Dynamic Light Scattering Study of AOT Microemulsions with Nonaqueous Polar Additives in an Oil Continuous Phase

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Microemulsions with entrapped nonaqueous polar solvents—glycerol (Gly), ethylene glycol (EtGy), and formamide (Form)—and an oil (isooctane or n-heptane) continuous phase were studied by dynamic light scattering (DLS). The largest hydrodynamic radii evaluated for the two former systems, by the method of extrapolation to infinite dilution, were respectively 56.5 and 28 Å. The method was not applicable to the latter system (formamide), making the determination of the hydrodynamic radius impossible. It was found that, in these microemulsion systems, the interactions between the droplets are more attractive than the ones observed in water-in-oil microemulsions, being larger in formamide and smaller in glycerol. The droplet structure remains spherical, but evidence of clusters was obtained in all the systems studied. Their formation is attributed to strong attractive interactions.

Introduction

Microemulsions are thermodynamic stable mixtures of two immiscible solvents (one apolar and the other polar) stabilized by an amphiphilic molecule, a surfactant. However, most systems studied are more complex, since a cosurfactant (usually an alcohol) and/or a salt are added to ensure the necessary stability.1

Nevertheless, some surfactants do not require a co-surfactant in order to encapsulate water-in-oil continuous microemulsions.2 Indeed, benzylidimethyl-n-hexade-cylammonium chloride (BHDC),3 dodecylammonium propionate (DAP),4 and sodium bis(2-ethylhexyl)sulfosuccinate, Aerosol OT (AOT), fall in this category.5 The last one forms anionic water-in-oil microemulsions which have been extensively studied by several techniques: small angle neutron scattering (SANS),6 small angle X-ray scattering (SAXS),6 time-resolved fluorescence quenching,7 freeze-fracture electron microscopy (FFEM),8 conductivity,9 and dynamic or static light scattering.10,11 These techniques provided ample evidence for the formation of spherical aggregates with entrapped water in the inner core (pool) while the surfactant molecules form a layer that stabilizes the water/oil interface. These systems are usually called reversed micelles dispersed in oil (w/o). For high dispersed phase volume fractions complex structures are observed due to attractive interactions between the droplets.1,2,7–9 In some conditions, an inversion between oil-continuous and water-continuous phases was observed and disordered bicontinuous structures were formed.1,2 These processes are dependent on composition,1 presence of additives (like salts, cosurfactants, polymers, and other polar solutes),1,2,7–9 temperature,1 pressure,9,10 structure of the apolar solvent molecule (size of the carbon chain and presence of aromatic moieties like benzene and toluene),1,7 density,16,18 and dielectric constant of the apolar solvent.16,19

The first reports of microemulsions in which water was substituted by polar solvents like glycerol and formamide appeared in 1984.20–22 These systems have potential practical use in organic reactions like esterification20 and polymerization.24 Their phase behavior is similar to those of water-in-oil microemulsions.22,25–27 In fact, the formation of spherical aggregates similar to reversed micelles...
was demonstrated by Robinson et al.\textsuperscript{22} and Visser et al.\textsuperscript{28} for an n-heptane/AOT/glycerol system. The authors have shown that these aggregates were stable only for small molar ratios of glycerol and surfactant (referred to later as \(g_0\)), with the maximum value around 3, which was considerably smaller than that of water (\(g_0 = [\text{H}_2\text{O}]/[\text{AOT}] > 10\)). However, studies dealing with the structure and sizes of those systems are very scarce and not quantitative.\textsuperscript{29}

In this work, we wish to report the coexistence of spherical monodisperse reverse micelles with clusters of reverse micelles in oil–continuous (isoctane and n-heptane) AOT/microemulsions containing nonaqueous polar solvents, glycerol (Gly), and ethylene glycol (EtGy) at low molar ratios of polar solvent to surfactant. Using the technique of dynamic light scattering, we have determined aggregate sizes in these systems\textsuperscript{30,31,32,33} and have also obtained evidence for cluster formation due to strong attractive interactions between droplets. The extension of the present work to the inclusion of another nonaqueous polar solvent, formamide (Form), showed that, in this case, very strong attractive interactions are present, preventing the formation of monodisperse reverse micelles, and origin the larger aggregates instead.

