Dynamics of water-containing sodium bis(2-ethylhexyl)sulfosuccinate (AOT) reverse micelles: A high-frequency dielectric study

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The high-frequency dielectric response of AOT reverse micelles in n-heptane and CCl_4 has been measured in the range $0.01-20$ GHz as a function of the water-surfactant ratio (W). A relaxation phenomenon has been observed which is connected to the single particle dynamics. This dielectric relaxation depends on surfactant hydration and is markedly affected by interparticle interactions. At low values of the volume fraction ϕ of dispersed matter (water + AOT), interparticle interactions are negligible and the behavior of the dielectric relaxation vs W has been interpreted in terms of two coexisting diffusion mechanisms: the reorientation of the whole micelle and the "free" diffusion of the completely hydrated AOT ion pairs. As ϕ is increased, interparticle interactions start to play a role and the dielectric relaxation is considerably affected by the nature of the external oil and by the addition of small amounts of electrolyte. [S1063-651X(96)03007-3]

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In a recent paper we reported the results of a detailed experimental investigation of dielectric and IR properties of very dilute samples of AOT reverse micelles in CCl_4 [1]. A relaxation phenomenon was observed in the microwave region reflecting some properties connected to the single particle dynamics. The behavior of the relaxation time with W was successfully interpreted in terms of two coexisting diffusion mechanisms, whose relative weights depend on the reverse micelle hydration degree. The first mechanism is the orientation of the whole micelle while the second one is the "free" diffusion of the completely hydrated AOT "ion pairs."

The main aim of the present paper is to investigate the extent of the applicability of this physical picture as the system is modified and to examine the influence of interdroplet attractive interactions on the observed dielectric relaxation. Since intermicellar interactions can be modulated by changing the external oil and/or by adding small amounts of electrolyte, we have performed measurements on AOT reverse micelles in both n-heptane and CCl_4 with and without extra electrolyte. The experimental procedure has been previously described [1].

Figure 1 shows the dielectric spectrum of AOT–H_2O–n-heptane microemulsion at $\phi=0.2$ for $W=11$. Two distinct relaxation phenomena are present in the spectra: the principal one, in the 100 MHz frequency region [1,2], is entirely within the experimental frequency window; the second one, located at higher frequencies, is not completely resolved in this experiment. These spectra can be appropriately fitted by the superposition of a Cole-Cole and a Debye relaxation function, according to the equation

$$\varepsilon^*(\omega)=\varepsilon_\infty+\frac{\Delta\varepsilon_1}{1+(i\omega\tau_1)^{1-\alpha}}+\frac{\Delta\varepsilon_2}{1+i\omega\tau_2} \qquad (1)$$

being ε_∞ the high-frequency dielectric constant, ω the angular frequency of the applied field, $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ the low- and high-frequency dielectric increments, respectively, τ_1 and τ_2 the relaxation times of the two processes, and α a parameter characterizing the width of the relaxation function

around τ_1. Typical values of α around 0.2 have been obtained. Since the value of $\Delta\varepsilon_2$ increases with the water content in the samples and τ_2 is located close to the region of bulk water dielectric relaxation, the second relaxation has been attributed to the reorientation of the water molecules confined within the micellar core. A deeper discussion on the behavior of this relaxation is beyond the purposes of the present work.

Measurements have been also taken on AOT–H_2O–n-heptane samples characterized by higher values of ϕ where an additional relaxation phenomenon appears in the 1 MHz region becoming more and more pronounced for increasing values of the volume fraction. The dielectric properties of water-in-oil microemulsions in this frequency re-
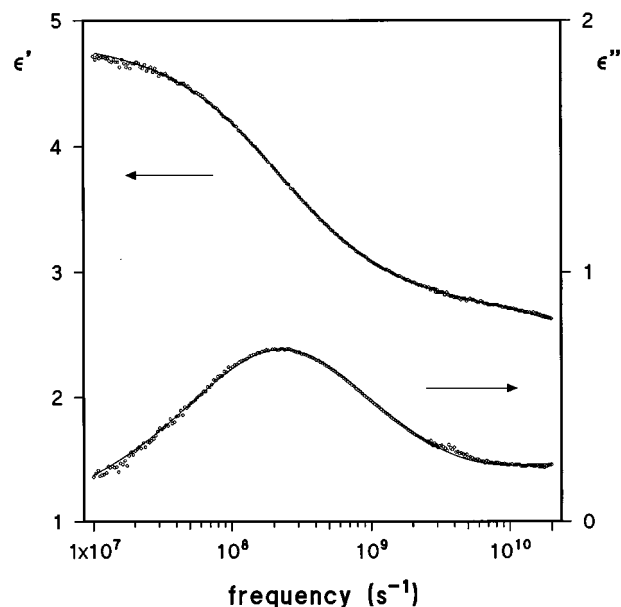

