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Conductivity and Relative Permittivity of Sodium *n*-Dodecyl Sulfate and *n*-Dodecyl Trimethylammonium Bromide

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The electrical conductivity and relative permittivity of the amphiphilics sodium *n*-dodecyl sulfate (SDS) and *n*-dodecyl trimethylammonium bromide (DTAB) were measured as a function of frequency (200 kHz to 20 MHz) at various concentrations. Both methods lead to similar values of the critical micelle concentration (cmc) for both surfactants despite the greater sensitivity of the relative permittivity to structural transformations derived from the formation of the micelles. The electrical conductivity is seen to be rather independent of frequency whereas the relative permittivity exhibits abrupt transitions in the neighborhood of the cmc. Tridimensional plots of the electrical conductivity as a function of the frequency and molar concentration show a gradual transition to the micellar state that takes place in the cmc concentration range. Relative permittivity values have been analyzed independently for concentrations above and below the cmc. In the micellar state both substances show a quadratic dependence of the relative permittivity on concentration. Below the cmc the relative permittivity shows a linear dependence on concentration in the monodisperse (SDS) region and a quadratic dependence in the polydisperse (DTAB) region. The relative permittivity is a better indicator of the existence of amphiphilic preaggregation than the electrical conductivity.

Introduction

The existence of a critical micelle concentration (cmc) indicates the presence of aggregation of amphiphilic molecules in solution. Several theoretical models such as the mass action model (Phillips, 1955; García-Mateos et al., 1990; Sarmiento et al., 1995) and the phase separation model (Shinoda and Hutchinson, 1962; Moro and Rodriguez, 1991) have been proposed to explain the results. The knowledge of the cmc is also important to the calculation of the thermodynamic parameters, which confirms the scientific interest of a precise determination of the cmc.

The cmc is a narrow concentration range where the physical properties of a amphiphilic solution show an abrupt change due to cooperative formation of micelles in the bulk solution. Several definitions have been proposed to explain this phenomenon (Hall, 1967; Tanford, 1974; Israelachvili et al., 1976). The concentration range strongly depends of the physical property observed, and the precision of the measurement is a function of the width of the transition region that shows the change in the physical property (Pérez-Rodríguez et al., 1998). This width is directly related to the existence of a preaggregation at concentrations lower than the cmc and the subsequent polydispersity of the medium. Thus, it is essential to employ physical methodologies which are highly sensitive to structural changes for determining the critical micelle concentration. In this study we have determined the critical micelle concentrations of sodium *n*-dodecyl sulfate and *n*-trimethylammonium bromide (SDS and DTAB) through measurements of the relative permittivity of the solutions at various frequencies. We have compared the results to the previous results of the cmc determined by electrical conductivity. The relative permittivity shows a greater sensitivity to both frequency and concentration changes

Table 1. Electrical Conductivity of Sodium *n*-dodecyl Sulfate at Various Concentrations for Different Frequencies at the Temperature 298.15 K

	$10^4\kappa'/(\mathrm{S\ m^{-1}})$		
$c/(\mathrm{mmol\ L^{-1}})$	200 kHz	2.1 MHz	20 MHz
2.0	133	131	126
2.5	155	152	148
3.0	200	198	194
3.5	223	220	215
4.0	268	266	261
4.5	291	288	282
5.0	337	334	329
5.5	359	356	348
6.0	403	401	395
6.5	427	424	415
7.0	467	464	458
7.5	489	486	479
8.0	523	521	514
8.5	543	540	534
9.0	564	561	556
9.5	581	578	570
10.0	595	592	588
10.5	611	608	600
11.0	622	620	616
11.5	639	636	631
12.0	647	645	645
12.5	665	663	660
13.0	671	669	671
13.5	694	692	692
14.0	698	696	698
14.5	720	718	719
15.0	723	721	724
15.5	744	742	742
16.0	746	744	748
16.5	768	767	766

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Table 2: Electrical Conductivity of *n*-Dodecyl Trimethylammonium Bromide at 298.15 K as a Function of Concentration for Different Frequencies

