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High-frequency dielectric properties of aerosol sodium bis-2-ethyl-hexylsulfosuccinate (AOT)–H_2O–CCl_4 systems in the reversed micellar phase

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The complex permittivity of sodium bis-2-ethyl-hexylsulfosuccinate (AOT)–H_2O–CCl_4 microemulsions has been measured by a frequency domain coaxial technique in the range 0.02–3 GHz as a function of molar ratio $W=[H_2O]/[AOT]$, for small amounts of water ($0.2<W<10$). A relaxation process has been observed, whose behavior as a function of W has been interpreted in terms of an increasing mobility of AOT ion pairs connected with the hydration process of the micellar aggregates.

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Microemulsions are multicomponent supramolecular liquid systems that currently constitute a very interesting and attractive field of research. Their structural and dynamical properties are the subject of many theoretical and experimental investigations. These systems consist of small surfactant-coated water droplets dispersed in an oil and interacting by means of a repulsive potential with a weak attractive tail. The size of the droplets can be varied by changing the molar ratio of water to surfactant (W). The aggregates containing a small amount of water are usually called reverse micelles, whereas microemulsions correspond to droplets containing a large amount of water molecules. By changing the concentration of the droplets these systems show a large variety of interesting physical phenomena, such as electrical conductivity percolation [1,2], glasslike behaviors [3,4], and phase transitions [5–7].

In recent years, many studies have focused on the three-component system sodium bis-2-ethyl-hexylsulfosuccinate (AOT)–water–oil, which forms a microemulsion phase over wide ranges of composition and temperature. The heterogeneous water confined in AOT reversed micelles has been investigated by many techniques [8–10]. These studies indicate that the properties of surfactant-trapped water pools differ from those of pure water and change strongly with water content if W is smaller than 6–10. The anomalous behavior of water at low W has been attributed to local interactions of water molecules with the Na^+ counterions and the strong dipole of AOT polar groups. A similar reasoning has been invoked to account for the behavior of the water close to biological membranes or proteins.

Information on the change of structure and dynamics of both the AOT shell and the water confined in the reverse micelles can be obtained from dielectric relaxation measurements. Most of the dielectric studies on reverse micelles are, however, performed at high volume fractions of the dispersed phase and the description of the data is usually related to dynamical percolation phenomena [1,2,11] accompanied by a sharp increase in the conductivity and a corresponding giant relaxation effect in the low-frequency region. Most of the studies on dielectric properties of microemulsions have therefore been conducted at relatively low (0.1–100 MHz) frequencies and little attention has been paid to the possible existence of a subsequent high-frequency dispersion. To the best of our knowledge there is only one previous investigation [11] of the dielectric properties of very dilute samples of AOT reverse micelles in n-decane extending up to microwave frequencies (0.001–1 GHz). In that study, concerning a sample at a molar ratio $W=40.8$, the occurrence was observed of a high-frequency dispersion characterized by a relaxation time of the order of 10^{-9} s and a dielectric increment of few units. This high-frequency dispersion seems to reflect some properties inherent in single particle dynamics and has been tentatively attributed [11] to motion of the surfactant polar anionic groups within the single droplets. In this respect it seems to be particularly appropriate to perform a series of dielectric measurements by varying W in the dilute region of the system, since the properties of the single microaggregate depend strongly on W, especially for the lowest values of W (<10).

In this paper the complex dielectric permittivity of AOT–water–carbon tetrachloride reverse micelles has been measured in the range 0.02–3 GHz at a fixed volume fraction of the dispersed phase ($\phi=0.1$) and a varying value of W in the region of small amounts of water ($0.2<W<10$). Carbon tetrachloride was chosen as the dispersing medium in order to reduce attractive interparticle interactions. In fact, it should be noted that, although the origin of attractive forces in microemulsions is still not clear [9], surfactant–solvent-oil interactions are thought to be a major factor [12]; the strength of this attractive interaction increases with the length of the solvent molecule and so it is expected to be less significant in carbon tetrachloride than in n-decane. Consistent with this, the behavior of both the diffusion coefficient and the viscosity of the AOT–water–carbon tetrachloride system is appropriately described in terms of a dispersion of independent spherical particles (the hard sphere approximation) for a volume fraction ϕ of the dispersed phase less than 0.1 [13,14].

