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Temperature and Composition Dependence of the Structure of Isooctane/AOT Microemulsion L₂ Phases with Glycerol and Formamide: A Light Scattering Study[†]

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Received April 10, 2000. In Final Form: July 5, 2000

Oil continuous isooctane/AOT microemulsions with a third polar component glycerol or formamide were studied with dynamic light scattering. Both temperature and dispersed phase volume fraction ϕ were changed. For the glycerol systems, it was found that well below the critical T_c and ϕ_c and/or at low glycerol concentrations, the molecular aggregates formed are similar to the aqueous reversed micelles. However an increase of attractive interactions between the droplets is observed, which is related to the formation of clusters. This effect is clearly seen when the ϕ_c is approached, where evidence for the existence of two populations (free reversed micelles and clusters) is obtained. When the ϕ_c is passed, the relaxation rate is fast and becomes single exponential, except for a long tail at lower temperatures, perhaps indicating the approach of a lamellar phase. The formamide system has single-exponential relaxation distribution and linear relationships with $\ln(\phi) - 1$ and does not show any evidence of cluster formation. It is suggested that the bending elastic constants in this system are rather low and saddle-splay structures seem to be preferred, due to different AOT polar head solvation by formamide.

Introduction

Microemulsions are thermodynamically stable isotropic mixtures of two imiscible components, an apolar solvent (oil) and a polar one (usually water), stabilized by a third component, a surfactant.[1] The latter are molecules having one or more apolar hydrocarbon chains and a polar headgroup, which can be anionic, cationic, neutral, or zwitterionic. One such molecule is the well-known sodium bis(2-ethylhexyl) sulfosuccinate (Aerosol OT or AOT), which is an anionic surfactant with an apolar double chain. This molecule is especially suitable for the formation of oil continuous microemulsions (L₂ phases) with water as the dispersed polar droplets.[2] Their spherical structure and size are related to the amount of water in solution given by the parameter $w_0 = [H_2O]/[AOT]$.[2] In general, a linear relationship between the hydrodynamic radius of the droplet, r_h, and w_0 is found as predicted by eq 1

$$r_h = 3 \frac{v_{H_2O}}{a_{AOT}} w_0 + \delta \qquad (1)$$

where v_{H_2O} is the volume of a water molecule, a_{AOT} is the interfacial area of an AOT molecule, and δ is the thickness of the interface. The temperature, the dispersed phase volume fraction (ϕ), and the nature of the oil have a low impact on the droplet structure.[2−6] The polydispersity of the molecular aggregates is relatively low, around 10−15%.[5,7−9] These molecular aggregates are normally known as *reversed micelles.*[2]

At high temperatures and/or ϕ, some important modifications may occur in microemulsions. Above a critical temperature T_c or critical volume fraction ϕ_c,[3] the conductivity of the sample dramatically increases.[3,10−13] This is the so-called percolation phenomenon,[3,11] caused by the aggregation of reversed micelles in infinite clusters in three-dimensional space. Frequently, this phenomenon is caused by the formation of bicontinuous phases, where both the oil and water phases are continuous.[1] Cluster formation has been linked to the importance of attractive interactions between reversed micelles.[6,9,14−24] One of the

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experimental methods used to probe these interactions is dynamic light scattering (DLS).[4,5,15–17,21–24]

Although aqueous microemulsions are suitable systems for many applications, those where water is substituted by another polar component have also been used in some instances. The introduction of glycerol, ethylene glycol, and formamide was made either to produce unique media for chemical reactions[25–27] or as an additive in aqueous microemulsions, to tune its physical properties.[1,28,29] Such microemulsions were first reported in 1984,[30–32] and since then the similarities with the aqueous systems have been highlighted.[22,32–39]

The microemulsions with glycerol are, probably, those having the greater similarities to the water systems. Fletcher et al.[32] studied the system *n*-heptane/AOT/glycerol and concluded that a typical reversed micellar structure is maintained. In a previous work,[22] it was found that there are strong attractive interactions between the droplets, leading to the formation of clusters. This conclusion was supported by viscosity, conductivity, and dielectric relaxation experiments made by another group,[38,39] since the critical percolation point occurs at lower T_c and ϕ_c than that in the water system. The oil/AOT/formamide systems are not, however, so readily understood. Few studies have been reported,[22,34,40–42] and these were highly inconclusive with respect to the structure of the molecular aggregates formed.

In this paper we continue the earlier work,[22] in order to elucidate the structure of these aggregates with temperature and composition. Differences between the glycerol (similar to water-in-oil microemulsions) and the formamide systems are elaborated. The glycerol microemulsions have been studied by changing and extending ϕ above ϕ_c. It is shown that a two-state scheme of reversed micelles and clusters may be used to describe glycerol microemulsions below ϕ_c, while above this point it will reflect critical concentration fluctuations in the system. In the formamide microemulsions, however, there is no

evidence for cluster formation below ϕ_c, and the results point to a situation in which the molecular aggregate size depends on both temperature and ϕ.

Experimental Section

Materials. AOT was purchased from Sigma and purified by solubilization with methanol in contact with active charcoal for 24 h and evaporation of the methanol under reduced pressure. After purification the surfactant was kept in a desiccator with $CaCl_2$. The isooctane (spectroscopic grade) was purchased from Aldrich and used as supplied. Spectroscopic grade glycerol and formamide were purchased from Aldrich and also used as supplied.

Light Scattering. The setup was described earlier.[43] The scattering cells were immersed in a thermostated bath of index-matching liquid (decalin). The light source was a laser (He–Ne, $\lambda = 632.8$ nm, 35 mW). In the case of low scattering samples an Ar ion laser was used ($\lambda = 488$ nm, 300 mW). The intensity autocorrelation function $g^2(t)$ was measured at an angle of 90°, after measurements with different angles had been made in order to check that there was a linear dependence on the relaxation rate with the square of the scattering vector, i.e., that the relaxations were diffusive. The temperature of the solution was always controlled.

