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## General discussion

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**Prof. Scholz** opened the discussion of Dr Dagastine's paper: When you change the solution composition you will, most probably, also change the probe–solution interface. Since your organic compounds are certainly slightly soluble in the aqueous phase, there may be adsorption competition among these organics and the ions on the probe surface. Thus it may happen that you get a layer of adsorbed organic molecules on the tip surface. In that case an attractive interaction between the tip and the droplet will not be a surprise. Can you really exclude such tip surface alterations?

**Dr Dagastine** responded: All the experiments are undertaken in saturated oil solutions. Butyl acetate is slightly water soluble whereas the octyl acetate is sparingly soluble in aqueous solution. The solubility of the butyl acetate in solution is the smallest with the sodium perchlorate. If there is adsorption to the hydrophilic surface, it is more likely to occur the higher the solubility, but the attraction is observed for the case with the lowest butyl acetate solubility. Furthermore, if adsorption of the organic solute onto the silica were an issue it would be expected that it would be more significant for octyl acetate than butyl acetate, yet no difference was seen.

**Prof. Unwin** said: I have several points and questions on your paper.

1. Following on from the comments of Prof. Scholz, could you describe how you treat the quartz spheres prior to your experiments and comment on how the surface chemistry of the quartz influences the force curves you measure? For example, how would the force curves differ for the extremes of a hydrophilic sphere, pre-treated with piranha solution, and a silanised hydrophobic sphere?
2. As a related point, could you comment on whether the force curves change when you make sequential measurements?
3. It is usual to find a statistical analysis of force curves derived from AFM measurements. Could you comment on the level of uncertainty in the force curves you measure and the various parameters you derive?

**Dr Dagastine** replied: (1) and (2): The attraction observed in the system is attributed to a specific ion effect, which seems unrelated to the hydrophobicity of the silica. In this study the silica spheres were exposed to a generated ozone atmosphere for 30 min just prior to use. One could expect that if the oil was coating the silica sphere then the observed behaviour could change after the initial measurement. This may be likely for hydrophobic surfaces, but not for this case of a hydrophilic silica sphere as discussed in the response to the previous question. Each force measurement is taken independently from the rest, sequential measurements do not exhibit large variations in force behaviour.

Although unrelated to the measurements presented in our paper we have included a review of the body of previous force measurements between rigid spherical particles and *either* oil droplets *or* bubbles where the hydrophobicity of the probe was modified. The first measurement of a particle between a deformable air–water interface with an AFM by Ducker *et al.* in 1994<sup>1</sup> varied the hydrophobicity of the silica probe, along with several other subsequent studies by Fielden *et al.*<sup>2</sup> and Presuss *et al.*<sup>3,4</sup> In Ducker's study the hydrophilic surface was exposed to water plasma and hydrophobic particles were created by chemisorbing a self-assembled monolayer of octadecyltrichlorosilane resulting with a water contact angle near 115°. For the hydrophilic case, the force behaviour exhibited a short-range attraction attributed to an attractive electrostatic double layer (EDL) force with a constant surface potential. The force behaviour with the hydrophobic silica exhibited a traumatic attractive jump-in before any EDL forces were observed. Also, upon addition

of anionic surfactant, these long-range attractions were no longer observed and EDL repulsion was observed. The hydrophobic interactions in these systems have led to estimations of the contact angle at the three phase contact line of bubble with the particle. Furthermore, a study by Yakubov *et al.*<sup>5</sup> used hydrophobic polystyrene microspheres interaction with an air bubble to probe the effects of line tension on the wettability with water.

The bubble particle interactions have repulsive van der Waals, but similar behaviour has been observed between rigid spherical particles and oil droplets. Mulvaney *et al.*<sup>6</sup> and Hartley *et al.*<sup>7</sup> performed measurements between hydrophilic silica and alkanes in inorganic electrolyte solutions. A DLVO force behaviour was observed with an EDL repulsion followed by a short-range attraction from van der Waals forces. Upon adsorption of surfactant onto the alkane-solution interface attraction was no longer observed. Aston and Berg have also observed long range attractions, attributed to hydrophobic force for the interaction between either polystyrene beads or silanated glass spheres and hexadecane droplets in aqueous solutions.<sup>8,9</sup> Again with the addition of surfactant these long range attractions were mediated or removed.

(3) The question of statistically significant atomic force microscopy measurements can sometimes have an ambiguous interpretation. Most studies, including this one, employ hundreds of individual force curve measurements. While this is a large number of measurements, it is by no means statistically significant if one takes into account the actual surface area probed on a given sample. The interaction area probed is several hundred square nanometers on a single sample that is a square centimetre. Perhaps several different samples are repeated, but this is still a small population to examine. To add to this complication is that force measurements with an AFM do not necessarily measure large ensemble averages of molecules. As an example, AFM is commonly used to measure the interactions of single molecules.<sup>10-12</sup> It is crucial that AFM investigations report all force behaviours observed, not just the one the investigators may deem statistically significant.

In this study, each type of experiment was repeated on a number of different occasions with different spheres, substrates and new solutions. The variability in the force data is within 10–20%, which is comparable to the error in determination of the cantilever spring constant.

- 1 W. A. Ducker, Z. G. Xu and J. N. Israelachvili, *Langmuir*, 1994, **10**, 3279.
- 2 M. L. Fielden, R. A. Hayes and J. Ralston, *Langmuir*, 1996, **12**, 3721.
- 3 M. Preuss and H.-J. Butt, *Langmuir*, 1998, **14**, 3164.
- 4 M. Preuss and H.-J. Butt, *J. Colloid Interface Sci.*, 1998, **208**, 468.
- 5 G. E. Yakubov, O. I. Vinogradova and H.-J. Butt, *J. Adv. Sci. Tech.*, 2000, **14**, 1783.
- 6 P. Mulvaney, J. M. Perera, S. Biggs, F. Grieser and G. W. Stevens, *J. Colloid Interface Sci.*, 1996, **183**, 614.
- 7 P. G. Hartley, F. Grieser, P. Mulvaney and G. W. Stevens, *Langmuir*, 1999, **15**, 7282.
- 8 D. E. Aston and J. C. Berg, *J. Colloid Interface Sci.*, 2001, **235**, 162.
- 9 D. E. Aston and J. C. Berg, *Ind. Eng. Chem. Res.*, 2002, **41**, 389.
- 10 V. T. Moy, E.-L. Florin and H. E. Gaub, *Science*, 1994, **266**, 257.
- 11 M. Rief, F. Oesterhelt, B. Heymann and H. E. Gaub, *Science*, 1997, **275**, 1295.
- 12 C. Friedsam, M. Seitz and H. E. Gaub, *J. Phys: Condens. Matter*, 2004, **16**, S2369.

**Prof. Hampe** asked: When considering the interaction between two liquid phases and a solid phase as has been done in the AFM experiments of Dagastine *et al.*, the question of wettability and contact angle springs into mind. *E.g.*, the phenomenon named ‘jump-in’ should have a correspondence in the complete wettability of the solid by one of the liquid phases. Have the contact angles of the systems been measured? And if so, what is the interpretation of the contact angle data in view of the AFM experiments?

