Influence of the pH-induced Ionization on the Conformation of Dodecyldimethylamine Oxide Micelles: A Radiowave Dielectric Relaxation and Light-Scattering Study

A. Bonincontro* and C. Cametti

Dipartimento di Fisica, Universita' di Roma "La Sapienza", and INFM, Unita' di Roma 1, Piazzale A. Moro 5, I-00185 Roma, Italy

S. Marchetti and G. Onori

Dipartimento di Fisica, Universita' di Perugia, and INFM, Unita' di Perugia, Via A. Pascoli, I-06123 Perugia, Italy

The dielectric properties of dodecyldimethylamine oxide [DDAO] in salt-free aqueous solutions under different pH conditions have been measured in the frequency range from 400 kHz to 100 MHz. DDAO is an amphyphile that may exist either in a neutral or a cationic protonated form, depending on the pH of the aqueous solution. This condition realizes, above the cmc, ionic or nonionic micelles in an easily controlled way. While the dielectric response of a neutral micelle, in the low-concentration limit, is rather flat, a dielectric dispersion occurs at pH values lower than pH = 7. This dielectric dispersion is attributed to an orientational polarization mechanism of the entire micelle, in addition to the usual Maxwell−Wagner effect. This orientational polarization is due to an electric dipole moment induced by protonation of the micellar surface. The average size of the micelle, considered as a rigid sphere of radius R_H, has been evaluated from the relaxation time of the observed dielectric relaxation. We found that R_H decreases with the increasing of the micellar ionization induced by acidic pH values. To obtain an independent evaluation of the micelle size, we have performed dynamic light-scattering experiments. These results are in a reasonable agreement with those derived by dielectric measurements. The influence of the ionic counterion species on the micelle size is briefly discussed.

1. Introduction

Alkylamine oxides are amphiphiles that exist either in a neutral or cationic protonated form, depending on the pH of the aqueous solutions. These systems represent a very interesting model for studying the effect of crossover between ionic and nonionic character of the single molecule on the structure of the micellar aggregate and have been the subject of increasing attention, both in fundamental and applied aspects, in the past few years.[1−6]

The effects of protonation of dodecyldimethylamine oxide [DDAO] have been extensively investigated and it was shown that DDAO in aqueous solutions becomes ionized at pH lower than pH = 7, the full protonation being approached at pH around pH = 2. Moreover, it has been found that the aggregation number (on the order of 60−80) changes with the degree of ionization.[1,2] Previous studies at low ionic strength indicate that these micelles are approximately spherical in shape, both in the neutral and protonated state.[7]

Frequency domain dielectric spectroscopy is a valid technique to evidence structural properties of micellar systems. Recently, we used this approach to study structural and conformational properties of proteins[8−10] and reversed micelles[11,12] in aqueous solutions.

Previous dielectric relaxation investigations[13−15] of charged colloidal particles in aqueous solutions showed that, in addition to the water relaxation in the gigahertz region, there is a dispersion located at around few hundred megahertz, attributable to the solute. Generally, this relaxation is interpreted as due to the counterion fluctuation at the micelle-solvent interface.[14,15] However, few systematic studies on dielectric properties of these systems have appeared and the interpretation of the experimental finding is not yet well established. More recently, Itatani and Shikata[16] performed dielectric measurements on DDAO at high concentration in a very wide range of frequency, from 1 MHz to 20 GHz. In that work, the experimental data were fitted by four overlapping Debye relaxation functions, and a possible interpretation was discussed.

Since both the degree of protonation and the ionic strength affect the micelle shape and size, DDAO system offers a valuable opportunity for a systematic study of the effects of the surface charge density on the dielectric behavior of these systems.

In the present paper, we report some dielectric measurements in dilute aqueous solutions of DDAO in the megahertz frequency range, where the process associated with the single micelle is relevant. In this frequency range, a well-characterized dielectric dispersion appears due to the formation of a fluctuating dipole moment induced by the protonation process. The overall dielectric process is attributed to the rotational relaxation mode of the entire micelle, modeled as a rigid sphere of radius R_H, partially overlapping to the interfacial relaxation mode, usually present in heterogeneous systems. From the rotational relaxation time, the average size of the micelle has been evaluated, together with its changes in the pH values of the aqueous solution. Dynamic light-scattering measurements performed on the same DDAO aqueous solutions reveal that two different populations are simultaneously present in the system, whose typical sizes lie in the range of 1−3 nm and 150−200 nm, respectively, the

---

* To whom correspondence should be addressed.

10672 *J. Phys. Chem. B, Vol. 107, No. 38, 2003*

Bonincontro et al.

smallest of them being in very good agreement with the size derived from the dielectric measurements. The influence of the pH changes and counterion species on the size of the DDAO micelles in aqueous solution is briefly discussed.

