THE COMPARISON OF TECHNOLOGY DEVELOPED BY ADVANCED WETTING TECHNOLOGIES PTY LTD WITH SURFACTANTS FROM OTHER LARGE MANUFACTURERS

A Report on AWT Technology

Introduction

Advanced Wetting Technologies Pty Ltd (AWT) has developed a new class of surfactants which physically behave differently to existing surfactant technology, resulting in dramatic improvements in the performance and cost of this critical sector of the global chemical market. The AWT innovation applies to all current applications of surfactants and is non-toxic. This is particularly relevant given the current focus on the environmental impact of fluoro and other toxic surfactants.

AWT has proven that surface tension alone is not a good wetting performance measure or predictor of a surfactant's performance when added to an aqueous solution. Surfactant performance is currently measured on the basis of its ability to reduce surface tension at time zero, and therefore does not take into account the time impact of the actual contact between the surface and the wetting liquid. Once contact occurs, the surface tension of the wetting liquid increases, therefore the interfacial energy increases and wetting slows down. This is described by a decaying exponential function. AWT has developed an effective mechanism to identify and address this increasing surface tension as measured by the reduced rate of reduction of the contact angle beyond the moment of liquid contact. In many AWT formulations there is little if any change in the surface tension of the wetting liquid after surface contact, resulting in a linear reduction in contact angle. This has significant implications for every sector of the enormous global chemical industry which relies upon surfactant processes.

The following report demonstrates this phenomenon, as well as the impact of AWT technology in transforming surfactant performance.

Subsequent wind tunnel testing of droplet distribution has also confirmed that unlike amphiphilic surfactants, AWT multiphase technology is not limited by the Marangoni Effect. This means that there is no surface tension difference between the edge of the drop and body of the drop which is the case with amphiphilic surfactants which results in the formation of fine droplets at the edge of the droplet due to lower surface tension causing spray drift. This is not the case with AWT technology.

Methodology

AWT has verified its technology performance by comparing its products to all classes of surfactants including non-ionic, cationic, anioic, Zwitterionic, and super-surfactants. AWT has also conducted this analysis against the Dow product Tergitol TMN-6, as well three BASF non-ionic surfactants as well as a standard non-ionic formulation from Huntsman. It is confirmed that AWT formulations out-performed all of these products.

A total of 91 formulations were tested at three different concentrations: 0.5%, 0.1% and 0.05%, with at least three replicates. This produced 1960 observations including graphs of contact angles over time periods of 0.5 seconds, 1 second, 1.5 seconds and 1 minute. Surface tension measurements of the formulations were obtained using pendant drop goniometry. The curves of both their pendant droplet and wetting droplet were measured by Laplace computation and images were produced for the curves for 88,000 wetting measurements and approximately 5,000 images measuring surface tension. All contact angle measurements were made on a hydrophobic Parafilm surface placed on a glass microscope slide. This technique was actually based upon one described to AWT by Dow. The variability of the surfaces was measured and estimates of the standard error and least significant differences were made along and across the roll of Parafilm. This required 20 separate pieces of Parafilm on separate slides using ultra-pure water, high surface tension water containing Teric N9 a non-ionic nonylphenol ethoxylate of nine moles of ethylene oxide per mole of phenol with a surface tension of about 32mN/m at a concentration of 0.5% in water, one of AWT mid-range formulations Evowet SS20 with a surface tension of about 24mN/m at a concentration of 0.5% water and pure water surface tension 72.86 mN/m. There were two replicates measuring variability in wettability across the roll of Parafilm and 20 different samples of Parafilm measuring variability and wettability along the roll of Parafilm. All measurements of contact angle were measured on the left and right hand sides of the droplet as well as the mean result. See *Figure 1* below. All experimentation was carried out on a KSV Goniometer placed on a 2 tonne slab of polished granite within a climate controlled room set at 20°C and 50% relative humidity at the Department of Applied Mathematics within the Research School of Physics at the Australian National University.

All comparisons within this report are at 0.5% concentration unless otherwise stated.

Subsequent to the data in this report there has been a significant amount of work carried out with agricultural formulations combined with AWT, existing commercial and developmental surfactants over short and longer time scales at concentrations down to 0.025%. At this level the true value of AWT technology is clearly demonstrated, i.e. the dose effect.

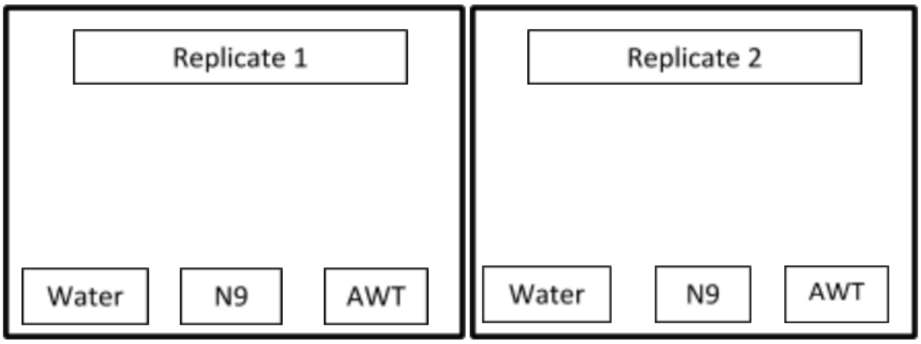


Figure 1: showing the layout of samples of different surfactants to determine the variability of the model surfaces. There were 20 such microscope slides with Parafilm with the above combination.

The system was calibrated with ultra-pure water (*see Figure 2*).

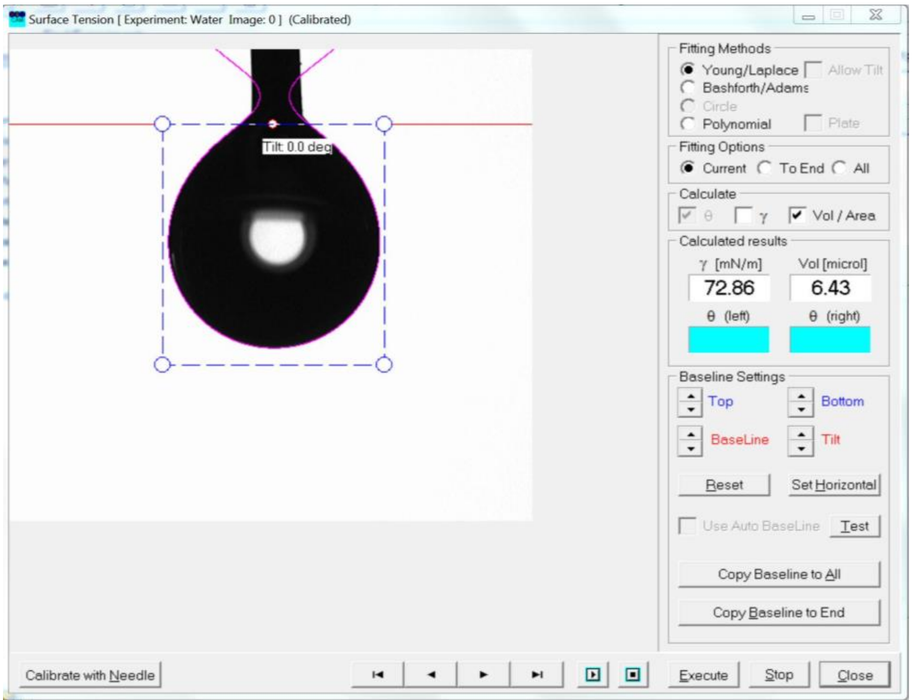


Figure 2: Surface tension of ultra-pure water

A typical contact angle measurement is seen in *Figure 3*. This was an example of a very fast system Rezex A2 after 1.92 seconds.

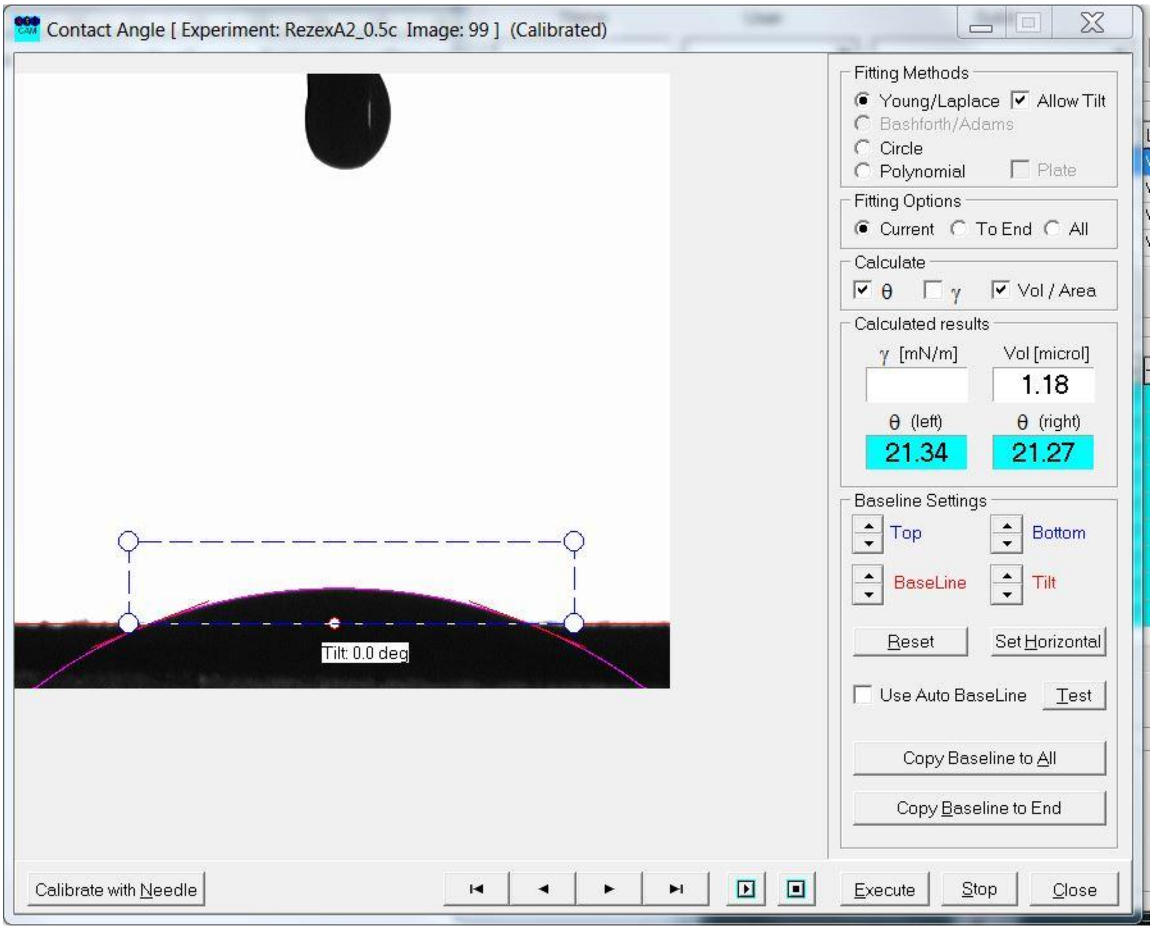


Figure 3: Contact angle measurement of a rapidly spreading AWT formulation Rezex A2.

Summary

Results

The results confirm that the currently published surface tension of amphiphilic surfactants in in aqueous solutions is only valid at the instant of contact with the wetting surface. Thereafter the surface tension rises thereby increasing the interfacial energy between the surface and the wetting liquid, resulting in a slowdown in the wetting process. This is due to the fact that these surfactants create micelles at very low solubility levels which have to break down to create a metastable equilibrium of surfactant molecules at the three phase interface for the wetting liquid to spread. Due to the equilibrium concentration of surfactant molecules in solution depleting as wetting progresses beyond the rate at which the micelles break down, there is an overall reduction in surfactant molecule equilibrium concentration at the three phase interface thus slowing wetting down. This is commonly known as the “stick/slip effect”. This is demonstrated by a reduction in contact angle graphically described by a decaying exponential function. It would in fact take an indefinite time for most surfactants to achieve a zero contact angle even assuming there is sufficient volume of water over an infinitely large surface.

AWT innovation increases the equilibrium concentration of the surfactant molecules such that they are in a stable and not a metastable state, i.e. micelle formation is inhibited. This results in the reduction in contact angle being close to linear during wetting. Therefore it can be predicted the time at which the contact angle approaches zero. Significantly, this enables a dose effect which facilitates far greater control over application usage and expense. This critical benefit has been proven in large scale agricultural spraying trials in which dosages had to be reduced to enable time for the herbicide to penetrate leaf stomata. This dose effect is believed to be unique to AWT technology.

Applications

In addition to the agricultural trialling mentioned above, the results of which have far exceeded expectations in that dose rates are less than 50% of existing adjuvants, AWT has been working with the largest Australian domestic paint manufacturer Dulux to address the critical application variables of drying and spreading. Again, the results have been extremely positive with Dulux, a subsidiary of a global chemical manufacturer, has committed to replace their previously used toxic fluoro surfactants with AWT technology.

Also, very significantly, AWT has been providing a formulation to a domestic firefighting foam producer which had previously only utilised fluoro surfactants to achieve the requisite spreading. While the AWT formulation provided did not quite achieve a surface tension result as low as the fluoros, it did meet the UK mil specification, UK DEF STAN 42-40/2, and was far superior in terms of foam expansion ratio and drainage rate. Most importantly, AWT technology is non-toxic, and given the current pressure to eliminate the usage of these 'forever chemicals', AWT is now working with this foam manufacturer in selling Class B firefighting foams within Australia. AWT has subsequently tested six formulations with a Class B foam and the results have been very positive in fire suppression. These formulations will be tested to the above UK standard. AWT is currently partnering with this company in submitting a number of tenders to defence departments of various national governments to provide fluoro free Class B firefighting foams. This includes testing at the Research Institutes of Sweden (RISE) where if successful such foams will be used the Swedavia the company that owns the ten largest airports in Sweden. AWT continues to undertake work on the surface tension of firefighting foams over various time scales and also agricultural applications at concentrations down to 0.025% which is one fifth the dose rates of commercial adjuvants.

Intellectual Property

AWT technology is currently covered by granted patents in the EU, USA, Canada, Australia and New Zealand as well as by PCT applications that were submitted in May 2018. These applications entered the National Phase examination process in November 2020. A further two PCT applications for non-aqueous systems were submitted in November 2019 and are due for publication in 2021.

Strategic Considerations

While AWT continues to develop further refinements to its technology and work with various partners mentioned in the applications above, the intention is to dispose of the business in its entirety, most likely to a global chemical producer which can fully optimise the enormous potential of the innovation. This potential can be seen in the granted and published patents.