FIG. 1. Real (ε') and imaginary (ε'') part of the dielectric permittivity vs frequency of AOT–H_2O–n-heptane microemulsions ($\phi=0.2$, $W=11$). (○): experimental points. (—): best fit according to Eq. (1).
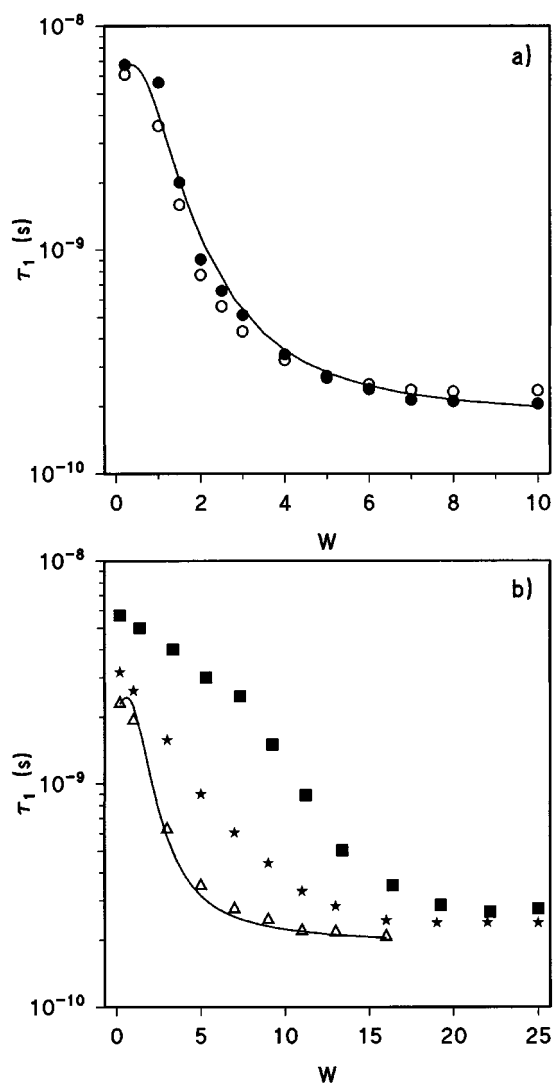
FIG. 2. Relaxation time (τ_1) as a function of W. (a) AOT–H_2O–CCl_4 microemulsions at $\phi=0.1$ (●) and $\phi=0.05$ (○). (b) AOT–H_2O–n-heptane microemulsions at $\phi=0.2$ (■), $\phi=0.1$ (★), and $\phi=0.05$ (△). (—): calculated according to Eq. (3).

FIG. 3. Relaxation strength ($\Delta\varepsilon_1$) vs W at selected ϕ values of AOT–H_2O–n-heptane microemulsions. In the inset a similar plot for AOT–H_2O–CCl_4 microemulsions is reported. Symbols and ϕ values are the same as in Fig. 2. The lines are guidelines for the eye.

gion was extensively studied and related to dynamical percolation phenomena [3–6]. In the present work we focus our attention to dilute samples ($\phi\leqslant0.2$), in which the 1 MHz relaxation is not significant, and to frequencies higher than 10^7 Hz.

