Applications

Note 152 | June 2007

# Development of a Process for High Throughput Surface Tension Measurement using the epMotion® 5075

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## Abstract

**A high throughput process for the preparation and testing of samples for their surface tension using the epMotion 5075 Liquid handling platform and Kibron delta-8 tensiometer has been successfully developed and implemented at the Centre for Materials Discovery. This allows multiple samples to be rapidly screened with a high accuracy, reproducibility and on a more cost effective scale. The process was shown to be over 500 times faster than manual traditional methods and allows swift studies to be carried out of formulation in the inks, surfactants, polymers, pharmaceutical and household care industries.**

## Introduction

Understanding the surface tension properties of aqueous surfactants and polymer materials is important for the pharmaceutical, inks, surfactant and household products industries. The traditional method of measuring surface tension is time-consuming so only a few compounds can be measured by a single user per day. The following technical note explains the background behind the measurement of surface tension and the manor in which a high throughput process for conducting this measurement was developed.

## Background

The traditional technique used to analyse surface tension is based on the measurement of the force of the 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 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 each place.

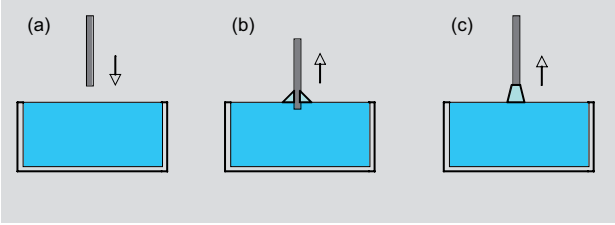


**Figure 1:** Diagram illustrating the maximum force method for surface tension measurement.

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 is time consuming (see figure 2). Therefore, there is a great need to increase the throughput of both surface tension sample preparation and measurement.

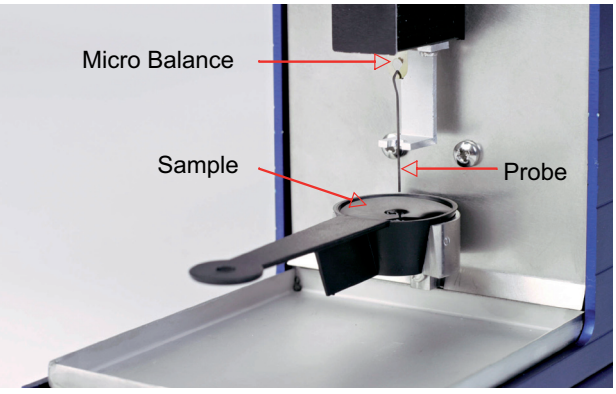


**Figure 2:** . Image of a typical manual tensiometer used for conducting surface tension measurements.

## Concept

At the Centre for Materials Discovery (CMD) a generic process for high throughput surface tension measurements of compounds and formulations has been developed. Using the Eppendorf epMotion 5075 LH automated liquid handling platform, large numbers of samples can be prepared quickly and accurately in 96 well microplates [3]. These are then fed into a Kibron Delta-8 surface tension plate reader where the surface tension of each well is measured [4]. As shown in figure 3a, the Kibron Delta 8 has eight du Nouy needle probes spaced in parallel on micro balances to fit the column of a 96 well plate. Between measurements the surface of these probes are then cleaned, using a furnace (figure 3b),thus allowing 96 surface tension measurements to be conducted within 3 minutes.

By using the epMotion 5075 LH automated pipetting system a highly flexible process has been created thus allowing researchers to deliver their surfactants or polymer samples directly from the laboratory in convenient and easy to handle formats, such as 1.5 ml Eppendorf centrifuge tubes. These are placed directly onto the deck where the epMotion 5075 then takes a small aliquot from each sample and prepares a serial dilution in a 96 well microplate using an aqueous medium. A daughter plate is then 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.

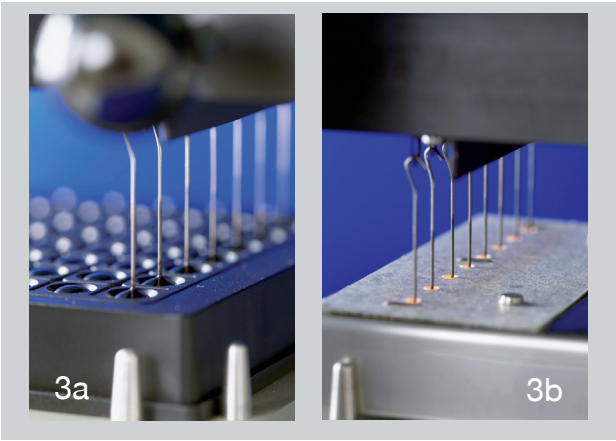


**Figure 3:** Kibron Delta 8 surface tension measurement with needle probes (3a). Cleaning of probes between measurements (3b).

