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THERMODYNAMIC STUDIES OF OCTYLTRIMETHYLAMMONIUM CHLORIDE IN WATER

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Densities, heat capacities, enthalpies of dilution at 298 K and osmotic coefficients at 310 K of octyltrimethylammonium chloride were measured as functions of concentration. From the experimental data, the partial molar volumes, heat capacities, relative enthalpies, nonideal free energies and entropies at 298 K were derived as functions of concentration. A comparison between the above data and those of dodecyltrimethylammonium chloride reported in the literature shows that the increase of the alkyl chain length shifts the apparent molar volume *vs.* concentration curves towards greater values and the heat capacity, relative enthalpy and free energy *vs.* concentration curves towards smaller values. By assuming the pseudo-phase transition model the properties of micellization (ΔY_m) were graphically evaluated. The ΔY_m values of OTAC compared with those of DTAC are consistent with the increase of the hydrophobicity by increasing the alkyl chain length.

Keywords: activity coefficients; enthalpies of dilution; heat capacities; nonideal entropies; nonideal free energies; octyltrimethylammonium chloride; osmotic coefficients; partial molar heat capacities; partial molar relative enthalpies; partial molar volumes; thermodynamics of micellization

Introduction

During last few years we have been performing a thermodynamic characterization of micellar systems. In particular, the thermodynamics of micellization in water [1–4] and the thermodynamics of solubilization of polar additives in micellar solutions have been investigated [5–8]. Recently, we have focussed on the interpretation of the effect of the nature of the head group on the profile of the bulk thermodynamic properties *vs.* concentration. Interesting information has been obtained by comparing these properties for alkyltrimethylammonium [1, 2], N-alkylpyridinium, [3] N-alkyl-N-methylpiperidinium [4] and N-alkylpiperidinium [4] chlorides. As a consequence of these results, we decided to study octylalkyldimethylammonium chlorides where the alkyl chain ranges between methyl

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and pentyl. The choice of octylcompounds is due to the fact that the their cmc values are sufficiently high to be thermodynamically analyzed in both the premicellar and postmicellar regions.

In this paper we report the volumes, heat capacities, enthalpies of dilution and osmotic coefficients (and, hence, the nonideal free energies and entropies) of octyltrimethylammonium chloride as functions of concentration.

Experimental

Materials

Octyltrimethylammonium chloride (OTAC) is a Tokyo Kasei product. It was crystallized from ethyl acetate and dried under vacuum for 48 h at room temperature.

D(+)sucrose and NaCl (Fluka products) were dried for at least 48 hours before use in a vacuum oven at 313 and 373 K, respectively.

All solutions were prepared by mass using degassed conductance water and their concentrations were expressed as the number of solute moles per kg of solvent.

Equipment

The densities of the solutions were measured with a vibrating tube flow densimeter (Sodev Mod. 03D) sensitive to 3 ppm or better. The temperature was kept constant at 298±0.001 K by using a closed loop temperature controller (Model CT-L, Sodev Inc.). The calibration of the instrument was made with water ($d = 0.997047\ \mathrm{g\cdot cm^{-3}}$) [9] and aqueous D(+)-sucrose solutions at different concentrations whose density values were taken from the literature [10].

The relative differences in heat capacities per unit volume between the surfactant solutions and water $\Delta\sigma/\sigma_o = (\sigma-\sigma_o)/\sigma_o$ were determined with a Picker flow microcalorimeter (Setaram). The specific heat capacities (c_p) of solutions of density d are related to $\Delta\sigma/\sigma_o$ through the equation

$$c_p = c_{p_o}\{1+\Delta\sigma/\sigma_o\}d_o/d \qquad (1)$$

where c_{p_o} and d_o are the specific heat capacity and density of water, respectively. The value of $4.1792\ \mathrm{J\cdot K^{-1}\cdot g^{-1}}$ was used for c_{p_o} [11].

