Thermochimica Acta, 205 (1992) 19–31
Elsevier Science Publishers B.V., Amsterdam

Thermochemical study of aqueous micellar solutions of some amphiphilic quaternary ammonium chlorides at 313 K

Bożenna Różycka-Roszak [1] and Emilia Fisicaro

Istituto di Chimica Fisica Applicata, Università di Parma, Via Spezia, 73-43100 Parma (Italy)

(Received 3 November 1991)

Abstract

The heats of dilution and osmotic coefficients of *N*-dodecyl-*N*-benzylmorpholinium chloride (DBeMC), *N*-dodecyl-*N*-methylmorpholinium chloride (DMeMC) and dodecyl-trimethylammonium chloride (DTAC) were measured by means of an LKB flow microcalorimeter and a vapor pressure osmometer at 40°C. The relative apparent and partial molar enthalpies, free energies and entropies were derived as a function of surfactant concentration. On the basis of the pseudo-phase separation model, the values of critical micelle concentration (c.m.c.) and enthalpy of micellization were graphically evaluated. Micellization heat capacities were also evaluated. The studies confirmed that the benzyl group of DBeMC behaves as a second chain with respect to the micellization process. It was also possible to estimate its "length" as similar to that of an alkyl chain of five carbon atoms. From these results, the packing parameter of DBeMC was evaluated and the formation of non-spherical aggregates by this surfactant was suggested.

INTRODUCTION

N-Dodecyl-*N*-benzylmorpholinium chloride (DBeMC) and *N*-dodecyl-*N*-methylmorpholinium chloride (DMeMC) show biological activity [1]. The compounds influence desorption of Ca^{2+} ion and transport of sulfate ion across liposome bilayers. DBeMC is more effective in both processes than DMeMC [2]. Previously this was interpreted as a result of changes in the structure of the head groups because the compounds were considered to have the same alkyl chain and different head groups. However, micellization studies [3] suggest that the benzyl group of DBeMC behaves as if it were a second hydrocarbon chain. In order to confirm the role played by the benzyl group, thermochemical studies of aqueous solutions of these compounds were undertaken.

Correspondence to: E. Fisicaro, Istituto di Chimica Fisica Applicata, Università di Parma, Via Spezia, 73-43100 Parma, Italy.

[1] Permanent address: Department of Physics and Biophysics, Agricultural University of Wrocław, Wrocław, Poland.

0040-6031/92/$05.00 © 1992 – Elsevier Science Publishers B.V. All rights reserved

The DMeMC compound differs from dodecyltrimethylammonium chloride (DTAC) by the presence of the morpholinium group in place of two methyl groups attached to nitrogen. In turn, DBeMC differs from DMeMC because of the replacement of the methyl group by the benzyl group. Thus, the compounds DMeMC and DBeMC, at least formally, can be treated as derivatives of DTAC which is why DTAC was also included in the study.

EXPERIMENTAL

Materials

All quaternary ammonium salts used in this study (see Fig. 1) were synthesized at the Technical University of Wrocław [1]. The solutions were prepared by weight, using freshly boiled doubly distilled water stored under nitrogen. Solution concentrations are expressed as molality *m* (mol kg^{-1}).

Measurements

The enthalpies of dilution were measured by an LKB 2107 flow microcalorimeter. The freshly prepared surfactant solutions, kept before injection at 40°C in a Heto cryothermostatic bath, were diluted into the "mixing" measuring cell of the microcalorimeter with CO_2-free water at ratio 1 : 1. The injection of the reactants into the calorimeter was done by means of a Gilson peristaltic pump, Minipuls 2, and their flows were determined by weight.

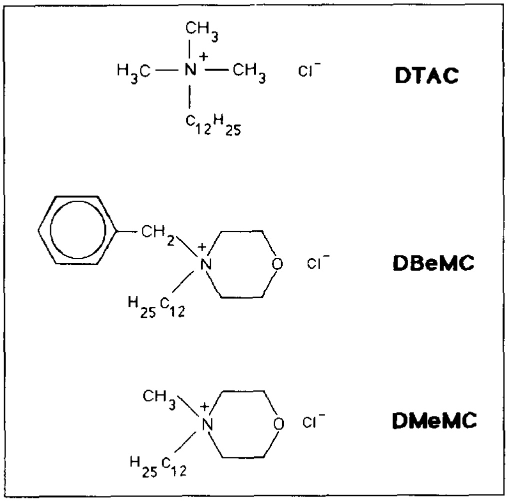

Fig. 1. Chemical formulas of the compounds under study: *N*-dodecyl-*N*,*N*,*N*-trimethylammonium chloride (DTAC), *N*-dodecyl-*N*-benzylmorpholinium chloride (DBeMC), *N*-dodecyl-*N*-methylmorpholinium chloride (DMeMC).

