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The Adsorption of Surfactants at the Air–Liquid Interface from Complex Mixtures, Measured by Specular Neutron Reflection[1]

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The specular reflection of neutrons, in combination with isotopic labeling, has been shown to be a powerful technique for the study of surfactant absorption at the air–liquid interface. It can be used to obtain adsorbed amounts in complex multicomponent systems and to determine the structure of the adsorbed monolayer. The adsorption of the alkyl polyoxyethylene nonionics surfactant and mixtures of anionic and cationic surfactants with the nonionic surfactants is described. The effects of temperature, electrolyte, and less polar solvents (the addition of sorbitol) to the adsorption and structure are discussed.

KEY WORDS: air–liquid interface; complex fluids; surfactant adsorption.

1. INTRODUCTION

The nature of adsorption of complex surfactant mixtures at interfaces is important in that most domestic and industrial applications involve mixtures. Mixtures are used in detergency applications either to optimize performance [1] or because commercial products involve impure materials. In applications and processing it is important to know the effects of modifying solvent quality, by temperature, added electrolyte, or additives such as sorbitol.

Neutron reflectivity, in combination with isotopic labeling, has been demonstrated to be an effective method to study surfactant adsorption at

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the air–liquid interface [2, 3]. It provides a direct and absolute method for the determination of adsorbed amounts for one-component [4] and multicomponent mixtures [5]. Furthermore, it enables the structure of the adsorbed layer to be determined in greater detail than has previously been possible by other techniques [6, 7].

We have investigated the effect of temperature and added electrolyte (both "salting in" and "salting out") on the adsorption of the alkyl polyoxyethylene oxide nonionic surfactants, $C_nH_{2n+1}(OC_2H_4)_mOH$ (abbreviated here to C_nE_m), for $C_{12}E_3$ to $C_{12}E_{12}$; the effect of sorbitol on the adsorption of $C_{12}E_6$ and the partitioning at the interface of the mixture sodium dodecyl sulfate, SDS/$C_{12}E_3$; and the effect of temperature on the partitioning at the interface of the mixture hexadecyltrimethyl ammonium bromide, CTAB/$C_{12}E_6$. Finally, we report the effects of the mixed water-sorbitol solvent on the structure of the $C_{12}E_6$ monolayer at the air–solution interface.

2. MEASUREMENTS

The neutron reflectivity measurements were made on the CRISP reflectometer [8] at the ISIS pulsed neutron source, Rutherford–Appleton Laboratory, UK. The white beam time of flight method was used at a fixed angle of incidence of 1.5°. The data were recorded over a wave vector transfer, κ (where $\kappa = 4\pi \sin \theta/\lambda$, θ is the glancing angle of incidence, and λ the neutron wavelength) range of 0.052 to 0.65 $Å^{-1}$. The absolute intensities were calibrated with respect to the reflectivity from D_2O, and a flat background determined by extrapolation to high κ values was subtracted from the reflectivity profiles; the detailed experimental procedures are described elsewhere [9].

The protonated surfactants were obtained from Nikkol (nonionics), BDH (SDS, CTAB), the alkyl-chain deuterated SDS (d-SDS), and D_2O from MSD Isotopes. The synthesis of the deuterium-labeled nonionic surfactants (alkyl-chain deuterated $C_{12}E_3$ to $C_{12}E_{12}$, and partially labeled compounds $hC_{12}hE_3dE_3$, $dC_{12}hE_3dE_3$) and the purification of all the surfactants were performed by standard procedures which are described in detail elsewhere [10, 11].

For a deuterated surfactant in null-reflecting water, nrw (a 92 mol% H_2O/D_2O mixture has a scattering-length density of zero, that is, a refractive index identical to air), the reflected signal arises only from the adsorbed surfactant layer at the interface. The adsorbed amount at the interface can then be evaluated by fitting the reflctivity to a model of a simple uniform layer, such that the area/molecule A is given by [4],

$$A = b/\tau\rho \tag{1}$$

where b is the neutron scattering length of the deuterated species, and τ and ρ are the model layer thicknesses and scattering-length densities. The surface excess, Γ (in mol · cm^{-2}), is then $\Gamma = 1/\mathrm{Na}A$ and Na is Avogadro's number. For a binary mixture the amount of each component adsorbed at the interface can be obtained by measuring the reflectivity as described above, but with each component in turn selectively deuterated. The scattering length of the protonated component is close to zero, small compared to the deuterated species. The area/molecule of each component is then related to the thickness and scattering length density of the uniform layer model by [12]

$$\rho = \frac{b_1}{A_1 \tau} + \frac{b_2}{A_2 \tau} \tag{2}$$

where $A_{1,2}$ and $b_{1,2}$ are the area/molecule and scattering length of each component. The errors associated with the determination of absolute adsorbed amounts have been discussed in detail elsewhere [4, 12] and are typically <5%. Figure 1 shows the reflectivity for $10^{-5}\,M\,C_{12}E_8$ in nrw and in 1 MNaCl/nrw at 30 C, and the corresponding uniform layer model fits. These results are typical of the reflectivity data for such systems.

