

Small Angle Neutron Scattering Study of Demixing in Micellar Solutions Containing CTAC and a Partially Fluorinated Cationic Surfactant

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Demixing of fluorocarbon and hydrocarbon surfactants to form coexisting fluorocarbon-rich and hydrocarbon-rich micelles has been studied by small angle neutron scattering in aqueous solution, using an equimolar mixture of cetyltrimethylammonium chloride and the partially fluorinated cationic surfactant *N*-(1,1,2,2-tetrahydroperfluorodecanyl)pyridinium chloride, with a deuterated pyridinium headgroup. Measurements have been performed under varying experimental conditions: in both pure aqueous solutions and with salt (0.10 M NaCl), at several contrasts for neutrons obtained by varying the H₂O/D₂O ratio, mainly at 25 °C but also at 60 °C to promote mixing of the surfactants. The experiments show that a substantial residual scattering is retained at the solvent composition where the average scattering length density of mixed micelles would match that of the solvent. It is moreover observed that, in solutions without added salt, a prominent correlation peak observed in 100% D₂O disappears at the match point. These observations are in accordance with a very broad composition distribution, possibly composed of two populations of mixed micelles of similar sizes but different compositions, but would not result from micelles with merely a highly inhomogeneous internal structure. Increasing the temperature from 25 to 60 °C reduces substantially the scattered intensity at zero angle at the match point, as expected for a less broad population of mixed micelles. In the numerical analysis, the scattering data for scattering vector $q \geq 0.02 \text{ \AA}^{-1}$ were analyzed by the indirect Fourier transform method to give the scattering at zero angle. From these data, the average micelle aggregation number was obtained as 76 at 25 °C and 54 at 60 °C. The contrast variation results for the intensity at zero angle give a measure of the width of the micelle distribution, which is obtained as $\sigma = 0.33$ at the lower temperature and $\sigma = 0.20$ at 60 °C. The result at the low temperature is compatible with the formation of two populations that are polydisperse ($\sigma = 0.07$) and centered around 18 and 82%; other broad distributions cannot be excluded.

Introduction

Mixtures of fluorocarbon and hydrocarbon surfactants in aqueous solution assemble either to form mixed micelles or to form coexisting populations of hydrocarbon-rich and fluorocarbon-rich micelles. Such a microscopic demixing was suggested early on^{1,2} but only in a few cases has uncontroversial evidence for it been presented. Some clear cases can be mentioned. Using a fluorinated and a conventional hydrophobic dye, the former preferentially soluble in micelles of mainly fluorinated surfactants and the latter preferring normal micelles, Haegel and Hoffmann³ demonstrated by ultracentrifugation that both types of micelles were present in a solution containing both sodium perfluorooctanoate (SPFO) and dimethyltetradecylaminoxide (TDMAO). For mixtures of lithium perfluorooctanesulfonate and lithium tetradecylsulfate, Asakawa et al.⁴ used gel filtration to clearly separate the two types of micelles. Other studies have given strong indications of demixing in several systems but are often convincing only for the specialists. To these belong several fluorescence studies^{4–11} and some NMR studies,^{12,13} in particular involving hexadecyltrimethylammonium chloride (CTAC) and *N*-(1,1,2,2-tetrahydroperfluorodecanyl)pyridinium chloride (HFDePC) which are the surfactants used in the present study.

In other systems, notably SPFO with sodium decanoate or sodium dodecanoate (or the corresponding mixtures with ammonium salts), the results or conclusions are conflicting.^{13–18} The careful small angle neutron scattering (SANS)^{19,20} and NMR²¹ studies of Caponetti et al. strongly suggest that only mixed micelles are formed in SPFO and sodium dodecanoate, but with an internal segregation of the fluorinated chains in the mixed micelles to form domains of fluorinated and hydrogenated chains.²¹ A similar internal segregation was also suggested to occur in CTAC/HFDePC, in addition to the demixing.¹²

In small angle neutron scattering (SANS), fluorinated surfactants and hydrogenated surfactants have quite different scattering length densities and would seem to be ideally suited for contrast matching experiments using H₂O/D₂O mixtures: one mixture would make the hydrocarbon surfactant invisible, another the fluorocarbon surfactant, and a third the mixed micelle. Attempts to utilize this method for demonstrating micellar demixing have not been successful, but they have either shown that only mixed micelles are present^{15,19,20} or been inconclusive. A recent contribution from this laboratory belongs to the latter category.²² In that study, mixtures of HFDe-*d*-PC (*d* indicates that the pyridinium headgroup is deuterated) and CTAC were investigated at three contrasts. Although the results showed a residual scattering at the contrast match point of the surfactant mixture (at 35 vol % D₂O), there was some uncertainty as to whether the observations really implied

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coexisting micelles of different compositions or if an inhomogeneous internal distribution of scattering length densities within the micelle could explain the results.