The enthalpies of dilution were measured at 298 K with a flow LKB 2107 microcalorimeter. The surfactant solutions were diluted in a 1:1 ratio with water. The injection of the solutions and water into the microcalorimeter was made by means of a Gilson peristaltic pump (Minipuls 2) and the flow of both the surfactant solution and water were determined by weight.

The osmotic coefficients (Φ) were determined by means of an Osmomat 070 (Gonotec) vapour pressure osmometer equipped with an automatic control unit. Measurements were made at 310 K, the lowest operating temperature suggested for aqueous solutions. The instrument was calibrated using an aqueous NaCl solution 400 mOsmol-kg^{-1}. The Φ accuracy is of the order of 1% at the lowest surfactant concentration analyzed and quickly improves to 0.2% when the surfactant concentration is increased.

Results and discussion

The apparent molar volumes V_Φ and heat capacities C_Φ of OTAC have been calculated by means of the following equations

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

$$C_\Phi = Mc_p + \frac{10^3(c_p - c_{po})}{m} \qquad (3)$$

where m is the molality of the solutions and M the molecular weight of the surfactant.

The apparent molar volumes and heat capacities together with the excess densities ($\Delta d = d - d_o$) and the relative differences in heat capacities per unit volume ($\Delta\sigma/\sigma_o$) of the solutions are summarized in Table 1, while the excess of the apparent molar properties with respect to those at infinite dilution ($Y_\Phi - Y_2^o$) as functions of concentration are shown in Figs 1 and 2, where dodecyltrimethylammonium chloride (DTAC) [2] plots are also shown for comparison. To compact the abscissa scale in these figures and in the following ones the logarithm of the concentration normalized for cmc is used. On the basis of the pseudo-phase transition model for micellization, the physical meaning of this scale is related to the nonideal free energies [12].

The standard (infinite dilution) partial molar volume and heat capacity were obtained from the dependence of the corresponding apparent molar properties in the premicellar region as functions of concentration by means of the following equation

$$Y_\Phi = Y_2^o + A_Y m^{1/2} + B_Y m + C_Y m^{3/2} \qquad (4)$$

where A_Y is the Debye-Hückel interaction parameter, B_Y and C_Y are pair and triplet surfactant-surfactant interaction parameters. The values used for A_Y at 298 K are 1.865 cm^3·mol$^{-3/2}$·kg$^{1/2}$ and 28.95 J·K^{-1}·mol$^{-3/2}$·kg$^{1/2}$ for volume and

Table 1 Volumes and heat capacities of octyltrimethylammonium chloride in water at 298 K

m / mol·kg^{-1}	$-10^3\Delta d$ / g·cm^{-3}	V_Φ / cm^3·mol^{-1}	V_2 / cm^3·mol^{-1}	$-10^3\Delta\sigma / \sigma_o$	C_Φ / J·K^{-1}·mol^{-1}	C_{p2} / J·K^{-1}·mol^{-1}
0.04537	0.441	217.37	217.28	1.75	746.8	745
0.08903	0.770	217.28	217.13	3.30	747.5	743
0.1282	1.091	217.20	217.02	4.86	742.2	742
0.1638	1.335	217.05	216.95	6.05	743.9	740
0.2019	1.675	217.11	216.89	7.61	740.3	739
0.2290	1.887	217.11	216.87	8.53	741.3	738
0.2857	2.324	217.09	216.86	10.36	743.7	737
0.3485	2.802	217.10	216.91	12.71	739.8	736
0.4014	3.140	216.96	217.01	14.39	741.2	736
0.4920	3.806	217.01	217.27	17.69	738.0	736
0.5697	3.779	217.04	217.60	22.66	713.0	524
0.6668	5.174	217.33	219.05	29.45	694.3	474
0.7056	5.467	217.39	219.40	33.17	679.3	466
0.8546	6.800	217.89	219.80	44.18	651.8	445
1.0037	8.094	218.29	220.00	57.29	618.9	436
1.1803	9.336	218.40	220.00	70.11	598.0	431
1.5098	11.683	218.75	220.00	96.17	557.6	441
2.0555	15.068	219.09	220.00	130.18	529.4	465