2. Experimental Section

2.1. Material. Dodecyldimethylamine oxide [DDAO] was purchased from Fluka and was used without any further purification. The solutions were prepared by weighing, using low-conductivity water ($\sigma = (1-2) \times 10^{-6}$ mho/m). The surfactant concentration was fixed to the value 20 mM, well above the cmc (about 1 mM). The pH of the aqueous phase was measured by means of a Crison micropH 2000 and changes in the pH conditions were obtained by adding negligible volumes of concentrated acidic solutions (HCl and H_2SO_4). Therefore, in the titration, the micelle concentration was substantially unchanged.

2.2. Dielectric Measurements. In the dielectric experiments, the permittivity $\epsilon'(\omega)$ and the dielectric loss $\epsilon''(\omega)$ were measured by means of a computer controlled Hewlett-Packard Impedance analyzer model 4194A, in the frequency range from 4×10^5 to 10^8 Hz. The measuring cell, described in detail elsewhere,[17] is a short section of a cylindrical waveguide which can be partially filled with the sample solution under investigation. The system behaves as a waveguide excited far beyond its cutoff frequency mode, and therefore, only the stray-field of a coaxial line-waveguide transition is used in the measurements. Cell constants were determined by calibration measurements with electrolyte solutions of known electrical conductivity, following the procedure reported elsewhere.[18] The uncertainties on $\epsilon'(\omega)$ and $\epsilon''(\omega)$ are within 1%. The temperature was fixed to 25.0 °C within 0.2 °C.

2.3. Dynamic Light-Scattering Measurements. Because the surfactant concentration for all the samples investigated is higher than the critical micelle concentration of DDAO (about cmc $\approx$ 1 mM[2]), we expect the presence of spherical micelles in aqueous solution (aggregation number on the order of 60−80). To characterize the size and the size distribution of the micellar aggregate, we employed a dynamic light-scattering method. This technique measures the normalized time autocorrelation function $g_2(t)$ of the scattered intensity according to

$$g_2(t) = \frac{\langle I^*(0, t)I(q, t)\rangle}{\langle I(q, t)^2\rangle} = A(1 + \beta [g_1(q, t)]^2) \qquad (1)$$

where $I(q, t)$ is the intensity of the scattered light at time t and at wavevector $q = (4\pi/\lambda)n_0 \sin(\vartheta/2)$, with λ the wavelength of the incident light, n_0 the refractive index of the aqueous phase and ϑ the scattering angle.

For suspensions having a narrow size distribution, the method of cumulants can be applied and the time electric field autocorrelation function can be expanded according to

$$g_1(q, t) \approx \exp(-\bar{\Gamma} t + \tfrac{1}{2}\mu t^2 + ...) \qquad (2)$$

where $\bar{D} = \bar{\Gamma}/q^2$ is the average diffusion coefficient weighted by the scattering intensity from which the z-average size of the diffusion particles is calculated from the Stokes−Einstein relationship

$$R_H = \frac{K_B T}{6\pi\eta\bar{D}} \qquad (3)$$

where η is the viscosity of the aqueous phase and $K_B T$ the thermal energy.
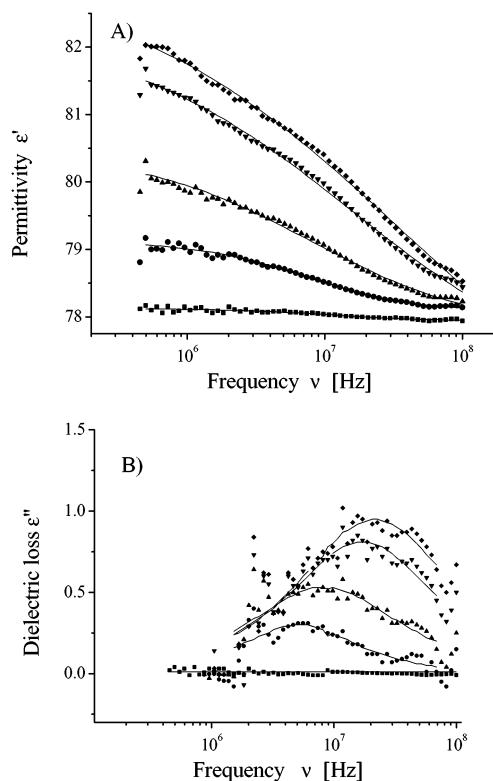

Figure 1. (A) Permittivity ϵ' as a function of frequency of DDAO aqueous solution at different pH values, in the presence of HCl: from bottom to top: pH = 8.12, 6.86, 6.20, 5.75, 5.55. The full line is the calculated values according to the sovraposition of two Debye-type relaxation functions (eq 5). (B) Dielectric loss $\epsilon''(\nu)$ as a function of the frequency ν for the samples as in part A. The dielectric loss is calculated from the total electrical conductivity $\sigma(\omega)$ according to the relationship $\epsilon''(\omega) = (\sigma(\omega) - \sigma(0))/\epsilon_0\omega$.