We have now made a new series of measurements at several contrasts in order to test whether demixing occurs. Mixtures containing equal concentrations (usually 16.5 mM) of CTAC and HFDe-*d*-PC were measured at different contrasts. Most of the samples contained 0.10 M NaCl to reduce the electrostatic interactions, but measurements in salt-free systems were made in D₂O and in a contrast matching solvent mixture. Measurements at a higher temperature, 60 °C, gave the scattering from completely mixed micelles.

In this contribution, we will present an analysis of results from contrast variation mainly based on the residual values at the match point of the intensities at zero scattering angle.

Experimental Section

Materials. The cationic fluorocarbon surfactant HFDe-*d*-PC (*N*-(1,1,2,2-tetrahydroperfluorodecanyl)pyridinium chloride with a deuterated headgroup) was a gift from Prof. Asakawa (Kanazawa University, Japan). The synthesis has been described.²³ Cetyltrimethylammonium chloride (C₁₆TAC) was prepared from the bromide salt (Serva, analytical grade) by ion exchange. The volume and scattering length densities of the surfactants were calculated from group contributions and atomic scattering lengths as $\nu = 616 \text{ \AA}^3$ and $\rho_{\text{HS}} = -0.24 \times 10^{10} \text{ cm}^{-2}$ for CTAC and $\nu = 593 \text{ \AA}^3$, $\rho_{\text{FS}} = 3.88 \times 10^{10} \text{ cm}^{-2}$ for HFDe-*d*-PC. In the calculation of the scattering length density, two-thirds of the scattering length of the counterion was included, approximately representing counterions associated with the micelle (the volume contribution from the counterion was neglected).

Small Angle Neutron Scattering. The SANS measurements were performed at the GKSS Research Centre, Geesthacht, Germany.²⁴ Three different instrumental settings (the sample-to-detector distance was varied from 0.7 to 4.5 m) were used. Experimental data were collected in the interval of the modulus of the scattering vector q ($q = 4\pi/\lambda \sin \theta/2$, where θ is the angle between the direct and scattered beam and $\lambda = 8.1 \text{ \AA}$ is the neutron wavelength) from 0.01 to 0.25 \AA^{-1} . All measurements were performed at 25 °C, unless otherwise stated.

The data were corrected for background scattering and put on an absolute scale by dividing them by the known scattering spectrum of pure H₂O.

Data Analysis by Indirect Fourier Transformation. Data analysis by indirect Fourier transformation (IFT) was performed at $q > 0.02 \text{ \AA}^{-1}$, where the effects of intermicellar interactions are negligible.²⁵ This yields the scattering at zero angle, $d\Sigma(0)/d\Omega$, and the radius of gyration without any presumptions regarding particle size and shape. The radius of gyration is given by

$$R_g^2 = \frac{\int_0^{D_{\text{max}}} p(r) r^2 dr}{2 \int_0^{D_{\text{max}}} p(r) dr} \quad (1)$$

where $p(r)$, the pair distribution function, is approximated by a linear combination of a number of basis functions. The value of D_{max} , the limit for the maximum dimension of the particle, was chosen so as to give a stable and smooth solution for the $p(r)$ function that after Fourier transformation was fitted to the experimental scattering data.

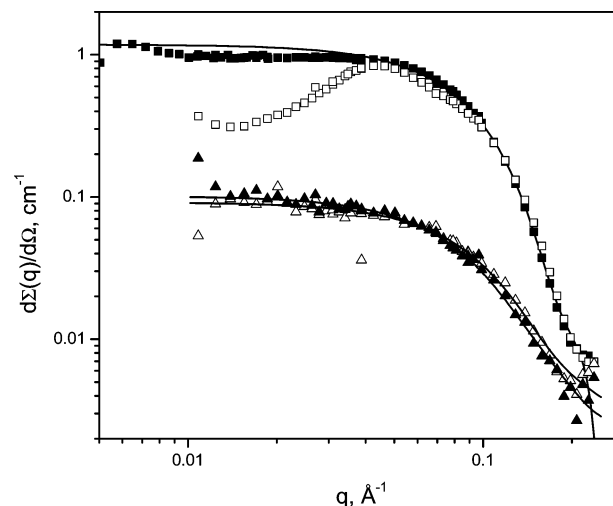


Figure 1. Scattering intensity as a function of scattering vector for samples with the same amounts of the surfactants HFDe-*d*-PC and CTAC (33 mM surfactant *in toto*). The empty symbols represent solutions without salt and the filled symbols represent solutions with 0.10 M NaCl, the squares represent solutions in D₂O and the triangles represent solutions at the match point, and the solid lines show the fit by IFT.