To give a better evidence of the effects of intermicellar interactions on dielectric spectra, the same measurements have been performed in CCl_4 where interactions are reduced by reducing the molecular size of the oil. In this case, the dielectric spectrum of all the investigated samples clearly shows the presence of the relaxation located in the 100 MHz–1 GHz region, very close to that observed in the systems containing n-heptane as a dispersing medium. The absence of dielectric dispersions in the 1 MHz region suggests the clustering process of reverse micelles in carbon tetrachloride to be negligible in the range of volume fractions here investigated. Also in this case, the interpolation procedure of the experimental data has been carried out using Eq. (1).

The behavior of the relaxation time τ_1 vs of W is shown in Figs. 2(a), 2(b) for all the investigated series of samples.
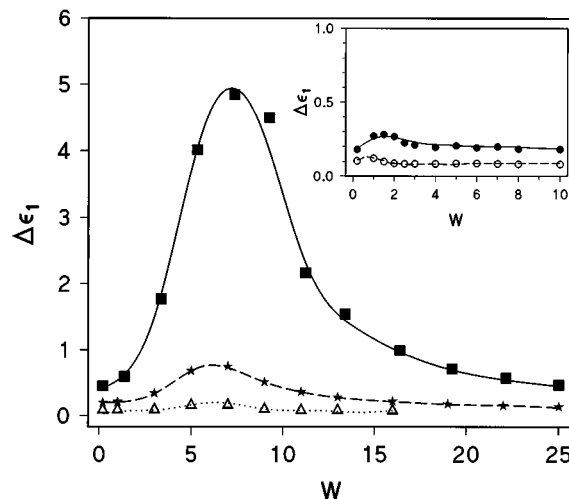
For each series, the experimental values of τ_1 exhibit a marked initial decrease followed by a region in which τ_1 keeps nearly constant. Concerning the initial decrease of τ_1 in CCl_4, it takes place in a narrow range between $W=0.2$ and $W=6$ and it does not depend on dilution. A similar behavior has been observed in the most dilute samples in n-heptane ($\phi=0.05$), but, different from CCl_4, a marked effect of particle volume fraction ϕ is here evidenced. Figure 2(b) shows a smoother and smoother behavior of τ_1 for increasing values of ϕ in n-heptane samples, as micellar interactions start to play a role. The presence of these interactions is also evident in the behavior of the relaxation strength $\Delta\varepsilon_1$ relative to AOT–H_2O–n-heptane microemulsions, as shown in Fig. 3. In particular, the experimental values of $\Delta\varepsilon_1$ attain a maximum for W close to 7–8. This maximum corresponds to a minimum for the percolation threshold [7,8] and it is likely connected to the interdroplet interactions. Moreover, Fig. 3 shows that the relaxation strength $\Delta\varepsilon_1$ in n-heptane increases faster than linearly in ϕ as expected when interactions take place. In CCl_4, the relaxation strength $\Delta\varepsilon_1$ keeps roughly constant in the whole investigated range of W, as shown in the inset of Fig. 3.

Previous neutron scattering, light scattering and viscosity measurements performed on these systems [8–10] suggested that interactions between the droplets are profoundly affected by the addition of small amounts of electrolyte and that the salted systems behave more like hard-sphere suspensions while having the same characteristic size of their unsalted counterparts. Following these suggestions we have tested the influence of the water salt content on the dielectric properties of the systems in n-heptane at $\phi=0.2$. The behavior of both $\Delta\varepsilon_1$ and τ_1 is reported in Fig. 4 together with that relative to samples in which pure water was replaced by a $0.5M$ NaCl brine. The figure clearly shows that, when NaCl is added to the solutions, the trend of the two dielectric parameters, as a function of W approaches the one that has been obtained for the systems in which interactions are lower. These results evidentiate the important role of the interparticle interactions in determining the behavior of the 100 MHz dielectric relaxation.
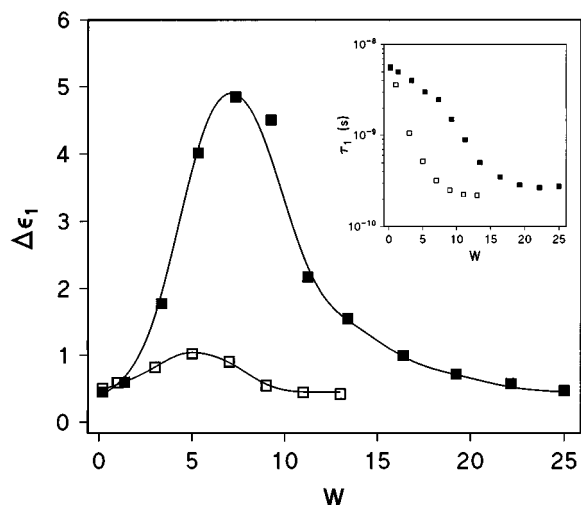
FIG. 4. AOT–H_2O–n-heptane systems $\phi=0.2$. Plots of relaxation strength as a function of W. (■): microemulsions containing H_2O; (□): microemulsions containing $0.5M$ NaCl brine. In the inset the evolution of relaxation time (τ_1) as a function of W for the same systems is reported. The lines are guidelines for the eye.