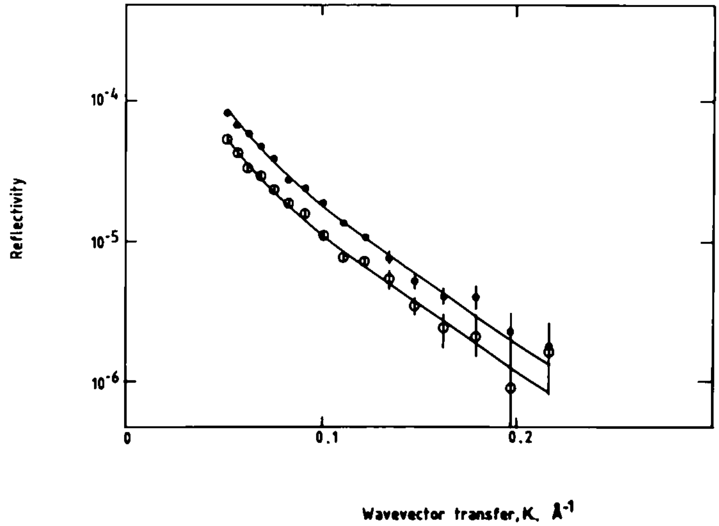

Fig. 1. Reflectivity for $10^{-5}\,M\,C_{12}E_8$ in nrw (○) and 1 M NaCl/nrw (●) at $t = 30°C$ (background subtracted); the solid lines are uniform layer fits for (○) $d = 16.6$, $\rho = 0.2 \times 10^{-5}$, and (●) $d = 17.3$, $\rho = 0.24 \times 10^{-5}$.

The structure information about the adsorbed layer is obtained either by model fitting [13] to the reflectivity profiles obtained from differently labeled surfactants by means of Fresnels equations or by the determination of partial structure factors [14]. In the latter approach it has been shown [15] that a set of neutron reflectivity profiles from samples of different isotopic composition can be analyzed by a direct method based on the kinematic scattering approximation. In the simplest isotropic-labeling scheme the scattering-length density for a surfactant layer at the air–water interface can be written as

$$\rho(z) = b_c n_c(z) + b_h n_h(z) + b_s n_s(z) \tag{3}$$

where n_i is the number density profile of labeled component i and b_i, its scattering length density. In this case c, h, and s refer, respectively, to the surfactant alkyl-chain and headgroup and the solvent. The kinematic approximation for the reflectivity $R(\kappa)$ may be written in terms of the partial structure factors, h_{ii} [15],

$$R(\kappa) = \frac{16\pi^2}{\kappa^2}\left[b_c^2 h_{cc} + b_h^2 h_{hh} + b_s^2 h_{ss} + 2b_c b_h h_{ch} + 2b_c b_s h_{cs} + 2b_h b_s h_{hs}\right] \tag{4}$$

where h_{ii} are the partial structure factors given by

$$h_{ii}(\kappa) = |n(\kappa)|^2 \tag{5}$$

and $h_{ii}(\kappa)$ is the one-dimensional Fourier transform of $n_i(z)$ [15]. The self partial structure factors, h_{ii}, contain information about the distribution of each labeled component and are modeled by Gaussian distributions for the different parts of the surfactant and a tanh distribution for the solvent [14, 15]. The cross terms provide directly information about the relative positions of the different components [15] and are characterized by a separation δ. $R(\kappa)$ and $h(\kappa)$ decay rapidly with κ, and for convenience they are evaluated and plotted as $\kappa^2 h(\kappa)$. For the labeling scheme in Eq. (3) the six partial structure factors in Eq. (4) can be obtained from the six different reflectivity profiles measured by means of different isotopic labeling schemes.

