

Surfactants at Expanding Liquid Surfaces, GR/M83797

Final Report

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1. Background

This project arose out of an EPSRC/Unilever funded programme in the mid-1990's in which we established the overflowing cylinder (OFC) as a platform for studying adsorption kinetics and Marangoni effects in surfactant solutions, using the cationic surfactant hexadecyltrimethyl ammonium bromide ($C_{16}TAB$) as a model system. Following the success of the earlier project, a new collaborative programme was launched with Dr. Julian Eastoe at Bristol to extend the study to a range of diverse surfactant systems and to develop quantitative models of surfactant adsorption. The Bristol group was tasked with the synthesis of surfactants (including deuterated materials for neutron reflection (NR)) and the measurement of dynamic surface tensions by light scattering and maximum bubble pressure (MBP) measurements. The Oxford group was responsible for laser Doppler velocimetry (LDV) and ellipsometry measurements and for the development of theoretical models. NR experiments were carried out jointly.

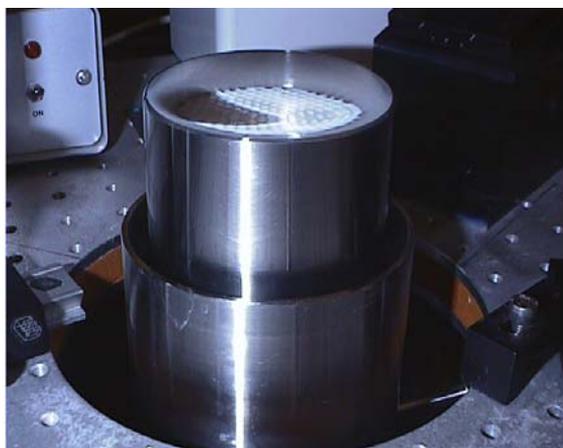


Figure 1. Photograph of an OFC. Water from a gravity feed flows upwards in the central cylinder and overflows the rim. A resistance plate and Teflon flow straightener ensure plug flow well beneath the surface.

The Bristol side of the project was funded under GR/M83780 for two years, and a final report was submitted in May 2002. Dr. Eastoe's report described in detail work in the early part of the project on two fluorinated sulposuccinates, di-CF₄ and di-HCF₆, including a comparison of

dynamic adsorption behaviour inferred from measurements by the MBP method and the OFC method. These results have also been published [1, 2] will not be repeated in this report.

2. Results

A. Methodology

The OFC dates back to the work of Padday and co-workers at Kodak in the 1940s, but surface characterisation was restricted to invasive measurements of the dynamic surface tension by the Wilhelmy plate method. In the early 1990s, Prins at Wageningen published a series of papers on the OFC highlighting the large surface accelerations arising from Marangoni effects in surfactant solutions. The surface velocity was measured by video recording of talc particles on the surface and by laser Doppler scattering. In our earlier project, we improved the design of the OFC and of the laser Doppler detection method and also developed ellipsometry, dynamic light scattering and neutron reflection as additional techniques for characterising the surface properties of surfactant solutions at expanding liquid surfaces.

To model adsorption kinetics it is essential to know the surface excess, Γ , under dynamic conditions. Historically, the surface excess has been deduced from the surface tension, σ , assuming that the equilibrium equation of state $\Gamma(\sigma)$ also holds under dynamic conditions. Direct measurements of the surface excess are much preferable, and to this end we demonstrated the feasibility of neutron reflectometry on the OFC. NR was applied to a number of surfactant systems in this project, but NR has a number of drawbacks, notably cost, the need for deuterated surfactants and the scheduling of beamtime. It would be much more convenient if the surface excess could be determined by a laboratory-based technique. In this project we investigated whether ellipsometry (for single component systems) and FTIR (for pure surfactants and mixtures) could provide such an alternative.

