

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/231663478>

Infrared and Dielectric Study of Ca(AOT)₂ Reverse Micelles

ARTICLE *in* THE JOURNAL OF PHYSICAL CHEMISTRY B · MARCH 1999

Impact Factor: 3.3 · DOI: 10.1021/jp9837028

CITATIONS

45

READS

26

5 AUTHORS, INCLUDING:



Daniele Fioretto

Università degli Studi di Perugia

177 PUBLICATIONS 2,830 CITATIONS

SEE PROFILE

Infrared and Dielectric Study of Ca(AOT)₂ Reverse MicellesD. Fioretto,[†] M. Freda,[‡] S. Mannaioli,[†] G. Onori,^{*,†} and A. Santucci[†]*Istituto per la Fisica della Materia, Unità di Perugia and Dipartimento di Fisica, Università di Perugia, Via Pascoli, I-06100 Perugia, Italy, and Dipartimento di Fisica and Istituto per la Fisica della Materia, Unità di Tor Vergata, Via della Ricerca Scientifica, I-00133 Roma, Italy**Received: September 14, 1998*

In this paper, we report on IR and dielectric spectroscopy of Ca(AOT)₂ reverse micelles containing water pools of different sizes. We investigate the effect of changing the nature of the counterion ($\text{Na}^+ \rightarrow \text{Ca}^{2+}$) on the hydration mechanisms and dynamics of AOT microaggregates. The hydration has been studied as a function of the molar ratio $W = [\text{H}_2\text{O}]/[\text{AOT}]$ by means of IR absorption of O–H stretching modes in the 3800–3000 cm^{-1} frequency range. The dynamical properties of the system have been investigated by dielectric permittivity measurements performed in the range 0.02–3 GHz, as a function of W . A relaxation phenomenon has been observed in this region, and a close connection between the behavior of the relaxation time vs W and the progressive hydration of AOT polar headgroups has been found, similar to the case of the NaAOT micellar system. These results could be interpreted in terms of two coexisting diffusion mechanisms: the reorientation of the whole micellar aggregate and the free rotational diffusion of the completely hydrated AOT headgroups.

1. Introduction

The surfactant sodium bis(2-ethylhexyl)sulfosuccinate (NaAOT) is known to form spherical, nanometer-sized, molecular aggregates in a variety of nonpolar solvents. The hydrocarbon tails of the AOT molecules are oriented toward the exterior of the aggregate, while the sulfonate headgroups with the sodium counterion are localized in the interior of the reverse micelle.^{1,2}

Particularly interesting is the ability of NaAOT microaggregates to solubilize relatively large amounts of water in their polar core, forming the so-called water pool. The radius of these spherical aggregates has been shown to increase linearly with the molar ratio $W = [\text{H}_2\text{O}]/[\text{AOT}]$.^{3–5}

Thermodynamical and spectroscopic properties of water in the water pool have been studied by means of a large variety of experimental techniques.^{1,2,6} These studies indicate that at low W values the solubilized water mainly exists as H₂O-bonded molecules whose static and dynamical properties are determined by local interactions with Na^+ counterions and surfactant headgroups. It follows that water confined into the microaggregates behaves anomalously; that is, its physical properties are somewhat different from those of pure water and change strongly with W . For high water content, the changes become smaller and smaller and the physical properties of the water pool asymptotically approach those of pure water.

In recent papers, the hydration of NaAOT reverse micelles in CCl_4 , n -heptane, and isooctane has been investigated by means of IR spectroscopy.^{7–10} The solubilization of water was described in terms of hydration of AOT headgroups, and the data indicate a maximum hydration number of three water molecules per AOT molecule.

More recently, a detailed dielectric investigation of the influence of both surfactant hydration and interparticle interactions on the dynamical properties of the NaAOT reverse micelles

was reported.^{11–15} The dielectric investigation was focused on the diluted region of the system (the volume fraction of the micellar phase was $\Phi = 0.1$ for all samples), where the model of dispersed droplets in a continuous medium is still valid, and in the region of small amounts of water added, where the properties of the system change strongly with water content. A relaxation phenomenon was observed in the microwave region whose behavior as a function of W , in the absence of interparticle interactions (dilute limit), was successfully interpreted in terms of two coexisting mechanisms: the reorientation of the whole micellar aggregate and the free rotational diffusion of the completely hydrated AOT headgroups. On the whole, our data revealed the dynamics of these systems to be richer than that usually reported in the literature, and evidenced the fruitful complementarity of IR and dielectric spectroscopy in understanding the role of hydration in the dynamics of reverse micelles.

