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Thermodynamic Properties and Conductivities of Some Dodecylsurfactants in Water

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Densities, heat capacities, enthalpies of dilution, osmotic coefficients and conductivities are reported for dodecylamine hydrochloride, dodecyldimethylammonium and dodecyltrimethylammonium chloride in water over a wide range of concentration. The last two properties were also measured for dodecyltrimethylammonium bromide. From the thermodynamic data partial molar volumes, heat capacities and relative enthalpies and nonideal free energies and entropies were derived as a function of the surfactant concentration. The cmc's and degree of counterion dissociation were also calculated from the transport properties. It is shown that the trends of volumes, enthalpies, free energies and entropies are quite regular whereas heat capacities present maxima and minima at concentrations which depend on the nature of surfactants. Corresponding changes were observed in the osmotic coefficients and specific conductivities. The thermodynamic functions of micellization were evaluated on the basis of the pseudo-phase transition model. Finally, the effects of the introduction of methyl groups in the hydrophilic moiety of the surfactant and of the nature of the counterion on the thermodynamic properties of monomers and micelles are examined.

KEY WORDS: Dodecylamine hydrochloride; dodecyldimethyl-ammonium chloride; dodecyltrimethylammonium chloride; dodecyltrimethylammonium bromide; conductivities, densities; heat capacities; enthalpies of dilution; osmotic coefficients; activity coefficients; partial molar volumes; partial molar heat capacities; partial molar relative enthalpies; nonideal free energies; nonideal entropies; thermodynamics of micellization; degree of counterion dissociation.

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1. INTRODUCTION

In a series of papers(1-8) on the effect of the nature of surfactants and solutes on the thermodynamics of solubilization of nonionic solutes in micellar solutions, we recently focused our attention on the effect of the presence of methyl groups in the hydrophilic moiety of surfactants.(9) The theoretical treatment of the bulk thermodynamic properties of solubilizate requires knowledge of the thermodynamics of micellization and of the degree of counterion dissociation.(1,3-5) In the case of ionic surfactants, the effect of the alkyl chain length and of the nature of the head group has been extensively investigated but little attention has been paid to the above mentioned CH_3 effect. To the best of our knowledge, the only papers where the hindering effect of methyl groups in the hydrophilic shell of micelles was analyzed, concern aggregation numbers,(10) cmc values(10) and compressibilities.(11) As far as the thermodynamics of micellization is concerned, from the dependence of the surface tension on the temperature, Aratono *et al.*(12) derived the entropy of micellization of dodecylammonium chloride and dodecyltrimethylammonium chloride. We have, therefore, investigated volumes, heat capacities, osmotic coefficients and enthalpies of dilution of dodecylamine hydrochloride, dodecyldimethylammonium chloride and dodecyltri-methylammonium chloride. Conductometric measurements were also carried out in order to evaluate cmc's and the degree of counterion dissociation. Finally, to study the effect of the nature of counterions on the thermodynamics of micellization, conductivities and osmotic coefficients were measured for dodecyltrimethylammonium bromide whose volumes,(1) heat capacities(5) and enthalpies of dilution(4) were reported elsewhere.

2. EXPERIMENTAL

Dodecyltrimethylammonium chloride (DTAC) and bromide (DTAB) and dodecylamine hydrochloride (DAC) (Sigma products) were crystallized twice from ethanol-acetone and then dried under vacuum at 60°C for at least 48 h before use. Dodecyldimethylammonium chloride (DDAC) was obtained by neutralization of the distilled dodecyldimethylamine (Sigma product) with aqueous HCl using 2-propanol as solvent. The water and 2-propanol were removed by flash evaporation. The solid DDAC was crystallized twice from ethanol-acetone and dried under vacuum at 60°C for 48 h before use. Solutions were prepared by weight using degassed conductance water whose specific conducitivity was less than 10^{-7} S-cm^{-1} and concentrations are expressed as the number of solute moles per kg of solvent.

Table I. Volumes and Heat Capacities of Dodecyltrimethylammonium Chloride in Water at 25°C[a]

m	$-10^3\Delta d$	V_ϕ	V_2	$-10^3\Delta\sigma/\sigma_0$	C_ϕ	C_{p2}
0.009827	0.159	280.98	280.9	0.24	1069	1065
0.01001	0.164	281.20	280.9	0.28	1055	1065
0.01493	0.232	280.41	280.9	0.36	1067	1065
0.02890	0.532	283.35	285.80	1.12	1017	647
0.02991	0.548	283.27	286.40	1.39	985.1	640
0.03961	0.778	284.66	287.70	2.92	874.4	598
0.04994	1.012	285.36	288.05	4.37	818.0	583
0.06303	1.323	286.18	288.36	6.60	746.9	566
0.07454	1.591	286.75	288.54	8.24	722.5	554
0.09779	2.091	286.79	288.72	11.65	683.2	540
0.1000	2.162	287.05	288.72	11.92	683.7	538
0.1244	2.700	287.29	288.74	15.66	652.1	532
0.1445	3.136	287.42	288.72	18.78	631.9	533
0.1789	3.906	287.77	288.68	23.76	615.6	554
0.1990	4.320	287.77	288.66	26.49	611.0	563
0.2505	5.368	287.79	288.60	33.30	603.6	581
0.2995	6.418	288.09	288.56	40.32	589.5	340
0.3243	6.906	288.10	288.53	44.97	567.0	530
0.3494	7.424	288.20	288.51	48.15	567.1	540
0.3694	7.784	288.13	288.48	51.02	562.1	538
0.3938	8.252	288.15	288.46	53.99	562.9	536
0.4448	9.195	288.13	288.41	61.10	561.8	535
0.4955	10.153	288.23	288.36	66.88	556.6	533
0.5977	11.948	288.24	288.20	79.17	552.4	529

[a] Units are: mol-kg^{-1} for m; g-cm^{-3} for densities; cm^3-mol^{-1} for volumes; J-K^{-1}mol^{-1} for heat capacities.

The densities of solutions were determined with a vibrating tube flow densimeter (Sodev Mod. 03D) sensitive to 3ppm. The densimeter was calibrated with water and vacuum. The temperature was kept constant at 25±0.002°C by a Heto proportional temperature controller. The relative differences in heat capacities per unit volume $\Delta\sigma/\sigma_0$ = $(\sigma\text{-}\sigma_0)/\sigma_0$ were determined with a Picker flow microcalorimeter (Setaram). Using a flow rate of about 0.01 cm^3-sec^{-1} and a basic power of 21.2 mW, the temperature increment was of approximatively 0.5°C. Heat capacity measurements of the surfactant solutions were carried out by taking water as reference solvent. The specific heat capacities (c_P) of solutions of density d are related to $\Delta\sigma/\sigma_0$ through the equation

Table II. Volumes and Heat Capacities of Dodecyldimethylammonium Chloride in Water at 25°C[a]

m	$-10^3\Delta d$	V_ϕ	V_2	$-10^3\Delta\sigma/\sigma_o$	C_ϕ	C_{p2}
0.009991	0.149	265.65	265.4	0.18	1031	1030
0.01298	0.187	265.09	265.4	0.23	1032	1030
0.01905	0.302	266.60	273.80	0.46	1009	890
0.02488	0.452	268.31	274.60	1.21	916.0	720
0.02949	0.576	270.36	274.80			
0.03491	0.685	270.49	275.00	2.48	827.1	574
0.04449	0.914	271.48	275.10			
0.04473	0.921	271.80	275.10	3.89	763.5	540
0.06926	1.518	273.03	275.16			
0.07497	1.646	273.10	275.16	8.54	652.2	500
0.07514	1.646	273.05	275.16	8.55	652.8	500
0.09855	2.202	273.65	275.16	11.95	619.7	490
0.1088	2.447	273.86	275.16	13.25	618.0	490
0.1193	2.700	274.07	275.16			
0.1249	2.819	274.04	275.16	15.03	621.7	495
0.1294	2.913	274.01	275.16	15.90	610.1	496
0.1597	4.420	274.20	275.16	20.87	572.6	502
0.1797	4.065	274.44	275.16	23.48	570.5	508
0.2096	4.695	274.38	275.16	27.69	559.5	517
0.2492	5.569	274.58	275.16	33.04	552.2	526
0.2943	6.514	274.62	275.16	38.54	553.0	533
0.3464	7.589	274.69	275.16	43.56	555.9	540
0.3978	8.638	274.79	275.16	51.18	548.5	540
0.4969	10.566	274.86	275.16	63.02	543.1	540
0.5663	11.868	274.91	275.16	70.65	543.1	540
0.5990	12.486	274.97	275.16	74.47	540.9	540
0.6936	14.143	274.97	275.16	83.30	548.4	540
0.8645	16.974	274.99	275.16	99.71	549.6	540