For a heterogeneous system, where the spectral profile of the scattered light is due to the superposition of multiLorentzian curves, $g_1(q, t)$ can be written as the Laplace transform of the spectrum of relaxation times

$$g_1(q, t) = \int_0^\infty G(\Gamma)e^{-\Gamma t}\,d\Gamma \qquad (4)$$

where Γ is the characteristic decay rate of the system and $G(\Gamma)$ is the weight factor in the relaxation time distribution. To obtain the distribution $G(\Gamma)$ of the decay rates, a constrained regularization method, CONTIN, was used to invert the experimental data.[19]

3. Results and Discussion

The complex dielectric constant $\epsilon^*(\omega) = \epsilon'(\omega) - i\epsilon''(\omega)$ of DDAO aqueous solutions, at the fixed concentration of 20 mM has been measured in the frequency range 100 kHz to 100 MHz, at different values of the pH of the aqueous phase, from about pH = 8 to pH = 5, corresponding to a change in the degree of ionization from 0 to 0.2. Two experiments were performed, using two different titrants, i.e., HCl and H_2SO_4. Figures 1 and 2 show the permittivity $\epsilon'(\omega)$ and the dielectric loss $\epsilon''(\omega)$ measured in these two sets of experiments, respectively. As can be seen, while the dielectric response of the micelle solution, under practically complete electroneutrality conditions (pH = 8), does not change appreciably, a dielectric relaxation appears at lower pH values, when the protonation of the HO−N group imparts a positive electric charge to the single micelle.
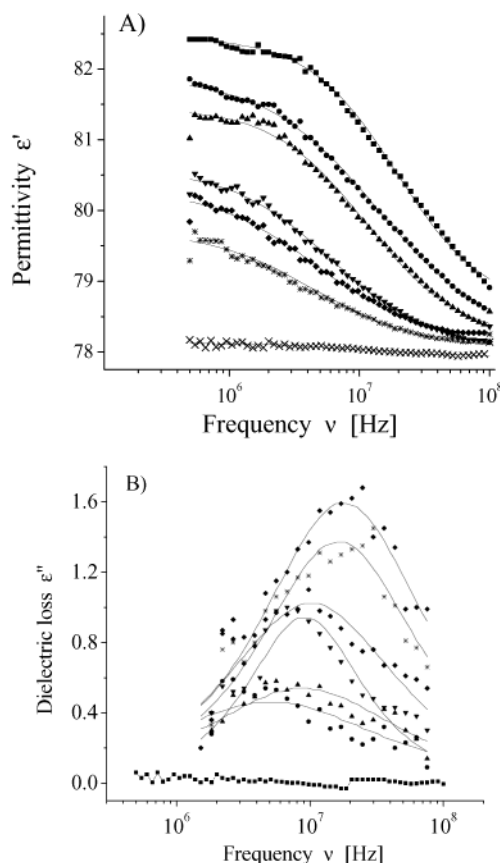
Dodecyldimethylamine Oxide Micelles

J. Phys. Chem. B, Vol. 107, No. 38, 2003 **10673**

Figure 2. (A) Permittivity ϵ' as a function of frequency of DDAO aqueous solution at different pH values, in the presence of H_2SO_4: from bottom to top: pH = 6.82, 6.25, 5.88, 5.47, 5.35, 5.09. The full line is the calculated values according to the sovraposition of two Debye-type relaxation functions (eq 5). (B) Dielectric loss $\epsilon''(\nu)$ as a function of the frequency ν for the samples as in Figure 2A.

Within the frequency window available in the present work, the observed dispersions, whose characteristic frequency falls in the range of about 1−100 MHz, are to be attributed to mechanisms associated with the single micelle, owing to the polar character that this structure assumes as a consequence of the protonation of the HO−N groups, due to the addition of the acidic tritants.

