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Temperature Dependence of Equilibrium and Transport Properties of Decyldimethylbenzylammonium Chloride in Aqueous Solutions

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Apparent and partial molar volumes of decyldimethylbenzylammonium chloride (C_{10}DBACl) at (15, 25, and 35) °C have been calculated from results of density measurements. The specific conductivities of the solutions have been determined at the same temperatures. The results served for the estimation of critical micelle concentration, cmc, ionization degree, β, and standard free energy of micellization, ΔG°_m, of the surfactant. From equivalent conductivity measured at 25 °C in the low concentration range, the transport number of the $C_{10}DBA^+$ cation has been estimated. The aggregation number, n, of the micelles has been estimated from the conductivity data.

Introduction

Alkyldimethylbenzylammonium salts are well-known for their germicidal activity and have found a broad application as antiseptics and disinfectants (Kopecky, 1996). The long-chain homologues (C14 and C16) form stable water/oil microemulsions (Jayalakshmi and Beysens, 1992). The micellar properties of such salts in aqueous solutions have been examined by various authors, and a survey of the results was presented in a recent paper (Del Castillo et al., 2000). This paper is a continuation of our conductivity and density measurements of C_{10}DBACl in aqueous solution.

Specific conductivity data at (15, 25, and 35) °C served for the evaluation of the temperature-dependent critical micelle concentration (cmc), the micelle ionization degree (β), and the standard free energy of micellization (ΔG°_m). The limiting equivalent conductivity (Λ_0) of the salt was calculated from conductivity results at 25 °C in the low concentration range. This value served for the estimation of the transport number (t_m) of the $C_{10}DBA^+$ cation and the aggregation number (n) of the micelles. The apparent and partial molar volume data were derived from density measurements at (15, 25, and 35) °C.

Materials and Methods

C_{10}DBACl was synthesized by quaternization of *N*,*N*-benzyldimethylamine with decyl chloride in ethanol and purified as described earlier (Del Castillo et al., 2000). The air-dried salt existed as a dihydrate, the amount of water being determined by the Karl Fischer method. Bidistilled water and solutions were properly degassed using an ultrasound unit.

Specific conductivity was measured by using a Kyoto Electronics conductometer, model CM-117, and, independently, on a different sample of C_{10}DBACl, using an Elmetron conductometer, model CX-732. The cell constants were determined at different temperatures using KCl solutions. The conductivity of the water was (1.8 ± 0.2, 2.3 ± 0.2, and 2.7 ± 0.3) μS cm^{-1} at (15, 25, and 35) °C, respectively. Weighed amounts of concentrated solutions of known molalities were introduced into the cells and were stirred continuously. The conductivities were measured at constant temperature while the solutions were diluted successively by adding predetermined amounts of water. Measurements made with selected samples at different temperatures show a repeatability better than 0.2% and 0.7% for the Elmetron and Kyoto conductometers, respectively. The cells were immersed in a thermostated bath, maintaining the temperature within ±0.01 °C. In each experiment, the conductivity of pure water was subtracted from the value indicated by the conductometer.

The measurements of densities were carried out with an Anton Paar DMA 60/602 vibrating tube densimeter operating under the static option, the accuracy of the instrument being $\pm 2 \times 10^{-6}$ g cm^{-3}. Solutions were prepared by mass using a Mettler H51 precision balance. The molalities of the solutions were prepared within an accuracy of ±0.0001 mol kg^{-1}. The temperature inside the vibrating tube cell was measured using Anton Paar DT 100-20 and DT 100-30 digital thermometers and was regulated better than ±0.01 °C using a HETO DBT thermostat. The apparatus was calibrated at atmospheric pressure before each series of measurements.

