

Surfactant-stabilised emulsions in amine units for LPG treating

Emulsion formation by surfactants is one of the most complex problems facing amine units treating refinery LPG

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Contamination in refinery liquefied petroleum gas (LPG) feed streams to amine units is one of the leading causes of process upsets and diminished throughputs. More detailed testing shows that, specifically, surfactants in the LPG are one of the most damaging contaminants affecting the process. Surfactants often pose a number of challenges such as LPG-amine solvent emulsification, amine solvent losses and downstream caustic unit contamination. In fact, surfactants in the feed LPG is perhaps one of the causes of low treating performance, often leading to copper strip failure. Surface active contaminants in LPG streams should therefore be sampled, analysed, and removed in order to enable processing plants to run smoothly. This article discusses how the stream LPG is sampled, revealing the presence of surfactants directly linked to emulsion formation and the associated amine solvent losses. Specialised methods for the presence of surfactants, such as surface tension and surface rheology evaluation, are examined, as well as techniques for on-site sampling of LPG. The article additionally discusses measures to be implemented to remove surfactants and eliminate their downstream effects.

Surfactant contaminants

Surfactants in the liquid LPG hydrocarbon phase feeding amine units can cause a number of detrimental effects, most predominantly LPG-amine solvent emulsification. Surfactants can also be present in the water phase if the LPG contains emulsified or free water. Emulsion formation inside the amine unit con-

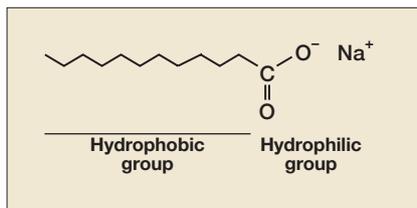


Figure 1 Example of a molecular surfactant

factor (treater) can then lead to several secondary problems such as the inability to meet H₂S removal specifications and amine solvent carry-over to downstream units. One of the most common and difficult challenges in processing units such as amine units is dealing with the various forms of surfactant ingress into the system.

Surfactants are interfacially active molecules. They generally consist of a polar section (head) or group and a non-polar group, generally hydrocarbon chains (see Figure 1). The polar part of the molecule can interact with polar solvents like water and is therefore also called the hydrophilic portion. The non-polar part, on the other hand, can interact with non-polar materials such as hydrocarbons and is therefore called the lipophilic or hydrophobic portion.

Surfactants can be classified

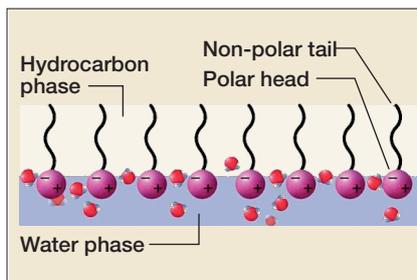


Figure 2 Example of surfactants populating a hydrocarbon/water interface

according to the charge of their polar head group:

- Anionic surfactants have a negatively charged head group
- Cationic surfactants have a positively charged head group
- Zwitterionic surfactants have a zwitterionic head group (positive and negative charge)
- Non-ionic surfactants have an uncharged polar head group.

Surfactants migrate preferentially to interfaces where they find the lowest and most energetically favourable conditions because of their two-component structure. At the water phase surface, for example, the surfactants orient themselves in such a way that the head group contacts the water and the hydrocarbon chain points to the hydrocarbon phase (see Figure 2). Thus, surfactants 'reside' in-between two phases as they can form strong interactions with both phases. The interfacial tension consequently decreases. The addition of surfactants often facilitates the mixing of non-polar and polar phases, which is used in many industries that use emulsions.

The decrease of the interfacial tension caused by surfactants becomes stronger as more surfactants are located at the hydrocarbon/water interface. Once the interface and hydrocarbon/water phases are saturated, the addition of more surfactants will not change the interfacial tension any further.