Results

A: Dow Chemical Tergitol TMN6

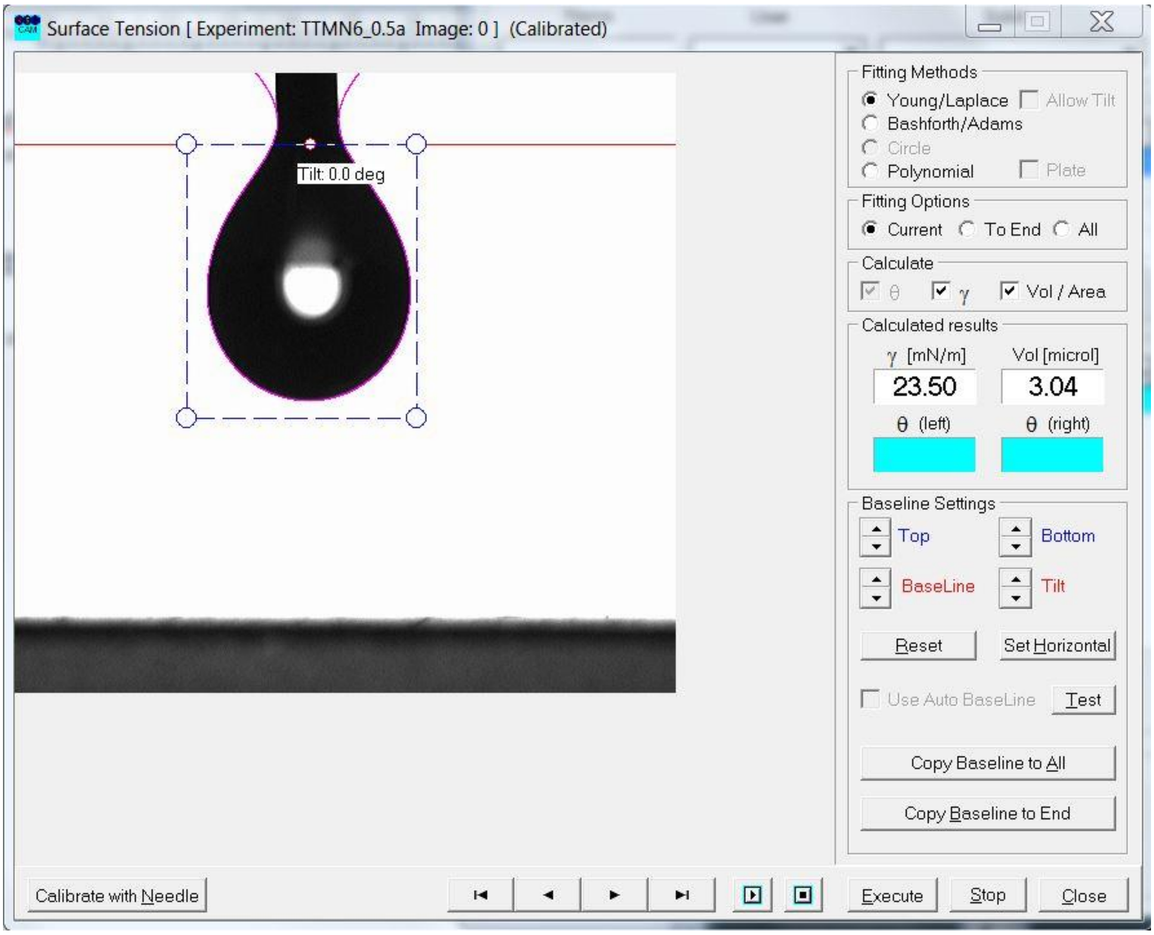


Figure 4: Surface tension of Tergitol TMN6.

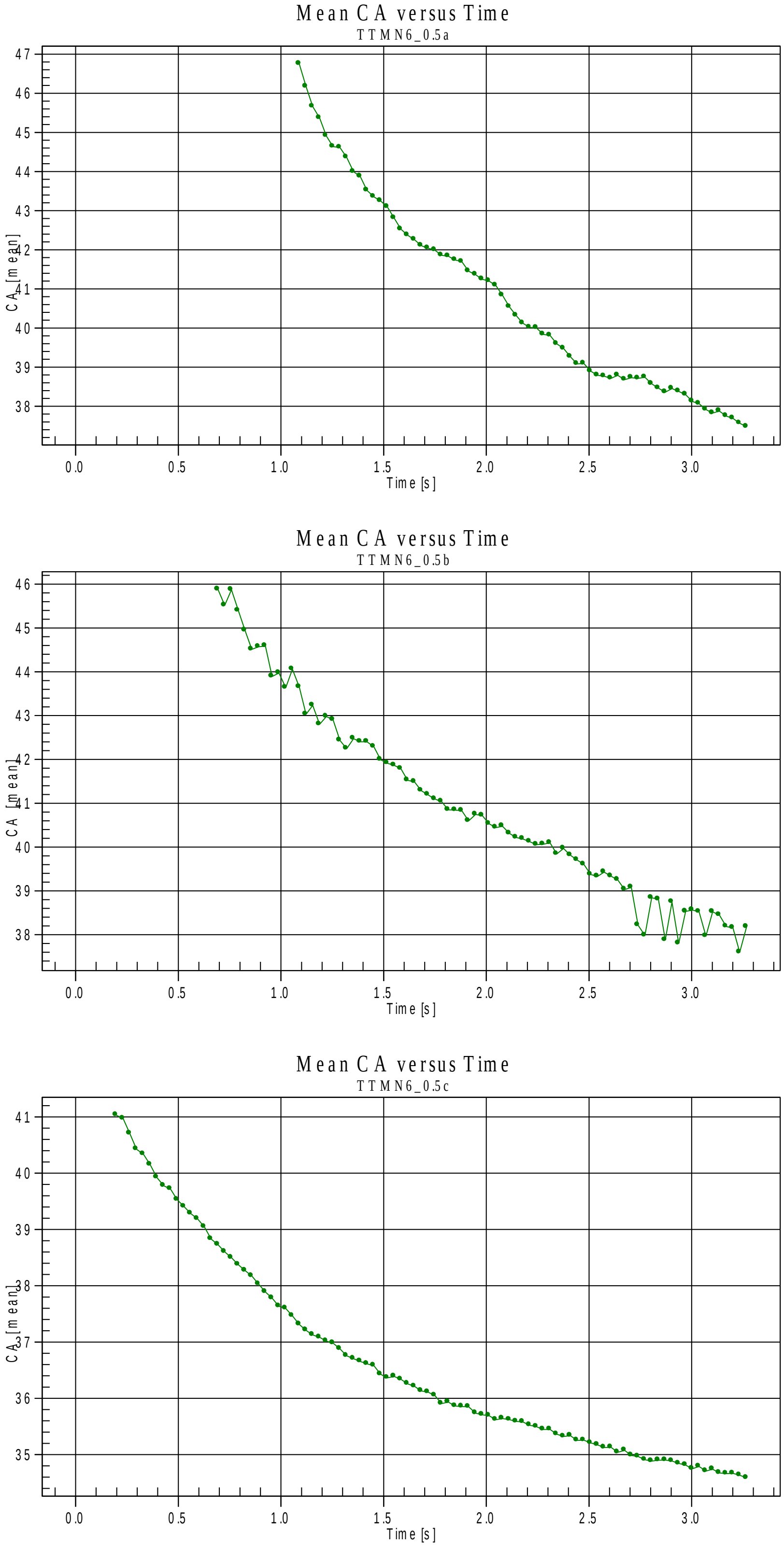


Figure 5: Graphs showing exponential decay of contact angle. After one minute the contact angle was 32.87° i.e. wetting slowed down considerably.

B: BASF Lutensol XL70

This product is a non-ionic alcohol ethoxylate used for Dishwashing, laundry, hard surface cleaning, food and beverage processing, food service and kitchen hygiene, commercial laundry and institutional cleaning.

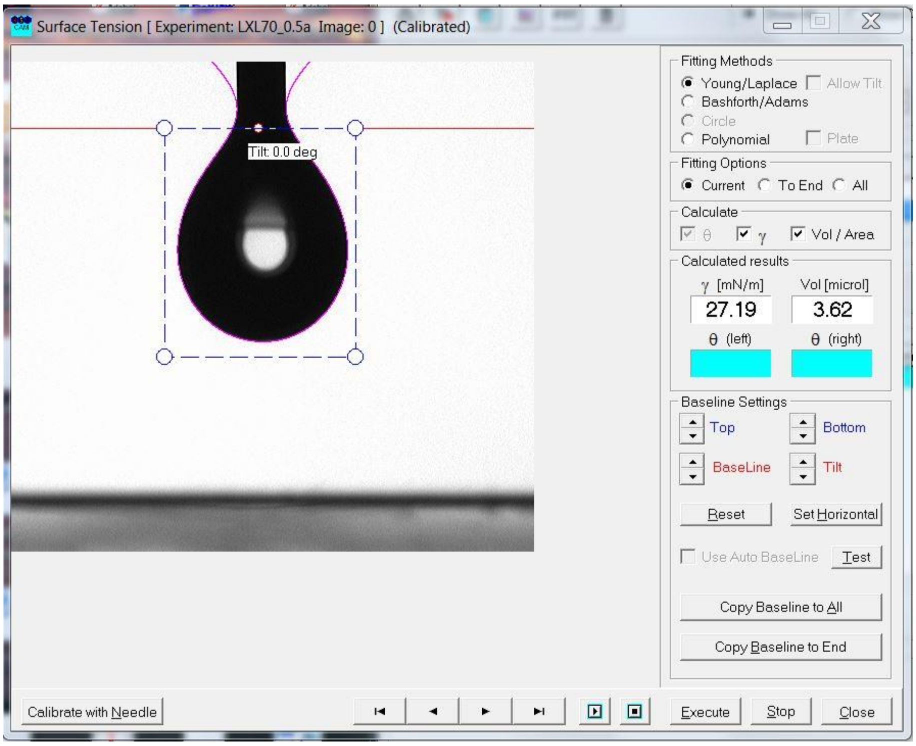


Figure 6: Surface tension of Lutensol XL70 @ 0.5% in ultra-pure water. Note good fit of curve giving a very good estimation of surface tension of this formulation. This was done many times and the range was 27.198 – 27.28 mM/m.

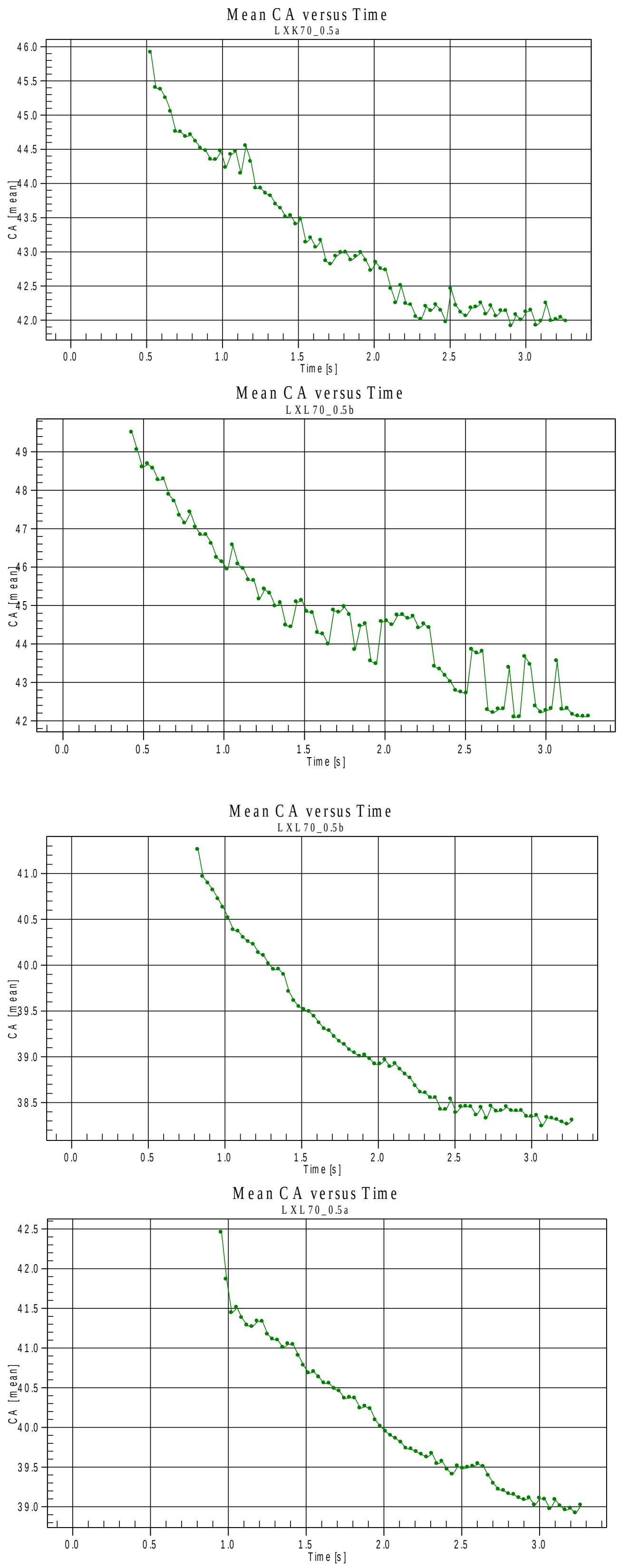


Figure 7: Graph of contact angle over time of Lutensol XL70, note the reduction of the rate of wetting i.e. contact angle does not change. The initial points of contact have been removed due to the hysteresis effect of the droplet on contact with the hydrophobic surface of the parafilm enabling a clearer picture of the rate of wetting. The rate of slowing of wetting can be described as a degrading

exponential function. After one minute the contact angle was 34.73°. As a result contact angle will ***never*** *achieve zero*

C: BASF Lutensol XP80

This product is a non-ionic alcohol ethoxylate used for Dishwashing, laundry, hard surface cleaning, food and beverage processing, food service and kitchen hygiene, commercial laundry and institutional cleaning.