[a] For units: see Table I.

$$c_p = c_{po}\,[1 + \Delta\sigma/\sigma_o]d_o/d \qquad (1)$$

where c_{po} (4.1792 J-K^{-1}-g^{-1})(13) and d_o (0.997047 g-cm^{-3})(14) are the specific heat capacity and density of water, respectively. The enthalpies of dilution at 25°C were measured with a flow LKB 2107 microcalorimeter. Measurements were carried out by diluting each surfactant solution of fixed composition with water. The injection of the solutions and of water into the microcalorimeter was made by means of a Gilson peristaltic pump (Minipuls 2) and their flows were determined by weight. The osmotic coefficients (Φ) were determined by means of a Knauer vapor pressure osmometer. Measurements were made at 37°C, the lowest operating temperature suggested for aqueous solutions. The instrument was calibrated using a standard (400 mOsmolal) aqueous NaCl solution. The accuracy of the osmotic coefficients is of the order of 1% at the lowest surfactant concentrations analyzed and quickly improves to 0.2% when the surfactant concentration is increased. Our data for DTAB at 25°C agree well with those recently reported by Dearden and Woolley.(15) For the conductance measurements a cell with unplatinized electrodes was used. The cell constant (2.834±0.001) was determined at 25°C by measuring the conductance of dilute solutions of aqueous KCl and using the equation of Lind *et al.*(16) All measurements were performed with the cell in a constant temperature oil-bath controlled within 0.005°C by a Hewlett-Packard 2804 A Quartz thermometer. The electrical resistence was measured at 2 kHz with a calibrated ac bridge.(17)

3. RESULTS

The apparent molar volumes, V_ϕ, and heat capacities, C_ϕ, of surfactants were calculated by means of the following equations

$$V_\phi = \frac{M}{d} - \frac{10^3(d-d_o)}{mdd_o} \tag{2}$$

$$C_\phi = Mc_p + 10^3(c_p - c_{po})/m \tag{3}$$

where d and m indicate the density and molality of solutions, respectively, and M the molecular weight of the investigated surfactant. The meanings of other symbols are the same as above.

As usual, the relative apparent molar enthalpies, L_ϕ, were derived from enthalpies of dilution defined by

$$\Delta H_{id} = L_{\phi,f} - L_{\phi,i} \tag{4}$$

where $L_{\phi,f}$ and $L_{\phi,i}$ refer to the final and initial concentrations, respectively. Due to the low value of the cmc of the present surfactants, the apparent molar enthalpy in the premicellar region is simply given by

$$L_\phi = 1973\sqrt{m} + Bm \tag{5}$$

where 1973 is the limiting Debye-Hückel slope for relative enthalpies. According to Eqs. (4,5), the B parameter was calculated by means of

Table III. Volumes and Heat Capacities of Dodecylamine Hydrochloride in Water at 25°C[a]

m	$-10^3\Delta d$	V_ϕ	V_2	$-10^3\Delta\sigma/\sigma_0$	C_ϕ	C_{p2}
0.008330	0.073	231.27	230.9	0	963.8	963
0.009472	0.078	230.76	230.9	0	961.6	963
0.01001	0.083	230.84	230.9	0	963.8	963
0.01296	0.108	230.88	230.9	0	962.1	963
0.01991	0.211	233.17	240.80	0.57	852.7	616
0.02603	0.334	235.46	241.30	1.23	782.5	580
0.03260	0.479	237.37	241.58	1.96	736.0	544
0.04206	0.658	238.37	241.74	2.98	694.7	507
0.04991	0.818	239.16	241.80	4.07	651.8	482
0.06055	1.012	239.54	241.80	5.44	617.2	457
0.06939	1.172	239.75	241.80	6.70	588.9	436
0.08999	1.532	239.97	241.80	9.25	561.1	404
0.1100	1.926	240.55	241.80	12.09	530.7	444
0.1230	2.169	240.73	241.80	13.48	531.6	478
0.1354	2.397	240.86	241.80	14.91	528.5	506
0.1479	2.623	240.95	241.80	16.31	526.8	530
0.1599	2.833	240.98	241.80	17.69	524.1	550
0.1901	3.380	241.18	241.80	20.46	534.6	570
0.1977	3.513	241.20	241.80	22.26	512.1	568
0.2063	3.667	241.25	241.80	21.89	539.8	564
0.2126	3.781	241.28	241.80	23.03	527.4	558
0.2152	3.819	241.25	241.80	20.88	578.9	555
0.2304	4.080	241.28	241.80	24.86	529.4	534
0.2668	4.702	241.34	241.80	29.78	508.7	480
0.3128	5.474	241.41	241.80	34.54	509.7	476
0.3512	6.124	241.50	241.80	38.91	505.5	468
0.3860	6.675	241.49	241.80	42.91	498.7	462
0.4396	7.554	241.59	241.80	48.64	495.3	451
0.4932	8.360	241.55	241.80	55.98	475.8	≈350
0.5987	9.856	241.42	241.80	69.47	451.1	≈300

[a] For units: see Table I.

$$\Delta H_{id} - 1973(\sqrt{m_f} - \sqrt{m_i}) = B(m_i) \qquad (6)$$

by plotting the quantity on the left hand side *vs.* $(m_f - m_i)$. Then L_ϕ can be calculated at all concentrations below the cmc by means of Eq. (5). For molalities greater than the cmc, a graphical method was used. This consists of applying Eq. (4) to the experimental points whose final con-

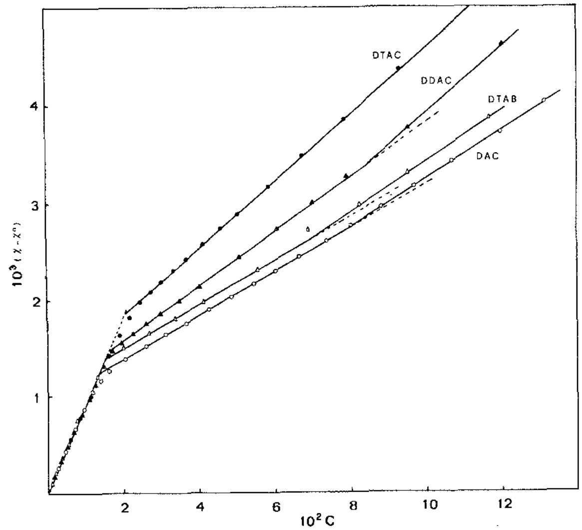

Fig. 1. Specific conductivities (ohm^{-1}-cm^{-}1) corrected for solvent *vs.* surfactant molarity. DAC, dodecylamine hydrochloride; DDAC, dodecyldimethylammonium chloride; DTAC, dodecyltrimethylammonium chloride; DTAB, dodecyltrimethylammonium bromide.

centration is lower than the cmc; in this way L_ϕ values at higher surfactant concentrations are obtained. Then, L_ϕ was plotted against m and by successive applications of this procedure L_ϕ in the whole concentration range was calculated.