Recently, the dielectric behavior of DDAO aqueous solutions has been investigated by Itamani et al.,[16] who have analyzed the dielectric response at a relatively high concentration, in a frequency range from 1 MHz to 20 GHz by means the sum of four Debye-type relaxation functions. The molecular mechanisms responsible for the observed dispersion have been associated respectively with the rotational relaxation of individual DDAO molecules into spherical micelles, with the formation of ion pairs between a protonated headgroup HO−H^+ and counterions (Br^-, in this case), with the rotation of intermolecular association particles formed between protonated and unprotonated DDAO molecules and, finally, with the relaxation due to the surface counterion distribution. Whereas the two fastest relaxation modes fall beyond our frequency window, the other two mechanisms occur in the same frequency range we have used in this work. However, owing to the low surfactant concentration we have investigated, the low ionic strength and the low degree of ionization induced by the titrant, the third relaxation mechanism (formation of intermolecular DDAO association) is unable to justify the strength of the dielectric effect we have observed. In fact, this mechanism associated with hydrogen bonding between protonated and

unprotonated DDAO monomers produces significant effects only at high ionic strength and high ionization degree.[20] Therefore, we propose a slightly different interpretation, substituting the mechanism due to the intermolecular association particles with the orientational relaxation of the entire micelle.

In fact, it must be considered that the exposition of charges on the micellar surface promoted by the protonation of the headgroups induced by pH changes is a random process yielding to an asymmetrical distribution of protonated headgroups at the micelle surface, and so an overall intrinsic electrical dipole moment appears at a low level of charge density. Moreover, it must be noted that a small anysotropy involving only some few units of elementary charge is able to produce, on a length on the order of the micellar diameter, a relatively high dipole moment, on the order of some hundreds of debye units. A further contribution might be due to even small deviations from spherical geometry. If we consider a micelle with a radius of about 2 nm, an orientational relaxation should occur at frequencies on the order of some megahertz, as experimentally observed. Therefore, we are encouraged to mainly attribute the observed dielectric dispersions to an orientational polarization of the entire micelle under the influence of an applied external electric field. The formation of polar micelles is a dynamic process, and then, at any pH value, two populations coexist, i.e., neutral and charged micelles. The decrease of the pH shifts the equilibrium toward charged micelles and, at the same time, promotes an higher dipole moment, almost until the degree of protonation is low. The consequence of this is an increase of the dielectric increment $\Delta\epsilon$ with decreasing pH, as experimentally observed.

On the other hand, in the frequency range investigated, a further dielectric polarization contribution must be taken into account, due to the heterogeneous character of the system. This contribution, known as Maxwell−Wagner interfacial polarization,[21] originates from the different electrical properties (permittivity and electrical conductivity) of the aqueous phase and the micellar structure. This effect has been extensively studied in aqueous colloidal suspensions for a long time[22−24] and its influence on the dielectric properties of heterogeneous systems is well established.[25]

On the basis of the above assumptions, the dielectric response in the frequency window investigated has been described, to a first approximation, by two partially overlapping dielectric dispersions, according to the relationship

$$\epsilon^*(\omega) = \epsilon_\infty + \frac{\Delta\epsilon_{MW}}{1 + i\omega\tau_{MW}} + \frac{\Delta\epsilon_r}{1 + i\omega\tau_r} \qquad (5)$$

where the dielectric increments $\Delta\epsilon_{MW}$ and $\Delta\epsilon_r$ and the relaxation times τ_{MW} and τ_r of the two dielectric dispersions are given by

$$\Delta\epsilon_{MW} = \frac{9}{2}\Phi\epsilon_m \frac{(\lambda_s)^2}{(\sigma_m + \lambda_s)^2} \qquad (6)$$

$$\tau_{MW} = \frac{\epsilon_0\epsilon_m}{(\sigma_m + \lambda_s)} \qquad (7)$$

and by

$$\Delta\epsilon_r = \frac{Cg\mu_0^2}{2\epsilon_0 K_B T} \qquad (8)$$

$$\tau_r = \frac{4\pi\eta R_H^3}{K_B T} \qquad (9)$$

TABLE 1: Dielectric Parameters at Different pH Values for DDAO in Aqueous Solutions Derived from the Analysis of the Dielectric Dispersions on the Basis of Two Partially Overlapping Debye-Type Relaxation Function (Eq 5)

titrant	pH	$\Delta\epsilon_r$	ϵ_∞	ν_r (MHz)	σ_m (mho/m)	R_H (nm)
HCl	8.12 ± 0.01	$\approx 0.3 \pm 0.2$	78.1 ± 0.01		0.0022	
	6.86 ± 0.01	0.7 ± 0.2	78.1 ± 0.01	20.3 ± 0.4	0.0052	1.37
	6.20 ± 0.01	1.0 ± 0.2	78.1 ± 0.1	29.4 ± 0.4	0.015	1.21
	5.75 ± 0.01	2.4 ± 0.2	77.9 ± 0.1	51 ± 2	0.029	1.01
	5.55 ± 0.01	3.4 ± 0.2	77.1 ± 0.1	54.7 ± 3	0.034	0.98
H_2SO_4	6.82 ± 0.01	0.8 ± 0.2	78.0 ± 0.1	6.1 ± 0.3	0.0060	2.04
	6.25 ± 0.01	1.0 ± 0.2	78.2 ± 0.1	7.2 ± 0.3	0.0068	1.93
	5.88 ± 0.01	1.7 ± 0.2	78.0 ± 0.1	10.2 ± 0.2	0.0077	1.72
	5.47 ± 0.01	2.2 ± 0.2	78.0 ± 0.1	29.4 ± 0.4	0.012	1.21
	5.35 ± 0.01	2.8 ± 0.2	78.2 ± 0.2	47.7 ± 0.6	0.015	1.03
	5.09 ± 0.01	3.5 ± 0.2	78.2 ± 0.1	79 ± 2	0.02	0.87