The almost dehydrated reversed micelles ($W=0.2$) exhibit a nearly rigid structure and, as previously suggested [1] the dielectric relaxation can be described in terms of the rotational diffusion of the whole micelle. Supposing the micellar aggregates to be approximately of spherical shape, the rotational diffusion time is given by the Debye-Stokes formula

$$\tau = 4\pi\eta R^3/k_B T , \qquad (2)$$

where η is the viscosity, R the micelle radius and $k_B T$ the thermal energy. Comparing the results obtained at different volume fractions, both in n-heptane and in CCl_4, reveals that the characteristic time τ_1 scales with the viscosity of the solution. At a given volume fraction ϕ, the micellar radius R has been estimated by inserting the viscosity of the solution [11] and the experimental time τ_1 in Eq. (2). This procedure has been applied to all the investigated samples and the results are reported in Table I; the values of the micellar radius calculated for different volume fractions ϕ are mutually consistent within the experimental errors and are also in agreement with the results reported in the literature [1,12].

It is known that, increasing the water content inside the micelles, the micellar radius R increases almost linearly [13] with W, so that τ_1 is expected to increase approximately with W^3 according to the Debye-Stokes Eq. (2). Different

TABLE I. Micelle radius (R) and apparent dipole moment (μ_{app}) of a surfactant molecule in the micelles ($W=0.2$).

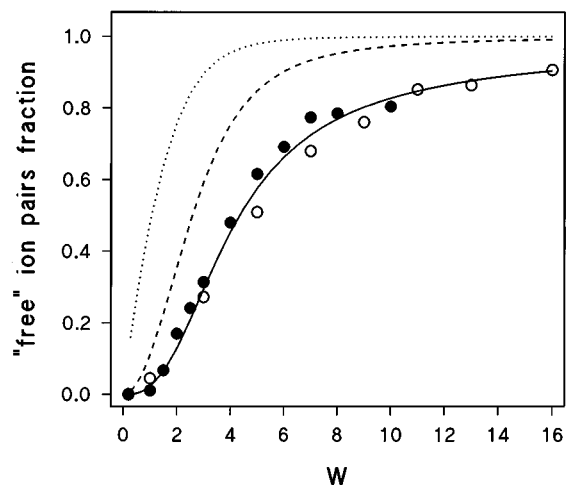| Oil	ϕ	R (Å)	μ_{app} (Debye)
CCl_4	0.05	12.0 ± 0.8	0.77
CCl_4	0.1	11.7 ± 0.7	0.76
n-heptane	0.05	11.8 ± 0.7	0.78
n-heptane	0.1	12.4 ± 0.6	0.75
n-heptane	0.2	12.8 ± 0.4	0.76

FIG. 5. Plot of the "free" ion pairs fraction $X(W)$ calculated according to Eq. (3). (●): AOT–H_2O–CCl_4 system at $\phi=0.1$; (○): AOT–H_2O–n-heptane system at $\phi=0.05$. Lines refer to the fractions of AOT ion pairs bound to at least one ($\cdots$), two ($- - -$), or three (—) water molecules as obtained from IR data.

