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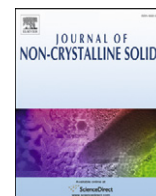
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Complexation of macrocyclic ligands in ionic SDS micellar solutions: A dielectric spectroscopy investigation

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ABSTRACT

The influence of two different macrocyclic ligands, [2.2.2] cryptand (C222) and 18-crown-6 (18C6) ether on the structural properties of sodium dodecyl sulfate (SDS) micellar solutions has been investigated by means of dielectric spectroscopy, in a frequency range from 1 kHz to 50 GHz. The dielectric spectra of SDS micellar solutions present three relaxation processes. In the MHz region, two different relaxations centered at about 30 MHz and 300 MHz, can be attributed to the micelle contribution, while, close to 20 GHz, the contribution of the bulk water orientational polarization is observed. The addition of ligands causes relevant changes in the overall dielectric relaxation spectrum. Significantly, the relaxation processes corresponding to the micelle component are largely modified by the presence of the different ligands investigated both in the relaxation frequency and in the dielectric strength, thus indicating a reorganization of the charged interface of ligand-decorated micelles. These changes are briefly discussed in the light of the phenomenology observed in attractive colloids, where the presence of a long-range electrostatic repulsive interaction and a short-range attractive interactions results in the presence of a well-defined cluster phase.

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1. Introduction

Aqueous micellar solutions of ionic surfactants represent an interesting colloidal system whose structural and dynamical properties have been carefully studied ever since the half of last century [1], not only because of the numerous applications in different technological fields, but also because it represents a model system in soft-matter physics. In fact, micellar solutions represent the simplest self-assembled amphiphilic vesicle which can mimic other more complex structures, such as oil-in-water microemulsions, bilayers vesicles and phospholipid membranes, sharing with micelles the same interfacial region between the external surface and the aqueous dispersing medium.

Sodium dodecyl sulfate [SDS] is one of the most employed and well-characterized ionic surfactant since it forms, by spontaneous self-assembly in water, a homodisperse and thermodynamically stable colloidal suspension of spherical micelles [2].

In the last years, the mechanism by which counterions or other charged entities could bind to ionic micelles and affect their structure was extensively investigated [3]. The ligand affinity to complex counterions seems to be the main driving force that induces changes in the micellar structure and, moreover, alters intermicelle interactions.

In this context, great attention was directed to the modifications in the micellar structure induced by specific counterion complexing molecules, such as macrocyclic ligands [4,5]. Due to their shape and size, macrocyclic ligands can recognize specific ions and/or small organic molecules at an interface [6]. This issue is particularly relevant when they interact with a micelle or close to a vesicular interface, thus modifying the interfacial properties depending on their specific chemical and structural properties. These properties find interesting applications in technological and industrial environments, such as the separation of ions and isotopes, transport across interfaces, liquid–liquid and liquid–solid phase-transfer reactions, dissolution of organic salts in apolar solvents, ion-selective electrodes [7–9]. Moreover, these macromolecules are considered models for carrier-mediated transport of cations across membranes, where micelles have been often used as membrane mimetic systems [10].

Despite the extensive investigations, the interfacial mechanism of interaction, the macrocycle location at the micellar interface of water-soluble macrocycles (crown ethers, cryptands, etc.) and changes in micellar structures have been long controversial (see [4,11–13] and refs. cited therein).

Recently, the behavior of sodium and lithium dodecyl sulfate micelles [14] upon the complexation of counterions by macrocyclic [2.2.2] cryptand was studied by small-angle neutron scattering. This investigation revealed that, in spite of the good solubility of the cryptand in water, C222 molecule is partitioned at micellar surface and penetrates below the polar head group region [14]. Interestingly,

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C222 molecule is able to decrease the effective micellar charge and the average aggregation number, as well as to increase the shell thickness. This picture has been also confirmed by molecular dynamics experiments [15].

Further studies on sodium dodecyl sulfate micelles in the presence of two different macrocyclic ligands, the cryptand C222 and the 18-crown-6 [18C6] ether have been carried out in order to clarify some aspects of the micelle-ligands complexation [11]. Preliminary results obtained by Dynamic Light Scattering, Electrophoresis and Small Angle X-rays Scattering show that the progressive screening of the surface charge, due to the neutralization effect of the surfactant by ligands, is accompanied by the aggregation of ligands-decorated micelles. Interestingly, size and overall charge of clusters appear to be related to the molar surfactant to ligands ratio (data not shown). These effects need to be further clarified in order to characterize this new cluster phase and to understand the mechanism of cluster formation and the stability and reversibility properties of the aggregates.

Recently, a great interest was directed towards the investigation of cluster phase formation, since it is related to the problem of spontaneous self-assembly of colloidal systems, where an electrostatic repulsion and a short-range electrostatic attraction coexist (for a review, see Bordini et al. [16] and references cited therein). In particular, in a large variety of systems, such as complexes between charged polymers (polyelectrolytes) and oppositely charged micelles, latex particles, dendrimers, ferric oxide particles, phospholipid vesicles (liposomes) and ‘hybrid niosome’ vesicles, the aggregation behavior is characterized by the presence of stable clusters close to the charge neutralization point. This aggregation cannot be completely justified within the framework of classical DLVO theory and has not been yet completely clarified [16].