Attractive interactions between droplets in these systems are discussed taking into account evaluated parameters and data analysis.

**Experimental Section**

**Materials.** The AOT was purchased from Sigma and re- crystallized in methanol.\textsuperscript{34} Further purification was achieved with active charcoal added to a suspension of AOT which was stirred for 1 day. The suspension was then filtered in order to remove the charcoal, and the solvent was evaporated with reduced pressure. The AOT obtained was dried in an exsicator with CaCl$_2$, kept at reduced pressure, for at least 2 days before use. After this procedure, the AOT was always stored in the exsicator.

The aim of this purification is to remove impurities resulting from the AOT hydrolysis.\textsuperscript{32} A completely dry AOT is difficult to obtain, and a residual amount of 0.25 molecules of water per AOT molecule is always present (confirmed by Karl Fisher titration of a AOT solution in isooctane).\textsuperscript{33}

Spectroscopic grade solvents were used without further purification. Isoctane was purchased from Lachsc; glycerol, formamide, and ethylene glycol were obtained from Aldrich. When not stated otherwise, the AOT concentration used was 0.1 M.

The isooctane viscosity was calculated from eq 1:\textsuperscript{10}

\[
\eta (\mu P) = \frac{161 000}{(148.5 + t)^{0.22}}
\]  

where \(t\) is the temperature in °C and the heptane viscosity was taken from the literature.\textsuperscript{34}

**Apparatus.** Dynamic light scattering measurements were performed using a multiangle apparatus (Brookhaven Corporation Limited) equipped with a He–Ne laser (127 Model, Spectra Physics, \(\lambda_0 = 632.8\) nm) with a 35 mW power. The diffused light was detected by a photomultiplier (placed at a fixed angle of 90° relative to the incident light) and analyzed with a 136 channel correlator (Model BI 2030AT). The samples were thermostated at 298 K using a water bath. The number of counts in the autocorrelation decay were always higher than 10$^7$. The solutions were filtered before use, through Millipore filters (0.1μm) directly into the optical cell. The observation angle was changed in order to check the accuracy of the diffusion coefficients measured.

**Data Analysis.** For a system of many spherical particles the observed intensity correlation \(g^2(\tau)\) function can be related to the electric-field correlation function \(g^1(\tau)\) and hence to the system intermediate scattering function \(F(q,r)\)

\[
g^2(\tau) = 1 + C \left( g^1(\tau) \right)^2
\]  

\[
g^1(\tau) = F(q,r)S(q)
\]

where \(\tau\) is the correlation time, \(S(q)\) is the static structure factor, \(C\) is a constant, and \(q\) is the wave vector equal to \(4\pi\sin(\theta)/\lambda\), defined by the scattering angle \(\theta\), the wavelength of the light \(\lambda\), and the refraction index \(n\).

In monodispersed solutions, the intermediate scattering function is given by\textsuperscript{35}

\[
F(q,r) = S(0) \exp(-Dq^2r)
\]

where \(D\) is the collective (mutual) diffusion coefficient.

The method of analysis used was the cumulants expansion.\textsuperscript{36} This method is based on the expansion in Taylor series of the expression that relates the autocorrelation curve \(g^2(\tau)\) with the experimental curve, giving the average values \(\langle I(\tau) \rangle\) and \(\langle (I(\tau) - \langle I(\tau) \rangle)^2 \rangle\). In a first-order expansion \(\langle I(\tau) \rangle = I(0)\) and

\[
\Gamma = Dq^2
\]

In a second-order expansion the polydispersity \(\sigma\) is given by

\[
\sigma = \frac{\langle (I(\tau) - \langle I(\tau) \rangle)^2 \rangle}{\langle I(\tau) \rangle^2}
\]