It is important to mention that solids such as iron sulphides can, under certain conditions, also act as a surfactant because the solids' surface can interact with both water and hydrocarbon phases at the same

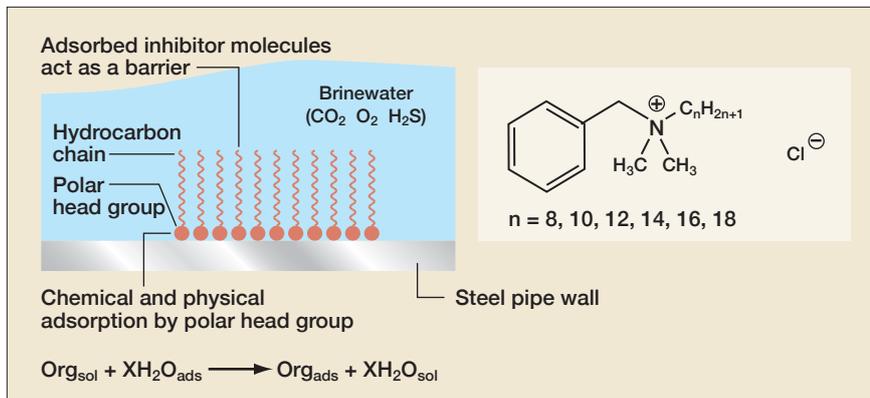


Figure 3 Left: example of the mechanism of a filming amine such as a quaternary ammonium salt (cationic corrosion inhibitor) Right: general structure of a simple filming amine corrosion inhibitor

time. For the purposes of this article, solid based surfactants (particles) will not be covered; only molecular surfactants as described previously are discussed.

Examples of some surfactants commonly found in hydrocarbon processing feed streams, such as amine units, include lubrication oils, produced water and upstream process additives. Lubrication oils from gas compressors typically contain a high percent base oil (most often petroleum fractions, called mineral oils) and about 10% additives for various functions, which often have surface active properties. Additives that deliver reduced friction and wear, increased viscosity, improved viscosity index, as well as resistance to corrosion, oxidation, ageing, and contamination in upstream processes also often have surface active properties. Upstream process additives, on the other hand, can be biocides, corrosion inhibitors, H₂S scavengers, or paraffin inhibitors to name a few. Corrosion inhibitors (filming amines or quaternary ammonium salts with alkanol segments) are an example of process additives with surfactant properties. **Figure 3** shows how a corrosion inhibitor

filming amine performs, and a possible general molecular structure. As with surfactants in general, a filming amine has a hydrophobic section (long alkyl chain called tail) and a hydrophilic section (polar ionic centre called head).

To illustrate this point, **Figure 4** shows the change in surface tension of distilled water compared to distilled water when used as a scrubbing agent for surfactants. The decrease in surface tension from 72 mN/m (millinewtons/metre) to 46 mN/m is a clear indication of surfactant presence. Similar effects are observed with some upstream process additives such as corrosion inhibitors. The decrease in surface tension leads to mechanically induced contamination (emulsions or foaming), and dissolved contaminants downstream as separation equipment loses its separation efficiency. Poor phase separation leads to multiple downstream impacts in addition to secondary effects such as solvent losses.

LPG and amine solvent emulsion formation

When a liquid hydrocarbon travels across the amine solvent inside the

amine unit contactor (treater) and liquid pockets or droplets cannot break the interfacial structure, they become encapsulated in the amine solvent aqueous liquid phase and form what is commonly referred to as emulsion. Emulsion is essentially a liquid droplet that will not merge (coalesce) with other liquid droplets because of the surrounding interface film. When a liquid treating amine unit has a solvent that experiences emulsification in the contactor (treater), it is initiated when certain contaminants are present or process perturbations occur beyond what the unit can tolerate. A decrease in surface tension will increase emulsification tendency, such as when some hydrocarbons are present. However, the emulsions are short lived and in most cases they are unnoticed. Surfactants, on the other hand, can greatly increase emulsion stability and emulsion tendency. When emulsification occurs, a number of operational changes may be observed.

Emulsification of the amine solvent can often lead to carry-over from the contactor with the treated hydrocarbon. Most amine units will have a separation vessel such as a knockout or separator drum at the contactor outlet to separate most amine solvent carry-over. Any carry-over from the amine contactor into the separator drum is often followed by a water wash stage to remove any emulsified amine solvent present in the treated liquid hydrocarbon. Amine solvent carry-over can also reach a number of downstream units such as dehydration plants, mercaptans removal plants or caustic treaters. In some cases, emulsification in the contactor is followed by foaming in a regenerator. This is also detrimental as rich amine solvents do not regenerate properly. In addition, carry-over with the acid gas can reach the sulphur recovery unit (SRU), flare systems or any other downstream process.