Surface excess determination by ellipsometry

There is no *a priori* reason why the coefficient of ellipticity, $\bar{\rho}$, of a surfactant film at the air-water interface should be a linear function of Γ . By a comparison of NR and ellipsometry data from the OFC, [3 ,4] we were able to show, however, that there is a good linear relationship between $\bar{\rho}$ and Γ for the family of cationic surfactants C_n TAB ($n = 12, 14, 16, 18$) and for the non-ionic surfactant $CH_3(CH_2)_7(OC_2H_4)_4OCH_3$ (C_8E_4OMe). The correlation for C_8E_4OMe is shown in Figure 2. Experiments were also conducted on the homologue $C_{10}E_4OMe$, but the NR experiments were unsuccessful due to small amounts of a bulk mesophase present even below the nominal cloud point. When these particles reached the surface they were ripped apart by surface tension forces and the resulting disturbance to the surface made NR impossible. It is interesting to note that there were no problems conducting ellipsometry measurements on the same systems, since ellipsometry is much less sensitive to vibrations.

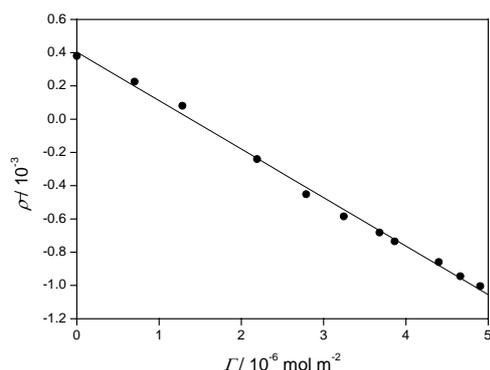


Figure 2. Linear relationship between the coefficient of ellipticity and the surface excess for the non-ionic surfactant C_8E_4OMe on the OFC.

These linear relationships can be understood in terms of an ‘oil film’ model of surfactant monolayers in which the hydrocarbon chain region behaves like a thin liquid oil film with a density similar to the parent hydrocarbon.

The ability of ellipsometry to provide absolute values of the surface excess is of particular value in other experimental situations (as in our own work on liquid jets [13]) in which alternative methods, such as NR or tensiometry, are difficult or impossible.

Dynamic surface excess determination by FTIR

The development of FTIR for studying composition and structure at the surface of flowing liquids was part of our original proposal, but was separately funded by the Petroleum Research Fund (PRF) and Kodak and therefore not formally part of this grant. Nevertheless, the FTIR experiments were treated as part of a single coherent project. In external reflection Fourier transform infrared (ER-FTIR) spectroscopy, a single-bounce IR spectrum is taken from the flowing surface of the OFC. This spectrum is dominated by the dispersion characteristics of water but has a small contribution (typically ≤ 1 part in 10^3) from the adsorbed surfactant layer and, at concentrations greater than a few mM, a detectable contribution from surfactant dissolved in the bulk. We have studied 3 surfactant systems by FTIR: C_{16} TAB, octaethyleneglycol monodecyl ether ($C_{10}E_8$) and ammonium perfluorononanoate (APFN).

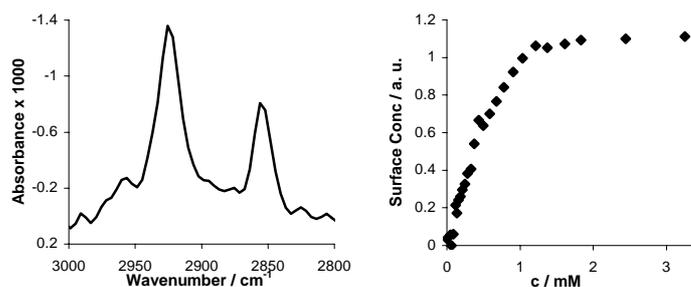


Figure 3. (left) ER-FTIR spectrum of 3.5 mM C_{16} TAB on the surface of an OFC. (right) Surface coverage of C_{16} TAB deduced by MCR of a data set of 26 raw CTAB spectra.