	$10^4 \kappa'$/S m^{-1}		
c/(mmol L^{-1})	200 kHz	2.1 MHz	20 MHz
1.0	100	98	94
2.5	243	240	236
3.0	290	287	283
3.5	336	333	329
4.0	382	380	375
4.5	429	426	421
5.0	475	472	467
5.5	520	518	512
6.0	566	563	557
6.5	612	609	602
7.0	657	654	647
7.5	700	698	688
8.0	746	743	734
8.5	793	790	781
9.0	842	840	830
9.5	886	884	874
10.0	928	925	916
10.5	973	971	960
11.0	1017	1015	1003
11.5	1061	1059	1046
12.0	1105	1103	1092
12.5	1150	1147	1135
13.0	1193	1190	1176
13.5	1237	1234	1222
14.0	1278	1276	1263
14.5	1318	1315	1302
15.0	1354	1351	1338
15.5	1382	1380	1366
16.0	1404	1401	1388
16.5	1421	1419	1406
17.0	1437	1434	1422
17.5	1451	1448	1436
18.0	1465	1462	1451
18.5	1478	1475	1464
19.0	1490	1488	1476
19.5	1502	1500	1488
20.0	1515	1513	1500

even in polydisperse solutions such as DTAB, and therefore it provides a more accurate way to experimentally determine of the cmc.

Experimental Section

Chemicals. Sodium *n*-dodecyl sulfate with a purity > 99% was obtained from Fluka, and *n*-dodecyl trimethylammonium bromide with a purity > 97% was obtained from Lancaster MTM Research Ltd. Solutions were made in double-distilled, deionized, and degassed water.

Apparatus and Procedure. Conductivities and relative permittivities of colloid solutions were measured with a HP 4285A Precision LCR meter equipped with a HP E5050A colloid dielectric probe operating in a frequency range between 200 kHz and 20 MHz. The probe was especially designed to avoid the polarization that occurs in the plain condensor probe. The cell design was conceived to obtain the highest degree of accuracy. It consists of a cylinder of 8 cm diameter and 5 cm height with the probe entrance at a side. This geometry ensures the probe head to be always surrounded by at least 2 cm of solution during the measurement process, which avoids possible interferences of the cell walls. The cell was inmersed in a Techne, model RB-12A thermostated bath equipped with a Tempunit TU-16A thermostat. Temperature control was achieved using an Anton Paar DT 100-30 thermometer, maintaining the temperature constant at 298.15 ± 0.01 K. To homogenize the solution, a Variomag 20P shaker was used.

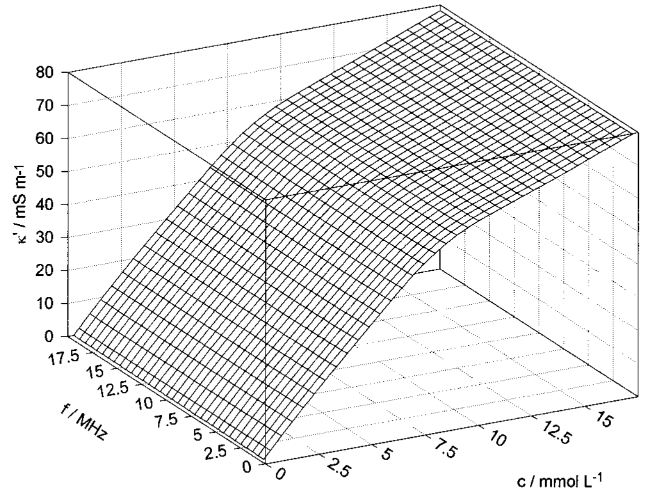

Figure 1. Plot of the real part of the electrical conductivity (k') of an aqueous solution of sodium *n*-dodecyl sulfate (SDS) against frequency and molar concentration at 298.15 K as given by eq 1 with the coefficients listed in Table 3. The critical micelle concentration is 8.21 mmol·L^{-1}.