The partial molar volumes, heat capacities and relative enthalpies were determined by drawing the best curve for the apparent molar quantities and then by calculating the partial molar quantities as $(\Delta m Y_\phi)/\Delta m$ from points interpolated at regular intervals on the lines.

Osmotic coefficient measurements were made in order to calculate the nonideal free energies. As said above, they were carried out at 37°C. Since other thermodynamic properties are at 25°C, osmotic coefficients were calculated at this temperature by means of Eq. (7)

$$\Phi_{298} = \frac{298-310}{2R(298)(310)}[(L_2 - L_\phi - 298(C_{p2} - C_\phi)] - \frac{(C_{p2} - C_\phi)}{2R}\ln\frac{298}{310} \quad (7)$$

where $(L_2 - L_\phi)$ and $(C_{p2} - C_\phi)$ are at 25°C.

The activity coefficients were calculated by means of the following equation

Table IV. Enthalpies of Dilution, Apparent and Partial Molar Relative Enthalpies of Dodecylamine Hydrochloride in Water at 25°C[a]

m_i	m_f	$L_{\Phi,i}$	$L_{\Phi,f}$	ΔH_{id}	$L_{2,i}$	$L_{2,f}$
0.008330	0.004168	485	280	-207	880	495
0.009472	0.004718	540	310	-226	980	550
0.01989	0.01070	1020	595	-426	1680	1090
0.04206	0.02082	1345	1035	-360	1510	1685
0.04989	0.02656	1360	1180	-182	1340	1710
0.06539	0.03249	1320	1275	-52	1040	1680
0.07352	0.03640	1280	1315	36	895	1610
0.09984	0.00621	1105	385	-745	420	690
0.1293	0.06803	890	1310	422	-10	985
0.1570	0.08294	690	1220	531	-370	710
0.2152	0.1057	345	1065	824	-960	320
0.2428	0.1285	155	900	710	-1190	-10
0.2989	0.1464	-115	760	872	-1560	-260
0.3988	0.1968	-520	430	938	-1830	-795
0.5004	0.2418	-790	170	999	-1800	-1185
0.5992	0.2946	-955	-95	868	-1640	-1540
0.7003	0.4129	-1040	-565	480	-1370	-1835
0.8002	0.3986	-1065	-510	555	-1040	-1830

[a] Units are: mol-kg^{-1} for m; J-mol^{-1} for enthalpies. The *B* parameter for fitting Eq. (5) is 3.66×10^4.

$$\ln\gamma_\pm = (\Phi - 1) - (0.39/2)\sqrt{m_o} + \int_{m_o}^{m} (\Phi-1)\,d\ln m \tag{8}$$

where -0.39 is the Debye-Hückel limiting slope. The experimental and theoretical Φ values converge at m_o which are 0.009 for DTAB, 0.006 for DTAC and 0.004 mol-kg^{-1} for DDAC and DAC. Details on Eqs. (7) and (8) are reported in the literature.(18)

The nonideal free energies and entropies were calculated by means of Eqs. (9,10), respectively

$$G_2^{ni} = 2RT\ln\gamma_\pm \tag{9}$$

$$G_2^{ni} = L_2 - TS_2^{ni} \tag{10}$$

Experimental and calculated thermodynamic data are reported in Tables I through XI. Table XII summarizes the equivalent conduc-

Table V. Enthalpies of Dilution, Apparent and Partial Molar Relative Enthalpies of Dodecyldimethylammonium Chloride in Water at 25°C[a]

m_i	m_f	$L_{\Phi,i}$	$L_{\Phi,f}$	ΔH_{id}	$L_{2,i}$	$L_{2,f}$
0.009991	0.005412	410	260	-150	700	310
0.02949	0.01595	1800	590	-1258	3640	1160
0.03491	0.01888	2040	840	-1173	3295	1640
0.04473	0.02424	2270	1355	-913	3110	3940
0.07524	0.04077	2520	2180	-379	2760	3175
0.09855	0.05368	2565	2370	-178	2570	2980
0.1088	0.05977	2560	2430	-119	2510	2910
0.1249	0.06965	2540	2500	-42	2410	2820
0.1797	0.1005	2440	2560	102	2110	2570
0.2096	0.1189	2380	2550	148	1985	2450
0.2492	0.1295	2310	2535	208	1835	2380
0.2496	0.1258	2310	2540	218	1830	2400
0.2943	0.1467	2250	2505	255	1695	2275
0.3463	0.1707	2165	2460	293	1570	2160
0.3978	0.1895	2090	2425	335	1470	2060
0.4969	0.2338	1965	2340	371	1340	1880
0.5663	0.2795	1890	2265	357	1280	1750
0.5990	0.2847	1850	2255	394	1260	1720
0.8645	0.4114	1650	2070	416	1195	1450

[a] For units, see Table IV. The *B* parameter for fitting Eq. (5) is 3.66×10^4.

tivities λ as a function of molarities *c*. It is well known that the cmc values are given by the intersection point of the slopes, below and above the cmc, of the specific conductivities χ *vs.* concentration (Fig. 1). The degree of the counterion dissociation β can be evaluated by means of the quadratic equation proposed by Evans(19)

$$10^3 S_2 = \beta^2 n^{2/3}(10^3 S_1 - \lambda_c) + \beta\lambda_c \qquad (11)$$

where $S_2=(d\chi/dc)_{post}$ and $S_1=(d\chi/dc)_{pre}$ are the slopes of the plot of χ *vs.* *c* above and below the cmc, respectively, λ_c is the equivalent conductance at infinite dilution of counterions and *n* is the aggregation number. Evans' equation was questioned(20) because it is based on the pseudo-phase transition model which does not account for the change of the monomeric surfactant concentration above the cmc. This approximation does not seem to be important since the β values calculated using the mass action model and the pseudo-phase transition model are in good agreement.(20) Nevertheless, in the case of DTAB by taking the value of

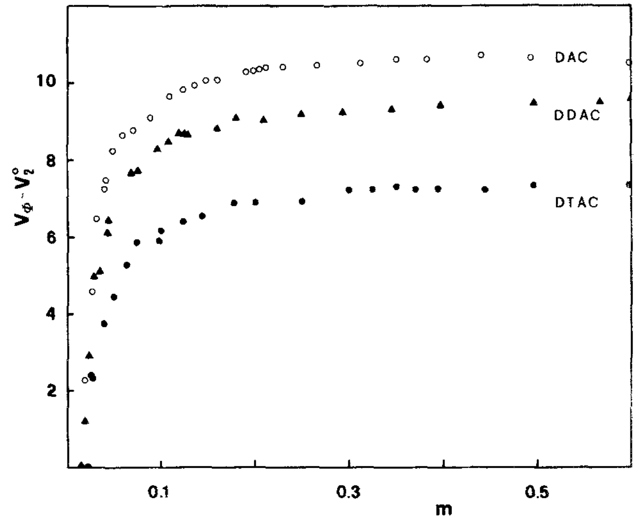

Fig. 2. Apparent molar volume (cm^3-mol^{-1}) *vs.* surfactant molality. DAC, dodecylamine hydrochloride; DDAC, dodecyldimethylammonium chloride; DTAC, dodecyltrimethylammonium chloride.

78.1(21) for λ_c (Br^-) and 55 for the aggregation number,(22) from Eq. (11) β was calculated to be 0.19, which is about 20% smaller than that from emf measurements.(10) As we will report in a forthcoming paper, more accurate β values can be obtained from the ratio of the slopes above and below the cmc of the plot of the specific conductivities *vs.* molarities

$$\beta = (d\,\chi/dc)_{post} \,/\, (d\chi/dc)_{pre} \tag{12}$$

Using Eq. (12) the literature β value for DTAB is recovered. The cmc and β values, the latter evaluated according to Eq. (12), are summarized in Table XIII. As Fig. 1 shows, positive deviations were observed in the post-micellar region around 0.07-0.10 *M* (depending on the nature of surfactant).