**Dr Dagastine** answered: The question of wettability is certainly relevant to the behaviour of force curves as mentioned in the responses to Prof. Unwin, but this question actually brings two separate points together. The first is what causes “jump-in” and the second is what happens once “jump-in” has occurred and how does this relate to wettability. The force measurement up to the point of “jump-in” is an equilibrium measurement where a description of the interaction force between the drop and the particle is sufficient to understand the force behaviour. The origin of jump-in is from an attractive surface force such that the gradient of the force is equal to the spring constant of the cantilever. This attractive force may be a macroscopic van der Waals force, which is attractive in this system; it could also be the result of a charge reversal or charge regulation in the electrostatic

double layer force. Both of these behaviours may not correspond to the wettability of the particle. For the hydrophobic force, where the mechanism and the origins of the force are not completely understood, this may correspond to the wettability behaviour of the system.<sup>1</sup> Thus, jump-in is not necessarily related to wetting. Also, the state after jump-in may not completely wet the particle. As mentioned above, the results of Ducker,<sup>2</sup> Fielden,<sup>3</sup> Preuss<sup>4,5</sup> and Yakubov<sup>6</sup> show that in some cases complete engulfment occurs and in others finite contact angles are measured from the formation of three phase contact lines. Another possibility pointed out from modelling by Bhatt *et al.*<sup>7</sup> and Dagastine and White<sup>8</sup> shows that if there are primary and secondary minima in the disjoining pressure, jump-in can take place between these minima, where the probe jumps from one attractive region to an inner repulsive one, where the two surfaces are not in contact.

1 J. N. Israelachvili, *Intermolecular and Surface Forces*, Academic Press, New York, 1992.

2 W. A. Ducker, Z. G. Xu and J. N. Israelachvili, *Langmuir*, 1994, **10**, 3279.

3 M. L. Fielden, R. A. Hayes and J. Ralston, *Langmuir*, 1996, **12**, 3721.

4 M. Preuss and H.-J. Butt, *Langmuir*, 1998, **14**, 3164.

5 M. Preuss and H.-J. Butt, *J. Colloid Interface Sci.*, 1998, **208**, 468.

6 G. E. Yakubov, O. I. Vinogradova and H.-J. Butt, *J. Adv. Sci. Tech.*, 2000, **14**, 1783.

7 D. Bhatt, J. Newman and C. J. Radke, *Langmuir*, 2001, **17**, 116.

8 R. R. Dagastine and L. R. White, *J. Colloid Interface Sci.*, 2002, **247**, 310.

**Prof. Schlossman** asked: Have you considered the relevance of elastic properties of the interface (*e.g.*, bending moduli, viscosity) on the description of the jump-in process?

**Dr Dagastine** replied: The question raises a good point about the dynamic process during jump-in, however this is irrelevant to whether jump-in is observed *or* the origins of the non-DLVO attraction observed in the paper. As mentioned in a previous response: “The force measurement up to the point of “jump-in” is an equilibrium measurement where a description of the interaction force between the drop and the particle is sufficient to understand the force behaviour. The origin of jump-in is from an attractive surface force such that the gradient of the force is equal to the spring constant of the cantilever.”

The description of the force measurement stops at the point of jump-in. The conditions to achieve jump-in are determined by the equilibrium interaction forces and the cantilever spring constant, but once the mechanical instability in the cantilever is reached this becomes a dynamic process. One would speculate that any time dependent phenomenon of the interface (*i.e.* interfacial rheological response, bulk viscosity, *etc.*) may contribute to the behaviour during the jump-in process.

**Prof. Rusling** asked: Is it possible to change the size of your particle probe into the nanometer range, and if so what would you expect the size effects to show?

**Dr Dagastine** replied: It is possible to change the probe radius to one-micron with standard particle attachment methods, but controlling the position of attachment with smaller particles can be difficult since most methods employ optical microscopy. It is likely that these difficulties could be overcome through novel attachment methods or new methods to micromanipulate particles. Using smaller particles may raise other issues not as relevant for larger particles. The spherical probe is used to provide well-defined geometry and a surface that is easy to characterize in contrast to an AFM tip, which is a much smaller dimension but the tip geometry can be irregular and difficult to characterize. The larger interaction area also provides an increased sensitivity if one scales by the interaction area or sphere radius. Another issue is that probes on the micron scale typically have surface roughness on the order of less than a nm for silica or 10 to 15 nm for polymer microspheres.<sup>1</sup> As the probe size scales down, the surface roughness does not necessarily scale with radius, thus for small particles the geometry may not be as well defined.

To speculate on how the force behaviour would change with size, one could employ the Derjaguin approximation<sup>2</sup> for a sphere and plate

$$F(D) = 2\pi aE(D)$$

where  $a$  is the radius of the probe and  $E$  is the interaction between flat surfaces. The overall magnitude and range of the force decrease with the interaction area. To respond to the comment by

Dr Liggieri, the above expression shows how the surface energy scales with radius for a solid liquid interface.

One can speculate on aspects unique to the measurement of liquid–liquid systems as well. The radial component of the force for this interaction scales by roughly the  $\sqrt{aD_o}$  where  $D_o$  is the intersurface separation, thus the interaction area is dependent on both intersurface separation and the probe geometry.<sup>3</sup> The closest approach of the probe will change as well. As mentioned in the paper, wrapping occurs for a number of these systems where only repulsion between the oil drop and the particle is observed. The pressure at which wrapping occurs is given by

$$\Pi(D_w) = 2\gamma\left(\frac{1}{a} + \frac{1}{R_o}\right)$$

where there is an inverse relation to the probe radius. With very small probe geometries, say 200 nm in radius, the wrapping pressure would occur at a much smaller separation. As discussed in the paper, if the wrapping thickness is smaller than the length scale of the ever-present van der Waals attraction, then it is likely that jump-in instead of wrapping would be observed.<sup>4</sup>

1 R. F. Conside, R. A. Hayes and R. G. Horn, *Langmuir*, 1999, **15**, 1657.

2 R. J. Hunter, *Foundations of Colloid Science*, Clarendon Press, Oxford, 1995.

3 D. Y. C. Chan, R. R. Dagastine and L. R. White, *J. Colloid Interface Sci.*, 2001, **236**, 141.

4 R. R. Dagastine and L. R. White, *J. Colloid Interface Sci.*, 2002, **247**, 310.

**Dr Horozov** asked: The jump-in or wrapping cases are related to the stability of the water film between the probe and oil drop.

Did you measure the stability of water films in a similar system *e.g.*, silica plates in water and approaching oil drops?