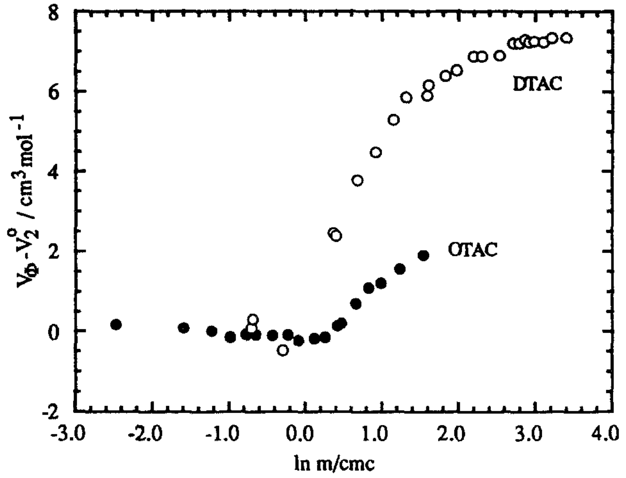

Fig. 1 Dependence on concentration of the excess apparent molar volumes with respect to those at infinite dilution for octyl- (OTAC) and dodecyl- (DTAC) trimethylammonium chlorides

heat capacity, respectively [13]. The values of the parameters obtained from Eq. (4) are reported in Table 4. From Y^o_2 for OTAC and DTAC, the CH_2 group contribution to the partial molar volume and heat capacity is 15.9 $cm^3 \cdot mol^{-1}$ and 80 $J \cdot K^{-1} \cdot mol^{-1}$, respectively, in agreement with the literature ones [14] of 15.9 $cm^3 \cdot mol^{-1}$ and 89 $J \cdot K^{-1} \cdot mol^{-1}$.

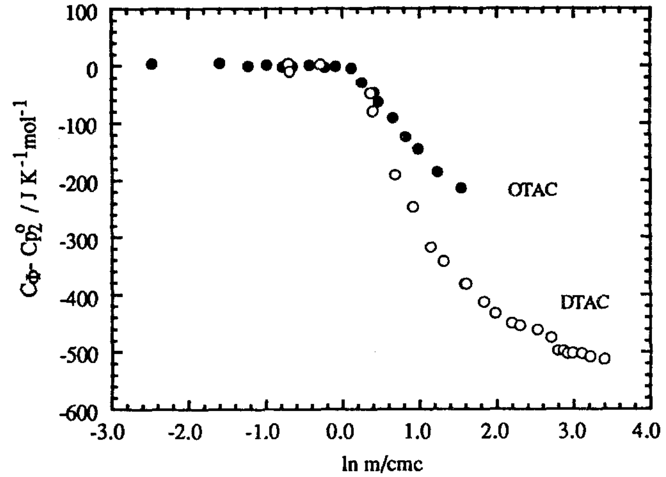

Fig. 2 Dependence on concentration of the excess apparent molar heat capacities with respect to those at infinite dilution for octyl- (OTAC) and dodecyl- (DTAC) trimethylammonium chlorides

As Figs 1 and 2 show, in the premicellar region $Y_\Phi - Y^o_2$ of OTAC slowly depends on concentration while in the micellar region it quickly changes. Moreover, the $Y_\Phi - Y^o_2$ *vs.* concentration trends do not practically depend on the alkyl chain length of the surfactant in the pre-micellar region, although a very few experimental data for DTAC are available, while they differ in the micellar region being the change, a expected, more important for the higher homologous.