4. DISCUSSION

The cmc values for DTAB(23) and for the three chloride surfactants(24) are reported in the literature. An excellent agreement was obtained for DTAB and DDAC whereas our values are about 10% smaller in the other two cases; however, our cmc value for DAC is very close to that reported by Herzfeld *et al.*(25) and to that calculated from the theory of Rao and Ruckenstein.(26) The large effect on β due to the nature of counterions and to the presence of methyl groups at the micel-

Table VI. Enthalpies of Dilution, Apparent and Partial Molar Relative Enthalpies of Dodecyltrimethylammonium Chloride in Water at 25°C[a]

m_i	m_f	$L_{\Phi,i}$	$L_{\Phi,f}$	ΔH_{id}	$L_{2,i}$	$L_{2,f}$
0.01011	0.005337	502	304	-170	904	537
0.01984	0.01044	873	515	-399	1608	929
0.03388	0.01791	2550	802	-1750	5100	1471
0.05865	0.03072	3665	2130	-1536	4950	4300
0.08949	0.04671	4015	3300	-802	4510	5280
0.1299	0.06723	4140	3810	-330	4130	4795
0.1596	0.08231	4110	3980	-124	3920	4595
0.1864	0.09570	4050	4050	8	3760	4440
0.2278	0.1165	3960	4145	139	3530	4240
0.2608	0.1377	3890	4140	206	3420	4080
0.3008	0.1555	3810	4120	289	3195	3950
0.3537	0.1784	3710	4070	375	2980	3810
0.3853	0.1952	3645	4035	401	2880	3710
0.4413	0.2232	3540	3970	448	2690	3560
0.5001	0.2380	3435	3940	636	2520	3480
0.5876	0.2764	3285	3865	588	2300	3300
0.7164	0.3414	3090	3730	628	2020	3035
0.8026	0.3884	2985	3650	640	1850	2860

[a] For units, see Table IV. The B parameter for fitting Eq. (5) is 3.00×10^{4}.

lar surface is noteworthy. The progressive introduction of CH_3 groups increases the volume of the polar group, decreases the density charge at the micellar surface and hence increases β. This increase is much larger than that obtained for the CH_2 contribution in the linear alkyl chain (0.02). A similar effect was already observed for compressibilities.(11) As far as the nature of counterions is concerned, β for DTAC is 0.15 units larger than that for DTAB. Robins and Thomas(27) using Eq. (11), found that β of dodecylaminoethanol hydrochloride is 0.07 units larger than that of the corresponding hydrobromide [by using Eq. (12) the difference becomes 0.10] whereas Dorshow *et al.*,(28) by means of light scattering measurements on hexadecyltrimethylammonium surfactants, found a difference of 0.05 units. The difference of 0.15 units we have found from DTAC and DTAB is a consequence not only of the counterions hydration(29) but also of the different structure of the micelles.

Table VII. Osmotic Coefficients of Dodecylamine Hydrochloride (DAC), Dodecyldimethylammonium Chloride (DDAC),Dodecyltrimethylammonium Chloride (DTAC) and Dodecyltrimethylammonium Bromide (DTAB) in Water at 37°C

m	Φ_{310}	m	Φ_{310}	m	Φ_{310}	m	Φ_{310}
DAC		DDAC		DTAC		DTAB	
0.008330	0.9409	0.009991	0.9408	0.01011	0.9410	0.009006	0.9646
0.009472	0.9272	0.02949	0.5699	0.01984	0.8980	0.01146	0.9592
0.01989	0.6292	0.03491	0.4983	0.03388	0.6285	0.01402	0.9345
0.04206	0.3442	0.04473	0.3902	0.05865	0.4028	0.02086	0.7386
0.04989	0.2970	0.07514	0.2741	0.08949	0.2916	0.02842	0.5480
0.06539	0.2339	0.09855	0.2326	0.1299	0.2321	0.03199	0.4675
0.07352	0.2118	0.1088	0.2204	0.1596	0.2099	0.03587	0.4319
0.09984	0.1667	0.1249	0.1972	0.1864	0.1912	0.04733	0.3320
0.1293	0.1407	0.1294	0.1988	0.2278	0.1776	0.05004	0.3152
0.1570	0.1267	0.1597	0.1827	0.2608	0.1708	0.05774	0.2912
0.1952	0.1138	0.1797	0.1708	0.3008	0.1630	0.07014	0.2325
0.2152	0.1087	0.2096	0.1613	0.3537	0.1602	0.07993	0.2156
0.2428	0.1041	0.2492	0.1523	0.3853	0.1555	0.09964	0.1882
0.2989	0.0953	0.2838	0.1499	0.4413	0.1522	0.1138	0.1702
0.3988	0.0864	0.3404	0.1439	0.5001	0.1530	0.1484	0.1521
0.5004	0.0804	0.3978	0.1410	0.5876	0.1526	0.1968	0.1394
0.5992	0.0743	0.4182	0.1390	0.7164	0.1534	0.2260	0.1309
0.7003	0.0697	0.4969	0.1390	0.8026	0.1541	0.2945	0.1176
0.8002	0.0690	0.5663	0.1364			0.3900	0.1174
0.9846	0.0715	0.6417	0.1377			0.4922	0.1130
		0.8645	0.1402			0.5908	0.1094
						0.7876	0.1069

4.1. Standard Heat Capacities and Volumes

The low cmc values of the surfactants investigated here do not allow an accurate evaluation of the dependence of the apparent molar volumes and heat capacities from the surfactant concentration in the premicellar region. So, the standard (infinite dilution) properties were evaluated as the average values of the experimental points in this region. Since the standard partial molar volumes and heat capacities generally show excellent group additivity, we have tested the above hypothesis whenever it was possible. From the standard heat capacities and volumes of tetraalkylammonium chlorides and bromides the difference between Br^- and Cl^- is 7.1 cm^3-mol^{-1} for volumes and -4 J-K^{-1}-mol^{-1} for heat capacities.(30) From these differences and from the standard partial molar volume(1) and heat capacity(5) of DTAB (obtained by additivity rule) the corresponding properties for DTAC are: V°(DTAC)= 281.3 cm^3-mol^{-1} and C°_{p}(DTAC)=1045 J-K^{-1}-mol^{-1}. Similarly, V°(DAC) and C°_{p}(DAC) were calculated from octylamine hydrobromide data,(31) the CH$_2$ group contribution (16 cm^3-mol^{-1} for volume and 89 J-K^{-1}-mol^{-1} for heat capacity) and the above difference between Br$^-$ and Cl$^-$. The calculated values are: V°(DAC)= 230.6 cm^3-mol^{-1} and C°_{p}(DAC)= 982 J-K^{-1}-mol^{-1}. V°(DAC) can be also evaluated by adding 32 to the value of 198.9 cm^3-mol^{-1} reported by Kale and Zana(32) for the standard partial molar volume of decylamine hydrochloride. Experimental volumes and heat capacities reported in Table XIII agree with the above calculated values within 0.4 cm^3-mol^{-1}and 19 J-K^{-1}-mol^{-1}, respectively. From data of Table XIII the contribution to V°_{2} and C°_{p2} for the replacement of the first two H atoms with CH$_3$ groups in the head group of alkylammonium surfactants can be calculated. The average values for each substitution, obtained as the differences between DDAC and DAC, are 17.2 cm^3-mol^{-1} and 34 J-K^{-1}-mol^{-1} for volumes and heat capacities, respectively. The substitution of the third H atom with a CH$_3$ group, obtained from DTAC and DDAC, gives the values of 15.5 cm^3-mol^{-1} and 34.5 J-K^{-1}-mol^{-1} for volumes and heat capacities, respectively. So, it seems that the progressive replacement of an H atom with a CH$_3$ group contributes with a constant amount to heat capacity whereas it is not so for volumes. However, it is to be stressed that if our V°(DDAC) is overestimated by 1 cm^3-mol^{-1}, volumes behave like heat capacities. Unfortunately, there is no investigation on shorter alkyl chain homologues which could allow the evaluation of V°(DDAC) by the additivity rule.