When charged colloidal particles interact with oppositely charged macroions, as multivalent ions or polyelectrolytes, the electrostatic repulsive interactions between adsorbed macroions at the particle surface drive the formation of a non-uniform distribution of the electrical charge at the particle surface, which appears as ‘decorated’ by discrete domains of charge with alternate signs (‘charge-patches’).

As Velegol and Twarog [17] have shown, a non-uniform distribution of the electric charge at the surface of colloidal particles results in an inter-particle potential that, even in the case of like-charged particles, has an attractive component and, in certain conditions, a potential barrier arises, favoring the stabilization of clusters of finite size.

For example, the presence of a long-lived cluster phase of finite size observed in oppositely charged liposomes–polyelectrolyte co-suspensions can be due to a fine balance between long-range repulsive and short-range attractive interactions, both of electrostatic nature [18,19].

A similar mechanism may be invoked to explain the aggregation of charged SDS micelles in the presence of macrocyclic ligands which, due to the complex structure of the molecule, can complex the interfacial counterions at the micelle surface, thus decreasing the overall charge of micelle itself and yielding a non-homogeneous ‘charge patch’ distribution of the ligand-decorated (LD) micelle, which may furthermore drive the LD-micelle aggregation cluster.

In this work, we investigated the radiowave dielectric properties of a two-component aqueous ionic micellar solutions of SDS in the presence of two macrocyclic ligands, [2.2.2]cryptand [C222] and 18-crown-6 [18C6] ether, which are recognized to be specific complexing agents for sodium [20] and are able to modify the structural and the dynamic properties of the SDS micellar system [14,21].

We performed a set of dielectric measurements on C222-SDS and 18C6-SDS systems in an extended frequency range, from 1 kHz to 50 GHz, in order to evidence the presence of the different relaxations processes characterizing the ligands–micelle system. The comparison between the dielectric spectra of SDS micellar suspension and the ones obtained in the presence of the two C222 and 18C6 macrocyclic

ligands suggests that the ligand/SDS system behaves as a two component system, where single complexes of ligands and micelles (ligand-decorated (LD)-micelles) coexist with a cluster phase formed by LD-micelles. This evidence opens further perspectives to the investigation of the aggregation behavior of LD-micelles. These aggregates can be considered as a new colloidal system, where electrostatic attraction and repulsion in competition among themselves coexist, giving rise to a cluster phase whose intriguing properties have not yet been well-defined.

2. Experimental

2.1. Materials

Aqueous micellar solutions of sodium dodecyl sulfate [SDS, $C_{12}H_{25}SO_4Na^+$, Mw = 288.4 Da] were prepared at the surfactant concentration 8 % wt:wt, well above the critical micelle concentration (cmc = 8.3 mM at 25 °C [1]). SDS was purchased from BDH, England (purity 99%). Water was from a Millipore Milli-Q apparatus. [2.2.2]-cryptand [C222] and 18-crown-6 [18C6] ether were obtained from Merck and used as received. The chemical structure and a molecular model of the C222 and 18C6 have been reported by Evans et al. [12].

The surfactant concentration was kept fixed at 8 % in weight for all the samples. Three different concentrations of C222 and 18C6 ligands were investigated (0.5, 1.0, and 1.5 ligand/surfactant molar ratios).

2.2. Dielectric measurements

The dielectric and conductometric spectra of SDS and ligand aqueous suspensions have been measured in the frequency range from 1 kHz to 50 GHz. In the low-tail of the frequency range investigated, two radio-frequency impedance analyzers, Hewlett-Packard model 4294A (in the frequency range from 1 kHz to 10 MHz) and 4291A (in the frequency range from 1 MHz to 2 GHz) were employed. In the high-frequency tail, in the range from 0.5 to 50 GHz, an Agilent N5230 Vector Network Analyzer (VNA) was used.

In the low-frequency region, the dielectric cell consists of a short section of a cylindrical coaxial line, with a characteristic impedance of 50 Ω , directly connected to the input of the meter by means of a precision APC7 connector. The input impedance $Z^*(\omega)$ (magnitude $|Z|$ and phase angle ϕ) was converted to the complex dielectric constant $\epsilon^*(\omega)$ through an appropriate lumped element electrical circuit. The electrical and geometrical cell constants were determined by measuring the complex impedance of the cell filled with standard electrolyte solutions of known permittivity and electrical conductivity. Details of the dielectric cell and the calibration procedure have been reported elsewhere [22,23].

In the high frequency region, the Agilent N5230A VNA has been used with its dielectric kit probe Agilent 85070E. The probe is immersed into a liquid solution of the material under test, contained in a glass vessel. The solution is the electrical termination of the probe, that is a section of a transmission line. The analyzer measures the complex reflection coefficient S_{11} , from which the complex dielectric constant is obtained after a calibration procedure performed with air, short connection and Millipore water.

All the measurements have been carried out at temperature $T = 21.0 \pm 0.5$ °C.

3. Results and discussion

The dielectric spectra of the micellar suspension in the presence of the two ligands C222 and 18C6 as a function of the ligand/surfactant molar ratio have been measured for a fixed surfactant concentration of 8% (wt/wt) in water, at different ligand–surfactant molar ratios (0.5, 1.0, 1.5, respectively).

