Segregation of mixed micelles in the presence of polymers

Peter Griffiths,*[a] Richard Abbott,[a] Peter Stilbs[b] and Andrew Howe[c]

[a] *Department of Chemistry, University of Wales Cardiff, PO Box 912, Cardiff, UK CF1 3TB*
[b] *Department of Physical Chemistry, Royal Institute of Technology, Stockholm, Sweden S-100 44*
[c] *Kodak European Research, Headstone Drive, Harrow, Middlesex, UK HA1 4TY*

The diffusion behaviour of an aqueous mixture of the sugar-based non-ionic surfactant dodecylmalono-bis-*N*-methylglucamide DBNMG and the anionic surfactant of similar tail length, sodium dodecyl sulfate SDS, are examined in the presence of 5 mass% gelatin; the results clearly show that there are two types of mixed micelle present in the system arising through competition between gelatin and the non-ionic micelle for the anionic surfactant.

The interactions between common synthetic polymers, *e.g.* homopolymers,[1,2] hydrophobically modified polymers[3–5] and polyelectrolytes,[6,7] and selected surfactants have been studied extensively. Generally, the polymer/surfactant complex consists of spherical, monodisperse micelles adsorbed onto the polymer chain in a 'bead and necklace' manner.[8] The presence of the polymer stabilises the formation of the adsorbed micelles and these form at lower concentrations [denoted c.a.c. or c.m.c. (1)], compared with the polymer-free critical micelle concentration (c.m.c.). Recent theoretical modelling[9,10] of these systems is based on the fact that the polymer segments bind in the micelle palisade layer thereby partially shielding some of the hydrophobic core from contact with the continuous aqueous phase. This results in a decrease in the interfacial free energy of the system and hence, provides the driving force for the interaction.

In commercial polymer/surfactant systems, a single surfactant is rarely employed. Most often, a mixture of surfactants is present and synergistic or antagonistic effects are used to mediate and control the overall polymer/surfactant behaviour. The molecular basis for these effects is poorly understood but very important for the improvement of product formulations. It is possible however, to build up a picture of the structure of the polymer/mixed surfactant complex from a knowledge of the diffusion behaviour of the various components. Here, we present as far as we are aware, the first such attempt to do this.

The simultaneous measurement of the (self)-diffusion coefficient of each component present in a multi-component mixture can be achieved using pulsed-gradient spin-echo nuclear magnetic resonance, PGSE NMR. The normal procedure for measuring the self-diffusion coefficient of a species in a multi-component solution is to isolate a resolvable peak, extract the peak integral (intensity) or height for a series of spectra separated in time and fit the resultant exponential time decay. In many useful polymer/surfactant mixtures, resolvable peaks are not present and one must resort to the fitting of multi-exponential decays. For example, consider the data shown in Fig. 1(*a*). The most intense peak (at δ 1.45) corresponds to CH_2 groups present in both surfactants as well as the gelatin. A new data analysis has been developed however, to overcome this problem, called component resolved (CORE) PGSE NMR.[11] The fit to the data is given in Fig. 1(*b*). This approach significantly enhances the accuracy of the diffusion coefficients obtained. A further advantage of CORE PGSE NMR, is that the T_2 weighted 1D spectrum for each component is extracted from the component bandshape. Unequivocal assignment of the diffusion coefficient to each component is then possible.

Gelatin interacts strongly with SDS but not DBNMG, whilst SDS and DBNMG form mixed micelles in the absence of gelatin.[10,12–14] The self-diffusion coefficients of the three components SDS, DBNMG and 5 mass% gelatin are presented in Fig. 2 for a series of 5 mass% aqueous gelatin solutions containing 20 mM SDS and a range of DBNMG concentrations. The broken line corresponds to the diffusion behaviour of DBNMG in the presence of 5 mass% gelatin. This diffusion is slower by a factor of approximately two-thirds than that in the absence of gelatin owing to the obstructing effects of the polymer: the micelle has to diffuse around the gelatin, thereby increasing its diffusion pathlength. The diffusion of DBNMG is further retarded when SDS is present in the system indicative of binding to the much more slowly diffusing gelatin. The gelatin diffusion is an order of magnitude slower than that measured in the simple gelatin and gelatin/DBNMG solutions, again indicative of binding of surfactant micelles to the gelatin.