4.2. Thermodynamic Properties of Micellar Solutions

In Fig. 2 the excess volumes (V_{ϕ} - V°_{2}) are plotted as a function of molalities. The concentration dependence of (V_{ϕ} - V°_{2}) is similar to that of other surfactants. Just above the cmc the apparent molar volume increases sharply and hence slowly levels off. In the case of DAC it seems that V_{ϕ} tends to decrease starting from 0.45 mol-kg^{-1}. If the partial molar volumes are considered (not shown), it appears that beyond a maximum which occurs at about 0.1 mol-kg^{-1}, by increasing the surfactant concentration V_2 decreases monotonically for DTAC, reaches a plateau and then decreases for DDAC whereas it is essentially constant for DAC. Beyond the cmc by decreasing the number of methyl groups in the polar head of micelles the initial slope of the plot of V_{ϕ} *vs.* m in-

Table VIII. Osmotic and Activity Coefficients and Nonideal Free Energies, Enthalpies and Entropies of Dodecylamine Hydrochloride in Water at 25°C[a]

m	Φ_{298}	$-\ln \gamma_{\pm}$	$-G^{ni}$	L_2	TS^{ni}
0.008330	0.9440	0.0847	0.42	0.88	1.30
0.009472	0.9306	0.1061	0.53	0.98	1.51
0.01989	0.6242	0.5491	2.72	1.68	4.40
0.04206	0.3371	1.2203	6.04	1.51	7.55
0.04989	0.2887	1.3863	6.87	1.34	8.21
0.06539	0.2238	1.6537	8.19	1.04	9.23
0.07352	0.2013	1.7686	8.76	0.90	9.66
0.09984	0.1555	2.0687	10.25	0.42	10.67
0.1293	0.1320	2.3156	11.47	-0.01	11.46
0.1570	0.1193	2.4990	12.38	-0.37	12.01
0.1952	0.1051	2.7079	13.41	-0.96	12.45
0.2152	0.0990	2.8017	13.88	-1.19	12.69
0.2428	0.0919	2.9182	14.45	-1.56	12.89
0.2989	0.0837	3.1173	15.44	-1.83	13.61
0.3988	0.0766	3.3932	16.81	-1.80	15.01
0.5004	0.0694	3.6125	17.89	-1.64	16.25
0.5992	0.0649	3.7860	18.75	-1.37	17.38

[a] Units are: mol-kg^{-1} for m; kJ-mol^{-1} for energies.

creases as predicted from aggregation numbers. L_ϕ (see Fig. 3) behaves similarly to V_ϕ with the exception that at surfactant concentrations higher than a given value (0.05 for DAC, 0.10 for DDAC and 0.13 mol-kg^{-1} for DTAC) by increasing the surfactant concentration L_ϕ decreases because of the strong hydrophilic interactions in the micellar region. Trends like those reported in Fig. 3 are typical(31,33-36) for ionic surfactants. Beyond the maximum (with the exception of DAC for concentrations greater than about 0.4 mol-kg^{-1}), the lines for L_2 *vs*. m (not shown) are nearly parallel showing that the introduction of a CH_3 group yields an average contribution to the relative partial molar enthalpies of about 1.5 kJ-mol^{-1}. This contribution is surprising since it is known that nonionic surfactants display greater enthalpies than ionic. The present data seems to indicates that the steric hindrance of the CH_3 group confers to the micelles a weaker ionic character despite β changes in the opposite direction. Similar conclusions can be drawn by comparing DTAC with DTAB. Enthalpies and degree of counterion dissociation of DTAC are both much larger than those of DTAB showing that counterions play

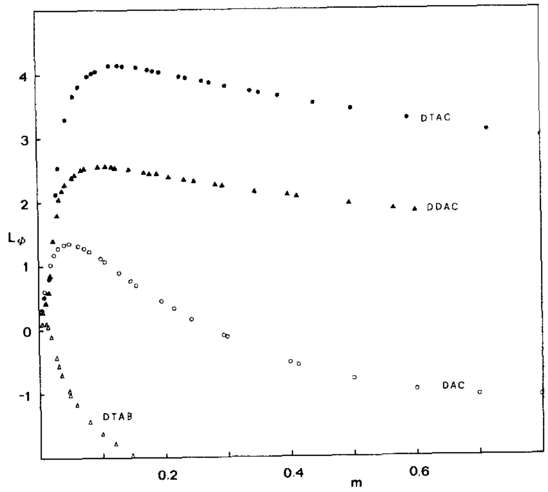

Fig. 3. Relative apparent molar enthalpy (kJ-mol^{-1}) *vs.* surfactant molality. DAC, dodecylamine hydrochloride; DDAC, dodecyldimethylammonium chloride; DTAC, dodecyltrimethylammonium chloride; DTAB, dodecyltrimethylammonium bromide.

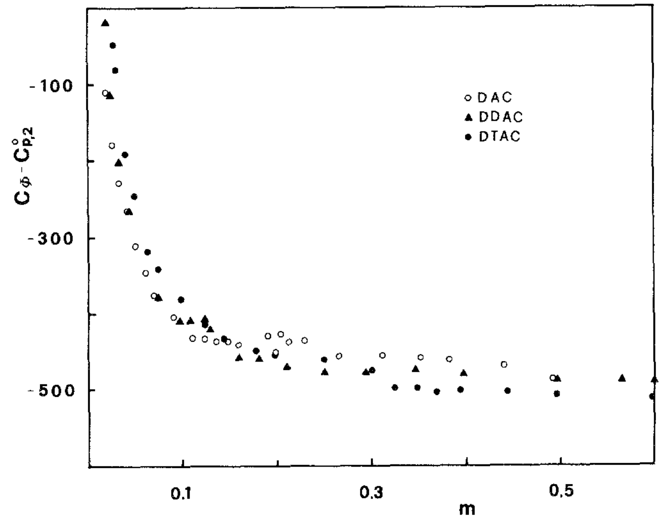

Fig. 4. Apparent molar heat capacity (J-K^{-1}-mol^{-1}) *vs.* surfactant molality. DAC, dodecylamine hydrochloride; DDAC, dodecyldimethylammonium chloride; DTAC, dodecyltrimethylammonium chloride.

Table IX. Osmotic and Activity Coefficients and Nonideal Free Energies, Enthalpies and Entropies of Dodecyldimethylammonium Chloride in Water at 25°C[a]

m	Φ_{298}	$-\ln \gamma_{\pm}$	$-G^{ni}$	L_2	TS^{ni}
0.009991	0.9431	0.0934	0.46	0.70	1.16
0.02949	0.5745	0.6582	3.26	3.64	6.90
0.03491	0.4983	0.8124	4.02	3.30	7.32
0.04473	0.3871	1.0614	5.26	3.11	8.37
0.07514	0.2685	1.5364	7.61	2.76	10.37
0.09855	0.2270	1.7837	8.83	2.57	11.40
0.1088	0.2146	1.8736	9.28	2.51	11.79
0.1249	0.1915	2.0067	9.94	2.41	12.35
0.1294	0.1932	2.0336	10.07	2.38	12.45
0.1597	0.1773	2.2221	11.01	2.21	13.22
0.1797	0.1657	2.3315	11.55	2.11	13.66
0.2096	0.1564	2.4704	12.24	1.98	14.22
0.2492	0.1473	2.6268	13.01	1.84	14.85
0.2838	0.1447	2.7407	13.57	1.72	15.29
0.3404	0.1388	2.9035	14.38	1.57	15.95
0.3978	0.1361	3.0412	15.06	1.47	16.53
0.4182	0.1341	3.0864	15.29	1.44	16.73
0.4969	0.1341	3.2366	16.03	1.34	17.37
0.5663	0.1314	3.3529	16.61	1.28	17.89
0.6417	0.1333	3.4598	17.14	1.24	18.38
0.8645	0.1366	3.7181	18.42	1.20	19.62

[a] For Units: see Table VIII.