We will report a preliminary phenomenological analysis of the dielectric spectra of the SDS micelles and the ones of the C222 and

18C6 ligand-SDS complexed micellar solutions. A detailed analysis of the dielectric spectra in terms of the standard electrokinetic model [24] together with the results from dynamic light scattering and SAXS measurements will be presented in a forthcoming paper.

3.1. SDS aqueous micellar solutions

The dielectric behavior of sodium dodecyl sulfate [SDS] aqueous solutions in the frequency range from 1 MHz to 50 GHz, at the temperature of $T = 21^\circ\text{C}$, is shown in Fig. 1. At the concentration investigated, $C = 8\%$ (wt/wt), the solution is composed by rather uniform-sized, spheroidal, self-assembled aggregates (micelles) with an aggregation number of the order of $N = 100$ and a diameter of $2R = 66 \text{ \AA}$ [21]. Due to the partial ionization of the sulfate groups, each micelle has a negative net surface charge density of the order of $\sigma = 2.7 \cdot 10^{-2} \text{ C/m}^2$ [21].

The dielectric spectra show three main relaxations centered at about 30 and 300 MHz and 20 GHz, respectively, besides a further dielectric relaxation at frequencies lower than 500 kHz, due to the effect of the electrode polarization. This latter contribution, caused by the polarization of the ionic atmosphere close to the electrode surface, is generally very huge and its magnitude increases with the decrease of the frequency with a scaling law $\sim \nu^{-\beta}$, covering any other possible polarization mechanisms. In our measurements, the tail of the electrode polarization contribution falls close to the region where the relaxation arising from the micellar contribution is expected, at about 30 MHz.

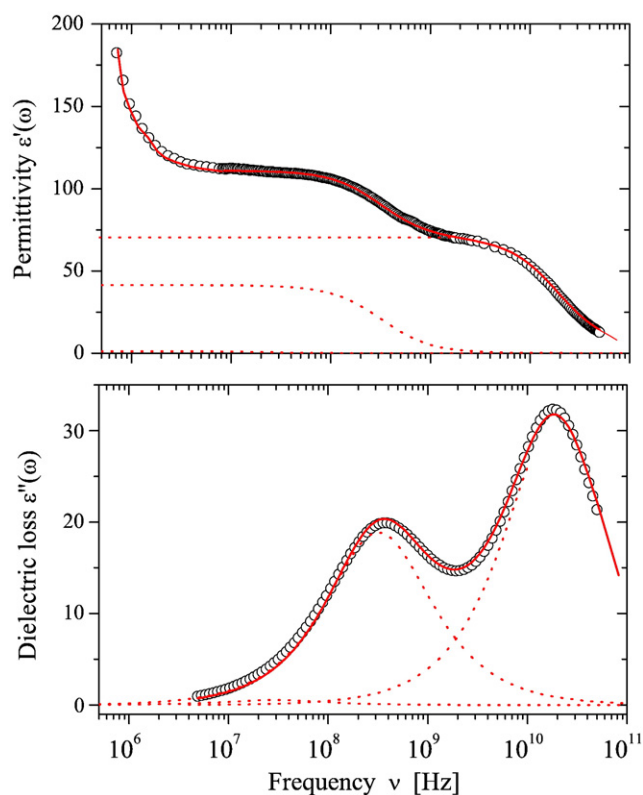


Fig. 1. Upper panel: the permittivity $\varepsilon'(\omega)$ as a function of frequency ν for SDS aqueous solution (8% wt/wt) at the temperature $T = 21 \pm 0.5^\circ\text{C}$. Full line represents the calculated values according to Eq. (1). The increase of the permittivity in the low-frequency region of the frequency window investigated is due to the beginning of the electrode polarization effect. Bottom panel: the dielectric loss $\varepsilon''(\omega)$ as a function of frequency. The three main relaxations falling at frequencies of the order of 30 MHz, 300 MHz and 20 GHz, respectively, are attributed to the polarization induced by the micellar phase and to the dipolar polarization of the aqueous phase.

The dielectric spectrum, once corrected from the electrode polarization effect, has been analyzed on the basis of the sum of three Cole-Cole relaxation functions, according to

$$\varepsilon^*(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_1}{1 + (i\nu/\nu_1)^{1-\alpha_1}} + \frac{\Delta\varepsilon_2}{1 + (i\nu/\nu_2)^{1-\alpha_2}} + \frac{\Delta\varepsilon_w}{1 + (i\nu/\nu_w)^{1-\alpha_w}} + \frac{\sigma_0}{i\varepsilon_0\omega} \quad (1)$$

where the first and the second process, characterized by the dielectric strength $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$, relaxation frequency ν_1 and ν_2 and spread parameter α_1 and α_2 , respectively, are attributed to the presence of the micellar phase and the third process, characterized by the dielectric strength $\Delta\varepsilon_w$, relaxation frequency ν_w and spread parameter α_w is attributed to the dipolar orientational polarization of the aqueous phase. ε_∞ is the high-frequency limit of the permittivity and σ_0 the d.c. electrical conductivity, ω the angular frequency of the applied electric field and, finally, ε_0 is the dielectric constant of free space.