Results and Discussion

Experimental measurements provide information of the complex electrical conductivity of the colloid solution. The measured real parts of the electrical conductivities of SDS and DTAB for different frequencies and concentrations above and below cmc are presented in Tables 1 and 2, respectively. These data were analyzed by means of the following function:

$$\kappa'(c,\omega) = \sum_{i=0}^{5} a_i c^i + b\omega \tag{1}$$

Here c is the molar concentration, ω is the frequency, and the a_i's and b are empirical constants. The computed values of the least squares fitted parameters for both SDS and DTAB are shown in Table 3 along with the respective fitting correlation. As can be seen in Figure 1, the concentration dependence of the electrical conductivity consists of a gradual decreasing of the slope from the monomer to the micellar state due to the formation of the association colloids and the consequent electric double layers (edl's) that reduce the concentration of free ions in solution (Varela et al., 1998). Even in substances that show a great degree of monodispersity, such as SDS, the determination of the cmc requires considerable numerical effort due to this relative insensitivity to concentration changes. The slow transition from the monomer state to the micellar state makes it almost impossible to obtain a single value for the critical micelle concentration. The values derived from the conductivity data applying the Phillips method

Table 3: Least Squares Fitted Values of Conductivity Equation (Eq 1) and Its Correlation for Sodium *n*-Dodecyl Sulfate and *n*-Dodecyltrimethylammonium Bromide at 298.15 K

	a_0	a_1	a_2	a_3	a_4	a_5	b	r^2
SDS	8.56	−1.52	2.54	−0.32	0.016	−0.0002	−0.036	0.9997
DTAB	−0.20	11.48	−0.81	0.11	−0.006	0.00009	−0.078	0.9997

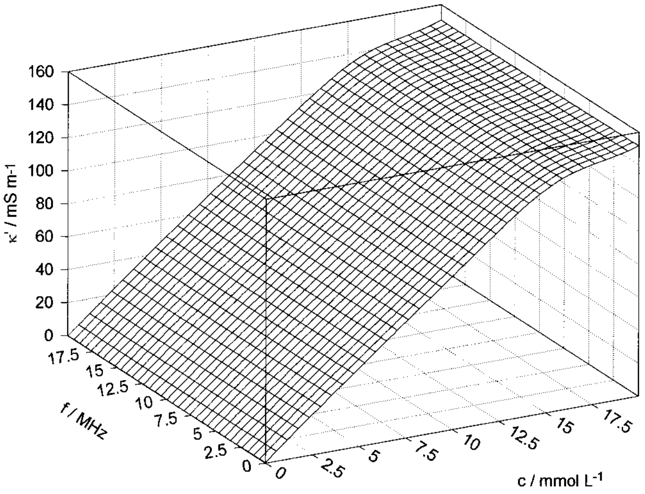

Figure 2. Plot of the real part of the electrical conductivity (k') of an aqueous solution of *n*-trimethylammonium bromide (DTAB) against frequency and molar concentration at 298.15 K as given by eq 1 with the coefficients listed in Table 3. The critical micelle concentration is 15.3 mmol·L^{-1}.

Table 4. Values of the Relative Permittivity of Sodium n-Dodecyl Sulfate at 298.15 K as a Function of Concentration for Different Frequencies

	ϵ'		
c/(mmol L^{-1})	200 kHz	2.1 MHz	20 MHz
2.0	75.9	77.8	78.5
2.5	73.8	76.9	77.9
3.0	76.0	77.6	78.7
3.5	73.7	76.6	78.0
4.0	76.2	77.3	78.8
4.5	73.6	76.0	78.1
5.0	76.3	77.0	78.8
5.5	73.9	75.9	78.1
6.0	76.5	76.9	78.9
6.5	73.9	75.5	77.9
7.0	76.8	77.0	79.1
7.5	74.8	76.0	78.8
8.0	76.9	77.1	79.3
8.5	75.1	76.0	78.9
9.0	77.6	77.7	79.7
9.5	75.7	76.5	79.0
10.0	78.3	78.2	80.2
10.5	76.6	77.3	79.6
11.0	79.1	78.9	80.8
11.5	77.6	78.0	80.3
12.0	79.5	79.3	81.1
12.5	78.5	78.6	80.8
13.0	81.4	80.4	82.2
13.5	79.5	79.5	81.8
14.0	80.9	80.4	82.2
14.5	80.1	80.1	82.4
15.0	81.8	81.1	82.8
15.5	80.8	80.6	82.5
16.5	81.1	80.9	82.8