Let us now discuss the excess heat capacities shown in Fig. 4. By increasing the surfactant concentration, $(C_{\phi} - C^{\circ}_{p2})$ for DDAC decreases continuously whereas those for DAC and DTAC show maxima and minima. These peculiarities could be ascribed to micellar structural transitions as suggested for alkyltrimethylammonium bromides(37-43) and alkylamine hydrochloride.(44) Whereas below the cmc the initial slope increases by decreasing the number of the methyl groups in the hydrophilic head group, at higher surfactant concentrations an inversion of these slopes occurs. The maxima and minima are small when the C_{ϕ} are examined but become more evident in the C_{p2} trends and when pentanol is used as a probe.(9)

Table X. Osmotic and Activity Coefficients and Nonideal Free Energies, Enthalpies and Entropies of Dodecyltrimethylammonium Chloride in Water at 25°C[a]

m	Φ_{298}	$-\ln \gamma_\pm$	$-G^{ni}$	L_2	TS^{ni}
0.01011	0.9441	0.1040	0.51	0.90	1.41
0.01984	0.9065	0.1914	0.95	1.61	2.56
0.03388	0.6339	0.5729	2.84	5.10	7.94
0.05865	0.4041	1.0727	5.31	4.95	10.26
0.08949	0.2887	1.4673	7.27	4.51	11.78
0.1299	0.2269	1.8100	8.96	4.13	13.09
0.1596	0.2046	1.9947	9.88	3.92	13.80
0.1864	0.1864	2.1381	10.59	3.76	14.35
0.2278	0.1727	2.3174	11.48	3.53	15.01
0.2608	0.1663	2.4364	12.07	3.42	15.49
0.3008	0.1471	2.5763	12.76	3.20	15.96
0.3537	0.1534	2.7083	13.41	2.98	16.39
0.3853	0.1483	2.7861	13.80	2.88	16.68
0.4413	0.1444	2.9062	14.39	2.69	17.08
0.5001	0.1447	3.0132	14.92	2.52	17.44
0.5876	0.1438	3.1527	15.61	2.30	17.91
0.7164	0.1439	3.3234	16.46	2.02	18.48
0.8026	0.1441	3.4206	16.94	1.85	18.79

[a] For Units: see Table VIII.

4.3. Osmotic Coefficients

Osmotic coefficients also seem to support the presence of transitions. Actually, as Fig. 5 shows, apart from the abrupt drop at the cmc, no peculiarities seem to be present in the plots of Φ *vs.* m. However, as we shall see later, according to the pseudo-phase transition model a linear plot is predicted for Φm *vs.* m. As Fig. 6 shows, the linear correlation was obtained but in correspondence with the maxima and minima observed in the C_ϕ *vs.* m plots, the slopes change. Also, in the case of DTAB a change of the slope occurs at about 0.08m, which corresponds approximately to the concentration at which the presence of a transition was earlier suggested.(43) No change in the slopes are obtained for nonyl- and decyltrimethylammonium bromides(45) whereas in the case of NaDS(46) the experimental point at the highest surfactant concentration reported in the literature deviates from the line. No tran-

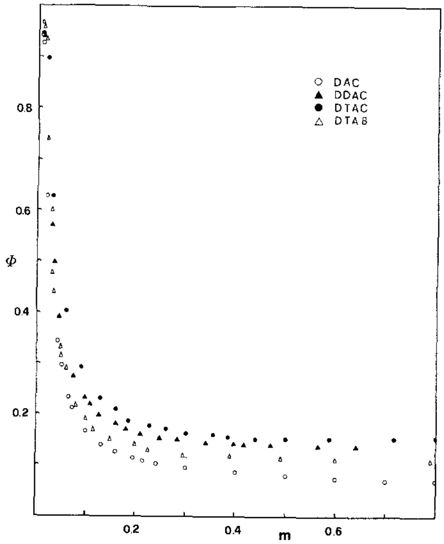

Fig. 5. Osmotic coefficient *vs.* surfactant molality. DAC, dodecylamine hydrochloride; DDAC, dodecyldimethylammonium chloride; DTAC, dodecyltrimethylammonium chloride; DTAB, dodecyltrimethylammonium bromide.

sitions are reported in the literature for the first two surfactants whereas a transition at about 0.25 mol-kg^{-1}, *i.e.* corresponding to the point that deviates from the line, was suggested for NaDS.(47-49) It seems that osmotic coefficients are very sensitive to the micellar rearrangements. However, it is to be stressed that Φ is sensitive to the number of particles, and then it cannot distinguish between the case in which the micellar rearrangement involves a change of the aggregation number, of the degree of the counterion binding or both. According to Lindblom *et al.*(39) a structural rearrangement of micelles should involve a change of the charge density and hence of β. So, the change of the slopes in the post-micellar region reported in Fig. 1 could be due to a change of β; this does not exclude a simultaneous change of *n*. The fact that the β change (if real) is very small does not imply that it is negligible as far as osmotic coefficients are concerned.

As Figs. 7 and 8 show, with the exception of entropies for DAC, the peculiarities observed in the Φ*m* *vs.* *m* plots disappear when the nonideal enthalpies, free energies and entropies are considered. Inspection of Fig. 7 shows that the removal of a CH_3 group from the polar head affects the nonideal enthalpies and free energies but not the entropies. However, at about 0.25 mol-kg^{-1} the nonideal entropies of DAC show a peculiar behavior which might be related to some sort of transition. As

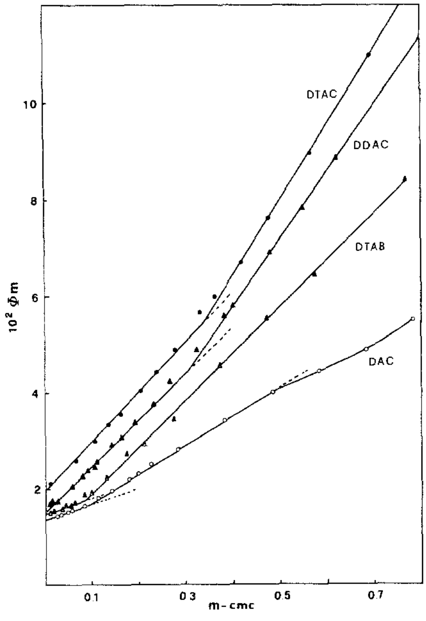

Fig. 6. Plots of osmotic coefficient times molality *vs.* surfactant molality according to the pseudo-phase transition model (Eq.13 of text). DAC, dodecylamine hydrochloride; DDAC, dodecyldimethylammonium chloride; DTAC, dodecyltrimethylammonium chloride; DTAB, dodecyltrimethylammonium bromide.

far as the effect of counterion is concerned, Fig. 8 shows that while nonideal enthalpies and entropies are markedly different when chloride ions are replaced by bromide ions, the same is not true for free energies.