Results and Discussion

The values of specific conductivity, κ, of C_{10}DBACl as a function of molality, m, at temperatures of (15, 25, and 35) °C are listed in Table 1. The data shown were obtained by using the Elmetron conductometer. Two linear segments in the conductivity versus molality plots can be displayed, and the cmc of the surfactant was taken as the intersection of the apparently straight lines. The degree of ionization, β, of the micelles was estimated from the ratio of the slopes of the two linear segments above and below cmc (Lianos and Lang, 1983). Assuming that micellization occurs according to the charged phase separation model of micellization (Mukerjee, 1961), the standard free energy

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Table 1. Specific Conductivity, κ, for the C_{10}DBACl−Water System at Different Temperatures

m mmol kg^{-1}	κ mS cm^{-1}	m mmol kg^{-1}	κ mS cm^{-1}	m mmol kg^{-1}	κ mS cm^{-1}	m mmol kg^{-1}	κ mS cm^{-1}
t = 15 °C							
78.7	3.540	57.1	2.983	42.2	2.544	28.9	1.890
74.6	3.438	54.9	2.922	39.9	2.449	27.3	1.793
71.0	3.342	52.9	2.870	37.9	2.356	25.9	1.703
67.7	3.261	51.1	2.816	36.0	2.257	24.5	1.624
64.7	3.180	47.8	2.721	34.3	2.168	23.4	1.550
61.9	3.112	44.8	2.629	32.8	2.079	22.3	1.484
59.4	3.044			30.7	2.000		
t = 25 °C							
78.9	4.527	52.9	3.602	34.1	2.679	25.7	2.023
74.7	4.383	49.4	3.466	32.7	2.580	25.0	1.962
71.0	4.253	46.4	3.343	31.5	2.483	24.3	1.908
67.7	4.136	43.7	3.229	30.3	2.392	23.3	1.828
64.6	4.029	41.3	3.117	29.2	2.308	22.5	1.754
61.9	3.928	39.2	3.010	28.3	2.229	21.7	1.687
59.4	3.838	37.4	2.901	27.3	2.156	21.0	1.624
57.0	3.754	35.7	2.785	26.5	2.088		
t = 25 °C (low concentration)							
1.995	0.189	1.456	0.138	1.081	0.103	0.7724	0.074
1.895	0.179	1.402	0.133	1.023	0.098	0.7421	0.071
1.804	0.171	1.352	0.129	0.9704	0.092	0.7141	0.068
1.722	0.163	1.305	0.124	0.9231	0.088	0.6881	0.066
1.647	0.156	1.221	0.116	0.8801	0.084	0.6640	0.064
1.578	0.150	1.147	0.109	0.8410	0.080		
1.515	0.144			0.8052	0.077		
t = 35 °C							
76.8	5.598	56.5	4.617	36.9	3.535	27.4	2.737
73.0	5.418	52.5	4.417	35.2	3.407	26.4	2.646
69.6	5.255	49.0	4.241	33.6	3.282	25.5	2.561
66.5	5.104	46.0	4.079	32.1	3.161	24.6	2.482
63.7	4.964	43.3	3.933	30.8	3.041	23.9	2.408
61.1	4.836	41.0	3.798	29.6	2.935	23.1	2.337
58.7	4.722	38.8	3.668	28.4	2.832		

Table 2. Values of Critical Micelle Concentration, cmc, Ionization Degree, β, and Standard Free Energy of Micellization, ΔG°_m, with the Kyoto Electronics CM-117 (a) and the Elmetron CX-731 (b) Conductivimeters

t °C	cmc(a) mmol kg^{-1}	β(a)	ΔG°_m(a) kJ mol^{-1}	cmc(b) mmol kg^{-1}	β(b)	ΔG°_m(b) kJ mol^{-1}
15.0	40.7	0.424	−27.2	39.1	0.421	−27.4
25.0	38.3	0.451	−27.7	38.7	0.424	−28.4
35.0	37.7	0.487	−27.8	37.9	0.519	−27.6