In this paper, we investigate the properties of water confined in reverse micelles of AOT, where the Ca^{2+} has replaced the Na^+ counterion. Therefore, the dielectric and IR properties of ternary systems formed by $\text{Ca}(\text{AOT})_2/\text{H}_2\text{O}/\text{CCl}_4$ are reported and compared with those of the corresponding NaAOT system. The aim is to study the effect of changing the nature of the counterion ($\text{Na}^+ \rightarrow \text{Ca}^{2+}$) on the hydration mechanisms and dynamical properties of AOT microaggregates. While the structure and properties of NaAOT reverse micelles are well-known, only a few papers recognize the influence of AOT counterions on the physicochemical properties of reverse micelles. In some cases, it has been shown^{16–19} that the nature of the counterion can influence the shape of the AOT microaggregates. However, small-angle neutron scattering (SANS) and viscosity measurements provide evidence of spherical aggregates in the $\text{Ca}(\text{AOT})_2$ system as for the NaAOT system.^{16–18} We expect that the ion–water interaction within the water pool changes by changing the metal cation and this might induce variations both in the hydration properties and in the dynamics of AOT reverse micelles.

* To whom correspondence should be addressed. SYMBIO@PERUGIA.INFN.IT.

[†] Università di Perugia.

[‡] Unità Tor Vergata.

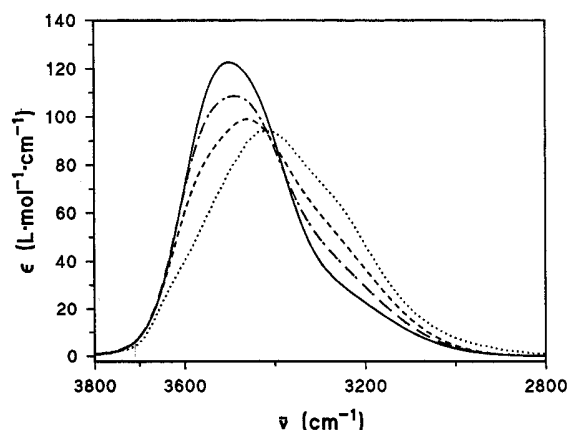


Figure 1. Molar extinction coefficient vs wavenumber for OH stretching of water in $\text{Ca(AOT)}_2/\text{H}_2\text{O}/\text{CCl}_4$ reverse micelle: (—) $W = 1.0$; (---) $W = 3.0$; (- · -) $W = 9.0$; (···) pure water spectrum.

2. Experimental Section

NaAOT 99% (Aldrich product), purified by recrystallization from methanol and dried in a vacuum, was stored in a vacuum over P_2O_5 . Ca(AOT)_2 was prepared as described elsewhere.^{17,18} Residual water [$W_0 = 0.2$ and 1.0 for NaAOT and Ca(AOT)_2 , respectively] was revealed by a Karl Fisher titrator and considered as a part of the total water in the mixture.

IR spectra were recorded by means of a Shimadzu model 470 IR spectrophotometer equipped with a variable path length cell and CaF_2 windows. Typical path lengths employed were $50 \mu\text{m}$ for AOT/ $\text{H}_2\text{O}/\text{CCl}_4$ mixtures. Pure water spectra were taken with a shorter path length.

The complex dielectric function of our samples was measured in the frequency domain by using an open coaxial cell consisting of a section of a transmission line with its center abruptly terminated. A detailed description of the experimental procedure is reported in ref 20. Measurements were performed in the $0.02\text{--}3 \text{ GHz}$ frequency range at 20°C . The mixtures under study were prepared by weighing, keeping the molar ratio W in the range $0.2\text{--}10$ and $1\text{--}9$ for NaAOT and Ca(AOT)_2 samples, respectively.

3. Results and Discussion

3.1. Infrared Measurements. Figure 1 shows the molar extinction coefficient of the O–H stretching absorption band for pure water and water in the $\text{Ca(AOT)}_2/\text{H}_2\text{O}/\text{CCl}_4$ system at selected values of W . It is evident from the Figure 1 that the molar absorption coefficient $\epsilon(\bar{\nu})$ changes with W ; however, the total peak area of the O–H stretching band increases linearly with water content according to the Beer's law

$$\epsilon_{\text{int}} = \frac{A}{[\text{H}_2\text{O}]d} = \int \epsilon(\bar{\nu}) d\bar{\nu} = 37 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1} \quad (1)$$

where d is the optical path length.