TABLE 1: Results Obtained from Indirect Fourier Analysis^a

sample filename	molar ratio FC/HC	solvent $X_{\text{D}_2\text{O}}$	$d\Sigma/d\Omega(0), \text{cm}^{-1}$	$R_g, \text{\AA}$	$D_{\text{max}}, \text{\AA}$
1P	1.039	1.00	1.20 ± 0.01	19.0 ± 0.2	60
2P	1.022	0.67	0.359 ± 0.005	18.0 ± 0.2	55
3P	1.006	0.499	0.156 ± 0.003	17.8 ± 0.4	60
4P	1.009	0.350	0.100 ± 0.002	20.1 ± 0.4	60
5P	1.000	0.198	0.163 ± 0.003	20.2 ± 0.4	60
6P	0.993	0.0482	0.341 ± 0.005	19.7 ± 0.2	60
1WS	1.00	1.00			
2WS	1.054	0.346	0.090 ± 0.002	17.9 ± 0.4	55
3WS	1.025	0.351	0.086 ± 0.002	17.9 ± 0.4	55
4WS	1.00	0.35	0.084 ± 0.002	17.5 ± 0.4	55
5WS	1.00	0.35	0.177 ± 0.003	17.9 ± 0.2	55
2PT	1.022	0.67	0.218 ± 0.003	16.1 ± 0.2	50
4PT	1.009	0.35	0.026 ± 0.002	16.6 ± 0.9	50

^a All samples but 5WS contain 33 mM surfactant *in toto*; 5WS contains twice that amount. The WS samples contain no added salt, and all others contain 0.10 M NaCl. The temperature was 60 °C in the PT samples; otherwise, it was 25 °C.

Results and Discussion

Salt and Salt-Free Solutions—External Demixing. Figure 1 shows the scattering curves for solutions with salt (0.100 M NaCl) and without salt in D₂O and at the match point of the mixture (35% D₂O).

The effect of salt in 100% D₂O is very clear. The prominent interaction peak in the salt-free solution disappears upon the addition of salt. In the contrast matching solvent mixture, however, the solutions with and without salt give rather similar results, with no indication of an interaction peak in the salt-free solution. The measurement with salt-free solutions at the match point was repeated several times with freshly prepared solutions (solutions 2WS, 3WS, and 4WS in Table 1) and also once with doubled surfactant concentration (5WS in Table 1). Not even in this case was any indication of an interaction peak observable in the scattering curve. There are some differences, however, between the salt-free and salt-containing solutions. The solution with salt gives a larger scattering at low q values which is an indication of a larger size of the micelles, as could be expected (compare Table 1; also, the radius of gyration is

larger in the presence of salt). The addition of salt also reduces the cmc and the concentration of free surfactant. This effect has little significance for the concentrations of micellized surfactants in the present case: the cmc's of the pure surfactants are for CTAC 1.3 and 0.1 mM in water and salt, respectively, and for HFDePC 2.3 and 0.2 mM,²⁶ and the free concentrations are lower in the mixtures.

To understand the lack of an effect of salt at the match point, we take our starting point in the "decoupling approximation" of Kotlarchyk and Chen²⁷ developed to handle size and shape polydispersity in weakly interacting systems, that is, without a coupling between the interparticle interactions and the polydispersities. The scattering cross section is

$$\frac{d\Sigma}{d\Omega}(q) = n_p[\langle |F(\vec{q})|^2 \rangle + \langle |F(\vec{q})|^2 \rangle (S(\vec{q}) - 1)] \quad (2)$$

where $d\Sigma/d\Omega(\vec{q})$ is the scattering cross section at scattering vector \vec{q} , n_p the number density of particles, $F(\vec{q})$ the form factor, and $S(\vec{q})$ the structure factor that in the present approximation is the average structure factor over all particles.²⁸ Usually, the brackets represent an average weighted by the distribution of particle size and orientation. In this case, however, the distribution of the particle composition is most important.

At high salt and low particle concentration, the structure factor is close to unity and eq 2 is reduced to

$$\frac{d\Sigma}{d\Omega}(q) = n_p \langle |F(\vec{q})|^2 \rangle \quad (3)$$

The same result would apply also without added salt in the case where, at the match point,

$$\langle |F(\vec{q})| \rangle = 0 \quad (4)$$

Obviously, if we were concerned with monodisperse, homogeneous micelles, only varying in composition and therefore contrast, this condition would be fulfilled at the match point. For eq 4 to be more generally valid, the micelles should be homogeneous and the variations of size and composition should not be correlated.

