

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Ionic Liquids in Solutions: from Simple Electrolytes to Surfactants

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Over recent decades ionic liquids (ILs) attracted the attention of many researchers as suitable systems for a wide range of applications. Favorable physical and chemical properties of ILs, such as high thermal and electrochemical stability, large liquidus range, non-flammability, biodegradability and recyclability, make them interesting to so-called green solvents with little waste, risk and hazard problems [1]. It has been found [2] that ILs are more complex than molecular solvents and thus their bulk and interfacial structures are markedly different. ILs show rich structural diversity both in the nature of ions that can be employed as well as in the organization of these ions in the liquid phase. By increasing the alkyl cationic side-chain length even the transition from the known spatially heterogeneous structure to a liquid crystal-like phase was observed [3]. However, the growing number of reviews dealing with the physico-chemical properties of ILs in their pure state has been extended to investigations of their mixtures with molecular co-solvents.

In this contribution first it will be shown, that ILs in solutions can serve as excellent model (electrolyte) systems, because they exist in diverse structure and the hydrophobic part of the cation can be vary almost optional. Investigations of ion association of ILs in diverse organic solvents reveal namely that their ion pairing is entropy driven and thus associated with cation desolvation, in line with the only moderate strength of cation-solvent interactions [4],[5]. The association of imidazolium based ILs as model 1,1-electrolytes in water solutions is weak but evidently dependent on the molecular structure (alkyl chain length), which also strongly affects the mobility of imidazolium cations [6]. According to experimental and computational results, hydrophobic hydration of the side chain on the imidazolium ring is most responsible for structure making/breaking properties of investigated imidazolium salts [7].

Next, ionic liquids with long alkyl chains will be discussed They behave similar to conventional surfactants forming aggregates in water [8],[9], but due to the possible variations in the chain length and counter-ions they are extremely appropriate for studying ion and isomer effects on self-assembly processes in solutions.

In summary, ILs exhibit properties from simple salts to liquid crystal-like structures and there are still many unexplored opportunities for manipulating their structure to control their functions and applications, especially in solutions.

Keywords: *Ionic liquids; Solutions, Electrolytes; Surfactants*

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A High-throughput Strategy for the Discovery of Multifunctional Ionic Liquids Reaction System

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Development of novel chemical processes with simplified reaction systems and work-up procedures is a great challenging task [1, 2]. Although ionic liquids are considered as a class of potential multifunctional materials to simplify traditional chemical processes, their rational design is difficult due to the complex interactions [3, 4]. In this work, a proof-of-concept strategy has been proposed to achieve an integration of high-throughput preparation of ionic liquids and in situ screening of their reaction-promoting performances in 96-well plates. The integrated approach then enables a facile identification of optimal ionic liquids from a 400-ionic liquid candidate pool for carbonyl-azide cycloaddition reactions. The functions of ionic liquid involve solvent, catalyst and separating assistant, simultaneously. The merits of the optimized ionic liquids-based processes have been demonstrated not only in the convenient and efficient synthesis of 1, 2, 3-triazolyl compounds, but also in the discovery of a new reaction for the chemical post-modification of free peptides.

This high-throughput strategy efficiently avoids the missing of some useful ionic liquids from combination of cations and anions due to the subjective bias, and gives a new pathway for the recognition of relationship between structure and properties of ionic liquids.

Keywords: *high-throughput strategy; functional ionic liquid; complex interactions; 1,2,3-triazolyl compounds; peptides post-modification*

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Utilization of Shrimp Shells with Ionic Liquids and Deep Eutectic Solvents

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The waste shrimp shells contain plenty of chitin, which can be extracted and converted to high-value products. The chitin and chitin-based products have been applied in various fields including medicine, agriculture, and textile industry, which is valuable and sustainable [1]. However, the traditional solvents for preparing chitin and chitin-based products are acid and base and special organic solvents, which no long meets the environment requirement now. Ionic liquids (ILs) and deep eutectic solvents (DES), as new generation green solvent, have low vapor pressure, designable structure, and numerous hydrogen bonding net. They provide new options for chitin extraction and utilization. Herein, this work used the shrimp shells as raw material to prepare chitin, chitin/Zn composite, and O-acylated chitin, providing alternation for waste shrimp shells utilization.

Chitin is prepared using choline-based ionic liquids (IL) from shrimp shells in one step. Under optimal conditions, the chitin with 92% purity was obtained, and the yield was up to 78%. Moreover, the chitin/Zn composite and O-acylated chitin were directly prepared from shrimp shells using DES urea/$Zn(OAc)_2 \cdot 2H_2O$ aqueous solution and choline chloride/organic acid, respectively. The used DESs all played three roles, namely decalcification, deproteinization, and function. Under the optimal conditions, the chitin/Zn composite with purity of 99.1% and 13.4% zinc was prepared, which showed good antibacterial effect. The O-acylated chitin with 98.6 % purity and DS of 0.46 was obtained under optimal conditions, showing exhibited antibacterial and anti-tumor effect.

Keywords: *Shrimp Shells, Ionic Liquid, Deep Eutectic Solvent, Chitin, Chitin-based Product*

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Acknowledgments

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A Mechanism Study on Absorption of Humid CO_2 by [Emim][Gly] Ionic Liquid

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As designable solvents, ionic liquids have many excellent properties and play an important role in CO_2 capture [1-3]. In this work, 1-ethyl-3-methylimidazolium giycinate ionic liquid ([Emim][Gly]) was synthesized and characterized, and then used to absorb CO_2 containing trace water. The effect of [Emim][Gly] ionic liquid's structure on humid CO_2 absorption capacity was investigated, and the absorption mechanism was studied by NMR and IR spectroscopy. The main conclusions are as follows.

1. It was shown that the melting point / glass transition temperature of the ionic liquid synthesized in this work was below -55℃, and the thermal decomposition temperature was higher than 200℃. Thus, [Emim][Gly] ionic liquid had good heat stability.
2. The [Emim][Gly] ionic liquid was used for humid CO_2 absorption. It was found that this ionic liquid could adsorb humid CO_2 in nearly 1:1 molar ratio. This absorption capacity was almost twice that of dry CO_2 absorbed by [Emim][Gly] ionic liquid.
3. Absorption mechanism studies have confirmed that in the preliminary stage of ionic liquid absorption of humid CO_2, the absorbed trace water had little effect on the absorption process. As the absorption time was increased to about 1h, the inhalation of H_2O resulted in the production of $[HCO_3]^-$ in the system and activation of the C2 site of the imidazolium cation. The activated site then reacted with CO_2 to form imidazolium-2-carboxylate (NHC-CO_2).

Keywords: *[Emim][Gly]; ionic liquid; humid CO_2; imidazolium-2-carboxylate.*

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CO_2 Separation Using a Hybrid Choline-2-pyrrolidine-carboxylic Acid/Polyethylene Glycol/Water Absorbent

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Developing novel hybrid absorbents is essential for CO_2 separation. In this study, the density and viscosity of a hybrid absorbent (choline-2-pyrrolidine-carboxylic acid/polyethylene glycol/water ([Cho][Pro]/PEG200/H_2O)) were measured experimentally, and its CO_2 solubility was also determined. The excess mole volume and excess Gibbs energy of activation of the hybrid absorbent were further estimated to understand the molecular structure and interactions between [Cho][Pro]/PEG200 and H_2O. The CO_2 solubilities in [Cho][Pro]/PEG200 and [Cho][Pro]/H_2O were analyzed and described using the Redlich–Kwong non-random-two-liquid (RK-NRTL) model. Furthermore, the CO_2 solubility in the hybrid absorbent was predicted using the RK-NRTL model and was compared with the new experimental results for verification. The effect of H_2O on the CO_2 absorption performance was further analyzed. The performance and cost of the hybrid absorbent were compared with those of other commercialized CO_2 absorbents. In addition, the recyclability of the hybrid absorbent for CO_2 separation was studied. The results of this study indicated that the hybrid absorbent could be promising for CO_2 separation.

Adsorption of Bacteria by Highly Efficient, Economic and Biodegradable Magnetic Coated Chitosan

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Adsorption can be considered as a versatile and green technology for waste water treatment because of no problem of sludge formation and secondary pollutants [1]. The use of magnetic based chitosan nano-adsorbent is very important because of their bio-degrability, non toxicity and easy preparation and handling, and separation from solution after adsorption experiments [2]. The current research focuses on the adsorption of both Gram positive and Gram negative bacteria on magnetic coated chitosan adsorbent. The results showed that magnetized chitosan was found to be an excellent adsorbent for bacteria removal. The PZC value for adsorbent was determined by salt addition method, while confirmation of composite formation and mechanism of adsorption was done by FT-IR. The morphology, surface area and thermal stability of adsorbent was performed by SEM, TEM, BET and TGA. It was observed that that bacteria adsorption was enhanced with increasing concentration of adsorbate and dosage amount. The adsorption process was maximum in pH range from 4-8 and temperature range from 20-50ºC. Langmuir adsorption isotherm was found to be well applicable to the equilibrium data and Pseudo first order kinetic model described well the kinetic data. Maximum adsorption capacity was observed to be 96%. Thermodynamic studies provided that the adsorption process is spontaneous and endothermic in nature.

Keywords: *Bacteria; Chitosan; Adsorption; Kinetics; Thermodynamics*

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Research Progress in Phase Equilibria of Salt-Water System at Low Temperature

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Various types of complex salts will crystallize out in the treatment processing of the salt lake brine, which results in the complexity of the process. The phase equilibria of different salt-water systems at different temperatures have been studied in this paper. The research shows that: for the salt-water systems associated with sulfate, the crystallization regions of complex salt sulfate-based appear at room temperature, even dot not disappear easily at high temperature; on the contrary, the low temperature can limit the generation of the sulfate-bsaed double salts, and the crystallization regions of that disappear or reduce; For the complex salts involved in nitrate and magnesium chloride, at high or low temperature, the crystallization regions become small or disappear. This phenomenon indicates that studying the phase equilibria of salt-water systems at low temperature is helpful to simplify the production process. Therefore, the low-temperature pretreatment can offer an alternative way for the treatment of brines in accordance with the necessity for current brine treatment processes to reduce the presence ofcomplex salts and be crucial for more pure products to be separated.

Keywords: *salt-water system; low temperature; phase equilibrium; double salts*

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Prediction of Vapor–Liquid Equilibria of Alcohol + Hydrocarbon Systems by ^{1}H NMR Spectroscopy

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The ^{1}H NMR chemical shifts of alcohol + hydrocarbon systems over the whole concentration range at 298.15 K were measured. Based on the concept of local composition (LC) [1], the concentration-dependent ^{1}H NMR chemical shift data of the OH and CH groups for 13 alcohol + hydrocarbon systems were correlated with only one energy parameter (Fig. 1), respectively. Using the parameters obtained from the spectra alone, the isothermal and isobaric vapor–liquid equilibria (VLE) data of the above-mentioned alcohol + hydrocarbon systems were predicted with satisfactory results (Fig. 2) [2]. By this way, the spectroscopic information can be used to predict VLE data of alcohol + hydrocarbon systems directly.

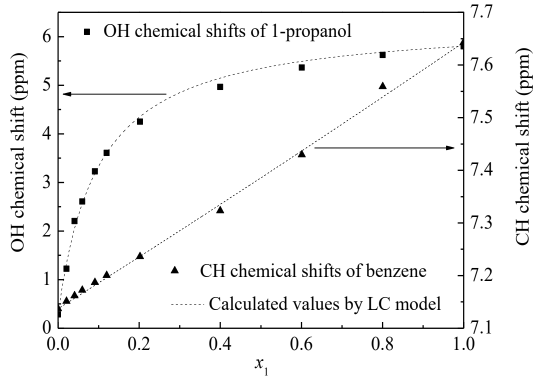

Fig 1. Comparison of the experimental and correlated ^{1}H NMR chemical shifts of 1-propanol(1)+cyclohexane (2) system.

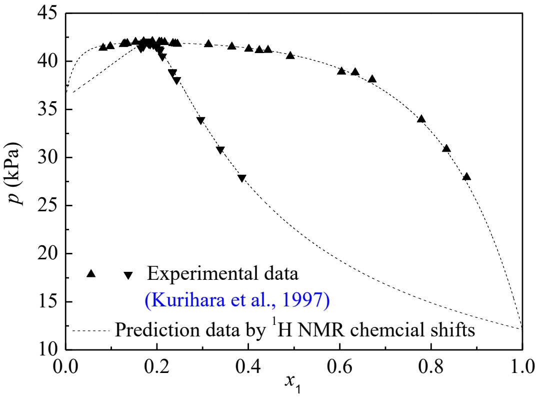

Fig 2. Comparison of the predicted VLE data and experimental data from the literature of 1-propanol (1)+benzene (2) system.

Keywords: *Phase equilibria; Thermodynamics; Microstructure; NMR; Local composition*

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Vapor-Liquid Equilibrium of HCl-H_2O System at Low Pressure

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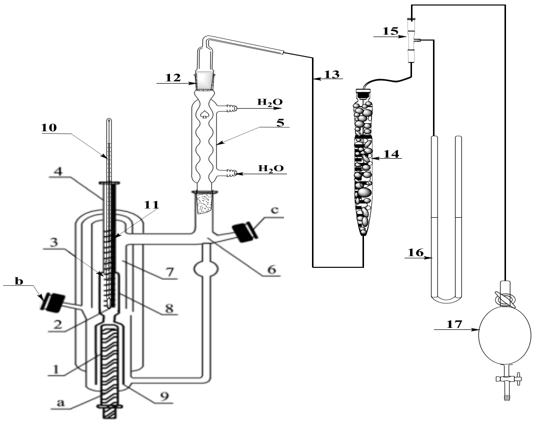
The dilute hydrochloric acid discharges from some salt lake chemical processes. There also exist plenty of bischofite resources in salt lakes of Qinghai Province, China. In order to collect basic data for the desorbtion of these dilute hydrochloric acid by the dehydration products of bischofite, the gas-liquid equilibrium of HCl-H_2O binary system at the low pressure in the Qinghai-Tibet Plateau was studied.

The geographical location of the experimental site was E101°45', N36°44', and the atmospheric pressure ranged from 77.1 kPa±0.42 kPa. The Vapor-liquid equilibrium data of the HCl-H_2O binary system was determined by a self-modified CE-2 type double-circulation vapor-liquid equilibrium glass reactor (Fig.1). Samples were measured using a ThermoFisher ICS-1100 ion chromatograph. The standard curve equation of Cl^- solution is $y=0.3163x-0.2106$, where the correlation coefficient is $R^2=1$ and the detection limit is 0.6882 μg/mL.

The experimental results indicated that, the azeotropic point of hydrochloric acid in aqueous solution is 101.21 ° C, and the azeotropic composition is 20.73% (Fig. 2) in this lower pressure experimental zone. Compared with the vapor-liquid equilibrium data (the azeotrope point is 108.6 ° C, the mass fraction of HCl in the azeotrope is 20.24%) under normal pressure, the azeotropic temperature at studied pressure is lowered by 7.39 ° C , indicating that the boiling temperature of the solution is significantly reduced, which is beneficial to the energy-saving and depletion of the desorption process. The mass fraction of HCl in the azeotrope is increased by 0.49%, which is favorable for the desorption and separation of salt to obtain a higher concentration hydrochloric acid.



1-heating chamber; **2**-liquid sample storage tank; **3**-vacuum insulation chamber; **4**-thermometer and thermocouple inlet; **5**-condenser; **6**-vapor phase sample storage tank; **7**-vapor-liquid separation chamber; **8**-vapor liquid riser; **9**-boiling chamber; **10**-thermometer; **11**-liquid paraffin; **12**-glass ground joint; **13**-latex tube (the same below); **14**-dry tube; **15**-glass three-way valve;**16**-U type differential pressure gauge; **17**-pressure ball; **a**-heating rod and thermocouple; **b**-liquid sample sampling port; **c**-steam sample sampling port

Fig 1. CE-2 type double-circulation vapor-liquid equilibrium glass reactor

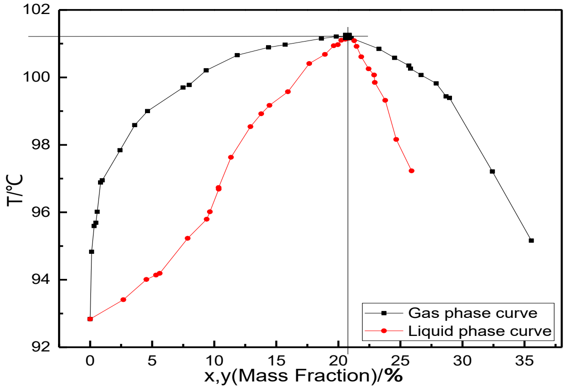


Fig 2. Vapor-liquid equilibrium phase diagram of HCl-H_2O system at low pressure

Keywords: *Vapor-Liquid Equilibrium; HCl-H_2O System; Low Pressure*

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Fabrication of Hierarchically Porous Materials by Using Supercritical CO_2

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A novel approach is provided to control the morphology and the structure of hierarchically porous materials (HPM), including carbon, organosilicon, metal-organic frameworks (MOFs), and carbon nitride, with well-ordered mesoporous and microporous structure by using supercritical/compressed CO_2. A surfactant solution (such as F127/MMA) was employed as the reactive system and the organic compound as the precursor with one-pot method by using supercritical/compressed CO_2 as the pore-forming or expanding agent. Specially, the morphology of the as-made HPM can be transformed by simply increasing the pressure of CO_2. Meanwhile, the porous structure of the obtained sample can be turned from mesopores/micropores to macropores/mesopores/micropores. The obtained HPM exhibits excellent performance in the CO_2 adsorption, medical materials for drug delivery carriers, and electrode materials for supercapacitors. Furthermore, the mechanism of the formation and transformation of HPM was discussed via investigating the solution. The result implied that CO_2 plays a decisive role to change the state of surfactant solution, leading to morphological and porous structural transformation of HPM. Different from conventional acid/base or inorganic additives as catalyst, CO_2 can not only be employed as an acid catalyst in the crosslinking of the precursors, but also be a controller of the structure transformation of HPM. This strategy can provide a novel route to develop architectural design of hierarchical porous materials in green processes.

Keywords: *Hierarchically porous materials; Compressed CO_2; Surfactant solution; self-assembly*

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Solubilities of 4-Aminoazobenzene and 4 Diethylaminoazobenzene in Supercritical Carbon Dioxide

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Supercritical carbon dioxide (sc-CO2) dyeing technology has been recognized as one of the innovative technologies of textile industries because environmental friendly compared to the conventional dyeing technology. To develop and design the sc-CO2 dyeing technology, solubility of dye, phase behavior, should be known well.

In this work, solubilities of 4-aminoazobenzene (C.I Disperse Yellow) and 4 diethylamino)azobenzene (Solvent Yellow 59) were measured at the temperature ranges of (323.15 to 383.15) K, and pressure of (12 to 25) MPa in supercritical carbon dioxide by a flow-type apparatus. The solubility of 4-(diethylamino)azobenzene was higher than that of 4-aminoazobenzene. It was found that the ethyl group addition on the 4-aminoazobenzene causes higher the solubility of the 4-(diethylamino)azobenzene in (sc-CO2). We apply six the empirical equations, namely, Mendez-Santiago – Teja [1], Chrastil, Kumar Johnston, Bartle, Galpati – Madras, Sung – Shim, also correlated thermodynamically by the regular solution model of the Flory-Huggins [2]. Good agreement between the experimental and calculated solubility of the dyestuffs was obtained.

Keywords: *Solubility; Supercritical carbon dioxide; azobenzene; amino; diethyl*

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The Structural Origins of Titanium Dioxide (TiO_2) Polymorphic Nucleation in Undercooling Melt

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Polymorphic nucleation behavior of TiO_2 that different crystal isomers (anatase/brookite/rutile) nucleated from undercooling melt widely exists in nature and practical industry, such as, mineral formation, plasma spray and thermal plasma oxidation, however, the current knowledge of this complicated nucleation phenomenon is largely insufficient. In this study, we investigate the efforts of molten TiO_2 structure on polymorphic nucleation by employing high-energy X-ray diffraction combining with aerodynamic levitation facilities, and expound the structural origins of the previously unexplained polymorphic nucleation phenomenon. Moreover, physically and chemically reasonable atomic configurations are generated based on the diffraction data through Reverse Monte Carlo (RMC) simulation. Here, we found that the chemical short-range order (CSRO, Ti-O polyhedra) of TiO_2 melt and corresponding crystalline phases are significantly different: the Ti-O bond length becomes short and the mean oxygen coordination number around Ti^{4+} ion decreases in melt. This structural dissimilarity depicts a nucleation barrier at atomic level. Comparing the structural deviation of CSRO between melt and crystal isomers, the mean Ti-O bond (1.875 Å~1.885 Å) in melt is closer to anatase (1.944 Å, 298 K) than brookite (1.951 Å, 298 K) and rutile (1.959 Å, 298 K), which positively indicate that anatase may have greater tendency to nucleate from undercooled melt prior to brookite and rutile. The undercooled melt structure of TiO_2 has significant temperature dependence, with the undercooling increasing, the predominant CSRO change from fivefold Ti-O polyhedra to crystal-like sixfold Ti-O polyhedra, which suggested a growing crystallization tendency. Additionally, from the view of near intermediate-range order (NIRO, the connection between CSRO), As the temperature decreases, crystal-like clusters (Ti-Ti[8], Ti-Ti[9] and Ti-Ti[10]) increase monotonically, while the other type clusters decrease. In contrast, anatase-like clusters (Ti-Ti[8]) are always more abundant than brookite-like clusters (Ti-Ti[9]) and rutile-like clusters (Ti-Ti[10]), which indicates the connectivity of Ti-O polyhedra are also similar with anatase phase. Our findings provide the underlying insights between evolution of crystal-like clusters in TiO_2 undercooling melt and polymorphic nucleation selection.

Keywords: *Polymorphic nucleation selection, undercooled TiO_2 melt, structure, X-ray diffraction, aerodynamic levitation.*

Novel Hydrophobic Ionic Liquid Based Microemulsion for Laccase Catalysed Reaction

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A hydrophobic ionic liquid (HIL)-based microemulsion is a promising medium for enzymatic reactions. It has the features of both ionic liquid and microemulsion. In this talk, the fish-shaped phase diagram method was applied to investigate the effects of surfactants, hydrocarbon alcohols (C5~C10), and HILs on the phase behaviour of the microemulsion stabilized by polyoxyethylene-type nonionic surfactant (C_nE_m). It has been found that small head group of the surfactant, high concentration of the alcohol and low cohesive energy density of the HIL result in low phase inversion temperature. These results are associated primarily with the dissolution and aggregation of surfactants in HIL as well as with the interface effect and the co-solvent effect of alcohols. Based on the phase behaviour, some bicontinuous microemulsions were formulated and their microstructures characterized. The effects of the composition/microstructure and temperature on the kinetic parameters of solubilized laccase were investigated. It is shown that temperature and alcohol are the key parameter affecting the catalytic performance of laccase. At ambient temperature, the optimum alcohol depends on the type of HIL as an oil phase. All the kinetic parameters indicate that [Omim]NTf_2/buffer/C_nE_m/1-hexanol bicontinuous microemulsion is a suitable medium for the laccase-catalysed reaction; in the $C_{16}E_{10}$ stabilized microemulsion the catalytic efficiency of laccase is as high as 95.3 mM^{-1} min^{-1}, which is 156 times higher than that in the water saturated [Omim]NTf_2 (0.607 mM^{-1} min^{-1}) at 35.0 °C.

Keywords: *Ionic liquid; Phase behavior; Microemulsin; Laccase; Kinetic parameters*

High Coupling Effect Between the Micellization, Ionic Condensation and Hydrophobic Absorption. Interpretation of the Co Catalytic Effect of $NaBPh_4$ over the Nano Polymerization of Styrene by the Zirconocene Dichloride in SDS Micelles.

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Generally, the micellization process is described as a first-order phase transition. Consequently, above cmc, the concentration of free monomers and the apparent charge eZ_{ap} of the micelles remain constants. In reality, colloidal nanoparticles are rather small systems characterized by non-homogeneous thermodynamic functions. It follows that the processes of micellization (of degree $1-\beta$) and ionic condensations of species "i" (each one of degree $1-\alpha_i$), are interdependent transitions more or less continuous. It is the case for SDS and TTAB micelles of $|eZ_s|$ structural charge, R radius and V_M volume, in hydro-organic solutions [1]. This nonlinear coupling extends if these two processes are accompanied by some absorptions of hydrophobic species "j" (each one of degree $1-\gamma_j$, with n_j particles into one micelle). This coupling can be expressed as following:

$Z_{ap} = \pm |Z_s|(\alpha - \beta)/(1 - \beta) - \sum_j (\pm n_j)(\alpha - \gamma_j)/(1 - \gamma_j)$; $\alpha = \sum_i \alpha_i$; $(1-\alpha)/(\alpha C_M) \cong V_M \exp\{(-Z_{ap}L_B/R)(1-R/d)\}$

C_M is the concentration and d is the radius of the ionic atmosphere surrounding a micelle.

Nano polymerizations of styrene in aqueous solutions, using SDS as emulsifier and $NaBPh_4$ as cocatalyst at room temperature appeared much more efficient than at high temperature (80 °C) polymerizations using the catalyst $[Cp_2ZrCl_2]$ alone [2].

The interpretation given by literature assumes that BPh_4^- hydrophobic anion forms a (clathrate) ion pair with the cationic hydrolyzed specie $[Cp_2ZrOH]^+$ what facilitates the incorporation of the catalyst inside the SDS. However, there is no experimental evidence of this 1-1 contact pair formation in water and it cannot be justified according to Bjerrum's criterion of ionic association. We therefore propose a new explanation based on the coupling described above. The different coupled steps are:

- Hydrophobic absorption of n_{BPh4^-} ions electrically compensated by the condensation of Na^+ counterions. - Electrostatic condensation of $[Cp_2ZrOH]^+$ species on SDS favored by the hydrophobic affinity of the two (C_5H_5) groups to the nonpolar side chains of SDS. - Formation of an ionic pair $Cp_2ZrOHBPh_4$ inside the micelle SDS, in conformity with the Bjerrum's criterion, because of the very low permittivity ε_M of the organic micro phase.

For a given total concentrations: $C°_{SD^-}$, $C°_{BPh4^-}$ and $C°_{[Cp2ZrOH]^+}$ of the mixed electrolyte, we estimate the number « n_{BPh4^-} » of absorbed BPh_4^- ions by one micelle SDS, in order to calculate the correspondent values α, β and γ, and the theoretical conductivity χ according to the Onsager - Kim - MSA theory of mixed electrolytes (including the dielectric friction undergone by the micelle) [3,4]. For $C°_{SD^-} >>$ cmc, the best fitting between calculated χ and experimental conductivity is obtained for $K_M \cong 10^{105}$ and $n_{BPh4} \cong 0.5$. K_M is the equilibrium constant of micellization so that:

$(1-\beta)/(\beta) = K_M|Z_s|(\beta C°_{SD^-})^{(|Zs|-1)}$

These results confirm the proposed mechanism as well as the high hydrophobic affinity $\Delta\mu°_{pair}$ of the ionic pair: $Cp_2ZrOHBPh_4$ [Catalyst - Co catalyst] to SDS micelles.

Keywords: *Sodium dodecyl sulfate; Styrene; Zirconocene dichloride; Hydrophobic affinity; Co-catalyst; MSA conductivity theory; Dielectric friction*

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AFM Study of pH-Dependent Adhesion of Single Protein to TiO_2 Surface

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The effect of pH-induced electrostatic conditions on the molecular interaction force of a single lysozyme molecule with TiO_2 is investigated using atomic force microscopy (AFM). The force between the charged or neutral lysozyme molecule and the TiO_2 surface is measured at different pH from 3.6 to 10.8. This molecular interaction force is independent of the surface geometric of the TiO_2, but it is found to be directly proportional to the contact area, given by an effective diameter of the lysozyme molecule, and is further qualitatively verified by the AFM-measured friction coefficients. The results of the Derjaguin–Landau–Verwey–Overbeek theory show that the pH can change the surface charge densities of both lysozyme and TiO_2, but the molecular interaction force at different pH is only dependent on the pH-induced effective diameter of lysozyme. The molecular interaction forces, quantified at the nanoscale, can be directly used to design high-performance liquid chromatography measurements at macroscale by tuning the retention time of a protein under varied pH conditions. They can also be applied to develop a model for predicting and controlling the chromatographic separations of proteins.

Keywords: *AFM; electrostatic condition, DLVO theory; molecular interaction force.*

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The Growth of Cage-like Uranyl Peroxide Nanoparticles: A Small-angle Scattering Study

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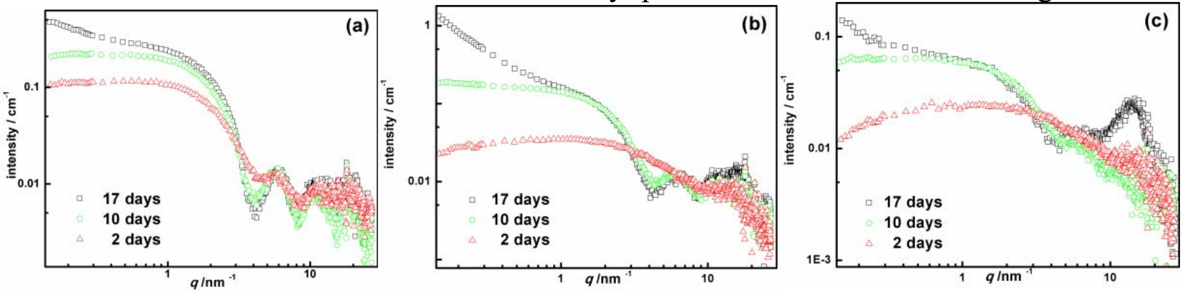
In the past 10 years, nanoparticles (NPs) or clusters based on actinides have attracted much attention in the fields of polyoxometalate chemistry, crystallography, mineralogy and nuclear fuel [1, 2]. In view of the importance of uranium technology, among the various actinide complexes the uranyl peroxide NPs have received special attention. Although the synthesis of uranyl peroxide NPs is straightforward, there is limited information on the structural evolution of dispersed uranyl peroxide NPs.

In this work, the temporal behavior (from days to 1 year) of uranyl peroxide NPs prepared with different LiOH/UO_2 molar ratios is studied. Small-angle X-ray scattering was chosen to explore the detailed structure of uranyl peroxide NPs because the electron scattering length of uranium atoms provides a strong contrast against the dispersion medium, and the cage-like structure exhibits pronounced oscillations. The present study provides an insight into the structural evolution and interactions of the uranyl peroxide NPs. The main findings are:



(1) Guinier analysis of the scattering curves indicated that the overall size of the uranyl peroxide NPs increased with storage time. Their structures were further analyzed by a spherical shell model fitting. Uranium24 (U24) particles consisting of 24 uranium atoms are formed in dispersion with Li/U = 7.7, whilst U28 particles are generated with Li/U = 3.1.

(2) The scattering data show that with increasing storage time, the attractive interactions between uranyl peroxide NPs become strong, as revealed by (a) the upturn of the scattering intensity at low *q*; and (b) the formation of precipitates. The formation of aggregates with hydrodynamic sizes of 200 to 1100 nm were also confirmed by the dynamic light scattering and transmission electron microscopy.

(3) After one year, the zeta potential of the upper part of the dispersions was -30 to -40 meV, and the precipitation ratios for the samples with Li/U = 3.1, 5.1, 7.7, were 0.36, 0.56, and 0.72, respectively. The NPs that remained in the dispersions were stable over one year due to electrostatic repulsion.

Keywords: *Uranyl peroxide; Nanoparticle; Small-angle scattering; Aggregation*

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Density Prediction for Aqueous Lithium Containing Multi-component Solution

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Salt Lakes are widely distributed in the Qinghai-Tibet plateau and abundant in high concentration of lithium, potassium and boron. The composition of salt lake brine can be represented as $Li^+–Na^+–K^+–Mg^{2+}–Cl^-–SO_4^{2-}–CO_3^{2-}–B_2O_3–H_2O$ system. Knowledge of the volumetric characteristics, such as density, has guiding role in salt lake brine evaporation process control and solar pond design [1]. Such data also provide valuable insight into the interaction behavior of mixed electrolyte solutions. The physical-chemical theories and approaches developed for the application to concentrated mixed electrolyte solutions can be very effectively used for the explanation and prediction of various processes occurring in natural hypersaline waters. One of such useful approached is the ion interaction model developed by Pitzer[2] which allows the prediction of thermodynamic properties of concentrated brine[3, 4]. In this paper, densities for binary and ternary systems have been measured by high precision vibrating-tube densitometer. The parameters of the Pitzer model were fit to the experimental density values. Densities of aqueous lithium containing multicomponent solution were calculated using the ion interaction model.

Keywords: *Density; Salt Lake Brine; Lithium; Pitzer Model*

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Modeling of Gas Solubility in Aqueous Electrolyte Solutions Using the Electrolyte Cubic-Plus-Association Equation of State

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Prediction of the solubilities for carbon dioxide and methane in aqueous inorganic salt solutions plays a key role in geological carbon storage, enhanced oil recovery and seawater desalination. And accuracy solubility calculations for carbon dioxide and methane in aqueous solutions of quaternary ammonium salts are important for semi-clathrate hydrate formation,

There are a few electrolyte Equation of State (EOS) for gas solubility calculation in wide temperature-pressure-salt molality (T-P-m) ranges. This work presents a thermodynamic modeling study for gas solubilities of carbon dioxide and methane in several aqueous solutions with the electrolyte Cubic-Plus-Association (e-CPA) EOS [1, 2]. The ion-gas interaction parameters are obtained by fitting the experimental data of gas solubilities. The model is extended to multi-salt solution systems with single salt-gas interaction parameters, and the model performance for these multi-salt systems is similar with that of single salt solutions.

The modeling results show that e-CPA can satisfactorily correlate gas solubilities in wide T-P-m ranges, with deviation around 7% for most systems. Compared with other electrolyte EOS, e-CPA can give better performance in wide T-P-m ranges. The salting-out effects and the effect of various factors (ion size, charge density, salt concentration) are also discussed, based on experimental data and the calculated values from e-CPA.

Keywords: *Gas Solubility; Aqueous Solution; e-CPA; Multi-salt*

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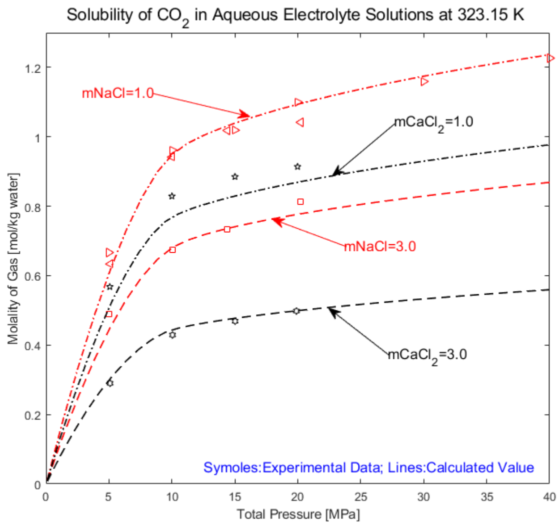

Isopiestic Measurements of Thermodynamic Properties for the Aqueous System ($LiBO_2 + Li_2B_4O_7 + H_2O$) at 288.15 K

Kaiyu Zhao[a], Kangrui Sun[a], Yafei Guo[a,*], Lingzong Meng[b], Tianlong Deng[a]

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Lithium borates not only occupy an important position in the modern inorganic industry, but also have been widely used in agriculture, metal smelting and chemical analysis for their excellent characteristics [1]. In the west of china, some salt-lake brines contain abundant lithium and boron, and consist of several types of hydrated lithium borates minerals. Due to the complex structure of lithium borates, it is highly desirable to study the thermodynamic properties and behaviors of its aqueous electrolyte solution [2], and fully understand ion-interactions among each ion.

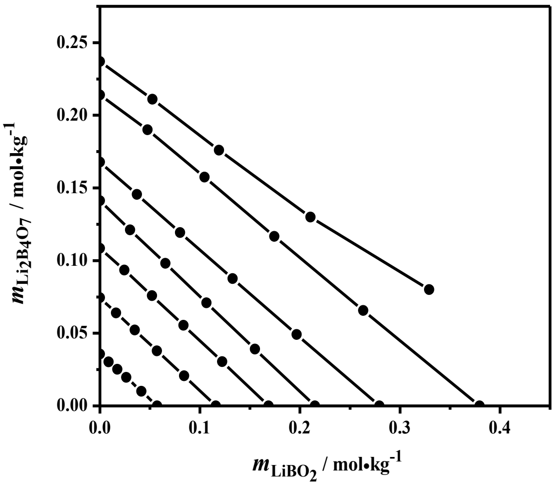

Fig. 1 Isopiestic equilibrium molalities of the system ($LiBO_2 + Li_2B_4O_7 + H_2O$) at 288.15 K.

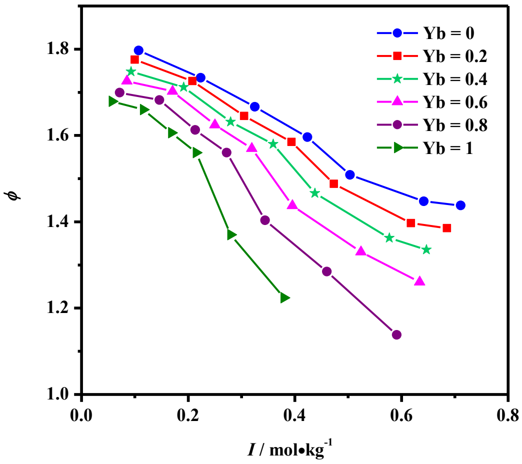

Fig. 2 Osmotic coefficients for the ternary system ($LiBO_2 + Li_2B_4O_7 + H_2O$) at 288.15 K.