This value for ϵ_{int} is found to be coincident to that of pure water and of water in NaAOT reverse micelles within the experimental errors.^{7,8} The IR spectrum of surfactant-entrapped water is significantly different from that of pure water, indicating that the water solubilized in the reverse micelles lacks the normal hydrogen-bonded structure of bulk water. In fact, one could observe from these spectra a decrease in the intensity for the low-frequency part of the OH absorption band as the water content is reduced; this behavior is qualitatively similar to that observed on increasing the temperature of pure water sample.

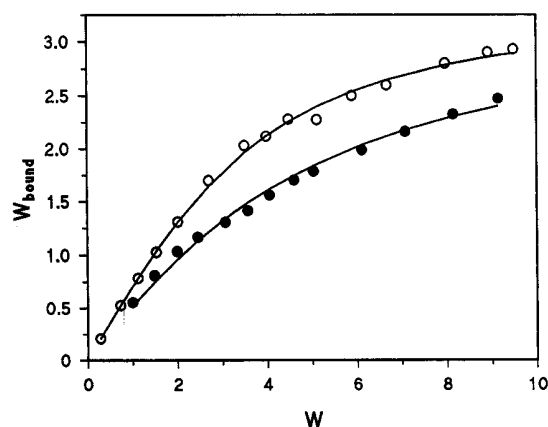


Figure 2. Concentration of bonded (W_{bound}) water in NaAOT/ $\text{H}_2\text{O}/\text{CCl}_4$ and $\text{Ca(AOT)}_2/\text{H}_2\text{O}/\text{CCl}_4$ systems vs total water concentration: (○) NaAOT/ $\text{H}_2\text{O}/\text{CCl}_4$ samples; (●) $\text{Ca(AOT)}_2/\text{H}_2\text{O}/\text{CCl}_4$; (—) fitting according to three-stage equilibrium model [see text and ref 7].

The low-frequency part of the O–H absorption band has been related to water molecules in more regular structures with unstrained H-bonds;^{9,21,22} therefore, the observed behavior suggests a minimal amount of water involved in a tetrahedral array of hydrogen bonds in the micellar water phase at low water content. These results substantially agree with that previously obtained for an NaAOT micellar system and indicate, as expected, a strong interaction of water molecules with surfactant polar heads (bound water) while the hydration shell is forming.^{7,8} According to these considerations, the spectra in Figure 1 have been analyzed assuming the existence of a continuous equilibrium between bound and bulk water, as quantitatively described for the corresponding NaAOT system in previous works.^{7,8} From this description, one could evaluate the molar fraction X_{bound} of bound water as a function of W ; the number W_{bound} of bound water molecules per AOT is then calculated using the relation

$$W_{\text{bound}} = X_{\text{bound}} W \quad (2)$$

Figure 2 shows the trends of calculated W_{bound} values vs W for NaAOT/ $\text{H}_2\text{O}/\text{CCl}_4$ and $\text{Ca(AOT)}_2/\text{H}_2\text{O}/\text{CCl}_4$ systems. These trends are qualitatively similar, showing for both micellar systems an asymptotic value of W_{bound} of about three water molecules per AOT headgroup at the highest W . However, single W_{bound} values of Ca(AOT)_2 samples are systematically lower than the corresponding ones for the NaAOT samples at the same W .

Thus, a smooth shift of the equilibrium bound \leftrightarrow bulk water toward a higher proportion of bulk water is observed in Ca(AOT)_2 with respect to NaAOT systems. This fact can be the result of a greater energy of interaction of water and AOT polar groups with Ca^{2+} with respect to Na^+ counterions.

The IR data for NaAOT system have been interpreted in terms of the existence of three binding sites per AOT group that could be filled from water molecules,⁷ and they have been treated assuming a three-stage equilibrium model to construct a hydrated shell around surfactant polar heads. Here, the same model is used to fit our data for Ca(AOT)_2 micelles. The results of the data fitting procedure are shown in Figure 2 by continuum curves for both samples; despite its great simplicity, this model seems also to reproduce very accurately the data for Ca(AOT)_2 micelles within the experimental errors.

