

Surface Behavior, Aggregation and Phase Separation of Aqueous Mixtures of Dodecyl Trimethylammonium Bromide and Sodium Oligoarene Sulfonates: the Transition to Polyelectrolyte/Surfactant Behavior

Ling Xiang Jiang,^{†,||} Jian Bin Huang,^{*,†} Alireza Bahramian,^{‡,||} Pei Xun Li,^{||} Robert K. Thomas,^{*,||} and Jeffrey Penfold^{§,||}

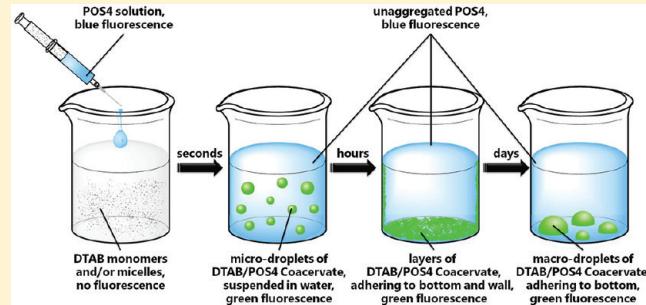
[†] Beijing National Laboratory for Molecular Sciences, State Key Laboratory for Structural Chemistry of Unstable and Stable Species, College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China

[‡] Institute of Petroleum Engineering, University of Tehran, Tehran, Iran,

^{||} Physical and Theoretical Chemistry Laboratory, University of Oxford, South Parks Road, Oxford, OX1 3QZ, U.K.

[§] Rutherford-Appleton Laboratory, Chilton, Didcot, Oxon

ABSTRACT: The properties and phase diagrams of aqueous mixtures of dodecyltrimethylammonium bromide (C_{12} TAB) with the sodium oligoarene sulphonates (POS_n), POS2, POS3, POS4, and POS6 have been studied using surface tension and neutron reflectometry to study the surface, and neutron small angle scattering and fluorescence to study the bulk solution. The behavior of POS2 and POS3 is reasonably consistent with mixed micelles of C_{12} TAB and POS_n -(C_{12} TA)_n. These systems exhibit a single critical micelle concentration (CMC) at which the surface tension reaches the usual plateau. This is contrary to a recent report which suggests that the onset of the surface tension plateau does not coincide with the CMC. In the POS3 system, the micelles conform to the core–shell model, are slightly ellipsoidal, and have aggregation numbers in the range 70–100. In addition, the dissociation constant for ionization of the micelles is significantly lower than for free C_{12} TAB micelles, indicating binding of the POS3 ion to the micelles. Estimation of the CMCs of the POS_n -(C_{12} TA)_n from $n = 1–3$ assuming ideal mixing of the two component surfactants and the observed values of the mixed CMC gives values that are consistent with the nearest related gemini surfactant. The POS4 and POS6 systems are different. They both phase separate slowly to form a dilute and a concentrated (dense) phase. Fluorescence of POS4 has been used to show that the onset of aggregation of surfactant (critical aggregation concentration, CAC) occurs at the onset of the surface tension plateau and that, at the slightly higher concentration of the phase separation, the concentration of POS4 and C_{12} TAB in the dilute phase is at or below its concentration at the CAC, that is, this is a clear case of complex coacervation. The surface layer of the C_{12} TA ion in the surface tension plateau region, studied directly by neutron reflectometry, was found to be higher than a simple monolayer (observed for POS2 and POS3) for both the POS4 and POS6 systems. In POS6 this evolved after a few hours to a structure consisting of a monolayer with an attached subsurface bilayer, closely resembling that observed for one class of polyelectrolyte/surfactant mixtures. It is suggested that this structured layer, which must be present on the surface of the dilute phase of the coacervated system, is a thin wetting film of the dense phase. The close resemblance of the properties of the POS6 system to that of one large group of polyelectrolyte/surfactant mixtures shows that the surface behavior of oligoion/surfactant mixtures can quickly become representative of that of true polyelectrolyte/surfactant mixtures. In addition, the more precise characterization possible for the POS6 system identifies an unusual feature of the surface behavior of some polyelectrolyte/surfactant systems and that is that the surface tension can remain low and constant through a precipitation/coacervation region because of the characteristics of two phase wetting. The well-defined fixed charge distribution in POS6 also suggests that rigidity and charge separation are the factors that control whether a given system will exhibit a flat surface tension plateau or the alternative of a peak on the surface tension plateau.



INTRODUCTION

Menger et al. recently reported some measurements on mixtures of dodecyltrimethylammonium bromide (C_{12} TAB) with various sodium oligoarene sulphonates (POS_n) from which they deduced the result that the air/water surface becomes saturated with surfactant at a concentration well below the critical

micelle concentration (CMC).¹² Thus, a plateau in the surface tension was reached at a concentration about an order of

Received: October 19, 2011

Revised: November 13, 2011

Published: November 18, 2011

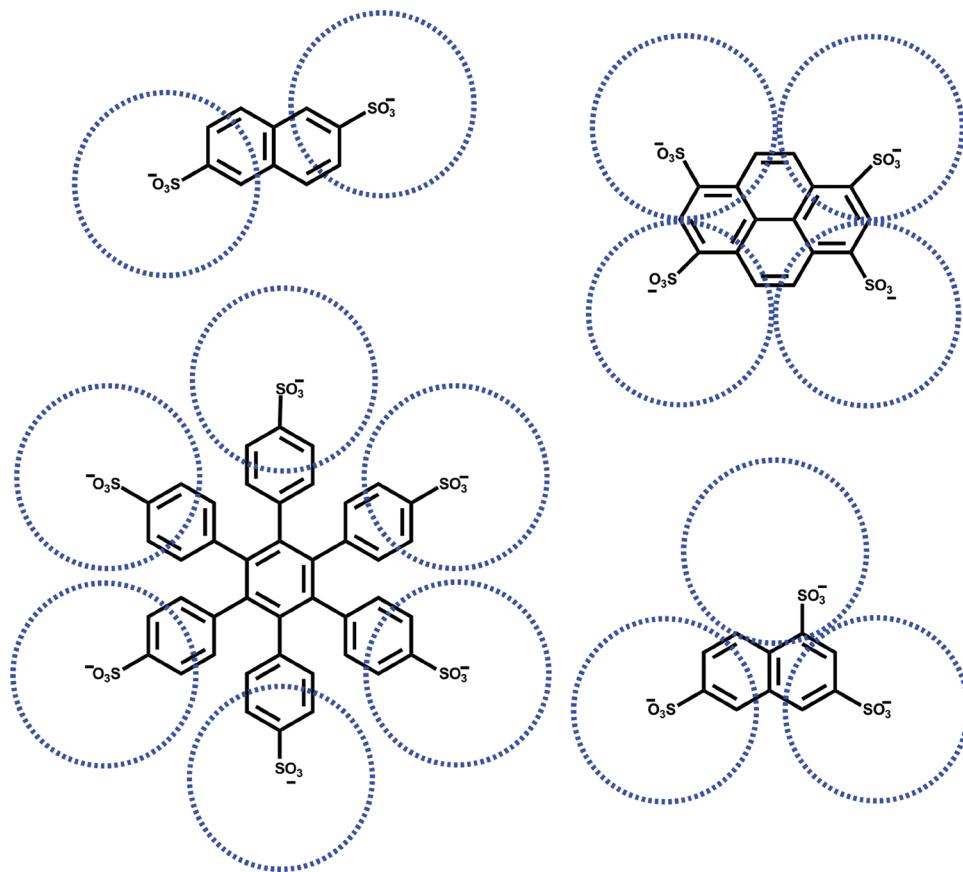


Figure 1. Chemical structures of the sodium oligoarene sulfonates, designated POS2, POS3, POS4, and POS6. The circles represent areas approximately equivalent to the cross sectional area (50 \AA^2) of a vertically attached C₁₂TAB molecule and their significance is discussed in the text. For simplicity, the benzene rings are drawn coplanar in the POS6 structure but in reality are tilted out of the plane.

magnitude lower than the CMC, as measured by conductivity, and Menger et al. interpreted this as an apparent violation of the Gibbs equation. The POS_n included in the study by Menger et al. contained from 1 to 6 sulfonates on a rigid framework at separations comparable with those in typical polyelectrolytes. Experiments on oligoamines of comparable charge³ suggest that in this charge range the surface behavior develops into that of polyelectrolyte/surfactant mixtures. An understanding of this development can be expected to help in understanding the often complicated phenomena that occur in polyelectrolyte/surfactant systems. Of added interest, the arene sulphonates have a rigid framework with charged groups more widely spaced than in the amines and the consequences of this difference from the amines may become evident in the oligoion limit.

The information that has been important in making progress in understanding the surfaces of polyelectrolyte/surfactant mixtures has been the surface coverage and structure of the surfactant. This is only accessible via neutron reflectometry (NR) and was not obtained by Menger et al. for the arene sulfonate/C₁₂TAB mixtures. In this paper we report NR results for C₁₂TAB interacting with four of the POS_n, shown in Figure 1. We have also repeated some of the surface tension measurements of Menger et al. To address more directly the question of the position of the critical micelle concentration (CMC), we have studied the solution structure of C₁₂TAB/POS3 mixtures using small angle neutron scattering (SANS). In addition, POS4 is fluorescent and we have made use of this to determine the CMC

of C₁₂TAB/POS4 mixtures directly by fluorescence. Finally, we have examined the macroscopic phase behavior of these mixtures. All of this leads to a more complete interpretation of the behavior in these systems than was possible in the papers of Menger et al.

EXPERIMENTAL DETAILS

POS2, POS4, hexaphenylbenzene (HPB), and the trisodium salt hydrate of 1,3,(6 or 7)-naphthalene trisulfonic acid were purchased from Sigma-Aldrich and used without further purification.