In this work, water activities and osmotic coefficients for the ternary system ($LiBO_2$ + $Li_2B_4O_7$ + H_2O) and its subsystem at 288.15 K with various ionic strength 0.0573-0.7112 mol·kg^{-1} were measured using an improved isopiestic device. The experimental results were treated by the Pitzer ion-interaction model, then, a series of parameters were obtained to describe the model.

Keywords: *Isopiestic measurements; Water activities; Osmotic Coefficients; Pitzer model*

Acknowledgements: Supports from the NNSFC (U1607123), the Key Projects of Natural Science Foundation of Tianjin (TD12-5004), the Innovative Research Team in Tianjin Colleges and Universities (TD13-5008) and the Yangtze Scholars and Innovative Research Team of the Chinese University (IRT_17R81).

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Inelastic X-ray Scattering Measurements of Copper/ethylene Glycol and Alumina/Water Nanofluids

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Recently, nanofluid, which is a fluid containing nanoparticles (NPs), has been focused on as a new heating medium for improvement of the heat exchange efficiency. The thermal conductively of ethylene glycol (EG) or water where a small amount of metal or metal oxide NPs is dispersed is larger than that of the pure solvent [1]. An increase in the thermal conductively exceeds that estimated by the Maxwell-Garnett theory. In order to elucidate the mechanism of the high thermal conductivity of nanofluid, inelastic X-ray scattering (IXS) of solvent is investigated. In IXS spectra of nanofluid, the collective excitation at momentum transfer of 2-20 nm^{-1} is observed as an acoustic phonon. The high-frequency sound velocity (HFSV) is obtained from a dispersion relation of the collective excitation. Since the HFSV reflects microscopic thermal conductivity and structural relaxation of solvent molecules in the framework of the generalized Langevin equation, the effect of nanoparticles on the thermal conduction and molecular dynamics of the solvent of nanofluids could be discussed.

IXS measurements of two types of nanofluids (Cu NPs/EG, alumina (Al_2O_3) NPs/water) were conducted using the high-resolution IXS spectrometer installed at BL35XU of SPring-8 in Japan. The IXS spectra were analyzed by a damped harmonic oscillator model [2] and by the generalized Langevin analysis [3]. The HFSV values for the nanofluids were determined in the momentum transfer range of 2.6 to 6.5 nm^{-1}. The values of HFSV increase with increasing the amount of Cu and Al_2O_3 NPs. The higher the concentration, the larger HFSV, which indicates that the collective dynamics of EG and water is affected by the existence of nanoparticles. Cu NPs affect the HFSV effectively. In contrast, although HFSVs increase with increasing Al_2O_3 amount in the case of the Al_2O_3/water system, the increase ratio is small. Compared with the results of thermal conductivity measurements of the same nanofluids, it was found that the enhancement of the thermal conductivity of nanofluid is strongly related to the collective dynamics of the solvent.

From the memory function of the generalized Langevin equation, the structural relaxation time of EG is determined in the Cu/EG system. The structural relaxation time became smaller with increasing Cu NPs amount. It is concluded that solvent dynamics affects the heat transfer mechanism of Cu/EG nanofluid. The IXS measurement of solvent in nanofluid could lead to the development of highly efficient nanofluids.

Keywords: *nanofluids; inelastic X-ray scattering; collective dynamics; thermal conduction*

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Microheterogeneity in Aqueous Solutions by Radiation Scattering and Computer Simulations

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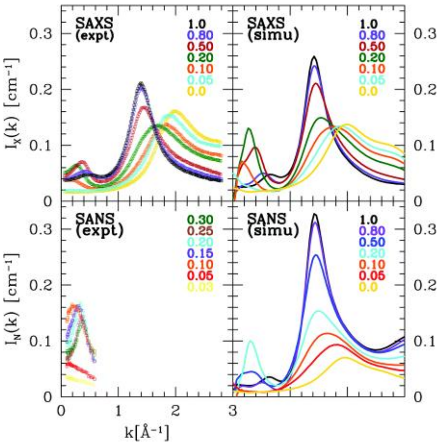
Mixtures of various amines with water are often characterized by the presence of strong self-aggregation of the two types of molecules, which leads to strong deviations from ideality of their thermodynamic functions, and can be detected by scattering methods such as small-angle neutron and X-ray scattering. In this presentation we discuss our recent results on various types of amines: cyclic amines such as piperidines and pyrrolidines, and linear short alkyl chain amines such as propylamine. The structure of these mixtures is investigated through X-ray and neutron scattering experiments, and computer simulations.

Both sets of data show a prominent scattering pre-peak, which first appears at propylamine mole fraction $x \geq 0.1$ around scattering vector $k \approx 0.2$ Å^{-1}, and evolves towards $k \approx 0.8$ Å^{-1} for neat propylamine [1-4]. The existence of a scattering pre-peak in these mixtures is unexpected, as no such features appear in aqueous solutions of very similar molecules such as linear or branched alcohols, or pyridine and its methyl derivatives[5]. The detailed analysis of the various atom–atom structure factors and snapshots reveals pre-peaks in the atom–atom structure factors, positive for like species and negative for cross species correlations, and their cancellation or not-cancellation results in peak in the measured structure factor. The way the amines bind with water produces a pre-peak through an imbalance of the positive and negative scattering contributions, unlike in short chain alcohols where these contributions compensate exactly. Hence molecular simulations demonstrate how chemical details influence the microscopic segregation in different types of molecular emulsions and can be detected or not by scattering experiments.



Keywords: *non-ideal mixing; small-angle scattering; computer simulation; microheterogeneity*

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Solution Chemistry and Trace Iodine Removal of High Salt Brine System

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At present, ionic membrane electrolysis is the most advanced technology for the mass production of caustic soda [1]. However, a lower concentration of iodine (< 0.2 mg L^{-1}) in high salt brines used for caustic soda production is crucial, otherwise iodine can be oxidized to higher oxidation states and produce insoluble precipitates in the alkaline environment of the ion membrane, resulting in reduced current efficiency and greatly decreasing the service life of the ion membrane [2-3]. In order to reduce membrane loss and caustic soda production costs, it is of practical significance to maximize the removal of iodine from high salt brine. However, the species of iodine and their corresponding contents are different in different process stage brines, which results in different iodine removal methods in each stage.

The speciation of iodine is mainly based on the combination of chromatographic separation and high-sensitivity detectors, especially in combination with inductively coupled plasma mass spectrometry (ICP-MS), due to its rapidity, low interference, low detection limit and high accuracy [4]. In this paper, the attention was given to the complex matrix of high salt brine from the chlor-alkali industry. Two types of anion exchange columns were tested to establish a rapid analytical method of iodine speciation applied to high salt brine by using a high multiple dilutions to eliminate matrix interferences. A high-efficiency separation anion-exchange column (Dionex IonPac AS-14) for iodate and iodide with 100 mM $(NH_4)_2CO_3$ solution at pH = 10 as mobile phase was proved, and the total running time of individual sample was within 8 min. Linear standard calibration plots were obtained in a concentration range of 1.0-100 µg L^{-1} for iodate and iodide, and the detection limits were 0.05 µg L^{-1} for the former and 0.20 µg L^{-1} for the latter. This method shows good sensitivity and precision to be used for high salinity samples from the chlor-alkali industry.

Keywords: *Speciation analysis; HPLC-ICP-MS; Iodate and iodide; High salt brine*

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Many-Body Effect Induces Gradual Crossover from Sub-diffusion to Normal Diffusion

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Dynamics of hydration water is essential for the function of bio-macromolecules. Previous studies have demonstrated that water molecules exhibit subdiffusion on the surface of bio-macromolecules; yet the microscopic mechanism remains vague. Here, by performing neutron scattering, molecular dynamics simulations, and analytic modeling on hydrated perdeuterated protein powders, we found water molecules jump randomly between trapping sites on protein surfaces, whose waiting times obey a broad distribution, resulting in subdiffusion. Moreover, the subdiffusive exponent gradually increases with observation time towards normal diffusion due to a many-body volume-exclusion effect.

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Novel Method to Evaluate Position-Dependent Diffusion Constant of Small Molecules in Heterogeneous Systems

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Understanding of mass transportation in heterogeneous systems such as electrode surface, biomembrane, and porous materials is crucial for various topics from the performance of fuel cells to drug permeation of biomembrane. One of the indispensable physical quantities to characterize such mass transportation is the position-dependent diffusion constant. For example, the position-dependent diffusion constant is necessary to evaluate permeability via solvation-diffusion model, in addition to free energy landscapes. Widespread conventional approach to evaluate the position-dependent diffusion constant includes Marrink and Berendsen's method [1] and Woolf and Roux's method [2], which are derived from the Langevin equation and the generalized Langevin equation, respectively. Consequently, these two methods are rigorous for systems with solutes much larger than solvents, as these equations are faithful in such systems. However, these methods are not necessarily suitable to systems where the size of solute is comparable or smaller than that of solvent. Hence, to reasonably evaluate the position-dependent diffusion constant of small solute, we propose a new method.

In the proposed method, we impose flat-bottom potential to a solute, whereby the molecule is restrained in a box. As the solute does not feel the force of the imposed potential at the flat bottom, we can collect segments of trajectory where the dynamics of solute is not affected by the imposed potentials. Using these segments of the solute trajectory, we calculate the mean square displacement (MSD) of the solute. Even though the dynamics itself in these segments is not affected by the imposed potential, statistics of trajectory, such as MSD, are dependent on the shape and the size of sampling space determined by the flat-bottom potential. To correct for this "shape factor", we numerically evaluated the correction function from simulations of diffusion of water. We will show that we can eliminate the shape factor of other systems by this correction function, and thereby that we can obtain the position-dependent diffusion constant.

To compare the new method with the conventional two methods, we calculated the position-dependent diffusion constant of hydrogen and oxygen in bulk water, as pilot cases. As these test systems are a homogeneous system, the diffusion constant can be obtained from MSD with good accuracy and this value is used as a reference for the position-dependent diffusion constant. Comparing this reference value and the position-dependent diffusion constants that are obtained with the three methods, we demonstrate outperformance of our new method over the conventional methods.

Keywords: *molecular dynamics (MD) simulation, heterogeneous system, position-dependent diffusion constant*

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Molecular Simulation of D-mannitol Polymorphs in Solution

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The crystal form regulation has gained more and more attention recently. In this paper, D-mannitol was taken as an example for the investigation of polymorphism in solution. In our previous study[1] on the cooling crystallization process of D-mannitol, it was found that the supersaturation of D-mannitol aqueous solution could affect the crystal form of the final nuclei. The stable β form of mannitol was favored at low supersaturation, whereas the metastable α form nucleated at high supersaturation and the least stable δ polymorph crystallized when the supersaturation was in the medium level.

During nucleation in solution， at least two processes should be involved. One is the desolvation of the solute molecules from the solvent, while the other is the interaction among the solute molecules to form crystal nuclei. The two processes might occur stepwise or at the same time. Geneally the interactions among molecules in the solution are quite complicated, which makes the nucleation process difficult to investigate, therefore the discussion on classic and one-step nucleation mechanisms is still going on with various evidences for one another.

In this paper, molecular simulation was used as the main tool to study the molecular behavior of D-mannitol in solution from the aspects of crystal structure, solution properties and nucleation process. First of all, the characteristics of D-mannitol molecules in different polymorphs were explored, which laid a foundation for the simulation of the molecular situation in the corresponding solution state. Then the molecular properties of D-mannitol polymorphs in supersaturation state was simulated. And the effects of solute-solvent and solute-solute interactions on nucleation were investigated. It was found that the nucleation of D-mannitol molecules depends not only on the desolvation of the solute molecules, but also on the interaction of solute-solute. Moreover, there is no direct correlation between the aggregated form of the D-mannitol molecules in the aqueous solution and the mode of D-mannitol molecules in the solid unit cell. However, based on the simulaiton, one might found that monomers and I type dimers of D-mannitol molecules in solution may favor the formation of delta form, and T type dimer may tend to form alpha form, while H type dimers and multimers may be beneficial to the formation of beta forms.

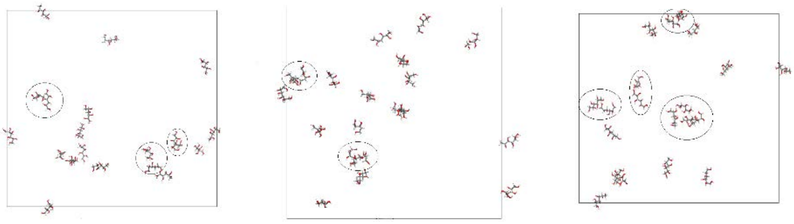
(a) (b) (c)

Fig 1. Distribution of D-mannitol molecules in solution with different supersaturations (with 20 solute molecules, (a) supersaturation: 2.92, (b) supersaturation: 1.90, (c) supersaturation: 1.27,).

Keywords: *D-mannitol, Polymorph, Molecular simulation, Solution, Nucleation*

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Insight into Understanding the Microstructure and Demulsification Mechanism of Temperature-responsive Ionic Liquid Microemulsion

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Microemulsions, which consist of two or more immiscible liquids and surfactants, have been successfully applied in the field of oil recovery, material synthesis, organic catalysis, cosmetic and pharmaceutical industry[1]. As different stability of microemulsions are required in various applications, how to realize the controllable deemulsification of microemulsions is very important and not an easy problem. A way to solve this problem is to build up the stimuli-responsive microemulsions. In recent years, temperature-responsive ionic liquid (IL) microemulsions become a hot topic [2]. However, little is known for their emulsification and demulsification mechanism.

In this work, a new microemulsion system comprising $[P_{4444}][CF_3COO]$, $[C_{12}mim]Br$ and water was constructed at 45℃. The effects of IL concentration and phase ratio of oil and water on the phase behavior of the microemulsion were investigated. It was found that the particle size of microemulsion increases sharply with increase of the temperature at a given concentration of IL. To understand the emulsification and demulsification mechanism of this temperature-responsive microemulsion at the molecular level, a serious of MD simulations were performed at different temperatures. After such simulations, it was found that the distribution of $[P_{4444}]^+$ and $[CF_3COO]^-$ was homogeneous and some small clusters comprised by the tail of $[C_{12}mim]^+$ were formed in the mixed system at low temperature. With the increase of temperature, $[P_{4444}]^+$, $[CF_3COO]^-$ and $[C_{12}mim]^+$ came to aggregate together, resulting in the formation of large clusters, and some water molecules were also dissolved in the clusters. The size of clusters became larger with incresing temperature, and $[P_{4444}][CF_3COO]$-in-H_2O microemulsion was formed at 318 K. Then the aggregation of $[P_{4444}]^+$ and $[CF_3COO]^-$ was enhanced, and an increased number of $[C_{12}mim]^+$ was distributed on the surface of clusters. Phase separation between ILs and water was generated at 358K in our simulations. It was concluded that the interaction between $[P_{4444}][CF_3COO]$ and H_2O play an important role in the emulsification and demulsification of temperature-sensitive microemulsions. In addition, the effect of IL concentration ($[P_{4444}]$ $[CF_3COO]$ and $[C_{12}mim]$ Br) on the microstructure of IL microemulsion were also revealed by molecular simulations. These findings provide some theoretical guidance for the further design of temperature-sensitive IL microemulsions.

Keywords: *ionic liquids; structure; interaction; molecular dynamic simulation*

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Structure Study of Ammonium Chloride Solutions by Spectroscopic Method and Molecular Dynamics Simulation

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X-ray scattering, Raman and molecular simulation were used to determine a series of ammonium chloride solutions at room temperature. The X-ray scattering results were analyzed by PDF theory. The reduced structure function F(Q) and the reduced pair distribution function G(r) were obtained. The excess Raman spectrum was used for spectral analysis. The results show that with the increase of concentration, the main peak position of G(r) which obtained by X-ray scattering moves to 3.16Å. The integral area of the first peak of the $g_{N\text{-}Cl}(r)$ which obtained by the molecular dynamics simulation increases gradually. The author speculate that this is due to the predominance of NH_4^+-Cl^- ion pairs in the high concentration solutions. The Raman spectrum and X-ray scattering results show that the hydrogen bonds in the aqueous solutions were disrupted with the increase of the ammonium chloride concentration.

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Keywords: *Ammonium chloride solution; Synchrotron radiation; X-ray scattering; Raman spectrum; Molecular simulation*

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Youth forum

Studying Phase Stability of Hen Egg-White Lysozyme Solutions with Molecular Dynamics

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Proteins are biological macromolecules that play an important role in key life processes. When proteins are dissolved in water these solutions are not necessarily stable. Aqueous protein solutions under certain conditions (temperature and protein concentration) can undergo vast changes. By decreasing the temperature the solution can undergo phase separation into, depending on the conditions, solid and liquid or two distinct liquid phases. These solution transformations can be described by a so-called thermodynamic phase diagram [1]. Irrespective of whether phase stability changes are beneficial (crystallization or formation of glassy solids) or harmful (formation of amyloid fibrils, causing neurodegenerative diseases) it is important to know the solution conditions and mechanisms under which they occur [2, 3]. Inter- and intramolecular interactions govern protein phase stability, therefore knowledge about them is crucial for the puzzling process of determining protein phase diagrams. One possible approach to investigate interparticle interactions is by using computer simulations. Especially all-atom simulations can provide detailed insight into the initial steps of protein oligomerization. In our study we have focused on the self-association process of hen-egg white lysozyme (HEWL) via atomistic molecular dynamics simulations. As protein concentration and temperature have a major influence on phase stability of aqueous HEWL solutions, the simulations were performed within (high HEWL concentration and low T) and outside (low HEWL concentration and high T) the experimentally established range in which liquid-liquid phase separation is observed. We were particularly interested in protein-protein and residue-residue radial distribution functions that provide a clear insight into the microstructure of the solution, and this also allowed us to decipher the mechanism of HEWL self-association. With the calculation of HEWL density fluctuations we were able to visualize the phase stability of HEWL solutions. Radius of gyration, hydration number and diffusion properties were also calculated.

Keywords: *lysozyme; protein aggregation; phase stability; molecular dynamics;*

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Reversible Phase Behavior Modulation of Azobenzene Ionic Liquid-based Emulsions by UV/vis Irradiation

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The balance between the long-term stability of the emulsions and its reversible emulsification-demulsification is an important issue in the field of emulsions. Environmental stimulus responsive ionic liquid-based emulsions provide a new way to solve this problem.[1] The use of light as an external stimulus is of particular interest because light has noninvasive character and can be delivered remotely and precisely in space and time.[2] However, the modulation of the phase behavior of ionic liquid-based emulsions by light irradiation has not been reported so far.

In this work, the photo-responsive emulsions were constructed by azobenzene-based ionic liquids, n-octane and water. Factors affecting the phase behavior of the emulsions, such as chemical structure and concentration of ionic liquids, phase ratio of oil and water, illumination time and intensity were investigated. It was found that, for a given ionic liquid, a stable emulsion could be formed when the concentration of the ionic liquid was above its critical micelle concentration, and the stability of the emulsion increased with increasing ionic liquid concentration. At a given concentration of ionic liquid, the stability of an emulsion decreased in the order: [C$_4$AzoC$_8$DMEA]Br > [C$_4$AzoC$_6$DMEA]Br > [C$_4$AzoC$_4$DMEA]Br > [C$_4$AzoC$_2$DMEA]Br. Upon UV irradiation, the emulsions underwent obvious demulsification, after further irradiation by vis-light, the system was emulsified again to form a stable emulsion. The structure of ionic liquids had a significant effect on the demulsification rate, which decreased in the following order: [C$_4$AzoC$_2$DMEA][Br] > [C$_4$AzoC$_2$Py][Br] > [C$_4$AzoC$_2$TMA][Br] > [C$_4$AzoC$_2$MIM][Br], [C$_4$AzoC$_2$DMEA][Br] > [C$_4$AzoC$_4$DMEA][Br] > [C$_4$AzoC$_6$DMEA][Br] > [C$_4$AzoC$_8$DMEA][Br]. For ionic liquids with the same alkyl spacer length, their demulsification rate is in agreement with their equilibrium isomerization rate, while for the ionic liquids with the same head group of the cation but different alkyl spacer length, ionic liquid with a smaller critical micelle concentration is not benefit for the demulsification.

Keywords: *Ionic liquid; Emulsion; Photo-responsive; Phase behavior modulation*

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Salt Lake Brines: Green and Abundant Catalyst for the Transformation of CO_2

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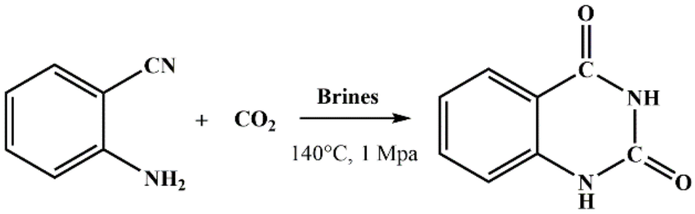
Carbon dioxide (CO_2) is promising C1 feedstock for green and sustainable chemistry. Transformation of this abundant, nontoxic, nonflammable and renewable C1 source into value-added chemicals by green and economical catalyst has drawn increasing attention [1]. Quinazoline-2,4(1H,3H)-diones and their derivatives are an important class of heterocyclic compounds with wide range of biological and pharmacological activities, and the atom-economic reaction between CO_2 and 2-aminobenzonitriles is an excellent route to yield quinazoline-2,4(1H,3H)-diones [2].



Scheme 1. Synthesis of quinazoline-2,4(1H,3H)-diones with CO_2 catalyzed by salt lake brines

Salt lake brines have been considered as the store house of mineral salts, and they are widely distributed in the worldwide scale, including America, Israel, Chile, China [3-4]. So far, researches on salt lake brines are mainly concentrated on the extraction of valuable and scattered elements. However, as far as we know, there is no report on using these green, abundant and easily available salt lake brines as catalysts. Herein, in this work, a series of basic salt lake brines were used for the first time to catalyze the reaction of CO_2 and a broad range 2-aminobenzonitriles to form corresponding quinazoline-2,4(1H,3H)-diones, as shown in Scheme 1. It was found that the abundant, inexpensive and available basic salt lake brines could efficiently promote the reactions of 2-aminobenzonitriles at low pressure of CO_2, and high yields of value-added products were obtained.

Keywords: *Salt lake brine; CO_2; quinazoline-2,4(1H,3H)-diones.*

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Hydration in Concentrated Alkali Metal Chloride Aqueous Solutions – The Winner Takes It All?!

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The structure of the hydrated alkali metal and chloride ions in aqueous electrolyte solution has been studied for a long time with a range of experimental methods.[1-3] In spite of this, the structure of the hydrated ions in aqueous solution is still debated, especially in industrially relevant highly concentrated solutions where the amount of water is not sufficient for complete hydration of the ions.

In our present study we have performed large angle X-ray scattering (XAS), chlorine K-edge X-ray absorption (XAS) measurements and theoretical simulations. Interestingly enough, by comparing the LAXS radial distribution function (Fig.1a) of the concentrated solution of the different alkali metal chlorides, one can conclude that the first two major peaks show changes which are proportional to the increasing ionic radius of the metal ion, while beyond it, the structure of the solution seems to be independent of the size of the metal ion. The chlorine XAS measurements revealed that the local structure around the Cl^- ion undergoes a substantial change with increasing concentration with Li^+ as a counter ion, while it retains in case of the other alkali metal ions, as illustrated in Fig. 1b and c.

All these observations and also theoretical calculations indicates that the ion with the highest hydration ability ($Li^+ > Na^+ \approx Cl^- > K^+ > Rb^+ > Cs^+$) is fully hydrated in one hydration shell, while the counter ion is not electrostatically attached to the hydrated ion through solvent shared ion-pairs in these highly concentrated solutions.

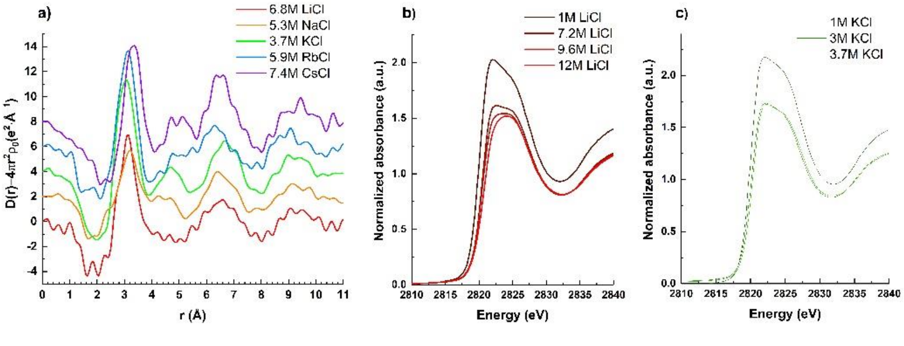

Figure 1. LAXS radial distribution functions of concentrated (LiCl) and saturated (NaCl, KCl, RbCl, CsCl) alkali metal chlorides (a) and normalized chlorine K-edge XANES spectra of LiCl (b) and KCl (c) aqueous solutions at different concentrations.

Keywords: *Alkali chlorides; Hydration structure; Chlorine K-edge XAS; LAXS; Theoretical calculations*

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Chemistry of Mg-borates in Sulfate-type Saline Lake and its Application in Boron Recovery From Brine

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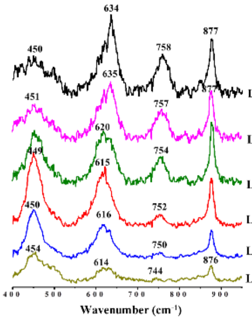
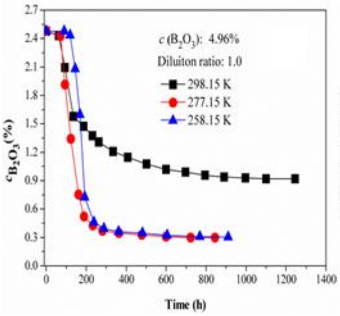
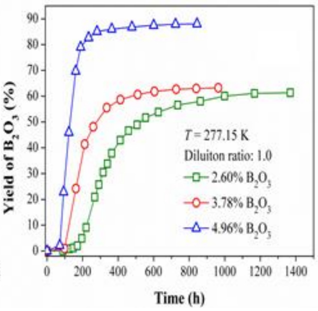
Boron resources are abundant in salt lakes of Qaidam Basin. Studies showed that borates have a high supersolubility and can be accumulated in the bittern during evaporation and remains stable for a few months at room temperature in the form of tetraborate $MgO{\cdot}2B_2O_3$ based on comprehensive statistics [1]. However, as this boron-concentrated brine was diluted with water, different Mg-borate salts precipitate from diluted brine, with types of salts vary depending on dilution ratio and working time [2]. This phenomenon is referred to as "crystallization by dilution," a process different from "crystallization by evaporation". Furthermore, since the boron content in precipitates was more than 35% in B_2O_3, which is much higher than boron ores (5 to 30% B_2O_3) in China, the high grade Mg-borate salts could be used as raw materials for industrial production of boron compound. Therefore, the "crystallization by dilution" would provide a more economical, environmentally friendly boron extraction method. The objective of the present study was to investigate the polyborate species in brine, phase transformation mechanism and kinetics of Mg-borates crystallization after dilution by Raman and kinetic model. Last, the obtained results were applied to the boron recovery from a sulfate-type salt lake by the dilution method.







The results showed that there were at least six polyborates present, $B(OH)_3$, $B(OH)_4^-$, $B_3O_3(OH)_4^-$, $B_4O_5(OH)_4^{2-}$, $B_5O_6(OH)_4^-$, and $B_6O_7(OH)_6^{2-}$, in the boron-concentrated brine, where $B(OH)_4^-$ and $B_4O_5(OH)_4^{2-}$ were the minor species in this brine. Diluting brines with water accelerated depolymerization of $B_5O_6(OH)_4^-$ and $B_6O_7(OH)_6^{2-}$ anions into $B(OH)_3$ and $B_3O_3(OH)_4^-$ ions and generated OH^- ions, causing the pH of the solutions to increase from 4.2 to more than 8.0. The calculated kinetic equations revealed the Mg-borates crystallization was dominated by the polynuclear layer controlled growth mechanism. Medium dilution ratios (0.50 to 1.0), high boron concentration (>3% B_2O_3), and lower temperature (below 273.15 K) were found to be more beneficial to the boron extraction from brine and the boron yield was more than 88% B_2O_3. The products obtained were only Mg-borates.

Keywords: *Salt lake; Polyborates; Raman spectrum; Kinetics* of *Mg-borate; Boron extraction by dilution*

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The Effect of Isotopic Composition on the Dielectric Relaxation of Water

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The small size of water as well as its unique hydrogen bonding network are at the heart of its extraordinary properties as a solvent. These features manifest themselves in high relaxation amplitudes and correlated reorientational dynamics in the complex permittivity spectrum. The dipolar relaxation of water take place at microwave frequencies and probed by dielectric relaxation spectroscopy (DRS). Even for neat water, however, the origin of different contributions to the observed spectra is still not fully understood.[1,2] To gain deeper understanding about the nature of dynamics, we investigate the effect of isotopic composition of water on the dielectric spectra of water. To this end we study $H_2{}^{16}O$, $D_2{}^{16}O$,[3,4] and $H_2{}^{18}O$ at temperatures ranging from 5 to 65 °C.

The spectra of all isotopes are well described by a superposition of two Debye-type (exponential) relaxation processes over the studied temperature range. We find the static dielectric constants to be practically the same for all three types of water, which can be explained by the very similar volume concentrations of dipoles. More profound differences are seen between the relaxation times of the main relaxation process (τ_1). This dominant relaxation mode corresponds to the cooperative reorientation of the hydrogen-bonded water network, and has been proposed to be due molecular jumps together with hydrogen bond breaking and re-formation. The substitution of hydrogen for deuterium ($H_2{}^{16}O$ vs $D_2{}^{16}O$) results in the previously reported increase of τ_1 by up to 30% (5 °C).[3,4] Remarkably, also the replacement of ^{16}O with ^{18}O leads to a 3–4% enhancement of τ_1. Conversely, the fast relaxation time ($\tau_2 = 0.1$–0.6 ps), which has been ascribed to small angular motions of water, seems to not change upon isotopic substitution of the oxygen. Hence, we find that the small difference in the collective relaxation of water, may be due to the slightly different moment of inertia for $H_2{}^{18}O$ and $H_2{}^{16}O$. On the other hand, the fast dynamics, which might be expected to be prone to inertial effects, seems to be rather insensitive to the oxygen isotope.

Analyzing the relaxation times applying the transition state theory,[2] the higher activation enthalpy of the relaxation of $D_2{}^{16}O$ correlates to the higher hydrogen bond strength of O–D vs O–H. For $H_2{}^{18}O$, on the other hand, the enthalpy of activation is the same as for $H_2{}^{16}O$, despite the higher relaxation times at all temperatures. Comparing the activation of Gibbs free energies and entropies, we found that the latter has a non-negligible contribution to the relaxation process and compared to $H_2{}^{16}O$, it is less positive for $H_2{}^{18}O$ yielding somewhat slower relaxation.

Together, we find that the replacement of H by D results in the well-known retardation of the cooperative relaxation of water, while the substitution of ^{16}O for ^{18}O leads to a minor, yet detectable, slow-down of the rate of dipolar relaxation.

Keywords: *dielectric relaxation; water isotopes; transition state theory; hydrogen bond*

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Exfoliation of Two-Dimensional Materials: The Role of Entropy

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Liquid-phase exfoliation (LPE) is the best-known method for the synthesis of two-dimensional (2D) nanosheets. Compared to enthalpy, entropy is hardly considered to be a factor in choosing energy-efficient solvents and has not even been verified to be negligible. In this work, we explore the entropy contribution in LPE by performing molecular dynamics (MD) simulation of the structural flexibility effect in graphene, hexagonal boron nitride (hBN), and molybdenum disulfide (MoS_2). Our results show that surface vibration favors the exfoliation of graphene and hBN and destabilizes the reaggregation of nanosheets in water at 300 K, whereas the opposite is found for MoS_2. The entropy change is found to be 41%, 48%, and 4% of the enthalpy gain for graphene, hBN, and MoS_2 in LPE, respectively, and 64%, 32%, and 56% in reaggregation, which amounts to a step advancement for solvent screening in LPE of 2D materials.

Keywords: *entropy; exfoliation; graphene; water*

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Interaction and Synergistic Effect of Heteroatoms in Co-Doped Graphene in Ionic Liquid-based Supercapacitor

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Recently, graphene has been widely used as an electrode material for supercapacitors, but the electrochemical performance of the graphene-based supercapacitor is far below its theoretical level[1]. The introduction of heteroatoms to graphene can change the electrical conductivity, surface activity and mechanical stability, and improve the electrochemical performance of graphene-based supercapacitor, which is very important for widening its application in energy storage[2]. Among many heteroatoms, the doping of nitrogen can adjust the electronic properties of graphene and improve the electrochemical properties of graphene for supercapacitors[3]. The sulfur has a large size and possesses an electron pair that is easily polarized and is used to incorporation into graphene for improving its chemical reactivity[4]. In addition, the heteroatom co-doping as compared with single doping, can effectively enhance the capacitive properties of graphene. Besides, Ionic liquids have the advantages of wide electrochemical window, high thermal and chemical stability. It is significance for improve the energy density of supercapacitors. In this work, we synthesized the nitrogen-sulfur co-doped graphene aerogel (NS-GA) using graphene oxide as the precursor and mercaptoethylamine as the dopant by hydrothermal method. The effects of the interaction between co-doped heteroatoms on the morphology and structure of graphene were investigated, and their advantages in improving the performance of graphene-based supercapacitors were explored. The results show that NS-GA has larger effective specific surface area compared with single-doped graphene aerogel, and possess interconnected three-dimensional multi-level pore structure. The large effective specific surface area provides a wider residence for the adsorption of ions, and the multi-level pore structure is beneficial to the electrolyte ions to rapidly diffuse and adsorb to the electrode surface. The material was electrochemically tested with 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIMBF$_4$) as electrolyte. The test results show that the specific capacitance of the supercapacitor based on NS-GA is 191.7 F g^{-1} at a current density of 1 A g^{-1}. When the power density is 993 W kg^{-1}, the energy density is as high as 105 Wh kg^{-1}. Compared with the single-doped graphene electrode material, the synergistic effect between the co-doped heteroatom is more helpful to improve the electrochemical performance of the material.

Keywords: *Ionic liquid; Graphene; Supercapacitors; Energy density*

Acknowledgments

Financial support from the National Natural Science Foundation of China (Nos. 21873026, 21573058, and 21303044) is gratefully acknowledged.

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Excited State Proton Transfer of Cyanonaphthol in High-temperature and High-pressure Alcohol: Effect of Solvent Polarity and Hydrogen Bonding Ability

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Supercritical fluid (SCF) has been extensively studied because of their unique physicochemical properties. Among them, hydrogen bonding (HB) solvents such as water and alcohols, are revealed to show interesting behavior as reaction media around the critical point mainly due to the local density enhancement around the solute molecule. To investigate how HB between solute and solvent affects the reaction dynamics, we have focused on the proton transfer (PT) dynamics of photo-acid in supercritical fluids with hydrogen-bonding ability[1]. In this presentation, we will discuss the PT dynamics of 5, 8-dicyano-2-naphthol (DCN2) assessed by the time resolved fluorescence spectrum at high temperature and high pressure methanol and ethanol (30 MPa isobar between 294 K and 543 K). The results are compared with those in n-alcohols under ambient condition (295 K and 0.1MPa) [2].

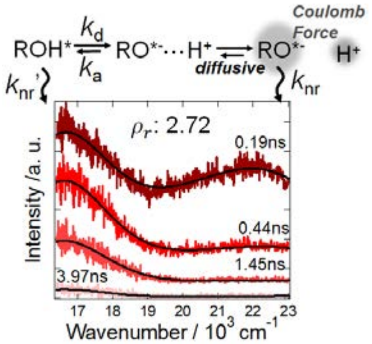

Figure 1. ESPT scheme and time-resolved fluorescence spectrum of DCN2 in methanol at 30 MPa and 373 K.

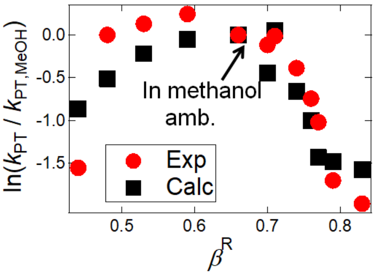

Figure 2. Correlation of rate constant and solvent's HB basicity (β)

Figure 1 shows the time resolved fluorescence spectrum of DCN2 in methanol at 30 MPa and 373 K. The band around 22000 cm^{-1} is fluorescence from the normal form (ROH*) and that around 17000 cm^{-1} is fluorescence from the proton dissociated form (RO^{-}*). The population dynamics of each species was extracted from the spectrum fitting to a sum of log-normal functions. From the population dynamics, PT rate constant of DCN2 was determined by solving the time-dependent diffusional motion of geminate species (RO^{-}*…H^{+}) in the Coulomb field according to the reaction scheme in Fig. 1[3]. Figure 2 is the plot of PT rate constant (k_{PT}) at various thermal conditions normalized by that in methanol under ambient conditions ($k_{PT,MeOH}$) against the HB basicity (β) of solvent. Black markers represent the rate constants obtained by the correlation with the solvent's β and the dipolarity scale (π*). The experimental trend of PT rate constants with β value is well captured by that determined by the calculation, which means PT kinetics is simply explained by the solvent HB property and polarity. The nonlinear correlation of the PT rate constant against β is due to the competing effect of β and π* (which is not shown in the figure.) An increase in β decreases the PT rate because of the stabilization of reactant, while an increase of π* increases the PT rate because of the stabilization of the transition state.