**Dr Dagastine** replied: The question is correct in that the wrapping or jump-in behaviour is dependent on the stability of the water film. The governing forces behind the film stability are primarily surface forces and interfacial tension. As discussed above, the conditions for wrapping (given in previous responses) are based on the presence of a sufficiently strong repulsion coupled with a sufficiently pliable interface, such that the liquid–liquid interface begins to reflect the curvature of the rigid probe. The wrapping separation or film thickness must be larger than the length scale of the attractive forces in the system, otherwise the probe and liquid–liquid interface jump-in and the stable film is not formed. Theoretical studies have shown that if the interaction forces are constant only changes in the interfacial tension can cause a transition from jump-in to wrapping as the interfacial tension is significantly decreased.<sup>1</sup>

The suggested film stability experiments are a considerably different physical situation where the radial length scale is orders of magnitude larger. For example, scanning angle ellipsometry measurements of oil droplets approaching a flat silica surface have a radial length scale on the order of tens of microns.<sup>2–4</sup> Studies using a modified SFA and a mercury drop approaching a flat silica plate also have a much larger radial length scale.<sup>5–8</sup> More classical experiments including the Scelkudo–Exerowa cell to examine thin film stability for foams have radial films on the order of millimetres.<sup>9</sup> The radial length scale of the “wrapping films” in the AFM measurement is on the order of  $\sqrt{aD_w}$  where  $D_w$  is the wrapping thickness. For these experiments this is on the order of 100 nm in the radial direction.

All of the film stability experiments mentioned above have hydrodynamic components and formation of barrier rings during drainage due to the larger radial length scale. The AFM measurements are equilibrium force measurements, thus hydrodynamic drainage effects are not observed and the force behaviour is independent of approach speed.

A comparison between the AFM measurements and the film stability experiments can be drawn for equilibrium behaviour. The equilibrium film in the stability measurements provides a measure of the disjoining pressure curve between a silica surface and liquid–liquid interface at a *single* separation. The thickness is measured very accurately and the disjoining pressure is estimated or calculated.<sup>3–4</sup> This is in contrast to the AFM experiment, where the applied force is varied and the *entire* disjoining pressure curve can be measured. There is the opportunity to compare this one point

disjoining pressure measurement to the AFM results which we are currently carrying out in parallel studies using AFM and scanning angle ellipsometry on the same oil system.

- 1 R. R. Dagastine and L. R. White, *J. Colloid Interface Sci.*, 2002, **247**, 310.
- 2 D. G. Goodall, M. L. Gee and G. W. Stevens, *Langmuir*, 2001, **17**, 3784.
- 3 D. G. Goodall, G. W. Stevens, D. Beaglehole and M. L. Gee, *Langmuir*, 1999, **15**, 4579.
- 4 D. G. Goodall, M. L. Gee, G. Stevens, J. Perera and D. Beaglehole, *Colloids Surf., A*, 1998, **143**, 41.
- 5 J. N. Connor and R. G. Horn, *Langmuir*, 2001, **17**, 7194.
- 6 J. N. Connor and R. G. Horn, *Rev. Sci. Instrum.*, 2003, **74**, 4601.
- 7 J. N. Connor and R. G. Horn, *Faraday Discuss.*, 2003, **123**, 193.
- 8 J. N. Connor, R. G. Horn and S. J. Miklavcic, *Uzbek J. Phys.*, 1999, **1**, 99.
- 9 A. Scheludko and D. Exerowa, *Kolloid Z.*, 1959, **165**, 148.

**Dr Sakoguchi** asked: I'm very interested in complex formation reaction at the liquid–liquid interface. What do you think about the possibility of using your technique in order to obtain information about the molecular structure at the liquid–liquid interface?

**Dr Dagastine** replied: A number of contributions in this discussion have shown excellent examples of how spectroscopic and novel physical chemistry methods can probe the orientation and structure of molecules at the liquid–liquid interface. The measurements of interaction forces with colloidal probe microscopy are very sensitive to the presence and structure of molecules at the liquid–liquid interface, but do not probe the molecular structure directly compared to spectroscopic methods. Colloidal probe microscopy at the liquid–liquid interface provides a method to develop quantitative correlations between the observed force behaviour and the molecules adsorbed at the interface or present in solutions. This type of structure–function relation can then be used effectively in understanding and controlling coalescence phenomena. The AFM measurement coupled with spectroscopic techniques may be an approach to probe both the interaction forces and molecular structure simultaneously.

**Prof. Unwin** asked: Have you considered using AFM to probe the potential distribution at liquid/liquid interfaces under electrochemical control, using either partitioning ions or an external source to control the potential across the liquid/liquid interface?

**Dr Dagastine** replied: We have not considered this, but it seems likely it could provide some insight into the behaviour observed in these systems. For the paper presented in this discussion the technique might create an added complexity since the observed force behaviour is dependent on the type of ion present. This type of approach has been used in the modified SFA with a mercury droplet,<sup>1,2</sup> but this has not been adapted to AFM for liquid–liquid interfaces.

- 1 J. N. Connor and R. G. Horn, *Langmuir*, 2001, **17**, 7194.
- 2 J. N. Connor and R. G. Horn, *Rev. Sci. Instrum.*, 2003, **74**, 4601.

**Prof. Girault** asked:  $\text{NaClO}_4$  will distribute to the organic more than  $\text{NaNO}_3$ . Therefore, the liquid/liquid interface will be changed according to the distribution.

Did you take that into account in your model?

**Dr Dagastine** responded: The model used in the paper presented for the electrostatic double layer force was the full numerical solution to the Poisson–Boltzmann equation between flat plates in aqueous solution using the numerical methods of Chan *et al.*<sup>1</sup> This model does not take into account ion size, the width of the interface, or the distribution of ions in the organic phase. The motivation behind using the less complicated model is based on several reasons. First, this modelling approach has proved successful with the force measurements between alkane with and without the addition of surfactant,<sup>2–4</sup> where all of the model input parameters were measured independently.<sup>5</sup> The separation distances encountered in most of the force measurements are in the region where the EDL force is expected to follow an exponential behaviour.

Since the force behaviour observed is dependent on the type of ion present, it seems plausible that some additional information may need to be included in the treatment of the electrostatic double

layer forces. It is also important to note, that varying the surface potential or charge by twenty to thirty percent did change the qualitative trends in the model predictions. This would imply that if there were a deviation from the expected EDL force behaviour it must be significant and not just a small perturbation to the surface charge or potential.

- 1 D. Y. C. Chan, R. M. Pashley and L. R. White, *J. Colloid Interface Sci.*, 1980, **77**, 283.
- 2 P. G. Hartley, F. Grieser, P. Mulvaney and G. W. Stevens, *Langmuir*, 1999, **15**, 7282.
- 3 S. A. Nespolo, D. Y. C. Chan, F. Grieser, P. G. Hartley and G. W. Stevens, *Langmuir*, 2003, **19**, 2124.
- 4 R. R. Dagastine, D. C. Prieve and L. R. White, *J. Colloid Interface Sci.*, 2004, **269**, 84.
- 5 S. A. Nespolo, M. A. Bevan, D. Y. C. Chan, F. Grieser and G. W. Stevens, *Langmuir*, 2001, **17**, 7210.