The sample preparation and the measuring technique have been described elsewhere [14,15]. All measurements were performed at (20.0 ± 0.1) °C.

Figures 1(a) and 1(b) show the dielectric spectrum (circles) of a sample at $W=5$ and $W=10$, respectively. The dielectric dispersion here investigated is located at a frequency about two decades higher than the one that has been widely investigated in the literature and related to the clus-

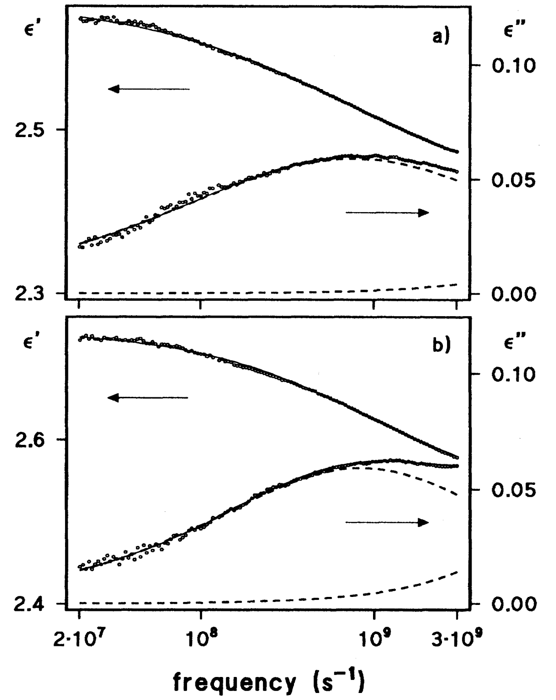

FIG. 1. Real (ε') and imaginary (ε'') parts of the dielectric constant of the AOT–H_2O–CCl_4 mixture vs frequency. (a) $W=5$, (b) $W=10$. (○), experimental points. (—), best-fit curves according to Eq. (1). Cole-Cole and Debye-type contributions to the best fit of $\varepsilon''(\omega)$ are also shown (- - -).

tering of microaggregates. Such a contribution was not observed at the value of ϕ chosen.

The frequency dependence of the complex dielectric constant $[\varepsilon^*(\omega)=\varepsilon'(\omega)-i\varepsilon''(\omega)]$ can be described in terms of Cole-Cole and Debye-type relaxation processes according to the equation

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

where ε_∞ is the high-frequency dielectric constant, ω is the angular frequency of the applied field, $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$ are the low- and high-frequency dielectric increments, respectively, τ_1 and τ_2 are the relaxation times of the two processes, and α is a parameter characterizing the width of the relaxation time distribution around τ_1.

The interpolation procedure of the experimental data as a function of frequency was carried out by fitting the values of both the real and imaginary parts of the dielectric permittivity by means of the Marquardt algorithm. The best-fit curves of the experimental spectra are reported in Fig. 1 (solid line) together with the Cole-Cole and Debye-type contributions to the best fit of $\varepsilon''(\omega)$ (dashed lines). The Debye dispersion is located at higher frequencies in the region of the relaxation of bulk water; in our experimental frequency range it makes only a small contribution which increases with increasing water content in the samples (see Fig. 1). On these grounds, this relaxation process has been attributed to the reorientation of water molecules confined within the micellar core. The present paper refers to the low-frequency relaxation process.