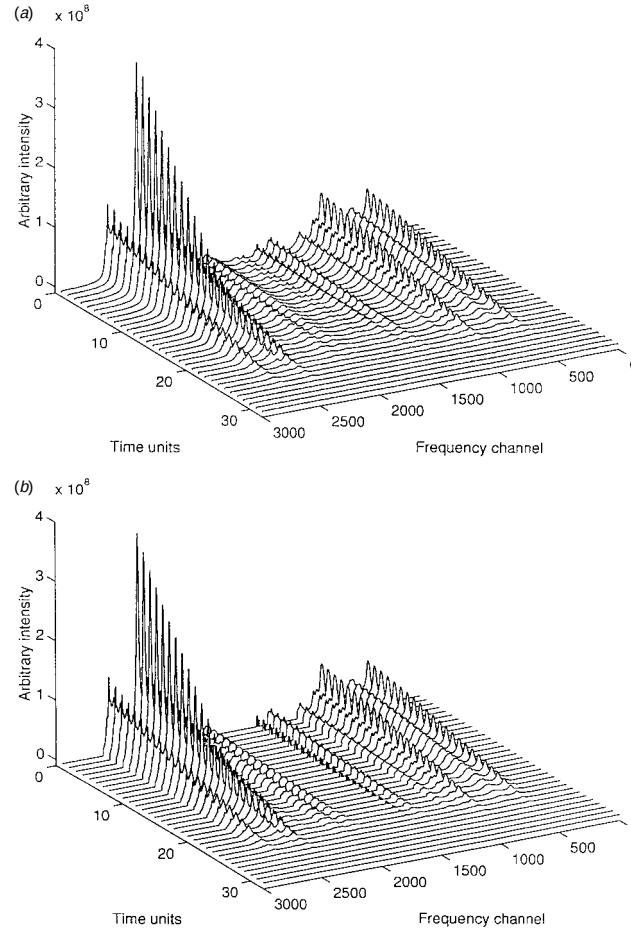

Fig. 1 (*a*) Experimental data for a 5 mass% gelatin solution containing 40 mM SDS and 5 mM DBNMG; (*b*) the CORE processed simulation

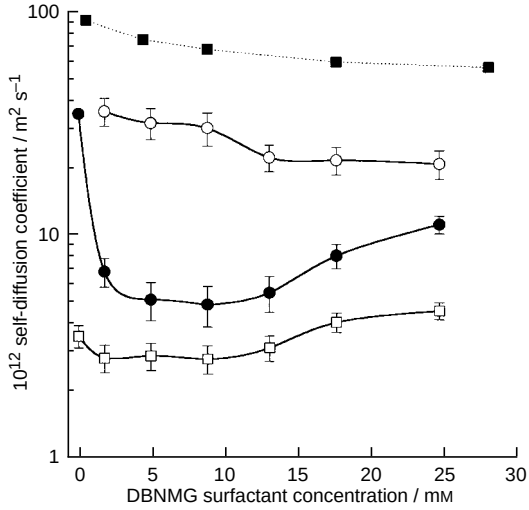

Fig. 2 Diffusion in 5 mass% aqueous gelatin/DBNMG/SDS solutions; gelatin (□), DBNMG (○), and SDS (●). The diffusion of DBNMG in the presence of 5 mass% gelatin only (■) is also shown.

The most striking conclusion however, comes from the behaviour of the SDS. If only one type of micelle is present in the system, and assuming that the unimer concentrations are low, the two surfactants should diffuse at the same rate. This is not observed. Since c.m.c.(1) for gelatin/SDS is higher than $c.m.c._{DBNMG}$, the concentration of unimeric SDS in the system should be greater than that of the DBNMG and hence, the self-diffusion coefficient of SDS should be greater than that of the DBNMG. This too is not observed. The highly unexpected, yet obvious conclusion is that two mixed micellar environments must be present, SDS-rich micelles bound to the gelatin and DBNMG-rich micelles present in solution.

At higher DBNMG concentrations, both the SDS and gelatin self-diffusion coefficients increase, the faster diffusing DBNMG-rich micelles in solution are 'pulling' SDS from the slower diffusing micelles bound to the gelatin. The SDS concentration bound to the gelatin therefore decreases, causing the diffusion of gelatin to increase.

Footnote and References

* E-mail: griffithspc@cardiff.ac.uk

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Received in Cambridge, UK, 29th September 1997; 7/07003I