The diffusion coefficient measured is related with the osmotic pressure \(\Pi\), and this relation can be described by the equation\textsuperscript{35}

\[
D = \Phi \frac{\Pi}{f} \frac{B}{\phi}
\]

where \(\phi\) is the volume fraction of the dispersed phase, \(\nu\) is the volume of a droplet, and \(f\) is the friction coefficient between the droplet and the continuous phase. For small volume fractions:

\[
\Pi \approx \frac{kT}{\nu} \Phi \left( 1 + \frac{B}{\phi} \right)
\]

where \(k\) is the Boltzmann constant, \(T\) is the absolute temperature, and \(B\) is the virial coefficient. In this case

\[
D = D_0 (1 + \alpha \phi)
\]

where the diffusing coefficient at infinite dilution \(D_0\)

\[
D_0 = \frac{kT}{f}
\]

relates with the friction factor \(f = 6\pi\eta r\), and, consequently, for spherical droplets, is inversely proportional to the hydrodynamic radius \(r\) and to the viscosity \(\eta\) of the continuous solvent. The dynamic virial coefficient \(\alpha\) is equal to \(1/3\) if the droplets behave as hard spheres and is negative if the attractive interactions between the droplets are stronger than the repulsive interactions.

This type of analysis is valid if there is only one population of aggregates (unimodal distribution). Should the distribution be not unimodal, another type of analysis must then be used.


\textsuperscript{(31)} Mengar, F. M. Am. Chem. Soc. 1979, 101 (22), 6732.


The most common ones are the EXPSAM, the inverse Laplace transform method, CONTIN, and the maximum entropy method (MEM). They give similar results consisting of a distribution function of the diffusion coefficients for the measured results. Due to the possibility of cluster formation in these systems, the EXPSAM and CONTIN methods were used in order to check whether the populations were unimodal or bimodal.

**Results**

The use of the Stokes–Einstein equation for the straightforward evaluation of hydrodynamic radii is only applicable to monodisperse spherical aggregates. In the microemulsions described in the present study, the existence of non-negligible interactions between aggregates makes the calculation of their sizes, by direct use of the apparent diffusion coefficients determined by DLS, impossible. The mean diffusion coefficients cannot only be linked to the mean particle size using the Stokes–Einstein equation for very dilute solutions. Furthermore, the diffusion coefficients obtained by the autocorrelation functions depend on the dispersed volume fraction \( \phi \). Therefore, extrapolation to infinite dilution must be performed in order to obtain the diffusion coefficient \( D_0 \), from which hydrodynamic radii can be calculated (eq 8b).

The method consists in fixing the molar concentration ratio of polar solvent to surfactant \( p_0 \) while changing the AOT concentration in order to have the same type of droplets but with different dispersed volume fractions.

Assuming that the microemulsion droplet is spherical, the volume of the inner core particle \( V \) is given by eq 9.

\[
V = \frac{4}{3} \pi r_3^3 \tag{9}
\]

where \( r_3 \) is the radius of the inner droplet core, \( n_{AOT} \) is the number of surfactant molecules with an interfacial area per AOT molecule \( a_{AOT} \), and \( V_s \) is the volume of a single molecule of polar solvent in the inner core.

Equally, the particle surface area \( A \) is given by eq 10.

\[
A = 4\pi r_3^2 = n_{AOT} a_{AOT} \tag{10}
\]

The hydrodynamic radius will then be given by

\[
r_h = 3 V_s p_0 + \delta \tag{11}
\]

where \( \delta \) is the thickness of the surfactant layer.

At a given temperature, a linear correlation is expected between the hydrodynamic radii and \( p_0 \), confirming the spherical shape of the aggregate.

The results obtained for the three systems studied—isoctane/AOT/glycerol, isooctane (n-heptane)/AOT/ethylene glycol, and isooctane/AOT/formamide—will be now described under separated headings.