(Phillips, 1955; Pérez-Rodríguez et al., 1998) are 8.22 mmol·L^{-1} and 15.2 mmol·L^{-1} for SDS and DTAB, respectively. For DTAB the transition is even more gradual than that for SDS, and this behavior is due to the presence of dimers and trimers in the bulk solution. This preaggregation produces an almost continuous growth of the edl, which attenuates the sharpness of the transition. On the other hand, Figures 1 and 2 also show that the electrical conductivity is almost independent of frequency for SDS and DTAB. The values of κ' in Tables 1 and 2 give the relative variations from 200 kHz to 20 MHz of <5% at 2 mmol·L^{-1} and of <0.3% at 16 mmol·L^{-1} for SDS and of <3% at 2.5 mmol·L^{-1} and of <1% at 20 mmol·L^{-1} for DTAB.

Table 5. Measured Relative Permittivity of *n*-Dodecyl Trimethylammonium Bromide at 298.15 K at Various Concentrations for Different Frequencies

	ϵ'		
c/(mmol L^{-1})	200 kHz	2.1 MHz	20 MHz
1.0	76.8	79.0	78.8
2.5	75.8	77.7	78.5
3.0	75.9	77.6	78.4
3.5	75.5	77.0	78.3
4.0	76.0	77.4	78.7
4.5	75.7	76.9	78.5
5.0	75.9	77.1	78.6
5.5	76.1	77.0	78.6
6.0	76.0	76.7	78.5
6.5	76.0	76.9	79.0
7.0	75.9	76.6	78.6
7.5	75.1	76.5	78.6
8.0	75.3	76.5	78.9
8.5	76.4	76.9	79.1
9.0	76.5	76.9	79.2
9.5	76.4	76.9	79.2
10.0	75.6	76.5	79.1
10.5	75.7	76.5	79.0
11.0	75.7	76.4	79.1
11.5	75.4	76.2	78.8
12.0	75.5	76.2	78.9
12.5	75.6	76.2	78.8
13.0	75.4	76.1	78.7
13.5	75.6	76.1	78.9
14.0	75.7	76.1	78.9
14.5	75.8	76.1	78.8
15.0	75.9	76.2	78.9
15.5	75.9	76.2	78.9
16.0	76.0	76.2	78.9
16.5	76.0	76.2	78.9
17.0	76.3	76.6	79.1
17.5	76.4	76.5	79.1
18.0	76.6	76.7	79.2
18.5	76.7	76.9	79.3
19.0	76.8	76.9	79.4
19.5	77.0	76.9	79.5
20.0	77.0	77.1	79.6

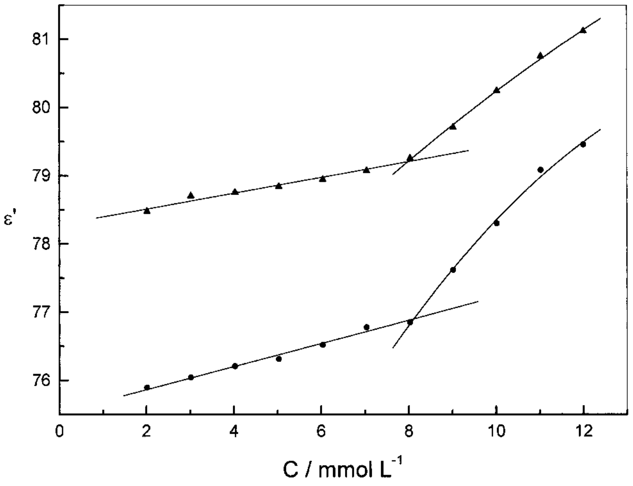

Figure 3. Relative permittivity of sodium *n*-dodecyl sulfate as a function of concentration at 298.15 K for 200 kHz (●) and 20 MHz (△). The solid line represents the linear (c < cmc) and quadratic (c > cmc) fitting curves corresponding to the parameters listed in Table 6.