Fig. 1, upper panel, shows the permittivity $\varepsilon'(\omega)$ as a function of the frequency and Fig. 1, bottom panel, shows the dielectric loss $\varepsilon''(\omega)$ obtained from the total dielectric loss, by subtracting the contribution of the conductivity loss $\sigma_0/\varepsilon_0\omega$, according to

$$\varepsilon''(\omega) = -\text{Im}[\varepsilon^*(\omega)] - \sigma_0/\varepsilon_0\omega \quad (2)$$

The curve fitting was carried out by the Levenberg–Marquardt method to minimize the sum of the residuals of the real part $\varepsilon'(\omega)$ and the imaginary part $\varepsilon''(\omega)$ of the complex dielectric constant $\varepsilon(\omega)$

$$\chi^2 = \sum_i [\varepsilon'_{\text{exp}}(\omega_i) - \varepsilon'_{\text{cal}}(\omega_i)]^2 + \sum_i [\varepsilon''_{\text{exp}}(\omega_i) - \varepsilon''_{\text{cal}}(\omega_i)]^2 \quad (3)$$

where the subscript *exp* and *cal* refer respectively to the experimental and calculated values. The simultaneous fit of the real and imaginary part of Eq. 1 to the experimental data ensures that the Kramer–Krönig relationships are fully verified.

The parameters deduced from the fitting procedure employed are listed in Table 1. The dielectric contribution due to the presence of the micellar component is characterized by a main dielectric relaxation process whose frequency is centered at 320 MHz, with a dielectric strength of $\Delta\varepsilon_1 = 41.5$, a spreading parameter $\alpha_1 = 0.07$ and by a smaller relaxation process centered at about 30 MHz, with a dielectric strength of $\Delta\varepsilon_2 = 1.2$ and a spread parameter α_2 close to zero.

The dielectric relaxation behavior of aqueous SDS solutions at 25°C was previously investigated by Barchini and Pottel [25] in the frequency range between 1 MHz and 30 GHz and by many other authors [26–28]. These authors analyzed the dielectric spectra by means of a superposition of a Cole–Cole or Debye relaxation functions for the micellar component and by a simple Debye relaxation function for the aqueous component, keeping its dielectric parameters (relaxation time and dielectric strength) fixed to the ones reported in literature [29]. The values of the parameters we obtain from our fitting procedure for SDS micellar solutions are in very good agreement with these previous data [25,28].

These two relaxations, characterized by frequencies of the order of some tens of MHz and some hundreds of MHz, respectively [26,27], are attributed to fluctuations of counterions at the micelle–aqueous phase interface. These findings are in good quantitative agreement with the Grosse model [30], that describes the two above stated relaxations as due to radial charge fluctuations of the diffuse layer and to the lateral movement of counterions bound to the micellar surface. Grosse [30] named these relaxations respectively δ - and γ -relaxations.

In the high-frequency region, our measurements clearly show the relaxation spectra associated with the bulk water orientational polarization process. For this relaxation process, we obtained the following values, $\nu_w = 19.2 \text{ GHz}$, $\Delta\varepsilon_w = 66$ and $\alpha_w = 0.05$, with ε_∞

Table 1

Parameters of the dielectric relaxations in SDS aqueous solution in the presence and in the absence of ligands C222 and 18C6 deduced from the fitting procedure of Eq. (1) to the experimental data.

	$\Delta\epsilon_1$	ν_1 [MHz]	α_1	$\Delta\epsilon_2$	ν_2 [MHz]	α_2	$\Delta\epsilon_w$	ν_w [GHz]	α_w
SDS	41.3	311	0.07	1.2	31	0	67	19.2	0.05
SDS-C222-0.5	13	307	0.04	22	34.5	0.039	59	17	0.05
SDS-C222-1.0	4	402	0.04	17	67.4	0.061	60	16	0.05
SDS-C222-1.5	4	402	0.09	18.5	57	0.09	58	14.5	0.05
SDS-18C6-0.5	13.5	322	0.038	18	42.6	0.07	63.5	17	0.044
SDS-18C6-1.0	8.4	353	0.084	17	66.0	0.07	60.7	16.5	0.044
SDS-18C6-1.5	6.7	380	0.084	16	80	0.05	58.5	15	0.044

close to 5, in agreement with the ones reported in literature ($\epsilon_\infty = 5.3$, $\tau = 8.3$ ps [26,29]).

3.2. SDS micellar solutions in the presence of macrocyclic ligands

Two different macrocyclic ligands were employed, cryptand C222 and crown 18C6-ether, added to the micellar solution at three different ligand-to-surfactant ratios of 0.5, 1.0, 1.5.

According to small-angle neutron scattering [SANS] measurements [14,21], both ligands solubilize at the micellar surface with the effect of increasing the thickness of the polar head region at the micelle interface, accompanied by a decrease of both the micellar surface charge and the micellar aggregation number.

This latter effect, in particular the decrease of the overall surface charge, may favor a micellar aggregation process, yielding to the coexistence of single LD-micelles and larger aggregates, as suggested by preliminary studies carried out by means of dynamic light scattering and SAXS measurements (data not shown). In the dielectric spectra of complexed LD-micelles, a large broadening and a significant shift towards lower frequencies, as far as the relaxation of the micellar component of the whole dielectric spectrum is concerned, are clearly evidenced. The second main relaxation, in the region of some GHz, the one we have attributed to the polarization of the aqueous phase, remains practically unchanged. In this case too, the dielectric spectra have been analyzed by means of a relaxation function given by Eq. (1).

