

Soft matter

Horizontal reflectometer FIGARO

Multilayers at interfaces of an oppositely charged polyelectrolyte/surfactant system resulting from the transport of bulk aggregates under gravity

Spontaneous multilayer formation at air/liquid and solid/liquid interfaces has been reported in a range of soft matter systems [2]. In many cases the mixed systems in question involve macromolecules. Repeating structures within the multilayer may be identified by the presence of a Bragg diffraction peak in specular neutron reflectometry measurements of a surface [3] or by off-specular neutron scattering [4]. A common interpretation of such observations is surface-induced self assembly, *i.e.*, spontaneous ordering of molecules induced by the presence of an interface in order to minimise its free energy.

Polymer/surfactant mixtures, which are used ubiquitously in formulations of countless household products such as detergents, have been shown to be extremely good candidates in the formation of multilayered interfaces [5]. It is also known that in the bulk solution strongly interacting mixtures form aggregates with internal molecular structure. The scope of the present work was to scrutinise whether the bulk aggregates could be involved in the formation of multilayered structures at interfaces and then determine the mechanism unequivocally.

We chose the strongly interacting mixture poly (diallyldimethylammonium chloride) /sodium dodecyl sulfate (Pdadmac/SDS) which had received recent attention because of a striking peak in its surface tension isotherm. Nevertheless it had been categorised as a system where interfacial multilayers were not expected, which prompted us to test whether any possible mechanism of formation of interfacial multilayers could be related to dynamic changes in the bulk phase behavior.

Some relevant visual observations concerning the bulk phase behavior of the system are represented in **figure 1**. For samples close to the charge match point of the oppositely charged polymer and surfactant, there is a suspension of bulk aggregates immediately upon mixing. With time the aggregates grow due to their lack of colloidal stability and under gravity the phase separation process becomes more evident. Depending on the isotopic contrast, the aggregates either float for polymer

Potential has been realised to make functionalised multilayered interfaces for use in electronic devices by molecular self assembly. Using neutron reflectometry measurements on FIGARO we have demonstrated a new mechanism of interfacial multilayer formation involving the self assembly of particles with internal molecular structure and their transport under gravity to surfaces of particular locations [1]. These findings may lead to optimised production of nanostructured interfaces involving a range of synthetic and biological macromolecules such as proteins or DNA.

with hydrogenated surfactant in deuterated water (left) yet they sink for polymer with deuterated surfactant in hydrogenated water (right). This difference arises due to changes in the relative densities between the aggregates and the bulk liquid when changing isotopic contrast. The same processes occur even for normal mixtures containing purely hydrogenated materials but here switching isotopic contrast was used as a tool to allow us to investigate the underlying physical chemistry more closely. These observations made us intrigued about the implications on the interfacial properties of these particles travelling in one direction or the other.

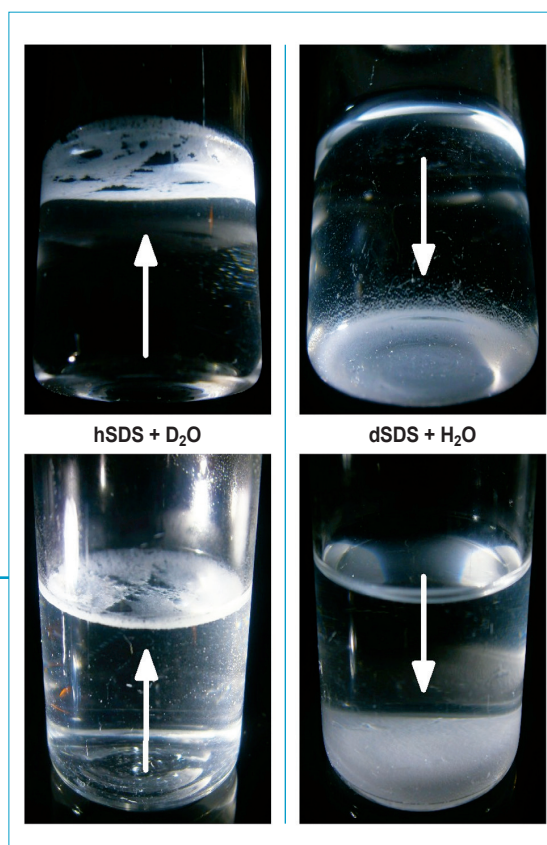


Figure 1:

Photos that highlight the directionality of the bulk aggregate transport for aged samples of Pdadmac/hSDS/D₂O (**left**) and Pdadmac/dSDS/H₂O (**right**). Perspectives are shown both from below the bottom surface (**top**) and above the top surface (**bottom**). The samples all contained 100 ppm Pdadmac, 0.82 mM SDS and 0.1 M NaCl which matched charge neutralisation of the bulk aggregates.