POS3 was obtained by recrystallizing the trisodium salt hydrate of 1,3,(6 or 7)-naphthalene trisulfonic acid from water three times (dissolved at 90°C and recrystallized at room temperature). ¹H NMR (600 MHz, D₂O): δ 8.83 (d, 1H), 8.69 (s, 1H), 8.61 (s, 1H), 8.54 (d, 1H), 8.14 (dd, 1H). ¹³C NMR (400 MHz, D₂O): δ 141.42, 139.86, 139.82, 132.84, 130.67, 130.10, 127.47, 126.71, 125.60, 124.05. ESI-MS: *m/z* 410.9 for [POS3 - Na]⁻, 194.0 for [POS3 - 2Na]²⁻.

The hexasodium salt of hexaphenylbenzene hexasulfonyl acid, POS6 was prepared as follows. 1.0 g of HPB was added under dry conditions to a 50 mL round-bottom flask, followed by the addition of 25 mL of dry CH₂Cl₂. The flask was placed in an ice/salt bath, and the reaction mixture stirred vigorously. Chlorosulfonic acid (7.5 mL) was then added dropwise (slow enough to keep the reaction temperature below 0 °C). The reaction was allowed to continue in the ice bath for 2 h. The mixture was then carefully poured into ice/water, giving a solid precipitate of the intermediate product, hexaphenylbenzene hexasulfonyl chloride. The precipitate was collected and suspended in 400 mL water. Concentrated

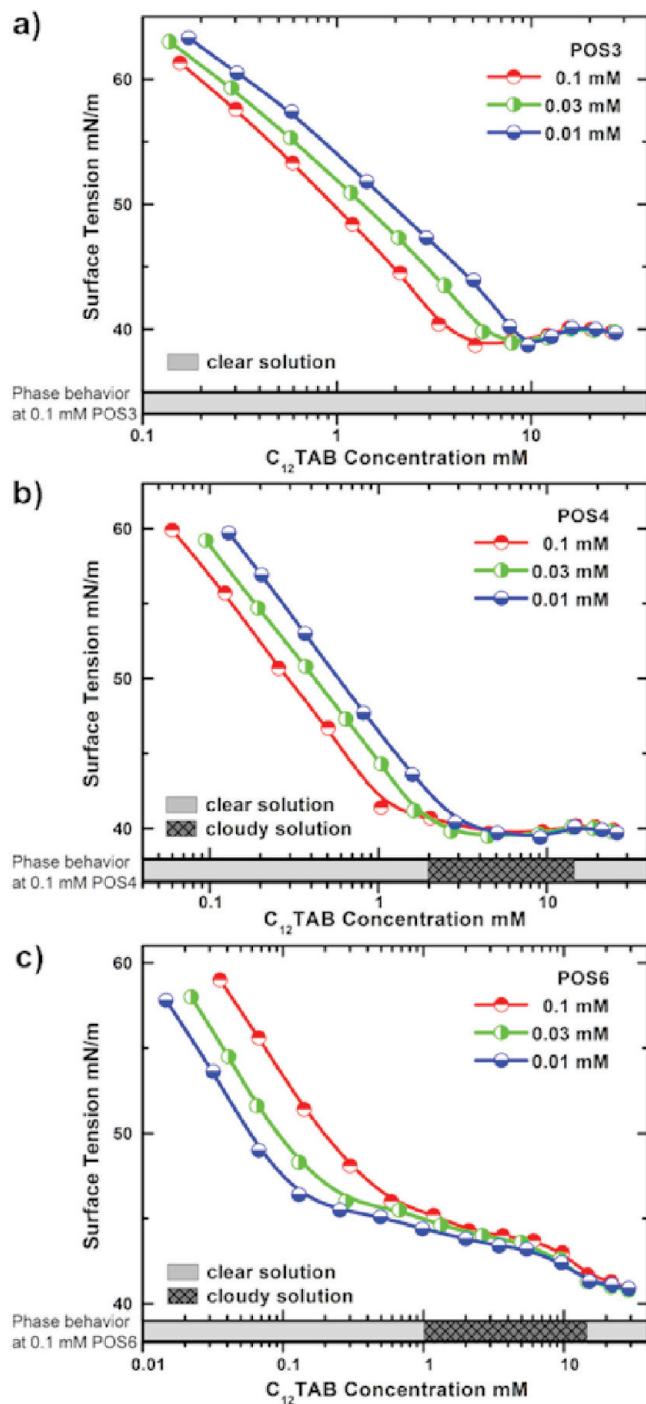


Figure 2. Variation of surface tension with the log of $C_{12}\text{TAB}$ at three different fixed concentrations of (a) POS3, (b) POS4, and (c) POS6. The dependence on POS_n concentration is reversed between POS4 and POS6. Along the bottom of each diagram is marked the range of cloudiness of the solutions.

NaOH solution was added slowly to the suspension and the suspension was vigorously stirred at 50°C for 12 h to dissolve the solid precipitate. The final solution was slightly basic and consisted of a mixture of POS_n and excess NaCl . NaCl was eliminated by dialysis (cellulose ester membrane tubes, Spectra/Por Float-A-Lyzer G2, MWCO: 100–500 D) against water. Elimination of NaCl was tested using concentrated AgNO_3 solution. Finally, the solution was freeze-dried. ^1H NMR (600 MHz , D_2O): δ 7.37 (d, 12H), 7.13 (d, 12H). ^{13}C NMR (400 MHz ,

D_2O): d 142.7 (6 C– SO_3Na), 140.2 (6 C para to the sulfonyl group), 139.6 (6 C of the substituted phenyl group), 131.8 (12 C ortho to the sulfonyl group), 124.3 (12 C meta to the sulfonyl group). ESI-MS: m/z 1122.9 for $[\text{POS}_6 - \text{Na}]^-$, 550.0 for $[\text{POS}_6 - 2\text{Na}]^{2-}$, 359.0 for $[\text{POS}_6 - 3\text{Na}]^{3-}$, 263.5 for $[\text{POS}_6 - 4\text{Na}]^{4-}$.

C_{12}TAB (Sigma-Aldrich) was purified by recrystallization from an acetone/ethanol mixture. Chain deuterated C_{12}TAB (dC_{12}TAB) was prepared from perdeuterated dodecylbromide and trimethylamine using a method described previously⁴ and purified in the same way as normal C_{12}TAB .

The neutron reflectivity measurements were made on the SURF reflectometer at the ISIS neutron source U.K.⁵ The measurements were made using a single detector at fixed angle of $\theta = 1.5^\circ$ with neutron wavelengths in the range 0.5 – 6.8 \AA^{-1} to provide a momentum transfer range 0.048 – 0.5 \AA^{-1} , the momentum transfer Q being defined as $Q = (4\pi \sin \theta)/\lambda$. For air/water measurements on null reflecting water, where there is no critical edge, the reflectivity was calibrated with respect to pure D_2O . Null reflecting water is a mixture of 92% H_2O and 8% D_2O with a scattering length density of exactly 0 and is therefore optically identical with air. Backgrounds measured from null reflecting samples were subtracted to provide the final reflectivity profile. These profiles were fitted using the program AFit⁶ which is based on the optical matrix method.⁷

The SANS measurements were made on the D11 diffractometer at the ILL, France⁸ at a neutron wavelength of 6 \AA and a sample to detector distances of 1.1, 5.0, and 16.5 m, to cover a Q range of 0.003 – 0.25 \AA^{-1} . The data were corrected for background scatter and detector response and converted to an absolute scattering cross section using standard procedures.⁹ The scattering patterns were modeled using the decoupling approximation, the core shell model, and a structure factor calculated using the rescaled mean spherical approximation calculation for a repulsive screened Coulombic intermicellar interaction, as described in full elsewhere.¹⁰

Fluorescence measurements were made on a Hitachi F-4500 fluorescence spectrometer. The excitation wavelength was set at 350 nm and emission spectra were recorded from 370 to 600 nm.

The surface tension measurements were made using a Kruss K10 maximum pull tensiometer with a Pt/Ir du Nouy ring. The tensiometer was calibrated by measurements in pure water before each set of measurements. The measurements were carried out at 298 K. The Pt/Ir ring and all associated glassware were washed in Decon 90, deionized water, and acetone and flamed immediately before use.

RESULTS

Identification of the CMC or CAC. Surface tension results for the systems POS3, POS4, and POS6 are shown in Figure 2. They have been done slightly differently from Menger et al. Rather than using a constant $\text{C}_{12}\text{TAB}/\text{POS}_n$ ratio we have made them at a constant POS_n concentration and varying C_{12}TAB concentration. However, we also made some measurements using the former method and these results are in reasonable agreement with those of Menger et al., the main ones of which are that a plateau in the surface tension is reached at a concentration well below the CMC of C_{12}TAB on its own and that the concentration of this point varies systematically downward as the degree of sulfonation (n) increases. There are some additional observations, which are not described in the papers of Menger et al. The most obvious of these is that for values of n of 2, 3 and 4, the onset of the plateau increases as the concentration of POS_n decreases, whereas for $n = 6$ it decreases with POS_n concentration. The latter is the same as was observed in mixtures of sodium poly(styrene sulfonate) with C_{12}TAB ¹¹ and we discuss this point in