Keywords: *Supercritical alcohol, proton transfer, Kamlet-Taft parameter, photoacid, time resolved fluorescence*

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Solution Structure of Sparingly Soluble Fluoride: Insights from Molecular Dynamics and Density Functional Theory Calculations

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Fluoride ions in the zinc hydrometallurgical system, when they are enriched to a certain concentration (say, more than 100 mg of F/L of solution), will harm the anode and cathode processes, and they need to be removed from the $ZnSO_4$ aqueous solution. CaF_2 and MgF_2 are sparingly soluble and thus the salt containing calcium and magnesium are usually used as preferred precipitants to remove fluoride. However, the effect of removing fluoride in practical zinc hydrometallurgical system is not good. Recently, the results of our group's solubility determination [1,2] display that solubility of CaF_2 and MgF_2 in the solutions containing $MgSO_4$, $ZnSO_4$ and $MnSO_4$ is higher ~50 times (averaged) than that in pure water, indicating that the ionic interactions in such system are very complicated. Consequently, the knowledge of species and structure of aqueous CaF_2 and MgF_2 solutions is crucial for predicting solubilities of fluoride complexes in different conditions by building reasonable thermodynamic model.

In this work, the solution structure of CaF_2 is investigated by molecular dynamics (MD) simulations and density functional theory (DFT) calculations. The DFT results display that the H_2O molecules bound with Ca^{2+} in the first coordinated shell are strongly attracted by F^- bound with Ca^{2+} in vacuum. This is ascribed to the strongly electronegativity of F^-. However, this situation is remitted in aqueous solution because of the H-bond formed with bulk water for F^-. MD simulations suggest that the CaF^+ species can be detected as $CaF(H_2O)_6^+$ or $CaF(H_2O)_5^+$. And a few $CaF_{2(aq)}$ species can also be detected as $CaF_2(H_2O)_5$ or $CaF_2(H_2O)_4$.

Dissociation constants for $CaF_{2(aq)}$ were calculated by performing series of distance-constrained ab initio MD simulations using CP2K. The free energies of the $CaF_{2(aq)}$ dissociation reactions were obtained by thermodynamic integration. These results are consistent with the experiments. This computational study provides an independent check that helps to evaluate the reliability of dissociation constants for the $CaF_{2(aq)}$ obtained by potentiometric method, and provide a means to determine the nature and stabilities of sparingly soluble fluoride complexes whose content beyond the detection limit of general spectroscopy.

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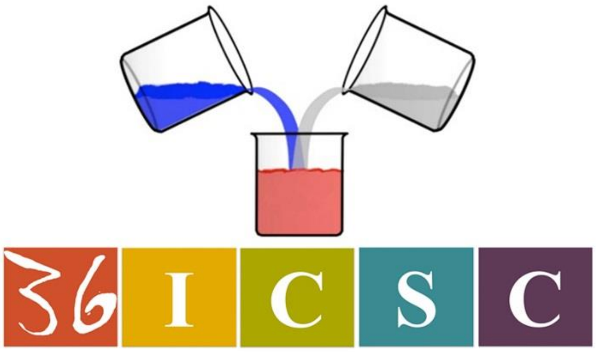

Poster Presentations

The Kinetics of Amino Acid Isomerization in Amyloid Beta Fragments Quantified by Real-Time ^{1}H-NMR

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Uncommon amino acid isomers have been found in a variety of peptides and proteins in a living body[1-4]. For example, isoaspartyl residues (isoAsp, Fig.1) is found to be produced in amyloid beta (Aβ) proteins. The appearance of isomers may cause major changes to protein structures, since different peptide chain orientations can induce an abnormal peptide backbone. The presence of isomers may be one of the triggers of abnormal aggregation and can induce the partial unfolding of protein leading to diseases.

It is challenging to analyze how such isomerization proceeds at each amino acid independently in situ. In this study, we performed a real time quantitation of isomerization of aspartyl (Asp) and glutamyl (Glu) residues in fragments of Aβ protein by using solution-state ^{1}H NMR in situ.

We succeeded in distinguishing isomerization from Asp to isoAsp residue in Aβ fragments, as well as the reactivity of glutamyl (Glu) residue. This enabled us to compare the isomerization of Asp1, Asp7, Asp23, and Glu3 systematically in various Aβ fragments, in terms of the kinetics of isomerization in real time. Finally, the analysis demonstrated the role of histidine (His) in regulating Asp isomerization; His showed an inhibitory effect on the progress of Asp isomerization, to avoid the accumulation of Asp isomers that might modify structures and functions in peptides.

Keywords: isomerization, NMR, aspartyl residue, glutamyl residue

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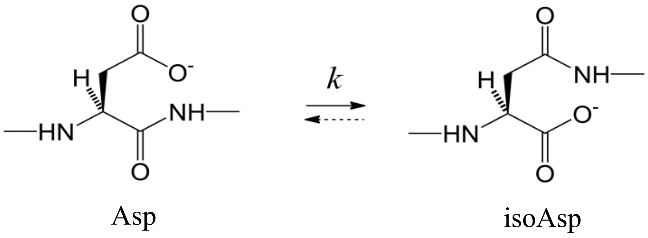

Fig 1. Isomerization of Aspartyl Residue in Peptides.

Volumetric Properties of Sodium Hypophosphite Aqueous Solution from 283.15 to 363.15 K at 101.325 kPa

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Densities of sodium hypophosphite aqueous solution (NaH_2PO_2) with the molality varied from (1.019143 to 10.43887) mol·kg^{-1} at temperature intervals of 5 K from 283.15 to 363.15 K and 101.325 kPa were measured by a precise Anton Paar Digital vibrating-tube densimeter. From the density data obtained in this work, the thermal expansion coefficient (α) and apparent molar volumes (V_Φ) were evaluated, and then the diagram of densities (ρ), expansion coefficient (α) and apparent molar volumes (V_Φ) against temperature and molality were plotted. There have been established the density increases sharply with increasing molality and declines moderately rising temperature. It was shown that the thermal expansion coefficient increase with enhancing temperature and molality simultaneously.

According to the Pitzer ion-interaction equation [1] of the apparent molar volumes, the Pitzer single-salt parameters ($\beta^{(0)v}{}_{MX}$, $\beta^{(1)v}{}_{MX}$, $\beta^{(2)v}{}_{MX}$ and $C^{\phi v}{}_{MX}$, MX = NaH_2PO_2) and their temperature-dependent correlation $F(i, p, T) = a_1 + a_2\ln(T/298.15) + a_3(T - 298.15) + a_4/(620 - T) + a_5/(T - 227)$ for NaH_2PO_2 were firstly obtained. The predictive apparent molar volumes fitted agree well with the experimental values, which indicated the single salt parameters and the temperature-dependent formula are available.

As regarding temperature-dependence coefficient parameters of the system $NaH_2PO_2 + H_2O$ were obtained involving of the least-squares method. All the thermodynamic and dielectric properties parameters of pure water involved in this article were calculated based on the IAPWS-95 equation [2] in this study.

Keywords: *Sodium hypophosphite, density, thermal expansion coefficients, apparent molar volumes, Pitzer ion-interaction model.*

Acknowledgements: Supports from the National Natural Science Foundation of China (U1607123 and 21773170), the Key Projects of Natural Science Foundation of Tianjin (18JCZDJC10040) and the Yangtze Scholars and Innovative Research Team of the Chinese University (IRT_17R81).

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Regulation of $MgCl_2$ on the Self-assembly of Ionic Liquid Surfactant ([C_{16}mim]Cl) in Aqueous Solutions

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Imidazolium-based ionic liquid surfactants can self-assemble into various structures in aqueous solutions, which are widely used in material science.[1] It was reported that the self-assembling behaviors of 1-hexadecyl-3-methylimidazolium chloride ([C_{16}mim]Cl) in aqueous solutions were strongly concentration-dependent, and both lamellar and non-lamellar structures could be formed by regulating the concentration.[2] Herein, we systematically studied the self-assembling behaviors of [C_{16}mim]Cl in aqueous solutions regulated by the concentration of $MgCl_2$, in which the content of [C_{16}mim]Cl was fixed at 20 wt% (only the mass of [C_{16}mim]Cl and water were considered). Differential scanning calorimetry (DSC) results showed that the phase transition temperatures, including the transitions from lamellar crystalline to lamellar gel and from lamellar gel to spherical aggregate, could be well regulated by the concentration of $MgCl_2$. Synchrotron X-ray scattering results indicated that the crystalline structure transferred to micelle directly upon heating in [C_{16}mim]Cl aqueous solutions in the absence of $MgCl_2$. However, a gel phase was observed amid the transformation from crystalline structure to micelle by rational regulating the concentration of $MgCl_2$. Fourier transform infrared spectroscopy (FTIR) was employed to examine the phase transition processes at submolecular level, which indicated that the ordering rearrangement of alkyl tails and the intermolecular interactions around headgroup regions exerted a joint effect on the phase transition behaviors in the studied system.

Keywords: *Ionic liquid surfactants; Self-assembly; Phase transition*

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Metal Ionic Liquids for the Cycloaddition of CO_2 under Ambient Conditions

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Ionic liquid (IL) is a molten salt composed of organic cation and inorganic anion which is liquid state at or near room temperature. ILs have many advantages over traditional organic solvents, i.e., non-combustible, good solubility properties, good thermal stability and chemical stability, easy to separate from other substances, and so on.[1] Due to their specific physical and chemical properties, ILs can be widely used in chemically fixed carbon dioxide, in particular to catalyze the reaction of carbon dioxide with epoxides to synthesize cyclic carbonates.[2] Here the metal ionic liquids (MILs) were prepared and characterized by thermogravimetric analysis, Fourier transform infrared spectroscopy, nuclear magnetic resonance and X-ray photoelectron spectroscopy (Fig. 1). The as-synthesized MIL can efficiently catalyze the cycloaddition of carbon dioxide and epoxides into cyclic carbonates at normal temperature and pressure with high catalytic activity and selectivity. It provides a new route for the chemical fixation of carbon dioxide.

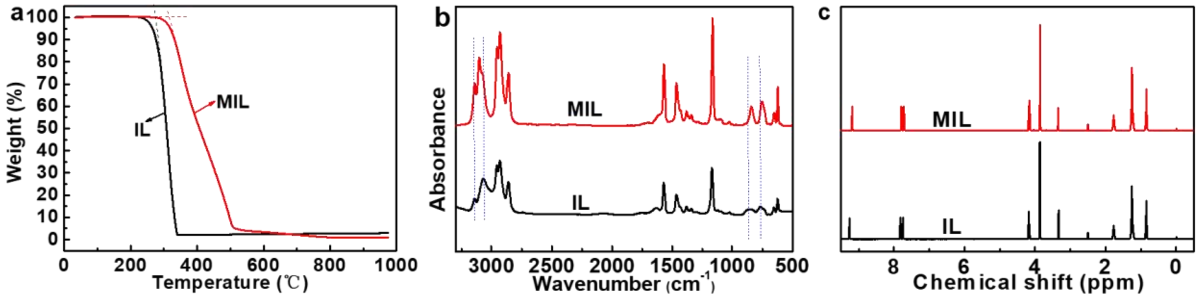

Fig 1. TG (a), FT-IR (b) and ^{1}H NMR (c) spectra of IL and MIL.

Keywords: *CO_2 cycloaddition; Ionic liquids; Epoxide; Cyclic carbonate*

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Basic Salt Lake Brines: Efficient and Sustainable Catalysts for Transformation of CO_2 into Quinazoline-2,4(1H,3H)-diones

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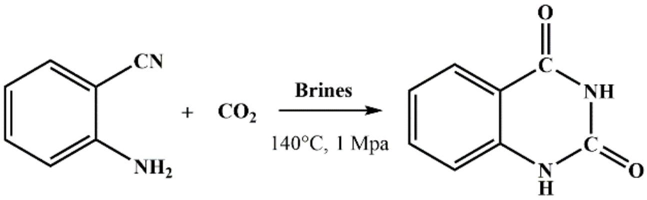
Carbon dioxide (CO_2) is promising C1 feedstock for green and sustainable chemistry. Transformation of this abundant, nontoxic, nonflammable and renewable C1 source into value-added chemicals by green and economical catalyst has drawn increasing attention [1]. Quinazoline-2,4(1H,3H)-diones and their derivatives are an important class of heterocyclic compounds with wide range of biological and pharmacological activities, and the atom-economic reaction between CO_2 and 2-aminobenzonitriles is an excellent route to yield quinazoline-2,4(1H,3H)-diones [2].



Scheme 1. Synthesis of quinazoline-2,4(1H,3H)-diones with CO_2 catalyzed by salt lake brines

Salt lake brines have been considered as the store house of mineral salts, and they are widely distributed in the worldwide scale, including America, Israel, Chile, China [3-4]. So far, researches on salt lake brines are mainly concentrated on the extraction of valuable and scattered elements. However, as far as we know, there is no report on using these green, abundant and easily available salt lake brines as catalysts. Herein, in this work, a series of basic salt lake brines were used for the first time to catalyze the reaction of CO_2 and a broad range 2-aminobenzonitriles to form corresponding quinazoline-2,4(1H,3H)-diones, as shown in Scheme 1. It was found that the abundant, inexpensive and available basic salt lake brines could efficiently promote the reactions of 2-aminobenzonitriles at low pressure of CO_2, and high yields of value-added products were obtained.

Keywords: *Salt lake brine; CO_2; quinazoline-2,4(1H,3H)-diones.*

Acknowledgements: The authors gratefully acknowledge financial supports from the National Natural Science Foundation of China (U1607123 and 21773170), the Application Foundation and Advanced Technology Program of Tianjin (15JCQNJC08300), the Program of Tianjin Education Commission (2017KJ015), the Innovative Research Team in Tianjin Colleges and Universities (TD13-5008) and Innovative Research Team of Chinese University (IRT_17R81).

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Speciation Analysis of Iodate and Iodide in High Salt Brine by High Performance Liquid Chromatography and Inductively Coupled Plasma Mass Spectrometry

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At present, ionic membrane electrolysis is the most advanced technology for the mass production of caustic soda [1]. However, a lower concentration of iodine (< 0.2 mg L^{-1}) in high salt brines used for caustic soda production is crucial, otherwise iodine can be oxidized to higher oxidation states and produce insoluble precipitates in the alkaline environment of the ion membrane, resulting in reduced current efficiency and greatly decreasing the service life of the ion membrane [2-3]. In order to reduce membrane loss and caustic soda production costs, it is of practical significance to maximize the removal of iodine from high salt brine. However, the species of iodine and their corresponding contents are different in different process stage brines, which results in different iodine removal methods in each stage.

The speciation of iodine is mainly based on the combination of chromatographic separation and high-sensitivity detectors, especially in combination with inductively coupled plasma mass spectrometry (ICP-MS), due to its rapidity, low interference, low detection limit and high accuracy [4]. In this paper, the attention was given to the complex matrix of high salt brine from the chlor-alkali industry. Two types of anion exchange columns were tested to establish a rapid analytical method of iodine speciation applied to high salt brine by using a high multiple dilutions to eliminate matrix interferences. A high-efficiency separation anion-exchange column (Dionex IonPac AS-14) for iodate and iodide with 100 mM $(NH_4)_2CO_3$ solution at pH = 10 as mobile phase was proved, and the total running time of individual sample was within 8 min. Linear standard calibration plots were obtained in a concentration range of 1.0-100 μg L^{-1} for iodate and iodide, and the detection limits were 0.05 μg L^{-1} for the former and 0.20 μg L^{-1} for the latter. This method shows good sensitivity and precision to be used for high salinity samples from the chlor-alkali industry.

Keyword: *Speciation analysis; HPLC-ICP-MS; Iodate and iodide; High salt brine*

Acknowledgements: Supported by the NNSFC (21773170, U1607123 and U1607129), the Key Projects of Natural Science Foundation of Tianjin (18JCZDJC10040), the Innovative Research Team in Tianjin Colleges and Universities (TD13-5008) and the Yangtze Scholars and Innovative Research Team in Chinese University (IRT_17R81).

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Thermodynamic Properties of CsCl + Tetramethylurea + Water Ternary System at 298.15K

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Activity coefficients and other related magnitudes such as osmotic coefficients, solvent activity, Gibbs free energy of the mixture (or of transfer) allow us to analyze the ion-solvent and ion-ion interactions occurring in the medium, as well as the structural implications played by the different components[1]. In this paper, the thermodynamic properties of CsCl in tetramethylurea (TMU) - water systems were investigated by potentiometric method at T = 298.15 K. The experiment data are correlated by the Pitzer and extended Debye-Hückel equations. The mean activity coefficients, osmotic coefficients, excess Gibbs free energies and standard solubility product of the ternary systems are calculated. The variation of these magnitudes in the ε_r-decreasing co-solvent (TMU-H_2O) is discussed in terms of the ion-solvent, ion-ion interactions, relative permittivity, ion radius in the solution.

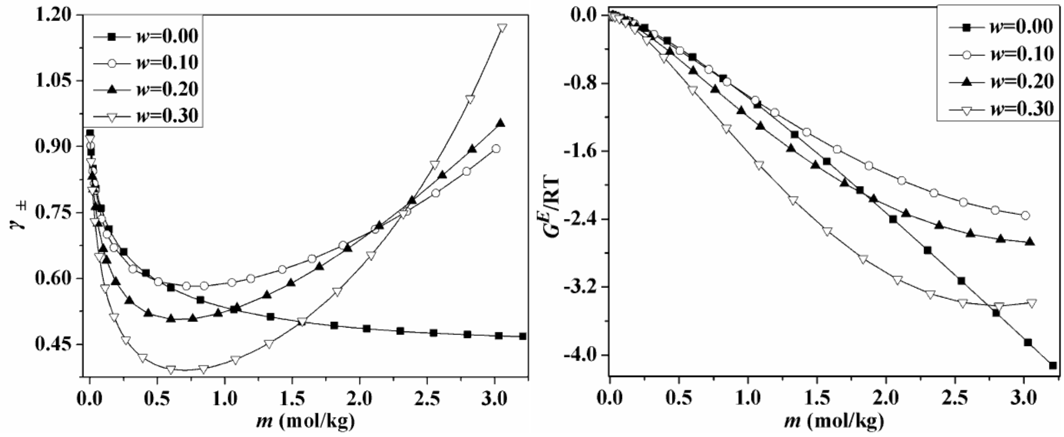

Fig 1. The average ion activity coefficient ($\gamma_{\pm}$) and excess gibbs free energy (G^E) of CsCl + TMU + H_2O systems at 298.15K

Keywords: *Tetramethylurea, CsCl, Potentiometric method, Thermodynamic properties*

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Improvement of Binary Interaction Coefficient in McAllister Three-body Viscosity Model

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Viscosity is an important transport properties of fluids, and can be obtained from experimental methods. However, for the binary mixtures of fluids, it is a difficult task to measure all the viscosities at different temperature, pressure and composition. Hence, viscosity prediction model of the mixtures is necessary. So far, many scholars have proposed different viscosity models, such as Frenkel model, Grunberg-Nissan model, McAllister three-body model. The most accurate of these is the McAllister three-body model. However, the binary interaction coefficient in the model can only be correlated through experimental data. Once the temperature changes, the viscosity needs to be re-measured and fitted, which is inconvenient.

In this work, the kinematic viscosities v_1 and v_2 of the pure component and the correction coefficients k_1 and k_2 are introduced into the binary interaction coefficient. We found that the correction coefficient varies linearly with temperature. Six different types of binary mixtures (methyl decanoate + alcohols, hexadecane + esters, isooctane + alcohols, butyl cyclohexane + alkanes, methyl tert-butyl ether + alkanes, ethanol + esters) were used to verify the model. Viscosity for lower and higher temperatures can be calculated using this improved model. It has also been found that there is a good parallel relationship between the correction coefficients of some mixtures of esters and alcohols. Therefore, the viscosity of the homologue can be derived by measuring only the viscosity of a mixture. The results are accurate enough for engineering applications.

Thermophysical Properties for Solutions of 1,2-hexanediol + Water Binary Mixtures at Different Temperatures and Atmospheric Pressure

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The thermophysical properties, such as density, speed of sound, and refractive index, are important for obtaining the fundamental data of various molecular liquids mixtures from different classes of compounds; these data are useful as well as in solutions theories and molecular thermodynamics, for confirmation and development of theoretical/ empirical models of pure fluids and mixtures and for understanding the behavior of interactions occurred between the components of these mixtures. The physico-chemical properties for the different organic binary mixtures are recently reported [1,2].

In this work, the thermophysical properties data for solutions of 1,2-hexanediol with water, have been measured at several temperature~~s~~ of (298.15, 308.15, and 318.15) K, atmospheric pressure, and in the whole range (0 to 1) of diol molar fractions.

Densities and speeds of sound data were obtained using the densitometer analyzer Anton Paar DSA 5000 M and the refractive indices data were measured using the Anton Paar RXA 170 automatic refractometer.

From the obtained experimental data, the related excess and deviation quantities, namely the excess molar volumes, the partial/apparent molar volumes, the isentropic compressibilities and the excess refractive indices were calculated.

The excess thermodynamic properties were correlated with the Redlich-Kister polynomial equation. The experimental excess molar volumes values have been also used to test the applicability of the Prigogine-Flory-Patterson (PFP) theory [3-5] and the results were analyzed in terms of molecular interactions between the components of the mixture.

Discussions concerning the experimental and calculated results in relation to the molecular interactions and structural effects between components of mixtures are presented. In the dilute range of composition, (0 to 0.25) diol mole fractions, the 1,2-hexanediol molecules form certain kind of aggregates, as shown in neutron scattering measurements[6].

Keywords: *1,2-Hexanediol, Thermodynamic properties, Prigogine-Flory-Patterson (PFP) theory, Microheterogeneity, Molecular interactions*

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Heat Capacity of $Rb_2SO_4(aq)$ and $Cs_2SO_4(aq)$ Solutions and Thermodynamics Modeling of $Rb_2SO_4 + H_2O$ and $Cs_2SO_4 + H_2O$ Systems

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Sulfuric acid or sulfate leaching process has been applied to extract Rb and Cs salts from lepidolite and pollucite. Liquor consisted of alkali metal (Li, Na, K, Rb and Cs) sulfates was produced in these processes. So knowledge of solubility and aqueous thermodynamic properties of such complex sulfate systems is essential to process design of further element separation from leaching liquor.

In this study, heat capacity of $Rb_2SO_4(aq)$ and $Cs_2SO_4(aq)$ solutions were determined from 288.15 K to 338.15 K and to concentration near saturation using a Calvet-type calorimeter. Combining heat capacity data with solubility and thermodynamic data reported in the literature [1-4], comprehensive thermodynamic models for the binary $Rb_2SO_4 + H_2O$ and $Cs_2SO_4 + H_2O$ systems were developed. The obtained models reproduce the activity, thermal and solid-liquid equilibria properties of the two systems over wide temperature and concentration ranges. The study laid a foundation of phase diagram simulation for complicated multi-component systems containing Rb and Cs sulfates.

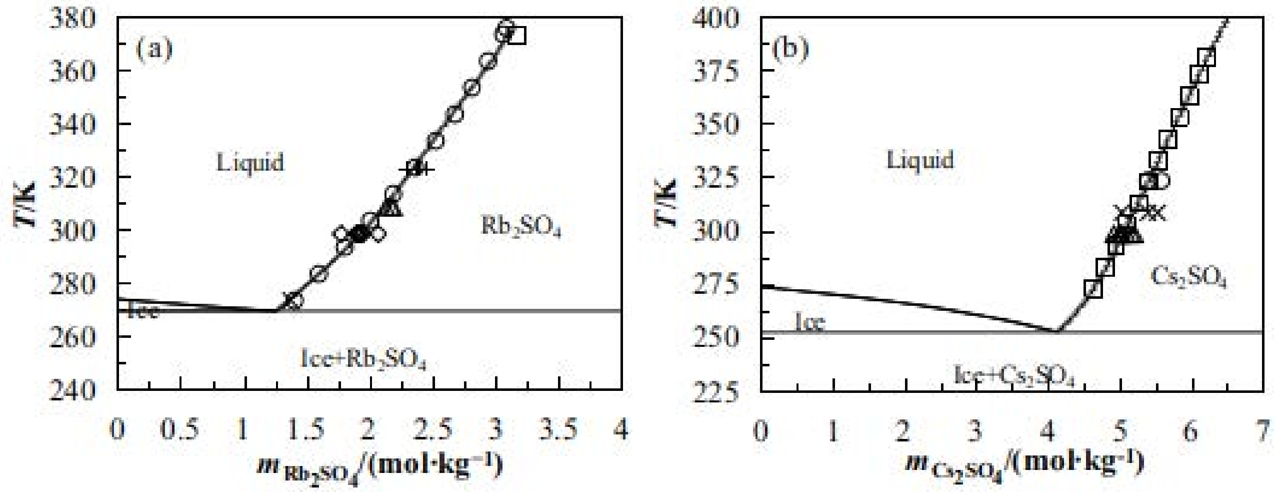

Fig. 1 Phase diagrams of $Rb_2SO_4 + H_2O$ and $Cs_2SO_4 + H_2O$ systems. Symbols are experimental data reported in literature, lines represent the model values. (a) $Rb_2SO_4 + H_2O$ (○ 273.15 K-375.55 K, × 273.15 K, ◊ 298.15 K, Δ 308.15 K, + 323.15 K, □ 373.15 K); (b) $Cs_2SO_4 + H_2O$ (□ 273.15 K-381.75 K, Δ 298.15 K, × 308.15 K, ○ 323.15 K).

Keywords: *Rubidium sulfate; Cesium sulfate; Heat capacity; Phase equilibria; Thermodynamic modeling*

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Molecular Dynamics Simulation of Temperature Influence on Ionic Hydration in $CaCl_2$ and $MgCl_2$ Aqueous Solutions

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The molecular dynamics simulations of aqueous $CaCl_2$ and $MgCl_2$ solutions with different temperatures, 298K, 323K, 373K respectively, were carried out to investigate the ionic hydration employing COMPASS force field of Materials Studio software package. The effect of temperature on the microstructure and dynamic properties of the solution were investigated. It was found that temperature has a certain effect on the structure of short-range hydration of Ca^{2+}, Mg^{2+} and Cl^- ions, but with the increase of the temperature, variation of hydration parameters of the three ions show different trends. The hydration number and hydration radius of Ca^{2+} increased gradually, simultaneously, the hydration number and hydration radius of Cl^- decreased in both solutions, while the hydration parameters of Mg^{2+} were hardly affected by temperature. Besides, the increase of temperature results in the increase of the self-diffusion coeffcients of Ca^{2+}、Mg^{2+}、Cl^-. This work can provide some theoretical basis for the development and utilization of seawater chemical resources.

Keywords: *$CaCl_2$ aqueous solution, $MgCl_2$ aqueous solution, Ionic hydration, Molecular dynamics simulation, Effect of temperature*

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Volumetric Properties and Ion-interaction Model for Aqueous Lithium Borate Solutions

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Densities of aqueous solutions of $LiB(OH)_4$ and $LiB_5O_6(OH)_4$ at solute molalities ranging from (0.03 to 0.97 or 1.13) mol·kg^{-1}, respectively, have been measured by using vibrating-tube densitometer at temperature intervals of 5 K from 288.15 to 323.15 K. The apparent molar volumes(Φ_{v}), standard molar volumes(Φ_v^0), apparent molar expansibilities(Φ_E^0), and coefficient of thermal expansion (α) in aqueous lithium metaborate and lithium metaborate solution have been calculated from the density data. The limiting appareut moler volume, Φ_E^0, and slope, S_{v}, are interpreted in terms of solute-solvent and solute-solute interactions, respectively. The Φ_E^0 values vary with temperature as a power series of temperature. Different thermodynamic parameters have been used to explore solute-solute, solute-solvent interactions and effect of concentration and temperature. According to the Heplers criterion, both lithium metaborate and lithium penta borate are water structure breaker. According to the Pitzer ion-interaction model of the apparent molar volume, the Pitzer single salt parameters of $LiB(OH)_4$ and $LiB_5O_6(OH)_4$ at different temperatures were obtained, and the correlation between Pitzer single salt parameters and temperature were given.

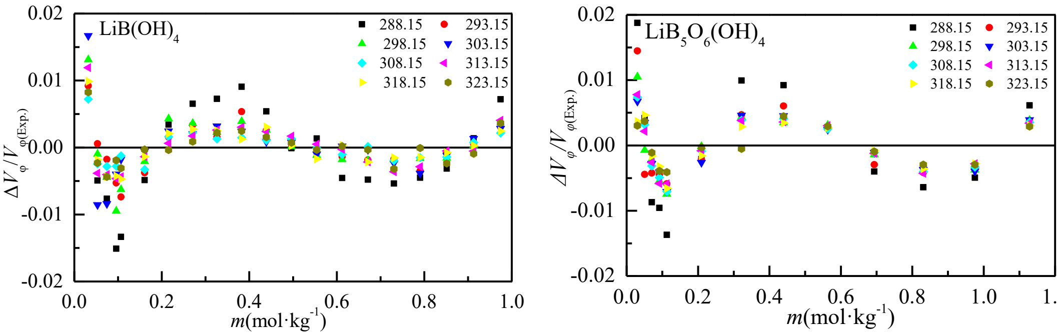

Fig 1. Relative deviations of the experimental apparent molar volumes V_φ at $288.15 \le T/\mathrm{K} \le 323.15$ for the system $LiB(OH)_4$-H_2O and $LiB_5O_6(OH)_4$-H_2O, as a function of the molality *m*, from the Pitzer model with the parameters

Keywords: *Lithium Borate; Density; Volumetric Properties; Pitzer model*

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Mean Activity Coefficients of KCl in KCl + $SrCl_2$ + H_2O Ternary System at 308 K by EMF Method

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Abstract: Electrolyte solution exists widely in nature, and the study of the thermodynamics properties of mixed electrolytes solution such as activity coefficients, osmotic coefficients, heat capacity, enthalpy, entropy and excess free energy is becoming more and more popular [1, 2]. In this work, the mean activity coefficients for KCl in the (KCl + $SrCl_2$ + H_2O) ternary system were determined by electrode potential measurements of the cell without liquid junction: K–ion selective electrode (ISE) | KCl (m_1), $SrCl_2$ (m_2), H_2O | Cl–ion selective electrode (ISE) at the total ionic strengths ranging from (0.0100 up to 1.0000) $mol \cdot kg^{-1}$ at 308.15 K for different ionic strength fractions y_b of $SrCl_2$ with y_b= (0.0, 0.2, 0.4, 0.6, and 0.8). The relationship diagrams between the mean activity coefficient of KCl and the ionic strength fraction were plotted. The Pitzer ion interaction parameters $\theta_{K^+ \cdot Sr^{2+}}$ and $\varphi_{K^+ \cdot Cl^- \cdot Sr^{2+}}$ were fitted respectively. Furthermore, those parameters obtained with the Pitzer model were used to calculate the values of the mean activity coefficients of $SrCl_2$. In addition, the osmotic coefficients, solvent activity and the excess Gibbs free energy for the mixed electrolyte system were also studied.

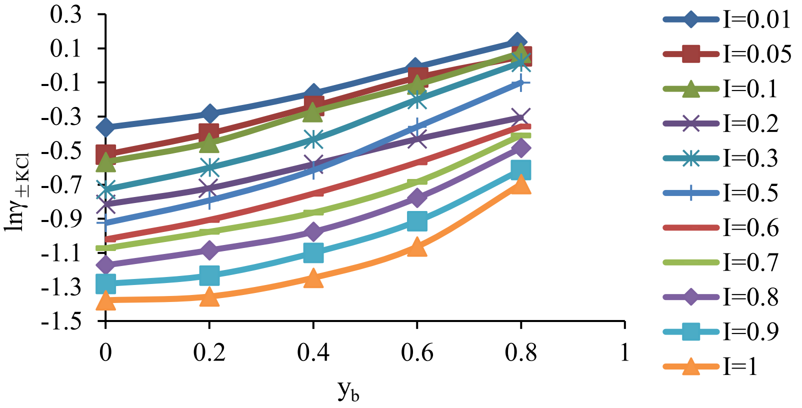

Figure 1. Plot of ln $\gamma_{\pm KCl}$ vs y_b for different ionic strengths I of the KCl-$SrCl_2$-H_2O ternary system at 308 K

Keywords: *Activity coefficients; Electrode potential; Ion selective electrode; Potassium chloride*

Acknowledgments

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Solubility and Model Simulation of Limited Solid Solution Containing System RbCl−CsCl−H_2O

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The solubility, phase diagram and their model simulation of the RbCl−CsCl−H_2O limited solid solution containing system, at relative wide temperature range, are of great importance for extracting rubidium and cesium resources from Chaerhan Salt Lake.

Up to now, there is only reported solubility of this ternary system at 298.15 K [1] and 323.15 K [2]. The reported solubility data at 323.15 K [2] are not quite reasonable that we evaluated, and the measured results shown that the equilibrium solid phase are pure salts (RbCl and CsCl), which are insistent with the situation of 298.15 K [1] that the solid phase are solid solution.

In this work, the solubility of the RbCl−CsCl−H_2O ternary system has been determined by two different methods, namely a Flow-Cloud-Point (FCP) method [3] and isothermal equilibrium method (IEM), from 298.15 K to 348.15 K. The measured results are consistent with each other, which indicate the reliability of the measured solubility, as shown in Figure 1 (a). Combining our previous work [3,4,5] for the RbCl−H_2O and CsCl−H_2O binary systems, the Pitzer model was used to evaluate the solubility and thermodynamic properties, to identify the equilibrium solid phases, of the RbCl−CsCl−H_2O ternary system from 298.15 K to 348.15 K. it is found that the equilibrium solid phases in the ternary system are two limited (regular) solid solution $(Rb,Cs)Cl_{(ss)}$ and $(Cs,Rb)Cl_{(ss)}$. The Lippmann diagrams for this limited solid solution containing system also have been presented, as shown in Figure 1 (b).

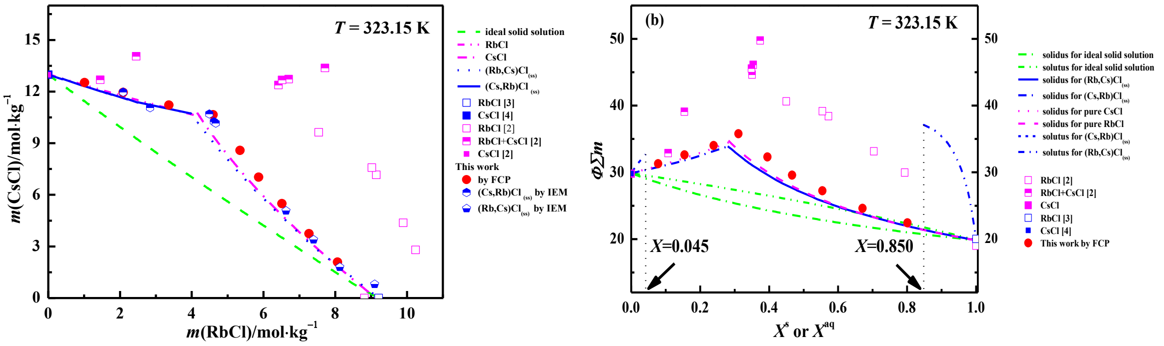

Figure 1. The solubility and Lippmann diagram of the RbCl−CsCl−H_2O ternary system at 323.15 K. (a) solubility (b) Lippmann diagram.

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Solubility Prediction of the Ternary System NaCl–SrCl₂–H₂O at 273 K and 308 K

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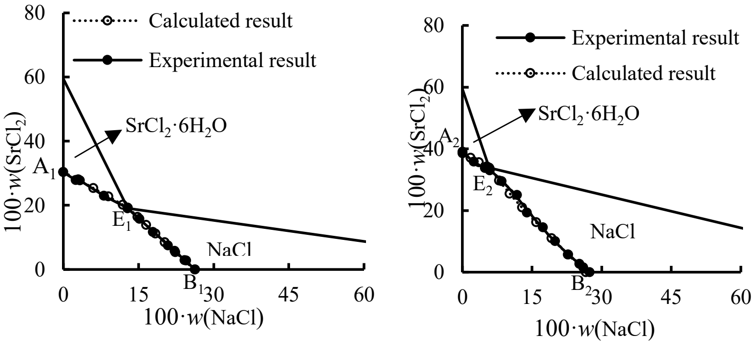
The underground brine of the Sichuan Basin in China is widely distributed and rich in resources. The studies of phase equilibria of systems containing strontium at various temperatures have practical guiding significance for the exploitation and utilization of underground brine. The Pitzer and H-W models are widely used in the solubility prediction of water-salt systems. In this paper, based on the solubilities of the ternary system $NaCl-SrCl_2-H_2O$ at 273 K and 308 K obtained in our experiment, the Pitzer and H-W models were employed to predict the solubilities of this ternary system at 273 K and 308 K. The single salt parameters ($\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ}) and solubility equilibrium constant of NaCl at 273 K and the Debye-Hückel constant A^{ϕ} were calculated according to the temperature-dependent equation in the literature [1], and those at 308 K were obtained from the literature [2]. The single salt parameters of $SrCl_2$ at 308 K were derived from the reference [3], while those at 273 K were fitted by linear regression fitting of solubility data. The solubility equilibrium constants of strontium chloride hexahydrate at 273 K and 308 K were calculated from the literature [4]. The mixing ion-interaction parameters $\theta_{Na,Sr}$ and $\Psi_{Na,Sr,Cl}$ were obtained by linear regression fitting of solubility data. Based on Pitzer and H-W equations, Particle Swarm Optimization (PSO) algorithm was adopted to calculate the solubilities of this ternary system. According to the calculated results, the comparison of calculated and experimental phase diagrams of the ternary system $NaCl-SrCl_2-H_2O$ at 273 K and 308 K were drawn in Figure 1. The results show that the calculated values are in accordance with the experimental data, which indicating that the parameters are reasonable and reliable.