**Isooctane/AOT/Glycerol Microemulsions.** Figure 1 shows the correlation between diffusion coefficients obtained directly from cumulants analysis and the dispersed phase volume fractions (glycerol plus AOT), for several \( g_0 = [\text{Gly}]/[\text{AOT}] \). As the amount of glycerol increases, the linear correlation becomes poor, especially for \( g_0 \) values close to the maximum amount of glycerol that it is possible to encapsulate in the isooctane/AOT system. This behavior indicates that the system deviates from eq 8a, meaning that microstructure changes are not accommodated by this simple equation. The linear fits to the data give as intercept \( D_0 \), while from the slope the dynamic virial coefficient is obtained.
The $R$ values (Table 1) are always negative, in accordance with the results published by Robinson et al.\textsuperscript{22} This indicates the predominance of attractive interactions between the droplets. It is also clear that the linear fitting is worse as $g_0$ becomes more negative. This fact suggests alterations of the droplet structure at high dispersed phase volume fraction and $g_0$ (nearthephase separation limit).

Figure 2 shows that the hydrodynamic radii correlate linearly with $g_0$, as predicted by eq 11, except for the higher value of $g_0 = 3.7$. Using $V_{\text{glycerol}} = 0.121$ nm$^3$,\textsuperscript{22} the estimation of the surface area of the AOT polar head was 0.41 nm$^2$, a very close value to the one calculated by Robinson et al. (also 0.41 nm$^2$ for the n-heptane/AOT/ethylene glycol system). The last experimental point out of the linear correlation between $r_h$ and $g_0$ was not used in the regression.

In Figure 2 the nonlinear correlation of the apparent "$r_h$" (obtained directly from $D$) with $g_0$ is also included. It is clear that the large positive deviation to linearity

<table>
<thead>
<tr>
<th>$e_0$</th>
<th>10$^6 D_0$, cm$^2$s$^{-1}$</th>
<th>$\alpha$</th>
<th>$r_h$, Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>2.11 (2.54)</td>
<td>-8.7 (-4.5)</td>
<td>21.7 (21.6)</td>
</tr>
<tr>
<td>2.0</td>
<td>1.62 (1.91)</td>
<td>-12.7 (-10.4)</td>
<td>26.5 (28.7)</td>
</tr>
</tbody>
</table>

Values in parentheses correspond to data in n-heptane/AOT/ethylene glycol.
obtained for $g_0 > 1$ is due to droplet interactions, which increase with the polar solvent content.

The polydispersity calculated from the second-order expansion of the cumulants is also shown. While this parameter is affected by the same restrictions as mentioned above for the apparent $r_h$, two distinct regions can be detected: below $g_0 = 1$, where the polydispersity is around 0.25, and above $g_0 = 2.5$, where the polydispersity decreases to around 0.15.

In order to check the presence of aggregates of different sizes, the CONTIN and EXPSAM methods were also used (see Figure 3). CONTIN analysis gave always only one distribution, while the EXPSAM method detects two distributions for high $g_0$. This indicates that two kinds of aggregates are possible: one giving a fast diffusion mode related with the individual aggregates (reversed micelles) and another slow diffusion mode which is related with clusters of reversed micelles.

**Isooctane (n-Heptane)/AOT/Ethylene Glycol Microemulsions.** Microemulsions with mixtures of ethylene glycol and water were studied by Hayes and Gulari. Recently, rather large apparent hydrodynamic radii $r_h$ were reported. Similar measurements, as those described in the previous section, were carried out for $e_0 = [EtGy]/[AOT]$ using as nonpolar solvent both isooctane and n-heptane. In this case the maximum amount of ethylene glycol which it is possible to encapsulate is smaller than that in the glycerol case. The extrapolation to infinite dilution, only needed for the higher values of $e_0$, obeyed eq 8a (Figure 4).