Data analysis was made by using the constrained regularization routine REPES.[43] This program is similar to the CONTIN method [44] but minimizes directly the sum of squared differences between the experimental and calculated intensity correlation functions ($g^2(t)$) using nonlinear programming. The experimental correlation function $g^2(t)$ is related to the electric-field correlation function $g^1(t)$ by $g^2(t) - 1 = \beta|g^1(t)|^2)$ where β is an empirical parameter describing the deviation from ideal correlation. The algorithm allows selection of a "smoothing parameter", *probability to reject P*—the higher this value, the greater the smoothing. A standard value of 0.5 was used in all analyses.

$g^1(t)$ can be written as the Laplace transform of the distribution of relaxation rates, $G(\Gamma)$

$$g^1(t) = \int_0^\infty G(\Gamma) \exp(-\Gamma t) \, d\Gamma \qquad (2)$$

where Γ is the relaxation rate and t the lag time. To obtain the relaxation times, (2) may be expressed as

$$g^1(t) = \int_0^\infty \tau A(\tau) \exp(-t/\tau) \, d \ln \tau \qquad (3)$$

Relaxation time distributions ($\tau A(\tau) = \Gamma G(\Gamma)$) were obtained by regularized inverse Laplace transformation and the diffusion coefficients calculated for each relaxation mode, at the peak of the distribution. Pre-exponential factors of these relaxation modes are the normalized areas of the distributions obtained from the analysis. The refraction indexes of both glycerol ($n_{25°C} = 1.4746$) and formamide ($n_{25°C} = 1.4475$) are greater than that of isooctane ($n_{25°C} = 1.3934$), ruling out optical matching.[5]

The scattered light intensity was converted into the Rayleigh ratio R_θ, using the ratio between scattered light intensity and incident light per scattered volume unit. To obtain this value, we used as reference a toluene sample at $\lambda = 632.8$ nm ($R_\theta^{toluene} = 1.40 \times 10^{-3}$ m^{-1}).

Results and Discussion

I. Isooctane/AOT/Glycerol Microemulsions. To study the effect of temperature and ϕ on the structure of these microemulsions, we selected two different situations corresponding to different behavioral trends. As in water systems, we define the variable $g_0 = $ [glycerol]/AOT which has an equivalent meaning to w_0. At $g_0 = 1.9$ the microemulsion is very similar to the aqueous system:[22] r_h still changes linearly with g_0 and the diffusion coefficient

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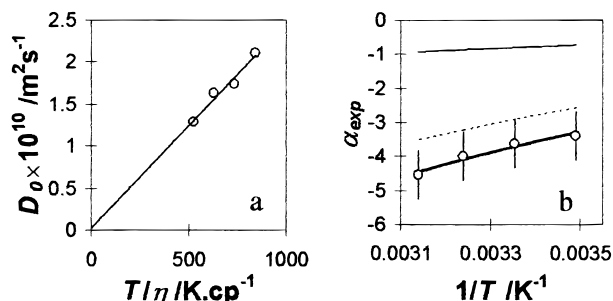(40) Arcoleo, V.; Aliotta, F.; Goffredi, M.; La Manna, G.; Liveri, V. T. *Mater. Sci. Eng. C* **1997**, *5*, 47.
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Figure 1. Relationship between the diffusion coefficient at infinite dilution D_0 and T/η (a) and the temperature dependence of the dynamic virial coefficient α_{exp} (b). α_{exp} was fitted with eq 6 (thick line) with $\Delta H_c = 5.6$ kJ mol^{-1} and $\Delta S_c = 24.3$ J (K mol)$^{-1}$, the thin line is the cluster contribution, and the dashed line represents $\tilde{k}_1$.

Table 1. Diffusion Coefficient at Infinite Dilution D_0 and Dynamic (α_{exp}) and Static (B_{exp}) Virial Coefficients Obtained for Isooctane/AOT/Glycerol $g_0 = 1.9$ Microemulsions

$T/°C$	$10^{10}D_0/m^2\ s^{-1}$	α_{exp}	B_{exp}
13.4	1.29	−3.40	3.86
25.0	1.63	−3.63	1.27
35.6	1.74	−4.00	1.40
45.4	2.11	−4.55	−0.17

also changes linearly with ϕ. Mathew et al. have determined the critical dispersed phase volume fraction ϕ_c for this system.[38] The value for $g_0 = 1.9$ corresponds to $\phi_c = 0.24$; i.e., [AOT]$_c \approx 0.45$ M. Thus, even at [AOT] = 0.2 M, we are well below ϕ_c. At $g_0 = 3.7$ deviations are observed,[22] which are attributed to the formation of clusters. ϕ_c is, in this case, equal to 0.11; i.e., [AOT]$_c \approx 0.17$ M. Since we worked until [AOT] = 0.2 M, ϕ_c is crossed at $g_0 = 3.7$.

(a) $g_0 = 1.9$. The autocorrelation functions for this g_0 were always single-exponential independent of either ϕ ([AOT] = 0.025 to 0.2 M) or temperature (between 13.4 and 45.4 °C) of the sample, confirming the results obtained earlier in this range of composition.[22] The intensity of the scattered light I was also measured. Both the diffusion coefficient and the ratio ϕ/I should have linear relationships with ϕ in solutions of dilute spherical particles,[22–24,45] as shown in eqs 4 and 5
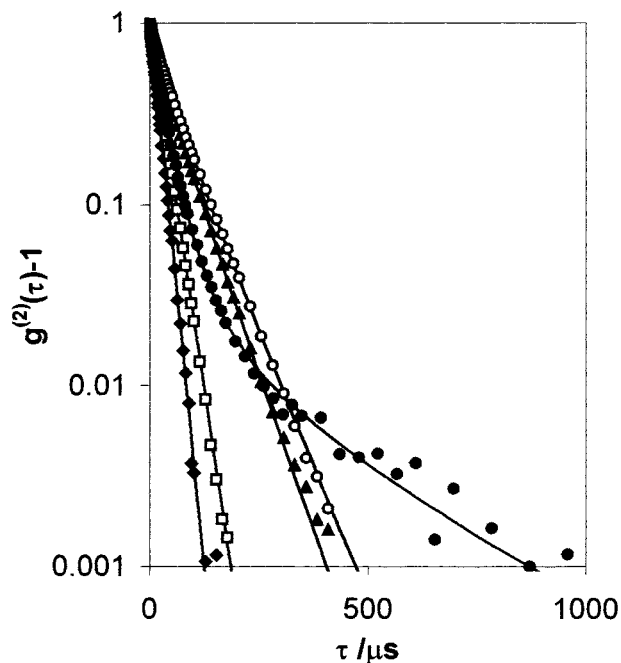
$$D = D_0(1 + \alpha\phi) \qquad (4)$$