Spectra of SDS-18C6 and SDS-C222 systems for different ligand-to-surfactant molar ratio, together with the single contributions obtained from the above stated deconvolution method, are shown in Figs. 2–5, respectively, as far as the permittivity $\epsilon'(\omega)$ and the dielectric loss $\epsilon''(\omega)$ are concerned.

The values of ν_1 , α_1 and $\Delta\epsilon_1$, corresponding to the relaxation of the LD-micellar component differ from the ones determined for the SDS micelles in the absence of added ligands. In fact, as previously described, the presence of different amounts of the added ligands can modify the aggregation behavior of the system. As a consequence, a modification of the dielectric spectra is expected.

The addition of the two ligands, at the different molar ratios, promotes a slight, but visible variation also in the spectra associated with the bulk aqueous phase. We observed that the frequency ν_w is reduced from 19.2 GHz to lower values, reaching a frequency close to 15 GHz at the larger concentration of ligands. Also the values of $\Delta\epsilon_w$ decrease of some units with respect to the case of pure SDS, with the increasing concentration of both ligands (see also Figs. 3 and 5). These modifications are correlated with the micelle–ligands complexation, which alters the interface of LD-micelles by progressive reduction of the surface charge [21], until a maximum amount of bound ligand is

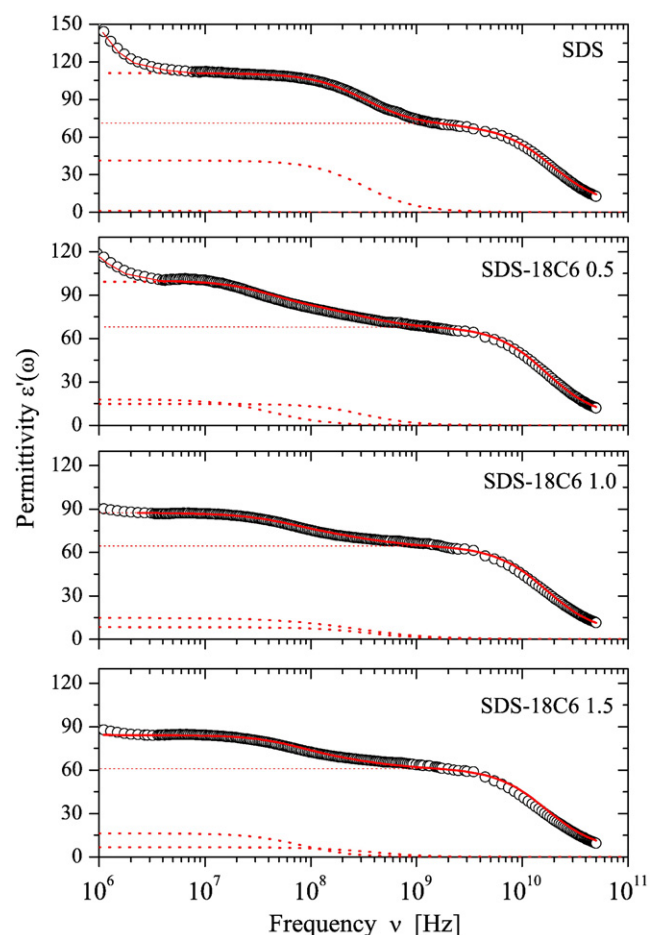


Fig. 2. Permittivity $\epsilon'(\omega)$ as a function of the frequency ν for SDS micellar aqueous solution (8% wt/wt) in the presence of different concentration of ligand 18C6 (ligand-to-surfactant molar ratio of 0.5, 1.0, 1.5). The spectrum of SDS aqueous solution in the absence of ligand is also shown (upper panel). Dotted lines represent the frequency behavior of the different relaxation processes employed in the deconvolution of the observed spectra.

reached at an equimolar ratio, where the percentage of ligand molecule per surfactant molecules at the interface is about 50%.

In a recent investigation of Buchner and coworkers [26,27] on the hydration and dynamics of SDS aqueous solutions at various surfactant concentrations, a careful analysis of dielectric spectra could show a small relaxation at approximately 2 GHz (~ 120 ps) which depends on the SDS concentration. This contribution was attributed to the water molecules with reduced mobility which are in contact with the hydrocarbon chain and to the ones hydrating the sulfate headgroups of SDS and, possibly, also to the bound Na^+ ions [26]. Bruce et al. [31] by means of MD simulations, supported this interpretation, since they observed that the motion of the water dipoles in the first two hydration layers around the headgroup oxygens is reduced by one or two orders of magnitude compared to bulk.

In our experimental conditions, we are unable to reveal the above stated relaxation of interfacial water which was revealed by Buchner et al. [26,27]. Nevertheless, it may be interesting to consider that the observed shift of the frequency ν_w of bulk water relaxation, that changes from 19.2 to 15 GHz, and the reduction of the dielectric strength ϵ_w , decreasing from 67 to values close to 60, may be actually attributed to the modification of the water spectra with respect to the two contributions of interfacial and bulk water. In fact, the presence of ligands at the micellar surface can modify the number of water molecules with reduced mobility, which are in contact with the surface of LD-micelles, with respect to the bulk molecules.