**Prof. Girault** asked: Why so few experiments with scanning probes?

**Dr Dagastine** replied: Over the last eight years scanning probe microscopy has been effective at measuring the interaction forces at liquid–liquid interfaces with colloidal probe AFM<sup>1–9</sup> as well as measuring the interaction forces between two oil droplets in aqueous solution.<sup>10</sup> One of the main complications using a scanning probe method is interfacial deformation creates difficulties in analysis and interpretation. There are a number of studies dedicated to just the analysis of the colloidal probe–liquid droplet experiment.<sup>8,9,11–16</sup> As mentioned in a response previously, colloidal probe microscopy at the liquid–liquid interface has been a useful method to develop quantitative correlations between the observed force behaviour and the molecules adsorbed at the interface or present in solution. There have also been a few imaging studies, but again droplet deformation gives rise to interpretation difficulties.<sup>17,18</sup> As the technological aspects of the scanning probe microscope improve, such as closed loop feedback in piezoelectric scanners and faster imaging times incorporated into commercial instruments, studies may become more common. Also, near field scanning optical microscopy (NSOM) can provide methods to perform spectroscopy on smaller length scales compared to traditional techniques.<sup>19</sup> NSOM can operate in a non-contact mode using light as the feedback signal, thus it may circumvent some of the difficulties encountered in AFM from interfacial deformation. The study of living cellular systems is an area with ever-increasing use of scanning probe methods.<sup>20</sup> This has also led to integration of AFM with a variety of methods including fluorescent microscopy, laser scanning confocal microscopy and some spectroscopy methods.<sup>20</sup> These studies range from very soft mammalian cells to more rigid bacteria and plant cells. If one expands the definition of a liquid–liquid interface to include a lipid bilayer, then there are a large number of experiments using scanning probe methods. It was unfortunate that there was virtually no representation at this discussion from the biophysics or physical chemistry communities using scanning probe methods with biological systems.

- 1 P. Mulvaney, J. M. Perera, S. Biggs, F. Grieser and G. W. Stevens, *J. Colloid Interface Sci.*, 1996, **183**, 614.
- 2 B. A. Snyder, D. E. Aston and J. C. Berg, *Langmuir*, 1997, **13**, 590.
- 3 P. G. Hartley, F. Grieser, P. Mulvaney and G. W. Stevens, *Langmuir*, 1999, **15**, 7282.
- 4 D. E. Aston and J. C. Berg, *Ind. Eng. Chem. Res.*, 2002, **41**, 389.
- 5 D. E. Aston and J. C. Berg, *J. Colloid Interface Sci.*, 2001, 235, 162.
- 6 G. Gillies, C. A. Prestidge and P. Attard, *Langmuir*, 2002, **18**, 1674.
- 7 G. Gillies and C. A. Prestidge, *Adv. Colloid Interface Sci.*, 2004, **108–109**, 197.
- 8 S. A. Nespolo, D. Y. C. Chan, F. Grieser, P. G. Hartley and G. W. Stevens, *Langmuir*, 2003, **19**, 2124.
- 9 R. R. Dagastine, D. C. Prieve and L. R. White, *J. Colloid Interface Sci.*, 2004, **269**, 84.
- 10 R. R. Dagastine, G. W. Stevens, D. Y. C. Chan and F. Grieser, *J. Colloid Interface Sci.*, 2004, **273**, 339.
- 11 D. Y. C. Chan, R. R. Dagastine and L. R. White, *J. Colloid Interface Sci.*, 2001, **236**, 141.
- 12 D. Bhatt, J. Newman and C. J. Radke, *Langmuir*, 2001, **17**, 116.
- 13 R. R. Dagastine and L. R. White, *J. Colloid Interface Sci.*, 2002, **247**, 310.
- 14 P. Attard and G. Gillies, *Aust. J. Chem.*, 2001, **54**, 477.
- 15 G. Gillies, C. A. Prestidge and P. Attard, *Langmuir*, 2001, **17**, 7955.
- 16 P. Attard and S. J. Miklavcic, *J. Colloid Interface Sci.*, 2002, **247**, 255.
- 17 S. D. A. Connell, S. Allen, C. J. Roberts, J. Davies, M. C. Davies, S. J. B. Tendler and P. M. Williams, *Langmuir*, 2002, **18**, 1719.
- 18 A. P. Gunning, A. R. Mackie, P. J. Wilde and V. J. Morris, *Langmuir*, 2004, **20**, 116.
- 19 A. Lewis, H. Taha, A. Strinkovski, A. Manevitch, A. Khachatourians, R. Dekhter and E. Ammann, *Nature Biotechnol.*, 2003, **21**, 1378.
- 20 R. M. Henderson, *J. Cell Sci.*, 2003, **116**, 761.

**Dr Bain** opened the discussion of Dr Liggieri's paper: Maldarelli and Liu have argued for a phase transition model in more hydrophobic members of the  $C_iE_j$  surfactants. You have used a re-orientation model. How would a phase transition manifest itself in your rheological measurements?

**Dr Liggieri** replied: Maldarelli and Liu argued for the formation of small aggregates (dimers, trimers, *etc.*).

The characteristic time associated with such transitions should be very short. Thus, in that case we would expect a system behaving according to the Lucassen–Van der Tempel (diffusion controlled relaxation) model. The phase transition should, however, influence the isotherm, and thus  $\varepsilon_0$ .

In a previous paper we have modelled the rheological behaviour of an adsorption layer presenting a surface phase transition from small to large aggregates, coupled to diffusional exchange.<sup>1</sup> Large aggregates were assumed to form above a critical surface pressure. The model predicts, in particular, the appearance of a discontinuity in the module of the surface visco-elasticity,  $|e|$ , at the critical surface pressure, due to the different packing of the molecules inside the aggregates.

The model has been successfully applied to explain/interpret the surface rheological behaviour of *n*-dodecanol adsorbed at water–air,<sup>2</sup> allowing kinetic and equilibrium parameters to be estimated.

1 R. Palazzolo, F. Ravera, M. Ferrari and L. Liggieri, *Langmuir*, 2002, **18**, 3592.

2 L. Liggieri, F. Ravera and M. Ferrari, *Langmuir*, 2003, **19**, 10233.

**Dr Cicuta** asked: Two experimental techniques are used, to give results over a wide frequency range. Could you comment on how you match the experimental conditions in the two set-ups, for example is the strain deformation the same? I see that in most cases the matching is very good, but in Fig. 9 of your paper, it seems less satisfactory.

**Dr Liggieri** replied: Both utilised methods rely on the linear response of the system for small area perturbations. Thus in the two set-ups we apply area variations of relative amplitude smaller than 0.2. In this range, in fact, the measured visco-elasticity is nearly independent of the relative perturbation amplitude. The two methods are however affected by different experimental errors which may cause some mismatch. For the elasticity measured by the capillary pressure tensiometer the error can be evaluated on the order of  $\text{mN m}^{-1}$ , which is compatible with the data reported in Fig. 9 of our paper.

**Prof. Unwin** asked: Eqn. (9) of your paper, which you used to fit your dynamic data, contains many variables, some of which you can obtain from equilibrium measurements. Nonetheless, you appear to derive three parameters from your dynamic measurements: the diffusion coefficient in solution; the reorientation rate; and the intrinsic surface viscosity. Could you comment on the precision with which these model-dependent parameters can be obtained using this method? I ask this partly because some of the diffusion coefficients appear high. For example, the value for the diffusion coefficient of  $C_{12}E_{23}$  in water of  $9.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$  is what one might expect for a small molecule rather than a surfactant.