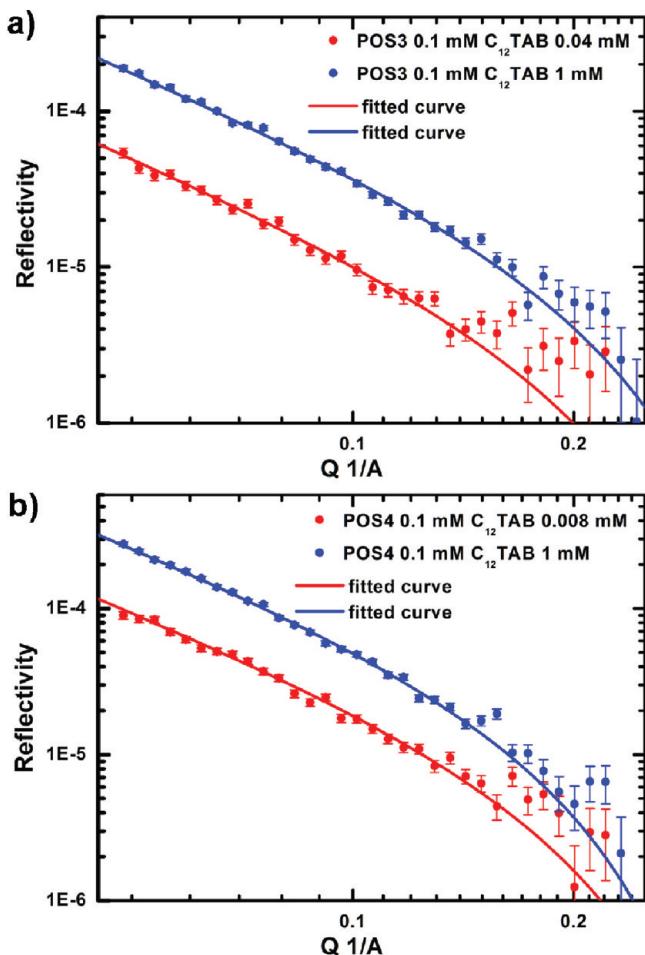


Figure 3. Neutron reflectivity profiles from $dC_{12}\text{TAB}/\text{POS}_n$ solutions in null reflecting water (NRW) in the presence of (a) POS3 and (b) POS6. The contribution to the observed signal is more or less entirely from the $dC_{12}\text{TAB}$. The fitted lines use a single uniform layer model.

the final section of the paper. A second observation, which also connects with polyelectrolyte/surfactant mixtures¹² is that the POS6 mixtures show a second plateau, close to the CMC of $C_{12}\text{TAB}$ on its own. Overall, the shape of the surface tension curves for pure $C_{12}\text{TAB}$ and for $C_{12}\text{TAB}$ with sodium poly(styrene sulfonate) are similar to those shown for the oligosulfonate mixtures but the break point (CMC/CAC) is about an order of magnitude higher or lower respectively. Also shown in Figure 2 is the range over which the solutions become cloudy. This was not commented on by Menger et al. but it occurs for the POS4 and POS6 mixtures in a range below the CMC of pure $C_{12}\text{TAB}$. The onset of cloudiness for POS4 is close to the onset of the surface tension plateau but for POS6 it is well above this point. POS2 and POS3 show no cloudiness. We comment in more detail on the cloudiness below.

We show two sets of NR results on the chain deuterated $C_{12}\text{TAB}$, $dC_{12}\text{TAB}$, in null reflecting water (NRW) in Figure 3. The results of fitting a uniform single layer to obtain the adsorbed amounts is shown for all four systems in Figure 4. There is no signal from NRW and in separate experiments we found that the signal from the POS_n was too weak to be observed. This is not surprising given the low estimated scattering length density of the POS_n species. At this isotopic composition the magnitude of the signal at low Q is therefore proportional to the square of the

surface coverage of surfactant. It can be seen that the coverage increases with $dC_{12}\text{TAB}$ concentration and reaches a plateau well below the CMC of $dC_{12}\text{TAB}$. The concentration at which the surface coverage reaches its maximum value decreases as n increases. From the known behavior of $C_{12}\text{TAB}$ on its own¹³ the adsorption in the presence of POS_n is greatly enhanced at low concentrations, that is the presence of POS_n induces adsorption of $C_{12}\text{TAB}$. In addition the adsorption of $C_{12}\text{TAB}$ in the presence of POS6 reaches a much higher value than in the other three systems and, at higher concentrations, the reflectivity shows the same type of pattern as observed in several surfactant/polyelectrolyte systems. This has been shown to correspond to a subsidiary layer of surfactant underneath the monolayer at the surface.¹² POS4 also shows an enhanced adsorption in comparison to POS2 and POS3 but no subsidiary layer could be reliably identified. Overall, the basic observations are consistent with the interpretation of Menger et al. that the adsorption becomes saturated at the same concentration as the surface tension reaches a plateau (marked by the arrows in Figure 4).

The most direct way to examine the nature of any aggregates in bulk solution is to use small angle neutron scattering (SANS). SANS results were made for $\text{POS}3/C_{12}\text{TAB}$ mixtures in $D_2\text{O}$ at a fixed concentration of 1 mM POS3 and concentrations of 0.4, 4, 8, and 20 mM $C_{12}\text{TAB}$. The middle two are in the range between the onset of the surface tension plateau and the CMC of $C_{12}\text{TAB}$. Figure 5 shows the scattering patterns for the three higher concentrations of $C_{12}\text{TAB}$ and these are characteristic of spherical micelles and show unequivocally that the CMC of the mixed $\text{POS}3/C_{12}\text{TAB}$ is much lower than for pure $C_{12}\text{TAB}$. The pattern at 0.4 mM is not shown. It gave a flat background signal, showing that there is no aggregation at 1 mM POS3 and 0.4 mM $C_{12}\text{TAB}$. Although the results were not done over a fine enough grid to establish a definite value of the CMC they do establish that it lies between 0.4 and 4 mM and it is therefore probable that it corresponds with the break point in the surface tension, which was found to be 1.5 mM for this concentration of POS_n . The detailed analyses of the micelles using the core–shell model are shown as lines in Figure 5. The micelles were found to be slightly elliptical, with $r_1 = 16.7 \text{ \AA}$ and $r_2 = 20.7 \text{ \AA}$ and the aggregation numbers were 96, 87, and 69 ± 4 at 4, 8, and 20 mM respectively. Aggregation numbers normally increase with concentration but here they do the opposite. This must be caused by the higher relative concentration of POS3 and suggests that the POS3 ion is more tightly bound to the micelle than Br^- . The values of the effective CMC, calculated from the overall concentration, aggregation number, and signal intensity, were 1.2, 3, and 8 mM for overall concentrations of 4, 8, and 20 mM respectively. These indicate that the CMC shifts with relative concentration of $C_{12}\text{TAB}$ and POS3, as would be expected for a mixture of surfactants. We discuss this further below but note here that this result shows unambiguously that the POS3 ions interact with the surfactant cation. Given this, the ion composition at the surface of the micelle almost certainly shifts progressively toward more bromide ions as the bromide/POS3 ratio increases. This is also shown by the 20 mM concentration where there is very little sign of an interaction peak in the micellar scattering, indicating a very low degree of dissociation on the micelles. The fitted value was found to be 0.05, which is both unusually low and compares with a much higher level of dissociation of pure $C_{12}\text{TAB}$ at the same 20 mM concentration, which was found to be 0.29.¹⁴ The large change between the two situations suggests that a number of POS3 ions are bound to the micelle at 1 mM POS3 and 20 mM $C_{12}\text{TAB}$. This has some implications for the conductivity behavior.

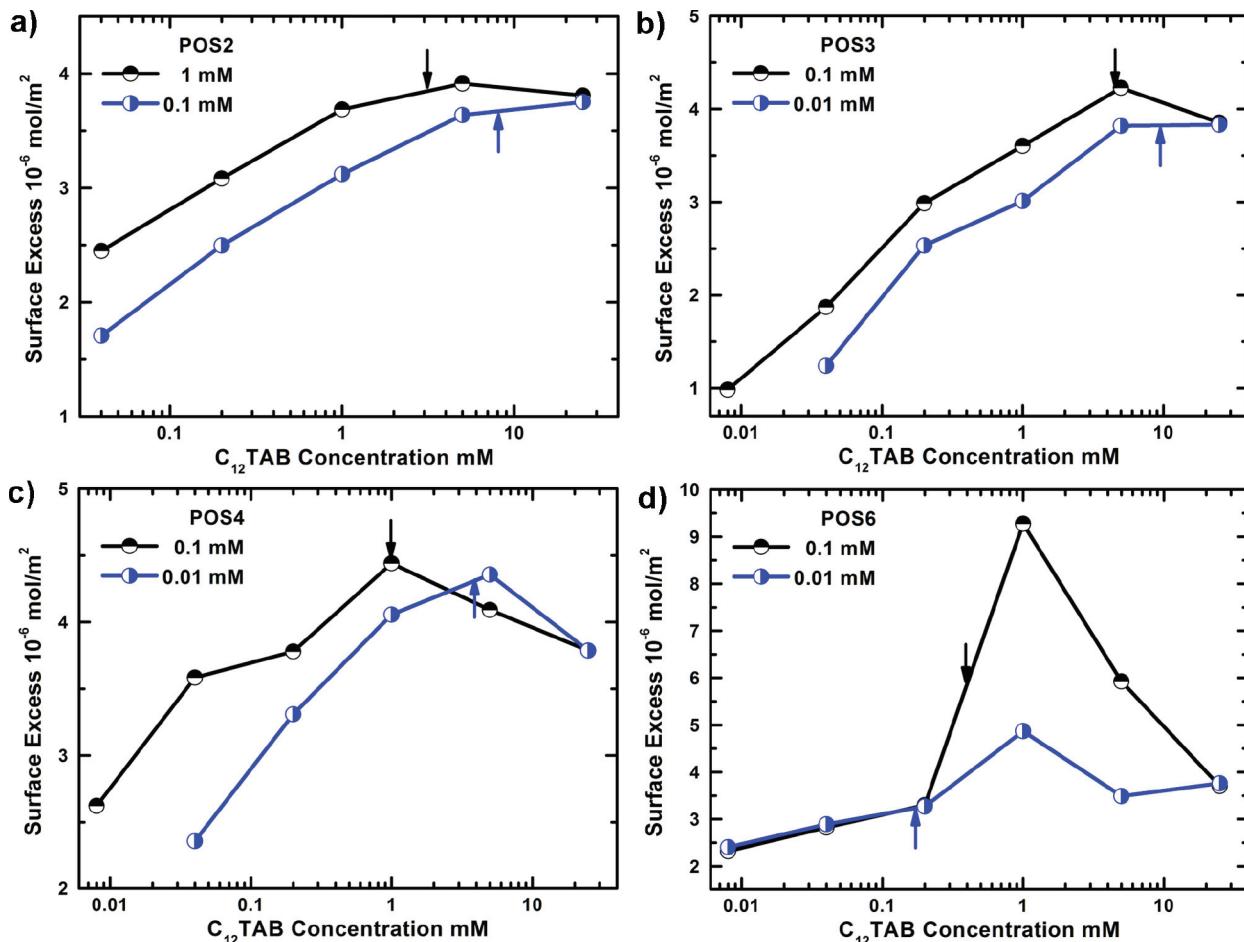


Figure 4. Adsorption isotherms determined from neutron reflectometry at two difference POS_n concentrations for (a) POS2, (b) POS3, (c) POS4, and (d) POS6. The arrows mark the onset of the plateau in the surface tension.