from this, τ_1 initially decreases and then keeps nearly constant as a function of W [see Figs. 2(a), 2(b)]. In a previous work [1] a quantitative description of the behavior of τ_1 as a function of W was reported in the case of AOT–H_2O–CCl_4 reversed micelles at $\phi=0.1$. For each value of W, we supposed the existence of a fraction $[1-X(W)]$ of surfactant ion pairs reorienting with the whole micelle with the Debye diffusion time $\tau_d(W)$ and of a fraction $X(W)$ of "free" ion pairs whose reorientation is characterized by a relaxation time, $\tau_0 < \tau_d(W)$. The value of τ_0 was fixed to the limit value of τ_1 at the highest molar ratios. The relaxation time τ_1 was expressed in terms of $\tau_d(W)$ and τ_0 according to the equation

$$\frac{1}{\tau_1} = \frac{X(W)}{\tau_0} + \frac{1-X(W)}{\tau_d(W)} . \qquad (3)$$

Starting from Eq. (3), in the present work we have calculated the fraction $X(W)$ of the "free" AOT ion pairs for samples in both CCl_4 ($\phi=0.1$) and n-heptane ($\phi=0.05$). To this aim, the experimental values of τ_1, the values of $\tau_d(W)$ calculated from Eq. (2), and the value of τ_0 have been inserted into Eq. (3) and the values obtained for $X(W)$ have been reported in Fig. 5. The values relative to the two solvents coincide within the experimental errors, as expected for an hydration process uneffected by the dispersing oil.

Previous IR studies [14,15] on these systems have shown that the spectroscopic properties of the water pool depend on W and, at constant W, they are practically independent of the concentration of the micellar phase and of the nature of the external oil in agreement with the assumptions of water encapsulated into the reverse micelles. In that case the experimental data were treated by assuming the existence of three independent binding sites per AOT molecule. The fractions of AOT molecules corresponding to the three possible hydration degrees are reported in Fig. 5 and compared with the values of $X(W)$ calculated from the dielectric measurements. We notice that the fraction of completely hydrated AOT ion

pairs superimposes to the values of $X(W)$; on the other hand, the fractions of the partially hydrated surfactant ion pairs significantly depart from the calculated values of $X(W)$. The continuous line in Fig. 2(a), 2(b) corresponds to the values of τ_1 calculated replacing the fraction of completely hydrated AOT ion pairs obtained from IR data in $X(W)$ of Eq. (3). It is noteworthy that results obtained from different experimental techniques are in very good agreement, thus revealing a fruitful complementarity of dielectric and IR spectroscopy in understanding the role of hydration in the dynamics of these systems.

In the previous discussion on the behavior of τ_1 as a function of W, the dielectric relaxation observed in the almost dehydrated reverse micelles ($W=0.2$) has been attributed to the rotational diffusion of the whole micellar aggregate. Moreover, as the water content inside the micelles is increased, an increasing number of completely hydrated AOT ion pairs is expected to achieve a mobility sufficient to reorientate independently from the microaggregate. The mechanism described above is also able to account for the observed dielectric relaxation strength at the extreme values of W. As a fact, for $W=0.2$ we have interpreted the experimental data of relaxation strength in terms of the rotational diffusion of the whole dehydrated micelle. The dipole moment μ_{mic} of the microaggregate has been estimated using the Debye extension of the Clausius-Mossotti equation as described in Ref. [1]. Using the value $N_a=17$ for the mean aggregation number of monomeric surfactant molecules in the two solvent oils, we have calculated the apparent dipole moment ($\mu_{app}=\mu_{mic}/N_a$) of a surfactant molecule in the micelles. The values obtained for μ_{app} (see Table I) do not appreciably depend on the oil and on the volume fraction of dispersed phase; for all the tested samples the value of μ_{app} obtained is in good agreement with that determined by Eicke and Christen [16].