3. RESULTS

The detail of surfactant micellisation and adsorption at interfaces in modified solvents is of much current interest [16]. The effect of the addition of sorbitol on the surface tension of water is consistent with negative adsorption at the interface in the absence of surfactant and positive adsorption in the presence of a nonionic surfactant such as $C_{12}E_6$. This suggests a direct interaction between the sorbitol and the ethylene oxide group. The surface-tension and neutron-reflectivity data [17] do, however, indicate that the adsorption of $C_{12}E_6$ at the air–water interface is unaffected by the addition of sorbitol. In a previous study we have used neutron reflectivity to determine the adsorption of the surfactant mixture SDS/$C_{12}E_3$ at the air–water interface [5] at a fixed bulk composition (65 mol% $C_{12}E_3$) over a wide range of concentrations in excess of the critical micellar concentration, cmc. The surface layer, in equilibrium with a bulk lamellar phase, demonstrates an evolving surface composition with concentration, the SDS concentration increases and that of $C_{12}E_3$ decreases, even though the surface tension is constant over this range of concentration. The surface composition was also in good agreement with the predictions of regular solution theory, RST [18]. We have investigated the effects of the addition of sorbitol on the surface composition of this mixture. The surface tension changes are less dramatic due to reduced ethylene oxide (EO)–sorbitol interaction. The neutron-reflctivity measurements show that the partitioning at the interface is unaffected by the addition of sorbitol. Figure 2 shows the proportion of SDS in the adsorbed layer obtained by neutron reflectivity for a 65 mol% $C_{12}E_3$/SDS mixture in a 300 g · L^{-1} sorbitol/0.1 *M* NaCl/water mixture and the predictions of RST for the pure-water solvent.

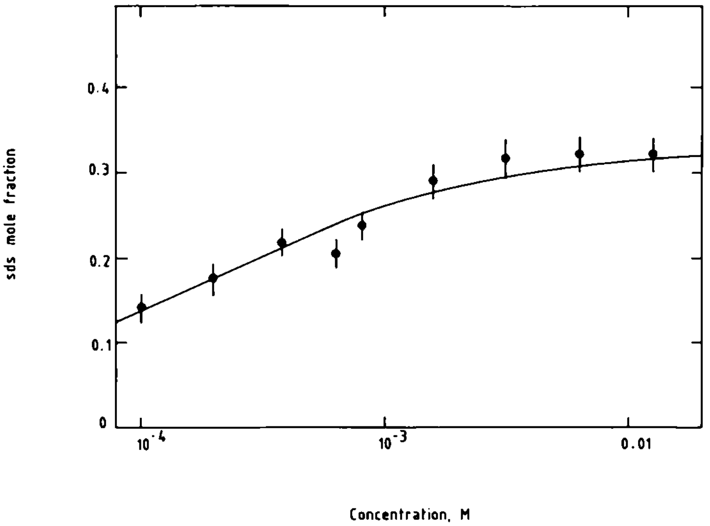

Fig. 2. Mole fraction of SDS at the air–liquid interface for a 65 mol% $C_{12}E_3$/SDS surfactant mixture in a 300 g · L^{-1} sorbitol/0.1 *M* NaCl/water mixture. The solid line is a prediction of RST for a pure-water solvent [5].

Table I. Changes in Area/Molecule, *A*, for 10^{-5} *M* $C_{12}E_8$ with Added Electrolyte at $T = 30°C$

	Pure water	0.1 *M* NaCl	1 *M* NaCl	0.1 *M* Na_2SO_4	0.5 *M* NaSCN
Area/molecule	86.0	79.0	67.0	77.0	90.0

In contrast to the situation of the modification of solvent quality by sorbitol, the addition of "salting in" and "salting out" electrolyte, in which there is also a specific interaction with the EO group, has no significant effect on the adsorption of nonionic surfactants at the air–liquid interface. Table I summarizes the changes in area/molecule for the addition of NaCl, Na_2SO_4, and sodium thiocyanate (NaSCN) for 10^{-5} *M* $C_{12}E_8$, and a similar trend is observed for $C_{12}E_6$ and $C_{12}E_{12}$.