The POS4 ion is a chromophore and its fluorescence can be studied without the need for a separate chromophore. Since fluorescence is highly sensitive to the molecular environment this property can be used directly to study the state of aggregation in the POS4/C₁₂TAB system. Figure 6(a) shows the fluorescence spectrum of 0.01 mM POS4 on its own and in the presence of 6 mM C₁₂TAB. The monomer fluorescence is in the range around 400 nm. A new peak appears in the presence of C₁₂TAB at around 510 nm. It is reasonable to interpret this as excimer fluorescence resulting from the close proximity of pairs of POS4 molecules in a micelle. In Figure 6(b), the intensity of the excimer fluorescence is plotted as a function of C₁₂TAB concentration at fixed 0.01 mM POS4. The concentration where the excimer fluorescence first appears is identified with the formation of aggregates, that is, the CMC (or critical aggregation concentration, CAC). Figure 6(c) shows that measurement of the onset of excimer fluorescence at different POS4 concentrations gives values of the CMC that coincide within error with the onset of the surface tension plateau. The fluorescence data therefore show that POS4 aggregation occurs at the same point as the onset of the surface tension plateau. POS4 was the only member of the series for which the fluorescence could be used to study aggregation. However, with the fluorescence data for POS4 and the SANS data for POS3, the break in the surface tension plots can probably safely be identified as the CMC or CAC for all four systems.

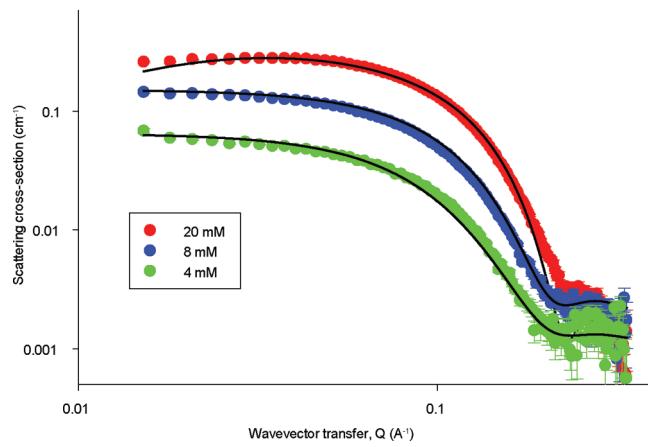


Figure 5. Neutron small angle scattering patterns of mixtures of POS3 and C₁₂TAB in D₂O at a fixed concentration of 1 mM for POS3 and concentrations of C₁₂TAB of 4, 8, and 20 mM (the CMC of C₁₂TAB alone is 15 mM) All three profiles can be fitted by a core–shell model of slightly elliptical micelles with aggregation numbers of 96, 87, and 69 ± 4, respectively.

In addition to the microstructure revealed by SANS and fluorescence measurements, the POS4 and POS6 systems also

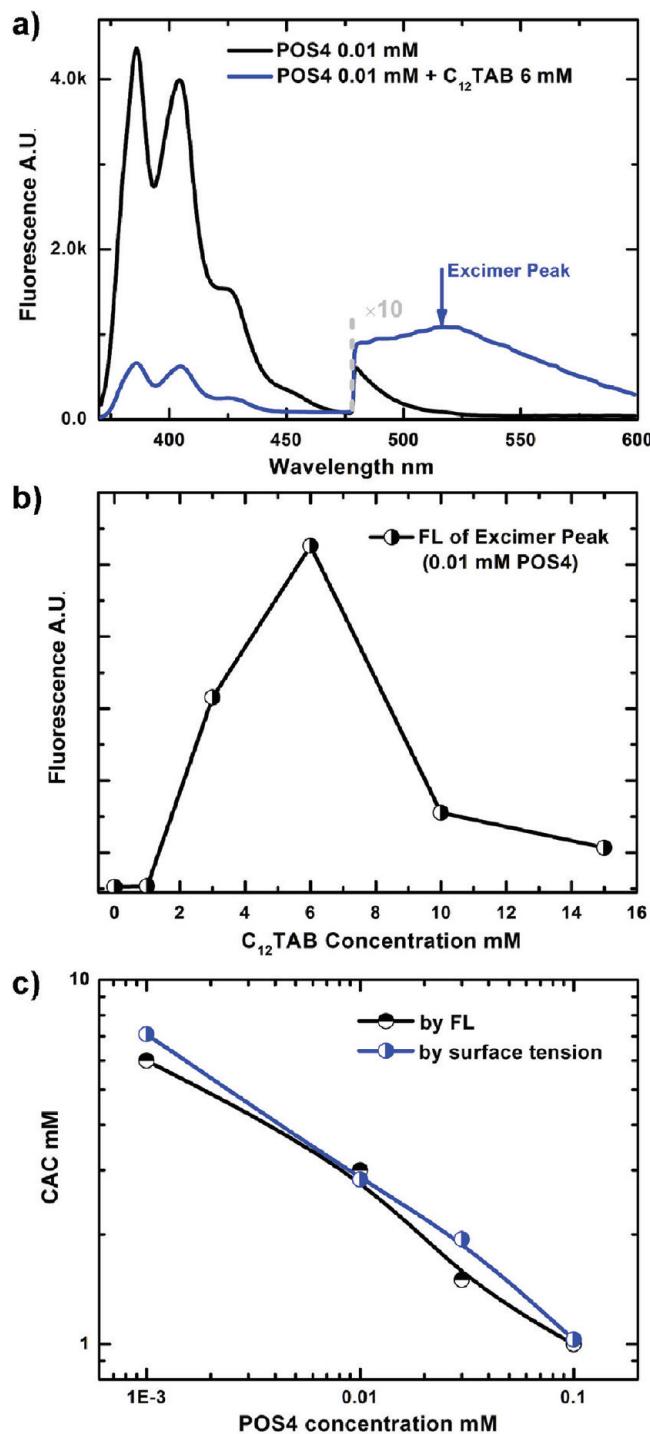


Figure 6. (a) Fluorescence spectra of POS4 in the absence and presence of C₁₂TAB, (b) the variation of the excimer fluorescence intensity with C₁₂TAB concentration at 0.01 mM POS4, and (c) comparison of the onset of POS4 excimer fluorescence and the onset of the surface tension plateau for different fixed POS4 concentrations.

show a well-defined phase behavior. Some indication of this has already been given in the shaded regions at the base of the diagrams in Figure 2. Not surprisingly, when a highly charged ion is mixed with an oppositely charged surfactant there is a tendency to precipitate out in the region of the charge neutralization point. As indicated in Figure 2 this does not happen for POS3 (nor

POS2, not shown) but there is marked cloudiness for the POS4 and POS6 mixtures. Examination over a longer time (hours and days) shows that this cloudiness slowly develops into a full phase separation into two liquid phases, one dilute (only blue monomer fluorescence) and one concentrated (strong green excimer fluorescence). This is shown diagrammatically in the upper part of Figure 7 and in photographs in the lower part of Figure 7. We have followed this phase separation with time and concentration using a variety of techniques, including simple photography. The phase diagram, with the two phase region marked in green, is shown in Figure 8. The phase separation develops only slowly but eventually droplets of the denser phase separate at the walls of the container and slowly fall to form a liquid layer at the bottom of the container. We emphasize that there is no solid precipitation in this process. Cryo-TEM images of the denser phase show some inner structure of the microdroplets, which weakly resembles that reported in the literature and which is usually attributed to a sponge phase.¹⁵ However, although we cannot identify the structure of the denser phase with certainty, it would be highly unlikely that such a phase separation could occur without aggregation in the dense phase. Figure 8 could then be taken as further evidence that aggregation occurs at C₁₂TAB concentrations well below its CMC at lower concentrations of POS4. The phase separation is very similar to that often described as coacervation,¹⁶ which normally occurs close to the charge neutralization point. Here it occurs at a charge ratio of only about 0.2 in the POS4 system (POS4:C₁₂TAB) indicating a strong interaction between the two species. We discuss the phase separation/coacervation further below.