where ϵ_m and σ_m are the permittivity and electrical conductivity of the aqueous phase, $\lambda_s = \lambda_{s0}/R_H$ is the counterion surface conductivity contribution at the micelle–water interface, Φ is the fractional volume of the micellar phase in the solution, C is the micelle concentration, $g\mu_0$ is the effective dipole moment of the single micelle (g is the Kirkwood molecular correlation parameter, generally assumed to be the unity, in dilute solution), and ϵ_0 is the dielectric constant of free space. ϵ_∞ is the high-frequency limit of the permittivity $\epsilon'(\omega)$.

The experimental data shown in Figures 1 and 2 were analyzed by means of the relaxation function given by eq 5.

As far as the Maxwell–Wagner dispersion is concerned, we calculated its contribution using the measured value for the ionic electrical conductivity σ_m of the aqueous phase and assuming a conductivity $\lambda_s = \lambda_{s0}/R_H$ of about 5×10^{-2} mho/m, this being a typical values in colloidal suspensions.[26] As far as the values of σ_m are concerned, these were measured in an aqueous solution in the presence of the two titrants investigated (HCl and H_2SO_4) at the given pH value. The fractional volume Φ of the dispersed phase was estimated to be on the order of $\Phi \approx 5 \times 10^{-3}$, on the basis of the surfactant concentration and a surfactant density of about 1 g/cm³. These quantities yield a dielectric increment $\Delta\epsilon_{MW}$ on the order of unity, with a weak dependence on the ionic conductivity σ_m, and a relaxation frequency $\nu_{MW} = 1/(2\pi\tau_{MW})$ that varies from about 5 MHz to about 500 kHz, as the ionic conductivity σ_m decreases from 0.03 to 0.002 mho/m, according to the change in the pH values, from about 5 (ionized micelle) to about 8 (complete electroneutral micelle). At low degree of protonation (high pH values), this dispersion is shifted toward low frequencies, and its contribution is negligible in the frequency window we have explored.

The dielectric parameters $\Delta\epsilon_r$, ϵ_∞, and $\nu_r = 1/(2\pi\tau_r)$ of the dispersion associated with the polar character of the micelle have been derived from a nonlinear least-squared minimization procedure, having subtracted the expected contribution due to the Maxwell–Wagner dispersion on the basis of the above quoted values for the conductivity λ_s, associated with the surface contribution. To a first approximation, since the surface protonation is relatively small for all the values of pH investigated, we have assumed λ_s to be independent of the micelle surface charge density. The results are shown in Table 1. The quoted uncertainties on the relaxation frequency ν_r, the dielectric strength $\Delta\epsilon_r$ and the high-frequency permittivity ϵ_∞ are based on a 95% confidence level. The overall goodness of the fit can be judge from the comparison between the calculated (eq 5) and experimental values of both ϵ' and ϵ'' shown in Figures 1 and 2.

It is noteworthy that a somewhat different analysis of our experimental data might provide further support to this approach. Recently, the dielectric relaxations of cationic micellar solutions

have been discussed by Baar et al.,[23] who analyze the two contiguous dispersions attributable to the micelle relaxation on the basis of the Grosse model.[15] Within this approach, the low-frequency relaxation mode reflects the counterion relaxation originated from the radial diffusion of counterions surrounding the charged micelle, resulting in the following dielectric parameters

$$\nu_1 = \frac{D}{2\pi R_H{}^2} \tag{10}$$

$$\Delta\epsilon_1 = \frac{9\Phi\epsilon_m (K_D R_H)^4 \left(\dfrac{\lambda_s}{\sigma_m}\right)^4}{4\left[(K_D R_H)\left(\dfrac{\lambda_s}{\sigma_m}\right)\left(\dfrac{\lambda_s}{\sigma_m}+1\right)+1\right]^2} \tag{11}$$

where K_D is the inverse of the Debye screening length.