Keywords: *Solubility; Strontium chloride; Pitzer model*



(a)273 K (b) 308 K

Figure 1. Calculated and experimental phase diagrams of the ternary system $NaCl-SrCl_2-H_2O$ at (273 and 308)K

Acknowledgments
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The Effect of Imidazolium-based Ionic Liquids [C_4mim][OAc] and [C_6mim][OAc] on Phase Behavior of DPPC

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Lipid bilayers are essential parts of cell membranes which are physical boundaries of cells. Ionic liquids have broad application prospects in biological systems. However, when ionic liquids leak into the environment, Some kinds of ionic liquids are difficult to biodegrade. So the ionic liquids will cause environmental pollution and endanger life of living things. The potential impact of ionic liquids on biological systems is still unclear, so it is important to study the interaction between ionic liquids and membranes.[1] DPPC is the main component of membrane lipids, and imidazolium-based ionic liquids are the most widely used types.[2,3] In this work, we study the effect of [C_4mim][OAc] and [C_6mim][OAc] on phase behavior of DPPC. For differential scanning calorimetry (DSC) results over a wide concentration range (DPPC: Ionic liquids from 1:0 to 1:5), the onset temperatures of main phase transition of DPPC decrease gradually from 41.5 ºC to 40.5 ºC and 38.0 ºC with the increasing concentration of [C_4mim][OAc] and [C_6mim][OAc], respectively. In DSC results, [C_6mim][OAc] causes the disappearance of the pre-phase transition peak of DPPC with high concentration of [C_6mim][OAc], these results indicate that [C_6mim][OAc] may affect the arrangement of head group of DPPC. For small-angle X-ray scattering (SAXS) results, the lamellar repeat spacings of the samples, DPPC:[C_4mim][OAc] = 1:0.5, 1:1, 1:2, 1:5, at 30 ºC in gel phase are determined to be 6.37 nm, 6.21 nm, 6.18 nm, 6.08 nm, respectively. These results show that the lamellar repeat spacings decrease gradually with the increasing concentration of [C_4mim][OAc]. The calculated electron density profiles show that [C_4mim][OAc] causes a reduction in dimension of the water layers with the increasing concentration of [C_4mim][OAc].

Keywords: *Ionic liquids; DPPC; Phase transition*

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Determination of Lithium in High Salinity Samples by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)

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Inductively coupled plasma optical emission spectrometry (ICP-OES) has the ability of multi-element simultaneous analysis [1-2], but it frequently suffers the serious interference of high concentration of coexisting ions in complex samples [3]. In order to realize the swift and accurate determination of lithium in brine, the analysis of lithium in high salinity sample by ICP-OES was carried out in this work. Results showed that the coexisting sodium, potassium, calcium and magnesium in sample will lead to serious interference, and the traditional internal standard method using whether yttrium or scandium as internal standard element cannot effectively solve this problem. However, when the total amount of NaCl, KCl and $MgCl_2$ in sample was no more than 40 g/L, the interference of these coexisting ions can be successfully solved by adding 10 g/L NaCl into both sample and standard solutions, and meanwhile Ca^{2+} in sample did not cause obvious impact when its concentration is no more than 1.8 g/L. The accuracy and reliability of this developed method were supported by the analysis of three kinds of samples with different matrix composition and also by the comparison with the results obtained by inductively coupled plasma mass spectrometry (ICP-MS). Only NaCl was used in this proposed method to match different coexisting ions, by which it successfully solve the problems of multi-ion match and the incapability of batch analysis by traditional method, and it therefore has important significance for the development and comprehensive utilization of lithium resource in brine.

Keywords: *Lithium; High salinity sample; ICP-OES; Interference*

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Efficient Separation of Phenol from Oils Using Environmentally Zwitterions Via Forming Deep Eutectic Solvents

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Phenolic compounds are important basic materials for the organic chemical industry, such as pesticides, medicines and preservatives[1]. The major sources of phenolic compounds include coal liquefaction oil, coal tar and petroleum, and biomass by pyrolysis[2]. The traditional method for separating phenolic compounds from coal tar oils uses aqueous alkaline solutions (such as NaOH) and then uses mineral acids (such as H_2SO_4) to recover the phenols[3]. The process can cause environmental pollution. Therefore, alternative methods to separate phenols from oil mixtures using a non-aqueous method were investigated.

Recently, Abbott et al. reported that deep eutectic solvent (DES) could be formed simply between a variety of quaternary ammonium salts and hydrogen bond donors (HBDs) [4], [5], which includes phenol. As we all know, zwitterion is also an ionic compound, such as betaine and L-carnitine, both of the two zwitterions contain quaternary ammonium group and carboxylic acid group. The oxygen on the carboxylic acid group has the function of halogen anion to act as hydrogen bond acceptors (HBAs). Our studies found that the zwitterion, betaine and L-carnitine, can interact with phenol to form DESs, which are insoluble with oils. This method can be used to separate phenol from oil. The effects of extraction time, temperature, ratio of zwitterion to phenol, and separation mechanism on the extraction via forming DES were studied. The results indicate that the extraction equilibrium can be reached at 5 min. The extraction rate is not sensitive to temperature at temperatures from 283.15 K to 328.15 K. The maximum extraction efficiency is 94% at conditions of initial phenol contents, 200.0 g/L; temperature, 298.15 K; mole ratio of L-carnitine to phenol, 0.6; extraction time, 5 min. Moreover, the zwitterion can be easily recovered and reused by ethyl ether without obviously mass loss and reduction in separation efficiency.

Keywords: *Separation; Phenolic compound; Oil; Zwitterion; Deep eutectic solvent*

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Apparent Molar Volumes of Sodium Arsenate Aqueous Solution from 283.15 K to 363.15 K at Atmospheric Pressure： An Experimental and Thermodynamic Modeling Study

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The densities of aqueous solution in the system $Na_3AsO_4–H_2O$ with the molality varied from (0.04165 to 0.37306) $mol·kg^{-1}$ were determined experimentally at temperatures intervals of 5 K from 283.15 K to 363.15 K and atmospheric pressure using a precise Anton Paar Digital vibrating-tube densimeter. The apparent molar volumes (V_{Φ}), thermal expansion coefficient (α) and partial molar volume ($\overline{V}_{B}$) [1] were obtained based on the experimental density data. The 3D diagram of apparent molar volume against temperature and molality as well as the diagram of thermal expansion coefficient and partial molar volume against molality were plotted. On the basis of Pitzer ion-interaction equation of the apparent molar volume model, the Pitzer single-salt parameters ($\beta^{(0)\upsilon}_{\mathrm{M.X}}$, $\beta^{(1)\upsilon}_{\mathrm{M.X}}$, $\beta^{(2)\upsilon}_{\mathrm{M.X}}$ and $C^{(\upsilon)}_{\mathrm{M.X}}$, MX = Na_3AsO_4) and their temperature-dependent correlation $F(i, p, T) = a_1 + a_2\ln(T/298.15) + a_3(T - 298.15) + a_4/(620 - T) + a_5/(T - 227)$ (where T is temperature in Kelvin, a_i are the correlation coefficients) for Na_3AsO_4 were obtained on account of the least-squares method [2], which is not reported in the literature. The predictive apparent molar volumes agree well with the experimental values, and those results indicate that the single-salt parameters and their relational coefficients of temperature-dependence for Na_3AsO_4 obtained in this work are reliable.

Keywords: *Density; Apparent molar volume; Thermal expansion coefficient; Partial molar volume; Sodium arsenate; Pitzer model*

Acknowledgements: Supports from National Natural Science of China (21773170 and U1607123), the Key Projects of Natural Science Foundation of Tianjin (18JCZDJC10040), the Innovative Research Team in Tianjin Colleges and Universities (TD13-5008) and the Yangtze Scholars and Innovative Research Team of the Chinese University (IRT_17R81).

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Correlation of the Solubilities of KCl in Mixed Solvents at 298K: $PEG_{1000/4000}$ + H_2O and Ethanol + H_2O

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Salting out is a method employed in crystallization for producing supersaturation solution by adding a third component to decrease the solubility of the salt of interest. In this field, some papers [1],[2] have reported the effects on the solubilities of alkalis salts by the addition of organic solvents to their aqueous solutions and our research group [3] has also done several ternary systems of PEG + alkalis salt + H_2O. By comparing the salting out rate of KCl in different mixed solvents, Fig.1 shows that the salting out rate increases with the increasement of C_2H_5OH or PEG and the rate of C_2H_5OH is larger than PEG_{1000} and PEG_{4000}.The reason why the salting out degree is different is that different types of alcohols introduced different steric hindrance and the binding ability of ions to water are also different. In addition to the above, we also use the modified Pitzer model[4] to predict the solubility of KCl in mixed solvents which contains six binary parameters and five mixture parameters. And Fig.2 shows that the modified Pitzer model to correlate solubility of KCl in above alcohols keeps good agreement with experimental values, providing useful information for the simulation of extractive crystallization processes of inorganic salts with a polymer or an alcohol.

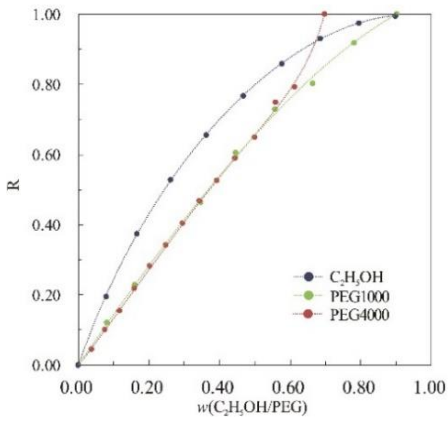

Fig 1. Salting out rate(R) of aqueous ternary system $C_2H_5OH/PEG_{1000/4000}$-KCl-H_2O at 298 K

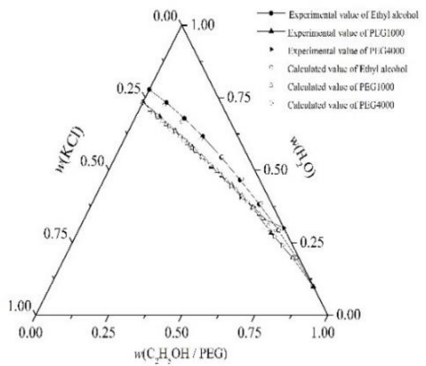

Fig 2. The experimental and calculation of aqueous ternary system $C_2H_5OH/PEG_{1000/4000}$-KCl-H_2O at 298 K

Keywords: *Pitzer model; ethyl alcohol; PEG; KCl; salting out rate.*

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Densities and Viscosities of Four Fatty Acid Esters at Temperatures from 303 K to 362 K and Pressures up to 30 MPa

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Fatty acid esters, a kind of stable chemicals, can be synthesized and obtained with highly purity at milder conditions. The esters, such as fatty acid methyl esters (FAMEs) and fatty acid ethyl esters (FAEEs), are of interested in industrial fields. Investigation shows that the main components of the biodiesel, which is a clean alternative fuel, are the mixtures of different FAMEs or FAEEs. Density and viscosity of fluids are two essential properties for its applications. For the biodiesel, the densities will affect the fuel injection equipment of the diesel engines, the injection pressure is usually about 15~50 MPa and the temperature is about 300~350 K. The values of the viscosity of biodiesel have the effects not only on the injection system but also on the atomization quality and combustion quality. Therefore, to carry out the experimental investigations on the densities and viscosities of FAMEs or FAEEs are necessary.

In this work, a set of high-pressure falling-body viscosity measurement system and high-pressure vibrating tube densimeter was designed and developed. The maximum measured temperature and pressure of the system were 373K and 45MPa, respectively. The experiment system was calibrated using three linear alkanes (dodecane, tetradecane, hexadecane), and it was determined that the viscosity measurement range of the system was between 0.576 and 4.081 mPa·s. Based on this, the high pressure densities and viscosities of four fatty acid esters (methyl decanoate, methyl laurate, ethyl octanoate, ethyl decanoate) was measured.

Keywords: *Falling-body viscometer; Vibrating-tube densimeter; Fatty acid esters; Density; Viscosity*

Study on the Stable Phase Equilibria of the Quaternary System Li^+, K^+//Cl^-, $B_4O_7^{2-}$–H_2O at 273 K

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Qaidam Basin has the advantages of wide distribution, excellent quality, abundant salt lake resources and so on [1]. Because of the unique geographical conditions of Qaidam Basin, it is beneficial to the study of phase equilibria of salt – water system at low temperature. Therefore, the results of phase equilibria provides a theoretical basis for extraction and separation technology of lithium resources in Qinghai Salt Lake [2].

The stable quaternary system Li^+, K^+//Cl^-, $B_4O_7^{2-}$–H_2O belongs to simple co-saturation type. The solubility curves of the hydrate salts are existed in the systems, and no double salt or solid solution. The stable phase diagram is constituted by two invariant points, five univariant solubility curves, and four solid phase crystalline regions corresponding to KCl, $K_2B_4O_7·4H_2O$, $Li_2B_4O_7·3H_2O$ and $LiCl·2H_2O$.

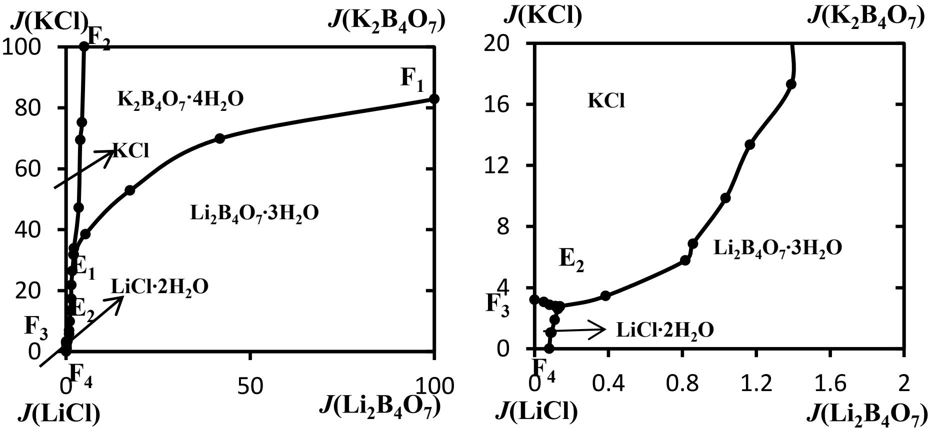

Fig 1. Phase diagram and partial enlarged diagram of quaternary system Li^+, K^+// Cl^-, $B_4O_7^{2-}$–H_2O at 273 K

Keywords: *Phase equilibrium; Lithium chloride; Solubility; Phase diagram*

Acknowledgments

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Insights Into the Microstructures of Three Alcohol–containing Binary Mixtures Using Excess Infrared Spectroscopy and DFT Calculation

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Hydrogen bond (H–bond) is omnipresent in nature with a remarkable effect on the properties of many fluids [1]. In recent years, a similar type of noncovalent interaction, the halogen bond (X–bond), has also attracted much attention [2]. In the present study, H–bonding patterns of t–BuOH in pure state and the H–/X–bonding properties of t–BuOH in CCl_4, $CHCl_3$, and DMSO-d_6 cosolvents over the whole range of concentrations were investigated by methods of ATR–FTIR, excess infrared spectroscopy [3] and DFT calculations. As a result of simultaneous H–bonding self–association and steric effects, t–BuOH forms supermolecular clusters of different sizes itself with the cyclic oligomers as the most stable structures. A detailed investigation on the optimized alcohol structures made it possible to characterize five types of hydroxyls, namely O^0H^0, O^1H^0, O^0H^1, O^1H^1, and O^2H^1, where the superscript indicates the number of H–bonds the atom involved. Depending on stretching vibrations, these hydroxyls fall over four spectral zones named as α, β, γ, and δ. This was considered as the basis for excess spectral assignments of binary mixtures. As the most controversial spectral region, the free O−H region corresponding to α and β zones were analyzed in more depth. By a combination of excess spectroscopy, quantum calculations and peak deconvolution, it was found that not only the alcohol monomers (αOH) and dimers (βOH), but also some heterogeneous t–BuOH−CCl_4/$CHCl_3$ complexes (βOH) contribute to the overall spectral shape (Fig. 1). In t–BuOH−DMSO-d_6 system, the much stronger cross interactions result in the positive excess band in γ zone, the zone attributed as the appearing dimer in t–BuOH−CCl_4/$CHCl_3$ mixtures.

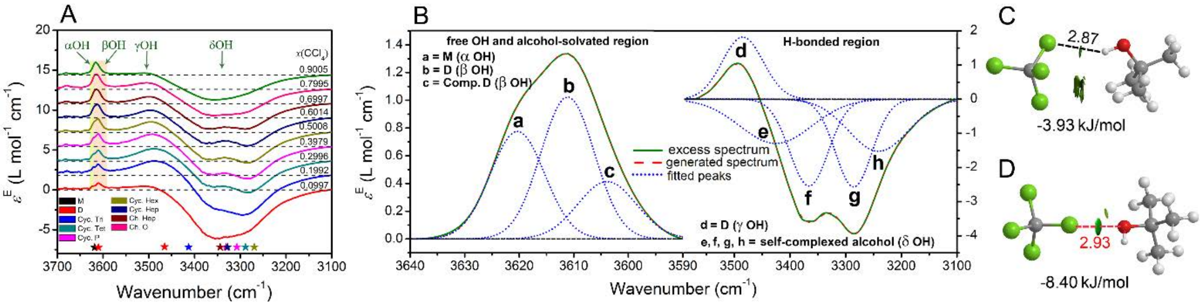

Figure 1. (A) Excess infrared spectra of υ(O−H) in t–BuOH−CCl_4 mixtures. (B) Deconvolution results of the free O−H region and H−bonded region excess spectra at equimolar composition. (C) H–bonding and (D) X–bonding interactions in 1:1 molar ratio of t–BuOH−CCl_4 mixture. Inset on (A), the theoretical averaged wavenumbers of the selected self–complexed alcohol structures shown as colored stars.

Keywords: *hydrogen/halogen bond; quasi–free O−H; monomeric O−H; excess infrared spectroscopy; DFT.*

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Molecular Study of Hepatitis B Virus with pgRNA in the Solution by Molecular Dynamics Calculation.

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Immature hepatitis B viruses (HBV) take nucleotides into its capsid and perform the reverse transcription there. It is not clear what kind of interaction invokes the absorption of nucleotides into the HBV capsid. In addition, the molecular picture of the HBVs in solution has not been clear. Therefore, to clarify that, we performed the long-time molecular dynamics (MD) calculation of HBV with pregenome RNA (pgRNA) in the solution.

Our calculation faithfully reproduced the HBV in experimental conditions. This was confirmed by the good agreement of the calculated root mean square fluctuation (RMSF), the radial electric density profile, and the radii of the HBV capsid with the experiments. The electric field analysis revealed that the HBV could not be recognized by any negatively charged substances which were placed 20 nm away from the center of mass the HBV. Within20 nm range, negatively charged substances feel repulsive forces originating from the negatively charged amino acids on the canyon of HBV. From these results, it is clear that the negatively charged substances such as the nucleotide approach the HBV floor in a random walk but by avoiding the canyon.

Pores exist around the 5, 2, 3, pseudo-3-folds rotational symmetry axis. We also calculated density and free energy profiles along these pores for a water molecule, a potassium ion, a sodium ion, and chloride ion. It has been reported that 5-fold rotational symmetry pore is small, and 2-fold rotational symmetry pore is hydrophobic. Water molecules experience a free energy barrier of roughly 2 kJ/mol in the 5- and 2-fold rotational symmetry pores, but the barrier is sufficiently small to be comparable to thermal energy. Therefore, water molecules can travel into/out the HBV capsid core. A large free energy barrier of 10 kJ/mol for the K+ and Na^+ ions exists in the 5- and 2-fold rotational symmetry pores. On the other hand, there is no free energy barrier for K^+ and Na^+ in the 3- and pseudo-3-fold rotational symmetry pores which are hydrophilic. Therefore, these ions are likely to travel into/out HBV capsid core by using 3- and pseudo-3-fold rotational symmetry pores. It is found that Cl^- ion cannot pass through 5-fold rotational symmetry pore, and a 10 kJ/mol free energy barrier exists in all other pores. Therefore, it is difficult for Cl^- ions to go in and out HBV capsid, unlike water molecules, K^+, and Na^+. From the calculated permeability rate, 3000 water molecules breathe in and out from HBV capsid within 1 ns. The calculated permeability rate of K^+ and Na^+ was about 70 ns^{-1}• $(mol/dm^3)^{-1}$. The calculated permeability rate of Cl^- was about 7-9 ns ns^{-1}• $(mol/dm^3)^{-1}$, which is 10 times slower than that of K^+ or Na^+. We also found that HBV capsid has the permselectivity of ions. Also, the free energy difference of K^+ and Cl^- between inside and outside of HBV capsid was -0.5 kJ/mol, meaning that these ions are slightly more stable inside the capsid.

Keywords: *all-atom molecular dynamics calculation, immature hepatitis B viruses*

Synthesis and Property Characterization on the Thermal Energy Storage Phase Change Materials Based on Octadecanoic Acid and Octadecanol

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Phase diagram is a powerful tool to guide the material study for understanding the important information of temperature, composition and phase state [1]. However, due to the single component of phase change material (PCM) often cannot meet the actual requirements, two or more components of different PCMs are required to synthesize the phase change materials with suitable phase change temperature and latent heat [2].

The conventional inorganic salt phase change materials such as sodium, potassium, calcium and magnesium have serious super-cooling and low phase change temperature, which cannot meet the needs of heat storage demands.

So the synthesis of phase change materials based on octadecanoic acid and octadecanol was studied. Those results can be summarized:

Firstly, suitable phase change temperature and high thermal conductivity PCM synthesized by using octadecanoic acid (C_{18}-acid) and octadecanol (C_{18}-OH) was obtained.

Secondly, the synthesized PCMs were encapsulated by the expanded graphite adsorption method. The thermal conductivity of PCMs increased 10 times than that of original PCMs. However, the phase transition temperature and latent heat decreased, respectively.

Finally, the composition of the composite PCMs as well as the systematic thermal chemical properties was introduced in this presentation.

Keywords: *Salt-water system solubility database; Composite PCM; Performance; Packaging*

Acknowledgments: Supports from the National Natural Science Foundation of China (U1407113, U1607123, U1607129), the Key Projects of Natural Science Foundation of Tianjin (18JCZDJC10040) and the Yangtze Scholars and Innovative Research Team of the Chinese University (IRT_17R81).

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ISLEC: A CALPHAD-Type Aqueous Solution Thermodynamic Modeling Software Based on A Pitzer-Simonson-Clegg Approach

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Thermodynamics and phase diagram of aqueous system are of importance in the design of industrial processes. CALPHAD (Computer Coupling of Phase Diagrams and Thermochemistry) technical aims to promote computational thermodynamics through development of models to represent thermodynamic properties for various phases which permit prediction of properties of multi-component systems from those of binary and ternary subsystems[1]. Combing the CALPHAD technical with excess Gibbs energy equations, e.g. Pitzer equation[2], Debye－Hückel equation[3,4], Davis equation[3,4], B-dot equation[3,4] et al., aqueous processes can be simulated. Several famous aqueous system modeling software[3-8] have been available and widely used in geochemistry, chemical engineering, hydrometallurgy, environmental and material sciences. Most of them used the Pitzer equation to describing the excess thermodynamic properties of aqueous phase, while some groups used other equations (i.e. e-NRTL equation[6], Extended UNIQUAC equation[7], MSE equation[8]) for modeling the properties of concentration aqueous solutions and mixed solvent systems. Relative to the original Pitzer approach, the mole-fraction based ion-interaction approach, that is the Pitzer-Simonson-Clegg approach[9] is of advantages in modeling the excess thermodynamic properties of concentrated brine system. In this study, we'd like to present some research advances on the development of CALPHAD-type aqueous solution thermodynamic modeling software based on a Pitzer-Simonson-Clegg approach. The software was name as ISLEC, which means *I*nstitute of *S*alt *L*akes *E*quilibrium *C*alculator and can be accessed at www.islec.net. In the software, Gibbs energy minimization approach was applied to solve the solid-liquid-gas equilibria of multi-component (indefinite number of component) and multiphase aqueous electrolyte systems and the Ipopt optimization library was introduced to optimize the total Gibbs energy function. Direct Gibbs energy minimization procedure was used without any phase stability analysis procedures. Comprehensive temperature-dependent models for some important industrial aqueous system have been developed on the ISLEC platform

Keywords: *Thermodynamics; Phase diagram; CALPHAD; Aqueous solution; Pitzer-Simonson-Clegg approach*

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Phase Equilibria of the Quaternary System ($KCl + CaCl_2 + SrCl_2 + H_2O$) at 288.15 K

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Strontium and its compounds have been used extensively in modern applications such as electronic, chemical engineering, metallurgy, military industry, light industry, medicine, optical and so on for their unique excellent characteristics. There are abundant oilfield brine resources with high-concentration of strontium in the western of China, especially in Nanyishan Section of the Qaidam Basin, China. Its average concentration of strontium can reach 5363.75 mg/L, which is far higher than the separate exploiting production-grade. The hydrochemistry is the calcium chloride type and the major chemical component of the oilfield brine belongs to the complex system of (Li−Na−K−Ca−Sr−Cl−borate−H_2O). It is well known that the phase equilibria and phase diagrams is the basis for describing the interaction of natural brine and salt minerals.

In this paper, experimental studies on the phase equilibria of the quaternary system ($KCl + CaCl_2 + SrCl_2 + H_2O$) at 288.15 K were determined with the method of isothermal dissolution equilibrium. Based on the experimental results, the phase diagram in this system were plotted. It was found that there are two invariant points, five univariant curves and four crystallization regions correspond to three single salts $SrCl_2{\cdot}6H_2O$, $CaCl_2{\cdot}6H_2O$, KCl and the solid solution (Ca,Sr) $Cl_2{\cdot}6H_2O$. $CaCl_2$ has the strong salting-out effect to KCl and $SrCl_2{\cdot}6H_2O$. The information of the phase diagram can be used to separate and purify the corresponding mineral salts from the concentrated brines.

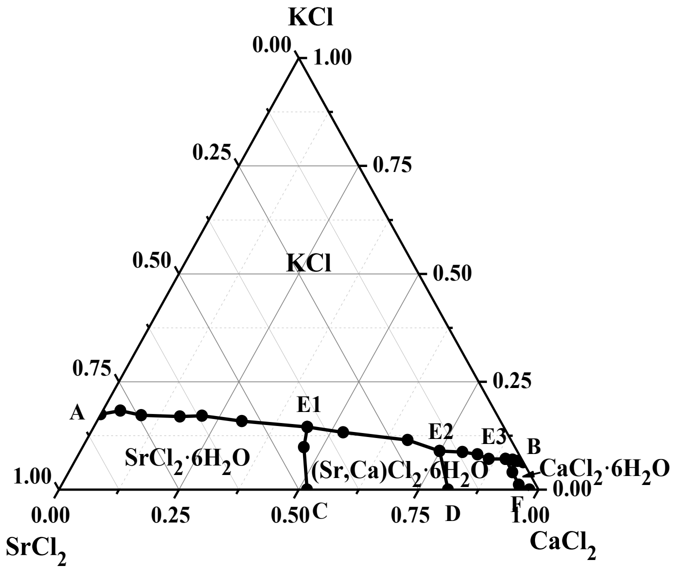

Fig 1. Phase diagram of the system at 288.15 K

Keywords: *Oilfield brine; Phase equilibria; Phase diagram; Solubility*

Acknowledgment: The work was supported by the Program of the National Natural Science Foundation of China (Grant No. 21406048 and U1507109), applied basic research plan of Hebei Province (13963103D), the Natural Science Foundation of Hebei Province (B2017202198), and the Natural Science Foundation of Tianjin (17JCYBJC19500, 15JCQNJC06100)..

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Correlation of Solubility of KCl/RbCl/CsCl-PEG$_{1000}$-H$_2$O at 298 K

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The purpose of the present work is to use the method of Zhu et al. [1] to correlate the solid-liquid equilibrium of alkali chlorides (KCl, RbCl, and CsCl) in PEG1000-H$_2$O mixed solvent at 298 K and this information can be used for the design of drowning-out separation processes. The modified Pitzer model[1], [2] assumed that the non-ionic solute (polymer) is a pseudo-solvent, and consequently the polymer + water components are equivalent to a solvent mixture, providing a new estimation of the binary parameters of the salt ($\beta^{(0)}$, $\beta^{(1)}$, and C^{φ}) and cross parameters between PEG1000(1) and salt(2) ($\beta_{12}^{(0)}$, $\beta_{12}^{(1)}$, $\beta_{12}^{(2)}$, C_{112}, and C_{122}) for its application which are upon calculating the mean ionic activity coefficient of the electrolyte in the solvent mixture. The solubilities of KCl/RbCl/CsCl-PEG1000-H$_2$O at 298 K were also compared with published data [3],[4] and modified Pitzer model [1],[2] for calculated data as shown in Fig. 1. It can be seen from the comparison of experimental and calculation diagrams that the predictive solubilities agree well with the experimental values.

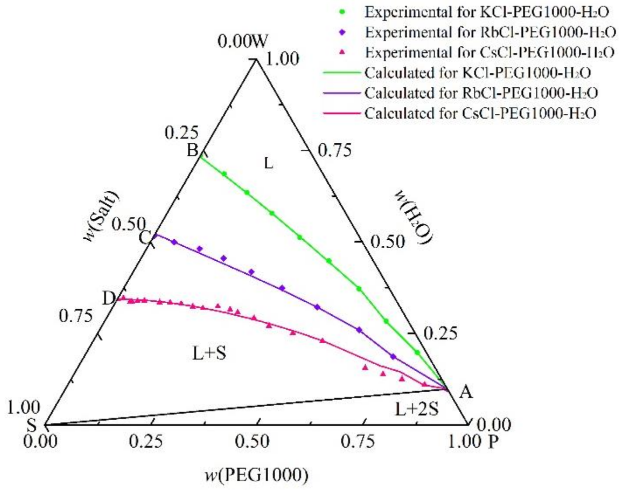

Fig 1. The experimental and calculation of aqueous ternary system KCl/RbCl/CsCl-PEG1000-H$_2$O at 298 K

Keywords: *Solid-liquid equilibrium; Correlation; KCl ; RbCl; CsCl*

Acknowledgements: Project supported by the NSFC(U1507111).

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Phase Equilibria and Phase Diagrams for the Ternary Aqueous System Containing Lithium, Sodium and Pentaborate Ions at 298.2 and 323.2 K and 101.325 kPa

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The salt lake brine located in the Qaidam Basin of Qinghai-Tibet Plateau is famous for its high concentrations of lithium, sodium, potassium and boron [1-2]. In the paper, the solubility data and physicochemical properties (refractive index and density) of the ternary system (LiB_5O_8 + NaB_5O_8 + H_2O) at 298.2 and 323.2 K and 101.325 kPa were investigated by the methods of isothermal dissolution equilibrium. According to the experimental data, The phase diagrams (Figure 1) were plotted, there was one invariant point, two univariant curves and two crystallization regions corresponding to sodium pentaborate pentahydrate ($NaB_5O_8\cdot5H_2O$) and lithium pentaboratepentahydrate ($LiB_5O_8\cdot5H_2O$). It was found that this system belongs to simple eutectic type at two temperatures, and neither double salts nor solid solutions were formed. The densities and refractive indices in the ternary system at 298.2 and 323.2 K are as similar as changing regularly with increasing of LiB_5O_8 concentration.

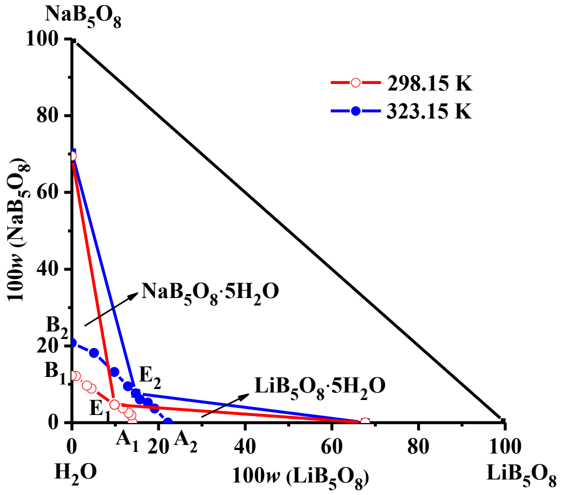

Fig 1. Phase diagram for the ternary system (LiB_5O_8 + NaB_5O_8 + H_2O) at 298.2 and 348.2 K.

Keywords: *Solid and liquid equilibrium; Lithiumpentaborate; Sodium pentaborate; Density and refractive index*

Acknowledgments: Supports from the National Natural Science Foundation of China (, U1607123 and 21773170), the Key Projects of Natural Science Foundation of Tianjin (18JCZDJC10040), the Innovative Research Team in Tianjin Colleges and Universities (TD13-5008) and the Yangtze Scholars and Innovative Research Team of the Chinese University (IRT_17R81).

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Solubility Phase Diagram of the Ternary System Li^+, Mg^{2+}/Cl^- (SO_4^{2-}) – H_2O at 348.15 K

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The ternary system $LiCl-MgCl_2-H_2O$ and $Li_2SO_4-MgSO_4-H_2O$ are one of the most important systems for lithium resource extraction from salt lake brine, which has been widely investigated. However, the solubility data of the ternary system $LiCl-MgCl_2-H_2O$ at 348.15 K has not been reported, and the reported solubilities[1]for the ternary system $Li_2SO_4-MgSO_4-H_2O$ at 348.15 K are not consistent with the calculated results with the model by Zhou[2]and Li[3]. In this work, we elaborately measured solubility diagram of the two sub-ternary systems at 348.15 K and the measured results are shown in Figure 1. Three kinds of solid phases $LiCl\cdot H_2O_{(s)}$、 $LiCl\cdot MgCl_2\cdot 7H_2O_{(s)}$ and $MgCl_2\cdot 6H_2O_{(s)}$ existed in the ternary system $LiCl-MgCl_2-H_2O$ at 348.15 K, which was reported for the first time. $MgSO_4\cdot 6H_2O_{(s)}$ as meta-stable was found in the ternary system $Li_2SO_4-MgSO_4-H_2O$ at 348.15 K.

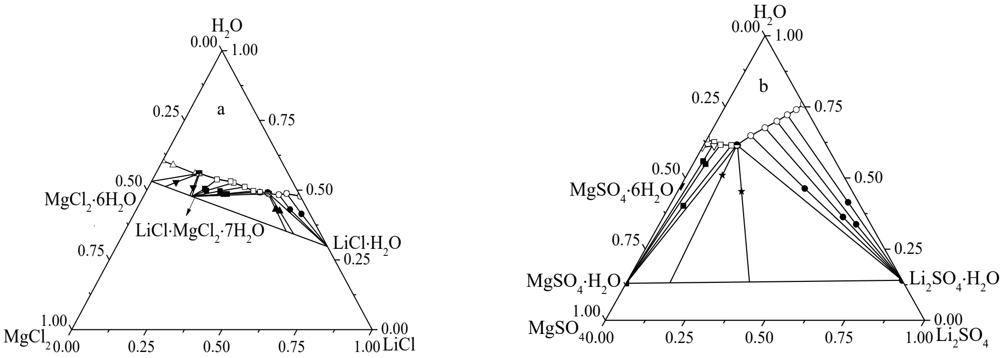

Figure 1. Solubility isotherms determined in this work. a) the ternary system $LiCl–MgCl_2–H_2O$ at 348.15 K: ○, Lc; ◓, Lc + LiC; □, LiC; ⬒, LiC + Bis; △, Bis. Completely filled symbols indicate wet solid phases. b) the ternary system $Li_2SO_4–MgSO_4–H_2O$ at 348.15 K: ○, Ls; ◓, Ls+ Kie; □, Kis; ▽, Hx. Completely filled symbols indicate wet solid phases.

Keywords: *Solubility*; *Lithium Chloride*; *Magnesium Chloride*; *Lithium Sulfate*; *Magnesium Sulfate*

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Phase Behavior of Tetramethylurea + CsCl + H_2O Systems at 298.15 K and 308.15 K

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Electrolytes exist in nature widely and are regarded highly by people for its wider applications. Tetramethylurea (TMU) is an excellent solvent in organic reactions groups. TMU-water is a mixture of a dipolar solvent and a protic solvent. Volumetric properties, enthalpies and heat capacities of the solution of tetramethylurea in water was investigated[1,2]. Recently, tetramethylurea - based electrolyte showed over 200 hours of cycling in lithium-sulfur batteries[3]. In this paper, the (solid + liquid) equilibrium (SLE) and (liquid+ liquid) equilibrium (LLE) of CsCl + tetramethylurea (TMU) + H_2O ternary systems were investigated at 298.15 K and 308.15K. The SLE and LLE data were correlated by the three parameter equation, the Othmer-Tobias and Bancroft equations. Moreover, the effect of temperature on binodal curves and tie-lines are investigated.