The expression for the particle form factor is

$$F_j(\vec{q}) = \int_{\text{particle } j} d\vec{r} [\rho_j(\vec{r}) - \rho_s] \exp(i\vec{q} \cdot \vec{r}) \quad (5)$$

where ρ_s is the scattering length density of the solvent and $\rho_j(\vec{r})$ the scattering length density in the particle. With respect to the homogeneity, the results in Figure 1 indicate that the internal inhomogeneity has little importance in the q range where the interaction peak appears. Since the average intermicellar distance determines the position of the interaction peak and the inhomogeneities occur on a much shorter length scale set by the micelle diameter, influence from the internal inhomogeneity should only be expected at q values substantially larger than the q_{max} value of the salt-free solution in D₂O. The results also suggest that either the variation of micelle size (aggregation number) is small or it is not strongly coupled to the variation of composition between the micelles. It seems rather unlikely that the latter is strictly true, but maybe the sensitivity to such a coupling is small. Contrast variation has been used to examine the polydispersity in microemulsions of the water-in-oil type, which consist of core-shell particles where the optical (contrast) polydispersity is a consequence of the size polydispersity.^{29,30} Even in this case, the effective structure factor was found to be close to unity at the match point.³¹

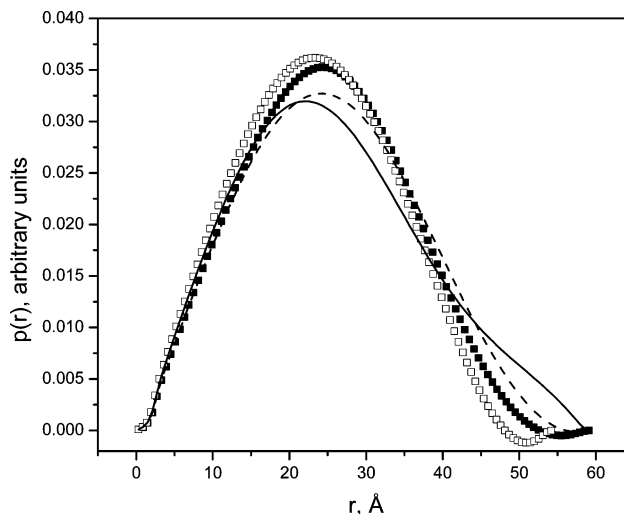


Figure 2. Pair distance distribution functions obtained under different contrast conditions: filled squares, $x_{\text{D}_2\text{O}} = 1$; empty squares, $x_{\text{D}_2\text{O}} = 0.67$ (match point of HFDe-*d*-PC); solid line, $x_{\text{D}_2\text{O}} = 0.35$ (match point of mixture); dashed line, $x_{\text{D}_2\text{O}} = 0.05$ (match point of CTAC).

From the results on salt and salt-free solutions in D₂O and at the match point, it is not clear whether we have a demixing into two populations of micelles with different average compositions or merely a wide composition distribution around a mean value. In the hope to answer this question, we have performed a measurement with systematic contrast variation for solutions containing 0.10 M NaCl.

Results from IFT Analysis: Pair Distance Distributions.

Values of the scattering at zero angle and the radius of gyration obtained from the indirect Fourier transformation analysis for different contrasts (H₂O/D₂O ratios) are collected in Table 1. Figure 2 presents some examples of the pair distribution functions obtained at different solvent compositions for the equimolar surfactant mixture.

As will be discussed below, all curves represent mixtures of micelles with widely varying compositions, containing both CTAC-rich and HFDePC-rich micelles. The curve for the solvent adjusted to the match point of one of the surfactants would then emphasize micelles enriched in the other surfactant. It is notable that $p(r)_{\text{max}}$ occurs at about the same distance when both CTAC and HFDePC are matched, indicating that the micelles are of similar sizes. At 35% D₂O, the two types of micelles contribute equally to the scattering. A closer examination of the scattering length densities shows, however, that at this point the contribution from the headgroup area of the HFDe-*d*-PC enriched micelles is particularly large compared to the contribution from the core, explaining the large involvement of the longest distances at this solvent composition. At 5% D₂O, both the core and surface of the HFDe-*d*-PC-rich micelles that dominate at this solvent composition show even larger contrasts, but the relative contributions are more equal (the ratio of the headgroup to core contrast is 4.3 at 35% and 1.8 at 5% D₂O, if it is assumed that the HFDePC enriched micelles contain 80% of this surfactant and 20% CTAC). An increase of $p(r)$ at long distances is still observed at 5% D₂O in Figure 2.

Contrast Variation for Salt Solutions—Magnitude of External Demixing. Let us now consider the results from the scattered intensity extrapolated to $q = 0$. At $q \rightarrow 0$, the form factor approaches unity irrespective of particle shape. At low micelle concentrations, with the electrostatic interactions screened by salt, $S(q)$ is close to unity as well. For monodisperse particles, the intensity is then

$$\frac{d\Sigma}{d\Omega}(0) = n_m V_m^2 (\bar{\rho} - \rho_s)^2 \quad (6)$$

where V_m is the dry micelle volume and n_m the number density of micelles. A plot of the square root of the zero scattering intensity versus solvent scattering length density would be V-shaped with the apex at zero intensity at the match point. In reality, there will always be some residual scattering at the match point, from an inhomogeneous distribution of the scattering length density within the micelle or, more importantly in the present case, from a distribution of micelle composition around the average, including a demixing into two micelle types with different contrasts. As discussed above, the inhomogeneous distribution should not affect the scattering at low q values. Demixing into separate populations of equally sized micelles or a single broad composition distribution around the average composition are possible sources of the residual scattering.