The high-frequency mode is assigned to the rapid tangential mode of bound counterions at the micelle surface, characterized by dielectric parameters given by

$$\nu_2 = \frac{\lambda_s + \sigma_m}{\pi\epsilon_0(\epsilon_p + 2\epsilon_m)} \tag{12}$$

$$\Delta\epsilon_2 = \frac{9\Phi\epsilon_m\left(\dfrac{2\lambda_s}{\sigma_m} - \dfrac{\epsilon_p}{\epsilon_m}\right)^2}{\dfrac{\epsilon_p + 2\epsilon_m}{\epsilon_m}\left(\dfrac{2\lambda_s}{\sigma_m} + 2\right)^2} \tag{13}$$

where ϵ_p is the micelle core permittivity.

In the present case, whereas the high-frequency relationships (eqs 12 and 13) for $\epsilon_p < \epsilon_m$ reduce to the results for the Maxwell–Wagner relaxation of a suspension of insulating particles covered by a conducting layer (the same relationships we quoted in this work, eqs 6 and 7), the low-frequency mode should be characterized by a relaxation frequency on the order of $\nu_1 \approx 5-10$ MHz and a dielectric strength $\Delta\epsilon_1$ on the order of $0.1-0.2$, too small to be observed within the present experimental accuracy. Consequently, within the present analysis, we conclude that the Grosse model[15] does not correctly describe the solute relaxation of DDAO aqueous solutions, where the ionic atmosphere relaxation of the low-frequency mode is substituted by the rotation of the intere micelle polarized by protonation. In the present case, the degree of ionization is relatively small ($\alpha = 0.2$ at pH $= 5$), resulting in a negligible counterion atmosphere relaxation that evidences the effect due to unsymmetrical protonation of the micelle (pH effect). Conversely, in the case of cationic micelles as those investigated by Baar et al.,[23] where the Grosse model applies, the symmetric

Dodecyldimethylamine Oxide Micelles

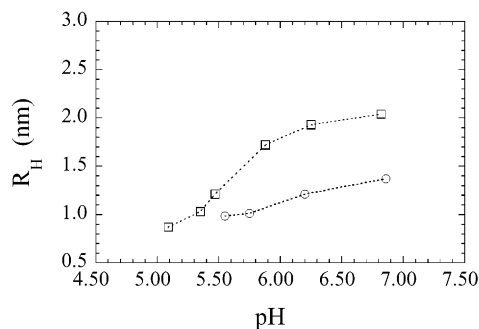*J. Phys. Chem. B, Vol. 107, No. 38, 2003* **10675**

Figure 3. Hydrodynamic radius R_H for aqueous DDAO micelles from two different titrants, calculated from the relaxation frequency of the observed dielectric dispersion according to the procedure described in the text: (○) HCl; (□) H_2SO_4.

distribution of the surface charge prevents the rising of a intrinsic dipole moment and, on the other hand, favors a relaxation mechanism based on the polarization of the ionic atmosphere.

As far as the proposed model is concerned, in both the two systems (aqueous solutions in the presence of HCl or H_2SO_4), the dielectric increment $\Delta\epsilon_r$ increases as the pH of the aqueous phase decreases, i.e., the protonation of the headgroups proceeds. The relaxation frequency ν_r shows the same trend, too. It has to be noted, moreover, that in the case of samples supplemented with HCl, the relaxation frequencies are systematically higher than to those supplemented with H_2SO_4. On the contrary, the dielectric increment $\Delta\epsilon_r$ is practically independent of the type of titrant employed to vary the pH of the solution.

From the relaxation time of the dispersion associated with the dipolar polarization (eq 9), we can evaluate the typical size of the micelle in the solution. The final results are shown in Figure 3, where we report the average radius R_H of the micelle population as a function of pH, for samples in the presence of Cl^- and SO_4^{2-} counterions. In particular, the dielectric measurements clearly suggest a decrease of the hydrodynamic radius as the ionization is increased, at acidic pH values. This decrease of R_H denotes a structural effect related to a reduction of the aggregation number, induced by the repulsive interactions. This effect is coherent with the decrease of the aggregation number reported in the literature.[2,27]

Moreover, the hydrodynamic radius is higher in the presence of SO_4^{2-} counterions in comparison to the corresponding values in the presence of Cl^- counterions, at the same pH value. Counterions SO_4^{2-} and Cl^- exert a shielding effect, stabilizing the micellar structure. Therefore, the differences observed in R_H might be explained considering the higher shielding action exerted by SO_4^{2-} in comparison to Cl^- counterions.