$$\frac{\phi}{I} \approx \frac{1}{G}\left(\frac{\partial n}{\partial \phi}\right)^{-2}\frac{3}{4\pi r_h^3}(1 + B\phi) \qquad (5)$$

where α is a hydrodynamic "virial coefficient" that gives a measure of the attractive interactions between droplets. The diffusion coefficient at infinite dilution D_0 is given by the Stokes−Einstein equation[45] and is inversely proportional to the r_h and the solvent viscosity η.

In a system of hard spheres, it is predicted that $\alpha \sim 1$,[45] while negative values result when attractive interactions are strong.[23,24] The relation between D and ϕ is linear for the ranges of T and ϕ studied, while for ϕ/I the data are relatively scattered. Table 1 summarizes the results of the linear regression of the experimental points. As expected, the α values are negative in accordance with previous results.[22]

From the correlation between D_0 and T/η in Figure 1a, the aggregate size can be extracted ($r_h = 28.1 \pm 1.7$ Å) using the Stokes−Einstein equation. This value agrees

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Figure 2. Scattered light intensity autocorrelation functions ($g^{(2)}(\tau)$) at 25 °C for different AOT concentrations ($\blacklozenge$, [AOT] = 0.025 M; $\square$, [AOT] = 0.075 M; $\blacktriangle$, [AOT] = 0.125 M; $\bigcirc$, [AOT] = 0.175 M; $\bullet$, [AOT] = 0.200 M) for isooctane/AOT/glycerol g_0 = 3.7 microemulsions.
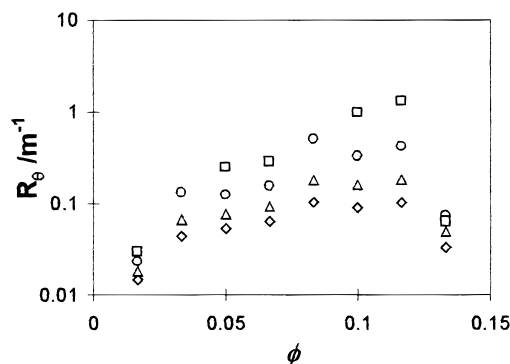
Figure 3. Rayleigh ratio R_θ versus ϕ for isooctane/AOT/glycerol $g_0 = 3.7$ microemulsions ($\diamond$, $T = 13.4$ °C; $\triangle$, $T = 25.0$ °C; $\bigcirc$, $T = 35.6$ °C; $\square$, $T = 45.4$ °C).

with the previous result obtained at 25 °C.[22] The temperature dependence of α (Figure 1b) is not, however, so straightforward. Kopper et al.[21] proposed a thermodynamic model based on the assumption that the reversed micelles form clusters according to a linear aggregation mechanism. They derived the expression
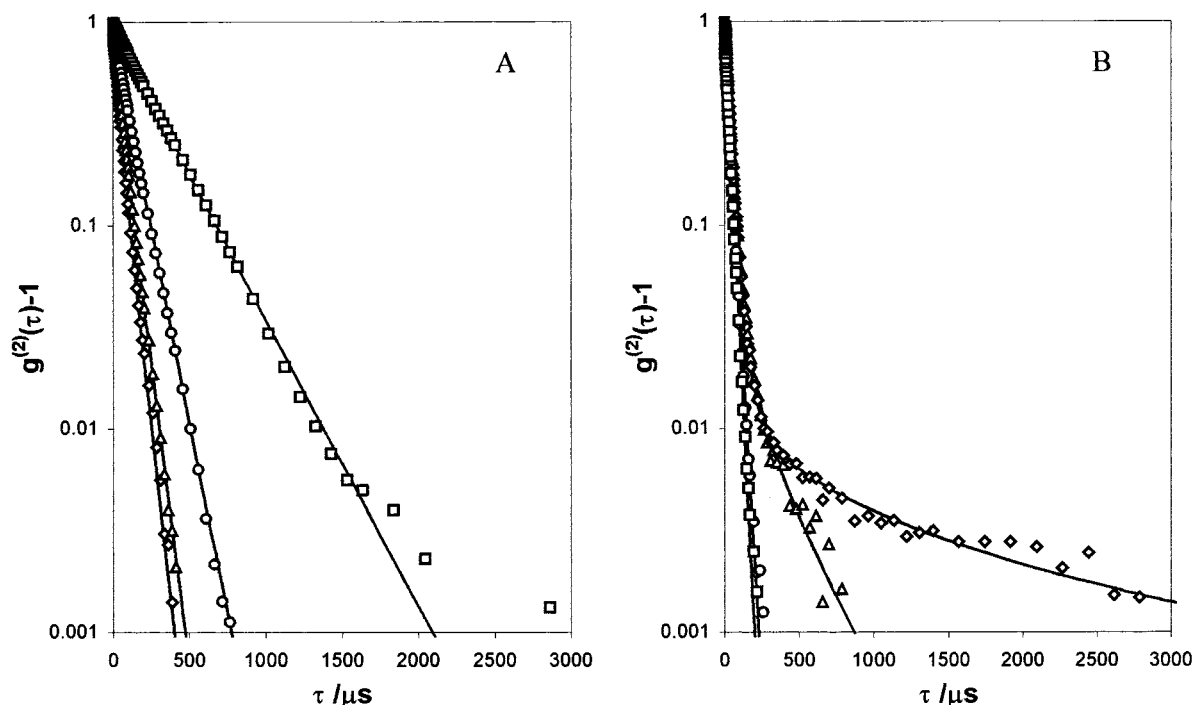
$$D_Z = D_1^0\left[1 + \phi\left(\tilde{k}_1 + \frac{2(D_2^0 - D_1^0)}{D_1^0}\exp\left(-\frac{\Delta G_c}{k_B T}\right)\right) + \cdots\right] \qquad (6)$$

where D_Z is the *z-averaged* effective diffusion coefficient, defined in the following manner:[21]

$$D_Z \equiv \frac{\sum\limits_{k=1}^{\infty}k\phi_k D_k}{\sum\limits_{k=1}^{\infty}k\phi_k} \qquad (7)$$