Both the acquisition of spectra with sufficient stability and the extraction of the surface coverage are non-trivial and we are developing multivariate curve resolution (MCR) techniques to analyse data sets. An example of the results for C_{16} TAB are shown in Figure 3. The sensitivity of the method is $<10\%$ of a monolayer for this surfactant and there is a linear relationship between the ‘weight’ of the CTAB component in the IR spectra and the surface excess determined by NR. We are currently extending these studies to binary mixtures of C_{16} TAB, APFN and $C_{10}E_8$. One publication is in press [5] and a second is in preparation.

Equations of State of Efficient Surfactants

Our work on the analysis of the adsorption kinetics of C_{16} TAB [6-8] highlighted the importance of reliable equilibrium isotherms for the analysis of kinetic data. Obtaining such isotherms for efficient surfactants (such as the C_nE_m family of non-ionic surfactants) is very difficult due to depletion effects and long equilibration times. Consequently, we realised that before we could analyse our data for the C_nE_m surfactants on the OFC, we would need a better way of determining equilibrium adsorption isotherms. The method we adopted was to equilibrate a bubble at a concentration where the surface excess was known (at or near the cmc) and then rapidly expand the bubble and measure the surface tension by drop shape analysis. By varying the expansion ratio (and hence the surface excess after expansion), we can construct an equation of state $\Gamma(\sigma)$. Lin and Maldarelli have independently proposed a similar approach, though our method of extrapolating to $t = 0$ allows measurements on solutions at much higher bulk concentrations. Our method has been published recently in *PCCP* [9].

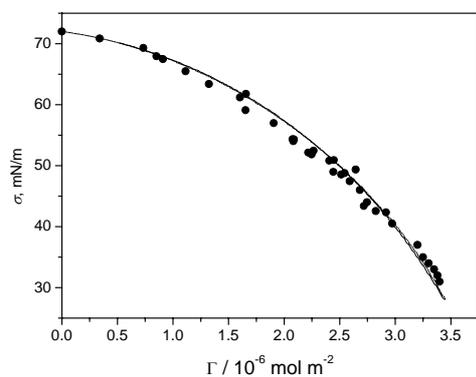


Figure 4. Equation of state for the non-ionic surfactant $C_{12}E_3$. Solid line shows a fit to a Frumkin isotherm and dotted line to a van der Waals isotherm.

Optical Tweezers

Initial experiments were undertaken at the Lasers for Science Facility at the Rutherford Appleton Laboratory to extend our studies of Marangoni effects to the oil-water interface, using pairs of oil drops trapped in oscillating optical traps (see reports to the CLF for details). We have applied successfully for access time to develop this approach further.

B. Surfactant systems

CTABs

The homologous series of C_n TAB surfactants ($n = 12-18$) was studied with and without added electrolyte. These studies addressed the effect of kinetic barriers, micellar breakdown and bulk phase mass transport on adsorption kinetics and Marangoni effects. Figure 5 shows the effect of the concentration of added NaBr on the surface expansion rate, θ , of C_{18} TAB. These results can be understood qualitatively in terms of the effect of salt on the state of aggregation in the bulk. In the absence of salt, the micelles are spherical, at 25 mM they are cylindrical and at 100 mM they are lamellar. The shape of the micelles has a dramatic effect on the mass transport of surfactant to the expanding liquid surface. The large accelerations observed at high bulk concentrations (where one might expect the surface to be saturated), even in the absence of salt, suggest that kinetic barriers and/or micelle breakdown is limiting the adsorption rate. For a quantitative analysis we will require micellar diffusion coefficients (e.g. from PFG-NMR) and micelle breakdown rates (e.g. from stopped flow): such measurements were not within the scope of this project but will form part of a forthcoming proposal.

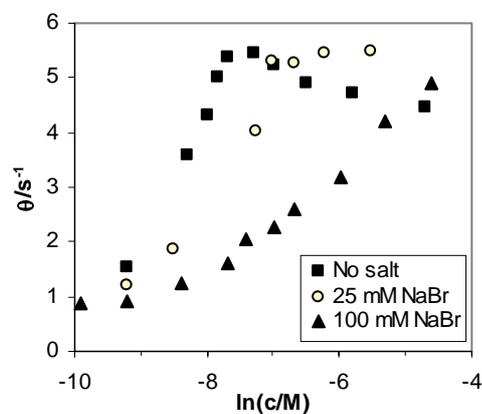


Figure 5. Effect of salt on the surface expansion rate, θ , for C_{18} TAB.