Furthermore, the three-stage equilibrium model enable us to calculate the fraction of AOT corresponding to three possible hydration degrees, namely the fraction of AOT hydrated with

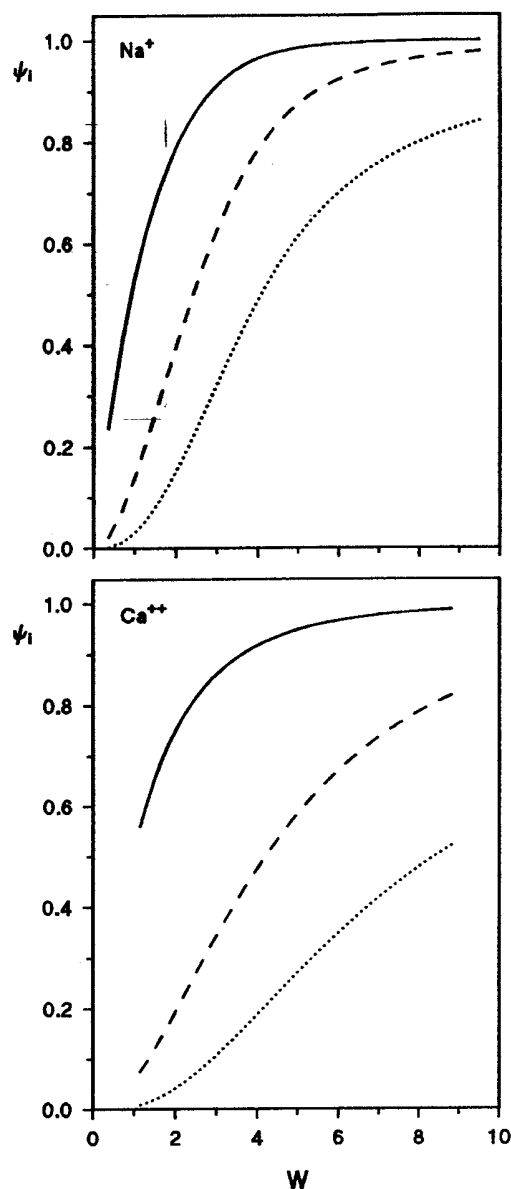


Figure 3. Plot of the fraction ψ_i of AOT ion pairs with at least one (—), two (---), or three (···) water molecules.

at least one (ψ_1), two (ψ_2), or three (ψ_3) water molecules; these fractions are plotted as a function of W in Figure 3 for both NaAOT and Ca(AOT)₂ systems. The fraction of AOT bound to at least one water molecule ψ_1 shows a trend strictly similar for both micellar systems; in contrast, significant differences appeared when we compare the fraction ψ_2 and ψ_3 of AOT with at least two water molecules or totally hydrated, respectively. In particular, the fraction of AOT totally hydrated in Ca(AOT)₂ increases much more slowly as a function of W than the corresponding one for NaAOT; at $W = 9$, the solubility limit for water in Ca(AOT)₂/H₂O/CCl₄ system, we see that ψ_3 in Ca(AOT)₂ is considerably lower than the corresponding value for NaAOT. These results seem to evidence that in Ca(AOT)₂ micelle the hydration shell around the polar heads of the surfactant is completed at higher water content with respect to the NaAOT micelle. It has been shown^{12,13} that the fraction ψ_3 plays an essential role in determining the intrinsic dynamics of the NaAOT micellar system; we expect that these differences in the values of ψ_3 could be related to a different dynamical behavior of the two systems.

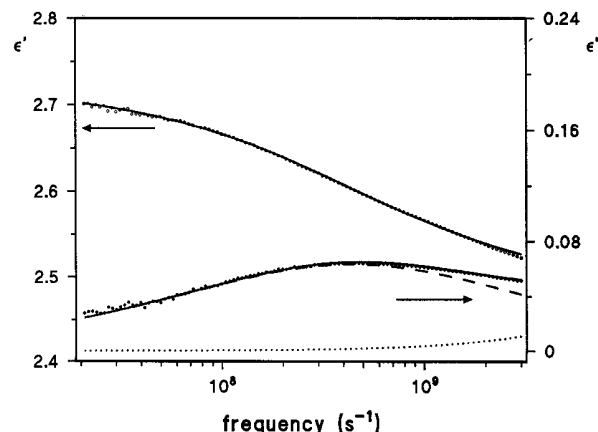


Figure 4. Real (ϵ') and imaginary (ϵ'') parts of the dielectric constant of the Ca(AOT)₂/H₂O/CCl₄ mixture ($W = 9$) vs frequency: (O) experimental points; (—) best fit according to eq 3. Cole–Cole (---) and Debye-type (···) contributions to the best fit of $\epsilon''(\omega)$ are also shown.