Menger et al. used conductivity to determine the state of aggregation of the surfactant/oligomer in the bulk solution and their results for a POS3/C₁₂TAB mixture are replotted in Figure 9. They concluded from this plot that the CMC was not at the surface tension break (2.9 mM) but that it was at 14 mM. We replot the data in Figure 9 and show an alternative fit with a quadratic curve fitted by least-squares. Within error there is no detectable break that could be identified reliably at either concentration. Thus, the interpretation that there is no break at 2.9 mM is reasonable but then, by the same criterion, there is no reason to identify a break at 14 mM. Conductivity measurements are normally sensitive to the position of the CMC but the technique may become ambiguous under certain circumstances, especially for more complex mixtures. The failure of the conductivity experiment to detect any transition in POS3, although one at 3 mM is indicated by the surface tension measurements, is almost certainly associated with the high charge on the POS3 ions and the pattern of their binding to the micelles. The separation of the charges in POS3, which is close to the Bjerrum length (about 7 Å for water), means that there is probably some binding of sodium counterions to the POS3. The contribution of the faster moving sodium ions to the conductivity would be lost by being attached to the more slowly moving POS3. When the C₁₂TAB ions aggregate with POS3 and Br⁻ to form micelles, the conductivity would be expected to increase much less rapidly with concentration and this is how a CMC would normally be detected. However, it may be that the accompanying release of bromide and sodium ions is sufficient to offset this reduction at least to a level where no distinct break is observed in the conductivity. A similar compensation effect occurs in some of the gemini cationic surfactants where ion association and premicellar association act in opposite directions.¹⁷ In the data of Figure 9 there is a progressively slower increase in the conductivity from the initial

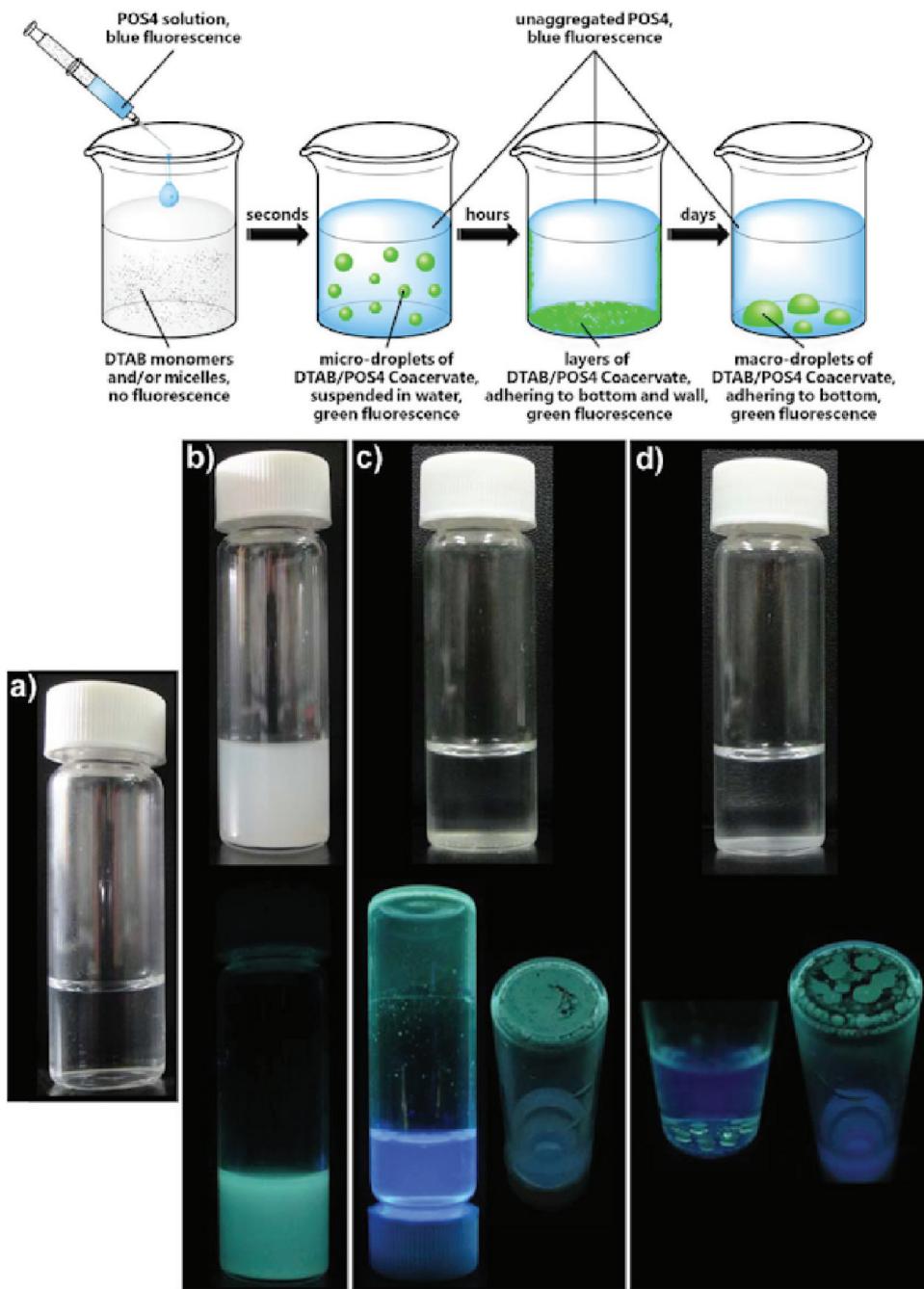


Figure 7. The phase separation in aqueous mixtures of POS4 and $C_{12}TAB$ (DTAB) at room temperature. The upper part of the diagram gives a schematic diagram of the direct observations and the lower part shows photographs of the fluorescence corresponding to the stages shown schematically above. The pale blue fluorescence is associated with monomer POS4 and the green fluorescence is associated with excimer emission.

surface tension break upward, but it is never as slow as for the pure $C_{12}TAB$ system above its CMC. We have not seen the other conductivity data of Menger et al., which may be less inconclusive than that shown in Figure 9.

That the conductivity should be affected by the composition of the counterions bound to the micelle is also suggested by the SANS data on POS3 at 20 mM, where the degree of dissociation was found to be unusually low. However, it is still surprising that Menger et al. did not see changes in the conductivity at the onset of coacervation in the POS6 system. These would be expected to be very evident, unless the measurements were made on too short a time scale. The

basic result is that misleading conductivity behavior conceals the fact that the onset of the surface plateau has the more normal and expected significance that it coincides with some kind of aggregation. The finer features of the differences between the four $POSn$ indicate that there are some very interesting changes as the size of the oligoion increases, in particular, the effect of $POSn$ concentration on the surface tension (and NR) data between 4 and 6, and that these features may be associated with the nature of the self-assembly in these systems, to which we now turn.

Self-Assembly in $C_{12}TAB/POS1$, $C_{12}TAB/POS2$ and $C_{12}TAB/POS3$. The results above show clearly that mixtures of $C_{12}TAB$ and

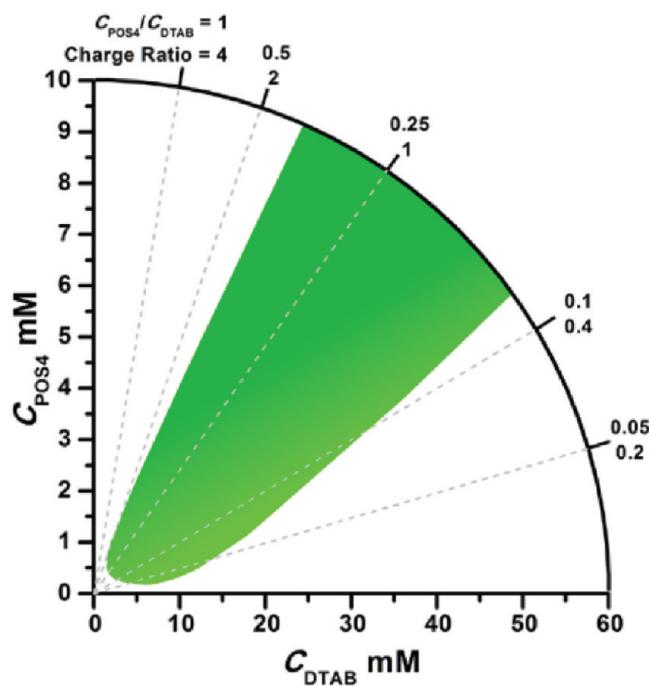


Figure 8. Phase diagram for mixtures of POS4 and C₁₂TAB (DTAB) at room temperature determined by measurements on the mixtures over several days. The two phase region is marked in green.

POS3 form normal micelles with no complications of phase separation, and that the CMC of the mixtures almost certainly coincides with the onset of the plateau in the surface tension. The variation of the CMC with composition suggests that the system is behaving as though it were a mixture of two surfactants. For the ideal mixing of two surfactants the CMC is given by

$$\frac{1}{c_{\text{mix}}} = \frac{\alpha_A}{c_A} + \frac{\alpha_B}{c_B} \quad (1)$$

where α are the bulk compositions, and c are the CMCs. A similar expression holds for the surface tensions but where the c now refer to the concentrations of the pure components and the mixture for a particular value of the surface tension.¹⁸ Since there is a strong charge interaction between the C₁₂TA and POS3 ions, the two surfactants making up the mixture will be C₁₂TAB and POS3-C_n where C is shorthand for the C₁₂TA ion and $n = 1-3$. The three possible POS3-C_n will each contribute a term to eq 1. However, POS3-C₃ will be by far the most surface active of the three and its formation is expected to be highly cooperative,¹⁹ so it should dominate the equation. Deviations from ideal mixing in surfactant systems almost always result from strong headgroup interactions and species of similar charge type normally interact close to ideally. Equation 1 should therefore apply approximately to the C₁₂TAB/POS3-C₃ mixture. The difficulty in applying the equation is that, although we know the proportions of the Br and POS3 ions in the system, the ratio of the two surfactants, i.e. the α value, is determined by the ratio of the equilibrium constants for the formation of the two surfactants, which we do not know. To circumvent this problem we first examine a solution for which the C₁₂TAB/POS3-C₃ ratio is as high as possible and we make the assumption that this completely converts the POS3 ion into POS3-C₃. We can then use the known composition and the observed mixed CMC to estimate the CMC of POS3-C₃. For 0.01 mM POS3 the mixed CMC (see Figure 2) is

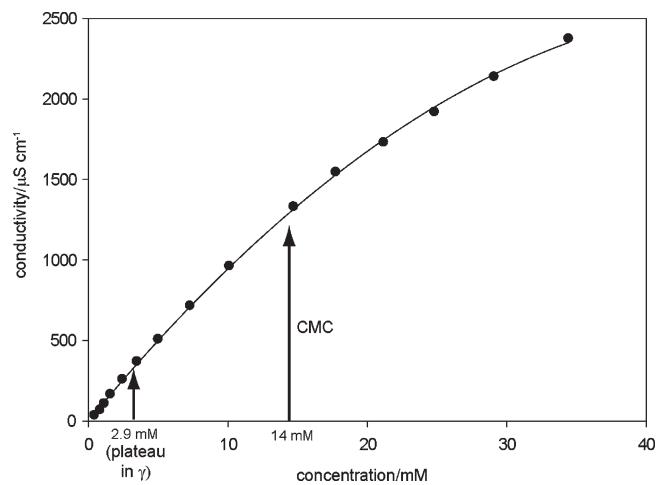


Figure 9. Conductivity of a POS3/C₁₂TAB mixture replotted from the graphical data in Figure 8. A quadratic curve, fitted by least-squares, has been drawn through the data to show that there are no obvious discontinuities.