The hydrodynamic radii were calculated from $D_0$ with the Stokes–Einstein equation, and the linear correlation with $e_0$ is presented in Figure 5. As expected, the radii are not dependent on the organic apolar solvent used, and the values obtained are of the same order as those obtained in isooctane/AOT/glycerol. At $e_0 = 2$ a pronounced deviation from the linearity is observed. This behavior is consistent with a higher attractive force $(\alpha = -10.4$ for the n-heptane/AOT/ethylene glycol and $\alpha = -12.7$ for the isooctane/AOT/ethylene glycol microemulsions, see Table 2). These values of $\alpha$ are much higher than those found in the similar microemulsions with isooctane/AOT/glycerol $(\alpha \approx -4.3$ at $g_0 = 1.9$, this work) and with n-heptane/AOT/glycerol $(\alpha \approx -4$ at $g_0 = 2)$. On the other hand, using an equivalent of eq 11, where $V_{EtGy}$ is the volume of a single ethylene glycol molecule $(0.0924 \text{ nm}^3)$, we found a value of $a_{EtGy}$ of $0.44 \text{ nm}^2$ for n-heptane/AOT/ethylene glycol and $0.43 \text{ nm}^2$ for isooctane/AOT/ethylene glycol. These values are similar to those found for the system with glycerol.

Analysis by both CONTIN and EXPSAM shows two distributions already at $e_0 = 1.5$ and at $e_0 = 2$ (Figure 6). A new diffusing mode is assigned to a cluster and supports the evidence of high attractive forces, provided by the $\alpha$ values.

**Isooctane/AOT/Formamide Microemulsions.** In these microemulsions, it was not possible to extrapolate to infinite dilution. The correlations between $D$ and dispersed phase volume fraction are very poor except for $f_0 = 1.0$ (Figure 7). The interactions between the reversed

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micelles of formamide microemulsions seem to be much stronger than those in the glycerol or even in the ethylene glycol systems. The use of both CONTIN and EXPSAM showed also in this case a bimodal distribution of diffusion coefficients (Figure 8).

**Discussion**

The comparison of results obtained for nonaqueous microemulsions with those of water-in-oil microemulsions shows that the interactions between the droplets are much more attractive in the former systems, but no evidence of bicontinuous structures was obtained. The $\alpha$ values are strongly negative, especially for concentrations of polar solvent close to the phase boundary. Whereas in an isooctane/AOT/water microemulsion no changes in the diffusion coefficient were detected until high volume fractions (above 0.3), in these nonaqueous microemulsions a decrease of diffusion coefficients is detected even for volume fractions smaller than 0.1. This is caused by the fact that the interface in water-in-oil microemulsions is rigid with a high curvature (which gives an $\alpha$ value of about $-1$) while with the nonaqueous polar solvents used here, glycerol and ethylene glycol, the interface is fluid. The interface is less rigid, perhaps due to a less effective hydrogen bonding between the surfactant head group and the polar protic solvent.

The formamide system is very difficult to study because strong deviations from eq 8 are observed. In this case, the formamide may not be a good solvent to stabilize the polar surfactant anionic head groups and an ion pair may be preferred with the Na$^+$ counterions very close to the negative oxygens of the sulfonate and carbonyl groups of AOT.

The $R_{AOT}$ obtained for glycerol and ethylene glycol microemulsions are similar and in good agreement with the value reported by Robinson et al. for n-heptane/AOT/glycerol microemulsions. The value is smaller than the one reported for water systems (between 0.6 and 0.5 nm$^2$), indicating that the AOT is either more packed in the interface or desorbed from the polar solvent interface. However, the values have a large uncertainty because the slope is relatively small.

The suggestion made by Hayes et al. that ethylene glycol could act as cosurfactant, in polar solvent-in-oil microemulsions using a mixture of ethylene glycol and water, is not consistent with data obtained in this work, since then it would be expected that both the size and surface area of the aggregate would increase. Alternatively, ethylene glycol may not separate as a monolayer but stay closer to the interface, explaining the larger attractive interactions between reversed micelles, compared to those observed with the glycerol system. Incorporation of zinc tetraphenylporphyrin in this system leads to an equilibrium between two spectroscopically distinct species which depends on the molar ratio of ethylene glycol and AOT, supporting the existence of a distinct nanophase.