3.2. Dielectric Measurements. Information on the change of structure and dynamics of both AOT shell and water confined in the reverse micelles can be obtained from dielectric relaxation measurements. A relaxation phenomenon in the microwave region has been recently observed in NaAOT/H₂O/CCl₄ diluted systems ($\Phi \leq 0.1$).¹² A very similar behavior is found for Ca(AOT)₂/H₂O/CCl₄ systems, as shown in Figure 4, where the dielectric spectrum of a Ca(AOT)₂/H₂O/CCl₄ sample at $\Phi = 0.1$ and $W = 9$ is reported. Two distinct relaxation phenomena are present in the spectrum, and as in the case of NaAOT/H₂O/CCl₄ system, the frequency dependence of the dielectric function $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ can be well described in terms of a sum of a Cole–Cole and a Debye-type relaxation function, according to the equation

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon_1}{1 + (i\omega\tau_1)^{1-\alpha}} + \frac{\Delta\epsilon_2}{1 + (i\omega\tau_2)} \quad (3)$$

where ϵ_∞ is the high-frequency (unrelaxed) dielectric constant, ω the angular frequency of the applied field, $\Delta\epsilon_1$ and $\Delta\epsilon_2$ 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 time distribution around τ_1 .

The best-fit curves of the experimental spectra are reported in Figure 4 (solid lines) together with the Cole–Cole and Debye-type contributions to the best fit of $\epsilon''(\omega)$ (dashed lines). The Debye dispersion is located at high frequencies, in the region of relaxation of bulk water; in our experimental frequency range, it makes only a small contribution which is found to increase with water content in the sample, as previously seen for NaAOT and Mg(AOT)₂ systems.^{11,23} For the sake of comparison, the dielectric increments of this relaxation process are reported in Figure 5 vs the water volume fraction $\Phi_v(\text{H}_2\text{O})$ in the samples, together with those of NaAOT and Mg(AOT)₂ systems. Within the experimental errors, the values of $\Delta\epsilon_2$ relative to these three different systems are mutually consistent. On these grounds, this relaxation process has been attributed to the reorientation of water molecules confined within the micellar core.

The present paper is focused on the low-frequency relaxation process, characterized by dielectric parameters τ_1 , $\Delta\epsilon_1$, and α . In this regard, Figure 6 shows the trend of τ_1 as a function of W for NaAOT and Ca(AOT)₂ systems; the values of $\Delta\epsilon_1$ and α vs W for the Ca(AOT)₂ system are reported in Figure 7. The

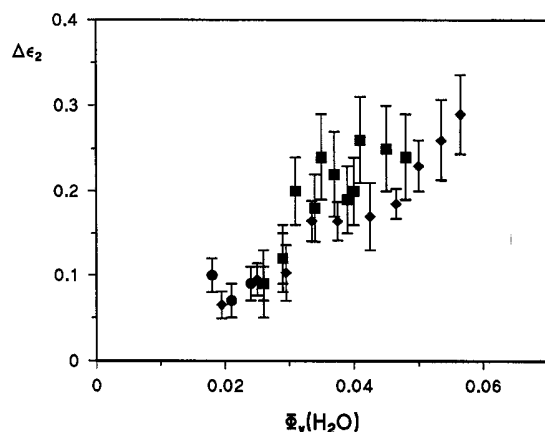


Figure 5. Dielectric relaxation amplitude for the Debye high-frequency relaxation as a function of total water volume fraction $\Phi_v(\text{H}_2\text{O})$: (●) $\text{Ca}(\text{AOT})_2/\text{H}_2\text{O}/\text{CCl}_4$; (□) $\text{Mg}(\text{AOT})_2/\text{H}_2\text{O}/\text{CCl}_4$; (◆): $\text{NaAOT}/\text{H}_2\text{O}/\text{CCl}_4$. The volume fraction of micellar phase is $\Phi = 0.1$ in all the samples.

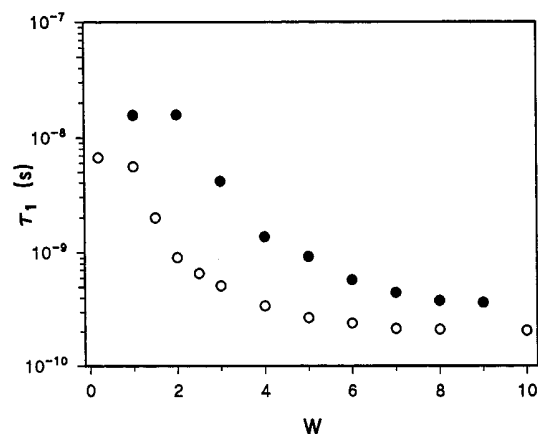


Figure 6. Relaxation time (τ_1) vs W for NaAOT and $\text{Ca}(\text{AOT})_2$ micelles ($\Phi = 0.1$): (●) $\text{Ca}(\text{AOT})_2/\text{H}_2\text{O}/\text{CCl}_4$; (○) $\text{NaAOT}/\text{H}_2\text{O}/\text{CCl}_4$.