Let us first consider the problem with a general composition distribution, $f(x_F)$, that can be specified to different cases. For simplicity, we assume that all micelles have the same aggregation number, or if there is a size polydispersity that it is not correlated with the composition. The surfactants are assumed to occupy equal volumes in the micelle (the volume of the tail was estimated as 453 and 459 Å³ for HFDe-*d*-PC and CTAC, respectively) so that also the average micelle volume is constant. The zero intensity is obtained as an integral weighted by the composition distribution

$$\frac{d\Sigma}{d\Omega}(0) = n_m V_m^2 \int_0^1 (\rho(x_F) - \rho_s)^2 f(x_F) dx_F \quad (7)$$

where

$$\int_0^1 f(x_F) dx_F = 1; \bar{x}_F = \int_0^1 x_F f(x_F) dx_F; \sigma^2 = \int_0^1 (x_F - \bar{x}_F)^2 f(x_F) dx_F \quad (8)$$

and the scattering length density of the micelle is

$$\rho(x_F) = \rho_{HS} + (\rho_{FS} - \rho_{HS})x_F \quad (9)$$

ρ_{FS} and ρ_{HS} are the scattering length densities of the fluorinated and normal surfactants, respectively. After some manipulation, we obtain

$$\frac{d\Sigma}{d\Omega}(0) = n_m V_m^2 [\sigma^2 (\rho_{FS} - \rho_{HS})^2 + (\bar{\rho} - \rho_s)^2] \quad (10)$$

A plot of the intensity versus the solvent composition (ρ_s is linearly related to the solvent composition according to $\rho_s = (6.95x_{D_2O} - 0.56) \times 10^{10} \text{ cm}^{-2}$) is shown in Figure 3 for samples with equal amounts of the two surfactants in 0.10 M NaCl. In addition to the new results, data from ref 22 are also shown. These data were obtained at a slightly larger surfactant concentration, 43.3 mM of total surfactant, and have been recalculated to correspond to 33 mM. Both sets fit very well to the parabolic relationship corresponding to eq 10

$$\frac{d\Sigma}{d\Omega}(0) = B_1 + B_2(x_{D_2O} - B_3)^2 \quad (11)$$

The parameter values B_1 , B_2 , and B_3 are 0.0985 ± 0.0015 , 2.63 ± 0.01 , and $0.353 \pm 0.001 \text{ cm}^{-1}$ for the new data and 0.128 ± 0.21 , 2.64 ± 0.14 , and $0.345 \pm 0.012 \text{ cm}^{-1}$ for the older data.

Comparing eqs 10 and 11, we find that B_3 is the value of x_{D_2O} at the match point. The value obtained, $x_{D_2O} = 0.35$, is in

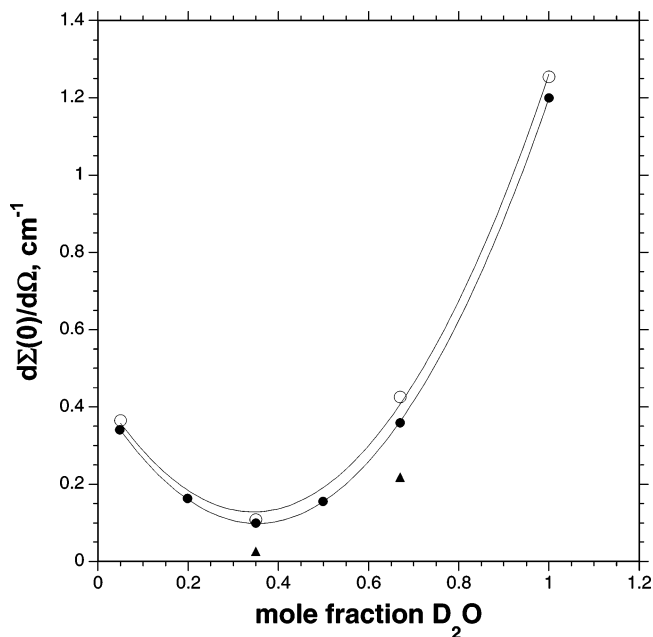


Figure 3. Zero intensity vs solvent composition for samples with a total surfactant concentration of 33 mM, half CTAC, half HDeFPC, in 0.10 M NaCl: (●) present results, 25 °C; (▲) results from 60 °C; (○) results recalculated from ref 22.

excellent agreement with the calculated value of the solvent composition at the match point for the equimolar surfactant mixture. The parameter B_2 gives $n_m V_m^2$, from which the micelle aggregation number may be calculated as $N_m = 76$. Finally, the ratio B_1/B_2 gives the quantity $(\rho_{FS} - \rho_{HS})^2 \sigma^2$, obtained as $1.81 \times 10^{20} \text{ cm}^{-4}$ ($2.34 \times 10^{20} \text{ cm}^{-4}$ for the older data). This results in $\sigma = 0.33$ (0.37 from the older results).