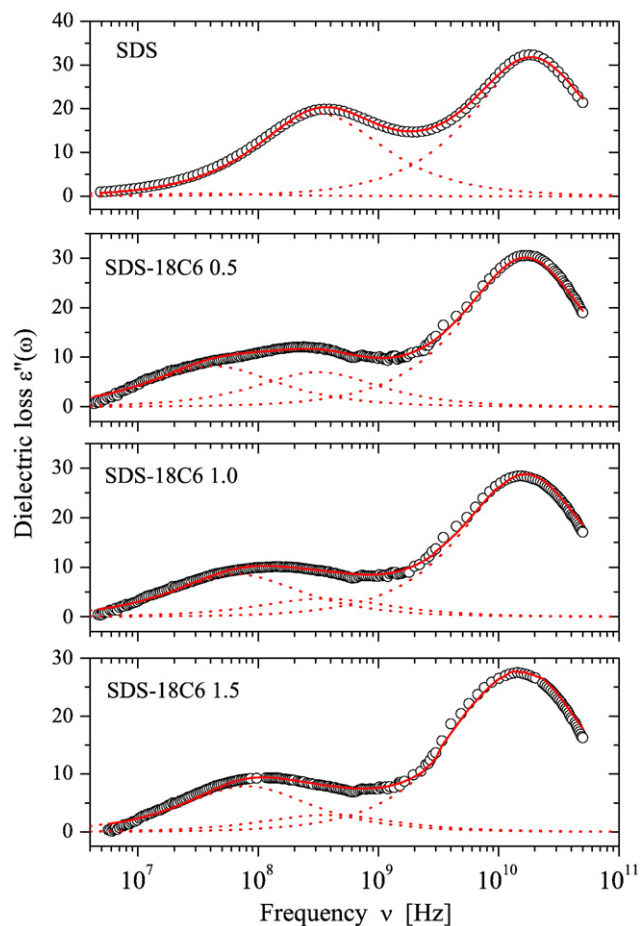


Fig. 3. Dielectric loss $\varepsilon''(\omega)$ as a function of the frequency ν for SDS micellar aqueous solution (8% wt/wt) in the presence of different concentration of ligand 18C6 (ligand-to-surfactant molar ratio of 0.5, 1.0, 1.5). The dielectric loss $\varepsilon''(\omega)$ has been obtained from the measured total loss by subtracting the contribution of the conductivity loss $\sigma_0/\varepsilon_0\omega$. The spectrum of SDS aqueous solution in the absence of ligand is also shown (upper panel) for comparison. Dotted lines represent the frequency behavior of the different relaxation processes employed in the deconvolution of the observed spectra.

In the presence of both the ligands investigated, a large effect is observed when we consider the parameters of the relaxation processes corresponding to the micellar component, which are largely modified with respect to the ones of the SDS micelles (see Table 1). The main contribution (centered around 300 MHz) in the case of pure SDS micelles, shifts towards higher frequencies with a concomitant decrease of the dielectric strength, with the increase of SDS-ligands molar ratio. Also the relaxation contribution centered at 30 MHz is shifted toward larger frequencies and its amplitude is largely increased. As above stated, these two contributions are due to the lateral conduction of the counterions bound to the micellar surface and to the radial charge fluctuation, respectively [30]. Our result suggests that a reorganization of the charged interface of LD-micelles occurs as a consequence of the interaction between ligands and micelles and the intensity of this effect appears to be connected to the amount of complexed ligand.

According to the model proposed by Evans and coworkers [4,32], the ligands remain attached to the micellar surface and screen, at least partly, the surface charge, due to a neutralizing effect of the surfactant head group. The size and the aggregation number of the micelles are decreased, as well as the thickness of the interfacial micellar layer [5,14]. In the case of C222, the interfacial adsorption of the ligand is driven by the hydrophobic repulsion of the exposed surfaces in the presence of an intermolecular repulsive electrostatic contribution due to the sodium ion trapped inside the ligand cage [14]. The dielectric

