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Dielectric spectroscopy by differential measurements in transmission lines on sodium dodecyl sulfate micelles in water

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Abstract

A sodium dodecyl sulfate micellar solution in water was studied by Broad Band Dielectric Spectroscopy to investigate the relaxation processes. The experimental complex permittivity vs. frequency was analyzed by fitting the experimental data to three different models. The simplest one uses two Debye relaxation processes, one for bulk water and one for micelles contribution. The second model uses a Debye relaxation process for water and a Cole–Cole one for micelles, the third uses two Debye relaxation processes instead of the Cole–Cole one. Step amplitudes and relaxation time constants were obtained for the different processes. The sample Ohmic conductivity was also studied.
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1. Introduction

Aqueous sodium dodecyl sulfate (SDS, $C_{12}H_{25}$-$SO_4^-Na^+$) micellar solutions were investigated by Broad Band Dielectric Spectroscopy (BBDS) in the frequency range $f = 100$ MHz–3 GHz. The study of the dielectric relaxation processes, characterized by the motion of dipolar species at molecular and supra-molecular level, probes the dynamics of the system. We chose the SDS system because the micelles microstructure is known from small-angle neutron scattering (SANS) [1–4]. On the contrary, the dynamic properties of the micelles are not yet understood.

After a preliminary study of the SDS micellar solutions with different concentrations [5], in this paper, one surfactant concentration was studied by several models to compare the results with those of other groups working on the same subject [6,7].

The micelle, dispersed in aqueous phase, is an aggregate of self-assembled surfactant molecules with the hydrophobic tails mainly located in the core and the hydrophilic polar heads at the surface. For the surfactant of this work, the head is composed by the sulfate group with one negative charge and by the positive sodium counterion. In the micelle, some sodium counterions are bound to the heads, the others are in a diffuse – or Gouy–Chapman – layer [8–10]. Thus we can distinguish among three concentric spherical regions: (a) the hydrophobic core of the micelle, (b) the interfacial layer in which polar head groups, some counterions and water molecules are located, and (c) the diffuse layer with the remaining unbound counterions in aqueous phase. If we name micelle the sum of core

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and interfacial layer, the negatively charged micelle is surrounded by a region with equal charge of opposite sign, the diffuse layer. The aqueous phase in which micelles are dispersed is composed of water and surfactant molecules in the monomeric state at the critical micellar concentration (cmc) (8.3 mM at 25 °C [11] for SDS micelles).

In the studied frequency range, the bulk water behavior is well described by a single Debye relaxation process with a relaxation time of $\tau_w \sim 8$ ps [12]. To study the relaxation processes, induced by the SDS addition to water, three different models were taken into account. The first model adds a single Debye relaxation process to that of water, a second model adds a Cole–Cole process instead of the single Debye to take into account the spread of relaxation processes. The third model uses two different Debye relaxation processes instead of the Cole–Cole or single Debye.

In our previous work [5], only the Cole–Cole model was employed.

2. Materials and methods

A micellar solution of SDS in water was prepared at surfactant concentration $C = 29.8$ mM. SDS was from BDH, England (purity 99%). Water was from a Millipore Milli-Q apparatus. The measurements were performed at temperature of 22.0 ± 0.5 °C.

An Anritsu MS4661A Vector Network Analyzer (VNA) was employed and a new double-differential method was used [13]. The measuring cells were pieces of coaxial transmission line machined from ISO316 steel and filled with the sample as dielectric; the outer and inner diameters of the cavity were 7.70 and 3.35 mm, respectively. Cell lengths of 30 and 80 mm were used. The cells had identical characteristics but for the length. All dimensions had an accuracy of 0.05 mm. The cell was connected to the VNA by two coaxial cables (Sucoflex 104 with type-N connectors). The scattering parameters of the cell were measured by the VNA to obtain the cell propagation constant $\gamma = \sqrt{(r + j\omega l)(g + j\omega c)}$, where r, l, g and c are the resistance, inductance, conductance and capacitance per unit length of the cell and ω is the angular frequency, $\omega = 2\pi f$. For the sample of this work, that is not magnetic, the constant r and l depend only on the cell material and do not change between empty and filled cells, while g and c are affected by the sample properties: $g = (\sigma + \omega\varepsilon_0\varepsilon'')/k$ and $c = \varepsilon_0\varepsilon'/k$, where σ is the Ohmic conductivity, ε_0 is vacuum dielectric permittivity, k is a cell geometric constant, ε' and ε'' are the real and imaginary part of the complex dielectric permittivity $\hat{\varepsilon} = \varepsilon' - j\varepsilon''$ (where $j^2 = -1$). By repeating the measurements with two cells of different length, both cells filled and empty, it is possible to cancel the contribution of the cell geometry and to extract the complex

permittivity and the Ohmic conductivity of the sample. The details of the calculations, the drawing of the cells and a full discussion of the method can be found in [13].