**Dr Liggieri** replied: In Table 2 the values of diffusion coefficients obtained from the elasticity data ( $D$ ), are compared with those ( $D_{\text{adk}}$ ) obtained by applying the Ward–Tordai model to experiments of adsorption kinetics at fresh interfaces (see Fig. 8 of our paper). For  $C_{10}E_5$  and  $C_{10}E_8$  the values agree within about  $2 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ . Assuming  $D$  to scale as the square root of the molecular weight, these values are also consistent with those measured by PFGSE-NMR (see for example, B. Faucompre *et al.*)<sup>1</sup>

The reported value for  $C_{12}E_{23}$  is actually larger than those of  $C_{10}E_8$  and  $C_{10}E_5$ , which is in contrast with its larger molecular weight. As stressed in the text, commercial  $C_{12}E_{23}$  samples were utilised, which may contain smaller  $C_iE_j$ 's and low molecular weight impurities, justifying the observation of a larger value of  $D$ . For this surfactant the value of  $D_{\text{adk}}$  is missing since the quality of results from adsorption kinetics experiments is very poor due to the strong surface activity of this surfactant.

Error estimation on parameters obtained by best-fit of multi-parametric systems is very difficult to give. The method provides anyway at least the order of magnitude of the re-orientation rate. The estimated value is probably much more accurate than when it is found independently of the surfactant concentration, as for example for C<sub>10</sub>E<sub>5</sub>.

1 B. Faucompre and B. Lindman, *J. Phys. Chem.*, 1987, **91**, 383.

**Dr Bain** asked: The rate constants,  $\nu_{\text{or}}$ , for reorientation of the surfactants are O( $10^2 \text{ s}^{-1}$ ), which is 6 orders of magnitude slower than equilibration times for surfactant monolayers in MD and MC simulations, for low surface coverages. What is the nature of the collective motions of the surfactant that gives rise to such (relatively) slow dynamics?

**Dr Liggieri** replied: A possible explanation for a collective behaviour could arise from the circumstance that, according to the physical view of the two-state model, the adsorbed molecules are highly packed already at rather low surface pressures. In fact, at small adsorption, molecules are allowed to adsorb in a status with high molar area. Thus, assuming for example the isotherm parameters for C<sub>10</sub>E<sub>5</sub> in Table 1, at the surface pressure of 5 mN m<sup>-1</sup>, corresponding to a bulk concentration of about 10<sup>-9</sup> mol cm<sup>-3</sup>, one finds already a surface coverage,  $\omega\Gamma$ , of about 0.8.

According to this view one should find larger values of the rate constant,  $\nu_{\text{or}}$ , in the range of very low surface pressures (say below 5 mN m<sup>-1</sup>). This range involves however very low bulk concentration and a vanishing rheological response, which makes these investigations nearly impossible.

**Dr Bain** commented: The reorganisation processes observed by Dr Liggieri and by other workers occur on timescales of milliseconds. Molecular simulations of surfactant layers typically equilibrate in nanoseconds, at least for systems that are not too dense. The nature of the collective processes that give rise to the slow reorganisation kinetics in surfactant monolayers remain a mystery and are a challenge for both simulators and experimentalists, since the timescales are long even for coarse-grained simulations and short for most spectroscopic or structural probes

**Dr Liggieri** responded: A possible justification for the occurrence of a collective behaviour assuming a two-state like model has been given in the previous answer to Dr Bain.

I agree that efforts should be made, in particular as far as simulation is concerned, to clarify these mechanisms.

Moreover, some “direct” optical techniques for adsorption investigation (ellipsometry, SHG) are probably mature enough to be applied to the highly dynamic situations related to surface rheology studies.

**Prof. Rathman** opened the discussion of Dr Mitani’s paper: The method involves deforming the interface, so that the interfacial area in the measurement region increases and decreases with the oscillations of the laser. When surfactants are adsorbed at the interface, the oscillation is probably so rapid that the surfactant does not have time to desorb and re-adsorb during each oscillation cycle; thus, the interfacial tension would not be constant. Even though oscillations are relatively small (< 10 nm amplitude) the change in surfactant surface concentration (molecules area<sup>-1</sup>) could be significant, and so the changes in interfacial tension would be significant.

**Dr Mitani** responded: In our experiments, we disregard the effect of the change of the surface density of the surfactant on the interfacial tension when the interface is deformed. The reason is that the density of the surfactant on the interface is low such as a gas, and the surfactant molecules can move freely on the surface, while they are limited to coming and going between the surface and the bulk. Therefore the small deformation of the interface does not change the interfacial tension, even when the modulation frequency of the interface is ~ 1 kHz. If the motion of the surfactant on the surface is limited, we can get the surface tension safely from the experimental spectrum by adding the elasticity term to the dispersion relation (eqn. (2.9) of our paper).

**Prof. Kornyshev** asked: Does your effect depend on polarization of incident light?

**Dr Mitani** replied: Because we used the optically isotropic liquids as the specimens and the pump laser penetrates the interface perpendicularly, the change of the light momentum at the interface is independent of the polarization of the pump light. If you measure the surface of a non-isotropic liquid such as a liquid crystal, the result would depend on the polarization of the pump light.

**Dr Liggieri** asked: The laser beam causes locally a heating of the interface. Has any effect been observed due to that local temperature increase?

**Dr Mitani** replied: Actually we observed that the interface deformed larger than the expected value in the LIM method when we used a pump laser of large intensity. We believe the cause of this to be the thermal expansion of the liquid on absorbing the pump light. Therefore we keep the intensity as low as possible in the measuring process. In addition, we measure the spectrum of the interface response, that is to say the time-dependent deformation. The liquid interface spends more time on expanding thermally than on deforming by light force, and we can divide the deformation caused by changing the light momentum and by heating. Accordingly we ignore the heating effect of the laser on the interfacial tension.

**Dr Grayeff** asked: Does Dr Mitani consider that the type of the initial standard water utilised in electrochemical experimental work is significant: different types of deionised water may contain different ionic ratios?

Comment:

(1) When an aqueous medium grade vermiculite solution is electrometrically measured the pH of the water (in this case tap water) can vary due to the ionic content of the water.

1 See Mitani's paper, Section A.

2 I. Lin, M. V. Smalley and S. G. Grayeff, *Overview of Vermiculite Modifications*, The Civil Engineering, Dept., The Technion.

**Dr Mitani** responded: In our experiments, we used distilled water without additional ions. The section A in our paper is the summary of our previous work, ref. 4 (of our paper), and we did not mention in detail the materials used in the experiments. As shown in section B, the concentration of ionic molecules in water such as surfactant or NaCl may easily change the surface or interfacial tension.

**Prof. Penfold** opened the discussion of Dr Zarbakhsh's paper: The results for the adsorption of C<sub>14</sub>TAB at the hexadecane–water interface is surprising for 3 reasons:

(i) We know from neutron reflectivity studies<sup>1</sup> that at the c.m.c. common small molecule surfactants adsorb at the air–water interface as a monolayer, and we have demonstrated this specifically for C<sub>14</sub>TAB.<sup>2</sup> Sub-surface ordering of micelles is observed, but at much larger concentrations  $\gg$  10 times the c.m.c.<sup>3</sup> Furthermore, in this regime of concentration micellar ordering has been predicted from computer simulations by Smit *et al.*,<sup>4</sup> at the oil–water interface.

