High Throughput Surface Tension Measurement

"Reducing Product Time to Market"

Neil L. Campbell*, Jon Weaver*

Centre for Materials Discovery, The University of Liverpool, Crown Street, Liverpool, L69 7ZD, United Kingdom*

ncampbell@materialsdiscovery.com

Abstract: Understanding the surface tension properties of aqueous surfactants and polymer materials is important for the pharmaceutical, coatings, paints, inks, surfactant and household products industries. The traditional methods of measuring surface tension are tedious and time-consuming, so only a few compounds can be measured by a single user per day. With the commercial drive to reduce product time to market the following process explains the background behind the measurement of surface tension and the manor in which a flexible high throughput process for conducting this measurement was developed at the Centre for Materials Discovery (CMD) for use in the research of surfactant and pH responsive polymers.

Eppendorf 5075LH PC Liquid Handling Platform

Kibron Delta-8 plate Surface Tension plate reader

1) Background

The traditional technique used to analyse surface tension is based on the measurement of the force of interaction between a probe and a surface of a fluid using a tensiometer. The probe used in these experiments is suspended from a balance and brought into contact with the interface of liquid to be tested. The forces measured by the balance as the probe interacts with the surface of the liquid can be used to calculate a number of physical properties including surface tension.

Factors affecting the forces in these measurements are: size and shape of the probe, contact angle of the liquid/solid interaction and the surface tension of the liquid. Some of these factors can easily be controlled such as the size and shape of the probe. Also a contact angle of zero is achieved by using probes made of a platinum/iridium alloy which insures complete wetting and easy and reliable cleaning.

The maximum pull force method used by the Kibron Delta-8 tensiometer (see figure 1) to measure surface tension is achieved by: (a) immersing a thin rod into the sample, (b) the vertical retrieval of the rod and (c) the measurement of maximum force needed to remove the rod from the liquid[1,2]. The technique requires a calibration factor obtained by measuring a liquid of known surface tension. In the case of the Kibron Delta-8 pure water is used to calibrate the instrument and used as a control in the last column of each plate.

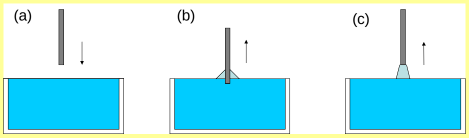

Figure 1. Diagram illustrating the maximum force method for surface tension measurement.

Measurements using a manual tensiometer are usually slow due to the low throughput of samples, as the sample setup, measurement and cleaning of the apparatus between measurements is time consuming (see figure 2). Therefore there is a great need to increase the throughput of both surface tension sample preparation and measurement.

Figure 2. Image of a typical manual tensiometer used for conducting surface tension measurements

2) Concept

At the CMD a generic process for high throughput surface tension measurements of compounds and formulations was developed. By using an Eppendorf epMotion 5075LH automated liquid handling platform, large numbers of samples can be prepared quickly and accurately in 96 well microplates. These plates are then fed into a Kibron Delta-8 surface tension plate reader where the surface tension of each well is measured. As shown in figure 3, the Kibron Delta-8 has eight du Nouy needle probes spaced in parallel on micro balances to fit the column spacing of a standard 96 well plate format. Between measurements the surface of these probes are then cleaned automatically using a furnace, thus allowing 96 surface tension measurements to be conducted within 3 minutes.

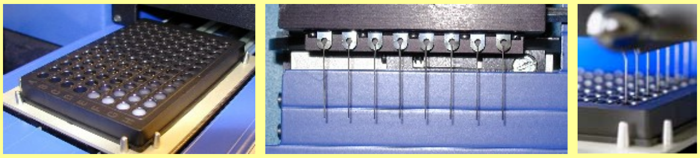

Figure 3. Kibron Delta-8 plate reader with multiple probes on individual microbalances.

By using the epMotion 5075LH liquid handler a highly flexible process has been created allowing researchers to deliver their surfactants or polymer samples direct from the synthesis laboratories in convenient and easy to handle formats, such as 1.5ml Eppendorf centrifuge tubes. These are then simply placed directly onto the deck where the epMotion 5075 takes a small aliquot from each sample and prepares a serial dilution in a standard 96 well microtiter plate using an aqueous stock solution. A replicate daughter plate is then carefully produced in a Teflon coated Kibron surface tension plate which allows the retention of a droplet shape meniscus onto which the surface tension probes can make contact as shown in figure 4.

Figure 4. Uniform sample preparation for high throughput surface tension measurement.

The data from the plates allows the calculation of surfactant critical micelle concentrations (CMCs), and air-water partition coefficient for each sample. This can also be used to show the effects of polymer mixtures on the surface tension with respect to changes in pH, and can be easily achieved by repeating the same process using dilution mediums of different pH in the Eppendorf epMotion 5075 reservoir racks. This enables rapid research to be conducted on selective pH responsive materials like those used in drug release technologies.