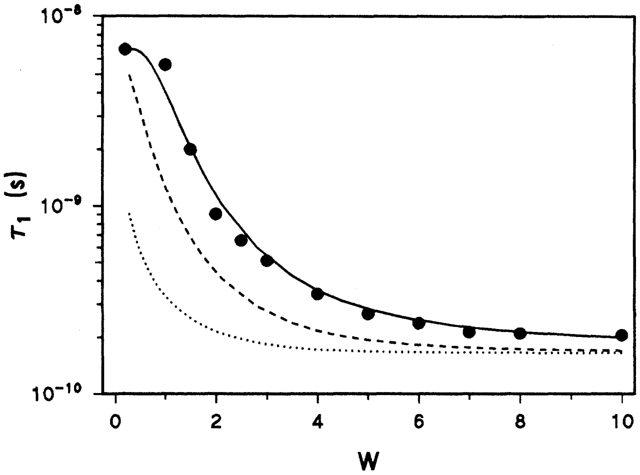

FIG. 2. (●), relaxation times τ_1 vs W for AOT–H_2O–CCl_4 mixtures. Lines have been calculated assuming for $\alpha(W)$ in Eq. (4) the fraction of AOT ion pairs bound to at least three (—), two (- - -), or one (· · ·) water molecules.

Figure 2 shows the values of the relaxation time τ_1 as a function of W. This figure shows a marked decrease in τ_1 up to $W\simeq 6$; for higher molar ratios, τ_1 keeps nearly constant. Similar results were obtained at a lower value of the dispersed phase volume fraction ($\phi=0.05$); this fact, according to results from diffusion coefficient and viscosity measurements [13,14], confirms that the role played by interactions between microaggregates in such dilute systems is not important.

In spite of the strong dependence of τ_1 on the degree of hydration of the micelles, the dielectric increment $\Delta\varepsilon_1$ and the shape parameter α (about 0.18 and 0.2, respectively, at $W=0.2$) keeps approximately constant as water is added to the solution. The following discussion will thus focus on the behavior of τ_1 as a function of the molar ratio W.

At low molar ratio ($W=0.2$) the micelles exhibit an almost rigid structure [16] and, according to previous suggestions [17,18], the observed dielectric dispersion has been attributed to the rotational diffusion of the whole micellar aggregates. In these conditions a τ_1 value of $(6.7\pm0.6)10^{-9}$ s has been obtained. Supposing the micelles to be approximately of spherical shape, the relaxation time depends, according to the Debye model, on the viscosity of the solution η and on the radius of the micelles R through the relation

$$\tau=\frac{4\pi\eta R^3}{k_BT}, \tag{2}$$

where k_BT is the thermal energy.

Inserting into Eq. (2) the viscosity value of the solution at $\phi=0.1$ [$\eta=(1.36\pm0.02)\times10^{-3}$N s m^{-2}] [14] a radius $R=(11.7\pm0.4)$ Å is obtained for the micelles. This result is consistent with the literature values [19–21].

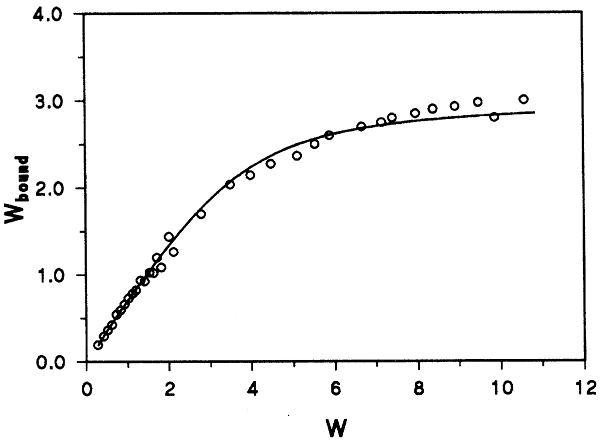

FIG. 3. Fraction of bound water molecules vs molar ratio. (○), calculated from experimental points. (—), calculated assuming the existence of three independent binding sites per AOT molecule [26].