Nonionics

The homologous series of $C_{12}E_m$ surfactants ($m = 3, 4, 5, 8$) and $C_{10}E_8$ were studied by LDV and ellipsometry. An example of the ellipsometric data is shown for $C_{10}E_8$ in Figure 6, showing the quality of the data that can be obtained. Methylated nonionics $C_{10}E_4OMe$ and C_8E_4OMe were also studied, the latter in conjunction with NR. For $C_{10}E_8$, below the cmc of 1 mM, we have converted

the measured ellipticities to surface excesses and attempted to fit these values to a diffusion-controlled monomer-only model (see below). For C_8E_4OMe , $C_{12}E_5$, and $C_{12}E_8$ we have sufficient experimental data to fit to our recently developed micellar model. For $C_{12}E_3$ we will require diffusion coefficient measurements and for $C_{10}E_4OMe$ we still need to determine the adsorption isotherm.

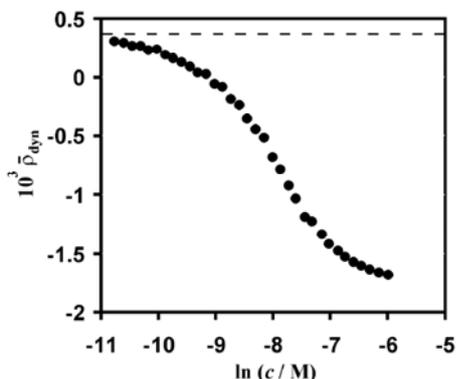


Figure 6. Coefficient of ellipticity of $C_{10}E_8$ as a function of bulk concentration in the OFC. The dotted line shows the value for pure water.

Fluorocarbons

Results for two fluorinated sulphosuccinates, di-CF4 and di-HCF6, have been described in the Final Report to GR/M83780. Last month, in our final shift at ISIS under this proposal, we acquired an excellent set of data on APFN. In the next few weeks, we will measure an equilibrium adsorption isotherm which, along with LDV data we have already, will enable us to analyse the adsorption kinetics in this (sub-micellar) system.

Other systems

Of the other systems listed in our proposal, we have a nearly complete data set on the AOT analogue, diheptyl-sulphosuccinate. There were problems with the NR measurements on this system, but we can use ellipsometry measurements to estimate the surface excess, under the assumption of a linear relationship between ρ and Γ . Linear alcohols proved problematic due to their volatility. We have also carried out some preliminary experiments on mixtures (see FTIR section above) and on polymer solutions (hydrophobically modified cellulose) to explore the utility of the OFC for studying these more complex systems.

C. Modelling of Adsorption Kinetics

Diffusion-controlled adsorption below the cmc

We first developed a diffusion-controlled model for surfactants below the cmc [6, 10], applicable to non-ionic surfactants and to ionic surfactants with and without added electrolyte. From the equilibrium adsorption isotherm, we can predict the surface excess for any bulk concentration and surface expansion rate. This value $\Gamma(\theta)$ can then be compared with the experimental values of Γ . $C_{16}TAB$, $C_{14}TAB$ and di-CF4 all showed diffusion-controlled adsorption. For $C_{12}TAB$ we studied the kinetics at fixed salt concentration and varying surfactant concentration, and fixed surfactant concentration and varying salt concentration. Agreement with a diffusion-controlled model was excellent [7].