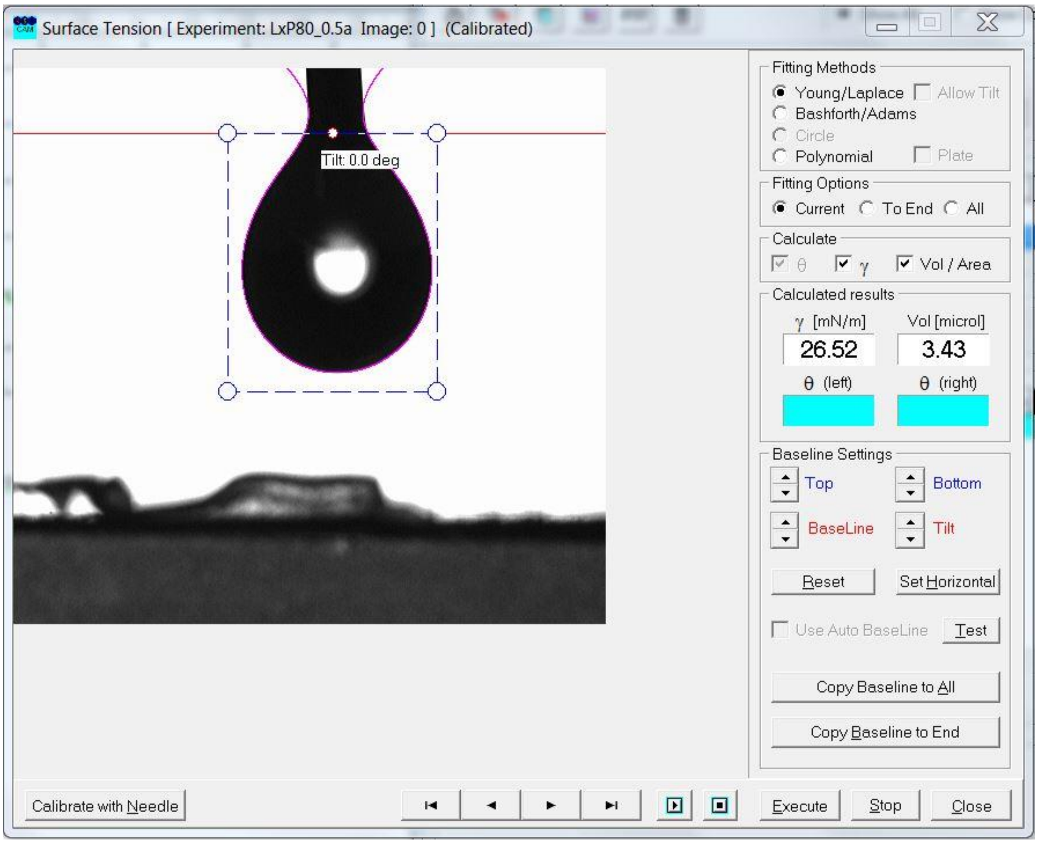
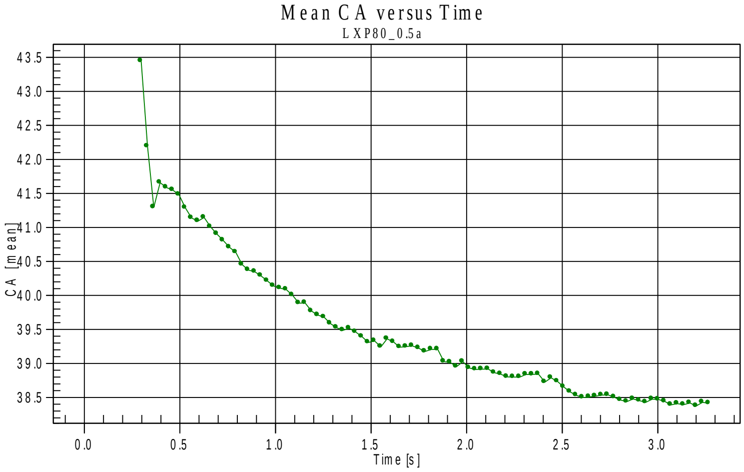
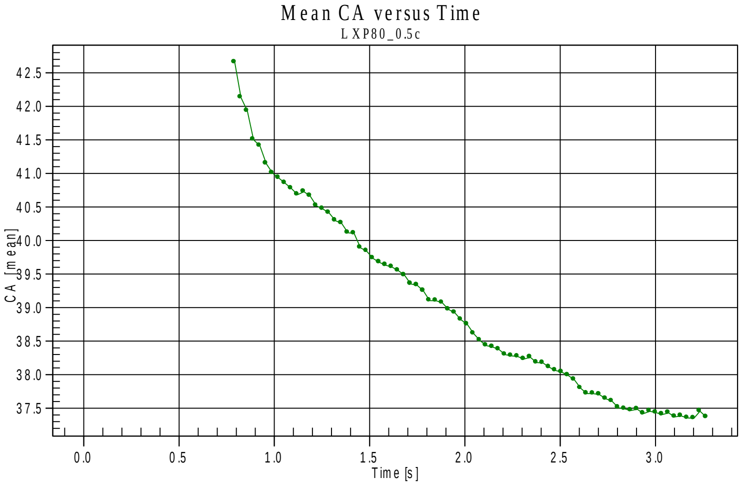
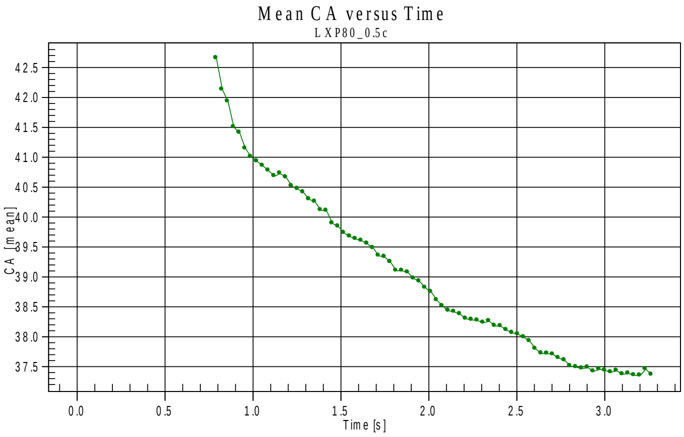


Figure 8: Surface tension of Lutensol XP80.


Mean CA versus Time
LXP80_0.5a
CA [mean]
Time [s]


Mean CA versus Time
LXP80_0.5c
CA [mean]
Time [s]


Mean CA versus Time
LXP80_0.5c
CA [mean]
Time [s]

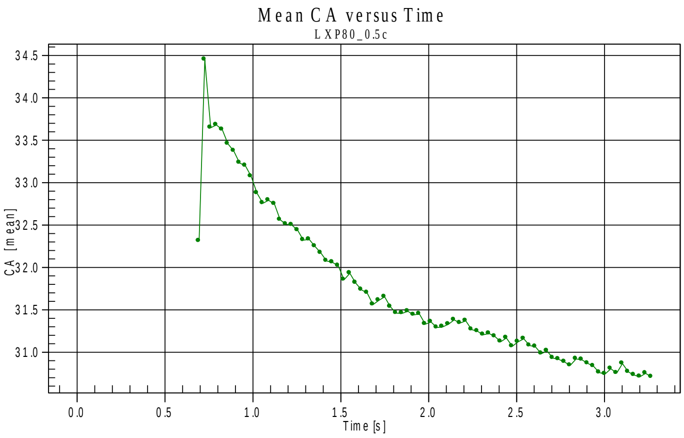

Mean CA versus Time
LXP80_0.5c
CA [mean]
Time [s]

Figure 9 (page 12): Graphs showing wetting of Lutensol XP80 note the flattening of the curve i.e. slower wetting and the extremely unlikely event that it will ever achieve a contact angle of 0°. Poor spreading and typical non-ionic amphiphilic surfactant behaviour i.e. decaying exponential curve demonstrating the limiting phenomena of micelle formation and breakdown to maintain surfactant molecular equilibrium just behind the three phase interface. Reduction in contact angle is only 5° and further spreading has stopped. After one minute the contact angle was 27.69°.

D: Plurafac LF120

Plurafac LF100 is a low foaming non-ionic surfactant.

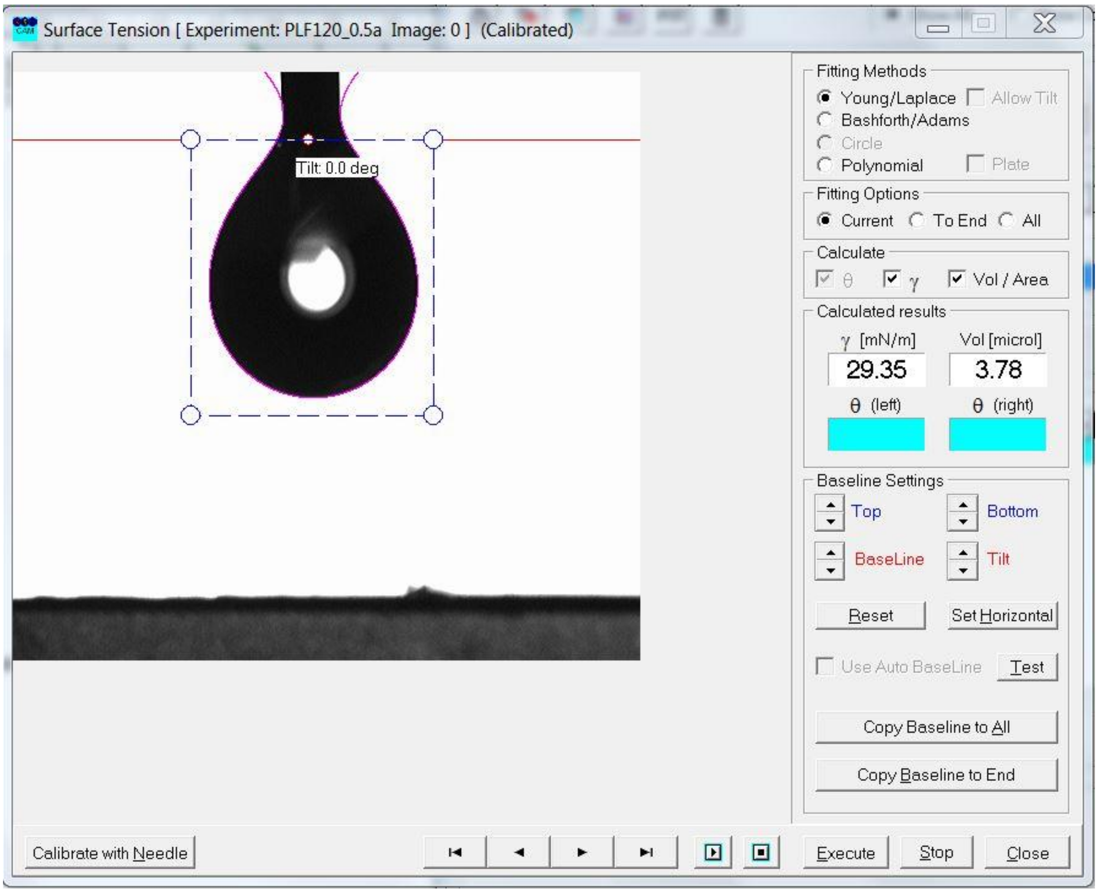
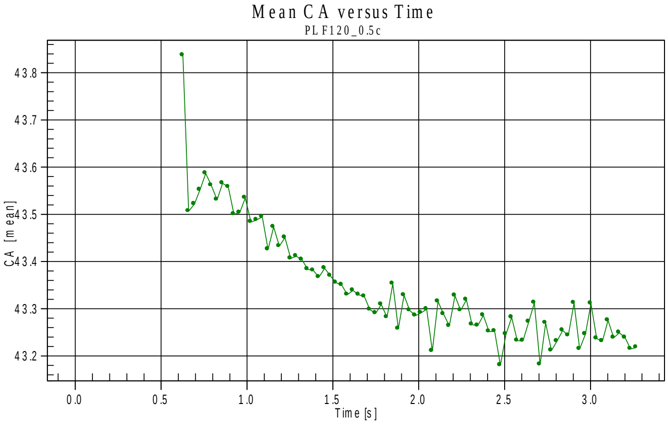
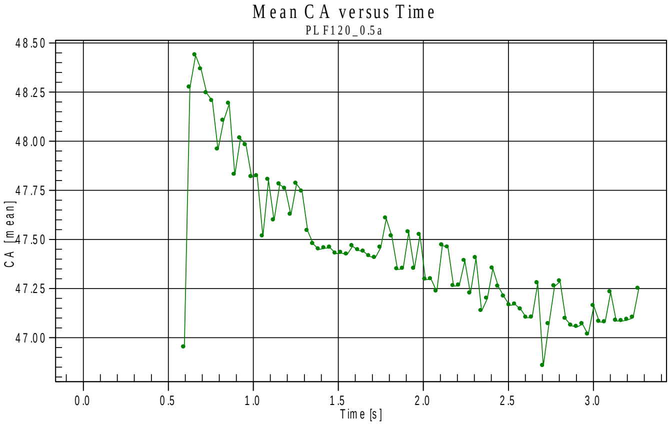
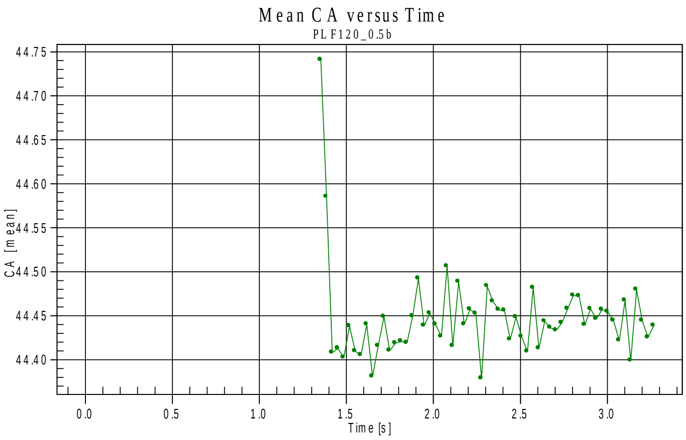


Figure 10: Surface tension of Plurafac LF120


Mean CA versus Time
PLF120_0.5c
CA [mean]
43.8
43.7
43.6
43.5
43.4
43.3
43.2
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Time [s]


Mean CA versus Time
PLF120_0.5a
CA [mean]
48.50
48.25
48.00
47.75
47.50
47.25
47.00
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Time [s]


Mean CA versus Time
PLF120_0.5b
CA [mean]
44.75
44.70
44.65
44.60
44.55
44.50
44.45
44.40
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Time [s]

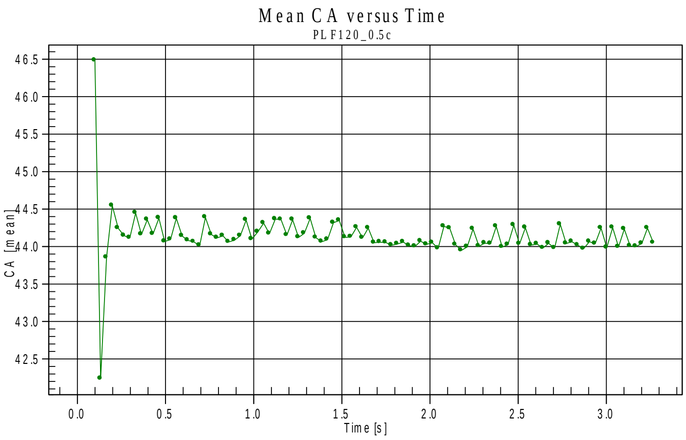

Mean CA versus Time
PLF120_0.5c
CA [mean]
46.5
46.0
45.5
45.0
44.5
44.0
43.5
43.0
42.5
0.0
0.5
1.0
1.5
2.0
2.5
3.0
Time [s]

Figure 12 (page 14): Graphs showing 4 examples of wetting of Plurafac LF120. All show that wetting performance is poor and there is no chance that a contact angle of 0° will ever be achieved and in fact there is very little reduction in contact angle. After one minute the contact angle was 42.39°.

E: Plurafac LF120 & AWT formulation

This is an example of where the addition of an AWT formulation makes this BASF surfactant far more effective.