The Debye extension of the Clausius-Mossotti equation has been used to estimate the dipole moment of the micelles at $W=0.2$. This equation can be written in terms of the molar fractions of micelles f_1 and of carbon tetrachloride f_2 as

$$\frac{\varepsilon-1}{\varepsilon+2}\left[\frac{f_1}{N_{01}}+\frac{f_2}{N_{02}}\right]=f_1\left[\frac{\varepsilon_\infty-1}{\varepsilon_\infty+2}\,\frac{1}{N_{01}}+\frac{\mu_{\mathrm{mic}}^2}{9\varepsilon_0 k_B T}\right]+f_2\left[\frac{\varepsilon_{\mathrm{CCl}_4}-1}{\varepsilon_{\mathrm{CCl}_4}+2}\,\frac{1}{N_{02}}\right], \tag{3}$$

where ε is the low-frequency dielectric permittivity of the solution, N_{01} and N_{02} the number of micellar microaggregates and solvent molecules per volume unit, respectively, μ_{mic} the micellar dipole moment, ε_0 the absolute dielectric constant of free space, and $\varepsilon_{\mathrm{CCl}_4}$ the dielectric constant of the solvent. Using a value of 17 [22,23] for the mean aggregation number of monomeric surfactant molecules in carbon tetrachloride, the resulting micellar dipole moment (μ_{mic}) is close to 14 D. The agreement between this value and that obtained by Eicke and Shepherd [24] lends further support to the idea that the relaxation phenomenon considered can be attributed to the whole micelle rotational diffusion.

It is to be noticed, however, that the experimental behavior of τ_1 with W does not agree with the Debye model. In fact, since the micellar radius R increases almost linearly with W [20], the Debye-Stokes equation predicts τ_1 to increase approximately as W^3. Conversely, the experimental results show a marked decrease in τ_1 up to $W\simeq 6$ and no appreciable changes at the highest W's. We notice that this behavior is typical of many other investigated properties of microemulsions [8,10,25] and it has been explained in terms of an initial hydration of the surfactant headgroups followed by formation of a water pool with a continuous equilibrium between bound and bulk water.

In a previous paper [26] the hydration of reversed micelles in carbon tetrachloride was investigated by means of IR spectroscopy. The results obtained are shown in Fig. 3, where the hydration number W_{bound} (mean number of bound water molecules per AOT molecule) is shown versus the molar ratio W. The values of W_{bound} increase steeply at low molar ratio and approach a nearly constant value close to 3 for W higher than 6. We emphasize that the behavior of W_{bound} in approaching its limiting value at the highest molar ratios is strikingly similar to that observed for the relaxation time τ_1 (Fig. 1). This result suggests a close connection between the behavior of τ_1 with W and the progressive hydration of AOT polar headgroups.

A ^{13}C NMR investigation [16] of AOT microemulsions has shown that the continuous hydration of the micellar aggregates corresponds to an increase in the mobility of the AOT carbon atoms which is much more pronounced for carbon atoms located closest to the polar headgroup of the surfactant molecule; this result agrees well with that obtained from nanosecond spectroscopy [16], suggesting a decrease in the stability of the interfacial AOT layer depending on the amount of water solubilized within the micellar aggregates. Similar conclusions can be inferred from electric conductivity [17] and quasielastic neutron scattering [27] data.

One can tentatively suppose that on increasing the amount of solubilized water, an increasing number of AOT ion pairs can achieve sufficient mobility to contribute separately to the relaxation process. The parallel evolution in τ_1 and W_{bound} as a function of W suggests that the progressive increase in the mobility of AOT polar headgroups continues until the hydration structure around them is almost complete.

The dielectric dispersion observed at the highest values of W is located close to a relaxation process observed in concentrated electrolyte solutions and attributed to the rotational diffusion of dipolar solute species (ion pairs) formed as the electrolyte concentration increases [28,29]. In our samples the ionic strength in the aqueous droplets is very high (>5 mole l^{-1}) with Na$^+$ counterions largely associated with SO$_3^-$ headgroups of AOT [30]. On these grounds we attribute the dielectric dispersion observed at the highest molar ratios to diffusive motions performed by the surfactant ion pairs. Further support to this interpretation derives from the analogies of the present relaxation process with that observed in colloidal solution of zwitterionic phospholipids and attributed to the zwitterionic part of the molecule [31].