Figure 4. Autocorrelation functions at different temperatures ($\diamond$, $T = 13.4$ °C; $\triangle$, $T = 25.0$ °C; $\bigcirc$, $T = 35.6$ °C; $\square$, $T = 45.4$ °C) for isooctane/AOT/glycerol $g_0 = 3.7$ microemulsions at two different ϕ values: (A), $\phi = 0.116$, [AOT] = 0.175 M; (B), $\phi = 0.133$, [AOT] = 0.200 M.

where ϕ_k is the volume fraction of clusters with k droplets and D_k is the diffusion coefficient of a cluster with k droplets. D_1^0 and D_2^0 are the diffusion coefficients for the reversed micelle and a dimer, respectively. ΔG_c is the free binding energy relative to isolated droplets. The term $\tilde{k}_1$ has the same origin as α in eq 4; i.e., it is an effective virial coefficient. This parameter is equal to

$$\tilde{k}_1 = 2B_2^{\text{eff}} - K_1 \qquad (8)$$

where K_1 is due to hydrodynamic interactions between the droplets and is approximately equal to 7.[45] B_2^{eff} is the virial coefficient that one could obtain from the intensity of scattered light and is given by the following expression:

$$B_2^{\text{eff}} = 4 - \exp\left(-\frac{\Delta G_c}{k_B T}\right) \qquad (9)$$

Fixing all parameters (K_1, D_1^0, D_2^0), it is possible to fit the model to our experimental results. However, the experimental error is large, which leads to a great uncertainty in the determination of enthalpic ΔH_c and entropic ΔS_c contributions in ΔG_c. The results were $\Delta H_c = 6 \pm 84$ kJ mol^{-1} and $\Delta S_c = 24 \pm 21$ J (K mol)$^{-1}$, showing that the variation of entropy is positive in accordance with previous calculations in water-in-oil microemulsions.[21] Noticeably, both contributions are less positive than those in the water systems. The enthalpic contribution may be even negative, but our results are not conclusive in this aspect. If this were the case, the clustering phenomena in glycerol-in-oil microemulsions would be not only entropy driven but also enthalpy driven. However we note that in order to have cluster−micelle equilibrium, ΔG_c should be around $1RT$, which is the result obtained.

The system at $g_0 = 1.9$ is clearly below the critical T_c and ϕ_c. Consequently, the results show the existence of essentially isolated reversed micelles and the system resembles the water-in-oil microemulsions. Evidence of this behavior comes from the single-exponential correla-tion functions obtained by the linear relationship between D and ϕ and also by the relationship between D_0 and T/η. The value obtained for r_h is very similar to that one obtained earlier,[22,32] showing that the size changes linearly with g_0.

Interestingly, the α values are smaller than those obtained in water-in-oil microemulsions. At $w_0 = 20$ (*n*-heptane/AOT/water system, $r_h \approx 50$ Å, a size that corresponds to $g_0 = 3.7$ reversed micelles), α is equal to -1.1,[16] and at $w_0 \approx 7.5$ ($r_h \approx 28$ Å, which corresponds to $g_0 = 1.9$), α should be even less negative according to the trend of the experimental results,[16] since attractive interactions should decrease with increasing size of the reversed micelles. Therefore our values ($\alpha \approx -4$) are clearly different from those in the water system, showing that attractive interactions between the droplets are greater in the glycerol system. The thermodynamic analysis, however, is not conclusive with respect to the details of these interactions due to large numerical errors. We only have evidence of a positive ΔS_c, in accordance with results in water-in-oil microemulsions.[21]

(b) $g_0 = 3.7$. Figure 2 shows the autocorrelation functions $g^{(2)}(\tau)$ at 25 °C at different ϕ. As expected, the relaxation rate becomes slower with an increase in [AOT]. However, on passing the critical ϕ_c the rate becomes faster. The intensity of scattered light R_θ increases with ϕ (Figure 3) assuming a maximum value at $\phi = \phi_c$. R_θ then drops again to low values. Temperature does not have a large effect on this behavior (only a small increase of R_θ is observed), and the relation of eq 5 is not observed.