The apparent molar relative enthalpies L_Φ were derived from the enthalpies of dilution ΔH_{id} by means of Eq. (5)

$$\Delta H_{id} = L_{\Phi,f} - L_{\Phi,i} \tag{5}$$

where $L_{\Phi,f}$ and $L_{\Phi,i}$ refer to the final and initial concentrations, respectively.

In the pre-micellar region Eq. (4) was applied to the apparent molar relative enthalpy so that by means of Eq. (5) the following equation was obtained

$$\frac{\Delta H_{id} - A_L\,(m_f^{1/2} - m_i^{1/2})}{m_f - m_i} = B_L + C_L\frac{m_f^{3/2} - m_i^{3/2}}{m_f - m_i} \tag{6}$$

where A_L= 1973 J kg$^{1/2}$·mol$^{-3/2}$ is the Debye-Hückel limiting slope for the apparent molar relative enthalpy at 298 K [13]. The B_L and C_L values derived from Eq. (6) are collected in Table 4. For molalities lower than the cmc, L_Φ values have been calculated by means of Eq. (4) and the B_L and C_L values. The procedure used to calculate L_Φ values at higher concentrations has been reported elsewhere [2, 3].

Table 2 Enthalpies of dilution, apparent and partial molar relative enthalpies of octyltrimethylammonium chloride in water at 298 K

m_i / mol·kg^{-1}	m_f / mol·kg^{-1}	$-\Delta H_{id}$ / J·mol^{-1}	$L_{\Phi,i}$ / J·mol^{-1}	$L_{\Phi,f}$ / J·mol^{-1}	$L_{2,i}$ / J·mol^{-1}	$L_{2,f}$ / J·mol^{-1}
0.08903	0.04531	135	467	321	765	480
0.1282	0.06501	217	604	387	1075	600
0.1638	0.08282	283	740	446	1395	720
0.2019	0.1019	396	900	511	1790	860
0.2290	0.1147	478	1023	555	2095	960
0.2857	0.1470	661	1305	674	2809	1240
0.3485	0.1690	920	1656	761	3705	1445
0.4014	0.1963	1095	1980	876	4540	1730
0.4920	0.2461	1417	2596	1105	6140	2300
0.5697	0.2793	1896	3181	1272	7660	2720
0.6668	0.3262	2290	3830	1527	7950	3375
0.7056	0.3378	2463	4080	1593	7940	3545
0.8546	0.4100	2689	4720	2035	7540	4685
1.0037	0.4753	2660	5140	2477	7180	5830
1.1803	0.5401	2413	5380	2952	6820	7065
1.5098	0.6802	1730	5675	3930	6490	7950
2.0555	0.8858	1021	5860	4820	6280	7450

The enthalpies of dilution and the apparent molar relative enthalpies at the initial and final concentrations are summarized in Table 2. Figure 3 shows the dependence of L_Φ on the concentration for both OTAC and DTAC. As it can be seen. the profile of OTAC is moved toward larger values with respect to that of DTAC such as observed for other surfactants.

In the pre-micellar region, the partial molar properties Y_2 have been calculated by means of Eqs (4) and (7) and the known A_Y, B_Y and C_Y parameters

$$Y_2 = \frac{\partial\,(mY_\Phi)}{\partial m} \qquad (7)$$

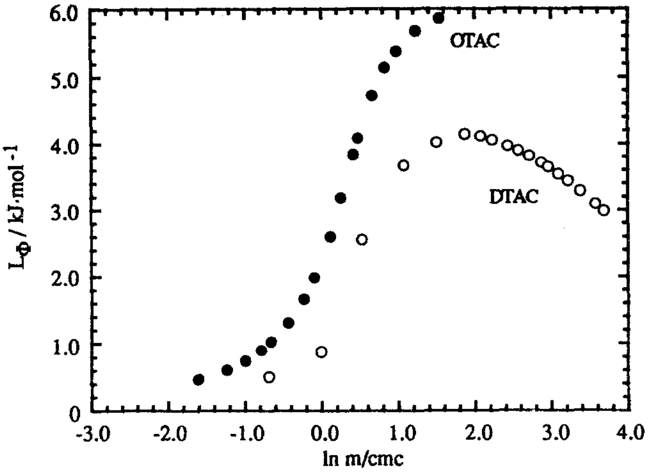

Fig. 3 Apparent molar relative enthalpies for octyl- (OTAC) and dodecyl- (DTAC) trimethyl ammonium chlorides as functions of concentration