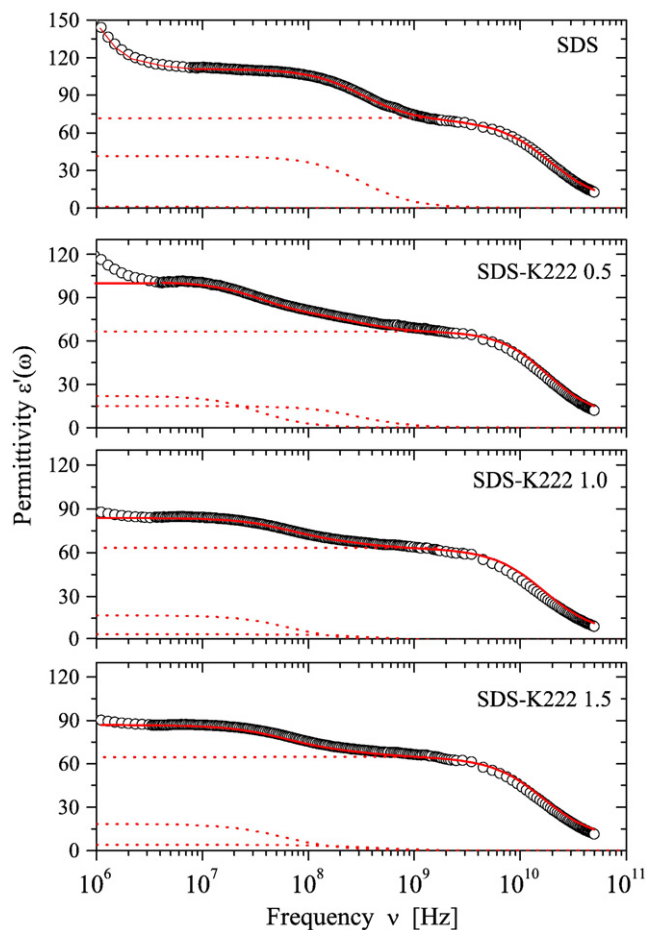


Fig. 4. Permittivity $\varepsilon'(\omega)$ as a function of the frequency ν for SDS micellar aqueous solution (8% wt/wt) in the presence of different concentration of cryptand C222 (ligand-to-surfactant molar ratio of 0.5, 1.0, 1.5). The spectrum of SDS aqueous solution in the absence of ligand is also shown (upper panel) for comparison. Dotted lines represent the frequency behavior of the different relaxation processes employed in the deconvolution of the observed spectra.

spectra of the LD-micelles appear modified as a consequence of the reorganization of the interfacial micellar layer in terms of surface charge, size and counterion mobility.

The relaxation times of γ - and δ -processes are more and more decreased with the increasing amount of bound ligand. These changes may be connected with a re-organization of the system with the increase of large aggregates of LD-micelles, which induces a longer relaxation time and an increased dielectric strength and a decrease of the number of single micelles which induces the observed decrease of the δ -relaxation.

Further investigations on the structural properties of this system, such as size and shape of aggregates, may contribute to an interpretation of the dielectric spectra, also in term of the standard electrokinetic model. These aspects of the complexation of ligands and SDS micelles will be considered in a forthcoming paper.

4. Conclusion

The relaxation processes occurring in SDS micellar solution upon complexation with two different macrocyclic ligands, the [2.2.2] cryptand and the 18C6 crown ether, were investigated by means of dielectric spectroscopy in a wide frequency range, from 1 kHz to 50 GHz. The dielectric spectra were analyzed by considering different contributions associated with the micellar component and the

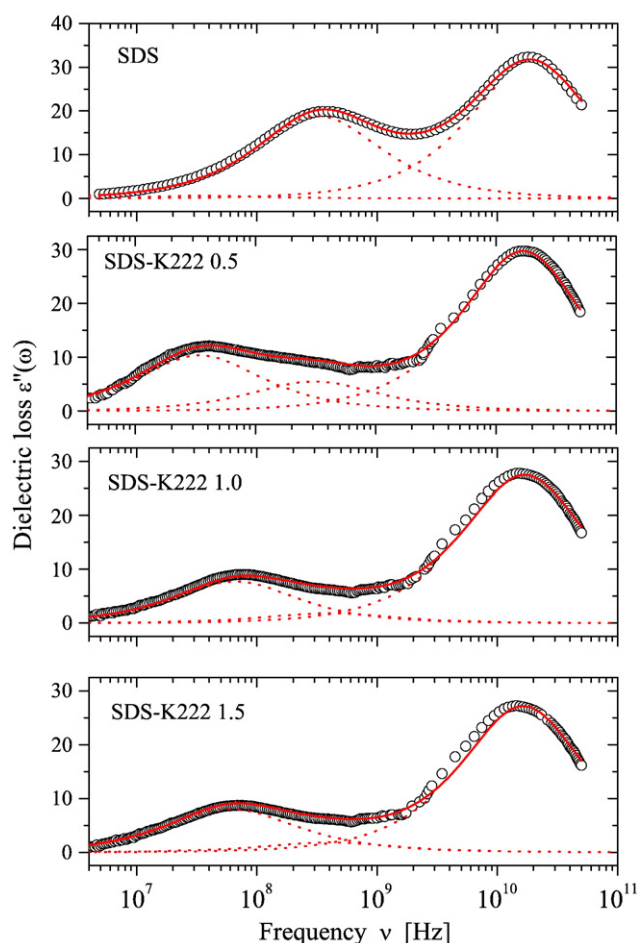


Fig. 5. Dielectric loss $\varepsilon''(\omega)$ as a function of the frequency ν for SDS micellar aqueous solution (8% wt/wt) in the presence of different concentration of cryptand C222 (ligand-to-surfactant molar ratio of 0.5, 1.0, 1.5). The dielectric loss $\varepsilon''(\omega)$ has been obtained from the measured total loss by subtracting the contribution of the conductivity loss $\sigma_0/\varepsilon_0\omega$. The spectrum of SDS aqueous solution in the absence of ligand is also shown (upper panel) for comparison. Dotted lines represent the frequency behavior of the different relaxation processes employed in the deconvolution of the observed spectra.

relaxation of the bulk water. Measurements evidenced the presence of three distinct relaxation regions, two of them due to the micellar component, a small one centered around 30 MHz and a main one at 300 MHz, and a larger one close to 20 GHz, corresponding to the bulk water relaxation contribution. The presence of both ligands deeply alters the dielectric spectra, with a broadening of the micellar contribution, due to a shift to higher frequencies of both the δ - and γ -relaxation and a redistribution of their dielectric strength,

corresponding to a modified LD-micellar interface in term of surface charge and thickness. The observed changes in relaxation behavior may be due to a new organization of the system, where the ligand-decorated (LD) micelles aggregate in large clusters, due to the progressive reduction of the surface charge. These results highlight the possibility of inducing the aggregation of LD-micelles by controlling the amount of complexed ligand at the micellar surface.