3. Results

The micellar solution was investigated at 22 °C with surfactant concentration of $C = 29.8$ mM, above the critical micellar concentration. Measurements have been performed taking 500 points in logarithmic scale on the frequency range from 100 MHz to 3 GHz. Fig. 1 shows the experimental dielectric spectra of water and of the SDS micellar solution.

The dielectric behavior of the bulk water is known from the literature [12] and it is characterized by two relaxation processes with relaxation time constants of ~ 1 ps and ~ 8 ps, ascribed to reorientation of free water molecules and to relaxation of the hydrogen-bound network of water.

In the studied frequency range, the water permittivity spectrum is well described by a single Debye relaxation process

$$\hat{\varepsilon}_w(\omega) = \varepsilon_\infty + \frac{\Delta\varepsilon_w}{1 + j\omega\tau_w}, \tag{1}$$

where ε_∞ is the water permittivity at high frequency adjusted for the contribution of free water molecules relaxation, $\Delta\varepsilon_w$ is the step amplitude of ε' and τ_w is the relaxation time constant due to the hydrogen-bound network. These values at 22 °C were taken from [14] ($\varepsilon_\infty = 5.72$, $\Delta\varepsilon_w = 79.45$, $\tau_w = 8.93$ ps) as their determination is well beyond our frequency range.

The addition of surfactant to water leads to changes of both the real and imaginary parts of the dielectric
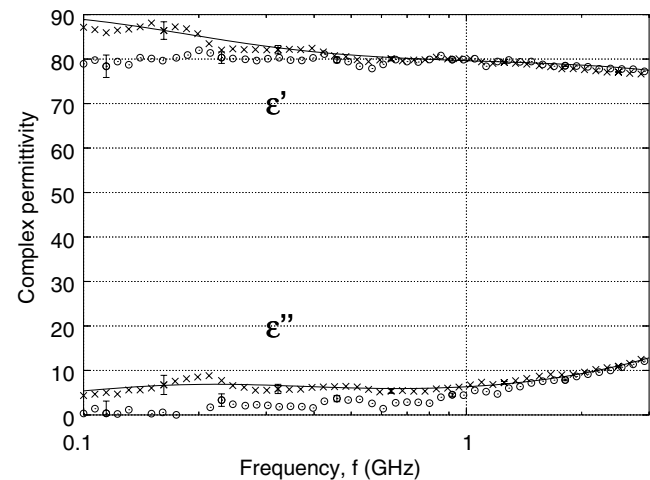

Fig. 1. Experimental dielectric spectra of water (○) and of 29.8 mM SDS micellar solution (×). Error bars are standard deviations. Solid lines are the fitted function of Eq. (4). Only a part of experimental points are drawn.

Table 1
Results of the fit of the complex dielectric permittivity spectrum by three models

Model	ϕ	σ (Ω^{-1} m^{-1})	$\Delta\varepsilon$	τ (ps)	h	$\Delta\varepsilon'$	τ' (ps)	χ^2
Single Debye	0.989 ± 0.001	0.091 ± 0.001	10.6 ± 0.2	670 ± 20				1.2
Cole–Cole	0.985 ± 0.001	0.085 ± 0.001	13.3 ± 0.5	850 ± 40	0.10 ± 0.01			1.0
Double Debye	0.989 ± 0.001	0.087 ± 0.001	10.9 ± 0.3	840 ± 30		1.2 ± 0.1	120 ± 10	1.0

permittivity through the investigated frequency range, suggesting the presence of some relaxation processes due to micelles formation. However, from the observation of the spectra it is not possible to distinguish among the several processes.

To fit the experimental data, three different models of the micelles contribution were used: a single Debye, a Cole–Cole and a double Debye relaxation model.

The whole expression of dielectric permittivity with the single Debye model is

$$\hat{\varepsilon}(\omega) = \phi\left(\varepsilon_\infty + \frac{\Delta\varepsilon_w}{1 + j\omega\tau_w}\right) + \frac{\Delta\varepsilon}{1 + j\omega\tau} + \frac{\sigma}{j\omega\varepsilon_0}, \quad (2)$$

where ϕ is the volume fraction of water in the sample, $\Delta\varepsilon$ and τ are the step amplitude in ε' and the relaxation time due to micelles; σ is the whole Ohmic conductivity of the micellar solution.

The relaxation process of micelles arises from the motion of the bound counterions in the interfacial layer [6,7,15–17].

