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ORIGINAL CONTRIBUTION

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Study of the dynamics of water/aerosol OT/*n*-heptane system by dielectric relaxation measurements

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Abstract Most of the previous dielectric studies on microemulsions and related systems have been conducted at relatively low frequencies where the dielectric response is sensitive to dynamic percolation phenomena. There is a lack of experimental studies at microwave frequencies where water plays a central role in dielectric relaxation. In this paper the dielectric complex permittivity of water/Aerosol OT/*n*-heptane microemulsions has been measured by a frequency domain coaxial technique in the range 0.02–20 GHz as a function of molar ratio $W = [\text{water}]/[\text{AOT}]$ at low volume fraction of the dispersed phase ($\phi = 0.1$ and $\phi = 0.2$). The data show two dielectric dispersions: The first located in the 100 MHz frequency region and the second at frequencies higher than 20 GHz. The evolution of the dielectric parameters of these relaxations has been studied as a function of the molar ratio W in the range $0 < W < 28$.

Key words Aerosol OT – dielectric spectroscopy – microemulsions – microwave – water pool

Introduction

Reverse micelles are spherical aggregates, nanometer sized, formed by certain surfactants in apolar media. The polar head groups of the surfactant molecules are directed towards the interior of the aggregate and form a polar core which can solubilize water (the "water pool").

Among the surfactants capable to form reverse micelles, bis-(2-ethylhexyl) sodium sulfosuccinate (AOT) has received particular attention in recent years. Thermodynamic and spectroscopic properties of water in reverse AOT micelles have been studied by means of a large variety of experimental techniques [1–3]. These studies indicate that the ratio $[H_2O]/[AOT]$ (W), more than the absolute amount of water or surfactant present in the hydrocarbon solvent, determines most of the structural and physical properties of the reverse micelles. At low W values ($W < 10$) the solubilized water exists mainly as H_2O-bound molecules whose static and dynamic properties are determined by the local interactions with the Na^+ counterions and the strong dipole of the AOT polar group. In this range of W, water in reverse micelles behaves "anomalously", i.e., its physical properties are somewhat different from those of bulk water and change strongly with W. With increasing the water content the changes become smaller and the physical properties of the water pool asymptotically approach those of pure water. The behavior of water bound to the inner surface of the AOT micelles is, in any effect, similar to the interfacial water present near the biological membranes or at protein surfaces; so, it is interesting to study the state of water in reverse micelles as a model of specific water in biological systems [4, 5].

Information on the change of structure and dynamics of both AOT shell and of water confined into the reverse micelles can be obtained from dielectric relaxation

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measurements. Yet, most dielectric studies on reverse micelles are performed at relatively low frequencies (0.1–100 MHz) and at relatively high volume fraction of dispersed phase and the description of data is usually related to a dynamic percolation phenomenon [6–9]. There is a lack of experimental studies at microwave frequencies where the dielectric response is dominated by the water component.

In this paper the dielectric complex permittivity of water/AOT/*n*-heptane reverse micelles has been measured by means of a frequency domain coaxial technique in the range (0.02–20 GHz as a function of molar ratio W at two different volume fractions of dispersed particles ($\phi = 0.1$ and $\phi = 0.2$). Our study was focused on the dilute region of the systems, where the model of dispersed droplets in a continuous medium is still valid, and to the region of small amounts of water ($0 < W < 28$) where the properties of the systems change strongly with water content.

Experiment

Measurements of the complex dielectric constant have been performed in the frequency domain using an open coaxial cell consisting of a section of transmission line with its center conductor abruptly terminated. A detailed description of the experimental procedure is reported in ref. [10]. We notice that, in the present experiment, the frequency range has been extended up to 20 GHz by use of an HP 8720 C Network Analyzer. Measurements on known materials have shown that the values of dielectric constants obtained by this technique differ from those reported in the literature by less than 1%.

All the tested samples have been prepared by weight, keeping constant the dispersed phase volume fraction and varying the molar water-surfactant ratio W in the range 0.2–28. The volume fraction ϕ of the dispersed particles has been calculated assuming an ideal mixing behavior. AOT 99% (Alfa product) purified by recrystallization from methanol and drying in vacuum, was stored in vacuum over P_2O_5. Some residual water molecules remained bound to the AOT molecules after the drying process of the surfactant. Water content in AOT/oil systems, measured by a Karl Fisher titrator, revealed the presence of 0.2 moles of water per mole of AOT. Such a small residual of water has been considered as a part of the total water in the mixtures. *n*-Heptane (Fluka product, purity > 99.5%) has been used without further purification. Deionized and bidistilled water has been employed to prepare the samples. The measurements have been performed at a fixed temperature of 20 ± 0.1 °C.