In the post-micellar region, Y_2 values were calculated by drawing the best curve for the corresponding apparent molar quantities as functions of molality and interpolating points at regular intervals [2, 3].

V_2, C_{p_2} and L_2 values are given in Tables 1–2.

Since, as previously mentioned, the osmotic coefficients Φ were measured at 310 K, the corresponding quantities at 298 K were calculated by means of the following equation [15]

$$\Phi_{T_o} = \Phi_T - \frac{T_o - T}{2RTT_o}\left[(L_2 - L_\Phi)_{298} - T_o\,(C_{p2} - C_\Phi)_{298}\right] - \frac{(C_{p_2} - C_\Phi)_{298}}{2R}\ln\frac{T_o}{T} \qquad (8)$$

where T_o and T are 298 K and 310 K, respectively.

Equation (8) was obtained by assuming the partial and apparent molar heat capacities to be temperature independent in the range considered. As Fig. 4 shows, the experimental osmotic coefficients as functions of concentration follow a decreasing curve with a break around 0.5 mol·kg^{-1}.

The activity coefficients were calculated by means of the following equation [11]

$$\ln\gamma_\pm = (\Phi - 1) + (2A_\Phi)\sqrt{m_o} + \int_{m_o}^{m}\frac{\Phi - 1}{m}\,dm \qquad (9)$$

where $A_\Phi = -0.39$ kg$^{1/2}$·mol$^{-1/2}$ is the Debye-Hückel limiting slope [13] and m_o the concentration at which the plot of the experimental and the calculated (by using the D-H limiting law) Φ values merge. The m_o value is 0.014 mol·kg^{-1}. The integral at the right hand side of Eq. (9) was solved graphically from plot of $(\Phi - 1)/m$ *vs.* m.

The nonideal free energies have been calculated as

$$G_2^{ni} = 2\,RT\,\ln\gamma_{\pm} \tag{10}$$

and the nonideal contribution to the partial molar entropies as

$$S_2^{ni} = (L_2 - G_2^{ni})/T \tag{11}$$

The osmotic coefficients at 310 and 298 K together with the activity coefficients, the nonideal free energies, enthalpies and entropies at 298 K are reported in Table 3.

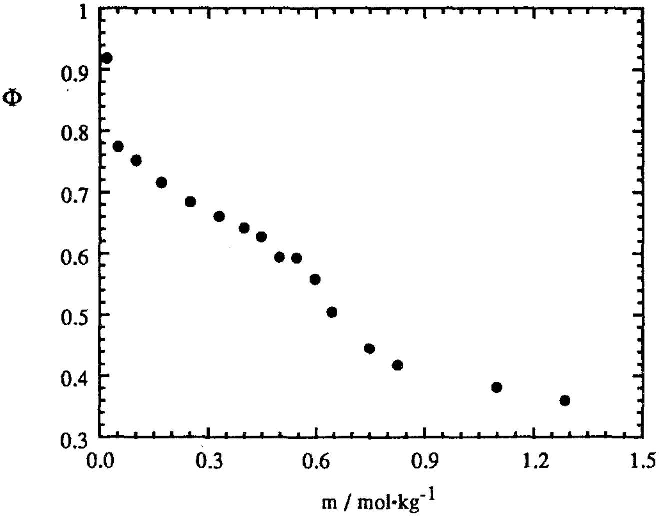

Fig. 4 Experimental osmotic coefficients of octyltrimethylammonium chloride as functions of concentration