A more careful examination of the autocorrelation functions shows that they are nearly single exponential well below ϕ_c (Figure 4). When the critical ϕ_c is approached, deviations from this behavior are observed, and the functions are clearly nonexponential for $\phi > \phi_c$. In this case, a nonexponential long tail is observed following a fast exponential decay. The tail is only observed over the percolation threshold, and it is highly temperature de-pendent. One can observe in Figure 4 the existence of a
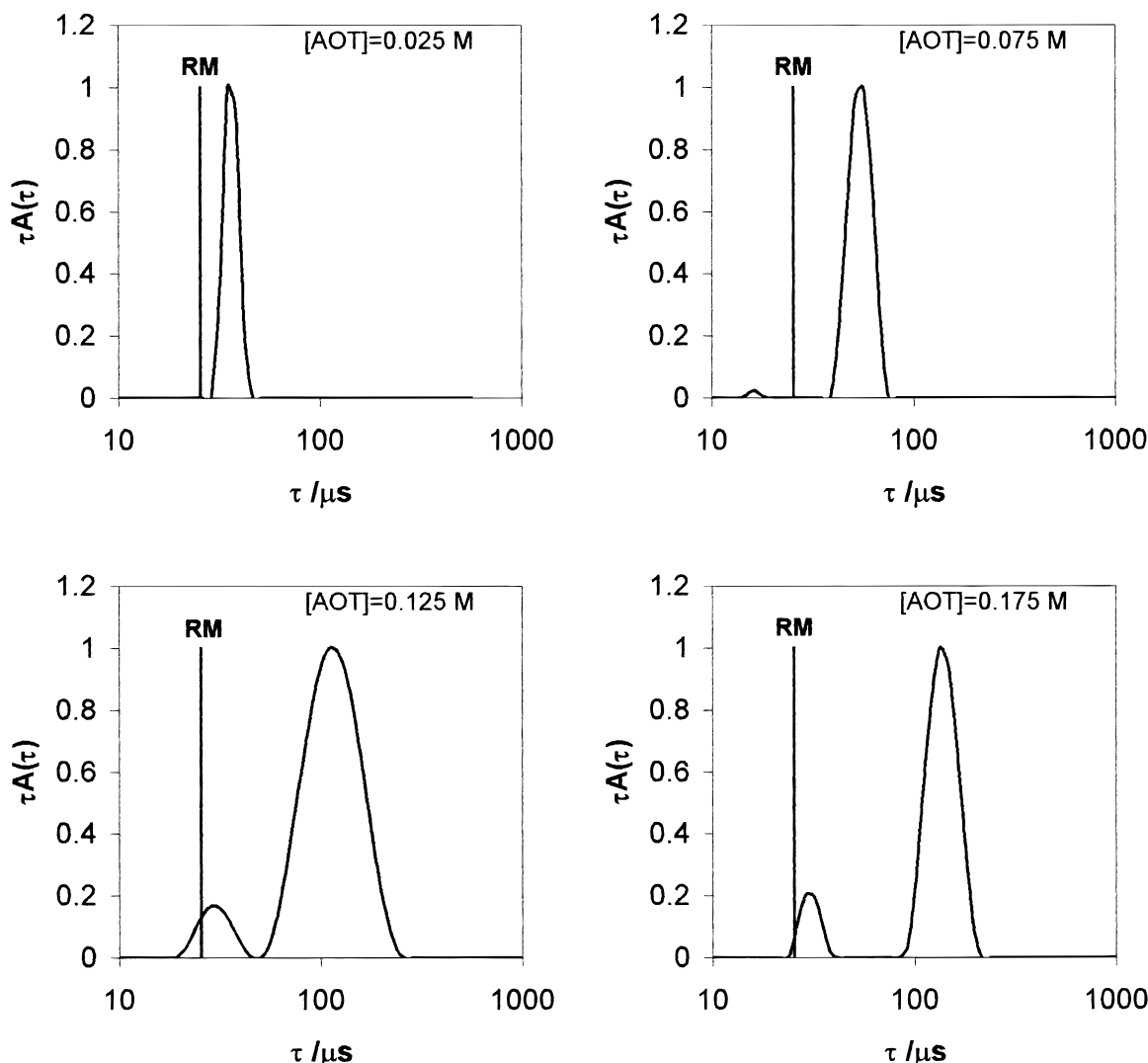
Figure 5. REPES analysis of the data in Figure 3 below or near ϕ_c. The expected diffusional relaxation mode of free reversed micelles is also indicated (RM).

long tail at 13.4 and 25 °C, fading away for higher temperatures. The initial part, however, does not seem to be temperature dependent within our experimental conditions.

The decay curves may be analyzed in different ways. REPES analysis treats the autocorrelation functions as a continuous distribution of relaxation times and enables the calculation of diffusion coefficients from the peaks (provided linear relationships of Γ with q^2 are observed). Another approach could be to fit to an empirical function, a so-called stretched exponential (or Kohlrausch−Williams−Watts function, KWW).[11] However, the analysis with a KWW function was not satisfactory, while a biexponential analysis is quite suitable for our results.

Figure 5 shows the results of the analysis with REPES for $T = 25$ °C. At low ϕ, we have only one relaxation mode which corresponds to single-exponential decay similar to those observed for $g_0 = 1.9$. At high ϕ, two peaks are observed, confirming the earlier results obtained with a linear autocorrelator.[22] The peak corresponding to the faster relaxation is near the expected value if only noninteracting isolated droplets (with the size expected for the reversed micelles in this system)[22,32] exist in the samples, while the slower relaxation is strongly ϕ-dependent. These results seem to support a two-state scheme, where we have a component deriving from diffusion of

isolated reversed micelles and a second component reflecting the relaxation rate of the cluster.

A two-state scheme is also suggested when the temperature is changed (Figure 6a). At 13.4 °C and for [AOT] = 0.175 M (in the critical T_c region), a broad and asymmetric peak is obtained, which splits in two peaks when the temperature is increased. On temperature increase, the cluster relaxation time becomes longer. However, for [AOT] = 0.2 M ($\phi > \phi_c$) the two-state scheme is not verified. The dominant peak is now the faster relaxation but does not correspond to that expected for the diffusion of isolated reversed micelles (Figure 6-b). With temperature decrease, both peaks broaden and the contribution of the slower relaxation increases.
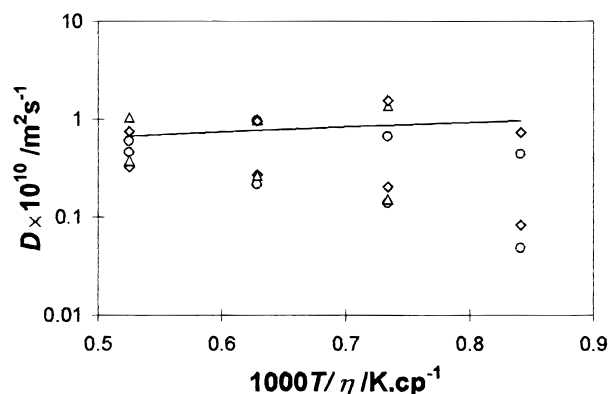
In Figure 7 we show the diffusion coefficients for $\phi < \phi_c$ versus T/η. The fast relaxation (D_{fast}) is identical, within experimental error, to the value expected for reversed micelle diffusion (at infinite dilution). The correlation length ξ obtained for D_{slow} according to