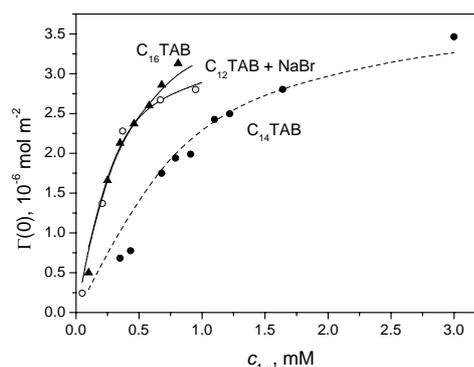


Figure 7. Experimental and theoretical values of the surface excess, on a diffusion-controlled model, for various cationic surfactants

In contrast, the adsorption of the non-ionic surfactant $C_{10}E_8$ appears not to be diffusion-controlled at any concentration at the mass transport rates studied on the OFC. This conclusion is in agreement with previous studies by Dr. Eastoe using the MBP approach.

Electrostatic barriers

We have carried out detailed modelling on the migration and diffusion fluxes within the electric double layer (EDL) in order to establish the conditions under which electrostatic barriers to adsorption might be significant [7]. We concluded that the EDL is unlikely to limit the adsorption rate for any ionic surfactants, with or without

electrolyte, except at strain rates, θ , much higher than those encountered on the OFC ($\theta \gg 10 \text{ s}^{-1}$).

Micelles

We extended the diffusion-controlled model to include micelles in the limit that the micellar break-down rate is fast on the timescale of θ^{-1} . This assumption permits an analytic solution to the mass transport equations [7]. Adsorption from $\text{C}_{14}\text{TAB} + 0.1\text{M NaBr}$ is found to be diffusion-limited both below and above the cmc. For $\text{C}_{16}\text{TAB} + \text{salt}$, the experimental surface excess is less than the diffusion-controlled prediction.

We have incorporated finite breakdown kinetics in two ways. First, in collaboration with Prof. Darton (Chem. Eng. oxford), we have implemented micelle kinetics in a finite-element CFD code within the commercial fluid modelling package FIDAP. Second, in collaboration with Drs. Howell and Breward of the Oxford Centre for Industrial and Applied Mathematics (OCIAM) we have developed asymptotic solutions to the mass transfer equations. These solutions show excellent agreement with experimental data for $\text{C}_{16}\text{TAB} + 0.1\text{M NaBr}$, with a rate constant for micelle breakdown of 20 s^{-1} [10]

D. Modelling of Marangoni Effects

The analysis of the coupled convection-diffusion problem in the OFC is greatly simplified by the separation of length scales: the diameter of the OFC is $\text{O}(10^{-1} \text{ m})$, the hydrodynamic boundary layer thickness is $\text{O}(10^{-3} \text{ m})$, the diffusion layer thickness is $\text{O}(10^{-5} \text{ m})$, the electrical double layer is $\text{O}(10^{-8} \text{ m})$ and the thickness of the monolayer is $\text{O}(10^{-9} \text{ m})$. We obtain the following relationship

$$\theta = \frac{2D(c_b - c_s)^2}{\pi\Gamma^2}$$

where c_b and c_s , are the bulk and sub-surface concentrations and D is the diffusion coefficient [6]. This equation is not sufficient to define the problem, however, since there is an infinite number of solutions with different expansion rates, θ . Breward and Howell have shown that there is a unique solution if the depth of the liquid flowing over the weir at the rim of the cylinder tends to zero. The value of $\Gamma(0)$ predicted by the model is in good agreement with experiment, even though the flow behaviour at the weir is unphysical. [11]

The problem of an undefined boundary condition (in this case, $\Gamma(0)$ at the centre of the cylinder), seems to be common to a number of problems in

free surface flows. When a surfactant solution emerges from nozzle, as in a liquid jet, Γ at the nozzle exit is similarly undefined [14].

One of our objectives is to apply insights gained from the OFC to other problems. Tiberg reported that the rate of penetration of surfactant solutions into hydrophobic capillaries was a linear function of time, in contrast to the more usual $t^{0.5}$ Lucas-Washburn behaviour. We have noted a close similarity between the fluid dynamics of capillary rise in hydrophobic capillaries and the OFC and are developing a model for capillary rise based on our understanding of the OFC. The OFC has also contributed to our understanding of drainage in foam lamellae [15].