4.4. Thermodynamics of Micellization

In order to evaluate the thermodynamics of micellization, a model for the micellization process must be assumed. Burchfield and Woolley(50) using their mass action model for ionic surfactants obtained thermodynamic properties of micellization often close to those calculated by means of the pseudo-phase transition model.(31,45) On the other hand, Maa and Chen(51) obtained comparable enthalpies of micellization of ionic surfactants using both the pseudo-phase transition model and the mass action model originally developed for nonionic surfactants.(52) In this case it was assumed that counterion binding does not play an important role on the energetics of the micellar solutions whereas Figs. 3 and 8 of this paper indicate that it is not so. Probably, all these models lead to close values for the thermodynamics of micel-

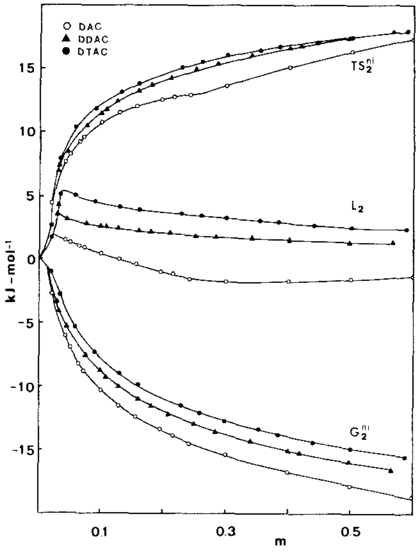

Fig. 7. Effect of the removal of CH_3 groups from the hydrophilic moiety of surfactant on the nonideal contribution to free energy, enthalpy and entropy. DAC, dodecylamine hydrochloride; DDAC, dodecyldimethylammonium chloride; DTAC, dodecyltrimethylammonium chloride.

lization since they make use of an implicit or explicit extrapolation procedure. A more appropriate test could be done by computing other quantities; the aggregation number is the most important of them since independent measurements are possible. If this is done, very large differences are obtained. For example, from the osmotic coefficients of nonionic surfactants more reasonable values of *n* were obtained by using the mass action models.(50,52) Also, with the hypothesis of ideal behavior of micelles and monomers, the pseudo-phase transition model leads to the following equation for the osmotic coefficients of ionic surfactants

$$\Phi m = m_c + [(1+\beta n)/2n]\,(m - m_c) \qquad (13)$$

where m_c is the cmc. Equation (13) predicts (see Fig. 6) a linear correlation between Φm and $(m\text{-}m_c)$. However, from the slope of this plot meaningless negative *n* values are calculated. Since we are interested in the thermodynamics of micellization, the simpler pseudo-phase transition model was used. Following this model a given thermodynamic property of micellization is obtained by extrapolating at the cmc the trends, above and below the cmc, of the corresponding partial molar property as a function of molality.(31,33) Let Y_s and Y_m be the extrapo-

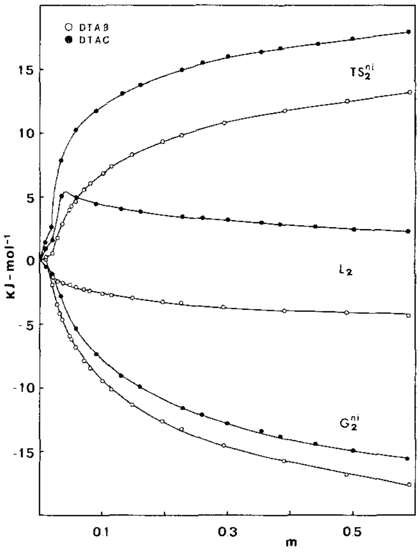

Fig. 8. Effect of the nature of counterion on the nonideal contribution to free energy, enthalpy and entropy. DTAC, dodecyltrimethylammonium chloride; DTAB, dodecyltrimethylammonium bromide.

lated partial molar quantities of surfactant at the cmc in the micellized and unmicellized states, respectively. The corresponding thermodynamic property for micellization (ΔY_m) is given by

$$\Delta Y_m = Y_s - Y_m \tag{14}$$

As far as the entropies of micellization (ΔS_m) are concerned, they can be evaluated graphically only if the excess partial molar entropies (S_2-S_2^o) are considered. They can be calculated by adding together the ideal mixing ($R \ln m$) and the nonideal (S_2^{ni}) contributions

$$S_2 - S_2^o = S_2^{ni} + R \ln m \tag{15}$$

Obviously, in the case of enthalpies the ideal contribution is zero whereas in the case of free energies it is $RT \ln m$. Since ΔG_m=0 at equilibrium, *i.e.* at the cmc, the entropy of micellization can be also calculated as

$$\Delta S_m = \Delta H_m / T \tag{16}$$

For example, Fig. 9 shows the plots of the excess free energies (G_2-G_2^o), enthalpies (H_2-H_2^o = L_2) and entropies (S_2-S_2^o) *vs.* *m* for DTAC. As can be seen, a discontinuity at the cmc is present for enthalpies and

Table XI. Osmotic and Activity Coefficients and Nonideal Free Energies, Enthalpies and Entropies of Dodecyltrimethylammonium Bromide in Water at 25°C[a]

m	Φ_{298}	$-\ln \gamma_\pm$	$-G^{ni}$	L_2	TS^{ni}
0.009006	0.9655	0.0530	0.13	-0.07	0.20
0.01146	0.9591	0.0653	0.32	-0.05	0.37
0.01402	0.9342	0.1008	0.50	-0.03	0.53
0.02086	0.7177	0.3797	1.88	1.30	0.58
0.02842	0.5296	0.6815	3.38	1.56	1.82
0.03199	0.4497	0.8216	4.07	1.62	2.45
0.03587	0.4150	0.9213	4.56	1.70	2.86
0.04733	0.3177	1.1947	5.92	1.92	4.00
0.05004	0.3014	1.2494	6.19	1.94	4.25
0.05774	0.2781	1.3746	6.81	2.08	4.73
0.07014	0.2202	1.5790	7.82	2.24	5.58
0.07993	0.2038	1.6986	8.41	2.35	6.06
0.09964	0.1770	1.9049	9.43	2.55	6.88
0.1138	0.1593	2.0334	10.07	2.71	7.36
0.1484	0.1415	2.2791	11.29	2.91	8.38
0.1968	0.1290	2.5387	12.57	3.17	9.40
0.2260	0.1204	2.6687	13.22	3.28	9.94
0.2945	0.1061	2.9203	14.46	3.62	10.84
0.3900	0.1075	3.1731	15.72	3.92	11.80
0.4922	0.1037	3.3869	16.77	4.14	12.63
0.5908	0.1009	3.5545	17.60	4.30	13.30
0.7876	0.1004	3.8171	18.91	4.46	14.45

[a] For Units: see Table VIII.

entropies but not for free energies since at the cmc micelles are forming. In the case of DDAC, to evaluate ΔS_m by graphical extrapolation, the curve in the pre-micellar region was drawn by adding points interpolated from the plot of S_2^{ni} *vs.* m by assuming a linear correlation for $0 < m <$ cmc. Table XIII summarizes the thermodynamic properties of the micellized and unmicellized surfactants at the cmc together with the thermodynamic properties of micellization using the above model. As the data in Fig. 9 and Table XIII show, the entropies of micellization directly evaluated agree well with those calculated as $\Delta H_m/T$, confirming that at the cmc $\Delta G_m=0$. The above comparison and plots such as those reported in Fig. 6 show that (at least for the present surfactants) the procedure used involves an accuracy better than 0.5 kJ-mol^{-1} and 1