$$\xi = \frac{k_B T}{6\pi\eta D_{slow}} \tag{10}$$

changes from 100 Å at $T = 13.4$ °C to 1000 Å at $T = 45.4$ °C. This would mean that the clusters would contain
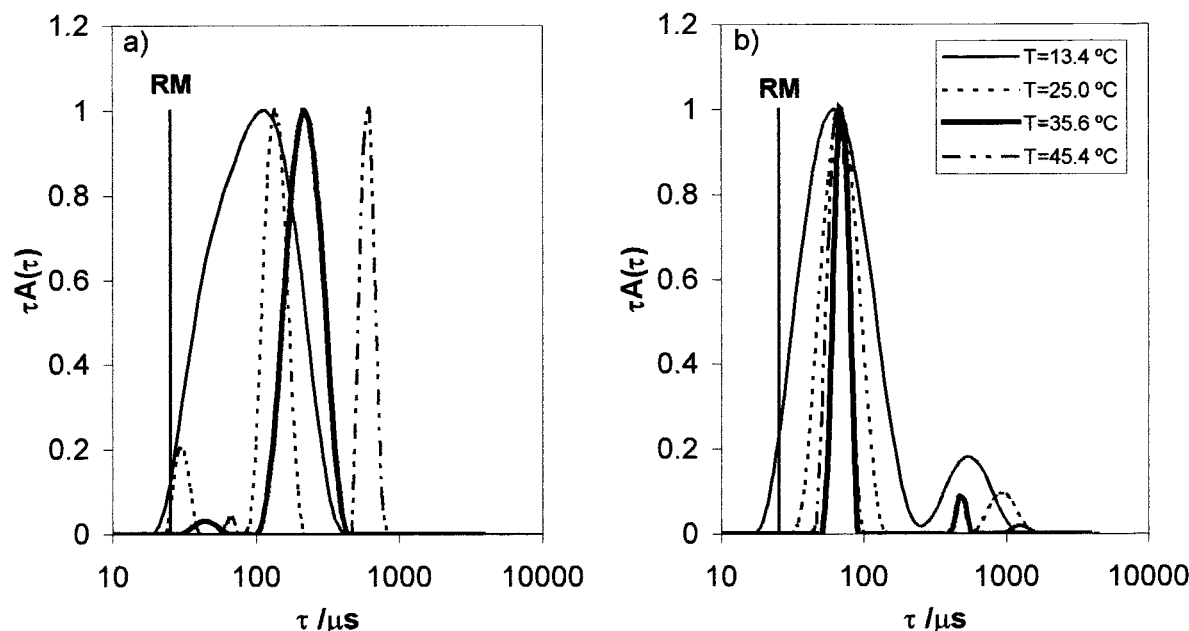
Figure 6. REPES analysis of the data in Figure 4: (a) [AOT] = 0.175 M; (b) [AOT] = 0.200 M. The expected diffusional relaxation mode of free reversed micelles is also indicated (RM).

Figure 7. Apparent diffusion coefficients obtained for both relaxations with REPES analysis from the two peaks of the distribution, for high ϕ ($\triangle$, [AOT] = 0.125 M; $\diamond$, [AOT] = 0.150 M; $\bigcirc$, [AOT] = 0.175 M). The line represents the expected value for the diffusion of a spherical particle with r_h = 56.5 Å (expected size for the reversed micelles at this g_0).[22]

between 8 (T = 13.4 °C) and about 1000 (T = 45.4 °C) reversed micelles.

For [AOT] = 0.200 M two relaxations are observed, depending on the temperature. The single-exponential decay has a relaxation time approximately equal to 55 μs. At lower temperatures, the slower relaxation is highly nonexponential, with τ_{aver} equal to 3860 μs (T = 13.4 °C) and 340 μs (T = 25.0 °C). This component vanishes at higher temperatures. This result is similar to the one obtained by Kotlarchyk et al.[46] in a study of L_3 phases of water-in-oil AOT microemulsions: a fast component (around 750 μs) was observed, which was followed by a slow one of around 1.5 s. The mechanisms attributed to these relaxations were, respectively, the Brownian movement of the interface and of the whole structure. The observation of a decrease in τ_{aver} (from 125 to 50 μs) with the increase of [AOT] from 0.175 to 0.200 M is also in accordance with observations in the water system,[46] where a decrease is also found when the ϕ_c is crossed (from 2 ms to 500 μs).

(46) Kotlarchyk, M.; Sheu, E. Y.; Capel, M. *Phys. Rev. A* **1992**, *46*, 928.

The long tail at lower temperatures might be caused by the conversion of the system to lamellar phases. It is known that lamellar phases have long average correlation lengths, which lead to long relaxation times.[46] This region, where a droplet-to-lamellar phase transition occurs, was found to be relatively large in water/AOT/decane microemulsions.[46] Nevertheless, a phase separation still does not occur, and the nature of the phase above the ϕ_c is not totally understood.

II. Isooctane/AOT/Formamide Microemulsions. As in the other cases, let us define the following parameter f_0 = [formamide]/[AOT]. In the previous study,[22] it was not possible to unravel the structure of these microemulsions. The relationship between D and ϕ was not linear, neither was that between r_h and f_0;[22] similar findings were presented by another group.[41] Also no evidence for cluster formation was found, and at high f_0, $g^2(\tau)$ was still single exponential, by contrast with the results obtained in the glycerol microemulsions.