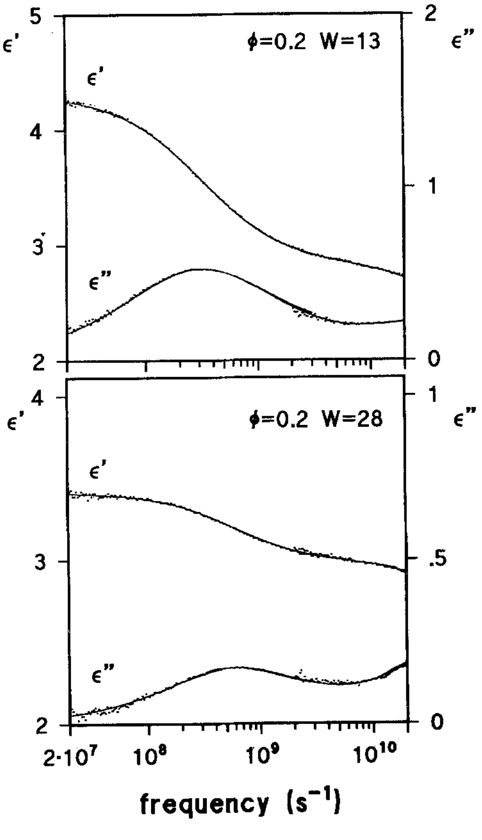
Results and discussion

Figure 1a, b show the presence of two relaxation regions: the principal one, located at about 100 MHz, is entirely within our experimental window; the second one, at higher frequencies, is not completely resolved in this experiment. The experimental spectra can be suitably fitted by the superposition of a Cole-Cole- and a Debye-type relaxation functions, according to the equation:

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

where ε_∞ is the high frequency dielectric constant, ω is 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 are the relaxation times of the two processes, and α is a parameter characterizing the width of the distribution of the relaxation times around τ_1 ($0 < \alpha < 1$). Equation 1 has been used to fit the experimental data of the real and the imaginary parts of the dielectric constant, simultaneously, by means of the Marquardt algorithm. The values of the parameters τ_1 and $\Delta\varepsilon_1$ obtained by this procedure

Fig. 1 Real (ε) and imaginary (ε') parts of dielectric constant as a function of frequency at selected W values



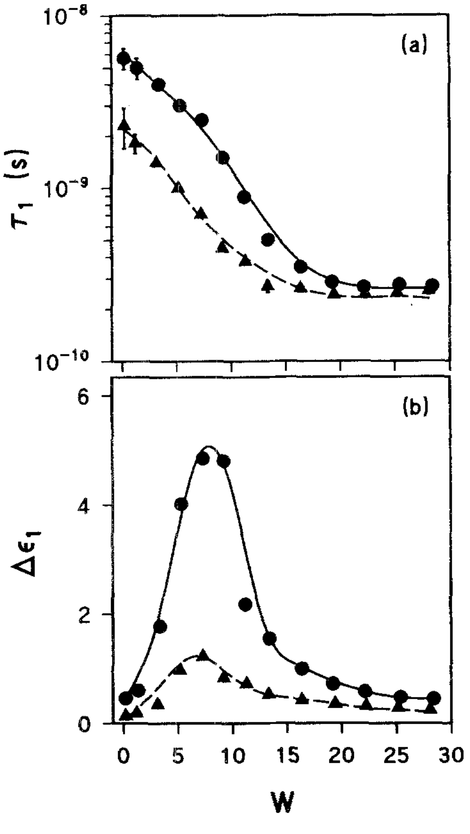
are reported in Figs. 2a and 2b as a function of the molar ratio *W*, for the two sets of measurements at different values of ϕ. Figure 3a and 3b show the values of τ_2 and $\Delta\varepsilon_2$ as a function of *W* for $\phi = 0.2$. The values of τ_2 and $\Delta\varepsilon_2$ for $\phi = 0.1$ are affected by errors too large to be reported here. The behavior of these parameters is discussed in the following, distinguishing the low and the high frequency relaxations.