To obtain an independent evaluation of the micelle size, we have performed dynamic light-scattering experiments on samples of DDAO aqueous solutions at the concentration investigated in the dielectric experiment. Figure 4 reports an example of the intensity correlation function of the scattered light for DDAO solution in the presence of HCl at $C = 20$ mM, pH $= 8.12$. The Laplace inversion of the correlation function, carried out by means of the algorithm CONTIN, yields two well-separated populations with some degree of polydispersity, as shown in Figure 4B, with average sizes of about 2.4 and 120 nm in diameter, respectively. For the same sample, at pH $= 5.55$, we again observe two well-separated populations with average sizes of about 1.75 and 250 nm, respectively. In these systems, there is the simultaneous presence of micelles and larger aggregates, whose relative concentrations span around 30−40%.

It is noteworthy that the average diameter of the micelle population is in good agreement with the values deduced from
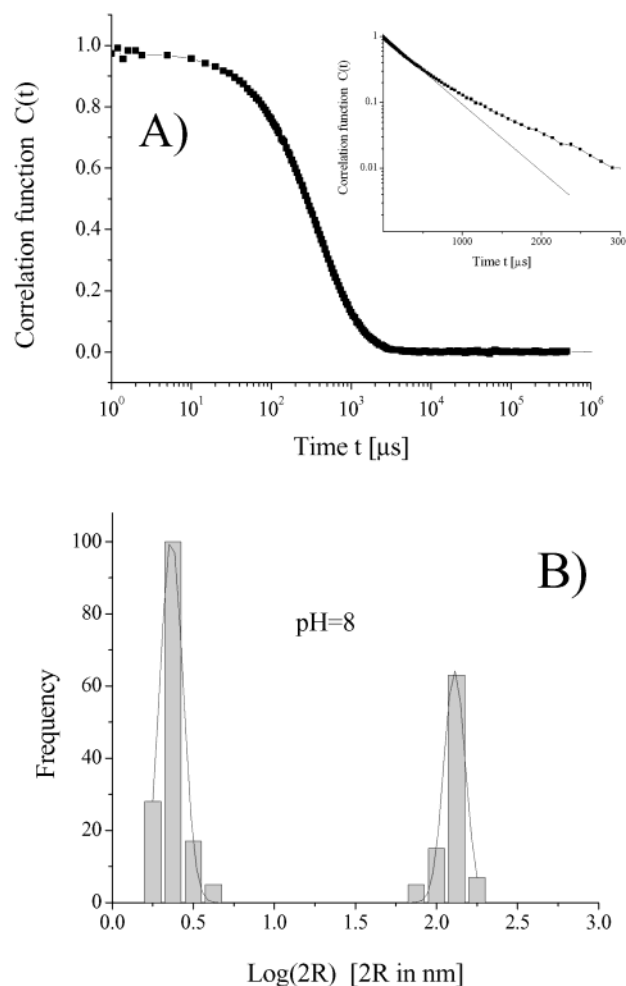

Figure 4. (A) Autocorrelation function of DDAO aqueous solution ($C = 20$ mM), at pH $= 8$. The inset shows the expansion of the autocorrelation function according to the method of cumulants. The slope of straight line gives the first cumulant to which corresponds a value of the average hydrodynamic diameter of about $2R_H = 3.8$ nm. (B) CONTIN analysis of the autocorrelation function showing the presence of two well-separated populations (with average sizes 2.4 and 127 nm, respectively).

the above stated dielectric analysis based on the orientational process of the micelle population.

It must be noted, however, that the results from dymamic light-scattering method differ from the values reported in the literature for similar DDAO samples in the same concentration range. This discrepance is due to the different algorithm used in the data analysis. In fact, if the light-scattering autocorrelation function is analyzed on the basis of the cumulant expansion, assuming particle monodispersity, we obtain, for each DDAO solution investigated, a simple decay rate to which corresponds an average hydrodynamic diameter of about $2R_H = 2.8$ nm at pH $= 5.55$ and about $2R_H = 3.8$ nm, at pH $= 8.12$. This latter value (uncharged micelles) is in good agreement with the value of $2R_H = 3.26$ nm reported by Warisnoicharoen et al.[28] and with the value of about 4 nm reported by Maeda et al.,[2] deduced by means of the method of cumulants.

We want to note that, if the dielectric data are analyzed in terms of a single Cole−Cole relaxation function, instead of two contiguous Debye-type dispersions (eq 5), we will obtain again a reasonable description of the data with a Cole−Cole relaxation spread parameter α on the order of 0.4. This means that the two different mechanisms we have above considered overlap, causing an unique averaged relaxation curve. Moreover, from

the "averaged" relaxation time, we could evaluate an average micellar size similar to that calculated from the cumulant analysis of the light-scattering measurement.