The effect of temperature on the adsorption of nonionic surfactants and mixtures involving nonionics is expected to be significant due to the dehydration of the ethylene oxide (EO) group. We have demonstrated that there is little effect of temperature on the coverage of the pure material, as shown in Fig. 3. However a significant variation is observed when the material is impure, due to the temperature dependent of the cmc of different C_nE_m's in the impure surfactant (the main impurities are nonionics of different EO length). The addition of electrolyte does not substantially

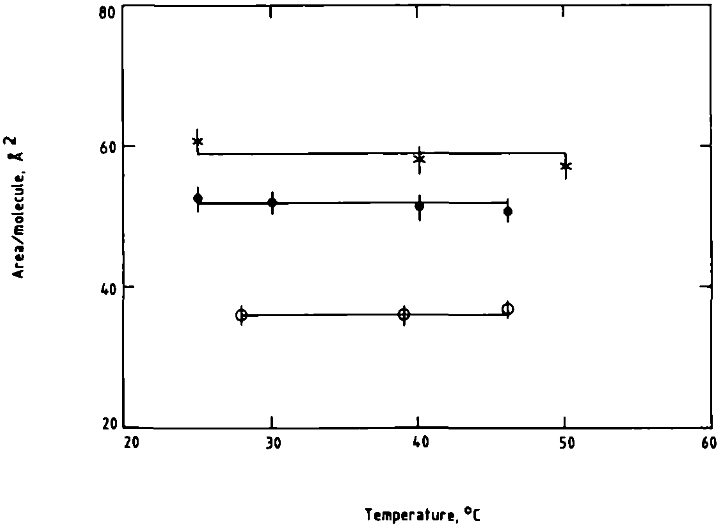

Fig. 3. The temperature dependence of the area/molecule for 5×10^{-5} *M* $C_{12}E_3$, 6×10^{-5} *M* $C_{12}E_6$, and 9×10^{-5} *M* $C_{12}E_8$ (at ~cmc).

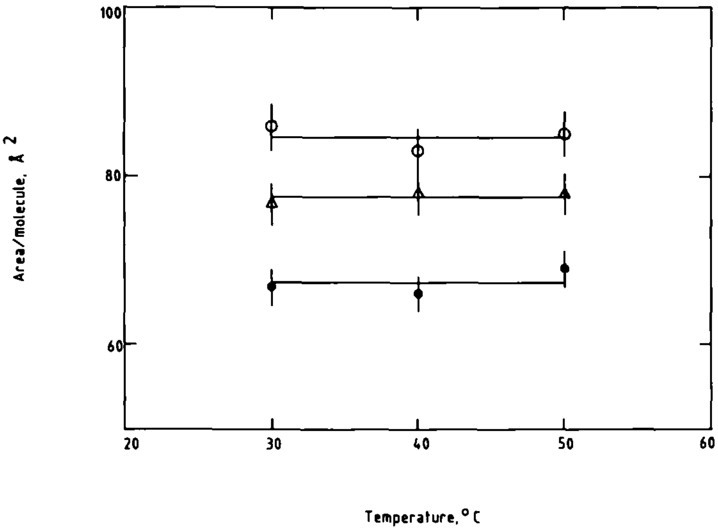

Fig. 4. The temperature dependence of the area/molecule of 1×10^{-5} *M* $C_{12}E_8$ in (○) pure water, (●) 1 *M* NaCl, and (△) 0.1 *M* Na_2SO^4.

alter this temperature invariance, as shown in Fig. 4. For $C_{12}E_8$ we have demonstrated that subtle changes in the structure of the adsorbed layer do occur [19]. With increasing temperature the alkyl-chain region becomes thicker, but the thickness of the EO chain region does not change. These differences and changes in the separation of the different fragments suggest that the layer is increasingly roughened at the higher temperatures and that the EO chain is significantly dehydrated.

From the previous discussions it is anticipated that temperature will affect the partitioning of surfactant mixtures involving nonionics. We have extensively studied the cationic/nonionic mixture of CTAB/$C_{12}E_6$ in 0.1 *M* NaBr [20]. At concentrations >cmc ideal mixing is essentially observed, and below the cmc departures from ideal mixing occurs.

Table II. Temperature Dependence of Area/Molecule, *A*, of CTAB and $C_{12}E_6$ in 2×10^{-5} *M* CTAB/$C_{12}E_6$/0.1 *M* NaBr Mixed Surfactants

Temperature (°C)	*A*, CTAB	*A*, $C_{12}E_6$
30	60.0	189.0
50	80.0	153.0

Preliminary measurements on the effect of temperature on the surface composition of mixtures for CTAB/$C_{12}E_6$ show a marked decrease in the surface excess of the CTAB and an increase in the adsorption of $C_{12}E_6$ with increasing temperature (see Table II). It is expected that such temperature-induced changes will have a pronounced effect on the structure of the mixed monolayer, and this is currently being investigated.