Figure 5 shows the dependence of G_2^{ni}, TS_2^{ni} and L_2 on concentration for both OTAC and DTAC. As it can be seen, for OTAC the free energy *vs.* ln*m*/*cmc* trend is moved down with respect to that of DTAC while the opposite behavior is observed for the entropy and the relative enthalpy. The difference observed between the free energy for OTAC and DTAC is due to the predominance of the entropic effect on that of the enthalpy. In addition, it is to be stressed that in the postmicellar region the slope of G_2^{ni} *vs.* ln*m*/*cmc* is essentially the same for the two homologues and that the difference in G_2^{ni} values is related to property at the cmc ($G_{2,m}^{ni}$) which, according to the pseudo-phase transition model, is the same for the surfactant in the unmicellized and micellized forms. On the basis of this model

Table 3 Osmotic coefficients at 310 and 298 K, activity coefficients, nonideal free energies, enthalpies and entropies at 298 K for octyltrimethylammonium chloride in water

m / mol·kg^{-1}	Φ_{310}	Φ_{298}	$-\ln\gamma_{\pm}$	L_2 / kJ·mol^{-1}	$-G_2^{ni}$ / kJ·mol^{-1}	TS_2^{ni} kJ·mol^{-1}
0.02000	0.919	0.920	0.0098	0.30	0.05	0.35
0.04997	0.774	0.775	0.2835	0.54	1.40	1.94
0.09977	0.752	0.755	0.4762	0.86	2.36	3.22
0.1700	0.716	0.720	0.6553	1.22	3.24	4.49
0.2497	0.684	0.694	0.7958	2.35	3.94	6.29
0.3295	0.661	0.676	0.9019	3.40	4.47	7.87
0.3982	0.642	0.662	0.9788	4.44	4.85	9.29
0.4456	0.627	0.657	1.0222	5.40	5.06	10.46
0.4973	0.594	0.623	1.0947	6.36	5.43	11.79
0.5455	0.593	0.621	1.1327	7.08	5.61	12.69
0.5968	0.559	0.588	1.2012	7.88	5.95	13.83
0.6429	0.505	0.527	1.2951	7.95	6.41	14.36
0.7483	0.446	0.463	1.4357	7.83	7.11	14.94
0.8268	0.419	0.432	1.5218	7.62	7.54	15.16
1.0969	0.382	0.389	1.7328	7.16	8.58	15.74
1.2858	0.360	0.362	1.8593	6.65	9.21	15.86

Units are: kJ·mol^{-1} for G_2^{ni}, L_2 and TS_2^{ni}

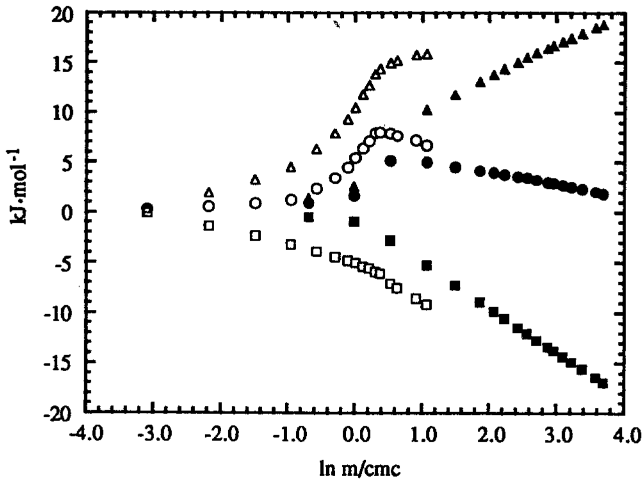

Fig. 5 Nonideal free energies (squares), enthalpies (circles) and entropies (triangles) of octyl- (OTAC) (open symbols) and dodecyl- (DTAC) (filled symbols) trimethylammonium chlorides as functions of concentration

and by assuming that the activity of the surfactant in micellar solution is constant the following equation was derived [12]

$$G_2^{ni} - G_{2,m}^{ni} = -\nu RT \ln m/cmc \tag{12}$$

where ν is the number of ions into which the electrolyte dissociates. According to Eq. (12) and as Fig. 6 shows, the slope of the plot of $G_2^{ni} - G_{2,m}^{ni}$ *vs.* ln*m*/*cmc* does not depend on the nature of the surfactant.