3) Example of a high throughput surface tension study of block copolymers

Hypothesis: The simultaneous use of an Eppendorf liquid handling robot and a Kibron Delta-8 high throughput surface tensiometer will allow determination of polymer surfactant adsorption isotherms with unprecedented speed, accuracy and reproducibility.

Experimental: 1 w/v % aqueous solutions of five amphiphilic block copolymers were prepared using distilled water and loaded into the Eppendorf liquid handling robot. The robot was programmed to perform 22 serial dilutions of each polymer solution (concentrations from 1.0 – 4.8 x 10-8 w/v %) into stock 96 well plates. 50 μL of each solution was transferred into standard Kibron Delta-8 96 well plates and characterised using the Kibron Delta-8 surface tensiometer. The 176 measurements were performed in approximately 5 minutes. The data from the 22 serial dilutions were combined using standard Kibron Delta-8 software procedures.

Results: The adsorption isotherms of the 5 amphiphilic block copolymers are shown in Figure 5.

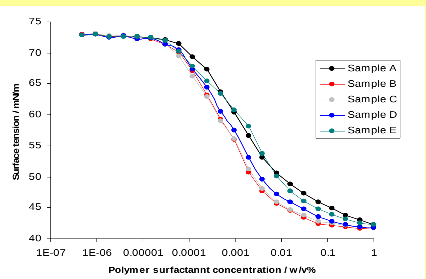

Figure 5. Surface tension isotherms for the 5 amphiphilic block copolymers.

Surfactant ID	Limiting surface tension / mN/m at 1 wv %	K_{aw}^{-1} / wv %	CMC / wv %
Sample A	42.28	8.0×10^{-5}	3.2×10^{-2}
Sample B	41.73	4.2×10^{-5}	1.2×10^{-2}
Sample C	41.89	4.0×10^{-5}	1.2×10^{-2}
Sample D	41.75	4.0×10^{-5}	1.8×10^{-2}
Sample E	42.25	3.8×10^{-5}	4.8×10^{-2}

Table 1. Limiting surface tension, CMC and *Kaw* for the individual isotherms.

Reproducibility: Reproducibility of the automated process was assessed by repeating the dilution of the same polymer sample across the entire plate, giving eight repetitions. The adsorption isotherms for this repeat experiment are well within acceptable tolerances and are shown in Figure 6 below.

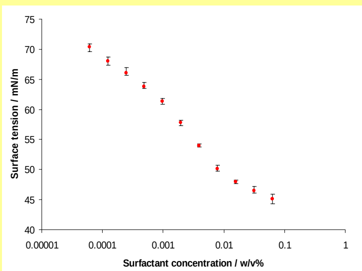

Figure 6. Repeat measurements of the adsorption isotherm for block copolymer 562C.

Discussion: K_{aw} indicates the affinity of a material to associate at the air-water interface and is a useful measure of hydrophobicity/hydrophilicity, which can also be used to assess a compounds membrane permeability[3], which is a useful measurement required in AMDE toxicity studies. The data suggests that each of the block copolymers have similar hydrophobicites with the exception of Sample A which appears to be more hydrophilic. CMC determination is a key parameter for the optimisation of aqueous formulations in a wide range of industrial sectors as it calculates the critical concentration at which amphiphiles associate into micellar structures. The CMC was shown to vary within a small range between the samples. The limiting surface tension is an indication of the surfactant efficiency. All samples appear to lower the surface tension of water to similar levels, however neither Sample A or Sample E had reached a plateau indicating that their limiting surface tensions may continue to decrease at higher concentrations. Further understanding of the effects of polymer molecular weight, architecture, functionality and hydrophile-lipophile balance (HLB) will allow the construction of useful structure-property relationships concerning the aqueous solution behaviour of novel amphiphilic materials, see Figure 7.

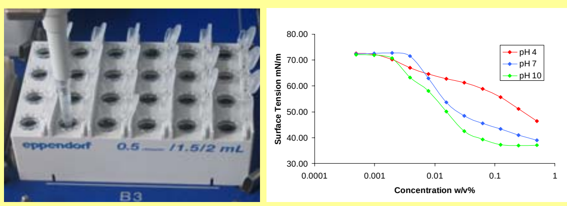

Figure 7. Sample preparation can be conducted from a large variety of user friendly formats to produce surface tension analysis plates. This process has also been used to produce pH profiles of responsive block copolymers tailored for selective encapsulation and release technologies.

4) Conclusions

At the Centre for Materials Discovery (CMD) we have established a work cell to conduct high throughput surface tension analysis. Currently 48 samples can be prepared and analysed every 30 minutes with a high degree of accuracy and reproducibility. The further increase in the sample throughput by the use of plate stacking is currently under development. This process developed at the CMD allows rapid research of industrially viable materials to be conducted in a cost effective manner and thereby reducing product time to market[4].

References:

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Acknowledgements:

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2. Kibron Inc – http://www.kibron.com/
3. The Centre for Materials Discovery – http://www.materialsdiscovery.com