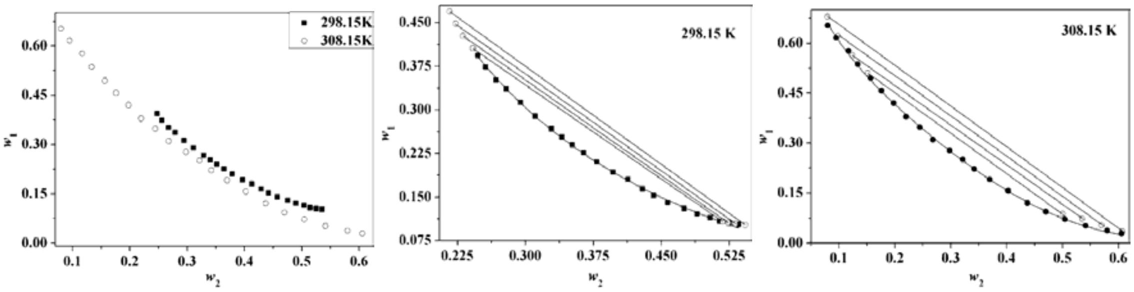

Figure 1. Binodal curves and tie-lines of the TMU (w_1) + CsCl (w_2) + H_2O (w_3)

Keywords: *phase behavior; Tetramethylurea; CsCl; Binodal curve, Tie-lines*

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The Stable Phase Diagram of the Quaternary Water-Salt System Li^+, Na^+, Cs^+ // SO_4^{2-} - H_2O at T = 298.2 K

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Salt lake brine and underground brine are mineral resources in the form of cesium as an aqueous solution. In the Qaidam Basin of the Qinghai-Tibet Plateau, there are many large and small sulfate-type salt lakes.[1] Cesium in the brine usually has low content (average of 0.034 mg/L Cs in Qaidam Basin salt lakes),[2] and coexists with potassium, sodium, lithium, rubidium, calcium, magnesium and so on.[3] For the sulfate type salt lake brine, the quaternary system Li_2SO_4 + Na_2SO_4 + Cs_2SO_4 + H_2O is one of the basis subsystems. Studying the phase equilibrium of salt lake brine is of great significance for the separation and extraction of cesium mineral resources. Thus, the phase equilibrium of lithium, sodium and cesium containing sulfate system has been presented here, using an isothermal dissolution method.

From the phase diagram (Fig.1), the information about the crystallization path, crystalloid forms and crystallization fields of different salts can be gotten as the follows.

The quaternary water-salt system Li^+, Na^+, Cs^+ // SO_4^{2-} - H_2O at T = 298.2 K is of a complex cosaturation type, with three double salts formed. Its phase diagram contains five invariant points, eleven univariant curves, and seven crystallization fields. There are two kinds of double salts formed for lithium and cesium sulfate, that are $Li_2SO_4·Cs_2SO_4$ and $Li_2SO_4·Cs_2SO_4H_2O$. The crystalline phase region of double salts is obviously larger than that of single salts, means the double salts are easier to form than single salts. Lithium and cesium are scarcely possible separated as Li_2SO_4 and Cs_2SO_4 from this system at 298.2 K just by evaporation and crystallization method.

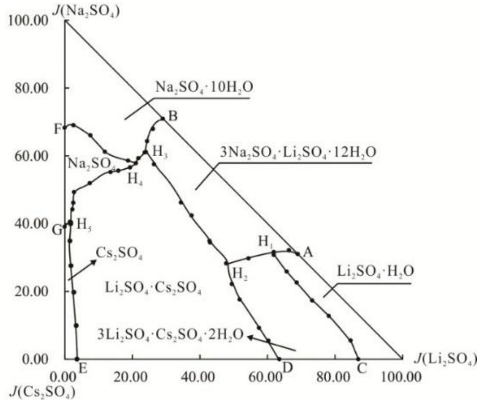

Fig.1 The planar projection diagram of the quaternary system Li^+, Na^+, Cs^+ // SO_4^{2-} - H_2O at 298.2 K.

Keywords: *stable phase equilibria; lithium sulfate; sodium sulfate; cesium sulfate; double salt*

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Micro-Hydration Structure of Aqueous Li^+ by DFT and CPMD

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In the present work, systematic studies on microscopic hydration structure of lithium ion hydrated clusters, $[Li(H_2O)_n]^+$ (n=1-20), are carried out by density functional theory (DFT) calculations at the ωB97XD/6-311++G(d,p) basis level and Car-Parrinello molecular dynamics (CPMD) simulations methods. The DFT calculation results reveal that the four-coordinated structure is favorable for $[Li(H_2O)_n]^+$ (n=1-20) clusters in the aqueous phase and the saturated structure of the second hydration layer is 8 water molecules when $n \geq 12$. The energy parameters calculation shows that the structures of the first and second hydration shells are relative steady. For $n>9$, the competitive effects of the second and third hydration layers on water molecules arise and the solvent-solvent interactions for outer hydration shell are strengthened. The results of bond parameters declare that the structure of inner hydration shell has little influence on the H_2O molecules of outer hydration layer when the first and second hydration spheres of Li^+ are saturated. The CPMD simulations exhibit that there are four water molecules with Li-O distance at 1.97 Å on average around each Li^+ in the first hydration shell. Li-O distance of the second hydration layer is around 4.10 Å. All of these results show good agreement with DFT calculations and CPMD simulations.

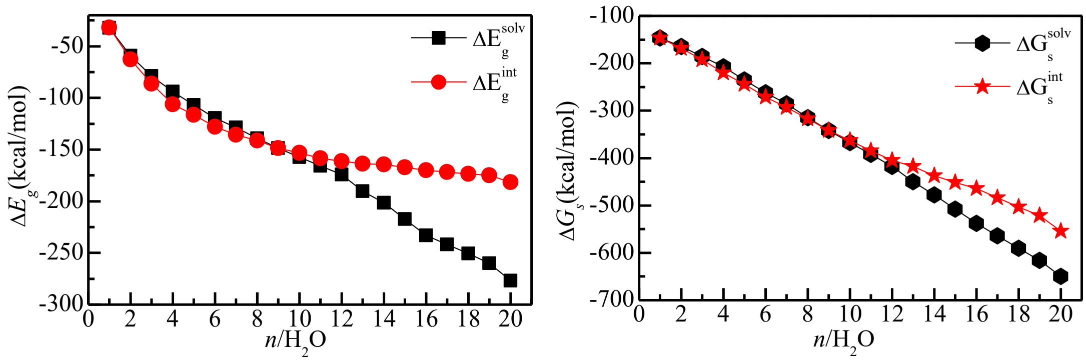

Fig 1. Variation of calculated interaction energies (ΔE_g^{int}, ΔG_s^{int}) and solvent stabilization energies (ΔE_g^{solv}, ΔG_s^{solv}) in gas (a) and aqueous (b) phase with the number of water molecules n for the most stable structures of $[Li(H_2O)_n]^+$ (n=1-20) clusters

Keywords: *$[Li(H_2O)_n]^+$ hydrated clusters, hydration structure, DFT, CPMD*

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Solubility and Model Simulation of Limited Solid Solution Containing System RbCl−CsCl−H_2O

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The solubility, phase diagram and their model simulation of the RbCl−CsCl−H_2O limited solid solution containing system, at relative wide temperature range, are of great importance for extracting rubidium and cesium resources from Chaerhan Salt Lake.

Up to now, there is only reported solubility of this ternary system at 298.15 K [1] and 323.15 K [2]. The reported solubility data at 323.15 K [2] are not quite reasonable that we evaluated, and the measured results shown that the equilibrium solid phase are pure salts (RbCl and CsCl), which are insistent with the situation of 298.15 K [1] that the solid phase are solid solution.

In this work, the solubility of the RbCl−CsCl−H_2O ternary system has been determined by two different methods, namely a Flow-Cloud-Point (FCP) method [3] and isothermal equilibrium method (IEM), from 298.15 K to 348.15 K. The measured results are consistent with each other, which indicate the reliability of the measured solubility, as shown in Figure 1 (a). Combining our previous work [3,4,5] for the RbCl−H_2O and CsCl−H_2O binary systems, the Pitzer model was used to evaluate the solubility and thermodynamic properties, to identify the equilibrium solid phases, of the RbCl−CsCl−H_2O ternary system from 298.15 K to 348.15 K. it is found that the equilibrium solid phases in the ternary system are two limited (regular) solid solution $(Rb,Cs)Cl_{(ss)}$ and $(Cs,Rb)Cl_{(ss)}$. The Lippmann diagrams for this limited solid solution containing system also have been presented, as shown in Figure 1 (b).

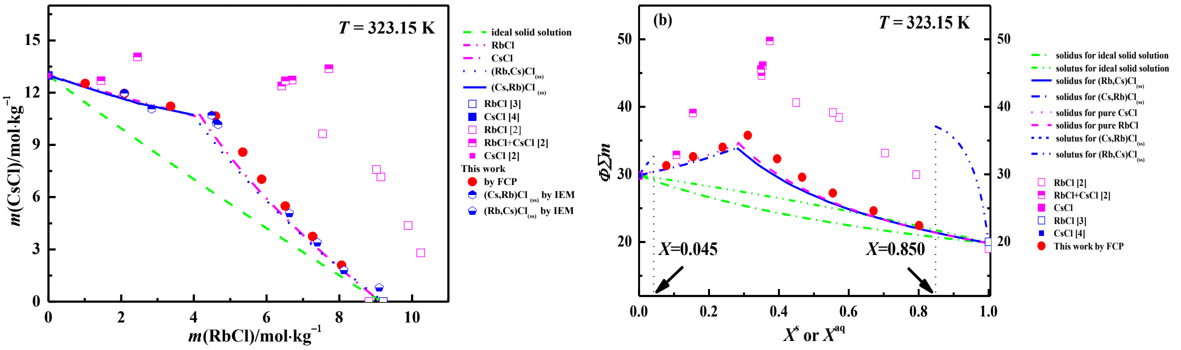

Figure 1. The solubility and Lippmann diagram of the RbCl−CsCl−H_2O ternary system at 323.15 K. (a) solubility, (b) Lippmann diagram.

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Solvent Extraction of Magnesium from Salt Lake Brines and Thermodynamics Study

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A novel extractive system (P204 + [P4446][NTf$_2$] + MIBK) has been established for magnesium extraction from the salt lake brine with high Mg/Li ratio to realize the separation of lithium and magnesium. The influence factors of extraction effect such as saponification rate, the pH of brine, phase ratio and composition of the organic phase were investigated. In addition, the extraction thermodynamics of this system was studied using an advanced microcalorimeter BT 2.15 and advanced thermodynamic software (AKTS, Switzerland). The reaction heat at 298.15, 313.15 and 328.15 K was determined. According to the heat flow data and the conversion method of Friedman, the kinetic parameters of activation energy (Ea) and pre-exponential factor (A) were obtained by advanced dynamic simulation methods [1],[2],[3]. The variations of reaction progress and rate versus time of the system had been simulated at different temperatures.

Keywords: *Magnesium; Extraction; Thermokinetics; Simulation*

Acknowledgements: Supports from the National Natural Science Foundation of China (U1607129 and U1607123), the Key Projects of Natural Science Foundation of Tianjin (HYHG 201701 and 201601), the Innovative Research Team in Tianjin Colleges and Universities (TD13-5008) and the Yangtze Scholars and Innovative Research Team of the Chinese University (IRT_17R81).

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Studies on the Mean Activity Coefficients of NaBr in the Ternary System NaBr-$SrBr_2$-H_2O at 308 K

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Electrolyte solutions have played an important mediating role in many organic and inorganic reactions. The thermodynamic properties of electrolyte solutions, such as activity coefficient, permeability coefficient, excess Gibbs free energy, etc., are important essential data of solution theory, in the development of thermodynamic models, process simulation, biology, geology and environmental studies [1]. Therefore, the study of the activity coefficient is one of the important contents of the theoretical study of electrolyte solution. In this paper, the mean activity coefficients of NaBr in the ternary system NaBr-$SrBr_2$-H_2O at 308 K were studied by electromotive force method (EMF).

In this experiment, a sodium ion selective electrode (Na-ISE) and a bromide ion selective electrode (Br-ISE) electrode were used to form a liquid-free potential reversible battery:

$$\text{Na—ISE} \mid \text{NaBr}\ (m_1),\ \text{SrBr}_2\ (m_2) \mid \text{Br—ISE}$$

The electromotive force values of NaBr in the single salt (NaBr) and the mixed salt (NaBr and $SrBr_2$) at different ionic strength ratios y_b of $SrBr_2$ (y_b=0, 0.2, 0.4, 0.6, 0.8) were measured at 308 K. The mean activity coefficients of NaBr in NaBr-$SrBr_2$-H_2O system were calculated by Nernst equations. According to the theory of the Pitzer model, the mean activity coefficients of $SrBr_2$ at 308 K were calculated [2]. Using the Matlab program linear regression related data, the Pitzer mixed ion parameters $\theta_{Na^+\cdot Sr^{2+}}$, $\varphi_{Na^+\cdot Br^-\cdot Sr^{2+}}$ are fitted and then the permeability coefficient Φ, water activity a_w, excess Gibbs free energy G^E are calculated respectively.

Keywords: *Activity coefficient; Electromotive force method; Pitzer model; Ion selective electrode*

Acknowledgements

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Studies on the Thermodynamic Properties of Electrolyte Solutions Containing Lithium Borates

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Lithium borates are widely used in many fields, such as modern life, industrial production and advanced technology, because of its excellent physical and chemical properties, which becomes a hot research at domestic and abroad [1]. However, it is difficult to separate and extract the lithium borates due to a supersaturation phenomenon existed in the brines containing borate [2]. In addition, borates in aqueous solutions can exist in several different species. Knowledge on thermodynamics properties of electrolyte solutions containing lithium borate is useful in characterizing solute-solvent and ion-ion interactions, which provides the basic scientific support of comprehensive utilization for lithium borates from salt lakes.

The heats of dissolution for lithium borates have been extensively measured by the microcalorimetry. According to the fundamental law of thermodynamics, the standard molar enthalpies of formation for lithium borates were obtained respectively. In addition, the mixing heats, heat capacities and volume properties of electrolyte solutions containing lithium borates have been also determined. Based on the Pitzer ion-interaction model, the Pitzer single-salt parameters and mixing parameters of lithium borates were acquired, which disclosed mechanism of interaction between particles in lithium borate electrolyte solutions and can enrich important thermodynamic fundamental data for the thermodynamic multi-temperature prediction chemical model of the salt lakes containing boron and lithium in China.

Keywords: *Lithium borate; Thermodynamics; Electrolyte solution; Ion interaction model*

Acknowledgements: Supports from the National Natural Science Foundation of China (U1607123 and 21773170), the Chinese Postdoctoral Science Foundation (2016M592827), the Innovative Research Team in Tianjin Colleges and Universities (TD13-5008) and the Yangtze Scholars and Innovative Research Team of the Chinese University (IRT_17R81).

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Correlation of the Solubility of $SrCl_2$ + NH_4Cl + H_2O Ternary System at 298 K with Pitzer Model

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The recovery of strontium chloride from strontium tailings and waste residue is of great significance for industrial development and environmental protection. The phase equilibrium study of strontium-containing systems provides a theoretical basis for the recovery of strontium chloride. Previously, we has finished the study of $SrCl_2$ + NH_4Cl + H_2O ternary system at 298 K which indicates that the system is of a simple type without solid solution or double salt formed.[1] In addition to the study of experimental phase equilibrium, Pitzer model can be used to predict the solubility of multi-group salt-water system.[2] In this work, binary parameters $\beta^{(0)}$, $\beta^{(1)}$ and C^{ϕ} of $SrCl_2$ and NH_4Cl can be obtained from corresponding literatures[3], [4], mixing parameters $\theta_{Sr,\ NH4}$ and $\psi_{Sr,\ NH4,\ Cl}$ were fitted according to experimental data in literature[1], and the solubility of $SrCl_2$-NH_4Cl-H_2O ternary system at 298 K were calculated using Pitzer equation. Analysis of the experimental and calculation phase diagrams show that the simulation data agree well with the experimental data.

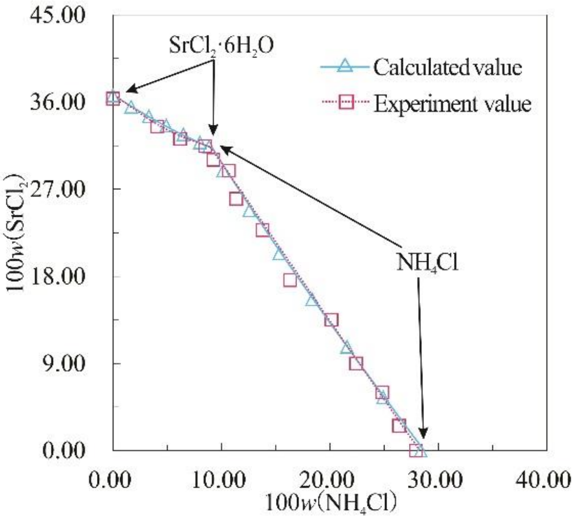

Fig 1. The calculated and experimental diagram of $SrCl_2$ + NH_4Cl + H_2O system at 298 K

Keywords: *Pitzer model; strontium chloride; solubility*

Acknowledgments: Project supported by Sichuan Science and Technology Program (2017JY0191).

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(Solid+Liquid) Phase Equilibria of LiCl + LiBO₂ + H₂O Ternary Systems and Raman Spectrum

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Boron exists in complex forms in aqueous solution, such as $B(OH)_4^-$、$B_3O_3(OH)_4^-$、$B_4O_5(OH)_4^{2-}$ and so on. The presence of these boron oxide anion is greatly affected by external factors, such as temperature, pH, and ionic strength. We need to know why $LiBO_2$ solubility increase with LiCl concentration in the ternary phase diagram of $LiBO_2$+LiCl+H_2O system, and how does the Boron existing forms change with temperature, pH and Li^+ concentration? Thus the set experiments of isothermal solid-liquid phase equilibria, isothermal forced evaporation, and liquid phase and solid species Raman testing were carried out.

The phase equilibrium experiments of $LiBO_2$+LiCl+H_2O system at 323.15K (figure 1) shows the anhydrous $LiBO_2$ occurring in the system, and the solubility of $LiBO_2$ increases with LiCl concentration, and two invariant points of ($LiBO_2 \cdot 2H_2O$+$LiBO_2$) and ($LiBO_2$+$LiCl \cdot H_2O$) existed. The isothermal forced evaporation for solution A under ambient pressure at 308K, the solid species $LiBO_2 \bullet 2H_2O$ formed and furtherly dissolved while liquid phase arrived to C point. The pH were changed from 10.52 to 9.18,. Raman Spectrums shows the same pattern of $B(OH)_4^-$ for A and C liquids. At co-saturated point B at 308K, the pH has a lower value of 6.61, but the Raman Spectrums is still same with the solution of A, and C (figure 2). Therefore, in the case of high Li^+ concentration, $LiBO_2$ exists in the form of $B(OH)_4^-$, when the aqueous solution is acid or neutral.

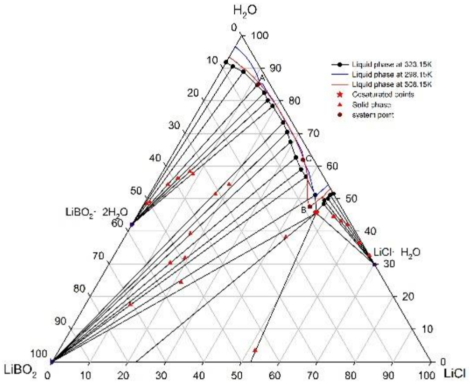

Figure 1. Phase diagram of the ternary system (LiCl+LiBO₂+H₂O) at 298.15K, 308 K and 338.15K

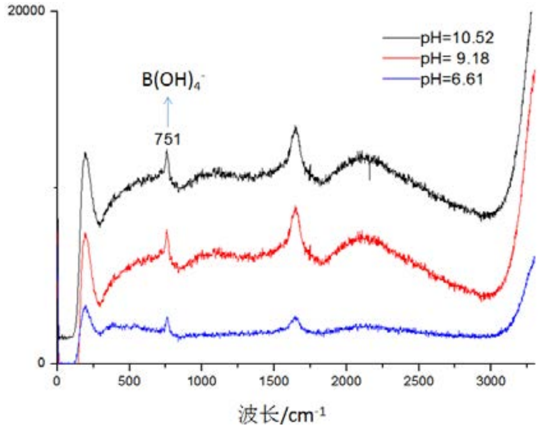

Figure 2. Boron exists in aqueous solution at different pH

Keywords: *LiCl+LiBO₂+H₂O, (Solid+liquid) phase, Raman Spectrum*

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Acknowledgments

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Solvent-induced Assembly of Mn(II) Coordination Polymers Containing 3,3',5,5' -biphenyltetracarboxylic Acid

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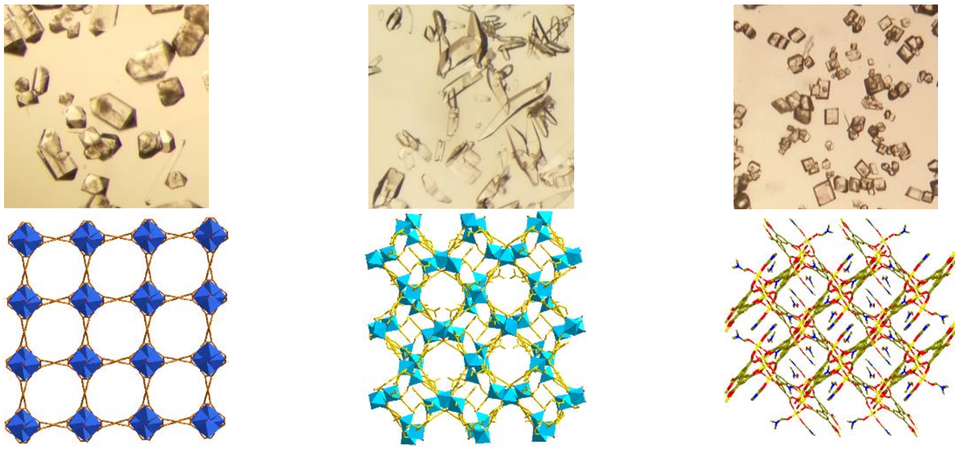
The solvents play an important role in the formation of coordination polymers (CPs) with special structure, therefore, it is of profound significance to explore the solvent effect on the directional growth of crystals. In this work, we successfully synthesized three new Mn(II)-CPs containing organic linker 3,3',5,5' -biphenyltetracarboxylic acid (H_4bptc) in different solvents. As see Figure 1a, triangular prism-shaped Mn(II)-CP-**1** was obtained in a mixed solution of DMF- ethanol- H_2O with the molar ratio of 1:1:1, and it is a typical 3D channel material with high absorption of dyes. Mn-CP-**2** (Fig.1b) has smaller pore channels compared with **1**, and it was obtained only in the mixture of DMF-ethanol (1:1) without the addition of water. The block Mn-CP-**3** (Fig.1c) was cultured in mixed DMF-H_2O (1:1) reaction media, and the solvent DMF was coordinated, and also filled the hole. The important role of solvent molecules was analyzed according to their physicochemical parameters.

Keywords: *Solvent-induced assembly; coordination polymers; crystal structure*



(a) **(b)** **(c)**

Figure 1. The crystal shape and structure of Mn(II)-CP-**1** (a), Mn(II)-CP-**1** (b) and Mn(II)-CP-**1** (c).

Vibrational Spectroscopic and Computational Studies on Formamide Solutions of Alkali-metal Ions

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Formamide (FA, $HCONH_2$) has been used as a solvent for many ionic compounds which are poorly soluble in water. Complexes of metals with FA and other amide molecules show coordination through the O atom almost exclusively, although amide molecules contain both O and N atoms as binding sites. In vibrational spectroscopic studies, a downshift of the CO stretch (ν_{CO}) frequency and an upshift of the CN stretch (ν_{CN}) frequency have been thought to be evidence for the O atom coordination. However, upshifts of both ν_{CO} and ν_{CN} bands were observed in Raman spectra for FA solutions of Li^+ [1]. The unusual results were interpreted by assuming a bidentate coordination of FA via both O and N atoms [1,2], instead of the usual O atom coordination.

We have carried out infrared (IR) spectroscopic studies on FA solutions of $LiClO_4$ and $NaClO_4$. Both ν_{CO} and ν_{CN} bands of FA are observed to undergo upshifts in the presence of Li^+ and Na^+; the observation is consistent with the previous Raman study [1,2]. We have also performed theoretical calculations for optimizing geometries and predicting vibrational spectra of $Li^+(FA)_n$ (n = 1–7) and $Na^+(FA)_n$ (n = 1–8) complexes as models of metal ions dissolved in FA. Polarizable Continuum Model (PCM) is incorporated to implicitly account for extra solvent molecules surrounding the complexes. The calculations indicate that bidentate $Li^+(FA)_2$ complexes are not consistent with the observed upshift of the ν_{CO} band, although such a coordination was assumed previously [1–3]. Instead, certain isomers of $Li^+(FA)_5$ and $Li^+(FA)_6$ complexes exhibit upshifts of both ν_{CO} and ν_{CN} modes, in spite of the usual monodentate coordination via the O atom. The theoretical IR spectra for these O-coordinated complexes are in overall agreement with the experimental spectrum for $LiClO_4$ in FA. These complexes are also successful in reproducing characteristic features observed in the previous Raman spectra for Li^+ in normal FA [1] and in deuterated FA, $HCOND_2$ [2]. Similarly, O-coordinated isomers of $Na^+(FA)_6$ and $Na^+(FA)_7$ complexes exhibit upshifts of both ν_{CO} and ν_{CN} modes. We reported the upshift of the ν_{CO} modes also for $Ca^{2+}(FA)_n$ and attributed it to large splitting of the ν_{CO} modes as a result of interactions among the CO oscillators [4]. The present calculations find that the magnitude of the splitting is larger in $Li^+(FA)_n$ than in $Na^+(FA)_n$ for a given n, probably because the charge density on the metal ion is higher in the former.

It has been generally accepted that the metal–ligand interactions solely determine the direction of frequency shifts of the ligand vibrations. However, for the ν_{CO} modes of FA, the intermolecular interactions among the ligands also play a dominant role in determining the direction of the shift.

Keywords: *formamide; Li(I); Na(I); coordination modes; vibrational frequency shifts*

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Phase Equilibria in Ternary System $LiCl–Li_2SO_4–H_2O$ at 373 K

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The underground brines in Sichuan Basin, as an important enrichment area of liquid mineral resources in China, are rich in resources and excellent in quality. The underground brines located in western Sichuan Basin have become one of the most important liquid salt mining areas in China due to rich in high value resources such as lithium, potassium, magnesium, strontium, rubidium, boron, bromine and iodine [1]. According to the composition characteristics of underground brines that are rich in potassium, lithium and strontium in western Sichuan Basin, the stable phase equilibrium of ternary system $LiCl–Li_2SO_4–H_2O$ at 373 K was studied by isothermal dissolution equilibrium method. It was found that ternary system $LiCl–Li_2SO_4–H_2O$ belongs to hydrate I type and without complex salt and solid solution formation. The phase diagram consists of one invariant point, two crystallization regions ($LiCl·H_2O$, $Li_2SO_4·H_2O$) and two univariate curves. Compared with the phase diagrams under different temperatures, the phase diagrams of ternary system $LiCl–Li_2SO_4–H_2O$ are similar and without new solid phase formation [2]. The research results in this paper are not only a powerful supplement to thermodynamic database of the systems containing lithium, but also can provide important theoretical support for the comprehensive development and utilization of brine resources containing lithium.

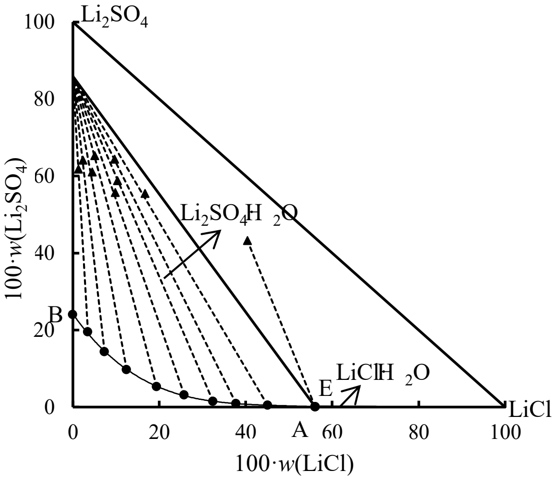

Fig 1. Equilibrium phase diagram of ternary system $LiCl–Li_2SO_4–H_2O$ at 373 K

Keywords: *Underground brines; Mineral resources; Phase equilibrium; Phase diagram; Thermodynamic database*

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Extraction of Cesium and Rubidium with Saponified 4-tert-butyl-2-(α-methylbenzyl) Phenol

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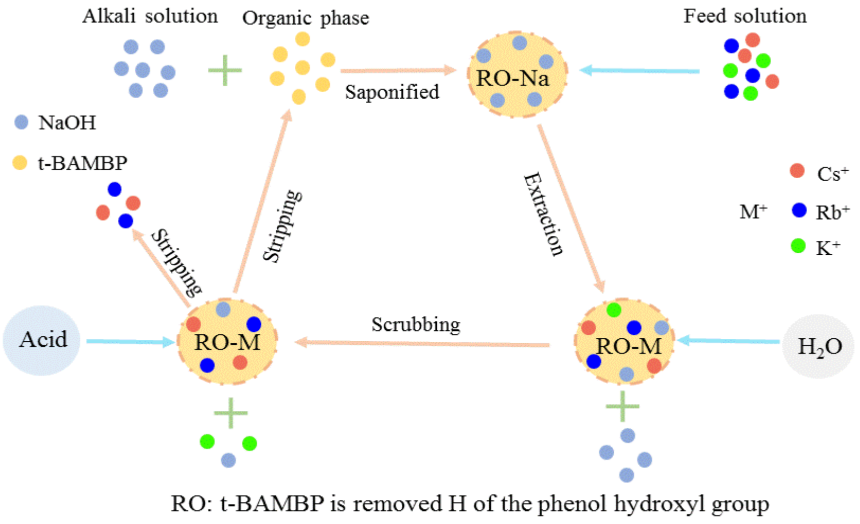
The present work shows the separation process of cesium (Cs^+) and rubidium (Rb^+) from potassium (K^+) solution. The process includes saponification, extraction, scrubbing, and stripping. Results indicate that saponified 4-tert-butyl-2-(α-methylbenzyl) phenol (t-BAMBP) has an excellent extraction effect, the optimal saponification conditions are 1 h employ 1.2 mol/L NaOH. Meanwhile, the Na^+ and NaOH are loaded into the organic phase. It's found that the optimum conditions of single-stage extract Cs^+ and Rb^+ are using 1.0 mol/L t-BAMBP and volume ratio of organic phase to the aqueous phase (O/A) of 1:1 at 288.15K, 99.5% Cs^+ and 46.7% Rb^+ are extracted into the organic phase. After three stages stripping by 1.2 mol/L HNO_3 at O/A of 5:1 for 4 min, 98.6% Cs^+ and 62.6% Rb^+ are stripped from the loaded organic phase. The kinetics of extraction and stripping reaches equilibrium at 5 min and 4 min, respectively. Both the extraction and stripping are exothermic reactions. The infrared spectrum studies indicate that t-BAMBP polymerize to form the dimer in the t-BAMBP while alkali metal ions are extracted, the dimers are dissociated after scrubbing and stripping. These present works show the extraction mechanism could be attributed to the ions exchange, and provide a potential way to separate Cs^+, Rb^+ and K^+.

Keywords: *t-BAMBP; Saponification; Extraction; Scrubbing; Stripping; Cesium; Rubidium*



RO: t-BAMBP is removed H of the phenol hydroxyl group

Fig 1. The process of seperation Cs^+, Rb^+ and K^+

Study on Metastable Phase Equilibrium of Ternary System Li_2SO_4-$Li_2B_4O_7$-H_2O 273 K

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Qinghai Qaidam Basin in China is rich in salt lake resources, of which boron reserves account for 25% of China. The development and utilization of salt lake resources effectively compensate for the scarcity of solid minerals in China. In recent years, there have been many reports on the phase equilibria of borate [1-3]. However, the metastable phase equilibria of the ternary system Li_2SO_4-$Li_2B_4O_7$-H_2O at 273 K have not been reported. Therefore, the metastable phase equilibria of the ternary system listed above were studied by isothermal evaporation method at 273 K in this work. The composition of corresponding liquid phase and solid phases were determined, and the metastable phase diagram of the ternary system was plotted. The results show that the ternary system Li_2SO_4-$Li_2B_4O_7$-H_2O at 273 K has no double salt or solid solution. The phase diagram contains one invariant point two isothermal evaporation curves and two crystallization fields (which are corresponding to $LiBO_2 \cdot 8H_2O$ + $Li_2SO_4 \cdot H_2O$).

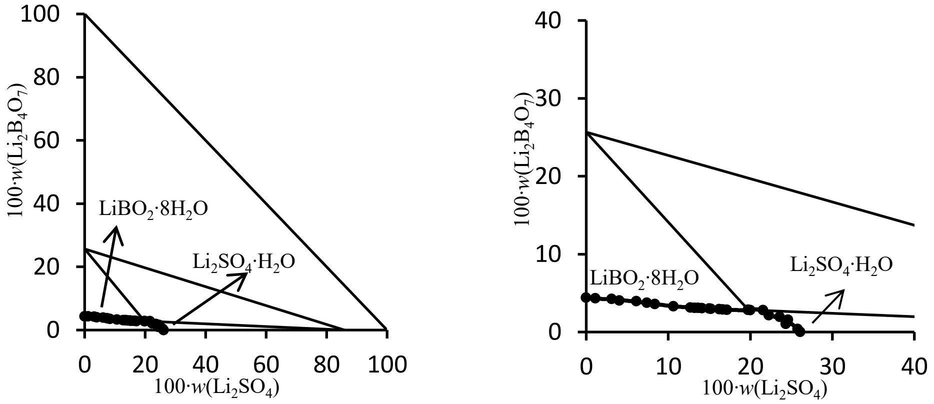

Fig 1. Metastable phase diagram and partial enlarged diagram of the ternary system Li_2SO_4–$Li_2B_4O_7$–H_2O at 273 K

Keywords: *Lithium borate; Isothermal evaporation; Metastable ; Phase equilibrium*

Acknowledgments

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Measurement and Correlation of Solubility of Myo-inositol in Water + Ethanol Binary Solvent System

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The myo-inositol solubility in water + ethanol solvent system was measured at temperatures ranging from 293.15 K to 318.15 K at atmospheric pressure by using the gravimetric method. Solubility data was correlated with the combination version of the Jouyban-Acree and van't Hoff models. By compared with the solubility of myo-inositol in binary water + acetic acid solvent system, it can be concluded that the viscosity and polarity could be the major factors influencing the solubility behavior of myo-inositol in the binary systems water with ethanol and acetic acid. The thermodynamic properties, such as Gibbs energy, enthalpy, and entropy were obtained from these experimental solubility data by using the van't Hoff analysis [1] and Gibbs equations [2].

Keywords: *myo-inositol; solubility; viscosity; polarity; thermodynamic properties.*

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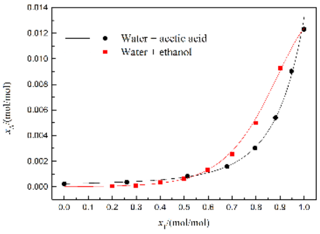

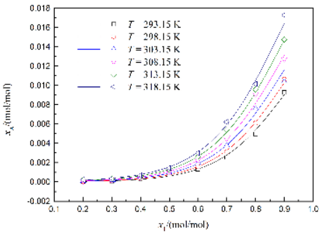

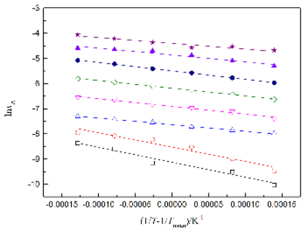

Preparation of Nitrogen Doped Carbon Quantum Dots Based on a Natural Deep Eutectic Solvent as the Functional Monomer for Specific Recognition of Cu^{2+}

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Natural deep eutectic solvents [1] (NADESs) are a large family of solvents that show many similarities with ionic liquids. As an emerging research field, NADESs have already received significant research attention from chemistry scientists. In this work, the nitrogen doped carbon quantum dots [2] based on L-arginine/Glycol NADES and urea were designed for their good dispersion. The physiochemical characterization [3] results suggested that the nitrogen doped carbon quantum dots with diameters ranging from 3 to 6 nm were successfully synthesized. The optical properties data indicated that the nitrogen doped carbon quantum dots exhibited excellent optoelectronic properties, excitation-dependent and pH stability. The nitrogen doped carbon quantum dots exhibited bright blue fluorescence emission (wavelength~365 nm) under UV-light with an excitation wavelength of 259 nm. Our study indicated that Cu^{2+} strongly quenched the fluorescent intensity of the nitrogen doped carbon quantum dots compared to other metal ions. These were characterized by several approaches including FT-IR, In situ IR, TEM, Fluorescence spectra, absorption spectra in the ultraviolet-visible, Excitation and emission spectrum and Dark box ultraviolet analyses experiments. These results demonstrated that the nitrogen doped carbon quantum dots with excellent properties have potential applications in environment.