Table XII. Equivalent Conductivities of Dodecylamine Hydrochloride (DAC), Dodecyldimethylammonium Chloride (DDAC), Dodecyltrimethylammonium Chloride (DTAC) and Dodecyltrimethylammonium Bromide (DTAB) in Water at 25°C[a]

c	λ	*c*	λ	*c*	λ	*c*	λ
DAC		DDAC		DTAC		DTAB	
0.002767	94.76	0.001787	95.59	0.002107	94.12	0.002075	96.76
0.004661	93.37	0.003556	94.16	0.003907	92.80	0.003769	95.31
0.007207	92.28	0.005047	92.99	0.006111	91.45	0.005507	94.10
0.009602	91.25	0.006904	92.05	0.008703	90.20	0.007909	92.68
0.01176	89.06	0.008863	91.10	0.01120	89.14	0.01059	91.38
0.01388	83.67	0.01068	90.38	0.01381	88.16	0.01331	90.21
0.01614	77.76	0.01252	89.72	0.01626	87.29	0.02001	74.96
0.02041	67.94	0.01467	88.95	0.01902	86.05	0.02683	63.65
0.02586	58.84	0.01704	86.19	0.02169	84.00	0.03396	53.38
0.03099	52.87	0.01935	80.38	0.02451	80.61	0.04149	47.81
0.03640	48.36	0.02247	73.37	0.02709	77.05	0.05575	41.50
0.04246	44.65	0.02586	67.46	0.02992	73.36	0.06942	37.88
0.04845	41.90	0.02969	62.34	0.03313	69.69	0.04383	35.72
0.05439	39.86	0.03472	57.30	0.03667	66.27	0.09650	34.23
0.06003	38.29	0.04020	53.28	0.04108	62.81	0.1186	32.53
0.06637	36.85	0.05064	48.13	0.04575	59.84	0.1426	31.37
0.07321	35.63	0.06086	44.92	0.05024	57.51		
0.08000	34.64	0.07003	42.91	0.05841	54.23		
0.08789	33.69	0.07897	41.45	0.06729	51.65		
0.09647	32.86	0.09533	39.59	0.07845	49.26		
0.1065	32.09	0.1224	37.83	0.09277	47.16		
0.1188	31.35	0.1360	37.25	0.1104	46.03		
0.1310	30.79			0.1389	45.49		
0.1436	30.33						
0.1569	29.97						
0.1694	29.69						
0.1810	29.46						
0.2021	29.14						

[a] Units are: molarity for concentrations; cm^2-ohm^{-1}-mol^{-1} for conductivities.

J-K^{-1}-mol^{-1} for ΔH_m and ΔS_m, respectively. Looking at the effect of the nature of counterions on the thermodynamics of micellization, the data in Table XIII shows that entropy and enthalpy of micellization are positive for DTAC and negative for DTAB, their differences being about 17 J-K^{-1}-mol^{-1} and 5.1 kJ-mol^{-1}. The volume of micellization of DTAC is also greater by about 1.5 cm^3-mol^{-1} whereas heat capacity of micellization is about 35 J-K^{-1}-mol^{-1} smaller; the latter value is comparable to the difference in heat capacities found for the micellized forms of

Table XIII. Critical Micelle Concentration, Aggregation Number, Degree of Counterion Binding, Thermodynamic Properties in Water, Aqueous Phase and in Micellar Phase and Thermodynamic Properties of Micellization[h]

	DAC	DDAC	DTAC	DTAB
cmc	$0.0135,0.015^a$	$0.0158,0.016^a$	$0.0203,0.022^a$	$0.0152,0.0152^b$
n	108^a	66^a	51^a	55^c
β	0.25	0.31	0.37	$0.23,0.23^d$
V^o_W	230.9	265.4	280.9	288.4^e
V_m	230.9	265.4	280.9	288.4^e
V_S	241.8	275.2	288.9	294.9^e
ΔV_m	10.9	9.8	8.0	6.5^e
Cp^o_W	963	1030	1065	1049^f
Cp_m	963	1030	1065	1110^f
Cp_S	530	490	530	610^f
ΔC_m	-430	-540	-535	-500^f
$L_{2,m}$	1.46	1.06	1.76	0.12^g
$L_{2,S}$	2.13	3.68	5.40	-1.4^g
ΔH_m	0.67	2.62	3.64	-1.5^g
$(S_2-S^o_2)_m$	78.26	73.69	71.81	71.74
$(S_2-S^o_2)_S$	80.34	81.74	83.62	66.98
ΔS_m	2.08	8.05	11.81	-4.76
$\Delta H_m/T$	2.25	8.79	12.21	-5.0

[a] From Ref.24. [b] From Ref.23. [c] From Ref.22. [d] From Ref.10. [e] From Ref.1. [f] From Ref.5. [g] From data in Ref.4. [h] Units are: mol-kg^{-1} for cmc; cm^3-mol^{-1} for volumes; J-K^{-1}mol^{-1} for heat capacities and entropies; kJ-mol^{-1} for enthalpies. The subscripts W, m, S refer to water, aqueous phase and micellar phase, respectively.

hexadecyltrimethylammonium chloride and bromide.(42) We recall that a large difference was also observed for β and that counterion solvation alone cannot account for this large difference.

Looking at the effect on the thermodynamics of micellization due to the introduction of CH_3 groups in the hydrophilic moiety of surfactants, Table XIII shows that entropies and enthalpies increase linearly with the number of the introduced CH_3 groups. An increase of ΔS_m

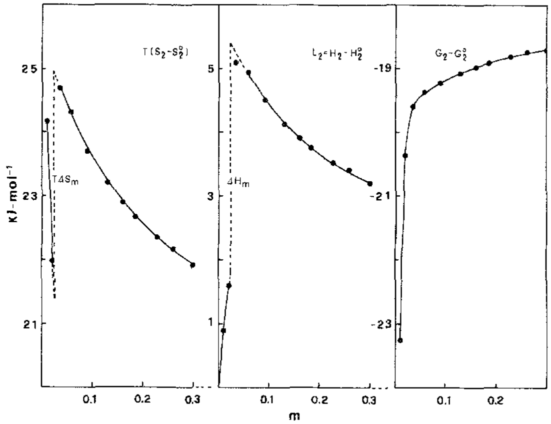

Fig. 9. Plots of the excess free energy, enthalpy and entropy *vs.* molality for dodecyltrimethylammonium chloride.

with methyl groups in the head group was also obtained by Aratono *et al.*[12] from the reported behavior of ΔS_m as a function of temperature, we have estimated their values for DAC and DTAC to be 4 J-K^{-1}-mol^{-1} estimated and 15 J-K^{-1}-mol^{-1}, respectively, which are comparable to those reported here. The increase of ΔH_m is clearly due to the increase of the relative partial molar enthalpy of surfactants in the micellized form whereas the increase of ΔS_m is due either to the increase of the partial molar entropy of surfactant of the micellized form or to the decrease of that quantity for the unmicellized form.

The replacement of a H atom with a CH_3 group contributes 3.2 J-K^{-1}-mol^{-1} and 1.0 kJ-mol^{-1} to ΔS_m and ΔH_m, respectively. It is noteworthy that these contributions are quantitatively the same as those for the removal of a CH_2 group in the aliphatic alkyl chain of the alkyltrimethylammonium surfactants.[34] As far as the volume of micellization is concerned, it decreases in a nonlinear way by increasing the number of CH_3 groups in the head group. It was reported[11] that decylamine hydrochloride is more compressible than decyltrimethylammonium chloride because of the stronger repulsive forces between the head groups at the micellar surface. This interpretation accounts also for the larger volume of micellization for DAC with respect to DDAC and DTAC. The average value for this contribution is -1 cm^3-mol^{-1}. Again, this contribution is opposite to that for the introduction of a CH_2 group in the hydrophobic moiety, which is 0.5 cm^3-mol^{-1}.[43] An accurate computation of the heat capacity of micellization (ΔC_m) is not always possible because of post-micellar transitions and hence of the uncertainty on the evaluation of heat capacity of surfactants in the micellized form. If these quantities are taken as the values at which the plots of C_p *vs. m* seem to tend below the structural transitions (values reported in Table XIII), ΔC_m does not change regularly with the number of CH_3 groups in the head group. However, each methyl group contributes about -30 J-K^{-1}-mol^{-1} which is still the same order of magnitude of that (-50 J-K^{-1}-mol^{-1}) for the introduction of a CH_2 group in the hydrophobic moiety.(43,53)

In conclusion, the substitution of a H atom by a CH_3 group in the hydrophilic moiety produces a change in the volume, enthalpy and entropy of micellization comparable to those for the removal of a CH_2 group from the hydrophobic moiety and heat capacity of micellization changes comparable to that for the introduction of a CH_2 group in the hydrophobic alkyl chain.

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