It is possible that, in the microemulsion with formamide, there might be some incorporation of the polar solvent in the interface, enhancing the interactions between droplets. Indeed, there are solutes (formamides and ureas) in water-in-oil microemulsions which tend to migrate to the interface.

Nonionic surfactants encapsulating formamide show a phase behavior identical to that displayed by water-in-oil systems. However, the amount of polar solvent that it is possible to encapsulate in the former is smaller and percolation seems to happen with lower temperatures and

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dispersed phase volume fractions. Structures with filaments of formamide were detected in the isooctane/CTAB/1-butanol/formamide system, and percolation was found in the formamide system with anionic surfactants.

The EXPSAM and CONTIN analyses gave good insight into the distribution of diffusion coefficients of all systems studied. The EXPSAM is a more sensitive analysis method, and bimodal distributions were obtained in glycerol, ethylene glycol, and formamide microemulsions. The CONTIN method gave broad distributions, which seems to indicate two populations: one constituted by individual spherical aggregates (reversed micelles) and another constituted by these individual aggregates interacting very closely and diffusing in a collective way. This analysis is apparently in contradiction with the one made with the cumulants, but conceptually it is natural that, in systems with high attractive interactions between droplets, the reversed micelles start to aggregate, especially near the phase boundary. The cluster formation happens also in water-in-oil microemulsions even with small attractive interactions, and Koper et al. showed that the virial coefficient α measured by cumulants is affected by the formation of these higher order aggregates. These higher order aggregates are clusters of reversed micelles, which maintain the spherical shape. Robinson et al. reported a high exchange rate of solutes in glycerol microemulsions which may be caused by the clustering phenomena. The results presented in this paper also support the Koper et al. model for the interpretation of α values: there should be two populations, then α is essentially a measure of the clustering process and not of attractive forces. This does not mean that the negative values may not reflect a strong attractive interaction between droplets. The reason why clusters may be forming can be that attractive interactions between the droplets are very strong.

Other contributions should be taken into account, including the possibility of more complex structures and, perhaps, the inexistence of reversed micelles. However, these structures should not be very different from the ones which are formed for glycerol microemulsions with high g₀, since the general behavior is very similar (including the polydispersity measured from the second cumulants). Bicontinuous structures are not likely to occur for these compositions and temperature, and possibly the aggregates are forming clusters of reversed micelles. The formation of “solvated” reverse micelles or microemulsions is likely to be associated with the ability of the encapsulated polar solvent to form a high degree of hydrogen bonds. According to the Kamlet and Taft polarity scale, the solvent proticity decreases in the following order: water > glycerol > ethylene glycol > formamide. An increase of attractive interactions will be expected to accompany the decrease of solvent proticity.

**Summary**

AOT microemulsions with the encapsulated nonaqueous polar solvents glycerol and ethylene glycol bear some similarities to the well-known water-in-oil microemulsions. However, the interface is more fluid, making the interactions between droplets more attractive.

At the temperature and compositions studied, there is no evidence for the formation of bicontinuous structures in these systems. The droplets remain spherical (similar to reversed micelles) and, due to strong attractive interactions, they assemble in clusters. As a consequence of this self-assembly, there is a coexistence of monodisperse reverse micelles and clusters of reverse micelles at relatively low molar ratios of polar solvent/surfactant.

When the encapsulated polar solvent is formamide, some aggregates and clusters are detected, but there is no evidence that monodisperse reverse micelles are formed in this case.

The attractive interactions increase in the order water < glycerol < ethylene glycol < formamide and are associated with the loss of stabilization of the polar surfactant head group by the polar solvent, which in turn is related to the decrease of hydrogen-bonding strength.

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