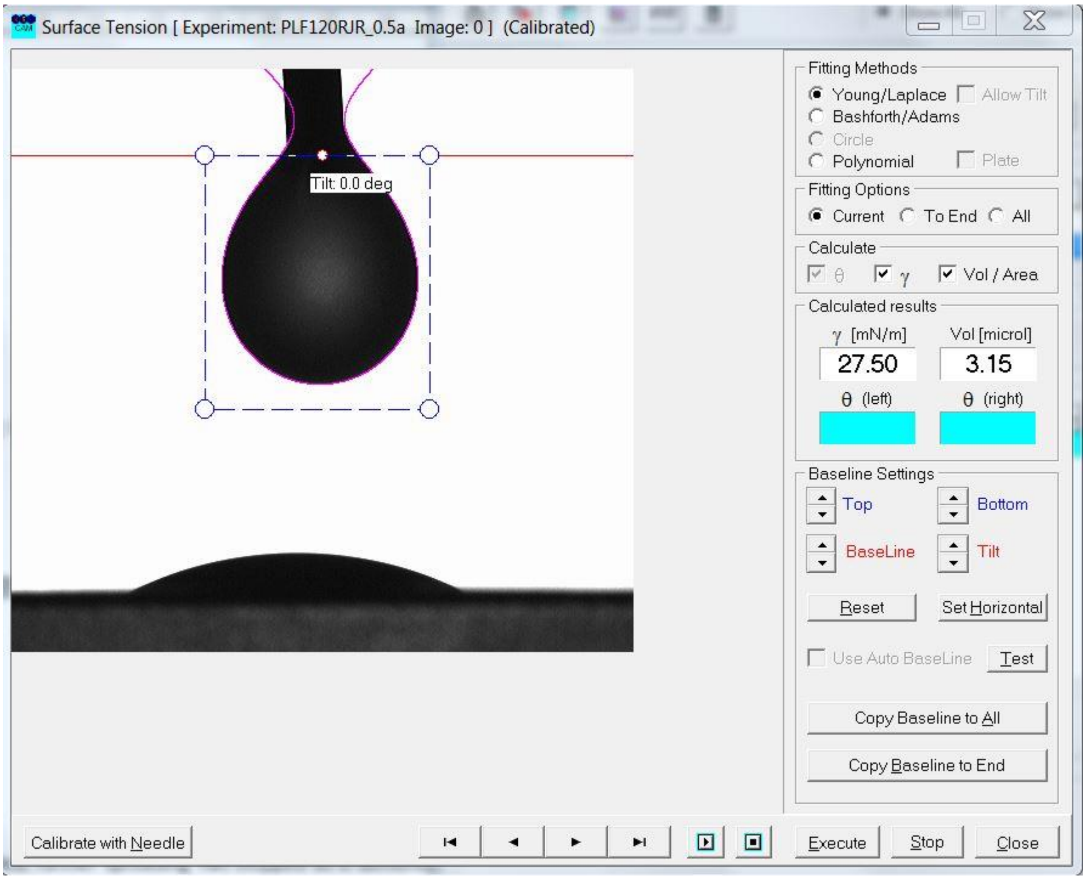


Figure 13: Surface tension of a combination of Plurafac LF120 & a AWT formulation below Plurafac LF120 itself.

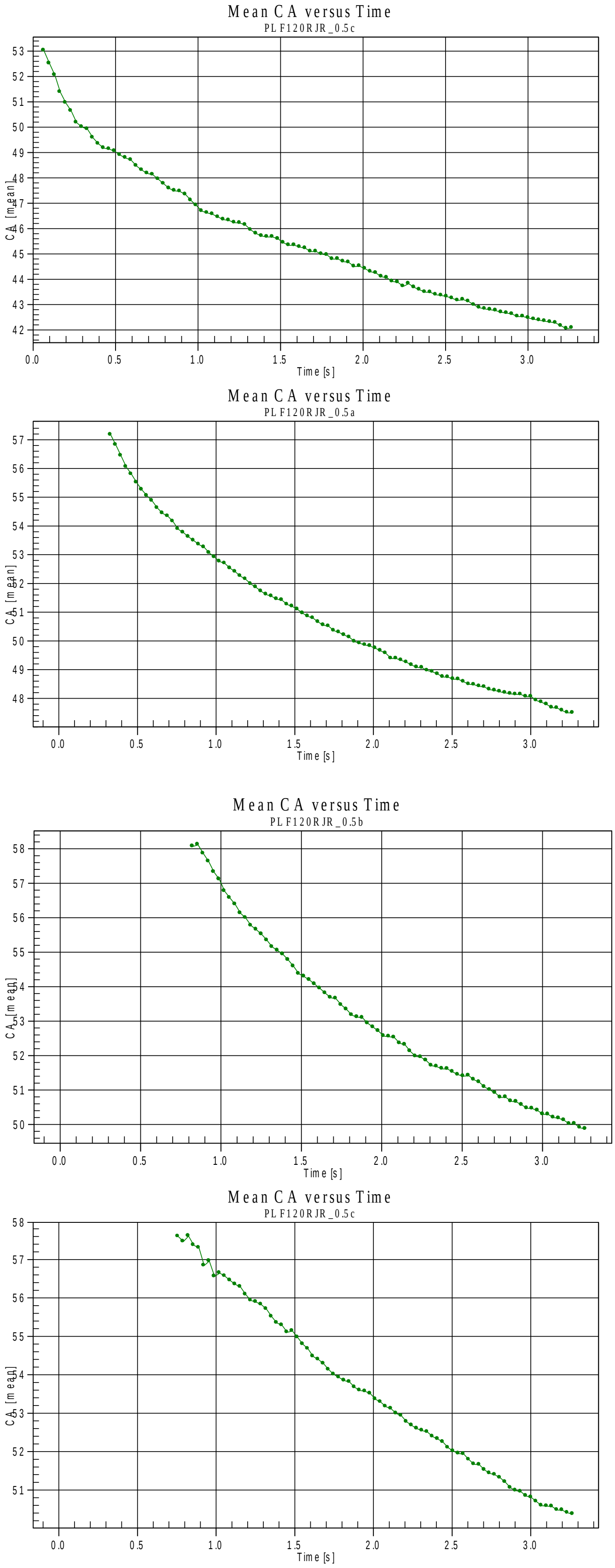


Figure 14: Graphs showing four examples of wetting of a Plurafac LF120 & a AWT formulation. All show that wetting performance is good and there is a high probability that a contact angle of 0° will be achieved. Plurafac LF120 and the AWT alcohol combination at 0.5%. Note the reduction in contact

angle of about 10°. Note the contact angle is continuing to reduce. After one minute the contact angle was 30.59°.

F: Huntsman Teric BL8

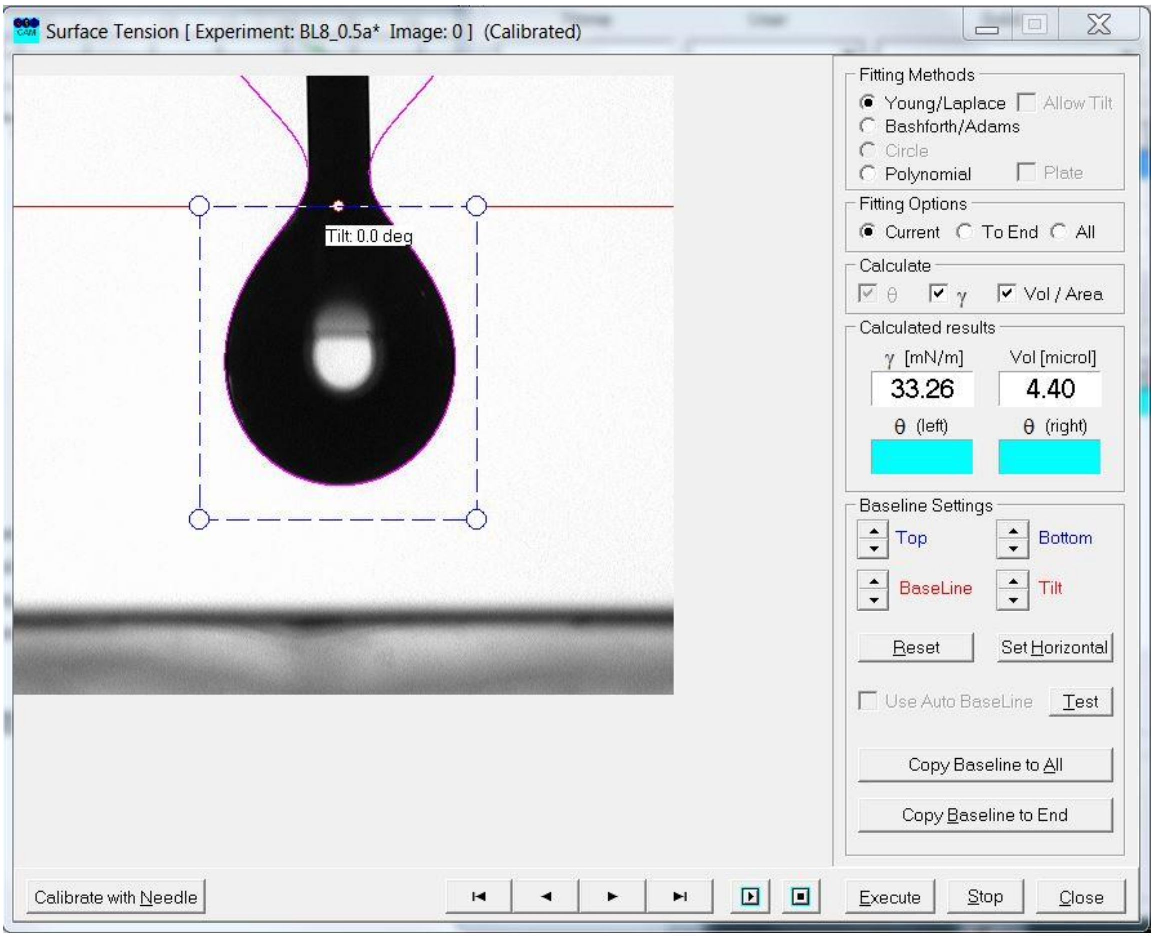
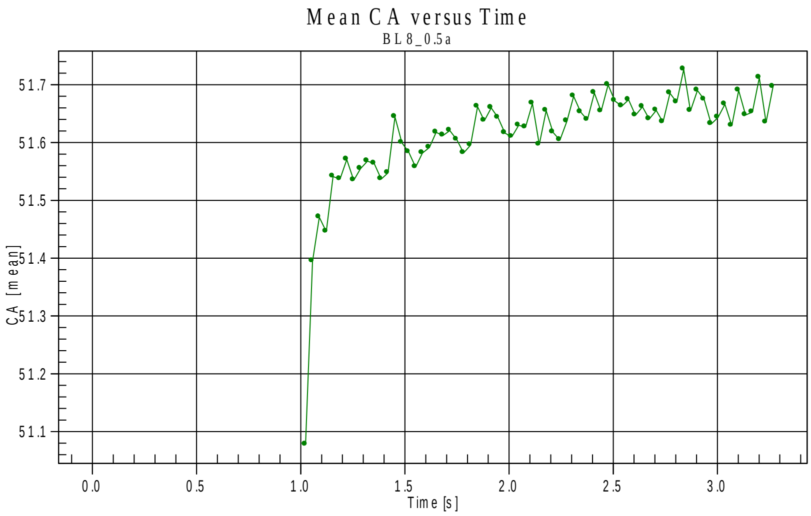


Figure 15: Surface tension of Huntsman Teric BL8.



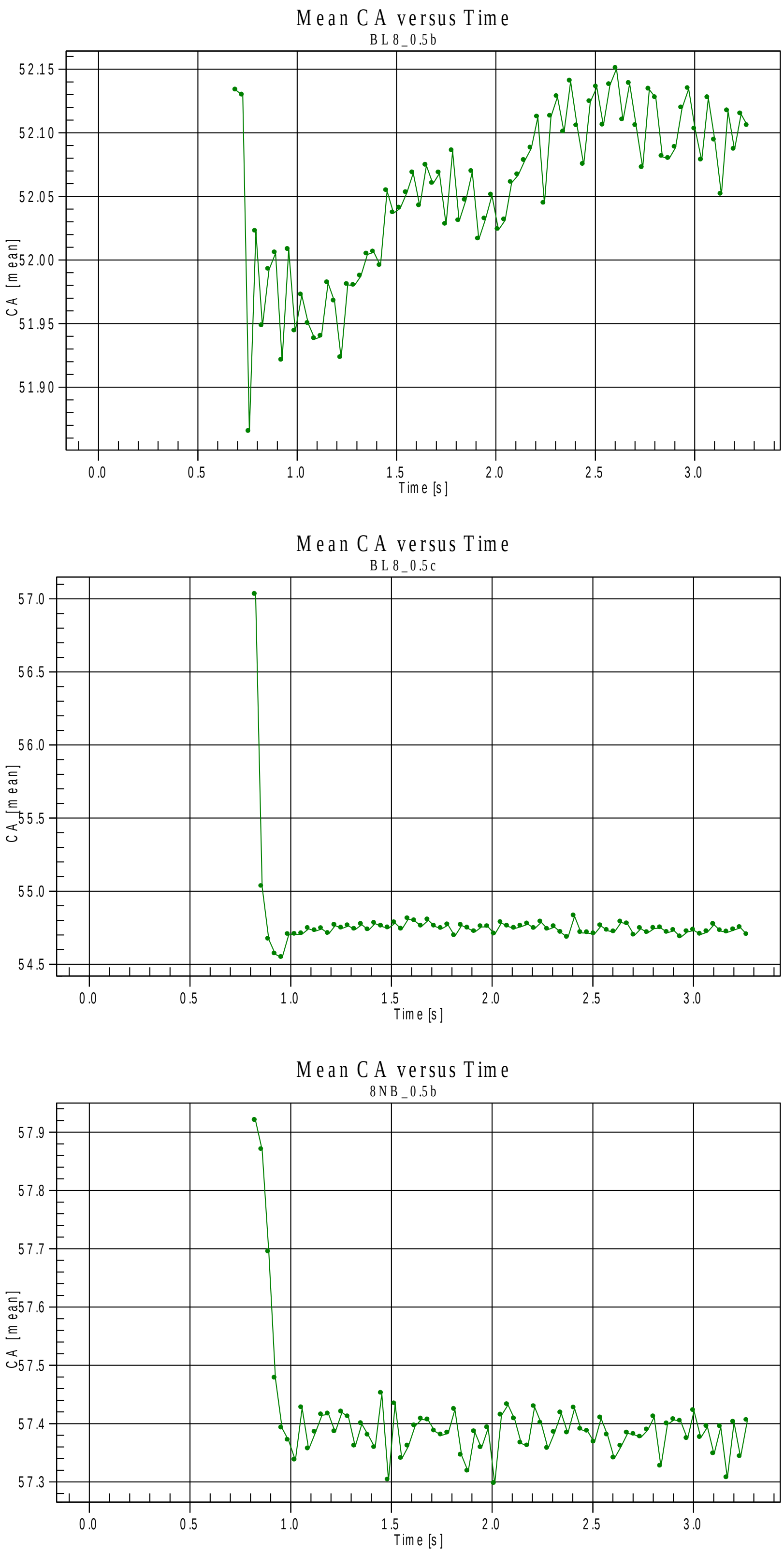


Figure 16 (above and p.18): Graphs showing the change of contact angle for BL8, note little change from droplet contact.