Antifoam or emulsion breaker addition is a common method to control the presence of foam or emulsions. However, the effectiveness of antifoams or emulsion breakers can be questionable as certain amine units use antifoam and expe-

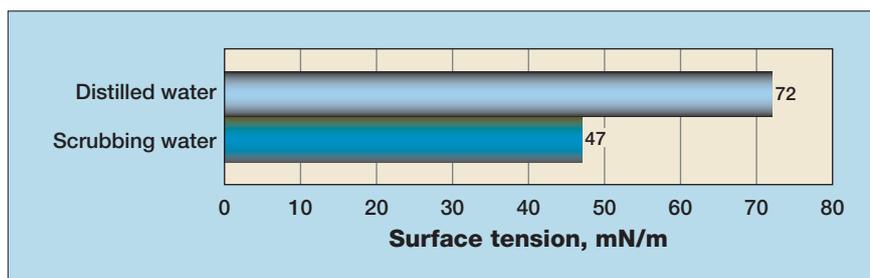


Figure 4 Surface tension of pure water in comparison with water contacted with surfactant

rience little to no effect in foam or emulsion minimisation. Some plants actually introduce antifoam or emulsion breakers to the amine unit on a daily basis, causing short-term benefits but also long-term harm to the amine solvent. In fact, antifoams or emulsion breakers should not be used on a constant basis, and root cause analysis of foaming or emulsification and elimination of the sources is often the best way to deal with a foaming emulsified amine solvent. Nevertheless, antifoams and emulsion breakers are still a valuable tool to use when sporadic upset incidents occur.

Amine solvent emulsification can have a number of root causes. Often, there is more than one root cause taking place simultaneously. Below is a list of the most prevalent causes of amine solvent emulsification:

- Ineffective inlet separation leading to contaminant bypass because of:
 - High velocity inside the amine unit contactor (mechanical shearing)
 - High concentration of suspended solids in the amine solvent (some solids can stabilise emulsions)
 - High soluble iron in the lean amine (rapid solids formation in the contactor)
 - Excess emulsion breaker injection (excess emulsion breaker use can induce emulsification or foam)
 - Incorrect emulsion breaker (some emulsion breakers will actually cause emulsification or foam)
 - Lean amine with surfactant contamination
 - Incorrect activated carbon (activated carbon exposed to phosphorous based activation)
 - Ingression of heavy phase hydrocarbons with the feed stream
 - Ingression of liquid contaminants (lubrication oils)
 - Surfactant based chemicals from upstream treating (such as corrosion inhibitors)
 - Contaminants present in the new amine solvent and or make-up water.

It is important to point out that amine solvent emulsification can be eliminated or greatly reduced in severity and/or frequency if efficient inlet separation is in place upstream of the amine contactor. In addition, it is necessary to have efficient amine



Figure 5 GASCO test units in operation for sampling feed LPG upstream of the amine unit contactor

solution filtration, effective activated carbon adsorption beds, and correct operations and maintenance.

Refinery LPG amine unit, surface rheology analysis and emulsion formation

A refinery was experiencing substantial difficulties with processing unsaturated LPG from the fluidised catalytic cracking (FCC) unit. Shortly after introducing LPG into the amine contactor, the LPG/amine solvent level was lost and amine carry-over occurred. Emulsion formation by surfactant contamination was the suspected culprit. These contaminants can originate from the lean amine feeding into the contactor or from the feed LPG into the unit. In addition, the plant had just begun operation after a turnaround. The contactor internals were modified during the turnaround to improve efficiency. This was done by:

- Replacing the existing ceramic packing with a larger diameter stainless steel Raschig ring packing to try to increase the void space in the column and reduce the perceived shear stresses on the LPG.
- Increasing the number of dispersion holes in the hold-down plate to amplify the active area on the plate.

The assumption was that with the new packing the tower would have additional open volume, improving

its operation. In both cases, the LPG-amine solvent interface was kept at the top of the contactor column, hence amine filled. After the turnaround, starting the amine contactor was practically impossible. Several changes in process conditions led to the same or similar outcomes. It was postulated that contaminants from the LPG feed were affecting the interface stability by emulsion formation.

Since the amine contactor could not be operated with stability and the H_2S levels were already very low, LPG was then bypassed around the amine unit and fed directly into the caustic treating system. Here the same phenomenon was experienced at the separator where caustic and LPG would not be properly separated. The loss of interface and emulsion formation would lead to carry-over of caustic with the treated LPG and large amounts of caustic being sent to the wastewater system.