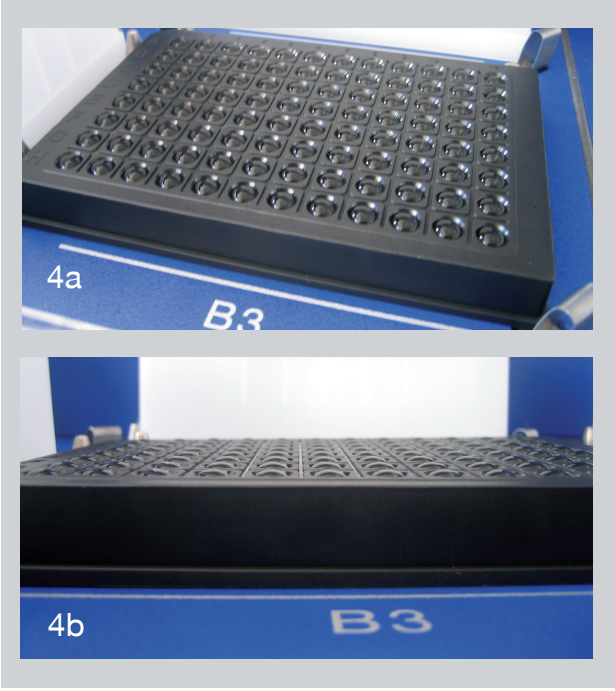


**Figure 4a and 4b:** Automated sample preparation for high throughput surface tension measurement. Please note the uniform shape of the droplet meniscus within samples.

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.

## Materials and Methods

**Process Technique**

The process is designed to be an easy to use service so even inexperienced liquid handling users can deliver their samples directly from the lab and conduct their measurements. The program allows up to 24 surfactant or polymer samples of known concentration to be placed on the deck of the Eppendorf epMotion 5075 LH in 0.5 ml, 1.5 ml and 2 ml centrifuge tubes (Figure 5).

After automated liquid level detection of each sample a 300 µl aliquot is then taken from each tube and placed into the first column of a standard 370 µl 96 well microplate. The last column is reserved for a control of pure water to which the measurement of each sample can be quantified. A serial dilution of the samples using an aqueous based medium is conducted before a 50 µl sample from each well is transferred to a 96 well Kibron measurement plate. This replicated plate is then transferred to the Kibron Delta 8 tensiometer. The probes are first stabilized before the surface tension of each sample in the plate is measured. The results of the measurements are then quantified against the in-plate control (pure water) and then transferred along with their relevant sample identification numbers to the Laboratory Information Management System (LIMS) where the data can be analysed by the users.