Equation 8 allows the average micelle dipole moment μ_0 to be evaluated from the dielectric increment $\Delta\epsilon_r$ associated with micelle rotational relaxation mode. For example, in the case of HCl aqueous solution at pH = 5.55, light-scattering measurements show a micelle population of about 0.65%, corresponding, for an average aggregation number of about 70, to a micelle concentration of $\sim 1 \times 10^{23}$ m^{-3}. These values correspond to a dipole moment of about 330 D, i.e., about three elementary charges over a distance of 3 nm.

In conclusion, our dielectric analysis, based on an orientational relaxation of the entire micelle, yields an evaluation of the size of the micelle in good agreement with that derived from direct measurements, carried out by means of dynamic light-scattering measurements. Both of the two above-mentioned techniques evidence an appreciable reduction of the micelle hydrodynamic radius with the decrease of pH.

References and Notes

(1) Zhang, H.; Dubin, P. L.; Kaplan, J. I. *Langmuir* **1991**, *7*, 2103.

(2) Maeda, H.; Muroi, S.; Kakehashi, R. *J. Phys. Chem. B* **1997**, *101*, 7378.

(3) Imaishi, Y.; Kakahashi, R.; Nazu, T.; Maeda, H. *J. Colloid Interface Sci.* **1998**, *197*, 309.

(4) Maeda, H.; Kanakubo, Y.; Miyahara, M.; Kakehashi, R.; Garamus, V.; Pedersen, J. S. *J. Phys. Chem. B* **2000**, *104*, 6174.

(5) Brackman, J. C.; Engberts, J. B. *Langmuir* **1992**, *8*, 424.

(6) Mel'nikova, Y. S.; Lindman, B. *Langmuir* **2000**, *16*, 5861.

(7) Ikeda, S.; Tsunoda, M.; Maeda, H. *J. Colloid Interface Sci.* **1979**, *70*, 448.

(8) Bonincontro, A.; Bultrini, E.; Calandrini, V.; Cinelli, S.; Onori, G. *J. Phys. Chem. B* **2000**, *104*, 6889.

(9) Bonincontro, A.; Bultrini, E.; Calandrini, V.; Onori, G. *P.C.C.P.* **2001**, *3*, 3811.

(10) Bonincontro, A.; Calandrini, V.; Onori, G. *Colloids Surf. B* **2001**, *21*, 311.

(11) D'Angelo, M.; Fioretto, D.; Onori, G.; Palmieri, L.; Santucci, A. *Phys. Rev. E* **1995**, *52*, 4620.

(12) D'Angelo, M.; Fioretto, D.; Onori, G.; Palmieri, L.; Santucci, A. *Phys. Rev. E* **1996**, *54*, 993.

(13) Barchini; Pottel, R. *J. Phys. Chem.* **1994**, *98*, 7899.

(14) Grosse, C.; Foster, K. R. *J. Phys. Chem. B* **1987**, *91*, 3073.

(15) Grosse, C. *J. Phys. Chem. B* **1988**, *92*, 3905.

(16) Itatani, S.; Shikata, T. *Langmuir* **2001**, *17*, 6841.

(17) Bonincontro, A.; Briganti, G.; Giansanti, A.; Pedone, F.; Risuleo, G. *Colloids Surf. B* **1996**, *6*, 219.

(18) Athey, T. W.; Stuckly, M. A.; Stuckly, S. S. *IEEE Trans. MTT* **1982**, *30*, 82.

(19) Provencher, S. W. *Comput. Phys. Commun.* **1982**, *27*, 213.

(20) Zhang, H.; Bubin, P. L.; Kaplan, J. I. *Langmuir* **1991**, *7*, 2103.

(21) Pauly, H.; Schwan, P. *Z. Naturforsch.* **1959**, *14B*, 125.

(22) Hasted, J. B. *Aqueous Dielectrics*; Chapman and Hall: London, 1973.

(23) Baar, C.; Buchner, R.; Kunz, W. *J. Phys. Chem. B* **2001**, *105*, 2914.

(24) Grant, E. H.; Sheppard, R. J.; South, G. P. *Dielectric behavior of biological molecules in solution*; Clarendon: Oxford, England, 1978.

(25) Pethig, R. *Dielectric and Electronic Properties of Biological Materials*; Wiley: New York, 1979.

(26) Ohshima, H.; Furusawa, K.; Eds. *Electrical phenomena at interfaces*; Marcel Dekker: New York, 1998.

(27) Garamus, V.; Kameyama, K.; Kakehashi, R.; Maeda, H. *Colloid Polym. Sci.* **1999**, *277*, 868.

(28) Warisnoicharoen, W.; Lansley, A. B.; Lawrence, M. J. *AAPS Pharmasci.* **2002**, *2*, 1.