9.3 mM in C₁₂TAB, i.e. a surfactant/ion ratio of 930. Substitution into eq 1 gives a value for the CMC of POS3-C₃ of 0.03 mM. A check using the measurement on the less saturated solution (0.03 mM POS3) gives 0.04 mM, indicating that saturation has been reached at the lower [POS3]. Thus, the 0.03 mM limit should be reasonably accurate. The value for POS2 is calculated from our own measurements at [POS2] = 0.1 mM, for which the mixed CMC is 7 mM, a surfactant/ion ratio of about 70. This gives 0.2 mM for the CMC of POS3-C₂. Using Menger's data for a surfactant/ion ratio of 15 and a mixed CMC of 3.9 mM gives 0.5 mM. This suggests that our much lower ion concentration has also approximately reached saturation. The only data available for POS1-C₁ is from Menger et al., where the ratio C₁₂TAB/POS1 was 5. This gives a value of about 4 mM for the CMC of POS3-C₁. Although a much lower surfactant/ion ratio will be necessary to saturate POS1 a factor of only 5 will probably overestimate the CMC of POS3-C₁ and the value of 4 mM should be regarded as an upper limit.

For any series of surfactants log CMC normally varies linearly with the number of carbon atoms and Figure 10 shows such a plot for POS1-C₁ to POS3-C₃. The plot is indeed approximately linear and the position of POS1-C₁ suggests that it is not too large an overestimate. The nearest possible comparison, between C₁₂TAB and the equivalent gemini surfactant with a xylol spacer,²⁰ gives a slope which is similar. Given that this gemini contains a similar spacer to that in POS2-C₂ this supports the simple interpretation that these three systems can be treated with the standard mixed micelle model.

Taking our results and the earlier ones of Menger et al. it can be concluded that the mixtures of POS1 to POS3 conform with the pattern expected for formation of species where the POS_n ion replaces wholly or partially the bromide ion to form various surfactants with stronger surface and self-assembling activities than the original C₁₂TAB. These mix with each other to give a single mixed CMC, which can be accounted for semiquantitatively by the standard mixing model. The micelles formed by POS3 and C₁₂TAB are not unusual and there is no unusual precipitation or cloudiness up to and including POS3. The low degree of ionization of the micelles in comparison with pure C₁₂TAB is also consistent with mixed micelles.

Phase Separation in C₁₂TAB/POS4 and C₁₂TAB/POS6. The POS4 and POS6 systems cannot be described with the

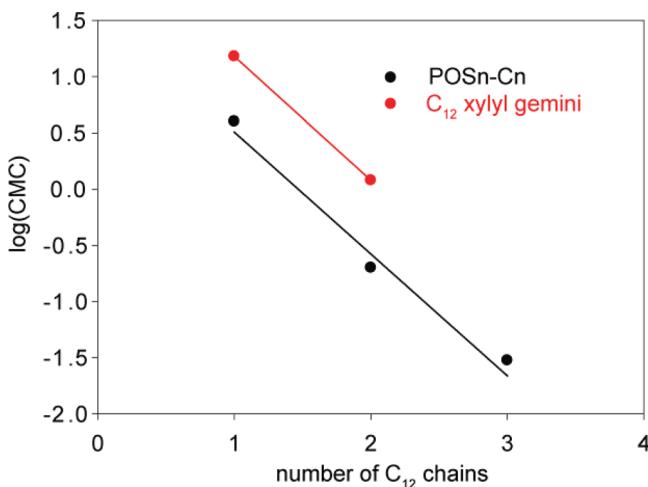


Figure 10. Plot of log CMC against number of chains for neutral surfactants formed by a POSn ion and the required number of C₁₂TAB ions. The CMCs were estimated from the observed mixed CMC at high C₁₂TAB/POSn ratios. Also shown are the values for C₁₂TABr and the gemini formed from two C₁₂DA chains connected by a xyl spacer.

same model as used for the lower members of the POSn series because phase separation is not characteristic of mixed micellar systems. It is helpful to start with a brief review of work on phase separations in related systems. Phase separations of this type are often termed coacervation and for this complexity of system are more particularly termed complex coacervation.¹⁶ They nearly always involve the addition of electrolyte (sometimes polyelectrolyte) to an aqueous solution, which brings about separation into two liquid phases, one very dilute in the original solute and one concentrated (the coacervate). The best-known types of coacervation are (i) aqueous polyelectrolyte/electrolyte mixtures,¹⁶ for which an underlying physical explanation has been given by Michaeli et al.,²¹ (ii) aqueous surfactant/electrolyte, e.g.,^{15,22} (or oppositely charged surfactant²³) mixtures, aqueous soaps, where the dilute phase is called lye, and (iii) polyelectrolyte/surfactant mixtures.^{24–26,27} Phase separations with some apparent similarity are those driven by the common salting out phenomenon so widely used in organic chemistry and exemplified by the addition of potassium carbonate to ethanol–water mixtures, which gives a concentrated phase containing 91% ethanol and a dilute phase of saturated aqueous potassium carbonate with a small amount of ethanol.²⁸ The main focus in cases of phase separations involving surfactants has been the structure of the dense (coacervate) phase and such evidence as there is suggests that this is often a sponge phase, for example,^{15,22} and the characteristics of the sponge phase have been identified both experimentally and theoretically.^{29–31,32} For our purposes the most important observations are that the basic structural unit in a sponge phase is a bilayer and that the sponge phase is usually adjacent to a standard lamellar phase in the phase diagram because this links up with the surface structure of C₁₂TAB/POS6.

Surface Behavior of C₁₂TAB/POS6 and C₁₂TAB/POS4. The fluorescence studies of the C₁₂TAB/POS4 system show that, while the dense phase contains a high enough concentration of surfactant for aggregation to occur, the surfactant/polyelectrolyte concentration in the dilute phase must be at or below the CAC because no signal from the aggregation is detected. Given this observation and the general observations on related systems above, we assume that this is also true for the C₁₂TAB/POS6

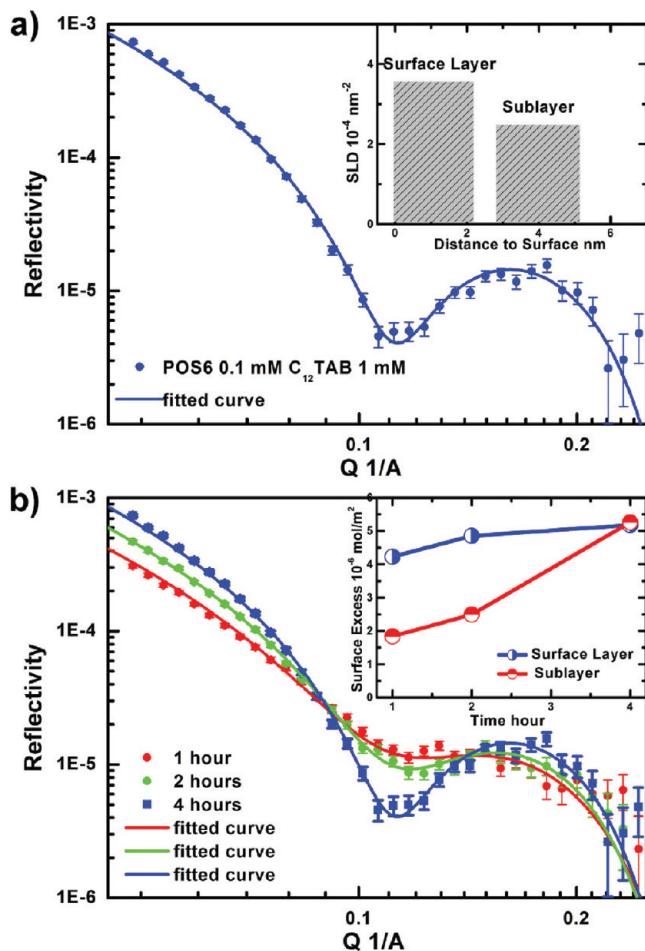


Figure 11. (a) Neutron reflectivity profiles of POS6/dC₁₂TAB at 1 mM in NRW and the distribution of C₁₂TAB required to fit it. (b) Development of the surface substructure with time in the same sample.

system. The neutron experiment was done on a time scale of hours so it is reasonable to assume that the neutrons observed the surface of the less dense dilute phase rather than that of the as yet unseparated mixture. What is then very surprising is that the neutron results show that the surface has a structured surface, even though there is no aggregation in the bulk dilute phase. This structure is well characterized by the interference fringe that is observed in the neutron reflectivity profiles of 0.1 mM POS6 and 1 or 5 mM C₁₂TAB. Figure 11a shows the 1 mM fringe after a long time and Figure 11b shows the slow development of this fringe with time. The fringe resembles those observed for several polyelectrolyte/surfactant systems and is characteristic of a monolayer at the air/water interface with a gap underneath it (here $6 \pm 1 \text{ \AA}$) followed by another surfactant layer (here about 28 \AA thick and with a density about 0.7 that of the monolayer). In polyelectrolyte systems this sublayer is usually close to a loosely packed bilayer, but here it is less dense. Note that the neutron experiment does not give any information about the lateral structure of the layer, which could be more complex than just a uniform bilayer.

Surface tension measurements are done more rapidly than the neutron experiments and our results, using the ring method, can be assumed to apply to the system before phase separation. This could be the explanation of why the surface tension shows no

break at the phase boundary, which occurs some way along the gently sloping plateau for the POS6 complex (see Figure 2). However, we have separately measured the tension of the dilute phase and found that it is the same as that of the unseparated mixture. That there is little difference between the surface tension of the unseparated mixture and of the dilute phase is then the more likely explanation of the smooth change in surface tension along the plateau.