We have demonstrated that the addition of sorbitol to $C_{12}E_6$ and mixed SDS/$C_{12}E_3$ surfactant solutions does not alter the adsorption pattern at the air–solution interface. It is expected that the sorbitol association with the EO groups will result in changes in the structure of the surfactant monolayer and especially in the conformation of the EO chain. We have used here our previous experience on $C_{12}E_6$ and $C_{12}E_8$ [5–7] to label partially the EO chain in order to obtain more detailed information on the EO chain conformation. Specifically we have deuterium labelled the three EO units at the free end of the EO chain such that the scattering length density is,

$$\rho(z) = b_c n_c(z) + b_{e1} n_{e1}(z) + b_{e2} n_{e2}(z) + b_s n_s(z) \tag{6}$$

where $e_{1,2}$ refer to the EO_3 group nearest of farthest from the alkyl chain. If it is assumed that the protonated EO_3 nearest the alkyl chain (e1) has a scattering length density of zero [7] then the reflectivity is,

$$R(\kappa) = \frac{16\pi^2}{\kappa^2} [b_c^2 h_{cc} + b_{e2}^2 h_{e2e2} + b_s^2 h_{ss} + 2b_c b_{e2} h_{ce2} + 2b_c b_s h_{cs} + 2b_{e2} b_s h_{e2} s] \tag{7}$$

A set of six partial structure factors is obtained from the reflectivities arising from the isotopic combinations of $dC_{12}hE_6$ in nrw and D_2O, $dC_{12}hE_3hE_6$ in nrw and D_2O, $hC_{12}hE_3hE_6$ in nrw, and hC_{12} hE_6 in D_2O. These partial structure factors describe the distributions of the alkyl chain, solvent, EO_3 group farthest from the alkyl chain and their relative positions and are discussed in detail elsewhere [15]. Figure 5 shows the partial structure factor h_{ce2}, which describes the relative positions of the EO_3 group and alkyl-chain distributions with and without added sorbitol. The solid lines are calculated curves for separations, δ_{ce2}, of 9.0 and 10.0 Å and are indicative of the sensitivity of the technique to changes in the structure. The number-density distributions of the different components obtained from this analysis are an appropriate way of demonstrating the structure of the monolayer. Figure 6 shows these distributions for the alkyl chain, solvent, and EO_3 group (e2) with and without added sorbitol ($300\,g \cdot L^{-1}$) and shows clearly that the addition of sorbitol has altered the structure of

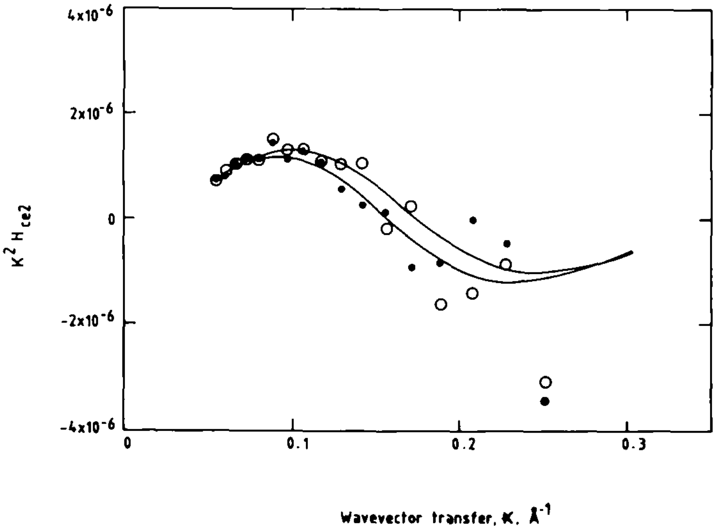

Fig. 5. Alkyl-ethylene oxide chain (e2) partial structure factor, $\kappa^2 h_{ce2}$, for 3×10^{-5} *M* $C_{12}E_6$ (○) in water and (●) in 300 g · L^{-1} sorbitol/water mixed solvent. The solid lines are calculated curves for δ_{ce2} of 9.0 and 10.0 Å, respectively.