To determine whether the quality of the LPG in terms of process contaminants was directly contributing to the amine contactor upsets, two Nexo Solutions GASCO liquid testing units were used to sample the feed LPG (see **Figure 5**). Water injection was used at the outlet of the second unit to scrub the LPG of any water soluble components. The first unit was used to remove any emul-

Surface tension analysis results	
Sample description	Equilibrium surface tension at 22°C (mN/m)
Injected scrubbing water	71.54
Hexanes (after contacting with scrubbing water)	19.02
Lean amine solution	44.78
Reagent grade DEA 30% in water (reference)	62.44
Distilled water (reference)	72.49
n-Hexane (reference)	18.38
Note: Hexanes is a mixture of hexane isomers, and n-hexane is a normal hexane (single isomer of linear structure)	

Table 1

sified and free water. The test was designed to determine two main aspects:

- 1) Free water carry-over from the upstream separator into the amine unit contactor.
- 2) Extract any water soluble contaminants by scrubbing of the feed LPG upstream of the amine unit contactor.

The first GASCO test unit showed that no free or emulsified liquids were present in the LPG feed. Attention then turned to the LPG scrubbing water samples. Samples of scrubbing water were extensively tested and analysed for the presence of surfactant. Pendant drop interfacial tension analysis was performed on four samples in order to understand the surface energetics in each sample. In general, surfactants in a solution will lower the surface tension while salts will increase surface tension. In addition, samples of the scrubbing water were contacted with hexanes to back-extract the contaminants. Further emulsification tests with distilled water and lean amine were conducted. The samples tested for interfacial tension were:

- Water (injected water used for con-

taminant scrubbing of the feed LPG)

- Hexanes (contacted with injected water)
- Lean amine solution
- Reagent grade DEA (30%) in water.

The results for the interfacial tension analyses are presented in **Table 1**. The surface tension of pure water and n-hexane are also shown for reference. In addition to interfacial tension analysis, a more comprehensive rheology study was performed on each sample.

Table 1 shows that the injection water tested has a surface tension only slightly lower than for distilled water. This suggests that the injection water has some amount of surfactant in it that slightly lowers the surface tension. Surface tension alone however does not provide enough information, and rheology is necessary to better understand the changes in water properties. Salts and other contaminants can elevate surface tension, masking any surfactant presence.

The hexanes contacted with injection water had a surface tension slightly higher than for pure hexanes. This suggests that the hexanes

Elemental analysis results for injected scrubbing water (after filtration by 0.45 micron PVDF membrane)

Element	Concentration, mg/l
Carbon	188
Oxygen	8.40
Hydrogen	64.2
Nitrogen	117
Sulphur	1930

Table 2

transferred some components, likely salts or ionic components, from the injection water that would raise the surface tension. The lean amine solution had a significantly lower surface tension than pure DEA in water, which suggests that some amount of surfactants is present in the lean amine that drastically affects surface energetics. In addition, the scrubbing water contacted with hexanes caused severe emulsion formation (see **Figure 6**). The scrubbing water treated with a demulsifier did break the emulsion somewhat. Treating the scrubbing water with activated carbon prior to contacting with hexanes, however, provided no emulsion resolution. The data suggested that the LPG did in fact have surfactant contamination.

The contaminants were extracted from the scrubbing water and analysed using elemental analysis and Fourier transform infrared spectroscopy (FT-IR). Both analyses showed consistency with nitrogen based quaternary ammonium salts scrubbed from the feed LPG into the amine unit. **Table 2** shows the elemental analysis performed on the scrubbing water itself. **Figure 7** and **Table 3** show the inferred spectroscopy spectrum and signal interpretations.

An elemental analysis of the injected scrubbing water for carbon, hydrogen, oxygen, nitrogen and sulphur was performed in order to understand the composition of contaminants extracted during the water injection. **Table 2** shows the results of the elemental analysis results.

An FT-IR analysis of the extracted material from LPG injected scrubbing was performed using an ATR equipped FT-IR spectrophotometer. The spectrum and signals were consistent with nitrogen based components and hydrocarbon residues.