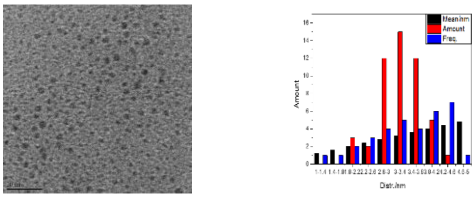

Figure 1. TEM image and particle size distribution of the nitrogen doped carbon quantum dots

Keywords: *Natural deep eutectic solvents; nitrogen doped carbon quantum dots; Cu^{2+} ion detection;*

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Highly Efficient and Reversible Inversion of a Pickering Emulsion Triggered by CO_2/N_2 at Ambient Conditions

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Emulsion inversion has great potential in applications such as materials science, chemical reactions, and drug delivery. Therefore, developing a simple and green approach to control emulsion inversion is highly desirable.[1],[2]

Herein, an octyl- and bis(2-hydroxyethyl)-3-amino-bifunctionalized silica microsphere (SM-O-BIS) is designed, prepared, and used to fabricate a Pickering emulsion. It is found for the first time that this Pickering emulsion can be easily and reversibly inverted from water-in-oil (w/o) to oil-in-water (o/w) by alternate bubbling of CO_2 and N_2 at room temperature and atmospheric pressure. The molar ratio of trimethoxyoctylsilane and bis(2-hydroxyethyl)-3-aminopropyltriethoxysilane plays an important role in emulsion inversion, and only in the molar ratio range from 1.12 to 1.30 could the material be used to achieve emulsion inversion. This unique inversion can be recycled multiple times without any deterioration. By utilizing the emulsion inversion strategy, encapsulation and release of curcumin molecules have been actualized on demand. The possible mechanism of emulsion inversion is also investigated by measuring zeta potential, water contact angle, ^{13}C NMR spectroscopy, and FT-IR spectroscopy. It is shown that reversible acid−base reaction of the bis(2-hydroxyethyl)-3-amino-terminated SM-O-BIS with CO_2 and thus reversible formation of hydrophilic ammonium bicarbonate led to a significant variation in hydrophilicity/hydrophobicity of the SM-O-BIS surface,[3] which was the main driving force for the CO_2/N_2-triggered emulsion inversion.

Keywords: *Pickering emulsion, emulsion inversion, CO_2, curcumin, encapsulation and release*

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This work is supported financially by the National Natural Science Foundation of China (No. 21603063, U1704251, and 21733011).

Study on Metastable Equilibria in the Quaternary System $LiCl–Li_2B_4O_7–KCl–K_2B_4O_7–H_2O$ at 273 K

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There are many salt lakes in Qaidam Basin of Qinghai province, which are rich in lithium, boron, magnesium and potassium [1]. In order to use such natural energies as the energy of the sun, the wind and low temperature condition to separate inorganic salt products from the salt lake brines with the method of natural freezing, the researth of stable and metastable phase equilibria and phase diagrams at low temperature is necessarily urgent [2]. Therefore, it is necessary to study the metastable phase equilibrium of salt lakes at 273 K under these conditions. It is of theoretical significance and practical value to carry out the study on the metastable phase equilibrium of the complex multicomponent system of the Qaidam Basin [3].

The metastable equilibria of the quaternary system $LiCl–Li_2B_4O_7–KCl–K_2B_4O_7–H_2O$ at 273 K was studied by the isothermal evaporation method. The quaternary system belongs to the simple co-saturation type, without complex salt or solid solution. There are two invariant points, five univariant curves and four crystallization fields corresponding to KCl, $K_2B_4O_7·4H_2O$, $LiBO_2·8H_2O$, and $LiCl·2H_2O$ in the phase diagram.

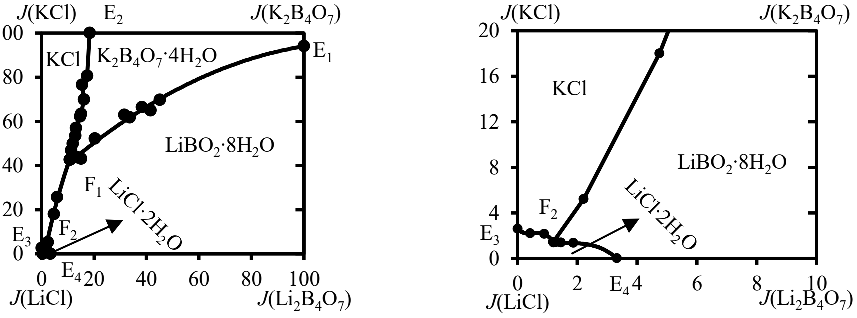

Fig. 1 Metastable phase diagram and partial enlarged diagram of quaternary system $LiCl–Li_2B_4O_7–KCl–K_2B_4O_7–H_2O$ at 273 K

Keywords: *Metastable equilibrium; Evaporation; Lithium; Solubility*

Acknowledgments

This project was supported by the National Natural Science Foundation of China (U1407108, 41873071).

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Solid–liquid Phase Equilibria of the Reciprocal Quaternary System (Na^+, Cs^+// Cl^-, SO_4^{2-} - H_2O) at 298.15 K and 0.1 Mpa

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Rare alkaline metal cesium (Cs) and its compound have wide applications in the fields of catalyst, medicine, electronic technology and aerospace in recent years[1]. In recent years, the exploitation of cesium turn to abundant liquid mineral resource such as salt lake brine, underground water, and geothermal brine. As we all know, the phase diagram of the salt-water system can provide essential fundamentals for the separation and purification process for minerals [2]. Therefore, in order to develop advanced methods for more effective and efficient extraction of Cs from aqueous solutions, the phase equilibrium study on the salt-water system containing Cs^+ is highly desirable.

In this paper, we used isothermal dissolution method to determinate the solid-liquid phase equilibria of reciprocal quaternary system (Na^+, Cs^+// Cl^-, SO_4^{2-} - H_2O) at 298.15 K and the corresponding physicochemical properties (refractive index and density) were determined. The dry salt phase diagram and the water content diagram were plotted. The reciprocal quaternary system was found that there are three invariant points, seven univariant curves, and six crystallization regions corresponding to single salts cesium sulfate (Cs_2SO_4), sodium chloride (NaCl), sodium sulfate (Na_2SO_4), mirabilite ($Na_2SO_4\cdot10H_2O$), a solid solution ($[Cs_{1-x}(Na\cdot H_2O)_x]Cl$) and a double salt ($CsCl\cdot2NaCl\cdot2H_2O$), respectively.

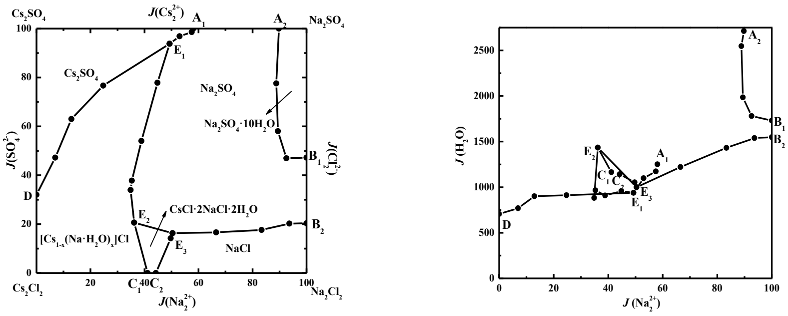

Fig 1. Phase diagram and water phase diagram of quaternary system (Na^+, Cs^+// Cl^-, SO_4^{2-} - H_2O).

Keywords: *Phase equilibrium; Reciprocal quaternary system; Cesium sulfate; Cesium chloride*

Acknowledgements: Supports from the National Natural Science Foundation of China (U1607123 and 21773170) , the Innovative Research Team in Tianjin Colleges and Universities (TD13-5008) and Yangtze Scholars and Innovative Research Team of the Chinese University (IRT_17R81) is acknowledged.

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Synthesis, Characterization and Physicochemical Properties Determination of Chelate-based Ionic Liquids

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Chelate-based ionic liquid is a new type of ionic liquid with potential application value. In this paper, a series of chelate-based ionic liquids were synthesized, and room temperature chelate-based ionic liquid were selected to measure their properties. At different temperatures, we measured the density, viscosity, conductivity and surface tension of these ionic liquids. Based on the empirical formulas in the literature, the lattice energy, and the molar enthalpy of vaporization of ionic liquids were derived.

In our work, a relatively rare ionic liquid cation was used, and the physicochemical properties of the synthesized chelate-based ionic liquid were compared with simple molten salts, ordinary ionic liquids and other chelate-based ionic liquids to obtain some laws. In addition, we can design specific chelate-based ionic liquids according to the existing property rules to achieve on-demand synthesis.

Keywords: *Chelate-based ionic liquids; Physicochemical properties; Lattice energy; The molar enthalpy of vaporization.*

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Apparent Molar Volumes for $Cs_2B_4O_7$ Aqueous Solution at Temperatures from (283.15 to 363.15) K and 101 kPa

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Alkali borates not only take up gradually a considerable position in the salt chemical industry [1], but also have been used extensively in numerous fields like, whisker materials for $Mg_2B_2O_5$ [2] and nonlinear optical materials for $CsLiB_6O_{10}$ [3]. A number of salt lakes with an abundance of cesium and boron resources are widely distributed in the west regions of China, and there are many kinds of hydrated cesium borates owing to the complex structure of borates. Studies on densities of electrolyte solutions are of great importance in characterizing the properties and structural aspects of solutions. In order to provide useful information in structural interactions for cesium borates and extract cesium resources in salt lake brines, it is extremely essential to study the volumetric properties for a successful thermodynamic model.

Densities for aqueous solutions of $Cs_2B_4O_7$ at the molalities of (0.18166 to 0.77600) mol·kg^{-1} were measured with an Anton Paar Digital vibrating-tube densimeter at temperatures from 283.15 K to 363.15 K and 101 kPa. According to experimental data, apparent molar volume (V_ϕ), partial molar volume ($\overline{V}_\phi$), and the coefficient of thermal expansion (α) of the $Cs_2B_4O_7$ aqueous solution were calculated, and their distributive behaviors against temperature and molality have been discussed in details. Considering the structure of $Cs_2B_4O_7$ in aqueous solution system is in the form of $Cs_2[B_4O_5(OH)_4]$, the Pitzer single-salt parameters ($\beta^{(0)v}_{\mathrm{M,X}}$, $\beta^{(1)v}_{\mathrm{M,X}}$, $\beta^{(2)v}_{\mathrm{M,X}}$ and $C^{v}_{\mathrm{M,X}}$) for $Cs_2[B_4O_5(OH)_4]$ as well as temperature-dependence correlations were obtained for the first time on the basis of Pitzer ion-interaction apparent molar volume model of electrolytes. The deviations of the experimental and calculated values of Pitzer single-salt parameters for $Cs_2[B_4O_5(OH)_4]$ are all within ± 0.1, indicating that the single-salt parameters and temperature relational coefficients obtained in this work are reliable.

Keywords: *Thermodynamic; Cesium tetraborate; Apparent molar volume; Pitzer model*

Acknowledgements: Supports from the National Natural Science Foundation of China (U1607123 and 21773170), the Key Projects of Natural Science Foundation of Tianjin (18JCZDJC10040), the Innovative Research Team in Tianjin Colleges and Universities (TD13-5008) and the Yangtze Scholars and Innovative Research Team of the Chinese University (IRT_17R81).

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Sensing Mechanism of *O*-azo Phenylboronic Acid-based Chemosensors for Saccharide: Color Change Caused by Solute-solvent Interaction

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Boronic acids rapidly react with polyol compounds to form tetrahedral boronate esters in aqueous solution. Many researchers have reported boronic acid-based chemosensors for saccharide[1], however, most of their sensing mechanisms have not been clarified.

In this work, we synthesized various *o*-azo phenylboronic acids (azoB) for the colorimetric sensing of saccharides, and clarified their sensing mechanisms.

UV-Vis absorption spectra of azoB1 ((E)-(5-(dimethylamino)-2-(phenyldiazenyl)phenyl)boronic acid) in various solvents are shown in Fig. 1. AzoB1 showed the π-π* absorption band at 350 – 500 nm in aprotic solvents, whreas in protic solvents (methanol in water (20%), methanol, and ethanol), it shifted bathchromically with the increase of absorption (Fig. 1). ^{11}B NMR study showed that azoB1 formed semi-tetrahedral boronate structure (Fig. 2) in a protic solvent (ROH), in which the inserted solvent molecule interacts with both the boron center and the β-nitrogen atom, as shown in Fig. 2. The formation of hydrogen bond between a protic solvent and the β-nitrogen atom, resulting in the stabilization of LUMO in azoB1,[3] would be responsible for the bathochromic shift.

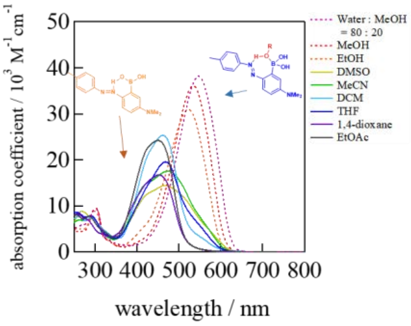


Fig. 1. UV-Vis. spectra of azoB in various solvents

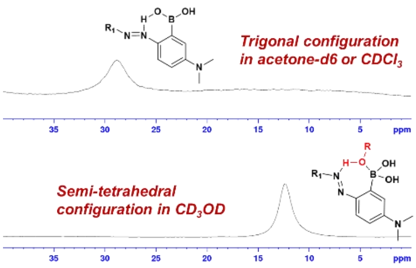
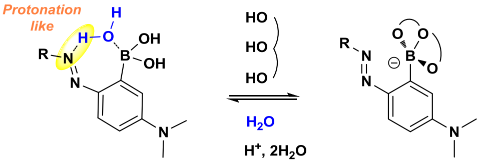


Fig. 2. ^{11}B NMR spectra of azoB in (a) $CDCl_3$ and (b) CD_3OD.

The addition of D-fructose to the methanolic aqueous solution of azoB1 exhibited distinct color change. UV-Vis. spectroscopic study showed that the absorption band of solvent-inserted azoB1 gradually disappeared, and simultaneously the π-π* absorption band of saccharide-coordinated azoB1 appeared, upon the addition of D-fructose. Therefore, the color change would result from the cleavage of the hydrogen bond between the *β*-nitrogen atom of azoB1 and a protic solvent molecule caused by the reaction with D-fructose (Scheme 1).



Scheme 1. Sensing mechanism of *o*-azoB for D-fructose in a protic solvent

The acid dissociation constants of azoBs (K_a^B) and the conditional formation constants for the reactions of azoBs with D-fructose at pH 7.4 (*K*') were determined spectrophotometrically. It was found that the linier free energy relationship held between log *K*' and pK_a^B.

Keywords: *Solute-solvent interaction; Aqueous solution; Boronic acid; Chemosensor; Saccharide*

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Solvent Effect on the Association of Cu(II)-chloride Complexes: Insight from UV-Vis, XAS and Molecular Dynamics

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Many association reactions occur in water, resulting in the associated species bound with water molecules in most cases. Consequently, it is very complex for aqueous solution systems because of the existence of the anion ion and solvent (water) molecules competitively coordinating with metal cation ion. The effects of both solute and solvent should be considered together for the association between anion and cation. However, the latter effect is assigned almost a secondary role in the form of a convenient medium in which to disperse solutes or even neglected, leading to some misunderstandings on the association behavior among these ions.

In this work, taking the Cu(II)-chloride speciation as an typical example, we show that a combination of UV-Vis, XAS, thermodynamic modeling and molecular dynamic computational methods provide a comprehensive picture on the structure, stability and formation of the Cu(II)-chloride complexes depending on the solvent effect. In both spectral experiments, the spectra data were collected by determining a series of solutions with various $Mg(ClO_4)_2$ concentration but containing constant Cu(II) and Cl^- concentration. These spectral evolutions are analogous with those of solution containing Cu(II) as a function of Cl^- concentrations. These indicate that the progressive replacement of H_2O by Cl^- around Cu^{2+} within the first coordinated shell occurs in the solution environment where the $Mg(ClO_4)_2$ concentration increases and simultaneously the water activity (free water molecule number) reduces (decreases) in spite of the constant Cl^- concentration. Molecular dynamics results show that existing Mg^{2+} or ClO_4^- ions destroy the second hydration shell which stabilizes the Cu(II)-chloride complexes, resulting in the increased exchanged probability of H_2O around Cu^{2+} and the Cl^- outside the second shell. These results suggest that solvent effect plays a more role on the heavy metal ionic association.

The Stable Phase Diagram of the Ternary Water-Salt System K^+, Rb^+ // SO_4^{2-} - H_2O at T = 298.2 K

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Salt lake resources in China are abundant and mainly distributed in Qinghai, Tibet, Xinjiang and Inner Mongolia.[1] Usually, the salt lake brine can be divided into four kinds, namely chloride type, sulfate type, nitrated type, and carbonated type. Thousands of sulfate-type salt lakes, large and small, have been found in Qinghai-Tibet Plateau.[2] Rubidium are rare and scattered in the brine; its applications are widely in the fields of nuclear energy, and space technologies. To understand the relations of interaction between rubidium and potassium in sulfate type brines, the phase equilibrium of system $K_2SO_4 + Rb_2SO_4 + H_2O$ at 298.2K has been investigated using an isothermal dissolution method. The equilibrated solid phases was identified by Schreinemakers' wet residue method and XRD patterns.

The measured phase equilibrium experimental results for the ternary system K_2SO_4 + $Rb_2SO_4 + H_2O$ at 298.2 K are plotted in Figure 1. As it shows, the ternary system K_2SO_4 + $Rb_2SO_4 + H_2O$ at 298.2 K is of a complex type, with a miscible solid solution formed. Its stable phase diagram consists of two invariant points(E_1, E_2), three univariant curves(AE_1, E_1E_2, BE_2), three crystallization fields correspond to sing salts K_2SO_4, Rb_2SO_4 and the solid solution [(K, Rb)$_2SO_4$]. The crystallization zone of the solid solution [(K, Rb)$_2SO_4$] almost occupies the entire phase region, means that in the aqueous containing with potassium and rubidium sulfate, solid solution is easy to be formed and the single salt crystals for potassium or rubidium sulfate are hardly obtained by evaporation

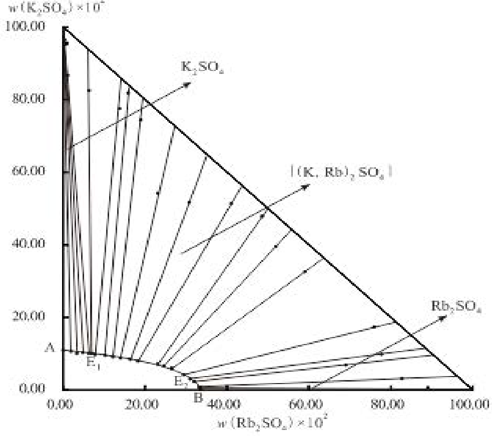

Fig 1. The stable phase diagram of the ternary system, K^+, Rb^+ // SO_4^{2-} - H_2O at 298.2 K.

Keywords: *stable phase equilibria; potassium sulfate; rubidium sulfate; solid solution*

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Theta Temperature of Poly(L-lactide) and the Relationship Between theta Temperature and Solubility Parameter, Interaction Parameter

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The theta temperatures of poly(L-lactide) in 2-hexanone, cyclohexanol, ethyl lactate, bromobenzene, cyclohexanone, and chlorobenzene were determined. At room temperature, poly(L-lactide) dissolved in above solvents. Each poly(L-lactide) solution has 13 concentrations. The cloud point temperatures of each poly(L-lactide) solution were measured by stepwise warming. According to the relation between volume fraction of poly(L-lactide) and cloud point temperature, the theta temperature of poly(L-lactide) solutions were obtained. The theta temperatures of poly(L-lactide) in 2-hexanone, cyclohexanol, ethyl lactate, bromobenzene, cyclohexanone, and chlorobenzene are 434.22 K, 422.12 K, 414.08 K, 408.00 K, 399.36 K and 392.46 K, respectively. The variation of theta temperature accords with the principle of similar solubility parameter. The theta temperature decreases with the decrease of the absolute value of the solubility parameter difference between poly(L-lactide) and the solvent. Meanwhile, the theta temperature decreases with the decline of interaction parameter. The closer the solubility parameter of the solvent and poly(L-lactide), the smaller the interaction parameter between the solvent and poly(L-lactide), the easier the solubility of poly(L-lactide), the lower the theta temperature. The exponential function can accurately express the relationship between theta temperature and absolute solubility parameter difference as well as the relationship between theta temperature and interaction parameter.

Keywords: *Poly(L-lactide); Cloud point temperature; Theta temperature; Solubility parameter; Interaction parameter*

Structure of Aqueous $CaCl_2$ Solutions by X-Ray Scattering and Density Functional Theory

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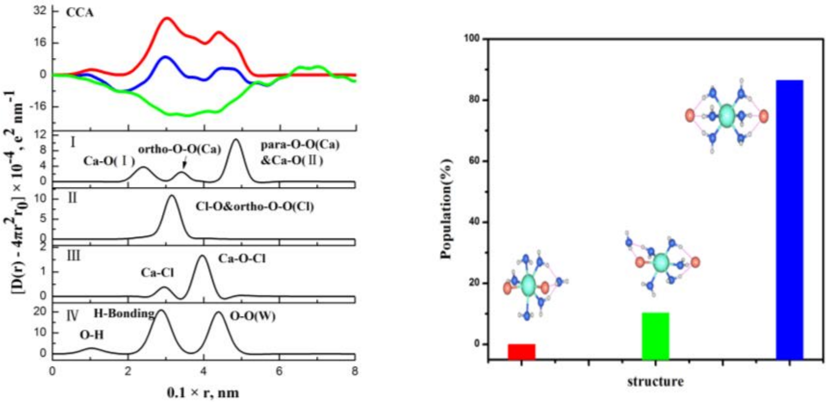
We report a structure analysis of aqueous calcium chloride solutions as a function of concentration at 298 ± 0.5 K by X-ray scattering. The radial distribution functions (RDFs) and theoretical partial radial distribution functions for O-O, Ca-O, Cl-O, Ca-Cl atom pairs are obtained from precise diffraction data processing (Fig. 1. a). The Ca-O(I) distance is 0.239~0.237 nm and the coordination number (*CN*) from 6.7 to 6.2 in the first hydration shell, which indicates an octahedron hydration geometry. The Ca^{2+} possesses a second hydration shell with the Ca-O(Ⅱ) distance range of 0.485~0.480 nm and the coordination number of 13~8. The Ca-Cl distance is 0.295 nm, while the coordination number is only 0.15 when the concentration is 6 mol/L, which confirms the lack of the virtual absence of Ca^{2+}-Cl^- contact ion pairs (CIP) even at high concentration. However, the Ca-O-Cl distance and the coordination number is 0.395~0.387 nm and 1.2~1.9, respectively. The principal change of concentration seems to be the entry of numerous numbers of Cl^- ions into the second hydration shell around Ca^{2+}, thus forming the Ca^{2+}-OH_2-Cl^- solvent-shared ion pairs (SIP). Meantime, in order to verify the accuracy of the experiment results, we got the most stable structure of $CaCl_2(H_2O)_6$ clusters by density functional theory (DFT). Then, we find that the distance of Ca-O(I) is 0.236 nm in the stable structures and the chloride and calcium ions are associated in the form of SIP (Fig. 1. b). DFT calculations were found to be in general accordance with the experimental findings. The results show that a clear picture of the structure of aqueous $CaCl_2$ solution has been acquired.



a b

Fig 1. a: Comparisons among experimental for (Ⅰ) hydrated calcium ion, (Ⅱ) hydrated chloride anion, (Ⅲ) ion association in sodium metaborate solutions at 298.15 K, and (Ⅳ) bulk water. **b:** The population of the $CaCl_2$ clusters by DFT calculations

Keywords: *Calcium Chloride; Aqueous Solution, X-Ray Scattering; DFT, Solution Structure*

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Scalable Exfoliation and Dispersion of Few-layer Hexagonal Boron Nitride Nanosheets in NMP-salt Solutions

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Two-dimensional (2D) hexagonal boron nitride (h-BN) has attracted more attention due to its great potentials for sensors, energy storage devices, temperature antioxidant materials, and composite materials [1]. However, compared with graphene, high efficient exfoliation of 2D h-BN from bulk h-BN powder is very difficult because of its special structure [2]. Therefore, it is necessary to develop highly effective exfoliation methods before any practical applications.

Here, we have developed a facile strategy for liquid-phase exfoliation of h-BN nanosheets in organic electrolyte solutions where N-methyl-pyrrolidinone (NMP) is used as an organic solvent, and sodium citrate, sodium tartrate, ammonium oxalate, potassium sodium tartrate or ethylenediaminetetraacetic acid disodium salt is used as a salt. It is found that the dispersion concentration of h-BN nanosheets has been greatly improved by using organic electrolyte solutions. For example, by addition of ethylenediaminetetraacetic acid disodium salt into NMP, the concentration of the exfoliated h-BN is 36 times that in neat NMP. Furthermore, approximately 85% of the h-BN nanosheets obtained in such a strategy is 1-4 layers. Mechanism study indicates that the strength of Lewis basicity of anion and size of cation of the salts play an important role in the exfoliation of h-BN by organic electrolyte solutions. The liquid exfoliation strategy reported here shows great promise for the mass production of high-quality few-layer h-BN nanosheets.

Keywords: *Hexagonal boron nitride; Liquid-phase exfoliation; NMP-salt solutions; Interactions*

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Liquid-liquid Equilibria for Ternary System CsCl + PEG + H_2O at 298 K: Effect of Different Polymer Molecular Weight

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The aqueous two phase system (ATPS) formed via combining polymer-polymer, polymer-salt dissolved in water, which separate into two phases in a critical thermodynamic condition. It was widely used for recovery of separation and purification of inorganic salts and biological molecules such as proteins and cells [1-3]. Generally, a hydrophilic polymer polyethylene glycol (PEG) was used in ATPS' studies because of its nontoxic and nonflammable. In this work, PEG (average molecular weight is 4000, 6000 and 20000 g/mol, respectively) were chose to study the liquid-liquid equilibrium for ternary system CsCl + PEG + H_2O at 298 K. And liquid-liquid equilibria data for binodal curve and tie-line were studied experimentally. Additionally, the composition, density, refractive index of both phases were determined, and tie-line length, slope of tie-line were also determined for the aqueous two phase system. The equilibrium phase diagram is shown in Fig.1. Furthermore, the effect of molecular weight of PEG was studied. A comparison of binodal for systems $PEG_{4000/6000/20000}$ + CsCl + H_2O has been done as shown in Fig.2. It can be observed that the binodal curve is to origin and the heterogeneous region is relatively larger with the increase of the molar mass of PEG.

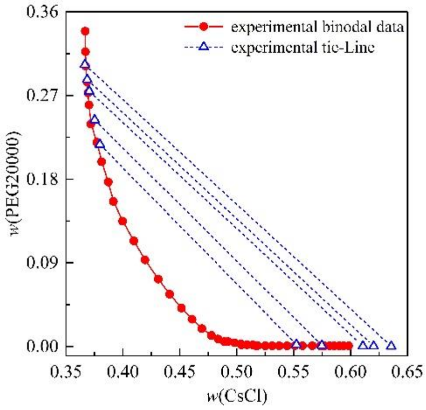

Fig 1. Experimental binodal curve and tie-line for CsCl - PEG_{20000} - H_2O at 298 K.

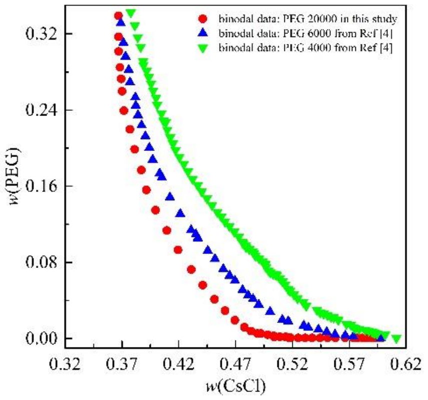

Fig 2. Diagram of comparison of bimodal curve for CsCl - $PEG_{4000/6000/20000}$ - H_2O at 298 K.

Keywords: *Liquid-liquid equilibria; polyethylene glycol; CsCl.*

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Sulfate Solution Physical Properties and Temperature-dependent Phase Diagram

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Qinghai has a large number of salt lakes, which are rich in salt resources such as potassium, magnesium, lithium and boron. Among them, the salt lakes such as the East and West Taijinar and Yiliping can be simplified to the six-element system of Li^+, Na^+, K^+, Mg^{2+}//Cl^-, SO_4^{2-}-H_2O. In order to express the physical properties and phase equilibrium of this system, this study focused on the physical and total temperature phase diagrams of the sulfate system, and the physical properties and full-temperature phase diagrams of four binary systems and six ternary systems including Li_2SO_4-H_2O, Li_2SO_4-Na_2SO_4 *el al.* were studied. The eNRTL model was used to determine the solution characteristic parameters, species parameters. The full temperature phase diagrams of four binary systems and six ternary systems were obtained. Figures 1 and 2 are two three-dimensional diagram, shows the full view of the ternary phase diagram from -20 ℃ to 100 ℃ under the normal pressure.

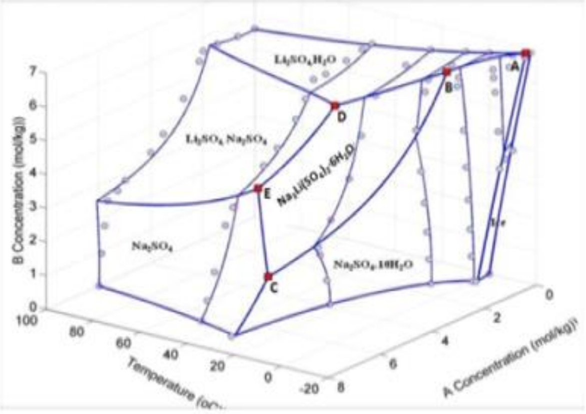

Figure 1. The three-dimensional full-temperature phase diagram of Na_2SO_4+Li_2SO_4+H_2O ternary system

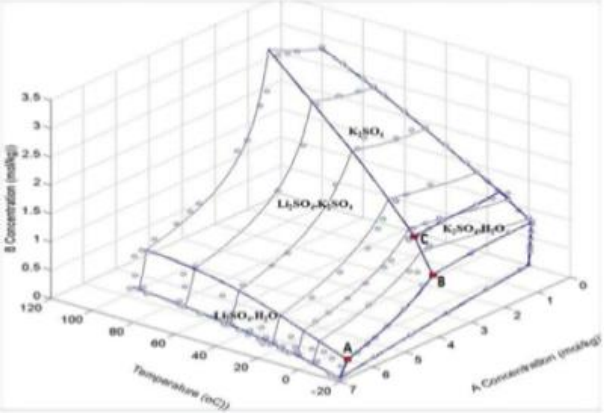

Figure 2. The three-dimensional full-temperature phase diagram of K_2SO_4+Li_2SO_4+H_2O ternary system

Keywords: *Li-Na-K-Mg-SO4 Aqueous system, phase diagram, eNRTL Model*

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Solid-Liquid Phase Equilibria in the Aqueous System Containing Potassium, Magnesium, and Borate at 308.15 K

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Salt lakes are widely distributed in the west of China, especially in the area of the Qinghai-Xizang (Tibet) Plateau. Dongtai Lake, Xitai Lake, and Yiliping Lake in Qaidam Basin are a subtype of magnesium sulfate brines famous for their abundance of lithium, potassium, magnesium, and boron resources. The brines mostly belong to the complex seven-component system of (Li + Na + K+ Mg+ Cl + SO_4 + borate + H_2O).

In this paper, experimental studies on the solubility, density and refractive index in the aqueous system containing potassium, magnesium, and borate at 308.15 K were determined with the method of isothermal dissolution equilibrium. Based on the experimental results, the diagrams of solubility, density and refractive index in this system were plotted. It was found that there are one eutectic point and two crystallization regions corresponding to the large area of inderite (L + $Mg_2B_6O_{11}\cdot 15H_2O$) and the relative small area of potassium borate tetrahydrate (L + $K_2B_4O_7\cdot 4H_2O$), respectively. Neither double salt nor solid solution was found in this system. The physicochemical properties (density and refractive index) in solution at 308.15 K change regularly with the increasing of potassium borate concentration. The calculated values of density and refractive index using empirical equations of the aqueous system are in good agreement with the experimental values.

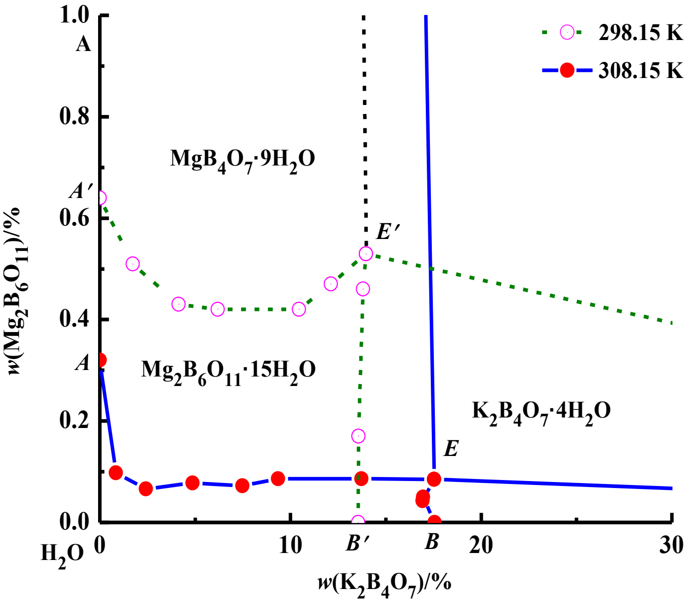

Fig 1. Phase diagram of the system at 298.15 K and 308.15 K

Keywords: *Stable phase equilibrium; Phase diagram; Solubility; Physicochemical property*

Acknowledgment: The work was supported by the Program of the National Natural Science Foundation of China (U1707602, U1507109, U1607123, 21773170, and 21106103), the Natural Science Foundation of Tianjin (17JCYBJC19500), and the Yangtze Scholars and Innovative Research Team of the Chinese University (IRT_17R81).

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Thermophysical Properties of Decanoic Acid Methyl Ester with Different Alcohols

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Due to the reducing fossil resources and seriously environmental problems, to find alternative fuels has become a major issue. With its excellent properties, biodiesel has been considered as an environmental-friendly and renewable alternatives for petroleum-based fuels. Biodiesel refers to mixtures of fatty methyl acids obtained from animal fat or vegetable oils with various alcohols by transesterification. Although the excellent properties of biodiesel, including better biodegradability, higher oxygen content, and lower sulfur content, however, some defects in biodiesel affected its further promotion. Poor fluidity at low temperatures will affect its use in filters and pumps. Higher molecular weight and higher viscosity of biodiesel will increase fuel consumption and soot volume.

Based on the above problems, it is reasonable to select an additive with low freezing point and low viscosity to add in biodiesel to improve the performance. Hence, the characteristics of mixtures of diesel/biodiesel, petrol/biodiesel, and alcohol/biodiesel have been reported in the literature. Investigation shows that adding alcohols in biodiesel will improve the low-temperature fluidity obviously, and the knowledge of thermophysical properties of alcohol/biodiesel mixtures is essential for further application. In this work, the densities and viscosities of decanoic acid methyl ester (one of the components of biodiesel) with three alcohols (including 1-propanol, 1-butanol and 1-pentanol) were reported. The excess molar volumes and viscosity deviations of the mixtures were calculated and correlated with the Redlich –Kister equation. For the prediction of viscosity, a modified McAllister four-body model was proposed.

Study on the Structure of Sodium Chloride Aqueous Solution by Synchrotron X-ray Scattering and Molecular Dynamics Methods

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X-ray scattering data of NaCl aqueous solutions was measured by the third generation diffractometer of Shanghai Synchrotron Radiation Facility (SSRF). The molar concentrations of the solutions are 0.172mol/L, 0.343mol/L, 0.699mol/L, 1.064mol/L, 2.832mol/L, 3.910mol/L, 5.289mol/L respectively at room temperature. Based on the X-ray scattering results, when the concentrations of NaCl aqueous solution increased, the characteristic peaks shifted from 12.6^{o} to 13.4^{o}. The pair distribution functions of different concentrations of NaCl aqueous solutions and pure water were obtained by PDF theory. The O-O peak gradually split into two peaks with the increase of concentration and the O-O peak was at 0.282nm. The structure of different concentrations of NaCl aqueous solutions was studied by molecular dynamic simulation, it indicated that the hydrogen bond structure of water molecules was destroyed by Na^+ and Cl^-, and the effect was particularly evident when the concentration was higher than 15%. It was found there are two hydrated shells around Na^+ and Cl^-, and the coordination numbers of ions decreased with the increase of ion concentrations. The self-diffusion coefficient of water molecules was much higher than that of Na^+ and Cl^-. The self-diffusion coefficients of both ions decreased with the increase of ion concentration. The hydrated radius of both ions decreased as the concentration increased. Through the exploration of this experiment, it provided some theoretical data and guidance for the development and utilization of seawater resources.

The authors thank beamline BL14B (Shanghai Synchrotron Radiation Facility) for providing the beam time and helps during experiments. This research work was supported by Natural Science Foundation of Hebei Province, China (B2017202246). Additional support was provided by Chinese National Key Research and Development Plan (2016YFB0600504), Key Research & Development Program Project of Hebei Province (18394008D), Science and Technology Planning Project of Fujian Province (2017Y4014), Program for Changjiang Scholars and Innovative Research Team in University (IRT14R14).