(ii) The total amount of C<sub>14</sub>TAB at the hexadecane/water interface (85 to 124 Å<sup>2</sup>) is low compared to what is measured at the air–water interface ( $\sim$ 45 Å<sup>2</sup> at the c.m.c.<sup>2</sup>). We have directly compared the adsorption of SDS at the air–water interface by neutron reflectivity<sup>5</sup> and at the hexadecane–water interface by SANS from SDS stabilised hexadecane in water emulsion.<sup>7</sup> From these measurements we observe rather similar amounts of adsorption at saturation at the two interfaces.

(iii) The thickness of the adsorbed layer is low compared to the surfactant chain length, and we have observed similar thicknesses for SDS.<sup>6</sup> However, this is in contrast to what is observed in slightly different circumstances. Lu *et al.*,<sup>7</sup> have measured the adsorption and structure of a cationic surfactant monolayer at the air–water interface to which dodecane is added (adsorbed) within the monolayer to saturation. (This can be considered as a nascent liquid–liquid interface). In this case the addition of the dodecane resulted in a larger alkyl chain thickness being measured for the cationic surfactant.

1 J. R. Lu, R. K. Thomas and J. Penfold, *Adv. Colloid Interface Sci.*, 2000, **84**, 143.

- 2 (a) E. A. Simister, E. M. Lee, R. K. Thomas and J. Penfold, *J. Phys. Chem.*, 1992, **96**, 1373; (b) E. A. Simister, R. K. Thomas, J. Penfold, R. Avegard, B. P. Binks, P. Cooper, P. D. I. Fletcher, J. R. Lu and A. Sokolowski, *J. Phys. Chem.*, 1992, **96**, 1383.
- 3 (a) J. R. Lu, E. A. Simister, R. K. Thomas and J. Penfold, *J. Phys. Chem.*, 1993, **97**, 13907; (b) E. M. Lee *et al.*, *J. Phys.*, 1989, **7**, 75; (c) E. M. Lee *et al.*, *Colloid Polym. Sci.*, 1990, **82**, 99.
- 4 (a) B. Smit, P. A. J. Hilbers, K. Esselink, L. A. M. Rupert, N. M. van Os and A. G. Schlijper, *J. Phys. Chem.*, 1991, **95**, 6361; (b) B. Smit, P. A. J. Hilbers, K. Esselink, L. A. M. Rupert, N. M. van Os and A. G. Schlijper, *Nature*, 1990, **348**, 624.
- 5 J. R. Lu, A. Marrocco, T. J. Su, R. K. Thomas and J. Penfold, *J. Colloid Interface Sci.*, 1993, **158**, 303.
- 6 E. Staples, J. Penfold and I. Tucker, *J. Phys. Chem. B*, 2000, **104**, 606.
- 7 (a) J. R. Lu, R. K. Thomas, R. Aveyard, B. P. Binks, P. Cooper, P. D. I. Fletcher, A. Sokolowski and J. Penfold, *J. Phys. Chem.*, 1992, **96**, 10971; (b) J. R. Lu, R. K. Thomas, B. P. Binks, P. D. I. Fletcher and J. Penfold, *J. Phys. Chem.*, 1995, **99**, 4113; (c) J. R. Lu, Z. X. Li, R. K. Thomas, B. P. Binks, D. Crichton, P. D. I. Fletcher, J. R. McNab and J. Penfold, *J. Phys. Chem.*, 1998, **102**, 5785.

**Dr Zarbakhsh** replied: We believe a single layer model does not fully describe our data. A single layer model does indeed give a low adsorbed amount, however, a two layer model yields a comparable adsorbed amount to that found at the air–water interface.

It may be possible that the monolayer oil experiment may not represent a true bulk oil/water interface.

**Dr Leermakers** asked: When equilibrating the system, surfactants may travel through the oil to the SiO<sub>2</sub> surface. Does this occur and is the surfactant pool in the interface sufficiently large to account for this loss of surfactant? In other words is the surfactant adsorption at the oil–water interface still in equilibrium with c.m.c.-level surfactant concentrations? Again in other words: What is the surfactant concentration in the water phase after equilibration?

**Dr Zarbakhsh** replied: The interface is in contact with c.m.c.-level concentrations of the bulk (relatively large reservoir  $\sim 20 \text{ cm}^3$ ) at all times.

On the matter of the surfactant travelling to the SiO<sub>2</sub>–oil interface, we are not sensitive to this although we plan to determine this in the future.

**Prof. Schlossman** asked: Your current models do not include the effect of interfacial roughness. Please comment on the effect of neglecting the roughness on the other parameters in your models. The ability to correctly identify the interfacial roughness depends critically on the background measurements. Please also comment on the method used to measure the background scattering.

**Dr Zarbakhsh** replied: As Prof. Schlossman suggests, the background levels can limit the ability to determine the true interfacial roughness. Currently we fit a constant background level to our reflectivity and this is found to be adequate for air–water interfaces. We currently do not subtract the background. We will, however, in the future by measuring the background either side of the specular peak. It is also important to reduce the true background, the dominant part of which originates from the sample/sample environment. We hope to achieve this by reducing the volume of the bulk solution and having a roughened silicon trough.

**Prof. Schlossman** asked: It would be helpful to identify a reference system that has been (or can be) studied by other techniques. For example, independent experiments and analysis of a common system by both X-ray and neutron reflectivity that provided complementary, but consistent, information on that system would provide a baseline to judge the capabilities of these techniques. Can you suggest appropriate systems for this type of study?

**Dr Zarbakhsh** replied: A well-defined water-soluble surfactant such as CTAB should also be characterisable using your X-ray technique. Currently we cannot use oil soluble surfactants, which would partition at solid–liquid interfaces.

**Dr Caruana** commented: I was very encouraged to hear that you have some preliminary analysis of the clean liquid/liquid interface (hexadecane/water) which gives the interfacial thickness to be 6 Å. We have used a different approach to stabilise a liquid/liquid interface in the form of an emulsion

and studied it with small angle neutron scattering. We determined the water/DCE interface to be very similar in thickness to what you quote.

**Dr Zarbakhsh** responded: Good. We are investigating the slight discrepancy for the bare interfacial roughness determined using neutrons and those reported using X-rays. The role of the oleophilic/trimethylsilane layer will also be investigated.

**Dr Caruana** asked: Would it be possible to use your technique to study the water/DCE interface? This would require the water layer to be frozen on the silicon block as the DCE is more dense.

**Dr Zarbakhsh** answered: Yes. There may be two possible ways to approach this problem:

(i) To spin coat a silicon block with 1,2-dichloroethane (DCE) and then fill the cell up upside down with water acting as a bulk phase. Then bending the neutron beam up to obtain the desired  $Q$ -range.

(ii) A thin water ( $D_2O$ ) layer could be deposited on a hydrophilic silicon block (evaporation, spinning or dipping) and frozen. DCE would then be spun on this layer (higher freezing point, so as not to damage the water film when bulk DCE is introduced) and then sandwich it by bulk DCE.