Table 3. Density, ρ, Apparent Molar Volume, V_ϕ, and Partial Molar Volume, V_2, of C_{10}DBACl at Different Temperatures

m mmol kg^{-1}	ρ g cm^{-1}	V_ϕ cm^3 mol^{-1}	V_2 cm^3 mol^{-1}	m mmol kg^{-1}	ρ g cm^{-1}	V_ϕ cm^3 mol^{-1}	V_2 cm^3 mol^{-1}
t = 15 °C							
0	0.999 097			58.3	0.999 259	309.4	314.2
10.2	0.999 148	307.3	307.2	66.9	0.999 246	309.9	314.4
14.9	0.999 172	307.2	307.1	71.2	0.999 235	310.3	314.3
19.5	0.999 195	307.2	307.2	78.2	0.999 223	310.6	313.8
25.7	0.999 225	307.2	307.2	98.5	0.999 185	311.3	314.3
31.6	0.999 255	307.2	307.8	134.1	0.999 104	312.2	314.7
37.2	0.999 274	307.4	309.0	150.8	0.999 074	312.4	314.1
41.9	0.999 288	307.6	310.8	186.9	0.999 004	312.8	314.1
49.6	0.999 280	308.5	314.0	318.1	0.998 778	313.3	314.3
55.3	0.999 267	309.1	314.9	439.3	0.998 591	313.5	314.3
t = 25 °C							
0	0.997 043			66.9	0.996 973	313.9	317.2
10.2	0.997 064	311.2	311.4	71.2	0.996 96	314.1	316.7
14.9	0.997 068	311.3	311.8	78.2	0.996 928	314.4	317.4
19.5	0.997 073	311.5	312.0	97.8	0.996 842	315.0	305.2
25.7	0.997 079	311.6	312.0	98.5	0.996 856	314.8	304.5
31.6	0.997 081	311.6	312.4	134.1	0.996 697	315.6	317.1
37.2	0.997 079	311.9	314.2	150.8	0.996 651	315.6	316.4
41.9	0.997 068	312.3	314.6	186.9	0.996 505	315.9	317.1
55.3	0.997 028	313.1	317.1	318.1	0.996 017	316.4	317.2
58.3	0.997 015	313.4	317.4	439.3	0.995 614	316.6	317.2
t = 35 °C							
0	0.994 027			58.3	0.993 871	316.6	318.5
10.2	0.994 021	314.7	314.7	66.9	0.993 82	317.1	320.4
14.9	0.994 017	314.7	314.7	71.2	0.993 792	317.3	319.9
19.5	0.994 013	314.7	315.1	78.2	0.993 756	317.4	319.5
25.7	0.994 002	314.9	315.5	97.8	0.993 64	318.0	320.1
31.6	0.993 994	315.0	315.2	134.1	0.993 423	318.6	320.1
37.2	0.993 987	315.0	315.1	186.9	0.993 14	318.9	319.8
41.9	0.993 981	315.0	318.5	318.1	0.992 445	319.4	320.0
49.6	0.993 911	316.3	321.7	439.3	0.991 892	319.4	319.6
55.3	0.993 881	316.6	318.4				

of micellization, ΔG°_m, was calculated from the relation

$$\Delta G^\circ_m = (2 - \beta)RT \ln x_{cmc} \tag{1}$$

where x_{cmc} is the value of critical micelle concentration expressed in mole fraction. The values of cmc, β, and ΔG°_m are collected in Table 2, where the results obtained with the two different instruments are included. The relative difference between the two values for cmc is <4%, and that for β is <7%. The obtained values for β are high in comparison with those of normal alkyltrimethylammonium salts, but they are comparable with those found for micelles formed by double-chained amphiphiles (Zana, 1980).

We have used the conductivity data obtained, for the low concentration range, (1.987 to 0.547 mM) of C_{10}DBACl at 25 °C to estimate, by extrapolation, the equivalent conductivity of the solute at infinite dilution, Λ_0. It amounts to 97.24 cm^2 S mol^{-1}. The concentrations needed for the purpose were calculated from the molality and density data. The limiting equivalent conductivity of the $C_{10}DBA^+$ cation Λ_0^{m+} equals correspondingly 20.93 cm^2 S mol^{-1} if the value of Λ_0 for the chloride anion is taken as 76.31 cm^2 S mol^{-1} (Vanysek, 1996). The transport number, $t_m = \Lambda_0^{m+}/\Lambda_0$, for the $C_{10}DBA^+$ cation at 25 °C amounts thus to 0.215.