The nature of the surface in two incompletely immiscible liquids has been thoroughly discussed by Rowlinson and Widom.³³ There are three interfacial tensions in the problem, the air/liquid tension of each of the liquid phases and the liquid/liquid tension. The experimental surface tension of the dilute phase is low. We do not know the tension of the dense phase and it would be difficult to measure because it is viscous. However, it is expected to be lower than that of the dilute phase, but not very much lower. Both phases should be coated with a monolayer but the dense phase will have some additional surface substructure. Although there seem to be no systematic studies of the effect of substructure on the tension, it is expected to contribute only a little extra to the value of the interfacial tension.³⁴ The little work that has been done on the tension in coacervate systems suggests that the tension between coacervate and dilute phases is low.¹⁶ If Antonow's rule applies (the highest of the three interfacial tensions is the sum of the other two) this is also consistent with a not too large difference between the tensions of the dense and dilute phases. The dilute phase is the less dense phase and will form the upper phase of the mixture. However, the phase with the lower air/liquid tension (here the dense phase) will spread as a thin film over the surface of the dilute phase because this lowers the free energy of the system. Rowlinson and Widom discuss the variety of possibilities for binary liquid systems in some detail and there are many subtleties, several of which have been observed experimentally, for example,^{35,36,37} However, there does not seem to be any discussion of the consequences when one of the liquids is a structured liquid.

On the basis of the discussion in Rowlinson and Widom the air/water interface of the dilute phase should be covered with a thin film of dense phase when there is phase separation. A thin film of incipient dense phase may also form as the concentration of phase separation is approached. The question then arises as to what could be the appearance of a thin film of a structured phase, such as a sponge phase. The situation is complicated because the structure of such a weakly structured phase is likely to be modified at a flat surface. Given that the basic unit of a sponge phase is a bilayer it is plausible that the thinnest possible film of dense phase consists of a monolayer plus a bilayer attached through the agency of the oligoion, as observed for C₁₂TAB/POS6. The C₁₂TAB/POS4 system has the same phase separation and same surface tension plateau as C₁₂TAB/POS6 but only a monolayer is formed. This can probably be attributed to the C₁₂TAB/POS4 system being intermediate between the simple mixed complexes of C₁₂TAB/POS3 and the trilayer structure of C₁₂TAB/POS6. The intermediate nature is supported by the coverage of the monolayer for POS4, which is significantly higher than the simple monolayers observed for POS2 and POS3 but evidently not sufficient for trilayer formation. One of the additional complications discussed by Rowlinson and Widom is the role of buoyancy and gravity in such wetting situations. In the neutron reflection experiments the use of deuterium labeled species may affect the densities of the two phases. In the experiments performed here the density of the dense phase will be enhanced

because the surfactant is deuterated whereas the solvent only contains 8% D₂O, but this does not seem to prevent the thin film of dense phase being formed at the air/water surface.

The change from forming mixed micelles in POS1–POS3 to forming lamellar based structures in POS6 can be understood from the structures of the POSn ions. Figure 1 shows the cross sections of a vertically oriented C₁₂TAB molecule marked as dashed circles. The lateral packing is such that the hydrophobic interaction between adjacent chains is favorable in all the complexes except POS6. For POS6 both the large gap at the center of the ion and the larger number of charged groups means that much of the cooperative interaction between hydrocarbon chains is lost. For example the intermediate species POS6-C₂⁴⁻ and POS6-C₃³⁻ have several configurations of the two surfactants where there is no hydrophobic attraction between the surfactant chains. Thus POS6-C₆ will be more surface active than the other members of the series simply because of the greater number of attached C₁₂TA, but its formation will be inhibited by the lack of cooperativity between surfactant chains. It will also be less easy for it to form spherical micelles as readily as the other POSn. Thus, any C₁₂TA ion attempting to occupy the central gap evident in Figure 1 will orient with its head-group pointing away from the aromatic rings. This will lead to a tendency to link up with other similar structures and hence to form lamellar structures, a tendency which will be reinforced by the large rigid area of the ion. A further weaker tendency to form lamellar structures, which is a function of the size of the rigid oligon, is that complexes can be formed with surfactant chains projecting on either side of the ion and this will assist the initiation and formation of the lamellar structures required for the eventual formation of a sponge phase.

Comparison with Polyelectrolyte/Surfactant Systems. The surface tension of all polyelectrolyte/surfactant mixtures at fixed low polyelectrolyte concentration but varying surfactant concentration initially decreases sharply to a plateau at a concentration often about 2 orders of magnitude lower than the CMC of the surfactant. On increasing the concentration along this plateau there is often an extensive range of concentration where the solution may become cloudy, there may be precipitation or there may be coacervation. The surface properties, tension and adsorption, divide into two patterns of behavior. In one, which we designate type A, the tension rises to a peak at some point along the plateau, and then falls back down to a limiting tension close to that of the free surfactant and in the region of the CMC. The lower concentration edge of the peak may or may not be sharp. Over the same concentration range, the surface coverage may deviate from a monolayer. Thus, it sometimes dips slightly at the peak in the surface tension. In the second pattern (type B) the tension stays more or less constant after the initial drop until it drops a little further to the second plateau close to the normal CMC. The behavior of the surface coverage in type B systems is quite different from that in A. Over much of the range a trilayer (a bilayer adsorbed with a small gap to the underside of the monolayer at the air/water interface) is formed, i.e. the coverage is approximately three times that of the saturated monolayer. Multilayers also often occur but these generally exist over a smaller concentration range than the trilayer. The trilayer/multilayer often disappears above the CMC and the start of the trilayer may or may not be at the concentration of the initial fall in tension.¹² The POS6/C₁₂TAB system completely conforms with the type B behavior. The close resemblance and the better defined experimental information available from the POS6/C₁₂TAB make it an interesting comparison.

The initial drop in surface tension occurs because of complexation of surfactant with polyelectrolyte and formation of a nearly saturated surfactant monolayer with some polyelectrolyte. A plateau results because complexation maintains the surfactant activity constant as the concentration increases, that is, this is a critical aggregation concentration (CAC). This is the same for both types of surface behavior. It is, however, easier to rationalize the type A behavior because the cloudiness that is nearly always observed indicates phase separation (precipitation or coacervation) or formation of aggregates in the solution, which will reduce the availability of polyelectrolyte/surfactant for surface adsorption and hence cause an increase in the surface tension. Further addition of surfactant reverses the charge on the complex, making it soluble and no longer surface active, saturates the polyelectrolyte, and the excess free surfactant then determines the rest of the surface behavior. This pattern is shown by the system SDS/PDMAAC in NaCl solution, where precipitation, surface coverage and tension were all followed carefully.³⁸ In addition, it was established that the surfactant was adsorbed in the form of a monolayer or less than complete monolayer throughout the changes in tension. The type B behavior is more difficult to explain because it is difficult to understand how the surface tension can be maintained at its plateau level, while precipitation or other bulk aggregation is occurring.

The model of Bell et al. rationalizes the two types of behavior by assuming a balance between separate equilibria for the formation of a surface complex ($CAC_{surface}$) and for a bulk surface complex (CAC_{bulk})³⁹ and then applying the Langmuir-Syszkowski equation relating surface tension and adsorption for each of the surface complex and the surfactant. The first complexation generates the surface active complex and causes the initial drop and onset of the surface tension plateau. In type A behavior bulk complexation occurs at a concentration not much higher than surface complexation, that is, the value of CAC_{bulk} is low enough to make formation of bulk complex dominant at higher concentrations. A surface tension peak then occurs when all the surface complex has been converted to bulk complex (note that this would also be true of precipitation and provided that the precipitate is in equilibrium with the solution the model is still valid). At higher concentrations the surface tension is determined by free surfactant. In type B systems, the value of CAC_{bulk} is relatively much higher, which allows the surface complex to dominate the surface behavior over the whole range of concentration. This interpretation implies that in the surface complex the surfactant interacts with polyelectrolyte in a way that stabilizes the extended form, so that it can align better with the surface, whereas in the bulk complex the surfactant stabilizes more coiled forms of the polyelectrolyte, which will not adsorb. This then suggests that the surfactant aggregates into micelles attached to the polyelectrolyte in the bulk complex. Fitting the model to a series of type A-behaving alkyl sulfate surfactants of varying chain length showed a good correlation of CAC_{bulk} with the strongly varying surfactant CMC, whereas $CAC_{surface}$ only had a weak chain length dependence,⁴⁰ both of which are consistent with the idea of the coiled and extended polyelectrolyte interactions. There are however some weaknesses in the model. The first is that the use of separate surface and bulk CACs seems artificial. Second, it does not account for phase separation in type B systems. Third, although the model explains both type A and type B systems in a simple way, the limiting surface tension at concentrations above the second plateau is predicted to be much too low in type B systems. This is because in practice the tension

at this point is close to that of pure surfactant but the model requires there to be an additional strong contribution from the stable surface complex.

The close resemblance of the properties of the POS6/C₁₂TAB system to the type B behavior suggests that the POS6 oligoion is large enough to be regarded as a polyelectrolyte, at least with respect to the surface behavior. Given this assumption, the much clearer delineation of the phase behavior offers a means of explaining some of the problematic aspects of type B systems. Moreover, the structural characteristics of POS6 indicate which factors could cause some systems to follow type B rather than type A behavior. The formation of the trilayer structure by the POS6/C₁₂TAB system indicates a very stable surface structure. Discussions of coacervation suggest that coacervation also relies on a strong stability of a bilayer.^{29–31,32} Through its rigidity and disposition of charge the POS6 ion is highly suited to forming lamellar structures and not well suited to participation in micellar structures. There is therefore a natural link between the basic oligoion structure, the structure of the dense (coacervate) phase and the trilayer surface structure, which suggests that type B behavior will be characteristic of more rigid polyelectrolytes. The POS6/C₁₂TAB system also shows experimentally that the effect of the removal of complexes on their availability for adsorption does not lead to an increase in surface tension. If the complex is strongly surface active the dense phase will have a lower surface tension than the dilute phase. As explained in the previous section this means that it will preferentially coat the air/water surface with an incipient layer of dense phase whatever the composition of the dilute phase. It is not generally known what phases are formed in type B polyelectrolyte/surfactant systems and polydispersity may further confuse the issue, but it is probable that unless the dense phase is physically removed, a mechanism similar to that for POS6/C₁₂TAB will ensure that the most stable surface structure will persist at the surface even after phase separation. Type B behavior should then be characteristic of polyelectrolytes with more rigid backbones.