Low frequency relaxation

Figure 2a shows that, at low *W*, the values of τ_1 depend on the value of ϕ being higher for the highest concentration of particles. The values of τ_1 rapidly decrease with increasing *W*, up to $W \approx 10$–15. For higher molar ratios, τ_1 becomes nearly constant, assuming the same value – within the experimental error – for the two sets of measurements.

The first relaxation is located in a frequency region about two decades higher than that extensively studied in the literature and usually related to a dynamic percolation phenomenon. To our knowledge, there is only one previous investigation of this relaxation [7]. In this work the dielectric properties of very dilute water in decane solutions containing AOT were studied as a function of temperature, at two different volume fractions of the coated water droplets ($\phi = 0.050$ and $\phi = 0.025$) and at a fixed molar ratio $W = 40.8$. The obtained results support the idea that the observed dispersion reflects the characteristics of the dynamics of the single particle components. Moreover, it is shown that, approaching the percolation threshold, this relaxation is partially masked by the one at lower frequencies, related to the percolation process, which becomes progressively predominant. In the present work, we study the dielectric properties of microemulsions below the percolation threshold [11] where the contribution of the percolation process is negligible in the investigated frequency window.

Fig. 2 **A** relaxation time and **B** dielectric relaxation amplitude for the low frequency relaxation vs. *W*. (●): $\phi = 0.2$; (▲): $\phi = 0.1$. Lines are a guide for the eyes



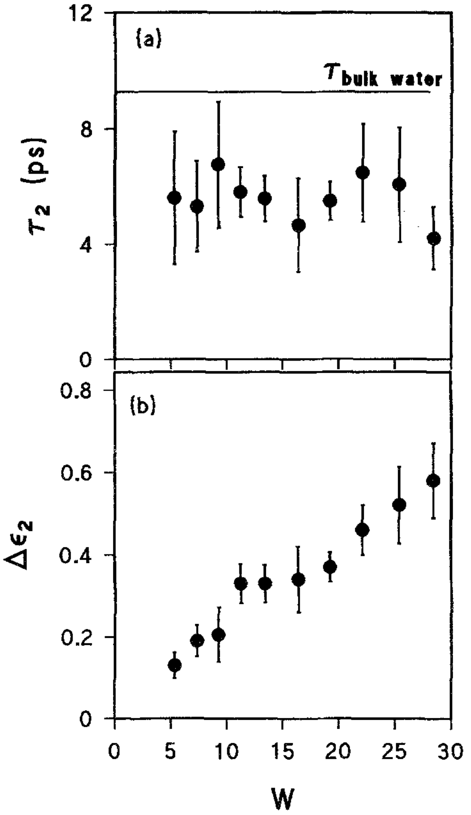


Fig. 3 **A** relaxation time and **B** dielectric relaxation amplitude for the high frequency relaxation vs. *W*. $\phi = 0.2$

The behavior of τ_1 is now analyzed as a function of the molar ratio *W*:

Low molar ratio *W*

In this case the water content inside the micelles is very low and a simple model to interpret the dielectric dispersion is the Debye one. According to this model the dielectric relaxation is attributed to the rotational diffusion of the spherical micelles having a permanent dipole. The relaxation time depends on the viscosity of the solution η and on the radius of the micelles R by the relation:

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

where $K_B T$ is the thermal energy. When the viscosity of the solution and the relaxation time τ_1 are replaced in Eq. (2), one can obtain the radius of the particle. For the sample at $W = 0.2$ and $\phi = 0.2$ ($\eta = 8.8 \times 10^{-4}$ Nsm^{-2} [11] and $\tau_1 = 5.7 \times 10^{-9}$ s), we obtain $R = 12.8$ Å. This result is consistent with the values given in the literature for the radius of the micelles at $W = 0.2$ ($R = 11.3$ [12] and $R = 13.8$ [13] obtained by geometrical estimations; $R = 14.5$ by sedimentation ultracentrifugation measurements [14]). For $W = 0.2$, the ratio between the relaxation times relative to the two volume fractions $\tau_1(\phi = 0.2)/\tau_1(\phi = 0.1) = 2.4 \pm 0.7$, is close to the ratio between the viscosity of the solutions at the same volume fractions $\eta(\phi = 0.2)/\eta(\phi = 0.1) = 1.7$, consistent with Eq. (2).