In this work, the temperature effect was studied in f_0 = 1.64 microemulsions. The latter is relatively high (phase separation occurs around f_0 = 1.9), where deviations from water-in-oil microemulsions are expected to be more pronounced. [AOT] was varied between 0.025 and 0.200 M (ϕ between 0.01 and 0.08), and the temperature was changed between 13.4 and 45.4 (as in the glycerol microemulsions). Again it is essential to establish whether we are above ϕ_c. The only known data are viscosity (η) and conductivity (σ) experiments performed by Arcoleo et al.[40] in the formamide/AOT/n-heptane microemulsions for f_0 = 0.52, 0.98, and 2.13. Volume fractions higher than 0.10 (until 0.5) were investigated, which are clearly higher than those studied in the present work. The results point to a situation in which ϕ_c is below 0.14 for f_0 = 2.13, while for f_0 = 0.52 and 0.98 it is higher than 0.50. Using the relations[38]

$$\log \sigma = A + B|\phi - \phi_c| \tag{11}$$

$$\log \eta = C + D|\phi - \phi_c| \tag{12}$$

where A, B, C, and D are parameters of the regression; a value for ϕ_c was estimated by optimizing the correlation
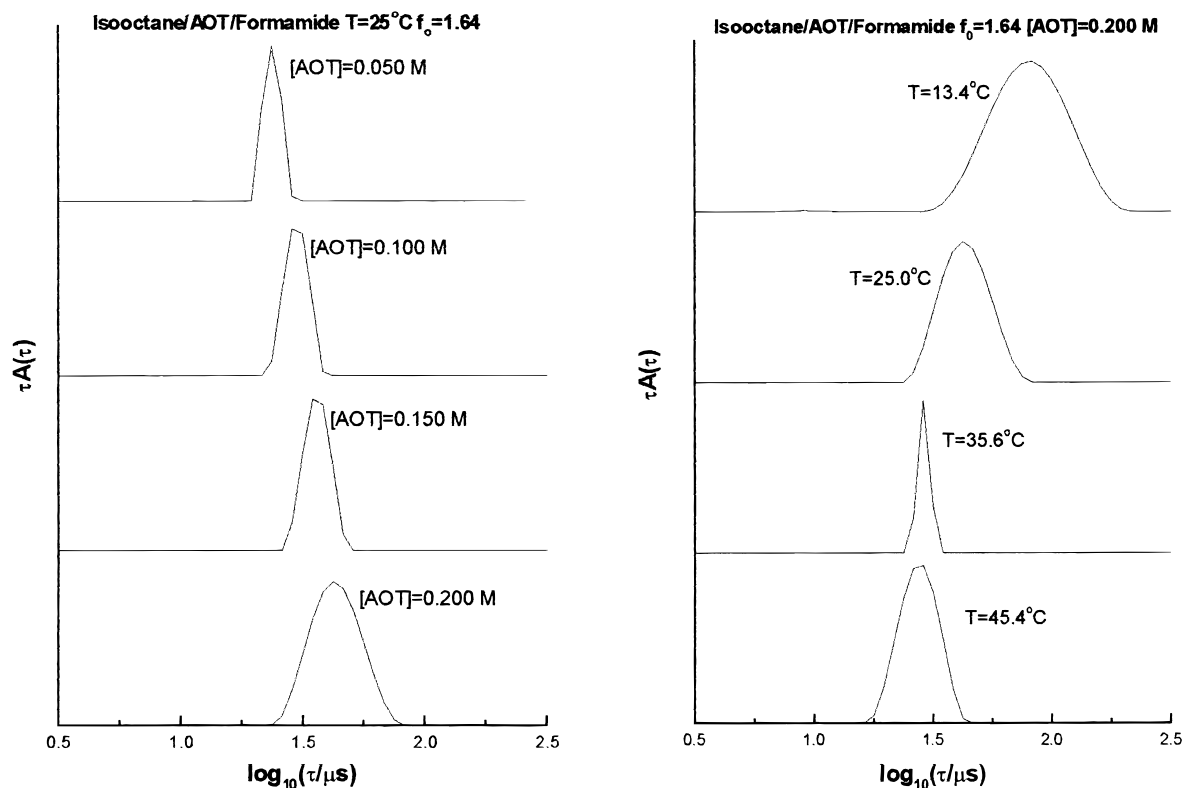
Figure 8. REPES analysis of the experimental data of isooctane/AOT/formamide $f_0 = 1.64$ microemulsions at different ϕ and T.

coefficient of the linear regression. It was found that ϕ_c should be around 0.07 and 0.08 at room temperature for this system (*n*-heptane/AOT/formamide, $f_0 = 2.13$).[47] In our case, the system (isooctane/AOT/formamide, $f_0 = 1.64$) is still relatively far from the cloud point ($f_0 = 1.9$); therefore we do not expect that ϕ_c would be less than 0.08, meaning that we are working below ϕ_c.

The autocorrelation functions obtained were single exponential at all temperatures and volume fractions (see Figure 8). The relaxation rate has a linear relationship with q^2, which leads us to conclude that this mode is mainly diffusive. There is no evidence of cluster formation, nor is a sharp transition, typical of critical points, observed.
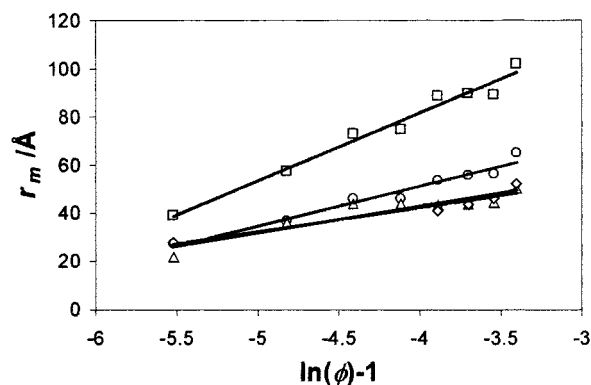
According to Helfrich,[48] the interface rigidity is related to the curvature energy F per unit area by

$$F = 2\kappa(H - c_0) + \tilde{\kappa} c_1 c_2 \tag{13}$$

where c_1 and c_2 are the surfactant monolayer main curvatures, c_0 is the surfactant monolayer spontaneous curvature (determined by surfactant molecules packing,[49] for $c_0 > 0$, aqueous dispersions are favored, for $c_0 < 0$, reversed systems are preferred), and H is the average curvature

$$H = \frac{1}{2}(c_1 + c_2) \tag{14}$$

For spherical aggregates with radius r, we may assume that $c_1 = c_2$ and $H = 1/r$, being positive in normal (micellar) phases and negative in reversed phases. κ and $\bar{\kappa}$ are the mean bending elastic constant (or rigidity) and the Gaussian bending constant, respectively.[1] A linear rela-

(47) Laia, C. A. T. Ph.D. Thesis, Instituto Superior Técnico, Lisbon, 1999.
(48) Helfrich, W. *Z. Naturforsch* **1973**, *28c*, 693.
(49) Mitchell, D. J.; Ninham, B. W. *J. Chem. Soc., Faraday Trans. 2* **1981**, *77*, 601.