The Cole–Cole model takes into account the spread of relaxation processes by addition of the parameter h

$$\hat{\varepsilon}(\omega) = \phi\left(\varepsilon_\infty + \frac{\Delta\varepsilon_w}{1 + j\omega\tau_w}\right) + \frac{\Delta\varepsilon}{1 + (j\omega\tau)^{1-h}} + \frac{\sigma}{j\omega\varepsilon_0}. \quad (3)$$

The double Debye model gives

$$\hat{\varepsilon}(\omega) = \phi\left(\varepsilon_\infty + \frac{\Delta\varepsilon_w}{1 + j\omega\tau_w}\right) + \frac{\Delta\varepsilon}{1 + j\omega\tau} + \frac{\Delta\varepsilon'}{1 + j\omega\tau'} + \frac{\sigma}{j\omega\varepsilon_0}, \quad (4)$$

where $\Delta\varepsilon'$ and τ' are introduced to describe an additional relaxation process probably due to the interfacial bound water molecules [7,16,17].

The experimental data were fitted to Eqs. (2)–(4) and the free fitting parameters were reported in Table 1.

4. Discussion

The fit quality was evaluated by the χ^2 value. This was higher for the single Debye model, indicating that this model is too simple to fit the experimental data. On the contrary, the Cole–Cole and the double Debye models give similar χ^2 values and close to 1. The single Debye model takes into account only the diffusion of interfacial (or bound) counterions. However, also the bound water molecules of the interfacial region presumably lead to another relaxation process, as also hypoth-

esized in [7,16,17]. Thus the double Debye model likely takes into account both counterions diffusion and water reorientation in the interfacial region.

The Cole–Cole model takes into account a spread of relaxation times, probably a weighted average of the above two interfacial relaxation processes [7].

Our experimental values of $\Delta\varepsilon$ and τ can be compared with those of the other groups.

Our data of Table 1 are in good agreement with Ref. [6], where $\Delta\varepsilon = 13.6$ and $\tau = 0.91$ ns were found by a Cole–Cole model used to study a SDS micellar solution at $C = 30$ mM and 25 °C.

In [7], where a sum of Debye relaxation processes is used to describe the dielectric spectra of a 25 mM SDS micellar solution at 25 °C, the values $\Delta\varepsilon = 4.08$, $\tau = 0.463$ ns, $\Delta\varepsilon' = 0.95$ and $\tau' = 0.158$ ns are reported. Our $\Delta\varepsilon$ and τ are higher, possibly because our lower frequency is too high to detect another low frequency relaxation process displayed in spectra of Ref. [7]. Our $\Delta\varepsilon'$ and τ' are in good agreement with [7].

The conductivity values of the sample for the three models are very similar, and are in agreement with $\sigma = 0.125$ Ω^{-1} m^{-1} [6] and $\sigma = 0.0905$ Ω^{-1} m^{-1} [7].

Taking into account the conductivity contributions of all the ions in the micellar solution, $\sigma = 0.090$ Ω^{-1} m^{-1} can be calculated as reported in [18]

$$\sigma = e^2 N_A[(u_{Na^+} + u_{DS^-})cmc + (\alpha u_{Na^+} + N\alpha^2 u_M)(C - cmc)], \quad (5)$$

where e is the electron charge, N_A is the Avogadro number, $u_{Na^+} = 3.24 \times 10_{11}$ kg^{-1} s is the Na$^+$ mobility [19], $u_{DS^-} = 1.48 \times 10^{11}$ kg^{-1} s is the DS$^-$ mobility [20], α is the micelle fraction of dissociated counterions, N is the average aggregation number, and u_M is the mobility of the micelle, with total radius R. From Stokes law $u_M = (6\pi\eta R)^{-1}$, where η is the water viscosity ($\eta = 1.000$ cps at 25 °C [19]). $\alpha = 0.181$, $N = 69.8$ and $R = 22.5 \times 10^{-10}$ m are available at 25 °C for a 25 mM concentration from SANS [1].

Our experimental value of σ (Table 1) is in good agreement with the value calculated by Eq. (5).

The ϕ values for all the models are very similar, and are in good agreement with the expected value, $\phi = (4/3)\pi R^3 N_A(C - cmc)/N = 0.988$.

In summary, the 29.8 mM SDS micellar solution was investigated by BBDS. The contribution of the micellized surfactant was analyzed by means of several models. Two relaxation processes were found to better

describe the dielectric spectrum. The main process, that arises from the motion of the bound counterions in the interfacial layer [6,7,15–17], is characterized by the step amplitude $\Delta\varepsilon = 10.9 \pm 0.3$ and the relaxation time constant $\tau = (840 \pm 30)$ ps, the other process, due to the interfacial bound water molecules [7,16,17], by $\Delta\varepsilon' = 1.2 \pm 0.1$ and $\tau = (120 \pm 10)$ ps. The micellar Ohmic conductivity was also measured, $\sigma = (0.087 \pm 0.001)$ $\Omega^{-1}\,m^{-1}$.

Acknowledgements

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