G: Combination of BL8 with AWT formulation

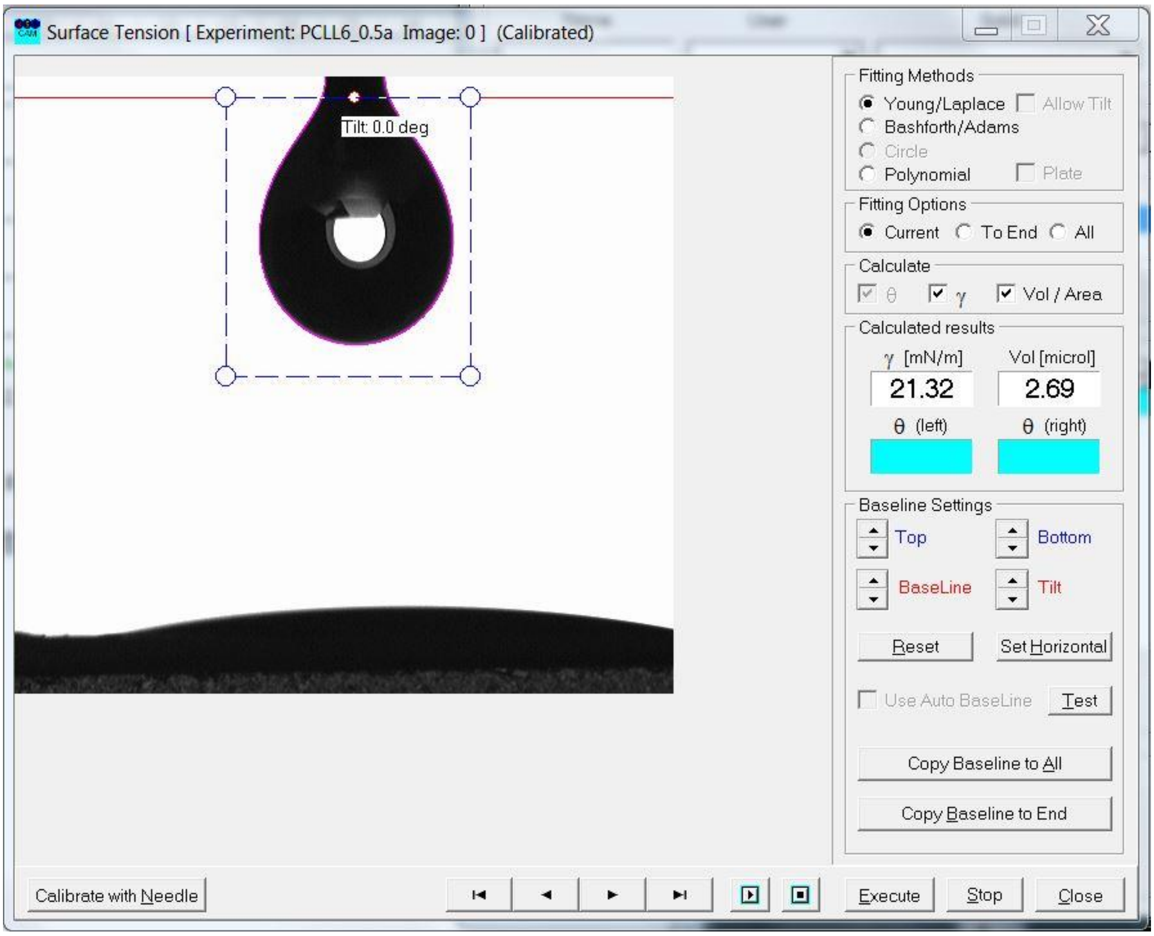
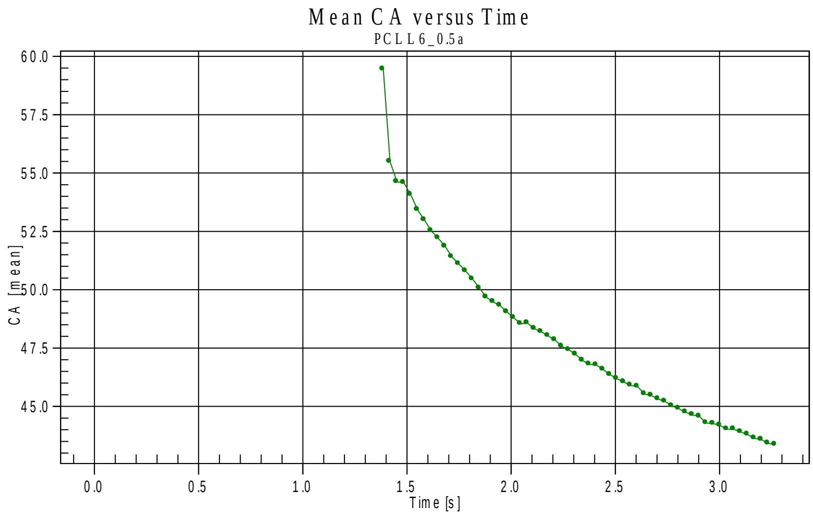
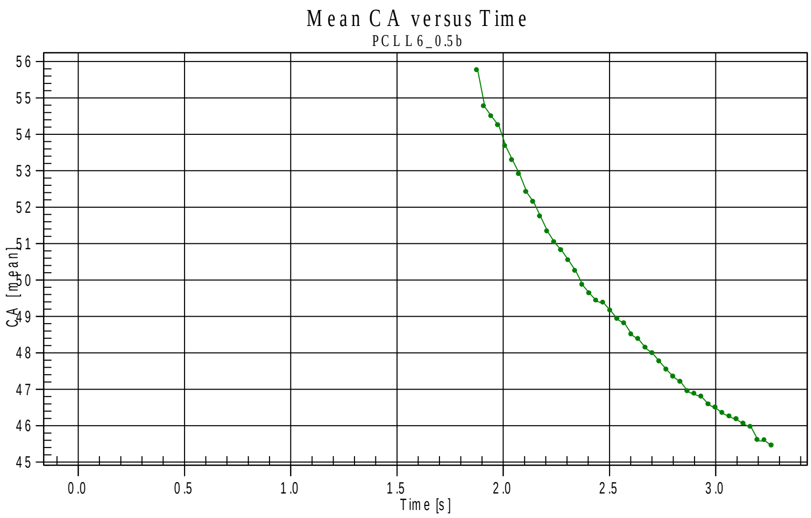


Figure 17: Combination of BL8 and an AWT formulation.





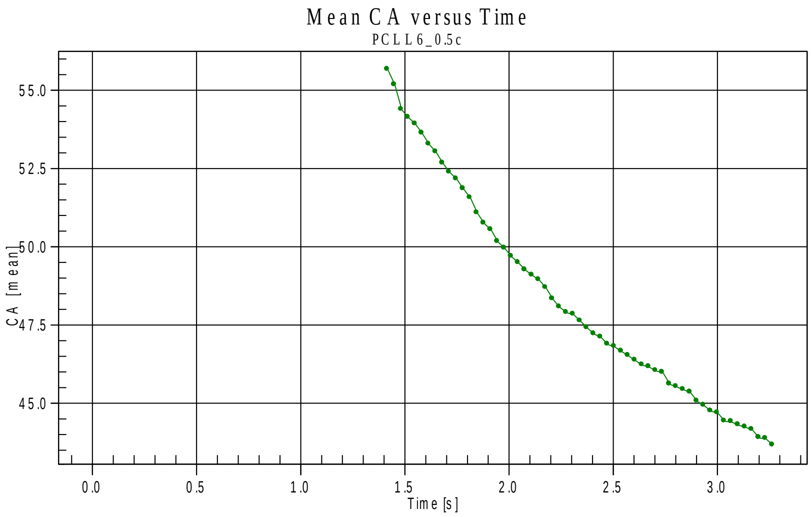


Figure 18: (above and p.20): Graphs showing very steep reduction in contact angle that is almost linear. After one minute the contact angle in the last example was 18.52°. Note comparison with straight BL8.

Results with AWT formulations alone

The most important characteristic about AWT formulations is that they are dose dependant, i.e. the concentration can be increased or decreased depending on the application. Where rapid wetting or spreading and not penetration is required such as in firefighting foams, coatings and contact resins, higher dose rates of AWT formulations may be required, especially in viscous fluids like paints and coatings where the surface must level prior to skinning and curing. In applications such as agricultural spraying, rapid wetting can be detrimental i.e. herbicides have to penetrate rather than spread over surfaces.

H.Rezex A2 Rapid spreader

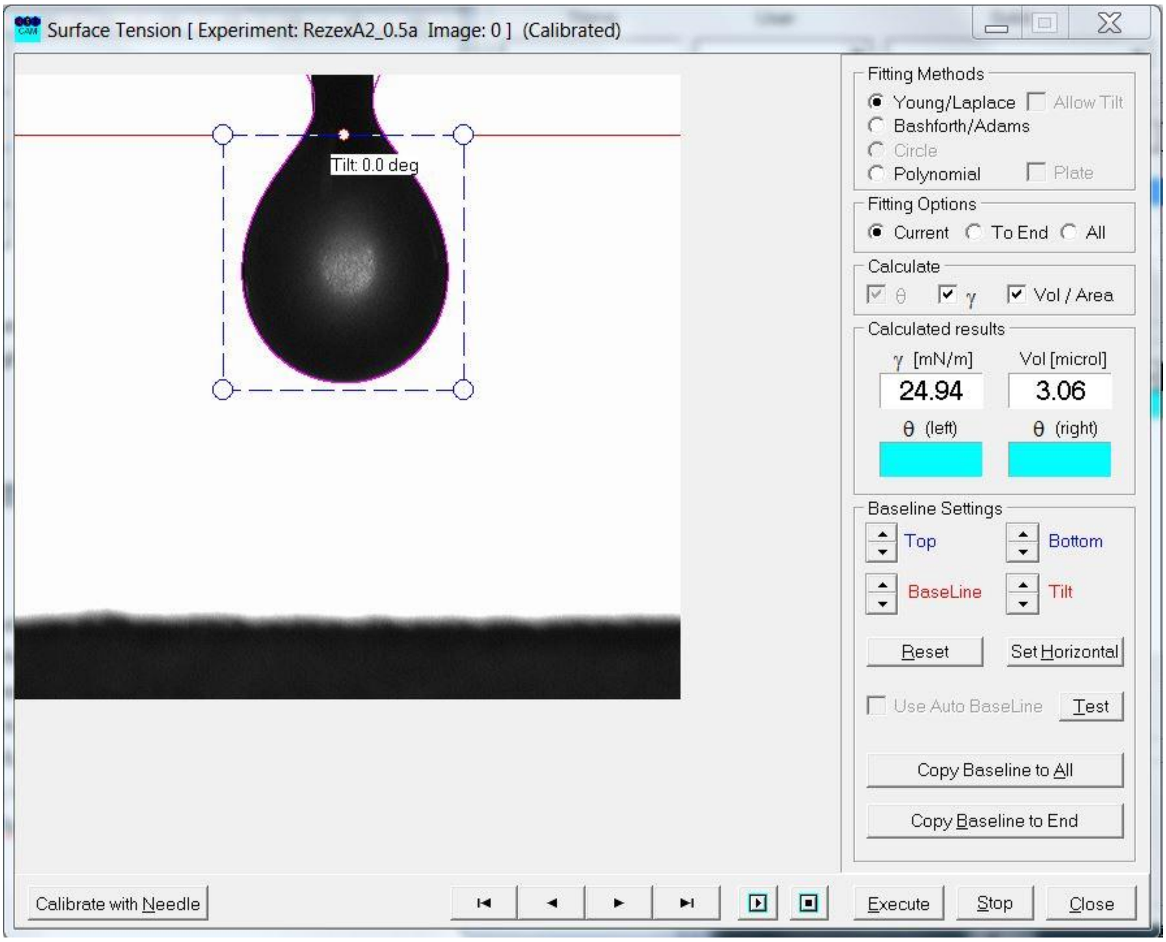


Figure 19: Surface tension of Rezex A2.

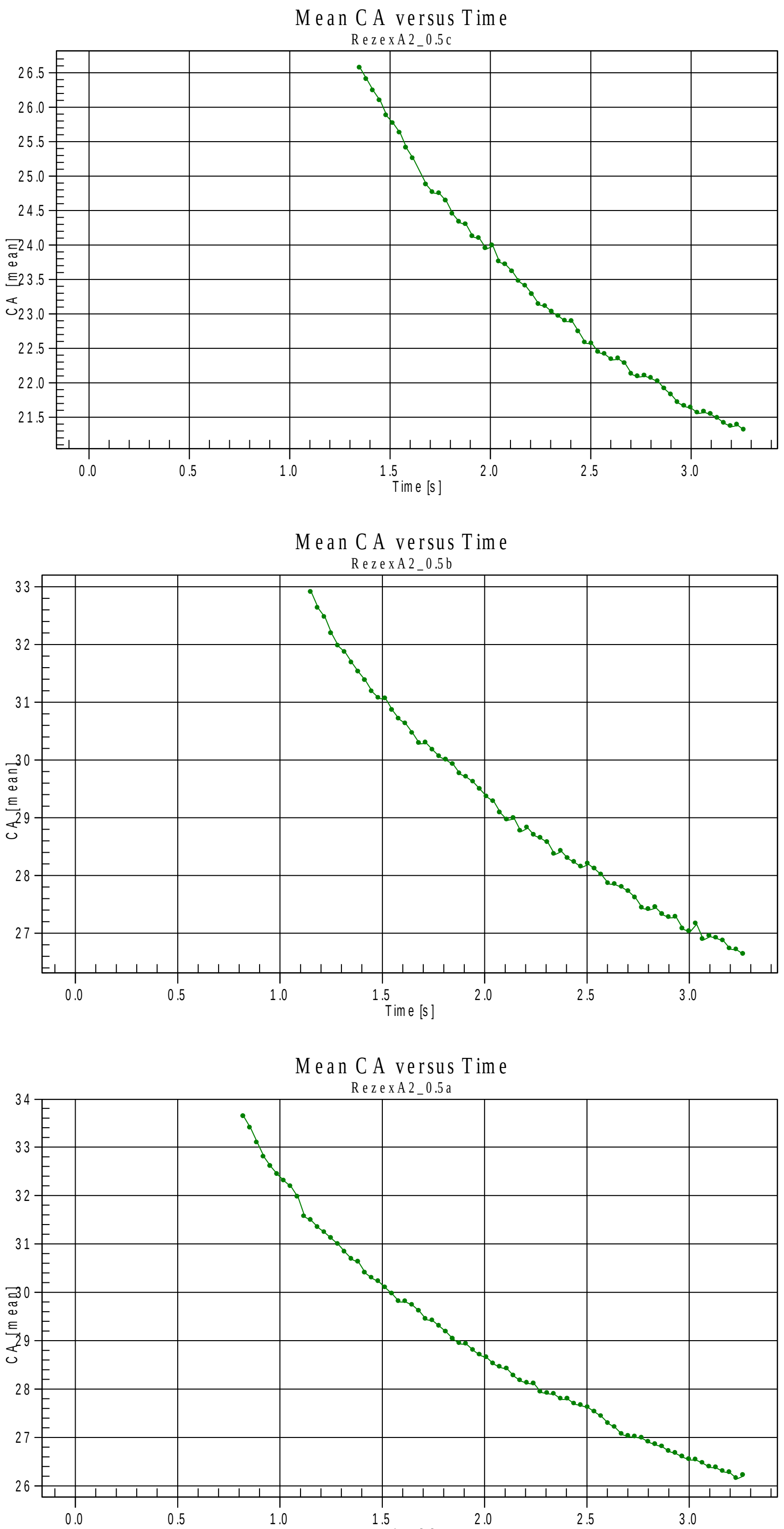


Figure 20: Showing the rapid wetting of Rezex A2. Note that the surface tension is not that low and yet it rapidly wets. At one minute the example in the third graph reached 16.41° clearly demonstrating that rapid wetting is still occurring.