Finally, we turn to the switch in the dependence of the CAC on the concentration of the POS_n ion on going from POS_n ($n \leq 4$) to POS6 (see Figure 2). The increase of CAC with POS6 concentration is paralleled in PSS/C₁₂TAB systems¹¹ but it is more or less independent of concentration in PDMDAAC/SDS systems,³⁸ which suggestss a connection between this and the type A/type B behavior. The observed trend can only be explained as there being insufficient surfactant relative to POS6 to form the surface active complex. Lowering the concentration of POS6 will increase the amount of surfactant per polymer only if it attaches itself randomly, rather than cooperatively, and this is consistent with the comments made about the POS6 structure above. It is also consistent with the idea that binding in type B systems creates structures that use links between the complexes on different polyelectrolyte molecules to form lamellae. That type A systems do not exhibit the same concentration dependence is consistent with the surfactant interacting more cooperatively within a single polyelectrolyte chain. However, these statements must be treated with caution because there is also the important element of exactly where the CAC is in relation to the concentrations being used. As n is increased in the POS_n the amount of surfactant required to create a surface active complex must also increase and, for a given POS_n concentration the relative surfactant concentration drops with n . As the POS6 concentration is lowered further than used in Figure 2, a point must come where the relative concentration of surfactant increases to a point where the value of the CAC must start to increase again.

■ CONCLUSIONS

The surface and bulk properties of mixtures of C₁₂TAB with individual members of a series of oligoarene sulfonates, POS2, POS3, POS4, and POS6 have been investigated by a variety of techniques. The results for the POS3 and POS4 mixtures show that the CMC or CAC of these systems coincides with the onset of a plateau in the surface tension, that is, there is no anomaly, as had been previously suggested.¹² Together with the earlier results of Menger et al. our results show that up to and including POS3 the mixtures can be explained in terms of mixed micelles of C₁₂TAB and POS_n-(C₁₂TA)_n with a single CMC and showing the usual surface tension plateau with an onset at the mixed CMC. There is a marked change in behavior for the POS4 and POS6 systems, which both phase separate. The POS4 system separates into a dense phase and a dilute phase, in which the surfactant concentration is at or below the CAC (coacervation). For POS6, although the dilute phase must form the upper layer of the mixture, the surface shows the presence of a structured surface layer, characteristic of a more concentrated phase, and its surface tension remains low. This paradox is explained in terms of wetting of the air/water surface of the dilute phase by a thin film of the more dense but lower surface tension phase. The close resemblance of the behavior of the POS6 system to one group of polyelectrolyte/surfactant mixtures shows that this ion is large enough to bring about polyelectrolyte type behavior. In comparison with polyelectrolytes, however, the POS6 is much better defined and the experimental information we have obtained is much more complete than possible for a polyelectrolyte/surfactant mixture. The greater detail of this information leads to possible new explanations for some of the unusual features of polyelectrolyte systems, in particular the smoothness of the surface tension plateau in one group of polyelectrolyte/surfactant mixtures.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: jbhhuang@pku.edu.cn (J.B.H.); robert.thomas@chem.ox.ac.uk (R.K.T.).

■ ACKNOWLEDGMENT

This work was supported by National Natural Science Foundation of China (20873001, 20633010, 21073006, and 50821061) and National Basic Research Program of China (Grant No. 2007CB936201). We also thank the staff and facilities of ILL, Grenoble, France, and ISIS, STFC, U.K., for support with the neutron beam facilities.

■ REFERENCES

- (1) Menger, F. M.; Shi, L. *J. Am. Chem. Soc.* **2009**, *131*, 6673.
- (2) Menger, F. M.; Shi, L.; Rizvi, S. A. A. *J. Am. Chem. Soc.* **2009**, *131*, 10831.
- (3) Penfold, J.; Thomas, R. K.; Zhang, X. L.; Taylor, D. J. F. *Langmuir* **2009**, *25*, 3972.
- (4) Simister, E. A.; Lee, E. M.; Thomas, R. K.; Penfold, J. *J. Phys. Chem.* **1991**, *96*, 1373.
- (5) Penfold, J.; et al. *J. Chem. Soc., Faraday Trans.* **1997**, *93*, 3899.
- (6) Thirtle, P. N.; Li, Z. X.; Thomas, R. K.; Rennie, A. R.; Satija, S. K.; Sung, L. P. *Langmuir* **1997**, *13*, 5451.
- (7) Born, M.; Wolf, E. *Principles of Optics*, 7th ed.; Cambridge University Press: Cambridge, U.K., 2003.
- (8) <http://www.ill.fr>.
- (9) Ghosh, R. E.; Egelhaaf, S.; Rennie, A. R. *ILL Internal Report ILL98GH14T* **1998**.
- (10) Hayter, J. B.; Penfold, J. *Colloid Polym. Sci.* **1983**, *261*, 1072.
- (11) Taylor, D. J. F.; Thomas, R. K.; Penfold, J. *Langmuir* **2002**, *18*, 4748.
- (12) Taylor, D. J. F.; Thomas, R. K.; Penfold, J. *Adv. Colloid Interface Sci.* **2007**, *132*, 69.
- (13) Lyttle, D. J.; Lu, J. R.; Thomas, R. K.; Penfold, J. *Langmuir* **1995**, *11*, 1001.
- (14) Hayter, J. B.; Penfold, J. *Colloid Polym. Sci.* **1983**, *261*, 1022.
- (15) Menger, F. M.; Sykes, B. M. *Langmuir* **1998**, *14*, 4131.
- (16) Kruty, H. R.; Bungenberg de Jong, H. G. *Colloid Science, Vol. II, Reversible Systems*; Elsevier: Amsterdam, 1949.
- (17) Li, P. X.; Dong, C. C.; Thomas, R. K.; Penfold, J.; Wang, Y. L. *Langmuir* **2011**, *27*, 2575–2586.
- (18) Clint, J. H. *J. Chem. Soc., Faraday Trans.* **1975**, *71*, 1327.
- (19) Pereira, R. F. P.; Tapia, M. J.; Valente, A. J. M.; Evans, R. C.; Burrows, H. D.; Carvalho, R. A. *J. Colloid Interface Sci.* **2011**, *354*, 670.
- (20) Li, Z. X.; Dong, C. C.; Thomas, R. K. *Langmuir* **1999**, *15*, 4392–4396.
- (21) Michaeli, I.; Overbeek, J. T. G.; Voorn, M. J. *J. Polym. Sci.* **1957**, *23*, 4843.
- (22) Menger, F. M.; Peresypkin, A. V.; Caran, K. L.; Apkarian, R. P. *Langmuir* **2000**, *16*, 9113.
- (23) Mukhayer, M. J.; Davis, S. S. *J. Colloid Interface Sci.* **1978**, *66*, 110.
- (24) Li, Y. J.; Dubin, P. L.; Have1, H. A.; Edwards, S. L. *Langmuir* **1995**, *11*, 2486.
- (25) Wang, Y. L.; Kimura, K.; Dubin, P. L.; Jaeger, W. *Macromolecules* **2000**, *33*, 3324.
- (26) Kumar, A.; Dubin, P. L.; Hernon, M. J.; Li, Y. J.; Jaeger, W. *J. Phys. Chem. B* **2007**, *111*, 8468.
- (27) Deng, M. L.; Cao, M. W.; Wang, Y. L. *J. Phys. Chem. B* **2009**, *113*, 9436.
- (28) Dervichian, D. G. *Discuss. Faraday Soc.* **1954**, *18*, 231.
- (29) Porte, G.; Appell, J.; Bassereau, P.; Marignan, J.; Skouri, M.; Billard, I.; Delsanti, M. *Phys. A* **1991**, *176*, 168.
- (30) Roux, D.; Safinya, C. R. *J. Phys. (Paris)* **1988**, *49*.
- (31) Roux, D.; Codon, C.; Cates, M. E. *J. Phys. Chem.* **1992**, *96*, 4174.
- (32) Strey, R.; Schomacker, R.; Roux, D.; Nallet, F.; Olsson, U. *J. Chem. Soc., Faraday Trans.* **1990**, *86*, 2253.
- (33) Rowlinson, J. S.; Widom, B. *Molecular Theory of Capillarity*; Clarendon Press: Oxford, U.K., 1982.
- (34) Kashchiev, D.; Exerowa, D. *Eur. Biophys. J.* **2001**, *30*, 34.
- (35) Moldover, M. R.; Cahn, J. W. *Science* **1980**, *207*, 1073.
- (36) Bonn, D.; Kellay, H.; Wegdam, G. H. *Phys. Rev. Lett.* **1992**, *69*, 1975.
- (37) Kellay, H.; Bonn, D.; Wegdam, G. H. *Phys. Rev. Lett.* **1993**, *71*, 2607.
- (38) Staples, E.; Tucker, I.; Penfold, J.; Warren, N.; Thomas, R. K.; Taylor, D. J. F. *Langmuir* **2002**, *18*, 5147.
- (39) Bell, C. G.; Breward, C. J. W.; Howell, P. D.; Penfold, J.; Thomas, K.; Robert *Langmuir* **2007**, *23*, 6042.
- (40) Penfold, J.; Tucker, I. M.; Thomas, R. K.; Taylor, D. J. F.; Zhang, X. L.; Bell, C. G.; Breward, C. J. W.; Howell, P. D. *Langmuir* **2007**, *23*, 3128.