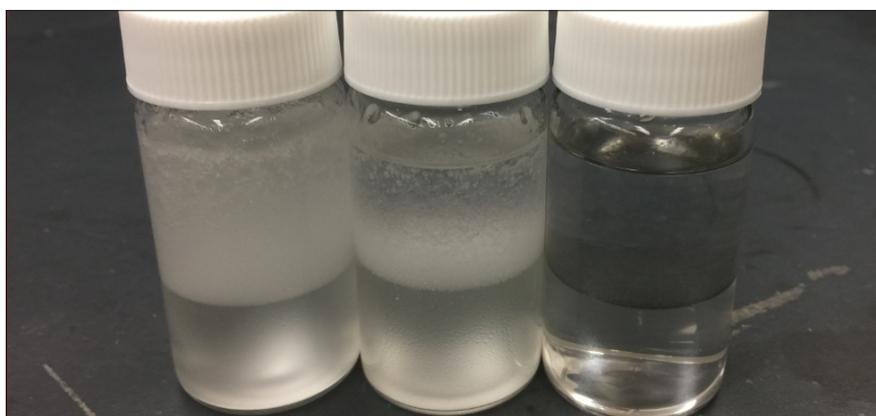


Figure 6 Scrubbing water contacted with a) hexanes (left) b) hexanes and 10 ppmv of demulsifier (centre) and c) hexanes and treating the scrubbing water with activated carbon (right)

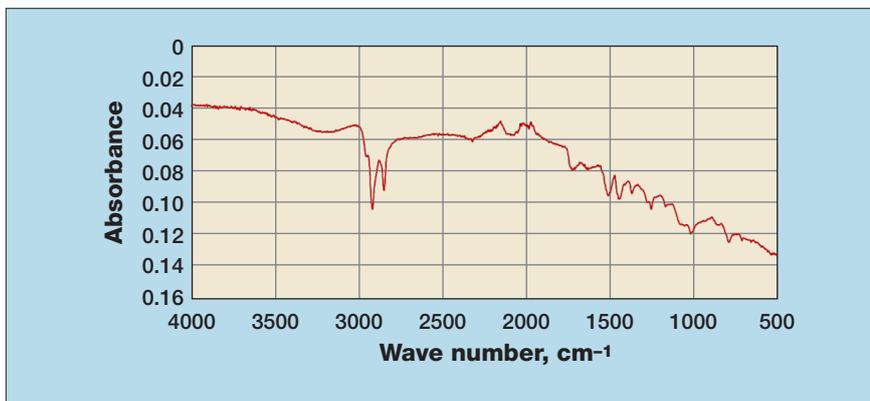


Figure 7 FT-IR spectrum of extracted material from the LPG injected scrubbing water

FT-IR spectrum peaks from extracted material of the LPG injected scrubbing water		
Frequency, cm ⁻¹	Vibrational motion	Suggested functionality
3500-3000	N-H, O-H stretch	Alcohol, amines
3000-2800	C-H stretch	Alkane from hydrocarbon chains
1715	C=O stretch	Carbonyls (ester or carboxylate)
1635	N-H stretch	Amines
1515	CH ₂ bend	Alkane from hydrocarbon chains

Table 3

Figure 7 shows spectral results and Table 3 shows the FT-IR signal interpretations. Comparative analysis showed consistency with quaternary ammonium salts with possible ester functionalities. The spectrum resembled closely generic quaternary ammonium based corrosion inhibitors used as process additives.

Conclusion and mitigation strategies

Emulsion formation (and to some extent foaming) caused by surfactants is perhaps one of the most complex problems facing amine units treating LPG in terms of process upsets. Surfactants can be present in the feed LPG in the water phase and/or the hydrocarbon phase. Often, these surfactants are associated with process additives used in units upstream such as filming amines. Removal of surfactants at source is the best strategy for its elimination. Once the surfactant is present in the amine solvent, there are limited avenues for its removal. In some cases, emulsion breakers are not effective in eliminating or reducing the emulsion. In addition, activated carbon can be ineffective in removing upstream process chemicals such as corrosion inhibitors that are also surfactants.

Water wash can be an effective

strategy to remove surfactants from the feed LPG. So can certain activated carbons to treat the LPG feed. Amine emulsion and foaming invariably will cause amine losses and, in plants not using proper emulsion breakers or antifoams, LPG feed rates (and by implication feed gas) might need to be reduced for controlling emulsion formation, amine carry-over and foam formation. Inlet testing using a slipstream and water scrubbing is one of the most effective ways to determine if surfactant contaminants are present in the feed. Emulsion and foaming tests are also instrumental in determining the effect of surfactants in emulsion and foam tendency and stability.

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