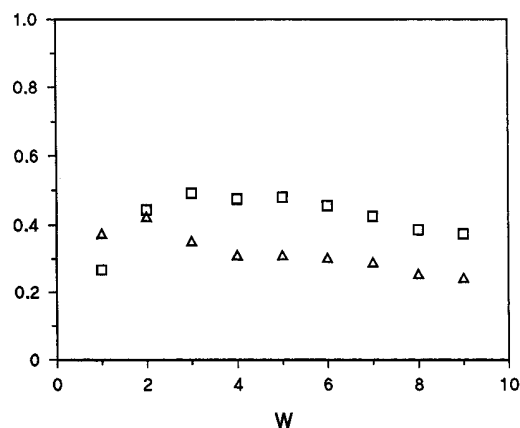


Figure 7. $\text{Ca}(\text{AOT})_2/\text{H}_2\text{O}/\text{CCl}_4$ system. Plot of the relaxation strength $\Delta\epsilon_1$ (Δ) and of the shape parameter α (□) vs W .

values of τ_1 (Figure 6) for the $\text{Ca}(\text{AOT})_2$ samples are systematically higher than those of NaAOT samples; however, for both micellar systems, the trend of τ_1 vs W exhibits an initial decrease followed by a region in which it is nearly constant. Both the relaxation strength $\Delta\epsilon_1$ and the shape parameter α (Figure 7) show, as the water is added to the solution, small but appreciable variations, which are more pronounced at lower water contents.

3.2.1. Dielectric Relaxation at Low Water Content. At the lowest water content ($W = 1$), the almost dehydrated reverse

$\text{Ca}(\text{AOT})_2$ micelle exhibits a nearly rigid structure^{12,13,24} and the dielectric relaxation can be described in terms of rotational diffusion of the whole micelle. Assuming an approximately spherical shape for the micellar aggregate, the rotational diffusion time is given by the Debye–Stokes formula,

$$\tau = \frac{4\pi\eta R^3}{K_b T} \quad (4)$$

where η is the viscosity of the solution, R the micellar radius, and $K_b T$ the thermal energy. Inserting in eq 4 the experimental time τ_1 , we obtain for the $\text{Ca}(\text{AOT})_2$ micelle at $W = 1$ a radius $R = (15.3 \pm 0.7)$ Å. This value is found to be consistent with the values reported in the literature.²⁵

Furthermore, the Debye extension of the Clausius–Mossotti equation^{12,14} has been used to estimate the apparent dipole moment μ_{app} of a single AOT group within the $\text{Ca}(\text{AOT})_2$ micelle ($W = 1$). We obtain for μ_{app} a value of approximately 0.7 D; this value is found to be consistent with the corresponding one for AOT group^{14,26} in a NaAOT micellar aggregate, and it is lower than that of the same isolated group for at least a factor of 10.²⁶ This result supports the idea of almost spherical-shaped $\text{Ca}(\text{AOT})_2$ micelles.^{17,18} In fact, an almost spherical symmetry in the distribution of dipoles causes a compensation effect which reduces the apparent dipole moment of the single AOT group with respect to that of the same isolated group.

The values of the shape parameter α higher than 0 ($\alpha = 0$ for a single Debye dispersion) indicate the existence of a distribution of relaxation times; in micellar solutions, this is often attributed to polydispersity in the radius and/or deviations from spherical form of the micelles. The addition of small amount of water (up to $W = 2$ –3) gives an increase of both the relaxation strength $\Delta\epsilon_1$ and of the shape parameter α . These results can be explained in terms of an increasing deviation from spherical form with water addition. In fact, the effective dipole moment of a single aggregate increases with deviations from spherical symmetry. Moreover, an increase of polydispersity in shape can account for the increasing values of α .

The further evolution of α and $\Delta\epsilon_1$ with W for $W > 2$ is related to the appearance of a different and faster relaxation process, as explained in the next sections.