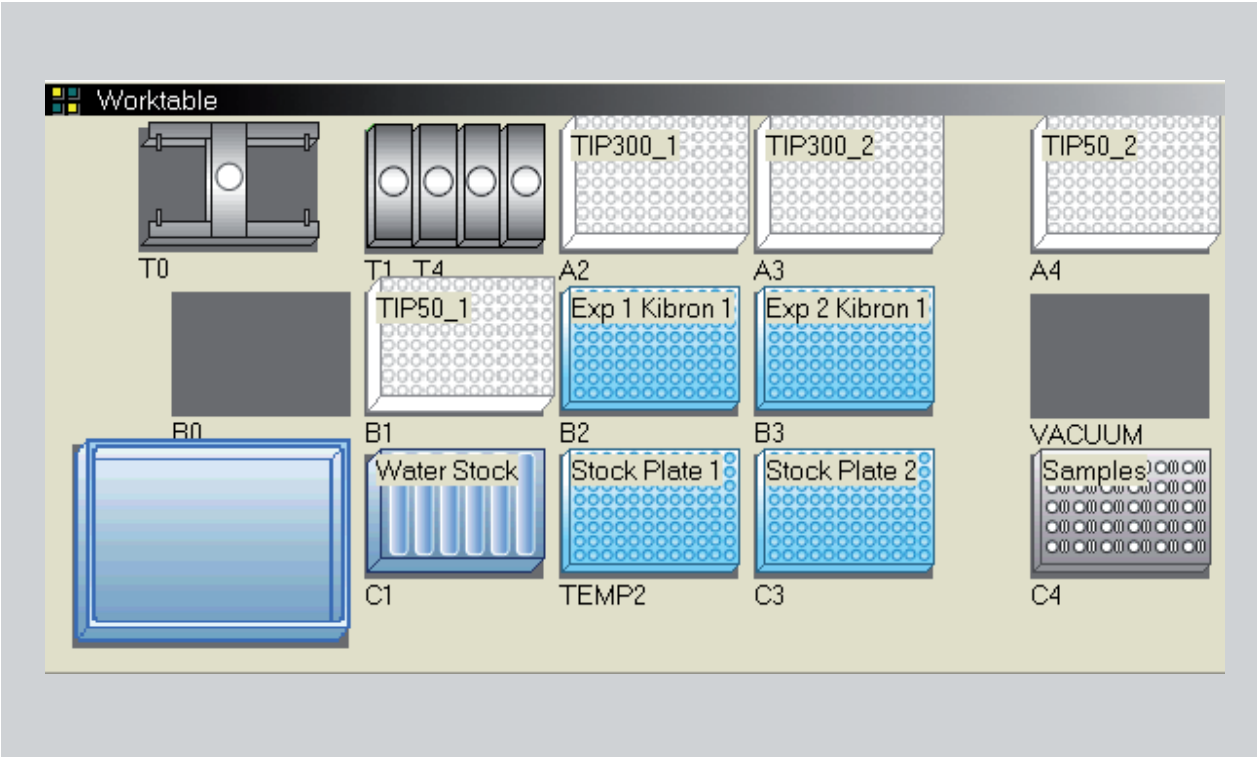


**Figure 5:** Eppendorf epMotion 5075 surface tension sample preparation deck layout.

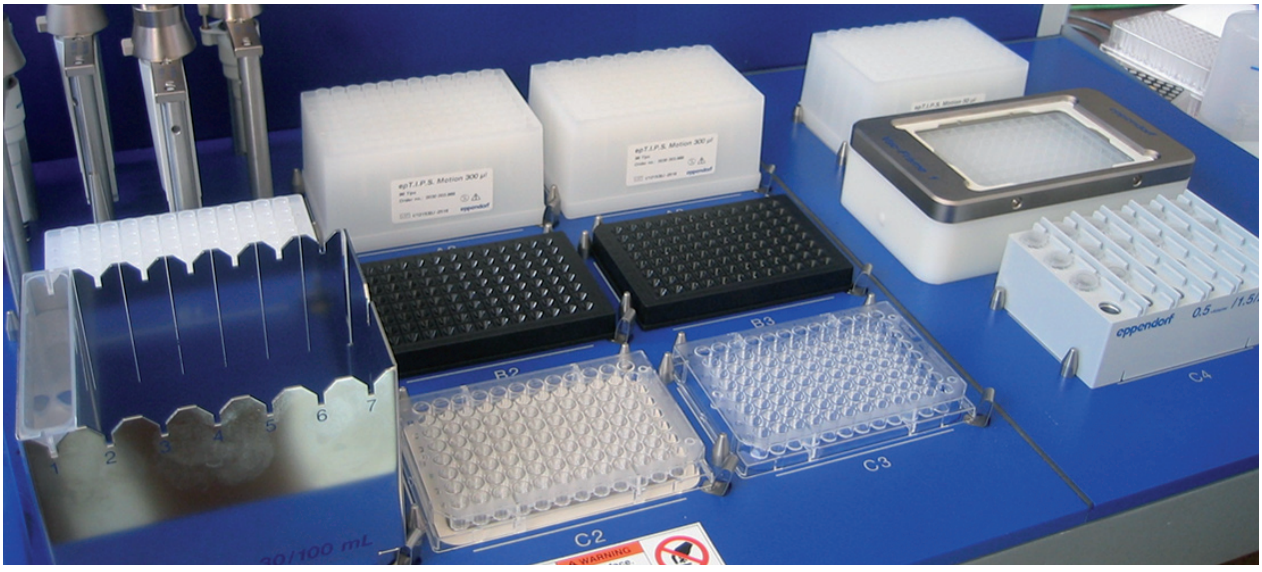


**Figure 6:** Image of flexible Eppendorf epMotion 5075 deck layout including interchangeable liquid handling heads, sample holder and reagent reservoirs.