I: Rezex A3 Linear spreading but slower than A2

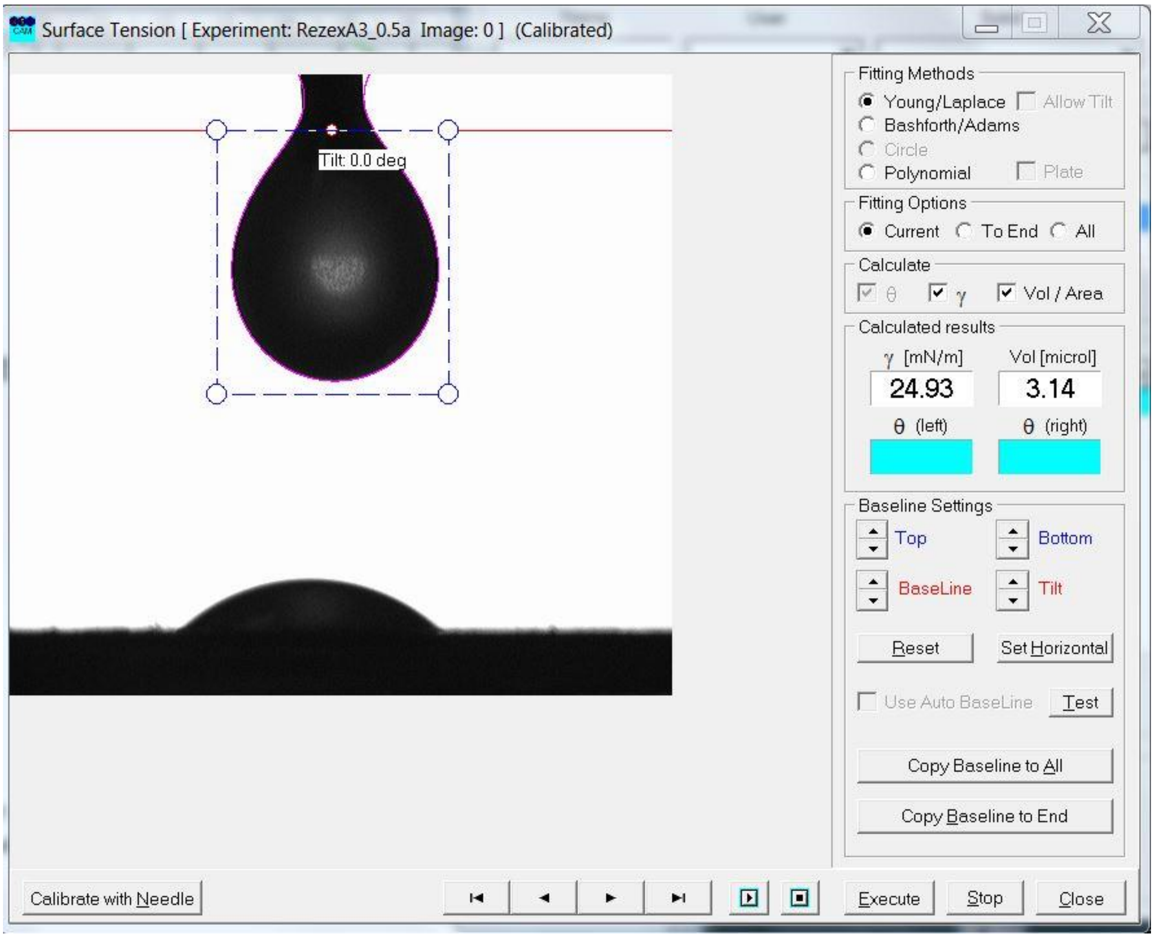
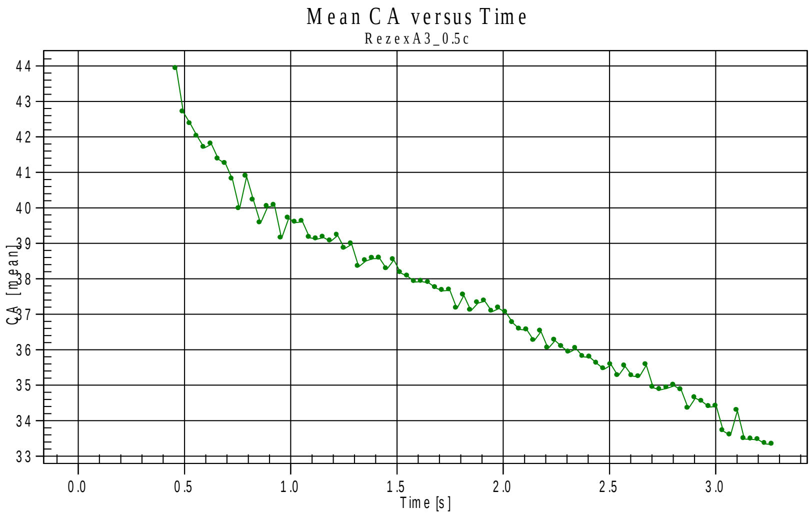
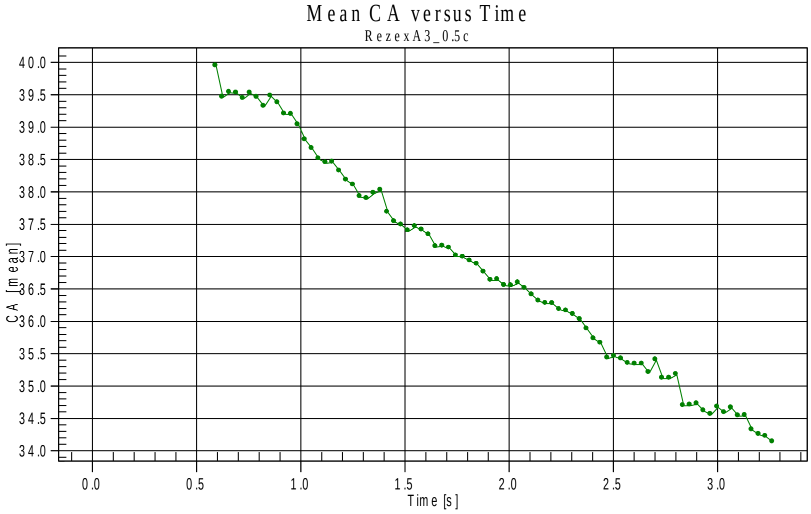


Figure 21: Surface tension of Rezex A3, almost identical to A2.





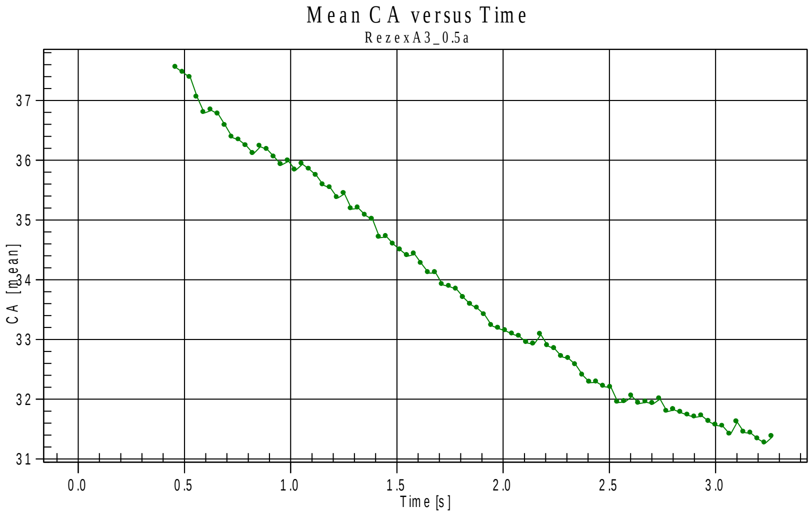


Figure 22 (above and p.24): Showing linear wetting but at a slower rate than Rezex A2. Note that the surface tension of both are virtually identical yet while the mechanism of wetting is the same the speed is different. This shows that surface tension per se is not a good predictor of wetting performance. After one minute the contact angle in graph 1 was 26.79°quite considerably more than for Rezex A2 (16.41°). It would still achieve a 0° contact angle but over a longer time scale.

J: Evowet/Rezex SS20

This surfactant while having a higher surface tension than the two fluoro surfactants I tried in a firefighting foam the actual firefighting mix containing 3% of a surfactant, including mine, overall with AWT surfactant **the firefighting foam spread more rapidly than the two containing fluoro surfactants.** This was confirmed in a production run of the foam at the manufacturer who has placed an ongoing order as fluoro's are chemicals of concern in Australia.

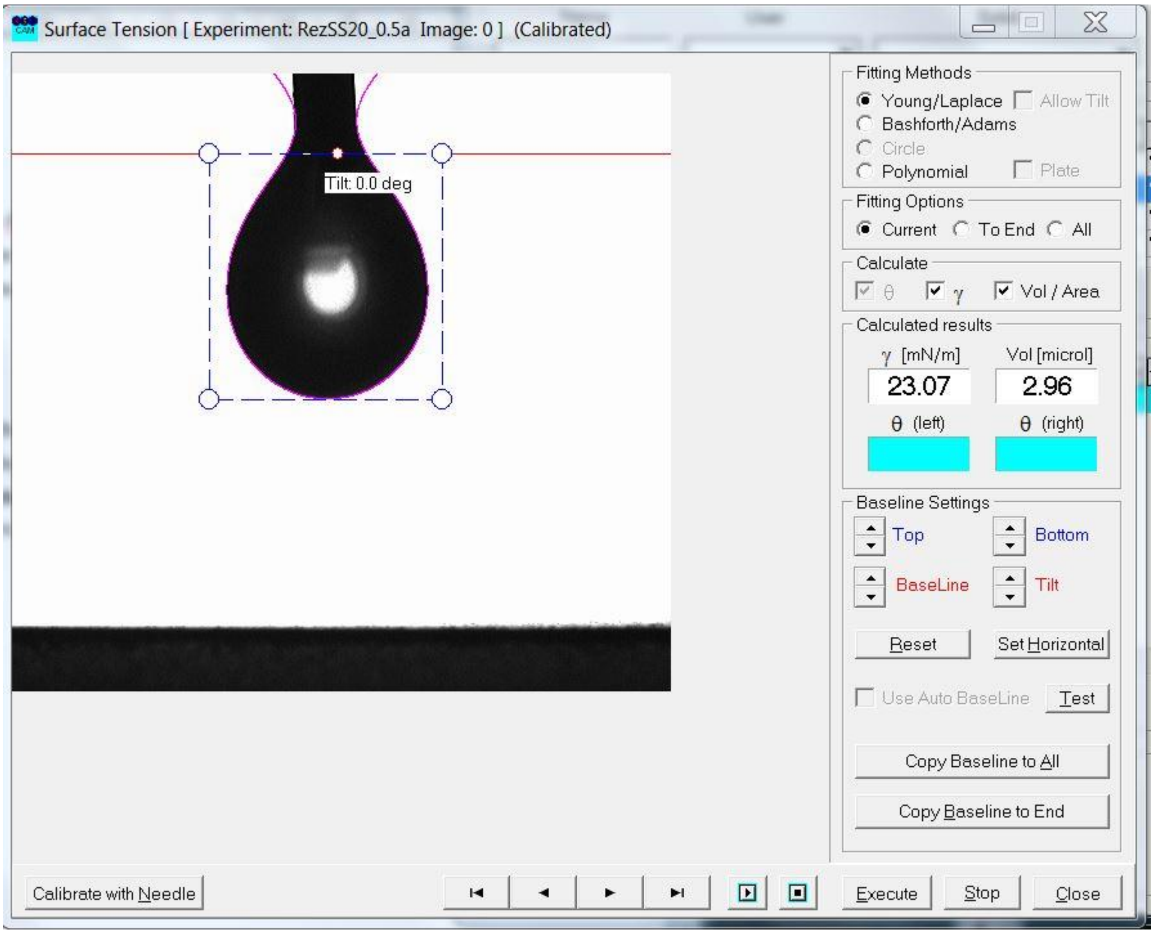
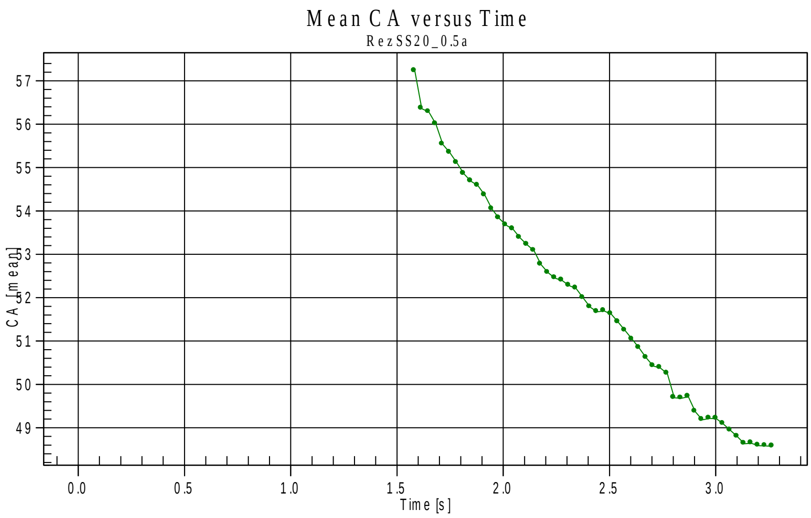
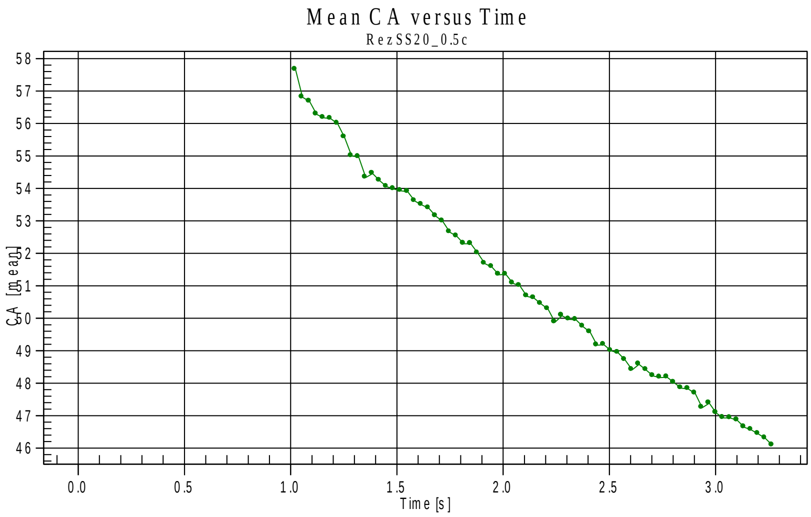


Figure 22: Surface tension of Evowet Rezex SS20. It is higher than a fluoro surfactant.