3. Project Management and Personnel Issues

The post-doc appointed on this project, Dr. Dmitrii Styrkas, resigned after one year to take up a position in industry. A nine-month hiatus ensued before his replacement, Dr. Dimitrina Valkovska, took up employment, as a consequence of which the project was granted a nine-month extension. Dr. Valkovska was a theoretician from the group of Peter Kralchevsky at the University of Sofia. Some time was lost in training Dr. Valkovska in the experimental techniques, but her background was invaluable to the project in developing theoretical models of adsorption kinetics. Dr. Valkovska resigned three months before the end of the project to return to Bulgaria to have her baby. The funds thus freed up were used to further the objects of the project in three ways: (i) One term's support for a DPhil student, Richard Campbell, to work on FTIR spectroscopy from the surface of the OFC. (ii) One term's support for a DPhil student, Michael Weiss, to incorporate micellar break-down kinetics into a CFD model of adsorption at expanding liquid interfaces. (iii) Support for a summer student, Philip Ash, to complete some ellipsometry measurements of nonionic surfactants in an OFC and to conduct trial experiments on polymer adsorption.

Failure of surface light scattering and maximum bubble pressure equipment at Bristol in 2001 prevented the acquisition of dynamic surface tension measurements except for the fluorosurfactants di-CF4 and di-HCF6. Full details are given in Dr. Eastoe's final report on GR/M83780.

This project benefited from the input of Prof. Richard Darton (Co-PI with Dr. Bain on GR/M73194), of two undergraduate project

students (Gemma Shearman – now a PhD student at Imperial – and Graham Geary) who carried out LDV measurements on some of the cationic and nonionic surfactants, of Richard Campbell who has been developing FTIR measurements on the OFC (jointly funded by the PRF and Kodak), and of Dr. Chris Breward and Dr. Peter Howell from OCIAM, who have worked on theoretical aspects of a number of projects related to dynamic liquid interfaces. The close collaboration between chemists at Oxford and Bristol, chemical engineers and applied mathematicians has resulted in a very fruitful – and enjoyable – project.

4. Research Impact

This work has generated considerable interest in worldwide academic and industrial community. The PI has given talks on this work at the Radke Award Symposium in New Orleans, at the ACS Meeting in San Diego, in Lund, Dunedin, Melbourne and Wellington, and at numerous universities in the UK. Kodak sponsored a student on the project. We have been invited to join a major project involving a consortium of ink jet companies as a result of this work and our related work on liquid jets. The work has been presented at the YKI in Stockholm and the Ian Wark Institute in Adelaide, two of the world's leading institutes for research in surface chemistry (both largely industrially funded). The Co-investigator, Dr. Eastoe, has given numerous research presentations incorporating this work including the Surfactants in Solutions series and the ACS Colloid Meetings. The PDRA presented the work at Eurofoam 2002 and at an ESF meeting in Barcelona. Dissemination into industry has been aided by our Advisory Panel Meetings, which include representatives from ICI, Kodak and Syngenta. The work has appeared in two invited review articles [1, 8] and an invited feature article for *PCCP* is in preparation.

The OFC is helping to shape our understanding of other practical problems involving free surface flows, such as jets, foams and capillary flows.

5. Future Research

We have acquired a significant amount of data that still requires quantitative analysis, and are generating more all the time through the work of undergraduate project students. To analyse these data, we will build on our links with Dr. Valkovska and the groups of Danov and Kralchevsky in Sofia, as well as OCIAM in Oxford. It is difficult to fund the Bulgarian leg of this collaboration, since UK funding agencies do not pay salaries for overseas

collaborators and the EU no longer favours bilateral projects.

To generate a definitive understanding of adsorption kinetics in micellar solutions will require a combined experimental and theoretical effort, including PFG-NMR and stopped flow measurements, in addition to LDV, ellipsometry and isotherm measurements. This will form the basis of a future collaborative grant application.

The ideas developed in this project are being taken forward as part of a large grant proposal on 'Next Generation Ink Jet Technology', which is currently under consideration by the EPSRC. This £2.7m proposal is co-ordinated by the Institute of Manufacturing in Cambridge and involves eight companies in the ink jet industry.

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