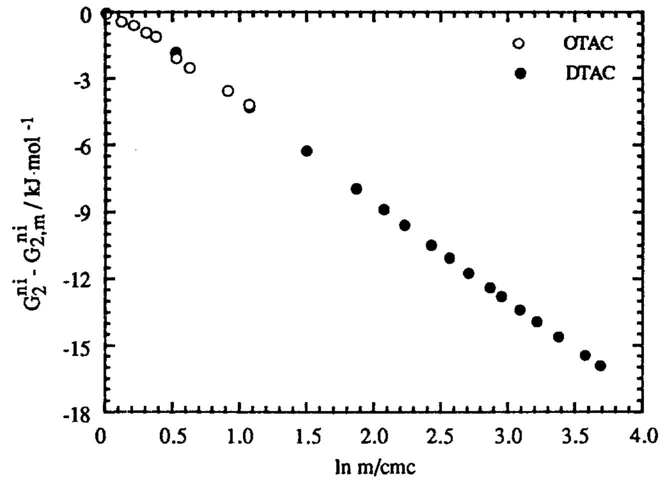

Fig. 6 Nonideal free energies, corrected for those at the cmc, of octyl- (OTAC) and dodecyl- (DTAC) trimethylammonium chlorides as functions of concentration

On the basis of the pseudo-phase transition model, the properties of micellization (ΔY_m) have been derived as differences between the extrapolated values at the cmc of the trend of the partial molar properties *vs.* concentration above (Y_s) and below (Y_m) the *cmc*

$$\Delta Y_m = Y_s - Y_m \tag{13}$$

The Y_m, Y_s and ΔY_m values are reported in Table 4 together with the corresponding ones for DTAC. As it can be seen, V_m and C_{p_m} values of OTAC are very close to those in the infinite dilution state because of the compensative effects between the different solute-solute interaction contributions. Since for DTAC [2] it was assumed $Y_m = Y_2^{\circ}$, the CH_2 group contributions to V_m and are same as those in the infinite dilution state. Moreover, the CH_2 group contribution to V_s (17.2 $cm^3 \cdot mol^{-1}$) and to C_{p_s} (20 $JK^{-1} \cdot mol^{-1}$) higher and lower, respectively, than the standard values in water agree with the literature data indicating that by decreasing the hydrophilicity of the solvent medium the volume increases and the

Table 4 Thermodynamic properties in water, aqueous phase and micellas phase and thermodynamic properties of micellization for octyltrimethylammonium chloride (OTAC) and dodecyltrimethylammonium chloride (DTAC)