Keywords: *X-ray scattering; molecular dynamic simulation; NaCl aqueous solutions; ion hydration; pair distribution functions*

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Tunable UCST-type Phase Behavior of Alkanolamine-based Deep Eutectic Solvents

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Deep eutectic solvents (DESs) are a new type of sustainable solvents. They have properties comparable to ionic liquids, especially, their potential as tunable solvents that can be customized to a particular type of chemistry.[1] Many reactions have already been studied in DESs, and cooperative action of DESs with molecular liquids is significant.[2] Partition coefficients of some compounds between DESs and molecular solvents have also been reported.[3] Reversible phase behavior control is important in proceeding from the start of the reaction to the separation of products. However, phase separation behavior of DESs in molecular solvents has not been reported.

Herein, a novel class of thermoresponsive DESs was designed and synthesized, where monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) were selected as hydrogen bond acceptor (HBA), while 4-methoxyphenol, 4-chlorophenol and 4-methylphenol were chosen as hydrogen bond donor (HBD). These DESs exhibited unique phase behaviour with water: the heterogeneously mixed solution became miscible upon heating, and it was separated into two phases again upon cooling. Such a reversible phase separation is a typical characteristic of upper critical solution temperature (UCST)-type phase behavior. The mechanism of UCST-type phase behavior of DESs was studied by using NMR, FT-IR in combination with DLS technique in detail. Since the phase could be controlled by changing the temperature in a few degrees, the UCST-type response of DESs-water mixture would be useful in various applications, such as extraction of biomolecules.

It was found that synergetic variations of HBAs and HBDs in aqueous DESs solution resulted in the randomly aggregated structure of globules during phase separation. Phase separation temperature of DESs-H_2O mixture was related with HBDs hydrophobicity and the basicity of HBAs. In addition, extraction of coumarin compounds was successfully carried out using the UCST behaviour of the DESs-water mixture, and the single-step extraction efficiency of 7-methoxycoumarin could be as high as 99%.

Keywords: *deep eutectic solvents; upper critical solution temperature; tunable phase separation*

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Lithium Ionic Sieve and its Adsorption Performance for Lithium from Underground Brine

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Lithium and its compounds are widely applied in industrial fields such as glass and ceramics, medicine, aerospace and batteries. Salt lake brine and sea water contain large amounts of lithium, more and more researches focus on the methods for lithium extraction, especially on the ionic sieve method. Commonly the lithium ionic sieves include manganese-base lithium ionic sieve, titanium-base lithium ionic sieve[1]. Among of them, the manganese-base lithium ionic sieve has several advantages like high selectivity for lithium, good Li^+ uptake capacity and recycled usability. At present, the three most reported manganese lithium ion sieve precursors are $LiMn_2O_4$, $Li_4Mn_5O_{12}$ and $Li_{1.6}Mn_{1.6}O_4$. Among of them, $Li_{1.6}Mn_{1.6}O_4$ has the largest theoretical adsorption capacity (72.9mg/g) and the most stable chemical properties.

However, the disadvantage of partial dissolution of skeleton structure in the elution process of manganese-base lithium ionic sieve had restricted its industrial application[2]. The solution loss may be caused by the trivalent manganese ions existing in the spinel structure of manganese-base lithium ionic sieve. Mn^{3+} can be produced disproportionation reaction in acid eluent to form Mn^{4+} and Mn^{2+}, while Mn^{2+} is easy to be dissolved in solution and causes the structural damage for the sieve. Reducing the dissolution loss of manganese is the key to successful preparation manganese-base lithium ionic sieves with stable structure. The average valence of manganese could be improved by cationic doped of other metal ions[3], which can inhibit dissolution loss, improve stability of spinel structure, improve exchange selectivity and recovery efficiency of lithium ion sieve [4].

Titanium has strong structural stability and could replace part of manganese ion in manganese-base lithium ionic sieves. Ti-O bond energy is greater than Mn-O bond, and can cause cell shrinkage and increase the average valence of manganese [5]. However, the effect of titanium doping on the adsorption properties of manganese-base lithium ion sieves in actual brines has been rarely reported. Considering the stability of titanium and improve service performance by reducing the dissolution loss of manganese, titanium doped manganese-base lithium ionic sieves can be used as new research direction.

Keywords: *lithium ionic sieve; dissolution; adsorption; titanium doped*

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Liquid Densities for Mixtures of Methyl Decanoate with N-propanol and N-butanol from 293.15 K to 363.15 K at Pressures up to 60MPa

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The development of industrialization has led to a sharp rise in the consumption of petroleum-based fuels. Petroleum-based fuels are non-renewable. Facing such a severe energy situation, it is necessary to seek alternative fuels which can be produced from resources available locally within the country, such as alcohol, biodiesel, vegetable oils etc. During the past decades, biodiesel has been studied as an excellent alternative for petroleum diesel. Since the early 1990s, various studies have been carried out on biodiesel[1-5]. Biodiesel is made from plant oils, animal fats and waste cooking oils through transesterification or esterification reactions[6]. It is considered as a renewable and clean fuel. The main component of biodiesel is fatty acid esters. The performance of biodiesel is also very similar to petroleum diesel fuel. However, the application of biodiesel is also facing a difficult technical problem. Compared with petroleum diesel fuel, the low-temperature flow properties of biodiesel are a key issue. However, researchers found it's economical and convenient to improve the cold flow performance by blending with some types of additives[7-11]. Density is one of the fundamental properties of fluid, and the experimental density data are essential for the application of a substance. However, we found it is very scarce for high pressure liquid density data of some fatty acid methyl ester and additive mixtures in the literature. Some researchers[12-14] just give a few density data of the pure components. It's necessary to extend the database of thermophysical properties of mixtures of fatty acid methyl esters and additives.

In this work, the experimental measurements for liquid densities of two binary systems of n-propanol plus methyl decanoate and n-butanol plus methyl decanoate were performed over the entire composition with a high-pressure vibrating-tube densimeter. The temperature ranges from 293.15 K to 363.15 K and the pressures were up to 60 MPa. The relative uncertainty of the measurement is estimated less than 0.001 with a confidence level of 0.95. High pressure density values were correlated by modified Tammann-Tait equation and the results are in good agreement with those from literatures. The derived thermodynamic properties, such as the excess molar volumes, the isothermal compressibility, and the isobaric thermal expansivity, were calculated from the experimental density data. The effects of pressure and temperature on the derived properties were also discussed.

Keywords: *Methyl decanoate, Short-chain alcohol additives, High-pressure liquid density, Derivative properties*

Studies on the Association Equilibrium Characteristic of Mg^{2+} and SO_4^{2-} by Raman Spectroscopy

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Magnesium Sulfate solution is an important electrolyte solution which is widely used in many fields, such as chemical industry, biology, metallurgy and so on. The characteristics and the association equilibrium of Mg^{2+} and SO_4^{2-} have been the focus of attention, which has important application values [1]. In this paper, the characteristic of ion association structure of SO_4^{2-} of 0.5mol/L、1.0mol/L、1.5mol/L、2.0mol/L $MgSO_4$ solution at the temperature of 5℃、10℃、20℃、30℃、40℃、50℃、60℃、70℃、80℃、90℃ were studied by Raman Spectroscopy combined with Gauss-lorentz peak fitting program. Furthermore, the ion association equilibrium constant K_R of $MgSO_4$ solutions were calculated.

It is generally recognized that there were four ion association structures of SO_4^{2-} as the free SO_4^{2-} ion, monodentate, bidentate and complicated contact ion pairs (CIPs) [2]. The spectra experiments results showed that the peak area and peak intensity of the ν_1-SO_4^{2-} characteristic peaks in $MgSO_4$ solution were linearly associated with the concentration of SO_4^{2-}. The free SO_4^{2-} ion was the main structure of ν_1-SO_4^{2-} characteristic peaks. During the process of the temperature increasing for high concentration of 1.5mol/L and 2.0mol/L $MgSO_4$ solution, the peak area and peak intensity of the ν_1-SO_4^{2-} characteristic peaks decreased, red shift phenomenon occurred in the peak position, and the symmetry of the peak changed. Accordingly, the content of free SO_4^{2-} ions decreased, the chance of monodentate contact ion pairs (CIPs) increased, but the content of bidentate CIPs and SO_4^{2-} groups structure changed irregularly.

Likewise, the ion association equilibrium constant K_R of $MgSO_4$ solution increased which showed that the ion association equilibrium moved to the right with the temperature increasing for 1.5mol/L and 2.0mol/L $MgSO_4$ solution, thus more CIPs generated. In dilute MgSO4 solutions, there were almost no bidentate CIPs and SO_4^{2-} groups structure detected, the ion association structure of ν_1-SO_4^{2-} characteristic peaks and K_R value changed irregularly.

Keywords: *Mg^{2+}; SO_4^{2-}; Raman spectroscopy; Association equilibrium*

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Phase Equilibria of Ternary System $LiCl–Li_2B_4O_7–H_2O$ at 273 K

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Qaidam Basin is an important inorganic salt reservoir in China [1]. Salt lakes in this area have the characteristics of large storage, complete types of salt lakes and high grade brine [2]. Therefore, the exploitation and utilization of resources in Qaidam Basin can offer an important raw material in the fields of chemical industry, medical treatment, construction, agriculture and metallurgy, and it is also of great significance to industrial production [3].

The stable phase equilibria of the ternary system $LiCl–Li_2B_4O_7–H_2O$ at 273 K were investigated by the isothermal dissolution equilibrium method. According to the experimental results, the phase diagram was plotted. The results show that the ternary system $LiCl–Li_2B_4O_7–H_2O$ at 273 K belongs to the simple co-saturated type, without complex salt or solid solution. The phase diagram contains one invariant point, two univariate curves and two crystallization regions (where the solids are $LiCl·2H_2O$ and $Li_2B_4O_7·3H_2O$). The area of the crystallization region $Li_2B_4O_7·3H_2O$ is much larger than that of $LiCl·2H_2O$, indicating that the solubility of $Li_2B_4O_7·3H_2O$ is much smaller than that of $LiCl·2H_2O$. The mass fraction of $Li_2B_4O_7$ in the equilibrium liquid phase gradually reduces, which indicates that LiCl has a certain salting out effect on $Li_2B_4O_7$.

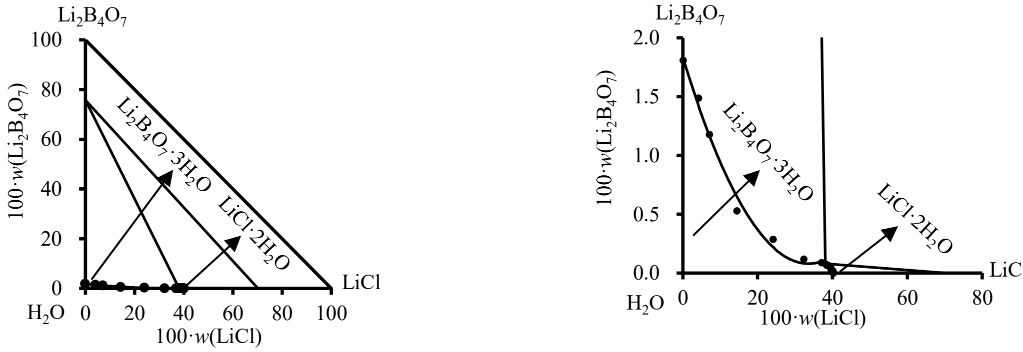

Fig 1. Phase diagram and partial enlarged diagram of ternary system $Li_2B_4O_7–LiCl–H_2O$ at 273 K

Keywords: *Phase equilibrium; Lithium chloride; Solubility; Phase diagram*

Acknowledgments

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Thermodynamic Modeling of $NaBO_2 + H_2O$ And $NaBO_2 + NaCl + H_2O$ Systems

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Metaborate species is dominate in alkali boron-containing aqueous solution. Knowledge of thermodynamic and phase equilibrium properties of multi-component metaborate aqueous solution is interested in many industrial processes. In this study, a thermodynamic model was developed for the $NaBO_2 + H_2O$ system base on the Pitzer-Simonson-Clegg (PSC) activity coefficient equation[1]. Model parameters were determined via simultaneously fitting the vapor pressure and solubility data reported in literature[2-5] and heat capacity data determined by us. The obtained model can well reproduce all the thermodynamic properties and phase diagram of the binary system for the temperature range from 250 K to 400 K (Fig. 1a). Based on the binary parameters of $NaBO_2 + H_2O$ and $NaCl + H_2O$ systems[6], a thermodynamic model for the ternary $NaBO_2 + NaCl + H_2O$ system was developed. The ternary model can reproduce the solubility isotherms reported in literature[7,8] and give a well behavior polythermal graph prediction (Fig. 1b).

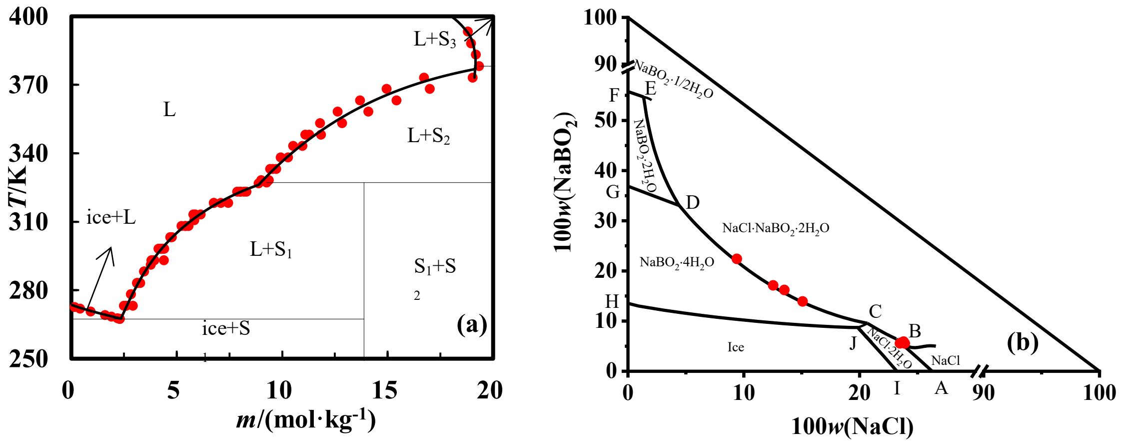

Fig. 1 Comparison of model values and literature values. ●: experimental values reported in literature; Lines: model predicted results. (a) Phase diagram of the $NaBO_2+H_2O$ system. L, Liquid, S_1, $NaBO_2 \cdot 4H_2O$; S_2, $NaBO_2 \cdot 2H_2O$; S_3, $NaBO_2 \cdot 1/2H_2O$; (b) Model predicted polythermal projection of the $NaBO_2 + NaCl + H_2O$ system.

Keywords: *$NaBO_2$+H_2O, $NaBO_2$+NaCl+H_2O, Heat capacity, Phase equilibrium, Thermodynamic modeling.*

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The Stable Phase Diagram of the Ternary Water-Salt System Mg^{2+}, Cs^+ // SO_4^{2-} - H_2O at T = 323.2 K

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Cesium, belongs to the rare metal, widely found in the salt lakes located in Qinghai-Tibet Plateau, which has been used in traditional applications such as electronics industry, glass ceramics, biochemistry, medicine.[1-2] In order to highly efficient exploiting cesium in sulfate brines, the phase equilibrium of the system containing with cesium sulfate and magnesium sulfate has been investigated at 323.2 K using isothermal dissolution method.

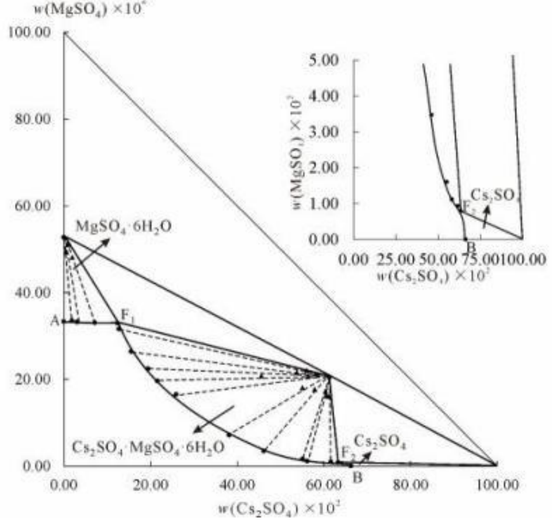

Fig 1. Stable phase diagram and partial enlarged drawing of the ternary system $Cs_2SO_4 + MgSO_4 + H_2O$ at 323.2 K

System $Cs_2SO_4 + MgSO_4 + H_2O$ at 323.2 K is of a complex system, with commensurate double salt formed. Its phase diagram at 323.2 K, as shown in Figure 1, consists of two invariant points and three isothermal dissolution curves. The two invariant points are all belong to commensurate type, cosaturated with two salts and one saturated solution. The cosaturated salts for the two invariant points are Cs_2SO_4 + $Cs_2SO_4 \cdot MgSO_4 \cdot 6H_2O$ and $MgSO_4 \cdot 6H_2O$ + $Cs_2SO_4 \cdot MgSO_4 \cdot 6H_2O$, respectively. The three univariant curves respectively correspond to salt Cs_2SO_4, $MgSO_4 \cdot 6H_2O$, and double salt $Cs_2SO_4 \cdot MgSO_4 \cdot 6H_2O$. The size order of the salt crystalline phase region is $Cs_2SO_4 \cdot MgSO_4 \cdot 6H_2O > MgSO_4 \cdot 6H_2O > Cs_2SO_4$, namely single salt Cs_2SO_4 is difficult to crystallize from this mixed solution.

Keywords: *stable phase equilibria;* magnesium *sulfate; cesium sulfate; double salt*

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Phase Equilibria of the Reciprocal Quaternary System (Li^+, K^+//Cl^-, $B_5O_8^-$ - H_2O) at 298.15 K and 101.325 kPa

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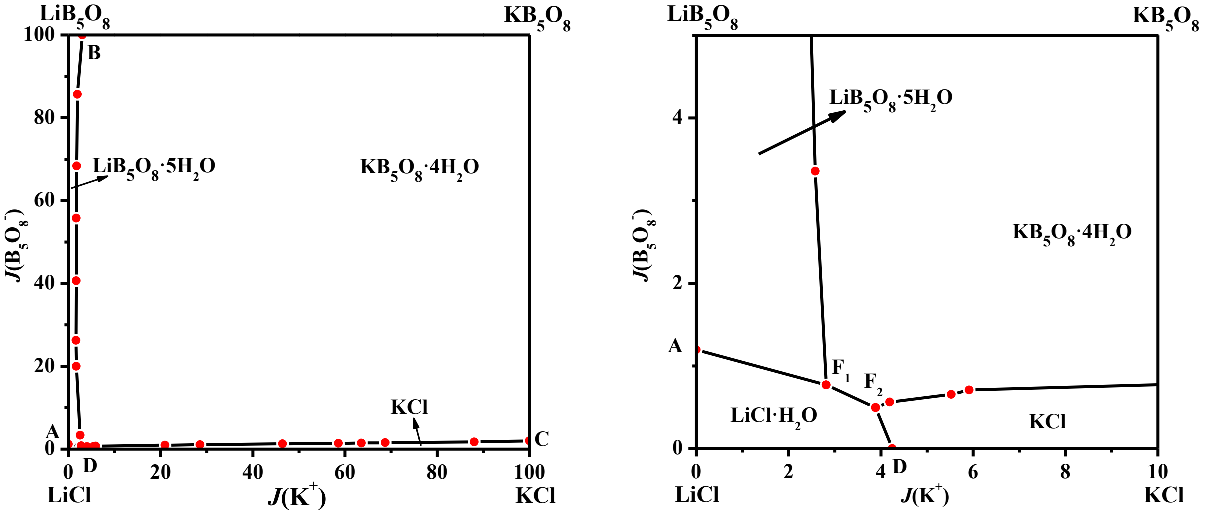
The reciprocal quaternary system (Li^+, K^+//Cl^-, $B_5O_8^-$ - H_2O) was studied using isothermal dissolution method [1-2]. Based on experimental method, the solubilities was available and the dry-salt phase diagram of this system was shown in Figure 1. As the Figure 1 had pointed out, there are two invariant points (F_1, F_2), five univariant curves (AF_1, BF_1, CF_2, DF_2 and F_1F_2) and four crystallization zones ($LiCl\cdot H_2O$, KCl, $KB_5O_8\cdot 4H_2O$, $LiB_5O_8\cdot 5H_2O$). The equilibrium solid phase of F_1 and F_2 were $LiCl\cdot H_2O$ + $LiB_5O_8\cdot 5H_2O$ + $KB_5O8\cdot 4H_2O$ and $LiCl\cdot H_2O$ + KCl + $KB_5O_8\cdot 4H_2O$, respectively. The crystallization area of $LiCl\cdot H_2O$ is smaller, while the crystallization area of $KB_5O_8\cdot 4H_2O$ is largest.



(a) (b)

Figure 1. Phase diagram (a) and enlarged diagram (b) in reciprocal quaternary systems (Li^+, K^+//Cl^-, $B_5O_8^-$ - H_2O) at 298.15 K.

Keywords: *Alkalis pentaborates; Phase equilibrium; Quaternary system*

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Dilution Enthalpies of the Aqueous Solutions on Lithium Borates and the Application of Ion-interaction Model

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Boron and its compounds play an important role in modern energy and material sciences including permanent magnetic, superconducting, boride cermets, boron-based fuel-rich propellants and borate whisker materials [1]. Lithium metaborate is a high-quality piezoelectric material for mobile communication, and lithium pentaborate can be used as a high quality laser material and so on [2]. In order to establish the thermodynamic model of brine systems and to utilize the valuable salt lake resources effectively and comprehensively, heat enthalpy knowledge on the salt lake system containing lithium and borate ions is of great significance not only to understand the ion-interaction between solute-solvent and solute-solute as well as the effects of ion strength, temperature on excess free energy, but also to provide fundamental data in predicting the crystallizing and evaporating behaviors of these salt lakes [3]. Studies on the thermodynamic properties of the salt lake brine systems containing lithium and borate ions is of great significance to establish the solubility predictive model of electrolytes to promote the industrial exploitation of those valuable salt lake resources effectively and comprehensively.

The dilution enthalpies of $LiBO_2$ (aq) from 0.03 to 0.80 $mol \cdot kg^{-1}$ and LiB_5O_8 (aq) from 0.05 to 0.90 $mol \cdot kg^{-1}$ at 298.15 K and 101.325 kPa were investigated using the microcalorimeter BT 2.15. The apparent molar enthalpies on the two species of lithium borates were obtained on the basis of experimental data, and then the diagrams of their apparent molar enthalpy against molality for $LiBO_2$ (aq) and LiB_5O_8 (aq) were also plotted. According to Pitzer ion-interaction equations, the Pitzer single-salt parameters ($\beta^{(0)L}_{MX}$, $\beta^{(1)L}_{MX}$, $\beta^{(2)L}_{MX}$, C^{L}_{MX}) for $LiB(OH)_4$ and $LiB_5O_6(OH)_4$ were obtained via fitting, which are not reported in the literature. The calculated apparent molar enthalpies for $LiBO_2$ (aq) and LiB_5O_8 (aq) agree well with the experimental values, which indicate that the Pitzer single parameters obtained are reliable.

Keywords: *Thermodynamics; Dilution enthalpy; Apparent molar enthalpy*

Acknowledgements: Supports from the National Natural Science Foundation of China (U1607123 and 21773170), the Key Projects of Natural Science Foundation of Tianjin (18JCZDJC10040), the Innovative Research Team in Tianjin Colleges and Universities (TD13-5008) and the Yangtze Scholars and Innovative Research Team of the Chinese University (IRT_17R81).

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Structure Study of Ammonium Chloride Solutions by Spectroscopic Method and Molecular Dynamics Simulation

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X-ray scattering, Raman and molecular simulation were used to determine a series of ammonium chloride solutions at room temperature. The X-ray scattering results were analyzed by PDF theory. The reduced structure function F(Q) and the reduced pair distribution function G(r) were obtained. The excess Raman spectrum was used for spectral analysis. The results show that with the increase of concentration, the main peak position of G(r) which obtained by X-ray scattering moves to 3.16Å. The integral area of the first peak of the $g_{N\text{-}Cl}(r)$ which obtained by the molecular dynamics simulation increases gradually. The author speculate that this is due to the predominance of NH_4^+-Cl^- ion pairs in the high concentration solutions. The Raman spectrum and X-ray scattering results show that the hydrogen bonds in the aqueous solutions were disrupted with the increase of the ammonium chloride concentration.

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Keywords: *Ammonium chloride solution; Synchrotron radiation; X-ray scattering; Raman spectrum; Molecular simulation*

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Viscosity of Mixtures of Dimenthyl Ether, Isobutene with Squalane in Saturated Liquid Phase

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Because of the requirement of sustainable development, environmental friendly refrigerants which has low ozone depletion and global warming potentials have attracted lots of attention. Some new refrigerants, such as dimenthyl ether(DME) and isobutene(R600a), was considered as substitutes of chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs). In the compression refrigeration cycle, the refrigerant may dissolved into the lubricants and form a vapor-liquid mixtures whose viscosity greatly affects the efficiency and reliability of the whole system [1]. Therefore, in order to enrich their thermodynamic properties, this work focused on the measurement of the viscosities of mixtures of DME or R600a with squalane.

The experimental viscosity system, includes the modified dual-capillary viscometer and equilibrium cell, were developed by our laboratory. The modified dual capillary method was based on the Poiseuille's law [2]. The viscosity of saturated liquid mixtures of dimenthyl ether or isobutene with squalane were measured at temperatures between 303.15 K and 343.15 K. The result show that the viscosity isotherms of mixtures decrease with the increase in mole fraction of squalane. The viscosity in the lower temperature zone decreased sharply with increasing mole fraction. The experimental data were correlated by the Hind model [3], and the average relative deviations were 5.61% and 5.79% for DME+squalane and R600a+squalane systems respectively, which may provide support for future research in the refrigeration field.

Keywords: *Vapor-liquid mixture; Viscosity; Squalane; Dimenthyl ether; Isobutene*

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Structure of Aqueous RbCl and CsCl Solutions in the GPa Range by Neutron Diffraction

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The abundance of rubidium and cesium in the earth's crust ranks in 16th and 40th, respectively. The extraction and metallurgy are very difficult due to their difficulty in forming a single mineral, so they are usually classified as "rare element". Large Rb^+ and Cs^+ are classified as structure breaking ions with lower charge densities, and the electrostatic interactions with anions or water are weak, compared to Na^+ in the alkali metal ions; their detailed hydration structure remains unclear. The hydration number of Na^+ does not change in an aqueous NaCl solution with increasing pressure due to their stronger electrostatic interaction, but that of Cl^- changes. High pressure and high temperature perturb the ion hydration and solvent structure, and thus experiment under extreme conditions will give us hints for understanding the nature of ion hydration and water. Neutron diffraction has the advantage to locate the hydrogen atom, and empirical potential structure refinement (EPSR) modeling combined with the diffraction data has been proved to be very successful in extracting the 3D structure of ion hydration and association and solvent water structure [1,2].

In this experiment, aqueous 3 mol/kg RbCl and CsCl solutions in D_2O are measured at 298 and 523 K and 1 and 4 GPa as well as an ambient condition by neutron diffraction on PLANET at J-PARC MLF, Tokai, Japan [3]. The structure factors are analyzed by EPSR modeling. The results show that pressure and temperature give different influences to structure factors (Fig.1). Pair correlation function, coordination number, triangle analysis, spatial density function can give a comprehensive information about the structure. Cs^+ (CN=7.34) has a larger average coordination number than Rb^+(CN=5.94). Tetrahedral ordering of water no longer exists in the GPa range.

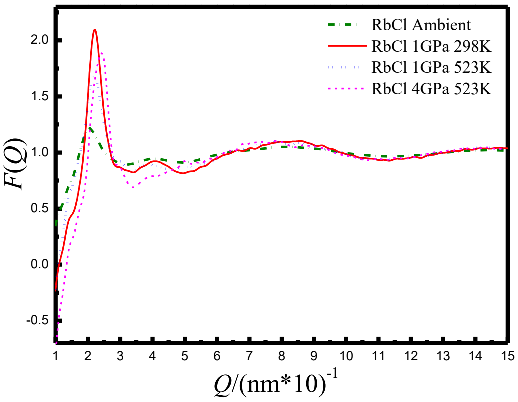

Fig. 1 Structure factors of 3 mol/kg RbCl solution in D_2O at various thermodynamic states

Keywords: *Neutron diffraction; EPSR; RbCl solution; CsCl solution; GPa*

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Supercritical Fluid for the Synthesis of Perovskite Nanocrystals

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Supercritical CO_2 is generally regarded as a green solvent because it is readily available, inexpensive, nontoxic, nonflammable, has adjustable properties, excellent mass transfer characteristics, and can be easily recaptured and recycled after use. Moreover, CO_2 has adjustable solvent power, zero or low interfacial tension and strong penetration ability characteristics that offer many advantages to replace conventional organic solvents, which has been widely used in extraction separation, material preparation and chemical reaction. All-inorganic metal halide perovskite (especially $CsPbX_3$, X=Cl, Br, I) nanocrystals have attracted intense research interest owing to their excellent photophysical properties, which are believed to be highly dependent on their morphologies. Here we demonstrate for the first time that the formation of perovskite nanocrystals by a supercritical fluid route. The morphology of the perovskite nanocrystals was characterized by transmission electron microscope (TEM) and different techniques. This study opens up new opportunity for synthesis of perovskite nanocrystals through a supercritical fluid route.

Keywords: *Supercritical fluid; Perovskite; Nanocrystals*

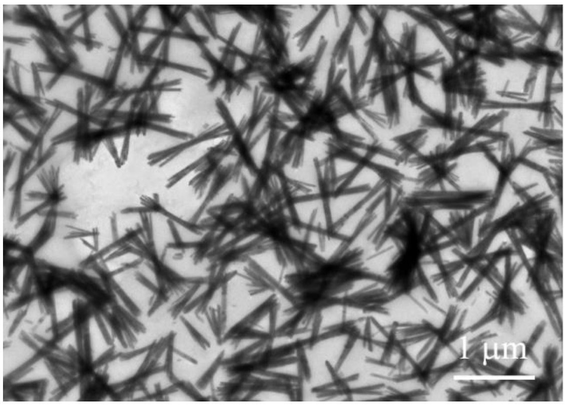

Fig. 1 TEM image of perovskite nanocrystals.

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Study on Separation Technology of Manganese Sulfate and Magnesium Sulfate in Manganese Electrolyte

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In the process of electrolytic manganese, magnesium ion was continuously enriched during the recycling of the electrolyte solution, which results in the increasing of magnesium impurity in manganese metal. Therefore, it is necessary to reduce the magnesium content in the electrolyte. In this study, the salt forming behavior of aqueous Mn^{2+}-Mg^{2+}-NH_4^+-SO_4^{2-} quaternary system were investigated. The experiments of solid-liquid phase equilibrium, isothermal evaporation and cooling crystallization were carried out.

Solid-liquid phase equilibrium data show that the complex solid-solution and double-salt were formed from system, and no way to separate $MgSO_4$ pure salt from the system. However, the isothermal evaporation process at high temperature, were found to be three stages: high-manganese double-salt (S_1), solid-solution (S_2) and high magnesium double-salt (S_3). So the strategy of separating manganese and magnesium content was proposed: (1) evaporation stage I to get manganese-ammonium sulfate double salt, (2) evaporation II to get the mixing salt mainly riched in solid-solution, which furtherly dissolved and recycle to evaporation I, (3) mother liquid of stage was cooled to separate magnesium-ammonium sulfate double salt, and the mother liquid was recycle to evaporation II.

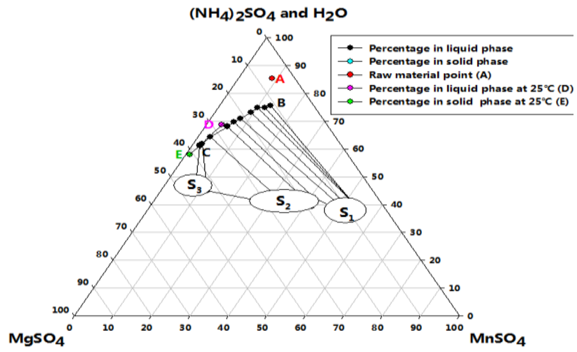

Figure 1. The qaternary system of Mn^{2+}-Mg^{2+}-NH_4^+-SO_4^{2-} at 373K

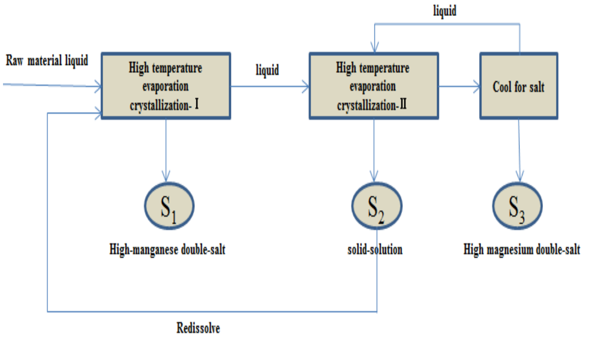

Figure 2. The process of separating salt of Mn^{2+}-Mg^{2+}-NH_4^+-SO_4^{2-}

Keywords: *$MnSO_4$-$MgSO_4$-$(NH_4)_2SO_4$-H_2O, crystallization law of salts*

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Acknowledgments

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Thermodynamic Modeling of the Solubilities of Boric Acid in Chloride and Sulfate Aqueous System: A Preliminary Study

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Boron is an important element in natural waters. High concentration of boron is very common in salt lake brines and radioactive wastewater. Knowledge of solubility and aqueous thermodynamic properties of boron-containing systems, especially with high salinity background (e.g. Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-}, F^-, OH^-, CO_3^{2-}, PO_4^{3+} et al.) is essential to boron extraction from brines and boron removal from wastewater. Comprehensive modeling of all the polyborate species in a system is still difficult even though some pioneers have made great efforts[1],[2]. In most situations, boric acid molecular H_3BO_3 will be the dominant species if the pH of the solution is below 5. Therefore, modeling of solubilities of boric acid in brine is relatively feasible and simple. After the interaction parameters between H_3BO_3 molecular and salts were well determined, systems with polyborate species will be studied further. In this preliminary study, boric acid solubilities in the H_3BO_3-MCl-H_2O and H_3BO_3-M_2SO_4-H_2O (M=Li, Na, K, Mg or Ca) systems were modeled over a wide temperature range using a Pitzer-Simonson-Clegg (PSC) excess Gibbs energy model framework in accordance with previous models[3]. Fig. 1 indicates the model results of H_3BO_3-NaCl-H_2O and H_3BO_3-KCl-H_2O systems are in good agreement with experimental data in literature[4].

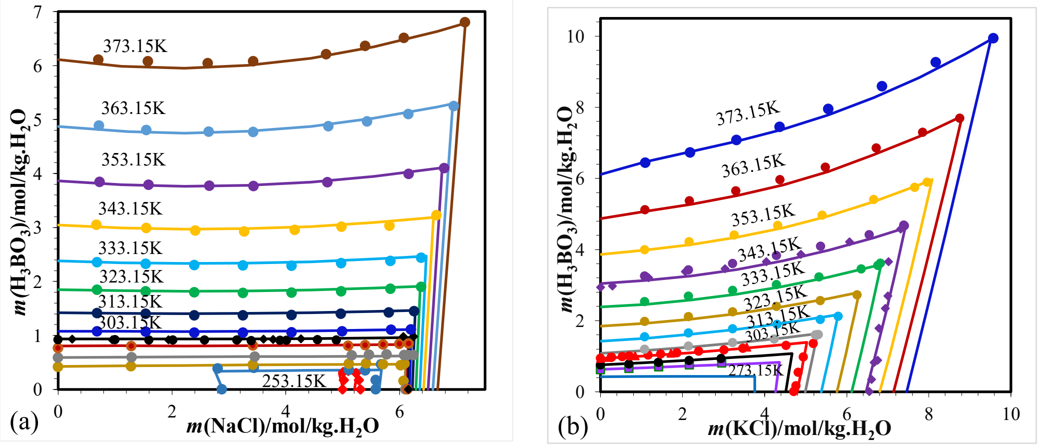

Fig 1. Solubility isotherms in H_3BO_3-NaCl-H_2O (a) and H_3BO_3-KCl-H_2O (b) systems. Lines represent modeling results and symbols represent experimental values in literature[4].

Keywords: *Boric acid; Sulfate; Chloride; Ternary system Solubility; Thermodynamic modeling;*

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Structure of Alkaline Aqueous $NaBH_4$ Solutions by X-Ray Scattering

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Sodium borohydride is a highly efficient and environmentally friendly chemical hydride. The concentration of NaOH is an important influence factor for BH_4^- hydration and Direct Borohydride Fuel Cell. However, there is little research on this issue are aviliable. In the present work the effect of different NaOH concentration on the structure of $NaBH_4$ solution by X-ray scattering were studied. The radial distribution function(RDF) for Na-O(I), Na-O(II), Na-B, B-O atom pairs are obtained from precise diffraction data processing. The Na-O(I) distance of the first hydrated layer of sodium is 0.234-0.246 nm and the coordination number (CN) ranges from 5.09 to 4.07, indicating the octahedral structure around the Na atom. The Na^+ possesses a second hydration shell with Na-O(II) distance range of 0.449-0.441nm and the coordination number (CN) of 8.1-4.2. With the increase of NaOH concentration, the coordination number of the first and second hydrate layers of Na^+ increases. The NA-B distance ranges from 0.280 to 0.271 nm, and the coordination number increases by about 1.1 with the increase of NaOH concentration. H_2O hydrates with BH_4^- through dihydrogen bonds with the B-O distance is 0.377-0.384nm . The coordination number of B-O is about 5.89 which increases of NaOH concentration. The hydrogen bond distance is in the range of 0.285-0.280nm and the dihydrogen bond length is 0.195nm.