Figure 9. Relationship between the sizes obtained for the molecular aggregates of isooctane/AOT/formamide $f_0 = 1.64$ microemulsions and $\ln(\phi) - 1$ at different temperatures ($\square$, $T = 13.4$ °C; $\bigcirc$, $T = 25.0$ °C; $\triangle$, $T = 35.6$ °C; $\diamond$, $T = 45.4$ °C).

tionship between r_m and $\ln \phi$ is predicted[50] due to the thermal motion that the droplet interface is subject to

$$\frac{r_m}{r_0} = \frac{2\kappa + \bar{\kappa}}{2\kappa} + \frac{k_B T}{8\pi\kappa}(\ln \phi - 1) \tag{15}$$

where $r_0 = c_0^{-1}$.

When the radius obtained is plotted versus $\ln(\phi) - 1$, linear relationships are obtained (Figure 9). Provided some value of c_0 is known, an estimation of κ and $\bar{\kappa}$ may be made. The value of a_{AOT} was actually obtained earlier by Bergenståhl et al.[34] for formamide/AOT/oil microemulsions. This value was around 0.75 nm², a little higher than that obtained in water and glycerol microemulsions. A quite low value for κ was estimated (around 0.05 $k_B T$), which increases with temperature; while $\bar{\kappa}$ has a positive

(50) Sicoli, F.; Langevin, D.; Lee, L. T. *J. Chem. Phys.* **1993**, *99*, 4759. Sicoli, F.; Langevin, D. *J. Phys. Chem.* **1995**, *99*, 14819.

Table 2. Bending Elastic Constants κ and $\bar{\kappa}$ Estimated for the Isooctane/AOT/Formamide $f_0 = 1.64$ Microemulsion Interface, for Different Values of a_{AOT}

| | $a_{AOT} = 0.50$ nm^2 | | $a_{AOT} = 0.75$ nm^2 | | $a_{AOT} = 1.00$ nm^2 | |
$T/°C$	κ/RT	$\bar{\kappa}/RT$	κ/RT	$\bar{\kappa}/RT$	κ/RT	$\bar{\kappa}/RT$
13.4	0.03 ± 0.005	0.43 ± 0.06	0.02 ± 0.005	0.44 ± 0.06	0.02 ± 0.005	0.44 ± 0.06
25.0	0.05 ± 0.005	0.41 ± 0.08	0.04 ± 0.005	0.42 ± 0.07	0.04 ± 0.005	0.43 ± 0.07
35.6	0.07 ± 0.015	0.42 ± 0.17	0.06 ± 0.01	0.43 ± 0.17	0.06 ± 0.01	0.44 ± 0.17
45.4	0.08 ± 0.015	0.43 ± 0.18	0.07 ± 0.01	0.45 ± 0.17	0.06 ± 0.01	0.46 ± 0.17

value of about 0.42 $k_B T$, almost independent of temperature (see Table 2). Changes in a_{AOT} to 0.50 or 1.00 nm^2 have little impact on the values obtained.

The κ values seem to be rather low, and when compared with the available values for water-in-oil microemulsions,[51] we notice that our results are at least 10 times smaller. On the other hand, our $\bar{\kappa}$ values are positive while those reported for water/AOT/n-octane are negative.[51] This suggests that in the formamide system, saddle-splay structures are more probable, while in water systems lamellar/droplet phases are preferred. This result was also reported for water/AOT/oil microemulsions when long chain oils such as n-dodecane are used.[51] Besides these aspects, it is noticeable that, in opposition to AOT water-in-oil microemulsions, reversed structures seem to be preferred at high temperatures. In fact, the behavior of water/AOT/oil microemulsions is opposite to that usually found in systems with neutral surfactants, where normal structures are preferred at high temperatures.[1] This effect is attributed to different solvation of the headgroup by water: neutral surfactants are less well solvated at higher temperatures, while in AOT the opposite happens. Similarly, we attribute the odd behavior in the formamide/AOT/isooctane system to poor solvation of the AOT polar heads by formamide at higher temperatures. Such an effect could lead to strong association at the interface between AOT and Na$^+$, with an overall neutral charge. A similar conclusion was made recently by Riter et al. in a combined work of FTIR spectroscopy and solvation dynamics in the same microemulsions.[42] FTIR results have shown that formamide retains a high degree of hydrogen bonding, showing little interactions of this type with the AOT polar head, which leads to a poor dissociation of the AOT ion

pair. This effect may be linked with the poor proticity of formamide as was already anticipated in our previous work.[22]

Nevertheless, further experiments with other techniques are required in order to establish the suggestion that AOT does not dissociate when polar components with a low proticity are entrapped into the reversed micelles, as the present work seems to suggest.

Conclusions

AOT glycerol microemulsions have close similarities with water-in-oil systems. At low g_0 and/or low ϕ the system is essentially made up of reversed micelles. When the glycerol concentration or the dispersed phase volume fraction increases, the droplets aggregate to form clusters. This is accentuated near ϕ_c, where a two-state scheme (reversed micelles and clusters) seems appropriate to describe the system. The formamide microemulsions are more complex, showing characteristics observed in systems with neutral surfactants. The aggregates appear to be globular, having an interface with low bending constants, which causes large variations of the aggregates size with both temperature and ϕ. A poor solvation of the AOT polar heads by formamide may be responsible for the novel features exhibited by these microemulsions.

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