3.2.2. Dielectric Relaxation at the Highest Values of W . With increasing the water content inside the micelle, the micellar radius R increases almost linearly with W , so that τ_1 is expected to increase approximately with W^3 , according to the Debye–Stokes law [see eq 4]. In our case, τ_1 initially decreases and then is nearly constant as a function of W (see Figure 6). In previous works,^{12,13} a quantitative description of the behavior of τ_1 as a function of W was reported in the case of NaAOT/ $\text{H}_2\text{O}/\text{CCl}_4$ reverse micelles at $\Phi = 0.1$. For each value of W , we supposed the existence of a fraction $[1 - X(W)]$ of surfactant headgroups reorienting with the whole micelle with the Debye diffusion time $\tau_D(W)$ and a fraction of free headgroups whose reorientation is characterized by a relaxation time $\tau_0 < \tau_D(W)$. The value of τ_0 for the NaAOT micellar system was fixed to the limiting value of τ_1 at the highest W ($\tau_0 = 1.9$ ns). This configuration is not to be considered as a static scenario because each AOT group experiences fluctuations in its local aqueous environment, with a characteristic time comparable to the mean residence time of a water molecule in the hydration shell of each ion. Since it is found experimentally²⁷ that this fluctuation rate is higher with respect to the intrinsic rates of the observed process (τ_0 and τ_D), we applied the so-called fast-exchange condition²⁸ to express the experimental relaxation time τ_1 in

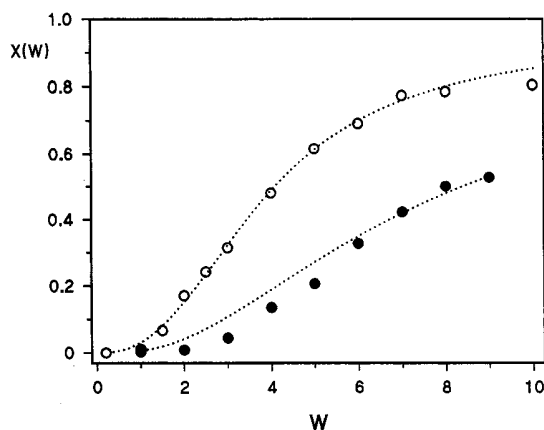


Figure 8. Plot of the free AOT headgroups fraction $X(W)$ calculated according to eq 4: (○) NaAOT/H₂O/CCl₄; (●) Ca(AOT)₂/H₂O/CCl₄; (···) fractions of AOT ion pairs bound to three water molecules as obtained from IR data.

terms of the τ_D and τ_0 .

$$\frac{1}{\tau_1} = \frac{X(W)}{\tau_0} + \frac{1 - X(W)}{\tau_D} \quad (5)$$

Starting from eq 5, we have calculated the fraction $X(W)$ of the free AOT headgroups for NaAOT and Ca(AOT)₂ reversed micelles by inserting into eq 5 the experimental values of τ_1 , the values of τ_D calculated according to Debye formula (4), and finally, a value of τ_0 of 1.9 ns (the same for the two systems). The values of $X(W)$ obtained from eq 5 are reported in Figure 8 for Ca(AOT)₂ and NaAOT; in the same figure, the fractions ψ_3 of totally hydrated AOT, as obtained from IR data (see Figure 3), have also been reported for both micellar systems. We notice that the fraction of completely hydrated AOT headgroups superimposes to $X(W)$ values for both NaAOT and Ca(AOT)₂. Furthermore, for both systems, the fractions of partially hydrated surfactant ion pairs (Figure 3) significantly depart from the calculated values of $X(W)$. These results confirm the hydration model above-reported,¹² for which only totally hydrated AOT headgroups can reorient itself in the applied electric field independently with respect to the micellar aggregate, while the partially hydrated AOT headgroups tend to rotate together with reverse micelle.

4. Conclusions

Our data show that the counterion substitution on the polar head of the surfactants provides significant variations in the formation and in the characteristics of hydration.

We found, for the Ca(AOT)₂ molecule, a surprising coincidence between the fraction $\psi_3(W)$ of AOT groups fully hydrated, derived from the analysis of IR data, and the fraction $X(W)$ of

AOT headgroups reorienting independently in the applied electric field, which comes from dielectric measurements. This coincidence, yet previously observed for NaAOT micelle, confirms that the dynamics of a single surfactant molecule in the micellar aggregate is closely connected to the hydration of polar groups. We notice that results on the same systems of two techniques, IR spectroscopy and dielectric spectroscopy, acting on very different time scales, provide a coherent quantitative description of the connections between hydration and dynamical properties of micellar systems.