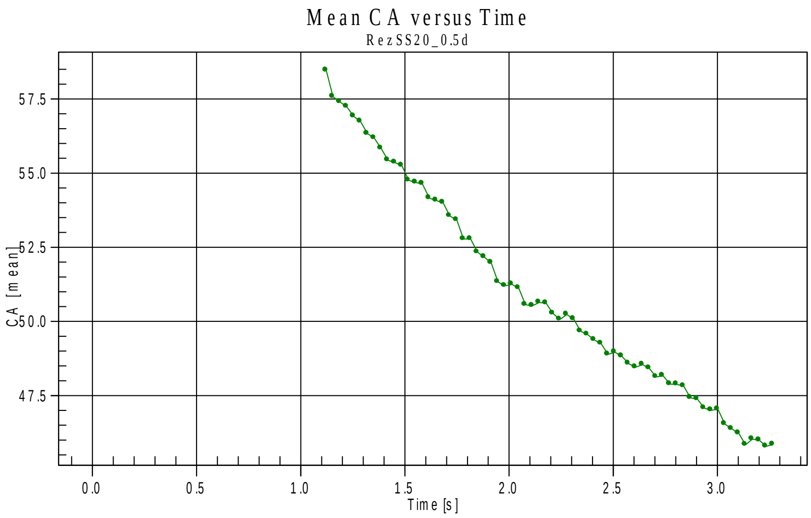
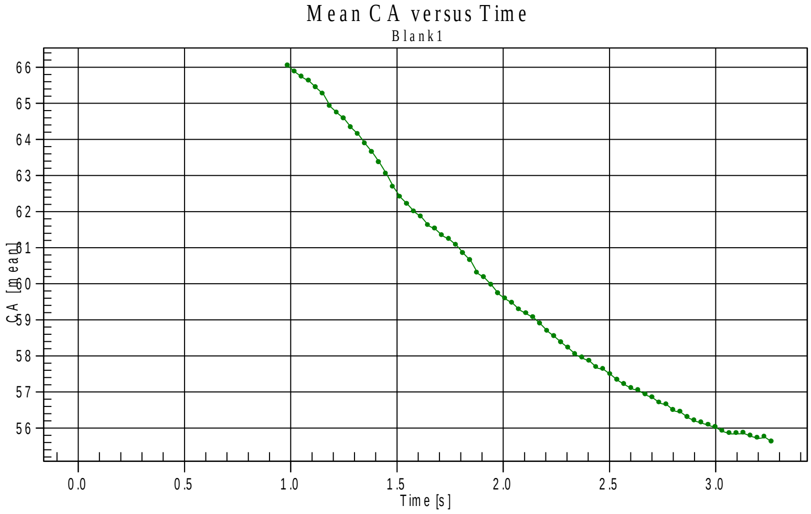
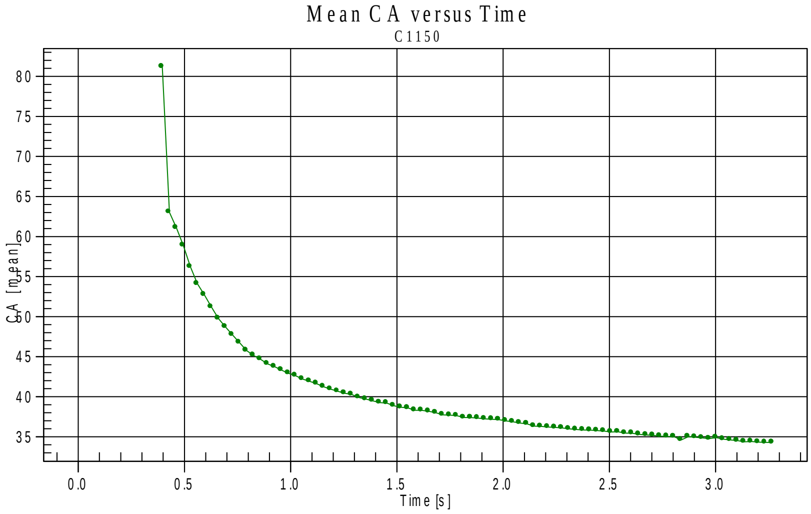


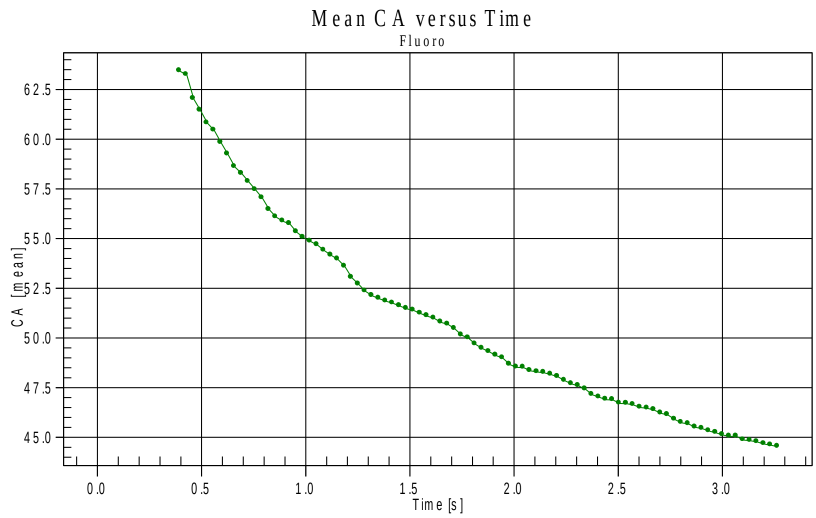
Figure 23: Showing rapid wetting of SS20. After one minute the contact angle was 23.06° in Graph 2.

K Firefighting foam comparison

The firefighting foam without any surfactant had a surface tension of about 28.5nmN/m. With the addition of 3% Fluoro surfactant Capstone 1150 at 3% the surface tension reduced to between 17.28 and 17.39 mN/m and with the second unnamed fluoro at 3% it was between 19.5 & 20mN/m. With Evowet SS20 (AWT) added at 3% it was between 24.31 and 24.57mN/m. This clearly demonstrates that surface tension is not a good predictor of wetting performance.







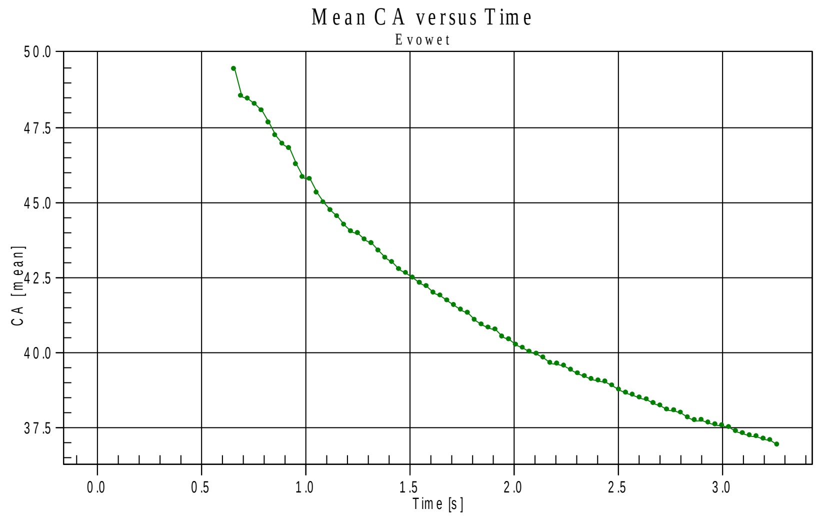


Figure 24 (above and p.28): Graphs from top to bottom, Foam with no surfactant, With Capstone C1150 fluoro @3%, with an unnamed fluoro @3% and with Evowet SS20 (AWT) at 3%. In order contact angles after one minute were 38.12°, between 22.86 and 24.73°, 10.91 to 12.39°, and Evowet 14.45 to 19.96° yet was spreading at a much more rapid rate at the end. It also had better water draining properties through the foam. The company wishes to pursue this new surfactant.

4: Other examples of high speed wetting formulations of AWT

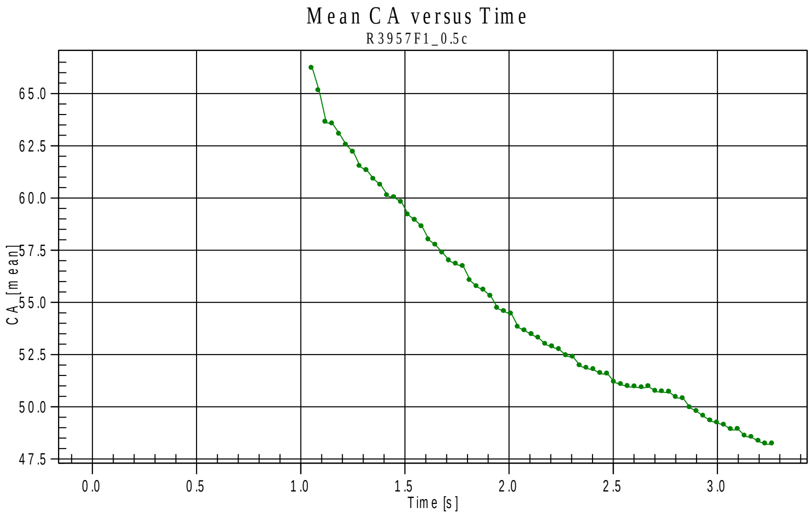


Figure 25: R3957F1, surface tension 22.43 mN/m, after one minute the contact angle was 17.87°.

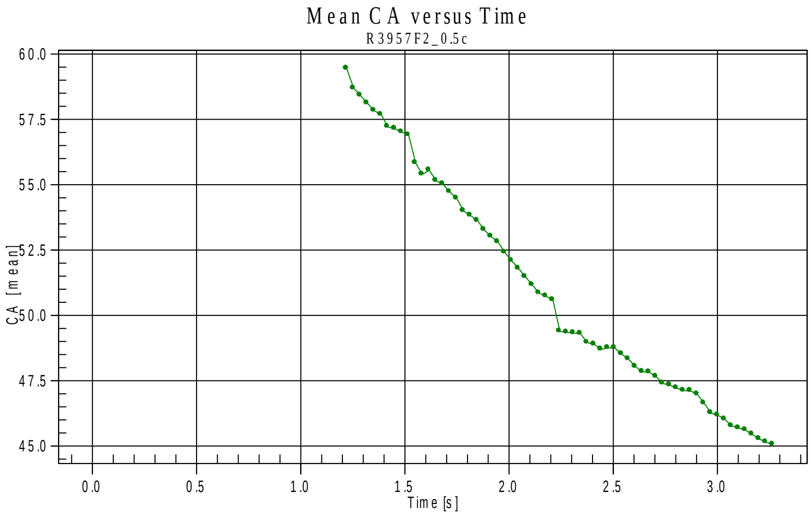


Figure 26: R3957F2, surface tension 21.85 mN/m, after one minute the contact angle was 15.61°.

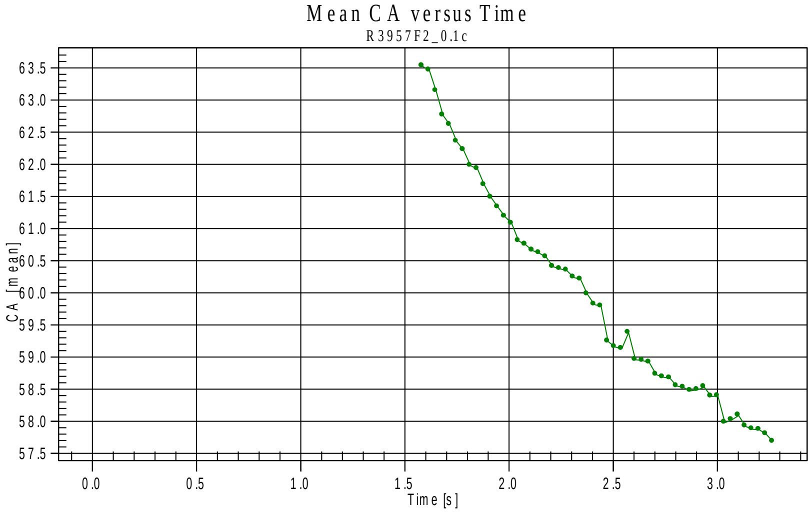


Figure 27: R3957F2 @ 0.1%, surface tension 24.89 mN/m, after one minute the contact angle was 20.21°. Note virtual linearity at the lower concentration. This is typical behaviour of these formulations.

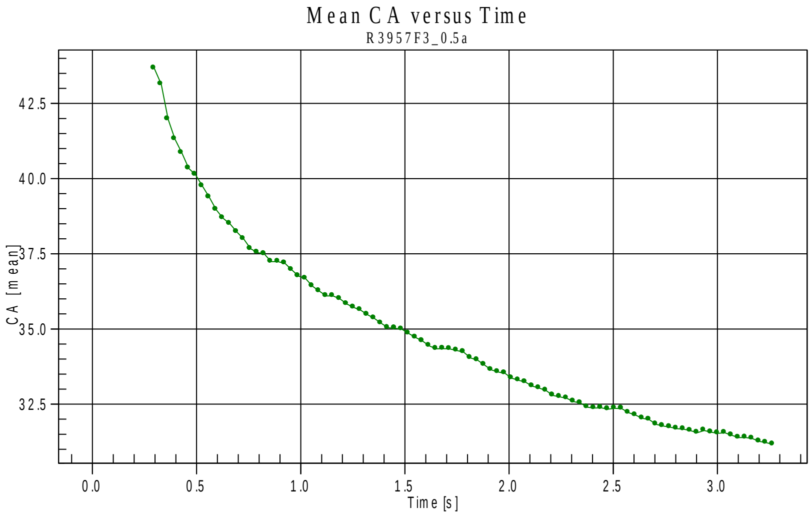


Figure 28: R3957F3, surface tension 24.78mN/m, showing slightly slower wetting, after one minute contact angle 25.86°.

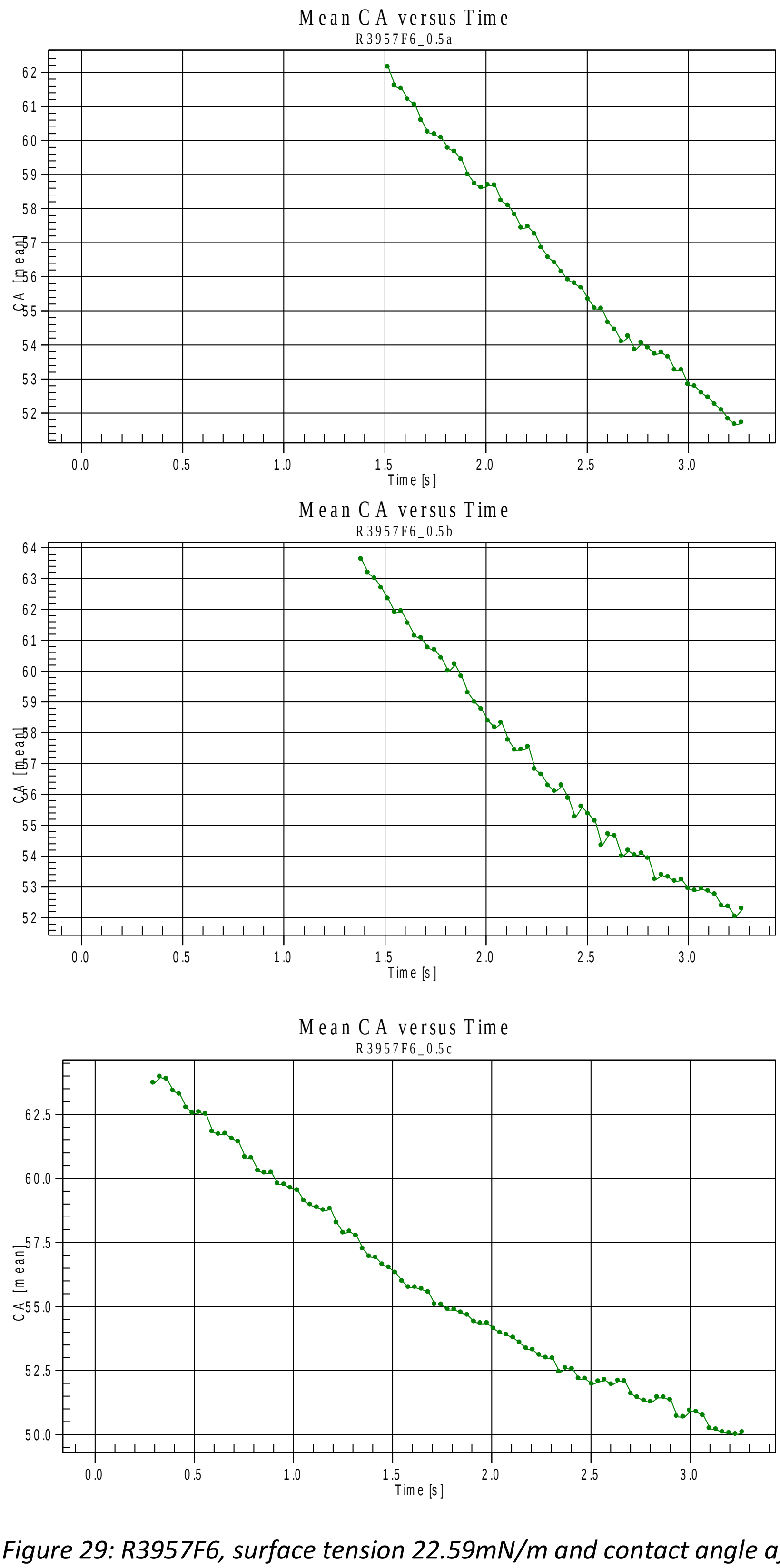
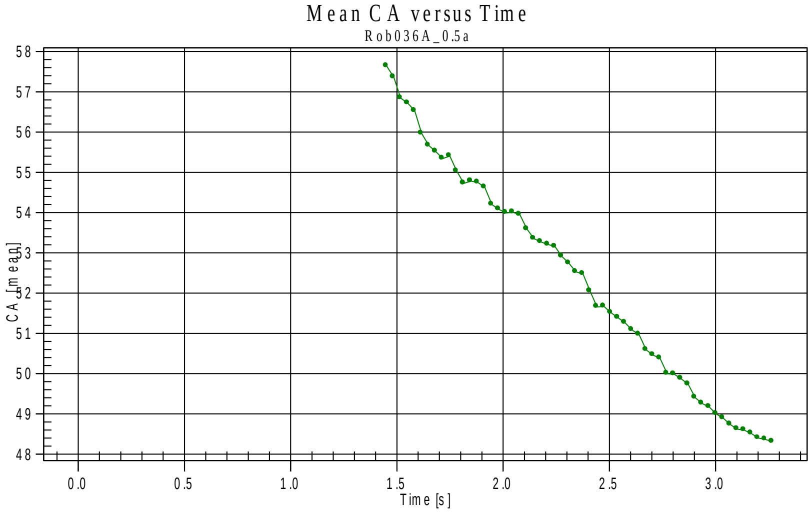