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References

- [1] R. Williams, J. Phillips, K. Mysels, *Trans. Faraday Soc.* 51 (1955) 728.
- [2] E. Sheu, S.H. Chen, *J. Phys. Chem.* 92 (1988) 4466.
- [3] V. Degiorgio, M. Corti (Eds.), *Physics of Amphiphiles: Micelles, Vesicles and Microemulsions*, North-Holland, 1985.
- [4] D.F. Evans, J. Evans, R. Sen, G.G. Warr, *J. Phys. Chem.* 90 (1986) 5500.
- [5] P. Baglioni, C.M.C. Gambi, R. Giordano, J. Teixeira, *J. Physica B* 231 (1995) 597.
- [6] R.M. Izatt, K. Pawlak, S.S. Bradshaw, R. Bruening, *Chem. Rev.* 91 (1991) 1721.
- [7] A.V. Baya, N. Poonia, *Coord. Chem. Rev.* 87 (1988) 55.
- [8] J.L. Arwood (Ed.), *Inclusion Phenomena and Molecular Recognition*, Plenum, New York, 1990.
- [9] F. Vogtle, *Supermolecular Chemistry*, Wiley, New York, 1991.
- [10] J.H. Fendler, Vol. chapter 2., *Membrane Mimetic Chemistry*, Wiley, New York, 1982.
- [11] P.A. Quintela, R.C.S. Reno, A.E.J. Kaifer, *J. Phys. Chem.* 91 (1987) 3582.
- [12] D. Evans, J. Evans, R. Sen, G. Warr, *J. Phys. Chem.* 92 (1988) 784.
- [13] G. Capuzzi, E. Fratini, F. Pini, P. Baglioni, A. Casnati, J. Teixeira, *Langmuir* 16 (2000) 188.
- [14] L. Scaffei, L. Lanzi, C.M.C. Gambi, R. Giordano, P. Baglioni, J. Teixeira, *J. Phys. Chem. B* 106 (2002) 10771.
- [15] N. Muzet, E. Engler, G. Wipff, *J. Phys. Chem. B* 102 (1988) 10772.
- [16] F. Bordini, S. Sennato, D. Truzzolillo, *J. Phys. Condens. Matter* 21 (2009) 203102.
- [17] D. Velegol, P. Thwar, *Langmuir* 17 (2001) 7687.
- [18] S. Sennato, D. Truzzolillo, F. Bordini, C. Cametti, *Langmuir* 24 (2008) 12181.
- [19] D. Truzzolillo, F. Bordini, F. Sciortino, C. Cametti, *Eur. Phys. J. E Soft Matter* 29 (2009) 229.
- [20] G.W. Gokel, *Crown ethers and cryptands*, Royal Society Of Chemistry, Cambridge, U.K., 1994.
- [21] P. Baglioni, C.M.C. Gambi, R. Giordano, J. Teixeira, *Colloids Surf. A* 21 (1997) 47.
- [22] S. Takashima, A. Casaleggio, F. Giuliano, M. Morando, P. Arrigo, S. Ridella, *Biophys. J.* 49 (1986) 1003.
- [23] F. Bordini, C. Cametti, G. Paradossi, *Biopolymers* 40 (1996) 485.
- [24] S.S. Dukhin, V.N. Shilov, *Dielectric Phenomena and the Double Layer in Disperse Systems and Polyelectrolytes*, Halsted, New York, 1974.
- [25] R. Barchini, R. Pottel, *J. Phys. Chem.* 98 (1994) 7899.
- [26] P. Fernandez, S. Schrodle, R. Buchner, W. Kunz, *Chem. Phys. Chem.* 4 (2003) 1065.
- [27] R. Buchner, C. Baar, P. Fernandez, S. Schrodle, W. Kunz, *J. Mol. Liq.* 118 (2005) 179.
- [28] L. Lanzi, L. Lanzi, M. Carlà, C.M.C. Gambi, *J. Colloid Int. Sci* 330 (2009) 156.
- [29] J.B. Hasted, *Aqueous dielectric*, Chapman and Hall, London, 1973.
- [30] C. Grosse, K. Foster, *J. Phys. Chem.* 91 (1987) 6415.
- [31] C.D. Bruce, S. Senapati, M.L. Berkowitz, L. Perera, M.D.E. Forbes, *J. Phys. Chem. B* 106 (2001) 10902.
- [32] K.A. Payne, L.J. Magid, D.F. Evans, *Colloid Polymer Sci* 73 (1978) 10.