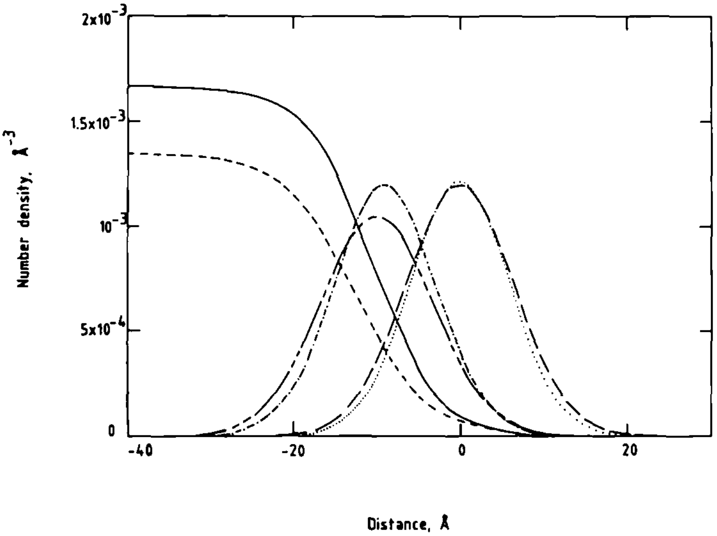

Fig. 6. $C_{12}E_6$ in water and water/300 g · L^{-1} sorbitol (solid line), water (dashed line), mixed solvent (broad dashed line), alkyl chain in water (dotted line), alkyl chain in mixed solvent (dashed–dotted line), e2 EO chain in water, and (dashed–dashed line) e2 EO chain in mixed solvent. The origin has been arbitrarily taken as the center of the alkyl-chain distribution.

the monolayer. The widths of the alkyl chain and e2 have both increased, and the separation between the alkyl chain and solvent, and e2 and solvent, has also increased. These results are consistent with an adsorption of sorbitol onto the EO chain, which gives rise to an increase in EO chain extension because of steric effects and a dehydration of the chain.

REFERENCES

1. M. Rosen, in *Phenomena in Mixed Surfactant Systems*, J. F. Scamehorn, eds. (ACS Symposium Series, Washington, DC, 1986), p. 311.
2. J. Penfold and R. K. Thomas, *J. Phys. Condens. Mater.* **2**:1369 (1990).
3. T. L. Crowley, E. M. Lee, E. A. Simister, R. K. Thomas, J. Penfold, and A. R. Rennie, *Colloids Surf.* **52**:85 (1990).
4. E. A. Simister, R. K. Thomas, J. Penfold, R. Aveyard, B. P. Binks, P. D. I. Fletcher, J. R. Lu, and A. Sokolowski, *J. Phys. Chem.* **96**:1383 (1992).
5. E. Staples, L. Thompson, I. Tucker, J. Penfold, R. K. Thomas, and J. R. Lu, *Langmuir* **9**:1651 (1993).
6. J. R. Lu, Z. X. Li, R. K. Thomas, E. Staples, I. Tucker, and J. Penfold, *J. Phys. Chem.* **97**:8012 (1993).
7. J. R. Lu, M. Hromadova, R. K. Thomas, and J. Penfold, *Langmuir* **9**:2417 (1993).
8. J. Penfold, R. C. Ward, and W. G. Williams, *J. Phys. E Sci. Instrum.* **40**:1411 (1987).
9. E. M. Lee, R. K. Thomas, J. Penfold, and R. C. Ward, *J. Phys. Chem.* **93**:381 (1989).
10. J. R. Lu, Z. X. Li, T. J. Su, R. K. Thomas, and J. Penfold, *Langmuir* **9**:2408 (1993).
11. J. R. Lu, E. M. Lee, R. K. Thomas, J. Penfold, and S. L. Flitsch, *Langmuir* **9**:1352 (1993).
12. J. R. Lu, R. K. Thomas, R. A. Aveyard, B. P. Binks, P. Cooper, P. D. I. Fletcher, A. Sokolowski, and J. Penfold, *J. Phys. Chem.* **96**:10971 (1992).
13. J. Penfold, in *Neutron, X-Ray and Light Scattering*, P. Lindner and T. Zemb, eds. (Elsevier, New York, 1991), p. 223.
14. E. A. Simister, E. M. Lee, R. K. Thomas, and J. Penfold, *J. Phys. Chem.* **96**:1373 (1992).
15. J. R. Lu, E. A. Simister, R. K. Thomas, and J. Penfold, *J. Phys. Chem.* **97**:6024 (1993).
17. E. Staples, L. Thompson, I. Tucker, J. Penfold, R. K. Thomas, and J. R. Lu, in preparation.
18. P. M. Holland, *Colloids Surf.* **19**:171 (1986).
19. J. R. Lu, R. K. Thomas, E. Staples, L. Thompson, I. Tucker, and J. Penfold, *J. Phys. Chem.* (in press).
20. J. Penfold, E. Staples, I. Tucker, P. Cummins, R. K. Thomas, A. A. Simister, and J. R. Lu, in preparation.