On the basis of the explanations given for this relaxation phenomenon at the lowest and highest molar ratios (reorientation of the whole micelle and rotational diffusion of "free" AOT ion pairs, respectively) we have attempted a quantitative description of the whole trend of τ_1 as a function of W. With this aim, two different relaxation times have been defined: a micellar Debye relaxation time $\tau_D(W)$, increasing with W^3, which accounts for the AOT ion pairs reorienting with the whole aggregate, and a lower relaxation time τ_0 for the reorientation of the "free" ion pairs chosen as the limiting value of τ_1 at the highest molar ratios. For each intermediate value of W we can suppose the existence of two different fractions of AOT ion pairs $\alpha(W)$ and $[1-\alpha(W)]$ referring to the surfactant ion pairs reorienting with characteristic times τ_0 and $\tau_D(W)$, respectively. This configuration is not to be considered as a static scenario: each AOT molecule, in fact, experiences fluctuations in its local aqueous environment with a characteristic time comparable to the mean residence time of a water molecule in the hydration layer of an ion. This mean residence time was found to be of the same order as the characteristic time of water rotational diffusion [32] (about 6×10^{-12} s in our experiment). The fluctuation rate of an ion pair hydration layer is thus faster than the intrinsic rates of the observed relaxation process by about two orders of magnitude. Under this "fast exchange" condition [33], the experimental time τ_1 can be expressed in terms of the two previously defined relaxation times $\tau_D(W)$ and τ_0 according to the equation

$$\frac{1}{\tau_1}=\frac{\alpha(W)}{\tau_0}+\frac{1-\alpha(W)}{\tau_D(W)}. \tag{4}$$

In the previously mentioned IR study [26] the data were explained by assuming the existence of three independent binding sites per AOT molecule; the fitting curve of the experimental data of W_{bound} versus W, according to this model, is shown as a solid line in Fig. 3. This model gives the opportunity of evaluating the fraction of AOT molecules corresponding to the three possible hydration degrees of AOT ion pairs. By replacing the fraction of completely hydrated AOT ion pairs (three water molecules per AOT ion pair) in $\alpha(W)$ of Eq. (4), the resulting trend of τ_1 as a function of W (solid line in Fig. 2) shows a very good reproduction of the experimental data. We emphasize that, since all the terms in Eq. (4) are given, the solid line in Fig. 2 is not the result of a fitting procedure. On the other hand, supposing that both the partially and completely hydrated surfactant ion pairs were able to reorientate separately, $\alpha(W)$ then refers to the fractions of AOT ion pairs with at least one or two hydration water molecules, respectively: however, the values of $\tau_1(W)$, calculated in terms of these two fractions, depart significantly from the experimental points (dotted and dashed lines in Fig. 2, respectively). From these results it appears that only the completely hydrated surfactant ion pairs acquire a sufficient mobility to provide a separate contribution to the relaxation process.

In conclusion, we report here a detailed investigation of diluted microemulsions as a function of the molar ratio W in the microwave region. A relaxation phenomenon has been observed whose behavior as a function of W is interpreted in terms of two coexisting diffusions mechanisms: the reorientation of the whole micellar aggregate and the free rotational diffusion of the completely hydrated AOT ion pairs. From these results it appears to be of interest to examine the influence of the interdroplet attractive interactions on the dielectric relaxation observed. Further measurements are presently in progress changing both the solvent oil in the micelle system and the temperature of the experiment.

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[1] M. A. Van Dijk, Phys. Rev. Lett. **55**, 1003 (1985).

[2] C. Cametti, P. Codastefano, A. Di Biaso, P. Tartaglia, and S. H. Chen, Phys. Rev. A **40**, 1962 (1990).

[3] S. H. Chen and J. S. Huang, Phys. Rev. Lett. **55**, 1888 (1985).