Composition Distributions. The only information concerning the composition distribution that is contained in the variation of the zero angle scattering with contrast is the standard deviation of the distribution, σ . Let us assume that this distribution is composed of two separate populations, with mean compositions given by the mole fraction of fluorinated surfactant in the micelle, $\bar{x}_{F,i}$ ($i = 1$ or 2). Each partial distribution has the same standard deviation, σ_p . For simplicity, we restrict ourselves to a 1:1 mixture of the two surfactants so that the average composition is 0.5. It can then be shown that

$$\sigma^2 = \sigma_p^2 + (\bar{x}_{F,1} - 0.5)(0.5 - \bar{x}_{F,2}) \quad (12)$$

If we first consider a single micelle distribution centered at $x_F = 0.5$ with $\sigma = 0.33$ (0.37), a very broad distribution would be required—too broad, in fact, to be a Gaussian on this interval from 0 to 1, as illustrated in Figure 4.

Complete demixing into pure hydrocarbon and fluorocarbon micelles would result in $\sigma = 0.5$. Earlier results from Asakawa et al.²³ suggest that the separation occurs into micelles containing 89 and 17% of HDeFPC, respectively, corresponding to $\sigma \geq 0.36$ (equality for $\sigma_p = 0$). Both values are larger than the experimentally determined value of $\sigma = 0.33$ and suggest that the demixing may be less far reaching, with the mean values of the demixed micelle populations closer together than assumed above.

If we assume a symmetric demixing, so that $(x_{F,1} - 0.5) = (0.5 - x_{F,2})$, and choose $\sigma_p = 0$, we obtain $x_{F,1} = 0.83$ and $x_{F,2} = 0.17$; with $\sigma_p = 0.07$, we have $x_{F,1} = 0.82$ and $x_{F,2} = 0.18$; and with $\sigma_p = 0.1$, the corresponding values are $x_{F,1} = 0.81$ and $x_{F,2} = 0.19$. The distribution from the last example is

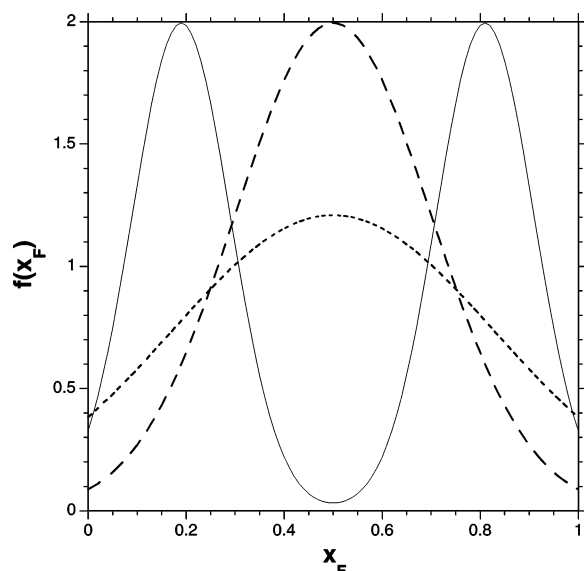


Figure 4. Examples of micelle distributions. The full drawn curve represents the demixed case with Gaussian peaks of $\sigma = 0.10$ at $x_F = 0.19$ and 0.81 . The broad dotted curve is a Gaussian at 0.5 with $\sigma = 0.33$, and the slashed curve is a Gaussian with $\sigma = 0.20$.

represented in Figure 4 and is seen to be too broad; just as the broad Gaussian distribution, it is truncated at the ends of the composition interval. The assumption of Gaussian distributions has no theoretical support, however. It is more probable that the demixed distributions are strongly skewed, as will be discussed next.

Nonideal mixed micelles are usually treated within the pseudo-phase-separation model using what is commonly called a regular solution approach.^{32–34} The regular solution results are characterized by a single interaction parameter that describes the deviation from ideal mixing. The results can be obtained from lattice models assuming that each surfactant molecule occupies a single lattice site and interacts only with its neighbors. As long as the surfactants are assumed to occupy equal space in the micelle (modeled as a two-dimensional lattice) and their interactions are characterized by a single parameter, the distributions for a 50:50 mixture are symmetric and the coexistence curve for demixing is necessarily symmetric around $x_F = 0.5$. Furthermore, the molecules are assumed randomly distributed on the lattice, so that the (free) energy of a molecule is assumed to depend on the average composition of its neighbor shell. In effect, the molecule is exposed to the mean field created by the lattice. Barzykin and Almgren³⁴ discussed the distribution of surfactants over equally sized micelles according to such models, also extended beyond the mean-field approximation. Some of their findings are summarized as follows. As the interaction parameter for a 50:50 mixture increases (temperature decreases) from zero in the ideal case toward the critical value and beyond, the distribution broadens from a binominal distribution ideally to a very broad, flattened distribution at the critical point and to two well-separated peaks at interaction parameters larger than the critical point. The critical value becomes larger and more strongly dependent on the size of the lattice when the mean-field approximation is removed. The two separated distributions are strongly skewed around their peaks and thus not well represented by Gaussian peaks. This is so already for the mean-field case (which leads to the regular solution expressions) and becomes more accentuated as one goes beyond this approximation.