Tables 4 and 5 contain the relative permittivity of aqueous solutions of SDS and DTAB, respectively, for concentrations above and below the cmc at various frequencies. These results are analyzed in terms of linear and quadratic fitting functions, as shown in Figures 3 and 4 for 200 kHz and 20 MHz for SDS and DTAB, and the results of the least squares fitting procedure are shown in

Table 6. Least Squares Fitted Values of the Relative Permittivity Equation $\epsilon' = ac^2 + bc + d$ for Sodium *n*-Dodecyl Sulfate and *n*-Dodecyltrimethylammonium Bromide for 200 KHz and 20 MHz at 298.15 K for Concentrations above and below the cmc

	SDS				DTAB			
	a/(mol^{-2}·L^2)	b/(mol^{-1}·L)	d	std dev	a/(mol^{-2}·L^2)	b/(mol^{-1}·L)	d	std dev
				ω 20 MHz				
c < cmc		0.16 ± 0.01	75.54 ± 0.04	0.04	0.02 ± 0.01	−0.70 ±0.39	84.13 ± 3.63	0.05
c > cmc	−0.04 ±0.02	1.66 ± 0.48	66.68 ± 2.39	0.09	0.04 ± 0.02	−1.41 ±0.79	63.93 ± 6.71	0.03
				ω 200 kHz				
c < cmc		0.11 ± 0.01	78.28 ± 0.04	0.04	−0.33 ±0.01	1.13 ± 0.32	66.34 ± 2.38	0.02
c > cmc	−0.01 ± 0.1	0.77 ± 0.24	73.97 ± 1.20	0.04	−0.02 ±0.01	1.13 ± 0.72	63.93 ± 6.70	0.04

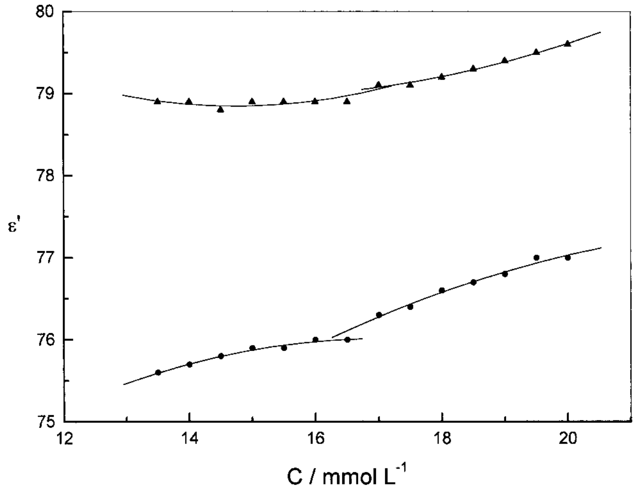

Figure 4. Relative permittivity of *n*-trimethylammonium bromide as a function of concentration at 298.15 K for 200 kHz (●) and 20 MHz (△). The solid line represents the quadratic fitting curves corresponding to the parameters listed in Table 6.

Table 6. This method is clearly more sensitive to variations of both concentration and frequency. Figure 3 demonstrates that SDS exhibits an abrupt transition in dielectric properties at the cmc that even changes the functional dependence from a linear to a quadratic one. While κ' depends linearly on concentration in both the monomer and the micellar state, ϵ' does not exhibit this uniformity in its concentration dependence. This may be explained in terms of the formation of the edl's, which introduce further contributions to the medium polarization and additional effects such as surface conductivity and others (Hidalgo-Alvarez et al., 1996) in response to the external frequency-dependent field. A similar behavior is obtained for DTAB, except for the effects of preaggregation at concentrations below the cmc that induce a quadratic dependence on the concentration of ϵ' in the pre-cmc region, as is shown by the nonzero coefficient of the quadratic term in Table 6 and is seen graphically in Figure 4. The values of the cmc obtained from dielectric constant measurements for both SDS and DTAB are respectively 7.91 mmol·L^{-1} and 13.01 mmol·L^{-1}, and they are lower than those obtained when applying the Phillips method to the conductivity data.

In conclusion, the dielectric properties of amphiphilic solutions are a more sensitive detector of structural modifications in bulk amphiphilic solutions than the electrical conductivity. Thus cmc's are more easily obtained from relative permittivity than from the corresponding conductivity data for both monodisperse and polydisperse media. The latter solution property is also more readily observed from relative permittivity measurements, as polydispersity is responsible for the nonlinear behavior of the relative permittivity as a function of concentration below the critical concentration.

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