**Prof. Deutsch** asked: The method of preparation of the thin oil layer between the silicon and water is very clever. I would like, however, to ask about the fits. Von Neumann reportedly said once that “with four parameters I can fit an elephant, and with five I can make him wiggle his trunk”. To assess the quality and significance of a fit it is important to know which parameters were varied in the fit and which were kept fixed, and at what values. Could Dr Zarbakhsh please expand on this for the fits shown in Figs. 3 and 4 of his paper?

**Dr Zarbakhsh** replied: The thickness and scattering length density of the oxide (oleophilic/trimethylsilane) film with added interlayer roughness were fixed. The oil layer thickness deduced from the attenuation from the  $0.26^\circ$  angle measurement was subsequently fixed.

The layer thickness and the scattering length density of the layer at the interfaces were fitted only. The uniqueness of this pair of parameters were ascertained by means of a contour plot of the weighted sum-of-squares deviations of two parameters, in this case the thickness and scattering length density of the interfacial slab.

These values were then used in our calculations (Figs. 3 and 4 of our paper) and reflectivities for all four angles were then calculated simultaneously.

**Prof. Samec** opened the discussion of Prof. Scholz’s paper: The three-phase electrode that you used is actually a membrane system (I),



where C represents the graphite electrode, M is the organic phase containing ferrocene species Fc, and W is the aqueous electrolyte solution containing anion  $X^-$ . The approximate thickness of the membrane can be estimated from the volume of the droplet as *ca.* 80  $\mu\text{m}$ . The electric current  $I$  is associated with the overall reaction (II),



The theory of amperometry for such a system should be based on a balance of the electric current, rather than on the electroneutrality condition, which of course applies to any finite volume element of space. Following our theoretical approach to such a system,<sup>1</sup> the applied potential  $E$  splits into two contributions plus a constant involving terms associated with the reference electrode,

$$E = \Delta_M^C \phi_{\text{Fc}^+/\text{Fc}}^{\text{O}'} + (RT/F) \ln[c_{\text{Fc}^+}(M)/c_{\text{Fc}}(M)] - \Delta_M^W \phi_{X^-}^{\text{O}'} + (RT/F) \ln[c_{X^-}(M)/c_{X^-}(W)] + \text{const} \quad (1)$$

Eqn. (1) is practically identical with eqn. (2) of your previous paper.<sup>2</sup> Assuming that the transport both inside the membrane and in the aqueous solution is controlled by the linear diffusion, the

interfacial concentrations  $c_i$ 's in eqn. (1) can be expressed using the convolution theorem as

$$\begin{aligned} c_{X^-}(\mathbf{M}) &= m/\kappa_{X^-}(\mathbf{M}) \\ c_{X^-}(\mathbf{W}) &= (m_{l,X^-} - m)/\kappa_{X^-}(\mathbf{W}) \\ c_{\text{Fc}}(\mathbf{M}) &= (m_{l,\text{Fc}} - m)/\kappa_{\text{Fc}}(\mathbf{M}) \\ c_{\text{Fc}^+}(\mathbf{M}) &= m/\kappa_{\text{Fc}^+}(\mathbf{M}) \end{aligned} \quad (2)$$

where  $m$  is the convolution current,

$$m = \pi^{-1/2} \int_0^t I(\tau)(t - \tau)^{-1/2} d\tau \quad (3)$$

The current vs. potential relationship then takes the form of an integral equation<sup>1</sup>

$$E = \Delta_{\mathbf{M}}^{\text{C}} \phi_{\text{Fc}^+/\text{Fc}}^{\text{O}'} - \Delta_{\mathbf{M}}^{\text{W}} \phi_{X^-}^{\text{O}'} + (RT/F) \ln \frac{m^2 \kappa_{\text{Fc}}(\mathbf{M}) \kappa_{X^-}(\mathbf{W})}{\kappa_{\text{Fc}^+}(\mathbf{M}) \kappa_{X^-}(\mathbf{M}) (m_{l,\text{Fc}} - m) (m_{l,X^-} - m)} + \text{const} \quad (4)$$

where  $m_{l,i} = \kappa_i c_i^0$  is the limiting convolution current, and  $\kappa_i$ 's are the mass transport coefficients comprising as the case may be the migration effect.<sup>1</sup> The equation for the reversible half-wave potential  $E_{1/2}^{\text{rev}}$  has the form depending on whether the transport is controlled by diffusion of the anion  $X^-$  in the aqueous phase (when  $m_{l,\text{Fc}} \cong m_{l,X^-} \geq m$ ), or by ferrocene species in the organic phase (when  $m_{l,X^-} \gg m_{l,\text{Fc}} \geq m$ ). In the former case, the substitution  $m = m_{l,X^-}/2$  into eqn. (4) yields

$$E_{1/2}^{\text{rev}} \approx \Delta_{\mathbf{M}}^{\text{C}} \phi_{\text{Fc}^+/\text{Fc}}^{\text{O}'} - \Delta_{\mathbf{M}}^{\text{W}} \phi_{X^-}^{\text{O}'} + (RT/F) \ln \frac{\kappa_{X^-}(\mathbf{W})^2}{2\kappa_{\text{Fc}^+}(\mathbf{M}) \kappa_{X^-}(\mathbf{M})} + (RT/F) \ln \frac{c_{X^-}^0(\mathbf{W})}{c_{\text{Fc}}^0(\mathbf{M})} + \text{const} \quad (5)$$

In the latter case, which apparently corresponds to your experimental conditions, the substitution  $m = m_{l,\text{Fc}}/2$  into eqn. (4) yields

$$E_{1/2}^{\text{rev}} = \Delta_{\mathbf{M}}^{\text{C}} \phi_{\text{Fc}^+/\text{Fc}}^{\text{O}'} - \Delta_{\mathbf{M}}^{\text{W}} \phi_{X^-}^{\text{O}'} + (RT/F) \ln \frac{\kappa_{\text{Fc}}(\mathbf{M})^2}{2\kappa_{\text{Fc}^+}(\mathbf{M}) \kappa_{X^-}(\mathbf{M})} + (RT/F) \ln \frac{c_{\text{Fc}}^0(\mathbf{M})}{c_{X^-}^0(\mathbf{W})} + \text{const} \quad (6)$$

Apart from the contribution from the mass transfer coefficients, eqn. (6) agrees with eqn. (1) of your paper.

- 1 Z. Samec, A. Trojáněk, J. Langmaier and E. Samcová, *J. Electroanal. Chem.*, 2000, **481**, 1.
- 2 G. Bouchard, A. Galland, P.-A. Carrupt, R. Gulaboski, V. Mirčeski, F. Scholz and H. H. Girault, *Phys. Chem. Chem. Phys.*, 2003, **5**, 3748.

**Prof. Scholz** responded: We have published a theoretical derivation and the experimental proof that the dependence of the formal potential on the logarithm of the anion concentration has an opposite sign depending on the ratio of the activities of the anions in water to that of dmfc in the organic phase.<sup>1</sup> In that publication the diffusion coefficients have been taken into account as well.

- 1 Š. Komorsky-Lovrić, M. Lovrić and F. Scholz, *Collect. Czech. Chem. Commun.*, 2001, **66**, 434.