[4] E. Y. She, S. H. Chen, J. S. Huang, and I. S. Sung, Phys. Rev. A **39**, 5867 (1989).

[5] M. W. Kim and J. S. Huang, Phys. Rev. B **26**, 2703 (1982).

[6] A. M. Belloq and D. Roux, Phys. Rev. Lett. **52**, 1895 (1984).

[7] J. Rouch, A. Sofonane, P. Tartaglia, and S. H. Chen, J. Chem. Phys. **90**, 3756 (1989).

[8] H. F. Eicke, in *Micelles*, Topics in Current Chemistry Vol. 87 (Springer, New York, 1980), p. 85.

[9] P. L. Luisi, M. Giomini, M. P. Pileni, and B. H. Robinson, Biochim. Biophys. Acta **947**, 209 (1988).

[10] Y. Chevalier and T. Zemb, Rep. Prog. Phys. **53**, 279 (1990).

[11] C. Cametti, P. Codastefano, and P. Tartaglia, Ber. Bunsenges. Phys. Chem. **94**, 149 (1990).

[12] J. S. Huang, J. Chem. Phys. **82**, 480 (1985).

[13] E. Sein, J. R. Lalanne, J. Buchert, and S. Kielich, J. Colloid Interface Sci. **72**, 363 (1979).

[14] G. Onori and A. Santucci, J. Colloid Interface Sci. **150**, 195 (1992).

[15] D. Fioretto, A. Marini, M. Massarotti, G. Onori, L. Palmieri, A. Santucci, and G. Socino, J. Chem. Phys. **99**, 8115 (1993).

[16] H. F. Eicke, J. Colloid Interface Sci. **65**, 131 (1978).

[17] J. S. Huang, J. Sowa, and S. Bhattacharya, J. Non-Cryst. Solids **131-133**, 335 (1991).

[18] S. Bhattacharya, J. Sowa, and J. S. Huang, Phys. Rev. Lett. **65**, 131 (1990).

[19] H. Yoshioka, J. Colloid Interface Sci. **95**, 81 (1983).

[20] M. A. V. Dijk, J. G. H. Joosten, J. K. Levine, and B. Bedeaux, J. Phys. Chem. **93**, 2506 (1989).

[21] B. H. Robinson, D. C. Steytler, and R. D. Tack, J. Chem. Soc. Faraday Trans. 1, **45**, 481 (1977).

[22] M. Ueno and H. Kishimoto, Bull. Chem. Soc. Jpn. **50**, 1631 (1977).

[23] K. Kon-no and A. Kitahara, J. Colloid Interface Sci. **35**, 636 (1971).

[24] H. F. Eicke and J. C. W. Shepherd, Helv. Chim. Acta **57**, 1951 (1974).

[25] P. L. Luisi and L. J. Magid, Crit. Rev. Biochem. Mol. Biol. **20**, 409 (1986).

[26] G. Onori and A. Santucci, J. Phys. Chem. **97**, 5430 (1993).

[27] P. D. I. Fletcher, B. H. Robinson, and J. Tabony, J. Chem. Soc. Faraday Trans. 1, **82**, 2311 (1986).

[28] J. Barthel, H. Hetzenauer, and R. Buchner, Ber. Bunsenges. Phys. Chem. **96**, 988 (1992).

[29] J. Barthel, H. Hetzenauer, and R. Buchner, Ber. Bunsenges. Phys. Chem. **96**, 1424 (1992).

[30] M. Wong, J. K. Thomas, and T. Nowack, J. Am. Chem. Soc. **99**, 4730 (1977).

[31] R. Pottel, K. D. Gopel, R. Henze, U. Kaaze, and W. Uhlendorf, Biophys. Chem. **19**, 233 (1984).

[32] K. Giese, Ber. Bunsenges. Phys. Chem. **76**, 495 (1972).

[33] J. E. Anderson, J. Chem. Phys. **47**, 4879 (1967).