Acknowledgment. This work was supported in part by a contribution from the Consiglio Nazionale delle Ricerche (Rome).

References and Notes

- (1) Eicke, H. F. *Micelles*; Springer: New York, 1980; p 85.
- (2) Chevalier, Y.; Zemb, T. *Rep. Prog. Phys.* **1990**, *53*, 279.
- (3) Kotlarchyk, M.; Chen, S. H.; Huang, J. S. *J. Phys. Chem.* **1982**, *86*, 3273.
- (4) Van Dijk, M. A.; Joosten, J. G. H.; Levine, J. K.; Bedeaux, D. *J. Phys. Chem.* **1989**, *93*, 2506.
- (5) Hilfiker, R.; Eicke, H. F.; Sager, W.; Steeb, C.; Hofmeier, U.; Gehrke, R. *Ber. Bunsen-Ges. Phys. Chem.* **1990**, *94*, 677.
- (6) Luisi, P. L.; Magid, L. J. *C. R. C. Crit. Rev. Biochem.* **1986**, *20*, 409.
- (7) Onori, G.; Santucci, A. *J. Phys. Chem.* **1993**, *97*, 5430.
- (8) Amico, P.; D'Angelo, M.; Onori, G.; Santucci, A. *Nuovo Cimento* **1995**, *D17* (9), 1053.
- (9) MacDonald, H.; Bedwell, B.; Gulari, E. *Langmuir* **1986**, *2*, 704.
- (10) Jain, T. K.; Varshney, M.; Maitra, A. *J. Phys. Chem.* **1989**, *93*, 7409.
- (11) D'Angelo, M.; Fioretto, D.; Onori, G.; Palmieri, L.; Santucci, A. *Colloid Polym. Sci.* **1995**, *273*, 899.
- (12) D'Angelo, M.; Fioretto, D.; Onori, G.; Palmieri, L.; Santucci, A. *Phys. Rev. E* **1995**, *52*, R4620.
- (13) D'Angelo, M.; Fioretto, D.; Onori, G.; Palmieri, L.; Santucci, A. *Phys. Rev. E* **1996**, *54* (1), 993.
- (14) Camardo, M.; D'Angelo, M.; Fioretto, D.; Onori, G.; Palmieri, L.; Santucci, A. *Prog. Colloid Polym. Sci.* **1996**, *100*, 177.
- (15) D'Angelo, M.; Fioretto, D.; Onori, G.; Santucci, A. *J. Mol. Struct.* **1996**, *383*, 157.
- (16) Giordano, R.; Migliardo, P.; Wanderling, U.; Bardez, E. *J. Mol. Struct.* **1993**, *296*, 265.
- (17) Eastoe, J.; Fragneto, G.; Robinson, B. H.; Towey, T. F.; Heenan, R. K.; Lang, F. *J. Chem. Soc., Faraday Trans. I* **1992**, *88*, 461.
- (18) Eastoe, J.; Towey, T. F.; Fragneto, G.; Robinson, B. H.; Williams, J.; Heenan, R. K. *J. Phys. Chem.* **1993**, *97*, 1459.
- (19) Bardez, E.; Wy, N. C. *Langmuir* **1995**, *11*, 3374.
- (20) Fioretto, D.; Marini, A.; Massarotti, M.; Onori, G.; Palmieri, L.; Santucci, A.; Socino, G. *J. Chem. Phys.* **1993**, *99* (10), 8115.
- (21) Luck, W. A. P. *Water: A Comprehensive Treatise*; Plenum Press: New York, 1973; Vol. 2, p 235.
- (22) Hallam, H. E. In *Structure of Water and Aqueous Solutions*; Luck, W. A. P., Ed.; Verlag: FRG, 1974; p 285.
- (23) Fioretto, D.; Freda, M.; Onori, G.; Santucci, A. *Prog. Colloid Polym. Sci.* **1997**, *105*, 256.
- (24) Bhattacharya, S.; Sowa, J.; Huang, J. S. *Phys. Rev. Lett.* **1990**, *65*, 131.
- (25) Maitra, A. *J. Phys. Chem.* **1984**, *88*, 5122.
- (26) Eicke, H. F.; Christen, H. *J. Colloid Interface Sci.* **1974**, *48*, 281.
- (27) Giese, K. *Ber. Bunsen-Ges. Phys. Chem.* **1972**, *76*, 495.
- (28) Anderson, J. E. *J. Chem. Phys.* **1967**, *47*, 4879.