An estimation of the micellar charge from conductivity data of aqueous detergent solutions can be made by applying the approach of Kimizuka and Satake (1962); they assumed that above the cmc there is only one kind of micelle of aggregation number n, with a degree of ionization amounting to β. An additional assumption that $\Lambda = \Lambda_0 + a\sqrt{I}$ (where a is a constant and I is the ionic strength) is valid in the pre- and postmicellar regions and leads to the equation

$$\left(\frac{\Lambda_0 - \Lambda}{\Lambda_0 - \Lambda_{cmc}}\right)^2 = \left(1 - \frac{\beta(1 + n\beta)}{2}\right) + \frac{\beta(1 + n\beta)}{2}\left(\frac{c}{c_{cmc}}\right) \tag{2}$$

where Λ_{cmc} is the equivalent conductivity of the solute just at the cmc. From the linear relation between $[(\Lambda_0 - \Lambda)/(\Lambda_0 - \Lambda_{cmc})]^2$ and c/c_{cmc}, the value of the aggregation number n can be inferred. The value of n can be obtained either from the intercept or from the slope. Both approaches yield comparable values of n, the mean value amounting to 48 ± 2.

The values of the density, ρ, of C_{10}DBACl in aqueous solutions at (15, 25, and 35) °C are listed in Table 3, together with apparent and partial molar volumes. The values of the apparent molar volume, V_ϕ, have been calculated from the expression

$$V_\phi = M/\rho - 10^3(\rho - \rho_0)/(m\rho\rho_0) \tag{3}$$

Table 4. Debye−Hückel Limiting Law Coefficient, A_v, Apparent Molar Volumes at Infinite Dilution, V_φ°, and at the cmc, V_φ^{cmc}, and Apparent Molar Volumes of Micellization, ΔV_φ^m, at (15, 25, and 35) °C

t	A_v	V_ϕ°	V_ϕ^{cmc}	ΔV_ϕ^m
°C	$cm^3\ kg^{1/2}\ mol^{-3/2}$	$cm^3\ mol^{-1}$	$cm^3\ mol^{-1}$	$cm^3\ mol^{-1}$
15.0	1.696	307.2	307.2	7.0
25.0	1.865	310.7	311.3	5.7
35.0	2.040	314.3	315.3	4.7

where ρ_0 is the density of pure water, M is the molar mass of the solute, and m is its molality. From this, the partial molar volume V_2 can be obtained as

$$V_2 = V_\phi + m(\partial V_\phi/\partial m)_{T,P} \qquad (4)$$

In the premicellar region, the values of V_ϕ can be expressed by the relation

$$V_\phi = V_\phi^\circ + A_v m^{1/2} + B_v m \qquad (5)$$

where V_ϕ° is the value of apparent molar volume at infinite dilution, A_v is the Debye−Hückel limiting law coefficient, and B_v is an adjustable parameter. The fit of the V_ϕ values to this equation enables us to obtain the limiting value of V_ϕ°. These values and the values of A_v for 1:1 electrolytes are listed in Table 4. In the postmicellar region, the values of V_ϕ have been fitted to the asymptotic function

$$V_\phi = V_\phi^{cmc} + \Delta V_\phi^m(m - \mathrm{cmc})/[B + (m - \mathrm{cmc})] \qquad (6)$$

where V_ϕ^{cmc} is the value of the apparent molar volume at the cmc and ΔV_ϕ^m is the difference between the limiting value at high concentration of surfactant and V_ϕ^{cmc}. It can be identified with the change in the apparent molar volume upon micellization. Values for these parameters are also listed in Table 4.

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