In order to obtain a further confirmation of the idea that this relaxation can be attributed to the rotational diffusion of the spherical micelles, we have used the Debye extension of the Clausius–Mossotti equation to estimate the dipole moment of the micelles dispersed in the solution at $W = 0.2$ and $\phi = 0.2$ [15]. This equation can be written in terms of the molar fractions of micelles and n-heptane, as:

$$\frac{\varepsilon - 1}{\varepsilon + 2}\left[\frac{f_1}{N_{01}} + \frac{f_2}{N_{02}}\right] = f_1 \cdot \left[\frac{\varepsilon_\infty - 1}{\varepsilon_\infty + 2} \cdot \frac{1}{N_{01}} + \frac{\mu_{\text{mic}}^2}{9\varepsilon_0 K_B T}\right] + f_2 \cdot \left[\frac{\varepsilon_{\text{hept}} - 1}{\varepsilon_{\text{hept}} + 2} \cdot \frac{1}{N_{02}}\right], \tag{3}$$

where ε is the low-frequency dielectric constant of the solution, f_1 and f_2 are the micelle and n-heptane molar fraction, respectively. N_{01} and N_{02} are the number of micelle and molecules of n-heptane per volume unit, respectively, μ_{mic} is the dipole moment of one micelle, ε_0 is the absolute dielectric constant of free space, ε_∞ is the high-frequency dielectric constant of micelles and $\varepsilon_{\text{hept}}$ is the dielectric constant of n-heptane. Equation (3) has been used to estimate the value of μ_{mic}, obtaining $\mu_{\text{mic}} \approx 13$ Debye. This value is in good agreement with that obtained by Eicke et al. ($\mu_{\text{mic}} \approx 15$ Debye) [16]. This result gives further support to the idea that the considered relaxation process is imputable, at the lowest values of W, to the whole micelle rotational diffusion.

Yet, it is to be noticed that the trend of the relaxation time τ_1 as a function of W does not agree with the given interpretation. In fact, increasing W, the radius of the micelles increases nearly linearly and, according to the Debye–Stokes equation, the relaxation time τ_1 should approximately increase as W^3. Different from this, the experimental results show that τ_1 decreases with increasing W up to values of W between 10 and 15, becoming nearly constant for higher values of the molar water-surfactant ratio. In order to give an interpretation to this behavior, we notice that many works in the literature [1–3] suggest that the structural and dynamical properties of water confined in the micellar core strongly changes increasing W up to values of about 10 and approach, at higher molar ratio, those typical of pure water. The result of our I.R. study on the properties of water solubilized in reverse micelles of AOT in n-heptane is reported in Fig. 4 [17]. In this figure the fraction of hydration water X_{bound} is plotted as a function of W. It can be seen that the value of X_{bound} rapidly decreases increasing W and becomes nearly constant for molar water-surfactant ratio higher than 15. One can easily notice that the trend of X_{bound} is strikingly similar to that observed for τ_1 as a function of W. We can thus try to relate the observed deviation of τ_1 from the Debye equation (2) to the growth of a water pool inside the micellar core. Since the properties of this water undergo remarkable changes in the initial range of W, the attempt of explaining the occurrence of this relaxation process using the models given in literature, which assume the dielectric properties of solubilized water to be those of bulk water, is possible only for the samples at the higher values of W.

High molar ratio W

Triphasic model of interfacial polarization

It is known that heterogeneous systems display a dielectric relaxation caused by charge accumulation at the interfaces between different phases [18]. For systems consisting of coated spherical particles uniformly distributed in a continuous medium, the Maxwell–Wagner model predicts the occurrence of two different dielectric dispersions whose relaxation times assume the approximate expressions:

$$\tau_A = \frac{\varepsilon_s}{\sigma_s}\varepsilon_0 \qquad \tau_B = \frac{\varepsilon_W + \frac{2d}{R}\varepsilon_s}{\sigma_W + \frac{4d}{R}\sigma_s}\varepsilon_0, \tag{4}$$

where σ is the *dc* conductivity, d the thickness of the surfactant shell, and the indices W and s refer to water core and surfactant shell, respectively. Replacing usual values for dielectric parameters for the different phases, Cametti et al. show that the model gives relaxation times at least