The models used in these theoretical discussions of micelle composition distributions are very simplistic and cannot be used

as a basis for quantitative interpretation of the experimental results. They do show, however, that the assumptions that the surfactants have the same size and are distributed among micelles of constant and composition independent size are consistent with a symmetric demixing, which is probably not strictly correct. Even within these assumptions, the distributions corresponding to the demixed partial populations would be strongly skewed around their peak values. Symmetric Gaussian distributions, as exemplified in Figure 4, are not to be expected close to the critical value of the interaction parameter.

A further complicating factor that we are presently investigating with small angle X-ray scattering (SAXS) measurements is the possible effect on micelle size of replacing H_2O for D_2O as solvent.

Effect of Temperature. Only two solutions were measured at $60\text{ }^\circ\text{C}$. This temperature is expected to be above the critical temperature so that only mixed micelles would be present,⁸ as also noted in NMR self-diffusion and fluorescence quenching studies.¹² Since the solvent composition at the match point should remain at $x_{D_2O} = 0.35$, the results from the two solutions are enough to determine the aggregation number and the distribution width from eq 10, in the same way as was done above, even though the uncertainty in these estimates will be high. The aggregation number is obtained as $N_{agg} = 54$ and the width of the distribution as $\sigma = 0.2$. The strong decrease of the aggregation number is reflected in the values of the radius of gyration reported in Table 1. The volume of the micelle, and hence the aggregation number, should be proportional to R_g^3 . The ratio of R_g^3 at 60 and $25\text{ }^\circ\text{C}$ for solutions 2P and 2PT is 0.72 , in excellent agreement with the ratio of the aggregation numbers at these temperatures, 0.71 .

The effect of a temperature increase on the residual scattering at the match point strongly supports the idea that an increased demixing occurs at the lower temperature. It should be noted, however, that the temperature increase from 25 to $60\text{ }^\circ\text{C}$ only changes the interaction parameter by a factor of 0.89 , so we would in both cases remain close to the critical point. Even at the higher temperature, the micelle distribution remains rather broad. For comparison, ideally mixed surfactants in a micelle with an aggregation number of 54 would have a binominal composition distribution with $\sigma = 0.10$.

Conclusions

Equimolar mixtures of CTAC and a partially fluorinated cationic surfactant, HFDe-*d*-PC, have been investigated by SANS measurements at six D_2O/H_2O solvent mixtures, also containing 0.10 M NaCl to reduce the electrostatic interactions. An indirect Fourier transform analysis of the scattering intensities for $q > 0.02\text{ \AA}^{-1}$ gave the scattering intensity at zero angle. An equation for the dependence of this quantity on the solvent scattering length density was deduced for the case of a distribution of micelle composition among equally sized micelles. The experimental results could be very well fitted to this equation, and from the fitting parameters, the micelle aggregation number was obtained as $N_m = 76$. The width of the composition distribution was obtained as $\sigma = 0.33$. This result is not compatible with a single Gaussian, since it would be too broad to be contained in the composition interval from 0 to 1 . It could be compatible with two Gaussian distributions centered at $x_{F,1} = 0.82$ and $x_{F,2} = 0.18$, with $\sigma = 0.07$.

From the present results alone, we only get the width of the composition distribution, and it is not possible to unambiguously settle the question of whether we have one broad distribution or two clearly separated populations. Simple model calcula-

tions³⁴ on demixing surfactant mixtures show that as the critical interaction parameter value is approached from the mixed region (high temperature) the distribution becomes very broad and flattened and in the region where demixing occurs the separated distributions are strongly skewed. The results show that at 25 °C the distribution is very broad and may well represent at least a beginning of separation, so that we are at least very close to the critical condition. At 60 °C, the limited studies show a strongly reduced width of the composition distribution, $\sigma = 0.2$ (and also a micelle aggregation number reduced to $N_m = 54$) which probably represents a single but still broad composition distribution.

In a salt-free D₂O solution, the scattering curve displays a prominent interaction peak that disappears in the match point mixture with 65% H₂O. We propose that this indicates that the micelles are of similar size, independent of composition.