A series of measurements on FIGARO's adsorption troughs showed us that a strong Bragg peak and clear off-specular scattering – both indicative of interfacial multilayers – were present under three strict conditions: (1) only for samples in the phase separation region, (2) only for fresh samples where a suspension of bulk aggregates was still present in solution, and crucially (3) only where the aggregate transport process occurs upwards in the direction of the air/water interface. The data were modelled to show that the relative sizes of the diffraction peak recorded in different isotopic contrasts were not consistent with a surface-induced self assembly mechanism. Instead the data were consistent with a mechanism where the interesting surface structures were observed only under conditions when the aggregates floated. Nevertheless, we lacked direct proof of this proposed mechanism involving bulk self-assembly and transport of aggregates under gravity because we could not make measurements with bulk air beneath the liquid for obvious practical reasons!

As a result we formulated a proof-of-principle experiment where we substituted air for hydrophobic solid crystals. This had the advantage that confined surfaces in different locations could be measured both above and below the liquid. Different isotopic contrasts were also measured: one involving polymer with hydrogenated surfactant in deuterated water where the aggregates floated (left) and one involving polymer with deuterated surfactant in hydrogenated water where the aggregates sank (right). This experiment involved the comparison of reflection up and down measurements in time-of-flight mode on FIGARO, which is a unique capability.

The hypothesis under test was that if the mechanism of interfacial multilayer formation were surface-induced self assembly driven by the minimisation of the free energy of the surface then the pair of experiments involving the same sample at different orientations should produce equivalent data, yet if the data are not equivalent then gravity may be a critical missing factor in tuning the interfacial properties. **Figure 2** shows unequivocally that the surface structure – shown here as off-specular scattering images of the neutron detector with baseline-corrected Bragg peaks from the specular reflectivity – is present only when the structured particles were travelling under gravity in the direction of the interface in question.

The bulk transport mechanism determined in this work [1] is an alternative route of formation of interfacial multilayers to surface-induced self-assembly. Clearly the two processes give rise to interfaces with very different structural and morphological properties. Also, while it is most intuitive to consider an air/liquid interface with air above a flat liquid surface this is not the situation in droplets and foams, which emphasizes the need to understand the link between dynamic changes in the bulk phase behavior and the interfacial properties of such systems more clearly.

We believe that our findings may be relevant to the functional properties of macromolecule/surfactant mixtures in a range of systems.

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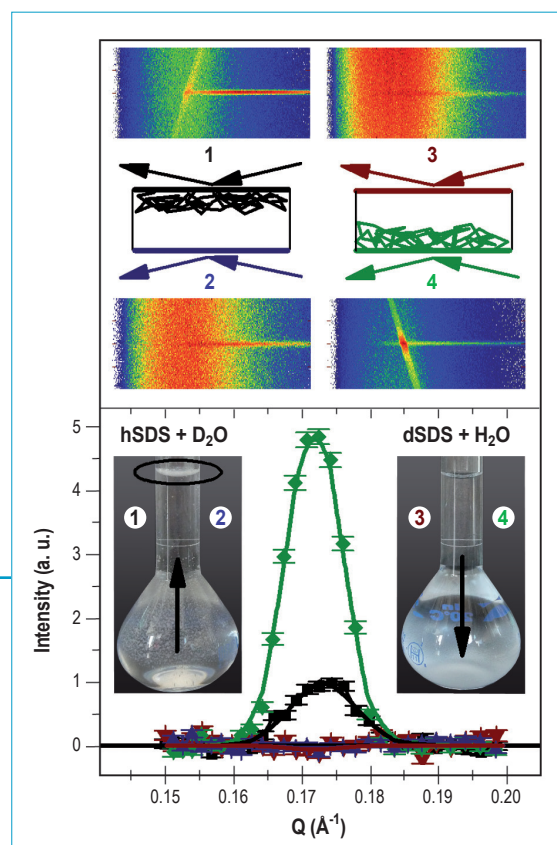


Figure 2:

(a) Neutron detector images comprising a color map of scattering for reflection angles of $\pm 1.5^\circ$ (vertical axis) with respect to the wavelength over a range of 1.5–10 Å (horizontal axis) from neutron reflectometry measurements on FIGARO of Pdadmac/SDS solutions at the hydrophobic solid/liquid interface.

(b) Bragg peak in the specular reflectivity profiles each with Gaussian fits, and additional illustrative photos of aged samples of Pdadmac/hSDS/D₂O (left) and Pdadmac/dSDS/H₂O (right). The samples all contained 100 ppm Pdadmac, 0.82 mM SDS and 0.1 M NaCl, and the data were recorded with a surface age of 27–36 hours.