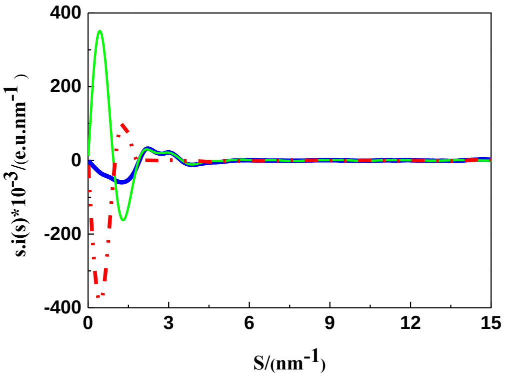

Fig 1. Structure Functions

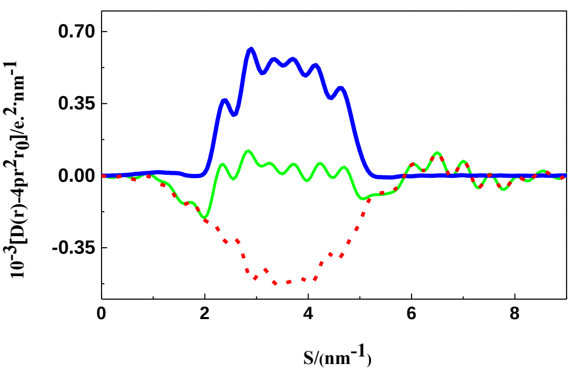

Fig 2. Radial Distribution Functions

Keywords: *X-ray Scattering; Sodium borohydride; Solution structure; Radial distribution function*

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Structure of Molten Nitrate(Hitec) by X-ray Scattering Study

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The structure of Hitec (53% KNO_3–7% $NaNO_3$–40% $NaNO_2$) nitrate molten salt at different temperature (T=150℃, 200℃, 250℃, 300℃, 350℃) were studied by X-ray scattering. The radial distribution functions and structure functions(Fig.1) of Hitec molten salt are obtained. The theoretical partial radial distribution functions of the interaction between Na–O, K–O, Na–N, and K–N atoms are given by model design and theoretical calculations. The plausible structure of Hitec nitrate molten salt is given, Na^+ forms hexa-coordinate octahedron structure with the Na–O(I) distances in the range 0.218 nm–0.226 nm and the coordination numbers from 5 to 6 in the first coordination layer, and the most possible configuration of Na^+ is that shares only one oxygen atom with NO_3^- or NO_2^-(Fig.2). The second coordination layer of Na^+ with the Na–O(II) distances in the range 0.430 nm–0.438 nm and the coordination numbers from 8 to 10. The K^+ forms 8 coordination with the K–O distances in the range 0.265 nm–0.276 nm and the coordination numbers from 4 to 8.6. The distances of Na–N in the rang 0.380 nm–0.392 nm and the coordination numbers from 3 to 6.5. The distances of K–N in the range 0.339 nm–0.348 nm and the coordination numbers from 1 to 3. The effect of temperature on melt structure is also discussed.

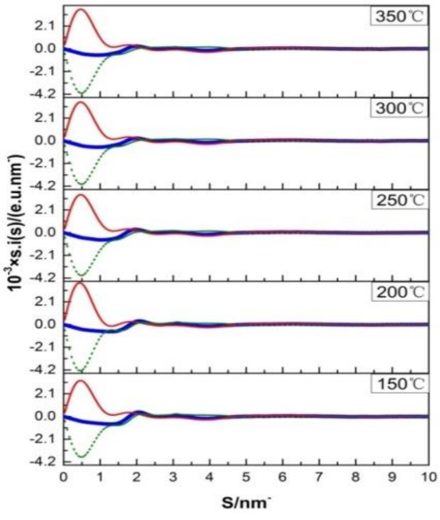

Fig 1. The structural functions of molten (Hitec)

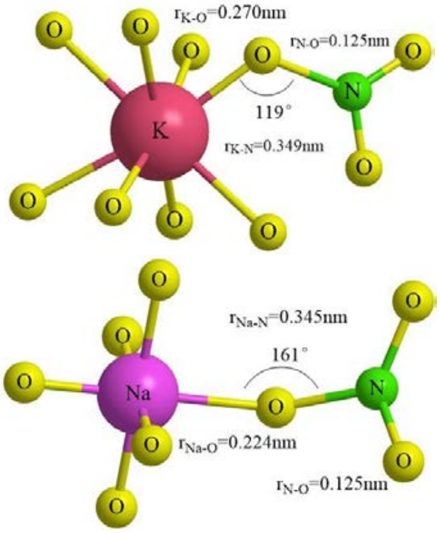

Fig 2. the most plausible configuration of ion paris in molten (Hitec,T=150℃)

Keywords: *X-ray scattering; Nitric acid molten salt; Melt structure;Radial distribution function.*

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In Situ Monitoring of the Adsorption Kinetics of Surfactants in Microchannel by Pulsed Streaming Potential Measurement

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Surfactants has been used in a great variety of industrial applications as detergents, foaming, emulsifiers, solubilizers, and wetting agents.[1] The adsorption of surfactant at the solid-liquid interface plays an important role in many technological and industrial applications, but the rapid time scales associated with the formation of an adsorbed surfactant layer at the solid–aqueous interface has prevented accurate investigation of adsorption kinetics.[2] New techniques with high temporal resolution will be need to monitor the adsorption kinetics of surfactants at the solid-liquid interface *in situ*. In this experiment, the adsorption kinetics of surfactants cetrimonium bromide (CTAB) and Didodecyldimethylammonium bromide (DDAB) were monitored based on the change of surface charge with pulsed (SP) measurement in five minutes. The effects of buffer concentration, pH, and solid surface on the adsorption kinetics of CTAB were also investigated. It is shown that there has a linear relationship between the initial SP change rate dE_r/dt with the concentration of CTAB in the same buffer solution, which concluded that the adsorption of CTAB at the solid-liquid interface controlled by diffusion model. The adsorption of DDAB show that there has a similar adsorption regime with CTAB, but compared with CTAB, DDAB takes longer time to reach equilibrium on the solid-liquid surface.

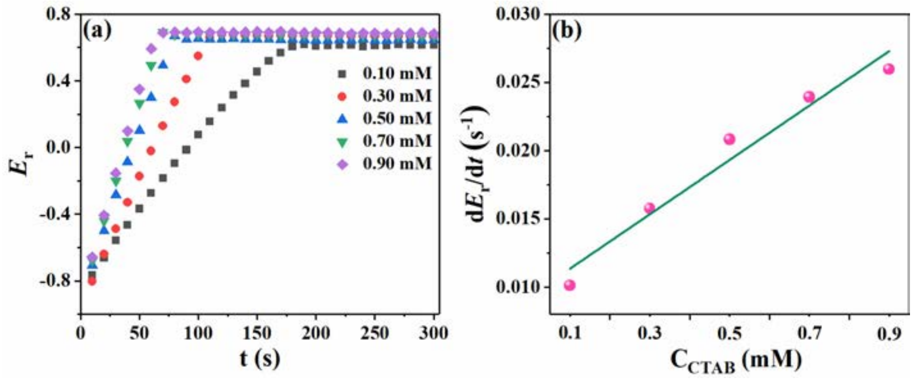

Figure 1. (a) The plots of relative SP E_r of CTAB with different concentrations onto bare silica capillaries changes along with time, the concentrations of CTAB are 0.10 mM, 0.30 mM, 0.50 mM, 0.70 mM, and 0.90 mM, respectively. (b) The linear relationship between the initial change rate dE_r/dt and the concentration of CTAB. Buffer solution is 5 mM PB, pH = 7.0.

Keywords: *surfactants; solid-liquid interface; adsorption kinetics; pulsed streaming potential; microchannel*

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Solubility of K_2SO_4 in ($PEG1000+H_2O$) Mixed Solvents at 298.15 and 308.15 K

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Potassium resources in China are abundant, however, potassium is mainly dependent on imports. In some papers, polymer or organic solvent is added to the water-salt system to obtain high-purity crystals by salting out effect[1]. Currently, the literature report of potassium sulfate in mixed solvent system is very rare. Therefore, the phase equilibrium study of K_2SO_4+PEG1000+H_2O ternary system was carried out, and compared the salting rate and solubility phase diagram with K_2SO_4+1-propanol+H_2O system in the reported literature[2]. Fig.1 shows that the temperature has little effect on salting out ratio, and the salting out ratio increases with the increase of the alcohol content in the solution at the same temperature. From the comparison in Fig.2, the solubility of potassium sulfate becomes larger when the temperature increases, and the solubility of potassium sulfate in the PEG1000+H_2O solution is greater than that in the 1-propanol + H_2O solution at the same temperature.

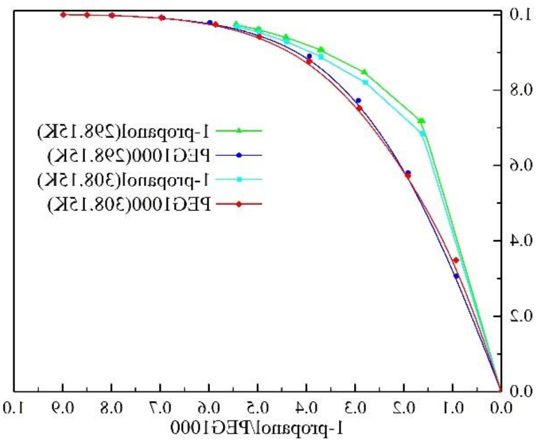

Fig 1. Salting-out ratio(R) for ternary system K_2SO_4 + PEG1000/1-propanol - H_2O at (298, 308) K

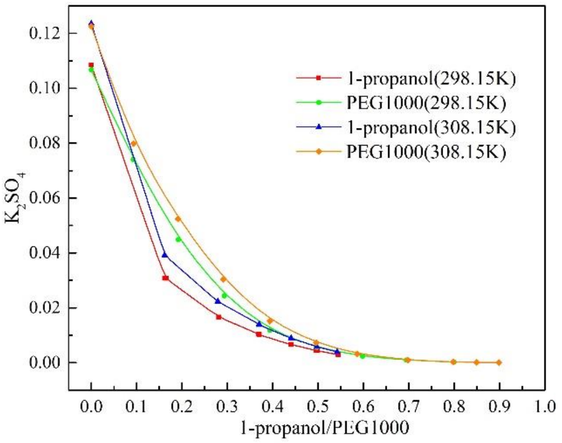

Fig 2. Solubility for ternary system K_2SO_4 + PEG1000/1-propanol - H_2O at (298, 308) K

Keywords: *phase equilibrium, salting out rate, solubility, mixed solvent*

Acknowledgements: Project supported by the NSFC(U1507111).

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Study on Lithium Enrichment and Potassium Extraction from Simulated Brine Solution

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In this study, Lithium enrichment and Potassium extraction were explored from 5L simulated brine solution with 0.028 wt. % Li^+, 6.0 wt. % K^+, and 4.8 wt. % CO_3^{2-}. Isothermal evaporation at 25 ℃ in a thermostat of the solution was prioritized, until lithium carbonate appeared in crystallizing solid, and the saturated solution containing 0.15 wt. % Li^+, 30 wt. % K^+, and 23.8 wt. % CO_3^{2-}.was obtained, then the high-pressure CO_2 was added for carbonization of the solution at room temperature in an autoclave (pilot pressure: 0.2-0.5 MPa, dwell time: 30min), the solution was converted into a solution system of Li^+， K^+//HCO_3^--H_2O, meanwhile, part of the $KHCO_3$ was precipitated and Li^+ was concentrated in the solution as $LiHCO_3$, followed by solid-liquid separation and washing, the solution composition was switched to 0.17 wt. % Li^+, 16.4 wt. % K^+, 10.4 wt. % CO_3^{2-}, and 6.0 wt. % HCO_3^-. Carbonization under the same conditions was continued until the $KHCO_3$ was no longer separated from the solution, the solution composition was switched to 0.19 wt. % Li^+, 9.6 wt. % K^+, 1.0wt. % CO_3^{2-}, and 13.0 wt. % HCO_3^-. The continued vaporization was carried out at 25ºC isothermal in a thermostat, the solids were continuously precipitated and accompanying regular solid-liquid separation until separated Li_2CO_3 appeared, the solution was eventually changed to a composition of 0.45 wt. % Li^+, 16.0 wt. % K^+, 13.2 wt. % CO_3^{2-}, and 3.4 wt. % HCO_3^-. The final measurement results indicated that, Li^+ in the simulated brine Solution could be enriched to more than 30 g/l, and the $KHCO_3$ precipitated at each stage could be vacuum dried at 80 C for 6 h, KHCO3 products could be obtained, and the recovery rate (calculated as the mass percentage of K^+) is 86.45%.

In addition, the study realizes the resource utilization of CO_2, and is easy to realize the recovery and recycling of the purified separation liquid, which is a green technology. By controlling pH value, solution density and crystallization time, the study can be connected with existing industrial evaporation and crystallization devices.

Keywords: *Simulated Brine Solution; Lithium; Potassium; Extraction*

Thermodynamic Model Calculation of Solid-liquid Equilibrium in Ternary System $NH_4Cl+MgCl_2+H_2O$ at 298 K

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In the salt lake resources of China, the separation of various elements affects the development and utilization of salt lakes especially for the extraction of Mg^{2+}, Li^+, and K^+. In allusion to this problem, some papers have reported that adding NH_4Cl can produce less soluble ammonium carnallite and then precipitate[1]. Phase equilibrium research is the basis for the development of brine resources. The solubility diagram gives the information about the crystallization behavior of salts. Yu et al. completed the phase diagram of $NH_4Cl + MgCl_2 + H_2O$ at 298 K[2]. Meanwhile, the Pitzer model was used to estimate the reliability of the solubility reported in the literature. In this work, the single salt parameters ($\beta^{(0)}$, $\beta^{(1)}$, C^{ϕ}) could be obtained in literatures[3-4]. Although mixed parameters ($\theta_{NH4,Mg}$, $\psi_{NH4,Mg,Cl}$) can be also acquired in literature[4], a slightly deviation can be observed as shown in Fig.1. Therefore, $\theta_{NH4,Mg}$, $\psi_{NH4,Mg,Cl}$ were fitted again according to experimental data from literature[2] in this study. A comparison of theoretical data and experimental value was done and it was shown in Fig.1. Results show that the experimental values are agree well with the calculated values.

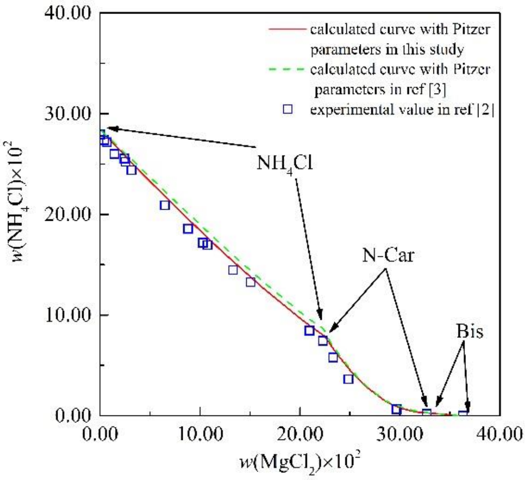

Fig 1. The calculated and experimental phase diagrams of NH_4Cl-$MgCl_2$-H_2O at 298 K; N-car: $NH_4Cl\cdot MgCl_2\cdot 6H_2O$; Bis: $MgCl_2\cdot 6H_2O$

Keywords: *Solubility; magnesium chloride; Pitzer model*

Acknoledgments: Project supported by Sichuan Science and Technology Program (2017JY0191).

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Study on the Dehydration Process of Magnesium Nitrate Hexahydrate

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Magnesium nitrate as a molten salt has the advantage of low melting point and low cost, and it can be obtained by dehydrating Magnesium nitrate hexahydrate. The dehydration process of magnesium nitrate hexahydrate was measured by simultaneous TG/DSC at different heating rates (1, 5, 10, 20°C/min). Especially a low heating rate (1°C/min) was chosen in order to improve the sensitivity of detection. It helps to pick up any small endothermic peaks and reflect the dehydration stages in detail. The TG and DSC curves of $Mg(NO_3)_2{\cdot}6H_2O$ is shown in Figure 1. First, magnesium nitrate hexahydrate was melting to liquid that was a concentrated aqueous solution of magnesium nitrate. With the loss of water magnesium nitrate dihydrate crystallized from the solution. When the temperature reached 131°C, magnesium nitrate dihydrate started to melting. The endothermic peak was clearly observed from the DSC curve at 1 °C/min heating rate. The dehydration process of $Mg(NO_3)_2{\cdot}6H_2O$ to $Mg(NO_3)_2{\cdot}2H_2O$ can be described from the phase equilibrium of aqueous solution of magnesium nitrate.

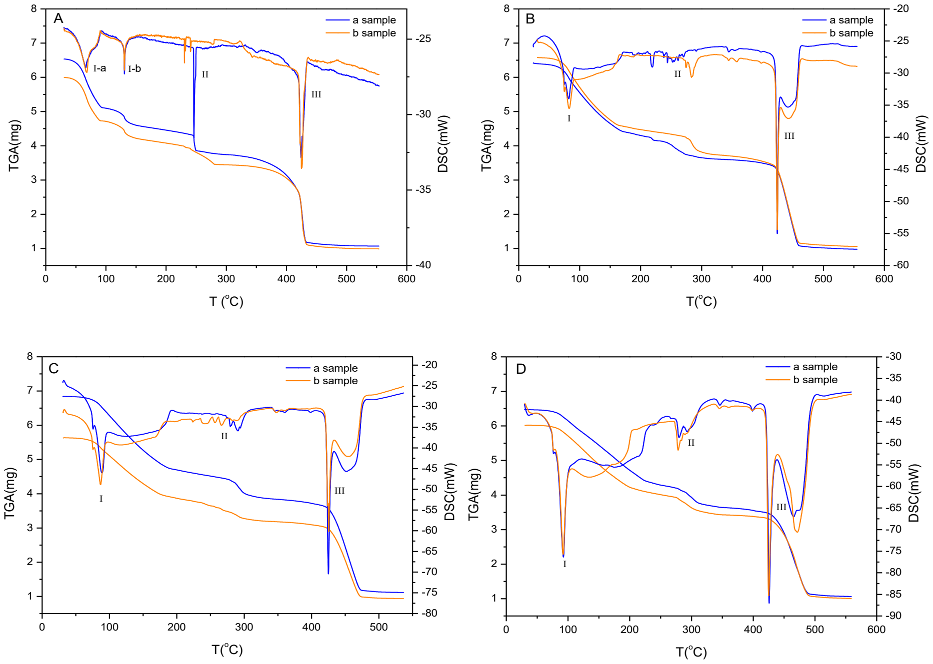

Figure 1. TG and DSC curves of $Mg(NO_3)_2{\cdot}6H_2O$ in N_2 (50mL/min) measured by simultaneous TG/DSC. (A) heating rate 1 °C/min, sample weights for a, b are 6.54 and 5.99 mg, respectively, (B) heating rate 5 °C/min, sample weights for a, b are 6.42 and 6.58 mg, respectively, (C) heating rate 10 °C/min, sample weights for a, b are 6.85 and 5.63 mg, respectively, (D) heating rate 20 °C/min, sample weights for a, b are 6.47 and 6.02 mg, respectively.

Local Microstructure Study on Pyridinium Ionic Liquids

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As a new type of green medium, room temperature ionic liquids (ILs) have received wide research attention due to their dramatic properties [1-3]. Microstructure and thermodynamic properties of ILs can be analyzed and predicted via molecular dynamics (MD) simulation [2], which is good for understanding the fundamental effects of ILs on physical and chemical processes.

The effects of temperature on the local microstructure and dynamics of pyridinium ionic liquids have been compared by analyzing their radial distribution and spatial distribution functions. It is showed in Fig. 1 that temperature increasing is advantageous to aggregations of the polar and nonpolar regions in the pyridinium ILs [4]. We concluded that the aggregation behavior with increasing temperature maybe results in different local solvation structure in polar and nonpolar regions with different solute-solvent interactions. Moreover, the microstructure and the microscopic dynamics of the mixture of ILs and acetonitrile have been studied [5]. It is found that the local microstructure of the polar region is different from the nonpolar region with different mole fraction of ionic liquids. Next, we will study the structure of pyridinium ILs on the surface of graphene.

Keywords: *Ionic liquids; Molecular dynamics simulation; Microstructure; Spatial distribution functions*

Fig 1. Spatial distributions of anions around cations in red color and those of CT4 around cations in yellow color at 293 K (left) and 373 K (right) for ionic liquid [BPy][BF_4] [4].

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Dihydrogen Bonds in Aqueous NaBD$_4$ Solution by Neutron and X-Ray Scattering: Concentration and Temperature Effects

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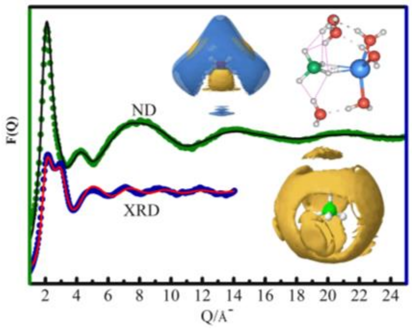
The dihydrogen bonds (hydridic-to-protonic interaction) influences the structure, reactivity, and selectivity in solution,[1] while little direct experimental evidences are available [2,3].

In the present work, X-ray Scattering, Neutron Scattering and Empirical Potential Structure Refinement (EPSR) modelling were employed to study the structure of alkaline aqueous NaBD$_4$ solutions at different NaBD$_4$ concentrations and temperatures. In alkaline NaBD$_4$ aqueous, about 5.6±1.6 water molecules are likely to bond to BD$_4^-$ *via* tetrahedral edges or tetrahedral corners without a very specific hydration geometry, giving rise to each hydrogen atom of BD$_4^-$ bound to 2.2±1.0 water molecules through dihydrogen bonds with the D-D distance of 1.95Å.



The number of dihydrogen bond decreases with increasing concentration, and increase with temperature. BH$_4^-$ and Na$^+$ form contact ion pairs dominatingly in the tetrahedral-edge-shared bidentate ligand form, with the Na$^+$-B distances of 2.82Å. Increasing NaBD$_4$ concentration aggravates the ion association between Na$^+$ and BD$_4^-$, while increase temperature decreases the ion association.

Keywords: *Borohydride, X-Ray diffraction, Dihydrogen bond, Ion pairs, EPSR*

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The Stable Phase Diagram of the Ternary Water-Salt System Na^+, Rb^+ // SO_4^{2-} - H_2O at 323.2 K

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As an essential industrial raw material, rubidium, a rare metal with the same unique properties, is widely used in the fields of energy, electronics, special glass, medicine and other high-tech fields. Sodium and rubidium in the form of brine are widely distributed in salt lakes and geothermal water in Qinghai and Tibet of China.[1,2] Sulfate type is an important water-salt system in Qinghai Salt Lake and the main component of the brine can be simplified as the complex system $Li^+ + Na^+ + K^+ + Rb^+ + Ca^{2+} + Mg^{2+} + Cl^- + SO_4^{2-} + H_2O$ with a great potential for extraction mineral resource.

Rubidium belongs to the typical scattered lithophile element group and cannot easily form an independent mineral in nature,[3] in addition, the global total reserves of rubidium is about 10 million 770 thousand tons, of which 10 million tons in the Saline Lake. As the most basic subsystem, the ternary system Na^+, Rb^+ // SO_4^{2-} - H_2O has been investigated at 323.2 K using the isothermal dissolution method.

According to the phase diagram (Fig. 1) of the system Na^+, Rb^+ // SO_4^{2-} - H_2O at 323.2 K, the system is of a simple type, no double salt or solid solution formed. The phase diagram consists two crystallization regions corresponding to Na_2SO_4 and Rb_2SO_4, one invariant point (commensurate invariant point - H_1) and two isothermal dissolution curves including H_1B and H_1A. Comparisons between the phase diagrams of Na^+, Rb^+ // SO_4^{2-} - H_2O at 298.2 and 323.2 K show that it is possible to obtain single salt of rubidium sulfate and sodium sulfate from the sulfate type old brines using ordinary evaporation crystallization or cooling crystallization method.

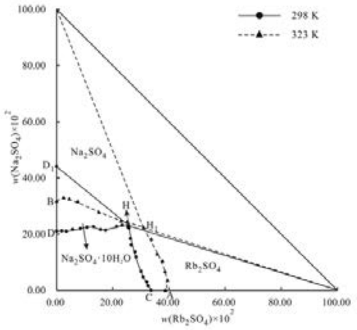

Fig 1 The stable phase diagram of the system Na^+, Rb^+ // SO_4^{2-} - H_2O at 323.2 K and 298.2 K.[4]

Keyword: *stable phase diagram; salt lake brines; sodium; rubidium*

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Structure Effect of Ionic Liquid to Enhance TBP Extraction for Effective Separation of Lithium and Magnesium

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Table 1 Ionic liquid with different anions enhanced TBP extraction and separation of Li^+ and Mg^{2+}

IL	E_{Li}(%)	E_{Mg}(%)	$\beta_{Li/Mg}$	IL	E_{Li}(%)	E_{Mg}(%)	$\beta_{Li/Mg}$
[Bmim]Cl	15.82	24.92	0.57	$[N_{4444}]$TFSI	26.69	18.88	1.57
[Bmim]Phen	29.58	34.44	0.80	[Bmbim]TFSI	83.87	15.61	28.36
[Bmim]FSI	42.61	26.46	2.06	[EMMP]TFSI	85.68	19.76	24.52
[Bmim]BF4	63.64	32.57	3.62	[PP14]TFSI	86.68	27.42	17.32
[Bmim]PF6	79.59	19.27	16.34	[P14]TFSI	87.25	21.33	25.23
[Bmim]TFSI	87.50	22.47	24.16	[Bmim]TFSI	87.50	22.47	24.16
---	---	---	---	[Bpy]TFSI	88.31	15.85	40.11

*E_{Li}(%): lithium extraction efficiency; E_{Mg}(%): magnesium extraction efficiency; $\beta_{Li/Mg}$: Li/Mg separation factor.

In order to study the structure effect of ionic liquids (IL) to enhance TBP extraction on separation of Li^+ and Mg^{2+}, IL with different anions and cations were selected for investigation. The extractant was prepared by combination of IL and TBP in different proportion. The organic phase and aqueous solution were mixed in a vials, and shaken well at a temperature of 298.0(± 0.5) K for 30 min to attain equilibrium. The concentrations of Li^+ and Mg^{2+} were measured by ICP-AES. The results (Table 1) showed that the separation efficiency of Li/Mg not only was affected by the hydrophobicity of the IL, the cation's polarity of IL also has a significant effect. This result might be attributed to the fact that most of the hydrophobic ILs can stay in the oil phase. As a result, $Li(TBP)_n^+$ transferred into oil phase through cation exchange process. Because most of the hydrophilic IL could be dissolved in the aqueous phase, therefore can't be function as a phase transfer exchanger, the Li^+ extraction efficiency was low. As the polarity of the cation was weaker, the cation exchange reaction at the interface was more difficult, thus the extraction efficiency of Li^+ and Mg^{2+} was also lower. Therefore, the hydrophobic IL with strong polar cations could enhance the TBP extraction efficiency for separation of Li^+ and Mg^{2+}.

Keywords: *Structure effect; Ionic liquid; TBP; Separation of lithium and magnesium*

Mechanism for Hydrolysis of Double Six–Membered Ring Tetraborate Anion

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$[B_4O_5(OH)_4^{2-}]$ is a representative borate anion with a double six–membered ring structure [1-6], but there is limited knowledge about the hydrolysis mechanisms of $[B_4O_5(OH)_4^{2-}]$. In this study, the structures and hydrolysis mechanisms of $[B_4O_5(OH)_4^{2-}]$ under different pathways in a neutral environment were studied at the MO6–2X/6–311++G (2df, 2pd) level of theory. The PCM solvation model was used to understand the fundamental chemistry of $[B_4O_5(OH)_4^{2-}]$ hydrolysis and transformation among borate anions. Our calculations show that the tetraborate ion undergoes three–step hydrolysis to form $[B(OH)_4^-]$ and an intermediate, $[B_3O_2(OH)_6^-]$. Other types of structures, such as chain and mesh structures, cannot be produced during these processes. $[B_3O_2(OH)_6^-]$ hydrolyzes to $[B(OH)_4^-]$ and $[B(OH)_3]$ in the last two steps. $[B_4O_5(OH)_4^{2-}]$ finally hydrolyzes to $[B(OH)_4^-]$ and $[B(OH)_3]$ in a molar–ratio of 2:2. Other species, such as $[B_3O_3(OH)_4^-]$ and $[B_5O_6(OH)_4^-]$, cannot be produced during this hydrolysis process. A distribution map of borate species was also used to explain transformations among borate anions in alkali tetraborate solutions. This study shows that $[B_4O_5(OH)_4^{2-}]$ always participates in the hydrolysis reaction, even with a decrease in concentration. $[B_3O_3(OH)_4^-]$, $[B(OH)_4^-]$, and $[B(OH)_3]$ have different roles in "water–poor" and "water–rich" zones. Concentration and pH of solution are the key factors that affect the distribution of borate ions.

Keywords: *Hydrolysis mechanism; Tetraborate anion; Polymerization; Distribution map of borate species*

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Recent Progress in Structure of Aqueous Polyborate Solutions

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Crystal structure of metal borates has been extensively investigated by X-ray and neutron diffraction, *etc*. However, the structure and properties in polyborate solutions have rarely been reported so far. Very complicated structure studies in aqueous polyborate solutions of Li, Na, K, Rb, Cs, and Mg have focused on by SR X-ray scattering(XRS), EXAFS, Raman, NMR, and DFT in the last decade years by our group. The density, conductivity and pH in aqueous polyborate solutions at 298.15 and 333.15K were measured in the present works. The polyborate species distribution were calculated from pH measurement and the main species in the solutions were confirmed by NMR and Raman spectra. For metaborate of alkali metal, the dominant species is always $B(OH)_4^-$ at any concentration, but the others negligible; For tetraborate of alkali metal, when concentration is at the extreme low range, there only $B(OH)_3$ and $B(OH)_4^-$ exist in the solutions. As concentration goes on increasing, $B(OH)_3$ and $B(OH)_4^-$ polycondensate to form more complex species. Of them, $B_4O_5(OH)_4^{2-}$ in the tetraborate solutions is a main species, $B(OH)_3$, $B(OH)_4^-$, and $B_3O_3(OH)_4^-$ minor, but $B_3O_3(OH)_5^{2-}$ and $B_5O_6OH)_4^-$ ignorable; As the solution continues to evaporate, $B_4O_5(OH)_4^{2-}$ eventually becomes a dominant species, consistent with the congruent compound $M_2B_4O_7 \cdot nH_2O$ (M=Li,Na,K,Rb,Cs) in the system M_2O-B_2O_3-H_2O (M=Li,Na,K,Rb,Cs). For pentaborate of of alkali metal, $B(OH)_3$ and $B(OH)_4^-$ are the main species at the extreme low concentration; The species distribution, Raman and NMR verify that the dominant species in the concentrated pentaborate solutions of Li and Na are pentaborate $B_5O_6OH)_4^-$, but it is surprising that main species of K, Rb, and Cs always are triborate monoanion $B_3O_3(OH)_4^-$. Although $M[B_5O_6OH)_4] \cdot nH_2O$ (M=Li,Na,K,Rb,Cs) are all congruent compounds in the system M_2O-B_2O_3-H_2O (M=Li,Na,K,Rb,Cs), the main species in the aqueous solutions are quite different because of different cation hydration distance(d), hydration number(CN) and their configuration, especially the charge(Z). For bivalent Mg^{2+}, three borate minerals, such as inderite ($2MgO \cdot 3B_2O_3 \cdot 15H_2O$), hungchaoite($MgO \cdot 2B_2O_3 \cdot 9H_2O$) and macallisterite ($MgO \cdot 3B_2O_3 \cdot 7.5H_2O$) exist in the MgO-B_2O_3-H_2O system at 298K. Of them, inderite is a congruent compound, but hungchaoite and macallisterite are incongruent. The species distribution and Raman spectra proved that the predominant species in the solutions of all magnesium borates is bivalent triborate $B_3O_3(OH)_5^{2-}$, the subordinate species is $B(OH)_4^-$ at low B_2O_3/MgO ratio and $B(OH)_3$ at high B_2O_3/MgO ratio, and the other anions are ignorable. Here the high Z of borate anion must match that of Mg^{2+}. The disappearance of divalent $B_4O_5(OH)_4^{2-}$ is agreement with incongruent nature. The DFT and XRS show that tetrahedral $Li(H_2O)_4^+$ (d=0.20nm, CN=4) and octahedral $Na(H_2O)_6^+$(d=0.236nm, CN=6) and $Mg(H_2O)_6^{2+}$ (d=0.210 nm,CN=6) in the first shell belong to Platonic polyhedra. However, $K(H_2O)_8^+$ (0.28 nm, CN=8, XRS and DFT), $Rb(H_2O)_8^+$ (d=0.293nm, CN=7.7-8.2, EXAFS), and $Cs(H_2O)_8^+$(d=0.320-0.326nm, CN=7.6-7.9, EXAFS) are inclined to Voronoi polyhedra. Therefore, the effect of cation Z and d on the structure of polyborate in aqueous solutions is deterministic, while hydrated-cation symmetry is secondary. Their hydrolysis order is: Mg>Li>Na>K>Rb>Cs, in step with hydration power. Among them, Mg^{2+} and Li^+ have a strong tendency to hydrolysis, but Na^+ scarcely hydrolyzes, especially Rb^+ and Cs^+ have a little protonation. X-ray scattering of aqueous alkaline boron hydroxide solution solution has firstly confirmed that dihydrogen bonds exist in the aqueous solution.

Keywords: solution structure; polyborate; X-ray scattering; dihydrogen bond; EXAFS

Basic Ionic Liquids Promoted Chemical Transformation of CO_2 to Organic Carbonates

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As one of the most important parts of chemistry, green chemistry has made significant contribution to the environmental improvement and economic benefit, and become a major target in the sustainable development of various countries and enterprises [1]. The synthesis of value-added bulk and fine chemicals by the using of renewable feedstocks and high efficient and stable green catalysts conform to the theory and practice of green chemistry, and therefore, has been attracting a lot of attentions and research.

Ionic liquids (ILs), especially basic ILs with unique physicochemical properties, have wide application in catalysis. Using basic ILs as catalysts for the conversion of cheap, abundant, nontoxic, and renewable CO_2 into value-added organic carbonates is highly significant in view of environmental and economic issues [2]. This work aims at giving a detailed overview on the recent advances on basic ILs promoted chemical transformation of CO_2 to cyclic and linear carbonates. The structures of various basic ILs, as well as the basic ILs promoted reactions for the transformation of CO_2 to organic carbonates are discussed in detail, including the reaction conditions, the yields of target products, the catalytic activities of basic ILs and the reaction mechanism

Keywords: *Basic ionic liquids; CO_2 chemical transformation, organic carbonates*

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Solubilities, Densities, Refractive Indices and pH Values for the Aqueous Ternary Systems ($LiCl + LiB_5O_8 + H_2O$) and ($Li_2SO_4 + LiB_5O_8 + H_2O$) at 288.15 K and 101 kPa

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Solubilities, densities, refractive indices and pH values of the ternary systems ($LiCl + LiB_5O_8 + H_2O$) and ($Li_2SO_4 + LiB_5O_8 + H_2O$) at 288.15 K and 101 kPa were studied using the isothermal dissolution method and the wet-residue method [1]. From the experimental data, the phase diagrams and the diagrams on physicochemical properties including density, refractive index and pH value against composition were plotted. The results show that two systems belong to simple saturation type, and no double salt or solid solution formed at 288.15 K. For the two systems, there are both in one invariant point, two isothermal dissolution curves and two crystallization regions including lithium pentaborate pentahydrate ($LiB_5O_8{\cdot}5H_2O$, Lb5), lithium chloride dihydrate ($LiCl{\cdot}2H_2O$, Lc2, in the former) and lithium sulfate monohydrate ($Li_2SO_4H_2O$, Ls1, in the latter). It was found that the area of the crystallization region of Lb5 was larger than that of Lc2 in the former system and Ls1 in the later system, and the results indicated that the solubility of lithium pentaborate was lower in the two systems. The densities and refractive indices in the two ternary systems at 288.15 K increased firstly and then decreased with the increase of LiCl and Li_2SO_4 concentration in the solution. However, the pH values present a contrary trend, which decreased firstly and then increased. The calculated values [2] of density and refractive index using empirical equations for the two ternary systems agree well with the experimental values.

Keywords: *Phase diagram; Solubility; Lithium sulfate; Lithium chloride; Lithium pentaborate*

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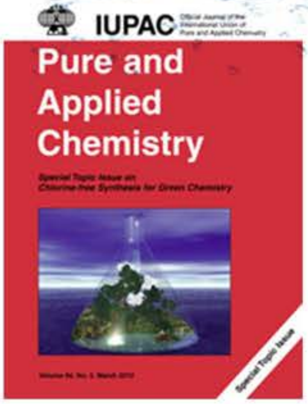
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