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References and Notes

- (1) Tiddy, G. J. T.; Wheeler, B. A. *J. Colloid Interface Sci.* **1974**, *47*, 59.
- (2) Mukerjee, P.; Mysels, K. J. *ACS Symp. Ser.* **1975**, *9*, 239.
- (3) Haegel, F. H.; Hoffmann, H. *Prog. Colloid Polym. Sci.* **1988**, *76*, 132.
- (4) Asakawa, T.; Miyagishi, S.; Nishida, M. *Langmuir* **1987**, *3*, 821–827.
- (5) Asakawa, T.; Amada, K.; Miyagishi, S. *Langmuir* **1997**, *13*, 4569.
- (6) Almgren, M.; Wang, K.; Asakawa, T. *Langmuir* **1997**, *13*, 4535.
- (7) Muto, Y.; Esumi, K.; Meguro, K.; Zana, R. *J. Colloid Interface Sci.* **1987**, *120*, 162.
- (8) Asakawa, T.; Okamoto, T.; Miyagishi, S. *J. Jpn. Oil Chem. Soc.* **1997**, *46*, 777.
- (9) Asakawa, T.; Saruta, A.; Miyagishi, S. *Colloid Polym. Sci.* **1997**, *275*, 958.
- (10) Asakawa, T.; Hisamatsu, H.; Miyagishi, S. *Langmuir* **1996**, *12*, 1204.
- (11) Asakawa, T.; Miyagishi, S. *Langmuir* **1999**, *15*, 3464.
- (12) Kadi, M.; Hansson, P.; Almgren, M.; Furo, I. *Langmuir* **2002**, *18*, 9243.
- (13) Carlfors, J.; Stilbs, P. *J. Phys. Chem.* **1984**, *88*, 4410.
- (14) De Lisi, R.; Inglese, A.; Milioto, S.; Pellerito, A. *Langmuir* **1997**, *13*, 192.
- (15) Burkitt, S. J.; Ottewill, R. H.; Hayter, J. B.; Ingram, B. T. *Colloid Polym. Sci.* **1987**, *265*, 628.
- (16) Clapperton, R. M.; Ottewill, R. H.; Ingram, B. T. *Langmuir* **1994**, *10*, 51.
- (17) Mukerjee, P.; Yang, A. Y. S. *J. Phys. Chem.* **1976**, *80*, 1388.
- (18) Shinoda, K.; Nomura, T. *J. Phys. Chem.* **1980**, *84*, 365.
- (19) Caponetti, E.; Chillura Martino, D.; Floriano, M. A.; Triolo, R. *Langmuir* **1993**, *9*, 1193.
- (20) Pedone, L.; Chillura Martino, D.; Caponetti, E.; Floriano, M. A.; Triolo, R. *J. Phys. Chem. B* **1997**, *101*, 9525.
- (21) Amato, M. E.; Caponetti, E.; Chillura Martino, D.; Pedone, L. *J. Phys. Chem. B* **2003**, *107*, 10048.
- (22) Kadi, M.; Hansson, P.; Almgren, M.; Bergström, M.; Garamus, V. M. *Langmuir* **2004**, *20*, 3933–3939.
- (23) Asakawa, T.; Hisamatsu, H.; Miyagishi, S. *Langmuir* **1995**, *11*, 478.
- (24) Stuhmann, H. B.; Burkhard, N.; Dietrich, G.; Junemann, R.; Meerwin, W.; Shmitt, M.; Wadzack, J.; Willumeit, R.; Zhao, J.; Nierhaus, K. H. *Nucl. Instrum. Methods Phys. Res., Sect. A* **1995**, *356*, 124.
- (25) Glatter, O. In *Small Angle X-ray Scattering*; Glatter, O., Kratky, O., Eds.; Academic Press: London, 1982.
- (26) Kadi, M.; Hansson, P.; Almgren, M. *J. Phys. Chem. B* **2004**, *108*, 7344.
- (27) Kotlarchyk, M.; Chen, S. H. *J. Chem. Phys.* **1983**, *79*, 2461.
- (28) Cabane, B. In *Surfactant Solutions. New Methods of Investigation*; Zana, R., Ed.; Surfactant Science Series 22; Dekker: New York, 1987; pp 57–145.
- (29) Arleth, L.; Pedersen, J. S. *Phys. Rev.* **2001**, *E63*, 061406.
- (30) Yan, Y. D.; Clarke, J. H. R. *J. Chem. Phys.* **1990**, *93*, 4501.
- (31) Pedersen, J. S. Private communication.
- (32) Holland, P. M.; Rubingh, D. N. *J. Phys. Chem.* **1983**, *87*, 1984.
- (33) Hoffmann, H.; Pössnecker, G. *Langmuir* **1994**, *10*, 381.
- (34) Barzykin, A. V.; Almgren, M. *Langmuir* **1996**, *12*, 4672.