**Prof. Janata** asked: Since the graphite electrode is in contact with both the aqueous and organic phase a mixed potential is formed. Has it been taken into account and/or eliminated?

**Prof. Scholz** replied: In all experiments performed so far, the potential was controlled externally. Since all electrode processes that, in principle, could occur at the graphite aqueous interface have much larger overpotentials than the studied process at the three-phase junction (and its extension), no effect of the graphite aqueous interface was detectable.

**Prof. Janata** asked: It appears that this “triple point” has a special significance in your experiment. Can you elaborate on this?

**Prof. Scholz** answered: Yes, indeed, the three-phase junction line is of special importance. Since the organic phase does not contain deliberately added electrolyte, its initial conductivity is very low. Only at the three-phase junction it will acquire by free partition an ionic conductivity that is sufficient to drive the coupled electron and ion transfer across the two interfaces graphite | organic phase and aqueous phase | organic phase. Since the electrode process creates  $\text{dmfc}^+$  and anions in the organic phase, the electrode reaction extends along these interfaces.

**Prof. Janata** asked: If the process is initiated at the triple point and then progresses to the rest of the electrode surface then there should be a transient current. Has this been observed and can you show such data?

**Prof. Scholz** replied: Until now, no potential step experiments monitoring current time transients have been performed by us.

**Prof. Karyakin** asked: By definition this system is a combination of thin layer–three-phase electrode. A three-phase electrode with thick organic layer would not have standard potential dependent on counter anion hydrophilicity.

**Prof. Scholz** replied: The term thin-layer electrode is misleading as the electrode consists of one or several immobilized droplets. The main feature is the three-phase arrangement. When a thick layer would cover the entire graphite surface, no electrochemical response can be measured because of the high resistance of the organic phase. However, in the three-phase arrangement, when the droplets are rather “thick” the response remains because of the unique feature of the three-phase junction that enables both the electron and ion transfer.

**Dr Walker** asked: Can you comment on whether or not the kinetics are different for the  $\text{L}(\text{solute}) \rightarrow \text{L}(\text{solvent})/\text{D}(\text{solute}) \rightarrow \text{D}(\text{solvent})$  vs.  $\text{L}(\text{solute}) \rightarrow \text{D}(\text{solvent})/\text{D}(\text{solute}) \rightarrow \text{L}(\text{solvent})$  systems?

If the kinetics are similar would that imply similar mechanisms of ion transfer?

Could different kinetics be used to differentiate different mechanisms of ion transfer?

**Prof. Scholz** replied: We could not see any differences for which different kinetics could be accounted for.

**Prof. Unwin** asked: Your analysis requires that the experimental response you measure is truly reversible. Mass transport in this system would appear to be complicated, with the reaction starting at the triple phase contact, where it will be characterised by high mass transport and resistive effects within the drop. Could you comment on the likely implications of such effects for your analysis, and whether resistive effects, in particular, have any influence on your data? The CV in Fig. 4 (of your paper) shows a peak to peak separation which appears to be close to 150 mV. What separation is expected for a reversible process at a droplet electrode of this type?

**Prof. Scholz** responded: The effect of the ohmic drop was studied in a theoretical simulation assuming, for reasons of simplicity, a conical form of the droplet.<sup>1</sup> Indeed it was found that the theoretical peak separation is between 125 and 150 mV, depending on the experimental conditions. The mid-peak potential may deviate by 7 mV from the thermodynamically expected value.

1 M. Lovrić and F. Scholz, *J. Electroanal. Chem.*, 2003, **540**, 89.

**Prof. Samec** addressed Prof. Unwin: Eqn. (4) in my comment above to Prof. Scholz’s paper indicates that the reversible voltammetric peak potential difference cannot take the value of 59 mV as for a univalent ion transfer across ITIES. Numerical calculation shows that the peak separation in this case is 91 mV.<sup>1</sup>

1 Z. Samec, A. Trojánek, J. Langmaier and E. Samcová, *J. Electroanal. Chem.*, 2000, **481**, 1.

**Prof. Kornyshev** asked: What is the nature of chiral effects in the free energy of transfer? Is it just the effect on van der Waals interactions?

**Prof. Scholz** replied: Yes, we suppose that the differences in van der Waals interactions are responsible for the different Gibbs energies of transfer.

**Dr. Wakisaka** asked: When you use a chiral organic phase, and a D-, L-mixture aqueous phase, is it possible to extract one optical isomer from the aqueous phase into the chiral organic phase, by controlling electric potential?

**Prof. Scholz** replied: In principle, such extractions should be feasible. However, since the energetic differences are very small, *i.e.*, the signals of mixtures are overlapping, a multi-step process will be necessary to achieve interesting separation yields.

**Dr Bain** asked: You have demonstrated that your voltammograms are not affected by transport rates across the liquid–liquid interface. Could one change the experimental parameters in order to probe chiral effects on transport rates across the liquid–liquid interface, or is diffusion/convection so complicated that it would be difficult to disentangle different kinetic processes?

**Prof. Scholz** replied: So far, we have not searched for effects of chirality on the kinetics of the process. Such effects can be expected and it would be interesting to study them.

**Dr Liggieri** commented: Interfacial tensiometric/rheometric methodologies can be very effective to investigate some aspects of the general items addressed in the discussion. Examples of these investigations are:

(1) Transfer across the interface of amphiphiles or of other species interacting with the adsorbed molecules can be investigated by the dynamic interfacial tension of freshly formed interfaces.<sup>1</sup>

(2) Nature and characteristics of the barriers to transport to/across the interface have been investigated by dynamic interfacial tension in well stirred bulks<sup>2</sup> and in drop shape tensiometers equipped with multiple feed systems.<sup>3</sup>

(3) Information about the interfacial layer structure and dynamic behaviour and about the relationships between bulk and interfacial properties are obtained by combining measurements of the  $\Pi$ - $c$  or  $\Pi$ - $A$  isotherms, of the dynamic interfacial tension (adsorption kinetics) and of the dilational and shear dynamic surface visco-elasticity (see our paper or ref. 4).

Technological advancement makes continuous improvements of these techniques possible and their full potential still needs to be explored. Significant progress will arise from coupling “fast” tensiometric/rheometric techniques (drop shape, oscillating bubble/drop, capillary pressure tensiometry) with optical ones (BAM, ellipsometry, SHG *etc.*); which is now at an initial stage.

1 M. Ferrari, L. Liggieri, F. Ravera, C. Amodio and R. Miller, *J. Colloid Interface Sci.*, 1997, **186** 40.

2 T. F. Svitova, M. J. Wetherbee and C. J. Radke, *J. Colloid Interface Sci.*, 2003, **261**, 170.

3 Miller *et al.*, *Food Hydrocolloids*, 2004, submitted.

4 L. Liggieri, F. Ravera and M. Ferrari, *Langmuir*, 2003, **19**, 10233.

**Dr Liggieri** added: At present we do not have reliable techniques for the measurement of dynamic interfacial tension (IT) and surface visco-elasticity working in the range of very low IT ( $< 1 \text{ mN m}^{-1}$ ). This range is very important for emulsion science and technology. It is then worth exploring the potential offered in this respect by the technique presented in Mitani’s paper.