Figure 29: R3957F6, surface tension 22.59mN/m and contact angle after one minute was 17.59° demonstrating not only linear but also very rapid wetting behaviour.



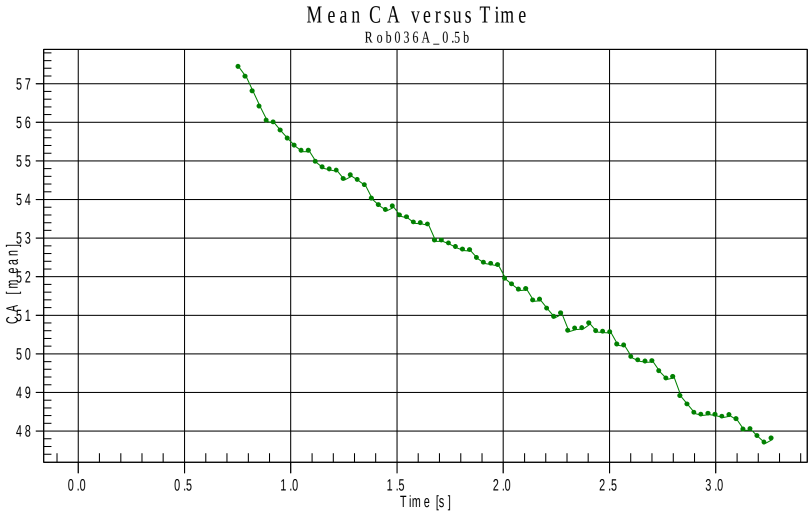


Figure 30: Formulation 036A, surface tension 22.51 and after one minute the contact angle was 22.10°showing very rapid wetting and again linearity of wetting.

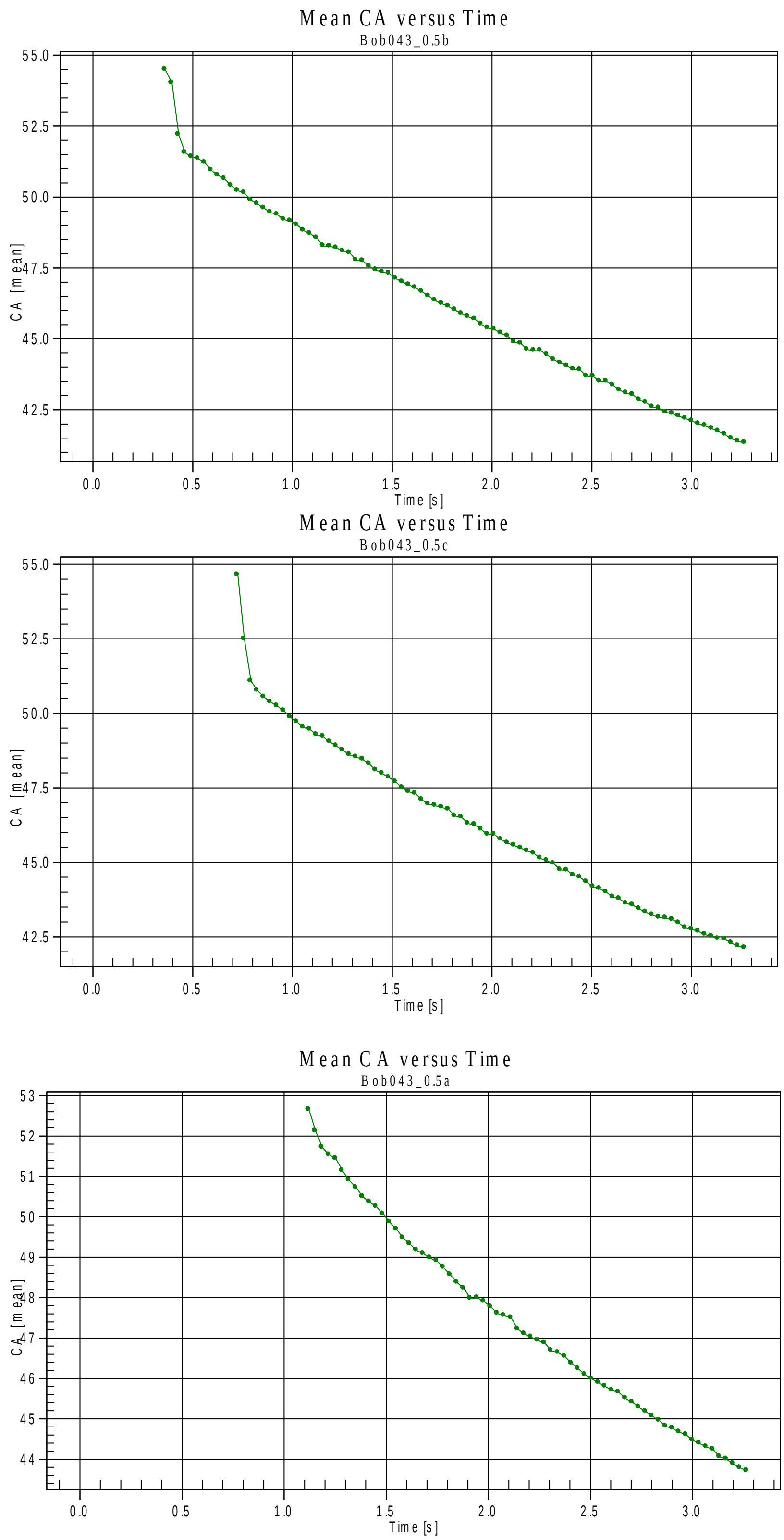


Figure 31: AWT formulation Bob043 at 0.5%, showing an almost linear reduction in contact angle where one could predict full wetting i.e. contact angle of 0°. The graphs show consistency of performance. Surface tension 25.2 and contact angle after one minute was 21.40°.

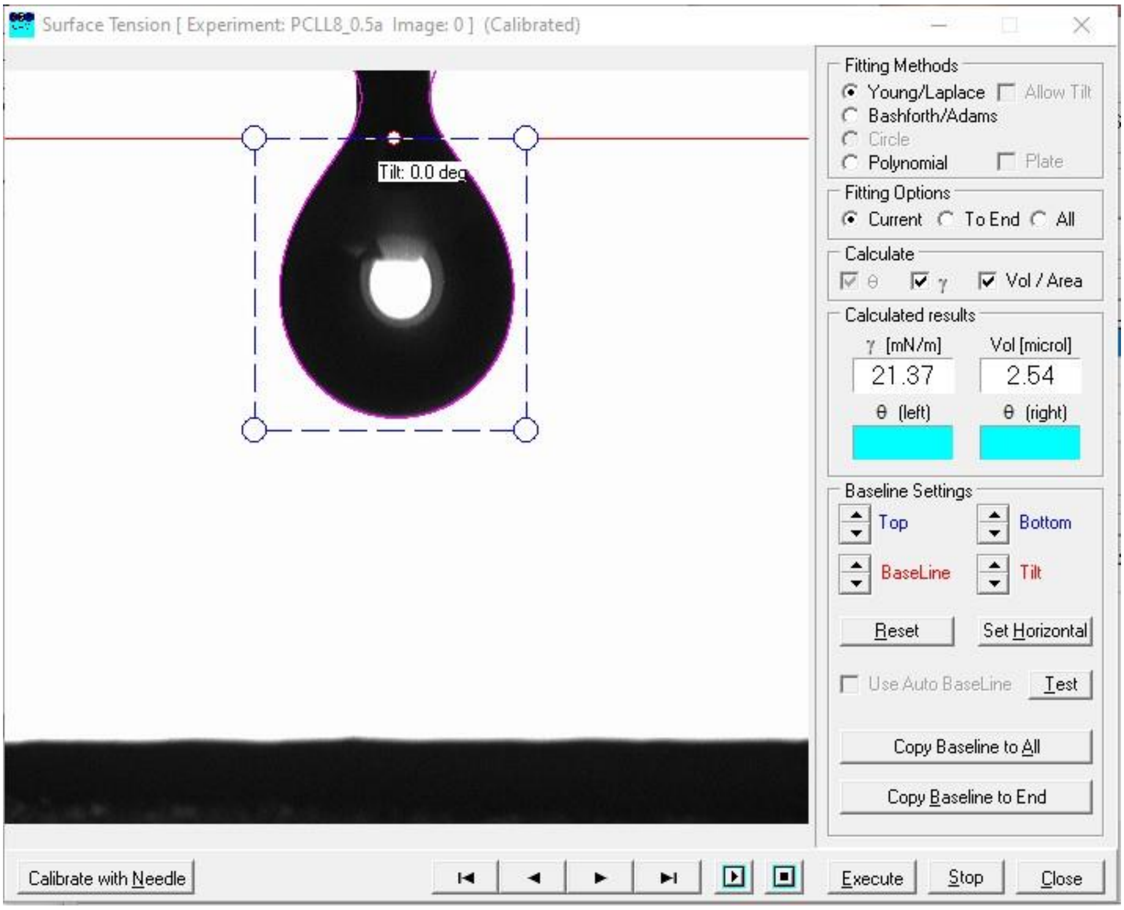


Figure 32: showing the surface tension of AWT formulation PCLL8 being 21.37mN/m.

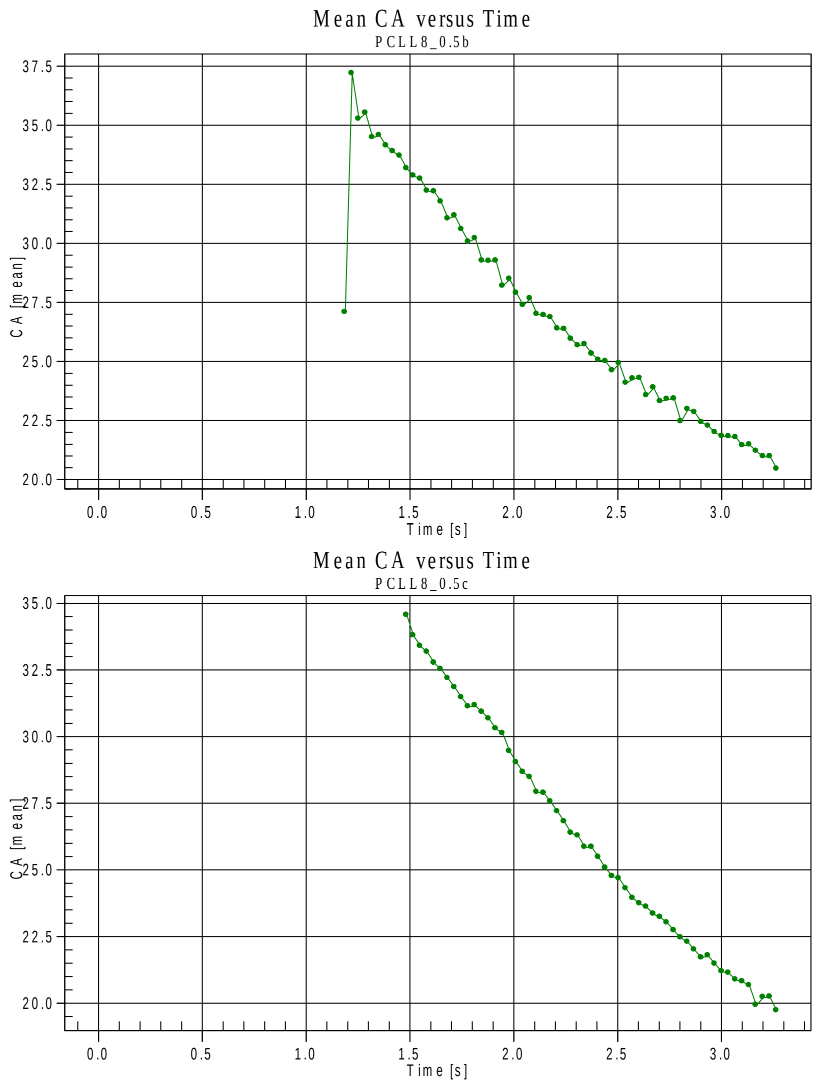


Figure 33: AWT formulation PCLL8 at 0.5%, showing an almost linear reduction in contact angle where one could predict full wetting i.e. contact angle of 0°.

Conclusions

There are dozens of examples that show the efficacy of the AWT system. Note that the linearity of the reduction in contact angle shows these surfactants do not exhibit the mechanism of micelle formation and then breakdown. This is the innovation of the AWT system. The above are just a sample of over 70 of AWT formulations that were tested. The experimental design was fully orthoganol. The highly significant factor from a fundamental physics perspective is that there was not a good relationship between surface tension reduction and wettability of AWT formulations. In addition there is not a good relationship of such with existing surfactants. This has been clearly demonstrated in the firefighting foam sector.

Agricultural spraying trials have shown success where the dosage of AWT formulations can be used at 20% of the dosage of existing, amphiphilic surfactants. It has also been used in broad acre 1000+ trials very successfully with one farmer wanting to change to one of AWT formulations immediately. AWT formulations are compatible with all of the major herbicides and have no phytotoxicity.