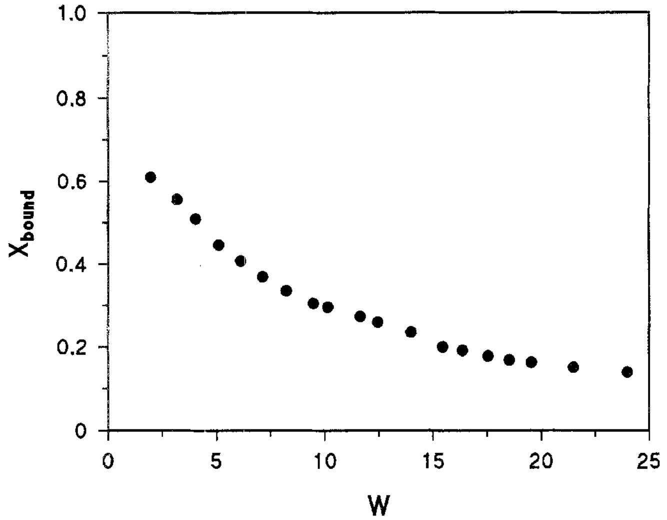


Fig. 4 Bound water fraction as a function of the molar ratio W [17]

a factor 20 smaller than the experimental ones [7]. Also in our case, the experimental value $\tau_1 = 2.7\,10^{-10}$ s obtained for the sample at $W = 28$ is much lower than the estimated ones $\tau_A \approx 3\,10^{-8}$ s and $\tau_B \approx 8\,10^{-7}$ s calculated by Eq. (4), assuming $\varepsilon_W = 80$, $\sigma_W = 10^{-4}\,\text{mho m}^{-1}$, $\varepsilon_s = 3.2$, $\sigma_s = 10^{-3}\,\text{mho m}^{-1}$ and $R = 52$ Å. These results lead us to exclude this mechanism as being responsible for the relaxation here discussed.

Counterion diffusion polarization

A possible polarization effect has been studied by Schwarz and Schurr [19] as caused by ionic diffusion in a layer adjacent to charged colloidal particles. In our case a similar phenomenon can be generated by the diffusion of counterions which are strongly linked to the surfactant polar groups so that they cannot be detached by the electric field, but can be displaced tangentially to the inner micellar surface. This polarization effect can be approximatively described by two Debye-type dispersions. The parameters of the relaxation closer to ours are given by:

$$\Delta\varepsilon \approx \frac{9\phi\dfrac{Re^2\sigma_0}{\varepsilon_0 K_B T}}{(2+\phi)^2} \qquad \tau = \frac{R^2}{2K_B T u}\,, \tag{5}$$

where e is the elementary electric charge, σ_0 is surface numerical density of SO_3^- groups, and u the bulk mobility of the counterions. Equation (5), used to estimate the values of σ_0 and u for the case $\phi = 0.2$ and $W = 28$, has given $\sigma_0 \approx 10^{-4}\,\text{Cm}^{-2}$ and $u \approx 10^{10}$ cgs units. These values must be compared with $\sigma_0 \approx 0.3\,\text{Cm}^{-2}$ expected under the hypothesis that the AOT molecules are fully ionized and with $u \approx 2$–$3\,10^8$ cgs units for the mobility of the Na^+ ions in water at this temperature. Also in this case, as in ref. [7], the values obtained for both the charge density and the mobility are far from the expected ones and the model seems not to be appropriate to describe the observed relaxation.

Diffusion of dipolar headgroups

The present relaxation shows some analogies with the case of aqueous colloidal solutions of zwitterionic phospholipids. In fact, also in these systems dielectric measurements show the existence of a dispersion located in the 100 MHz frequency region. This phenomenon was attributed to the motion of the zwitterionic part of the phospholipids, where the cationic group performs diffusive motion relative to the anionic group around axes perpendicular to the permanent electrical dipole [20]. Cametti et al. attempted to extend the above model to the surfactant microemulsion particles [7]. We also make this attempt, supposing that the dipolar headgroups of AOT play the role the zwitterions. According to this model, the dielectric parameters can be written as:

$$\Delta\varepsilon = \frac{9\phi n\mu^2 g/(\varepsilon_0 R K_B T)}{(2+\phi)^2\left[1+\left(\dfrac{1-\phi}{2+\phi}\right)\dfrac{\varepsilon_{\text{app}}}{\varepsilon_m}\right]\left[1+\left(\dfrac{1-\phi}{2+\phi}\right)\dfrac{\varepsilon_{\text{app}}+n\mu^2 g/(\varepsilon_0 R K_B T)}{\varepsilon_m}\right]} \tag{6a}$$