	OTAC	DTAC[a]
cmc / $\text{mol}\cdot\text{kg}^{-1}$	0.57[b]; 0.5[c] 0.44[d]	0.0203
V°_{2} / $\text{cm}^3\cdot\text{mol}^{-1}$	217.19±0.07	280.9
B_V / $\text{cm}^3\cdot\text{kg}\cdot\text{mol}^{-2}$	−7.1±0.8	
C_V / $\text{cm}^3\cdot\text{kg}^{3/2}\cdot\text{mol}^{-5/2}$	5.8±1.0	
V_m / $\text{cm}^3\cdot\text{mol}^{-1}$	217.4	280.9
V_S / $\text{cm}^3\cdot\text{mol}^{-1}$	220	288.9
ΔV_m / $\text{cm}^3\cdot\text{mol}^{-1}$	2.6	8.0
C°_{p2} / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	745±3	1065
B_C / $\text{J}\cdot\text{kg}\cdot\text{K}^{-1}\cdot\text{mol}^{-2}$	−115±34	
C_C / $\text{J}\cdot\text{K}^{-1}\cdot\text{kg}^{3/2}\cdot\text{mol}^{-5/2}$	89±45	
C_{Pm} / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	739	1065
C_{P_S} / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	450	530
ΔC_{Pm} / $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	−290	−535
B_L / $\text{kJ}\cdot\text{kg}\cdot\text{mol}^{-2}$	−4.2±0.2	
C_L / $\text{kJ}\cdot\text{kg}^{3/2}\cdot\text{mol}^{-5/2}$	9.5±0.3	
$L_{2,m}$ / $\text{kJ}\cdot\text{mol}^{-1}$	5.2	3.6
$L_{2,S}$ / $\text{kJ}\cdot\text{mol}^{-1}$	9.0	5.4
ΔH_m / $\text{kJ}\cdot\text{mol}^{-1}$	3.8	3.6
$T(S_2^{ni})_m$ / $\text{kJ}\cdot\text{mol}^{-1}$	10.0	2.1
$T(S_2^{ni})_S$ / $\text{kJ}\cdot\text{mol}^{-1}$	14.0	5.6
$T\Delta S_m$ / $\text{kJ}\cdot\text{mol}^{-1}$	4.0	3.5

[a]From Ref. [2]. [b]From volume data; [c]From heat capacity data; [d]From enthalpy and free energy data

heat capacity decreases. It is to be noted that the value obtained for the CH_2 group contribution to V_s agrees with that reported for other surfactants while it is not so for C_{p_s}. It is to be pointed out that different values for C_{p_s} (CH_2) are reported in the literature [3, 4, 12] as a consequence of the difficult evaluation of this quantity because of the presence of maxima and minima (postmicellar transitions) in the C_{p2} *vs.* *m* trends.

As it has been said above, according to the pseudo-phase transition model at the cmc the free energy of micellization is zero and, then, $\Delta H_m = T\Delta S_m$. This equality is verified, within the experimental uncertainties, from the data in Table 4. The self consistency of the data is also verified from the difference L_2-TS_2 at the cmc for both the unmicellized and micellized surfactant which is equal to the experimental value of $G^{0i}_{2,\mathrm{m}}$. Since the data are reliable, from the data in Table 4 we can observe that L_2 and TS_2 of surfactant in the unmicellized and micellized states decrease by increasing the alkyl chain length while ΔH_m and $T\Delta S_m$ do not change. Consequently, the CH_2 group contribution to both properties is zero while negative values are usually reported. This is not surprising, in fact since the additivity rule for the thermodynamic properties of micellization has been questioned in the past [3].

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Zusammenfassung — Für Oktyltrimethylammoniumchlorid wurden Dichte, Wärmekapazität, Lösungsenthalpie bei 298 K und osmotische Koeffizienten bei 310 K als Funktion der Konzentration gemessen. Anhand der experimentellen Daten wurden die partiellen Molvolumen, Wärmekapazitäten, relativen Enthalpien, die nichtidealen freien Energien und Entropien bei 298 K als Funktionen der Konzentration erhalten. Ein Vergleich obiger Daten mit den in der Literatur beschriebenen Daten für Dodecyltrimethylammoniumchlorid zeigt, daß längere Alkylketten die Kurve (scheinbares Molvolumen/Konzentration) zu größeren Werten hin verschiebt, die entsprechenden Kurven von Wärmekapazität, relativer Enthalpie und freien Energien hin zu kleineren Werten. Unter Annahme des Pseudeophasenübergangsmodelles konnten das Mizellisationsvermögen (ΔY_m)graphisch ermittelt werden. DieΔY_m-Werte für OTAC entsprechen - verglichen mit denen von DTAC - dem Anstieg der Hydrophobizität bei anwachsender Alkylkettenlänge.