## High throughput study

**Example of a high throughput study of the surface tension of a series of amphiphilic, linear block copolymers as a function of solution concentration**

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

**Experimental setup**

1 % (w/v) aqueous solutions of 5 amphiphilic block copolymers were prepared using distilled water and loaded into the Eppendorf epMotion 5075 LH. The liquid handling system was programmed to perform 22 serial dilutions of each polymer solution (concentrations from 1.0 % – 4.8 x $10^{-8}$ % (w/v)) into stock 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 6 minutes. The data from the 22 serial dilutions were combined using standard Kibron Delta-8 software procedures.

## Results and Discussion

The adsorption isotherms of the 5 amphiphilic block copolymers are shown in Figure 7.

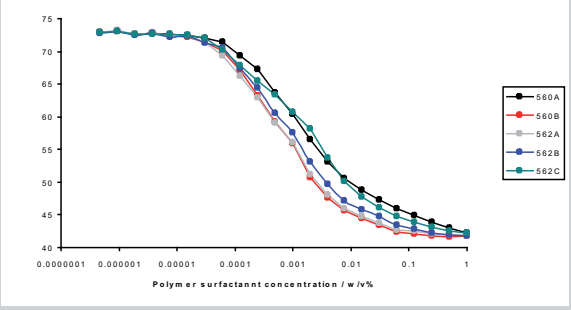


**Figure 7:** Adsorption isotherms for the 5 amphiphilic block copolymers.

The critical micelle concentration, (CMC) and the air-water partition coefficient, ($K_{aw}$) were calculated from the adsorption isotherms and are shown in Table 1.

**Table 1:** Limiting surface tension, CMC and $K_{aw}$ for the individual isotherms.

| Surfactant ID | Limiting surface tension / mN/m at 1 wv % | $K_{aw}^{-1}$ / wv % | CMC / wv % |
|---|---|---|---|
| 560A | 42,28 | $8.0 \times 10^{-5}$ | $3.2 \times 10^{-2}$ |
| 560B | 41,73 | $4.2 \times 10^{-5}$ | $1.2 \times 10^{-2}$ |
| 562A | 41,89 | $4.0 \times 10^{-5}$ | $1.2 \times 10^{-2}$ |
| 562B | 41,75 | $4.0 \times 10^{-5}$ | $1.8 \times 10^{-2}$ |
| 562C | 42,25 | $3.8 \times 10^{-5}$ | $4.8 \times 10^{-2}$ |

$K_{aw}$ indicates the affinity of a material to associate at the air-water interface and is a useful measure of hydrophobicity/hydrophilicity. The data suggest that each of the block copolymers have similar hydrophobicites with the exception of 560A 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 560A or 562C had reached a plateau indicating that their limiting surface tensions may continue to decrease at higher concentrations.

Further understanding of the polymer molecular weight, architecture, functionality and hydrophile-lipophile balance will allow the construction of useful quantitative structure-property relationships concerning the aqueous solution behaviour of novel amphiphilic materials.

## 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 within small tolerances and are shown in Figure 8.

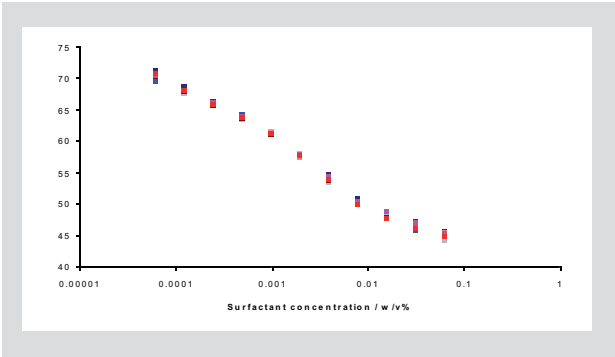


**Figure 8:** Repeat measurements of the adsorption isotherm for block copolymer 562C.

At the Centre for Materials Discovery (CMD) we have established a work cell to conduct high throughput surface tension analysis [5]. Currently 48 samples can be prepared and analysed every 30 minutes with a high degree of accuracy and reproducibility. Further increase of 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.

## References


[1] A.W. Adamson, Physical Chemistry of Surfaces, Wiley & Sons (1976)
[2] S.Wu, Polymer Interface & Adhesion, Marcel Dekker, N.Y.(1982)
[3] Eppendorf AG, http://www.eppendorf.com/epmotion/start.php
[4] Kibron Inc, http://www.kibron.com/
[5] The Centre for Materials Discovery, http://www.materialsdiscovery.com



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