$$\tau = \frac{1+\left(\dfrac{1-\phi}{2+\phi}\right)\dfrac{\varepsilon_{\text{app}}}{\varepsilon_m}}{D\left[1+\left(\dfrac{1-\phi}{2+\phi}\right)\dfrac{\varepsilon_{\text{app}}+n\mu^2 g/(\varepsilon_0 R K_B T)}{\varepsilon_m}\right]}\,, \tag{6b}$$

where μ is the effective dipolar moment of the a single AOT molecule at the interface with water droplet, n is the number of polar groups per particle surface area, ε_{app} is the equivalent permittivity of a dielectric homogeneous spherical particle which models the surfactant coated particle, ε_m is the permittivity of the continuous phase and D is the polar group rotational diffusion coefficient. In our case, the value of μ has been estimated from Eq. (6a) and from the experimental value of $\Delta\varepsilon_1 = 0.14$ relative to $W = 28$ and $\phi = 0.1$. For $g = 1$, we obtain the reasonable result, within the used approximations, $\mu \approx 14$ Debye, which can be compared with $\mu \approx 5$–6 Debye as obtained in ref. [21] for the case of AOT molecules dispersed in a nonpolar medium. Finally, we report the value $D \approx 1.6\,10^9\,\mathrm{s}^{-1}$ obtained from Eq. 6b and from the experimental value of τ_1.

Intermediate molar ratio W

On the basis of the previous discussion on the behavior of τ_1 at the extreme value of W, we can now try to explain the behavior of this relaxation time in the intermediate molar ratio region. At the lowest values of W, the micelles are almost dehydrated, the polar headgroups strongly interact in restricted regions, and the structure of the particles is almost rigid. In this case it is reasonable to attribute the observed dielectric dispersion to the rotational diffusion of the whole micellar aggregate. Increasing the water content in the micellar core (W), an increasing number of polar groups of AOT molecules can achieve enough mobility to contribute separately to the relaxation process. The observed fact that the values of τ_1 and X_{bound} arrive to saturation at the same values of $W \approx 15$ suggests that the progressive increase of mobility of AOT polar groups continues until the hydration structure around them is completed.

The variation of $\Delta\varepsilon_1$ vs W, shown in Fig. 2b, appears to be quite complex. We note that the curve has a maximum for W close to 8. Similar curves have already been obtained from conductivity, viscosity and static permittivity measurements on the same systems [6, 22]. In addition, the maximum at $W = 8$ corresponds to a minimum for the percolation threshold Φ_c [22]. It is generally assumed that the position of Φ_c corresponds to relative interactions of the system studied. So, as it has already observed [22], the complex shape of the experimental curves plotting conductivity, permittivity, viscosity versus W when Φ is constant can be related to attractive intermicellar interactions and to their changes along the experimental path followed (Φ constant, W variable).

High-frequency relaxation

Figures 3a and 3b show the trend of the dielectric parameters τ_2 and $\Delta\varepsilon_2$, relative to the high frequency dielectric dispersion, as a function of W. The relatively large error in their values can be attributed to the fact that the dispersion region is not completely contained in the available frequency window. On the other hand, to our knowledge, there are no previous experimental investigations on these systems extending up to such high frequencies. The considered dispersion is located in the frequency region typical of the relaxation of bulk water. We thus attribute this phenomenon to the reorientation of the dipoles of water molecules confined within the micellar core. This interpretation is also supported by the observed increase of the relaxation strength as a function of W (Fig. 3b). The experimental error in Fig. 3a is so large as to make impossible the singling out of a well-defined trend in the data. However, it is important to notice that the experimental values of τ_2 are lower than the value of the relaxation time relative to bulk water ($\tau = 9.3\,10^{-12}\,\mathrm{s}$ at $T = 20\,^\circ\mathrm{C}$ [23]), in the whole range of W. This result can be interpreted in terms of an increasing of the reorientation rate of water molecules confined inside micellar core. Similar results were obtained by dielectric measurements on electrolytic solutions [24].

Further measurements at lower temperatures are presently in progress in our laboratories in order to achieve a better insight into the dynamics of water confined in micellar cores.

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