At the highest values of W, the dispersed particles are usually depicted as spherical surfactant-coated water droplets with AOT ion pairs located at the surfactant-water interface; the observed dielectric relaxation phenomenon has been thus attributed to the fluctuating electric dipole moment imparted to the microaggregate by the diffusion of the AOT ion pairs. The dipole moment μ of an AOT ion pair has been considered as the microscopic origin of the orientational contribution ($\Delta\varepsilon_{ip}$) to the equivalent permittivity ε_p of the spherical particle suspended in an oil which models the microaggregate. Transforming the surface polarizability due to the AOT ''ion pairs'' diffusion at the surfactant-water interface into a volume polarizability of a reverse micelle substitute homogeneous sphere, $\Delta\varepsilon_{ip}$ has been written according to the equation

$$\Delta\varepsilon_{ip}=N_a\mu^2 g/4\pi\varepsilon_0 R^3 k_B T, \tag{4}$$

where R is the external micellar radius, and g the ''ion-pairs'' orientation correlation and/or local field correction factor. $\Delta\varepsilon_{ip}$ is related to the equivalent permittivity ε_p by means of the equation

$$\Delta\varepsilon_{ip}=\varepsilon_p-\varepsilon_{ph}, \tag{5}$$

where ε_{ph} is the high-frequency equivalent permittivity of the spherical particle.

The equivalent permittivity ε_p has been derived from the polarizability per unit volume of an homogeneous sphere suspended in an oil α_p using the equation [17]

$$\alpha_p=(\varepsilon_p-\varepsilon_m)/(\varepsilon_p+2\varepsilon_m), \tag{6}$$

where ε_m is the permittivity of the dispersing medium. At sufficiently low volume fractions ϕ, the values of α_p can be obtained from those of the microemulsion polarizability α, by means of the Clausius-Mossotti relation [17]

$$\alpha=(\varepsilon-\varepsilon_m)/(\varepsilon+2\varepsilon_m)=\alpha_p\phi, \tag{7}$$

where ε is the measurable permittivity of the mixture.

Once the values of the aggregation number N_a and of the micellar radius R are known, it is possible to estimate the AOT ion-pairs dipole moment μ from Eqs. (4)–(7). Assuming $g=1$, $N_a=59$, $R=27$ Å for the systems with $W=10$ in CCl_4 and $N_a=307$, $R=48$ Å for that with $W=25$ in n-heptane [17], a dipole moment of about 9 Debye has been obtained in both cases. This value is in good agreement with the value $\mu=7$ Debye reported in Ref. [16].

In conclusion, the model proposed to interpret the 100 MHz relaxation of AOT microemulsions is able to account for the experimental data of both relaxation strength and relaxation time of systems in CCl_4 and in n-heptane. Moreover, where interactions are present, the behavior of this relaxation has been shown to depend on W, on the nature of the solvent, and on the addition of small amounts of electrolyte. These interaction effects deserve further investigations for a better understanding their microscopic origin.

[1] M. D'Angelo et al., Phys. Rev. E 52, R4620 (1995).
[2] C. Cametti et al., Phys. Chem. 94, 149 (1990).
[3] J. Peyrelasse and C. Boned, J. Phys. Chem. 89, 370 (1985).
[4] C. Cametti et al., Phys. Rev. A 40, 1962 (1989).
[5] C. Cametti et al., Phys. Rev. Lett. 75, 569 (1995).
[6] Y. Feldam et al., Phys. Rev. E 51, 478 (1995).
[7] A. D'Aprano et al., J. Chem. Phys. 95, 1304 (1991).
[8] C. Boned and J. Peyrelasse, J. Surf. Sci. Technol. 7, 1 (1991).
[9] R. Ober and J. Taupin, J. Phys. Chem. 84, 2418 (1980).
[10] B. Bedwell and J. Gulari, J. Colloid Interface Sci. 102, 88 (1984).
[11] G. Onori and A. Santucci, J. Colloid Interface Sci. 150, 195 (1992).
[12] M. Kotlarchyk et al., J. Phys. Chem. 89, 4382 (1985).
[13] B.H. Robinson et al., J. Chem. Soc. Faraday Trans. I 80, 13 (1984).
[14] G. Onori and A. Santucci, J. Phys. Chem. 97, 5430 (1993).
[15] M. D'Angelo et al., Nuovo Cimento D 16, 1601 (1994).
[16] H.F. Eicke and H. Christen, J. Colloid Interface Sci. 48, 281 (1974).
[17] M.A. Van Dijk et al., J. Phys. Chem. 93, 2506 (1989).