Osmotic coefficients Φ were determined at 40°C by means of vapor pressure osmometer OSMOMAT 070-SA Gonotec, in which the molal decrease of vapor pressure of the solvent used is measured indirectly. The instrument was calibrated using an aqueous solution of NaCl (400 mOsmol kg^{-1}).

THEORY

How to obtain apparent and partial molar enthalpies from heats of dilution has been described in detail before [4–9].

With reference to the state of infinite dilution, the enthalpies of dilution ΔH_d are given by

$$\Delta H_d = \Phi_{L,f} - \Phi_{L,i} \tag{1}$$

where Φ_L are the apparent molar relative enthalpies and the indices f and i stand for the final and initial concentrations, respectively.

For an ionic surfactant in the premicellar region, the relative apparent molar enthalpy can be expressed by means of a polynomial in $m^{1/2}$. Stopping the serial expansion at the third term we obtain

$$\phi_L = Am^{1/2} + Bm + Cm^{3/2} \tag{2}$$

where A ($A = 2390$ J mol$^{-1/2}$ kg$^{1/2}$ at 40°C [10]) is the limiting Debye–Hückel slope for relative enthalpies, accounting for the long range solute–solute interactions. Parameters B and C are averaged from the experimental points in the premicellar region by a least-squares curve fitting

$$\Delta H_d - A(m_f^{1/2} - m_i^{1/2}) = B(m_f - m_i) + C(m_f^{3/2} - m_i^{3/2}) \tag{3}$$

In the micellar region, the apparent molar relative enthalpies are evaluated by means of eqn. (1) and by graphical interpolation, as described in detail in ref. 9.

The partial relative enthalpies L_2 are determined by drawing the best curve for the apparent molar enthalpies vs. m and then calculating the partial molar quantities as $\Delta(m\Phi_L)/\Delta m$ from points interpolated at regular intervals.

The osmotic coefficients are obtained as the ratio between the number of osmoles N_{osm}, which is directly read from the instrument, and the concentration of particles in solution νm, where ν is the number of ions generated upon dissociation

$$\Phi = N_{osm}/(\nu m) \tag{4}$$

Osmotic coefficients are related to activity coefficients by [6,7,11]

$$\ln \gamma_{\pm} = (\Phi - 1) - 2A_{\gamma}m_0^{1/2} + \int_{m_0}^{m} (\Phi - 1)\, \mathrm{d} \ln m \tag{5}$$

where A_γ is the Debye–Hückel limiting slope for the osmotic coefficients ($A_\gamma = 0.401$ mol$^{-1/2}$ kg$^{1/2}$ at 40°C [10]) and m_0 is the value of the concentration at which the experimental and limiting values of Φ converge.

The non-ideal free energies and entropies are related to the activity coefficients by

$$G_2^{\mathrm{ni}} = \nu RT \ln \gamma_\pm \tag{6}$$

and, if the partial molar enthalpies L_2 are known, the non-ideal entropies S_2^{ni} are given by

$$S_2^{\mathrm{ni}} = \left(L_2 - G_2^{\mathrm{ni}}\right)/T \tag{7}$$

The excess partial molar free energy and entropies can be calculated by adding the cratic term to the non-ideal contribution

$$G_2 - G_2^0 = G_2^{\mathrm{ni}} + \nu RT \ln m \tag{8}$$

$$s_2 - S_2^0 = S_2^{\mathrm{ni}} + \nu R \ln m \tag{9}$$

RESULTS AND DISCUSSION

The dilution heats and the apparent and partial molar quantities, obtained by means of eqns. (1)–(3), for the compounds under investigation are reported in Tables 1–3. The trends of the apparent and partial molar

TABLE 1

Enthalpies of dilution, apparent and partial molar enthalpies of DTAC at 313 K

m_i (mol kg^{-1})	m_f (mol kg^{-1})	ΔH_d (J mol^{-1})	Φ_{Li} (J mol^{-1})	Φ_{Lf} (J mol^{-1})	L_{2i} (J mol^{-1})	L_{2f} (J mol^{-1})
0.00989	0.00484	−182	460	250	810	460
0.01193	0.00582	−211	520	310	930	530
0.01248	0.00609	−255	550	320	960	540
0.01342	0.00655	−248	580	340	1040	580
0.01392	0.00681	−242	600	360	1060	590
0.01690	0.00828	−257	690	400	1260	700
0.01896	0.00926	−346	760	430	1400	760
0.01989	0.00969	−353	790	450	1450	800
0.02241	0.01093	−312	810	500	1400	880
0.02487	0.01217	−348	850	520	530	930
0.02984	0.01460	−99	700	610	−550	1100
0.03484	0.01706	177	480	690	−1320	1260
0.04807	0.02332	1042	−160	830	−2050	900
0.06157	0.03001	1208	−550	700	−2350	−550
0.08001	0.03878	1167	−927	240	−2500	−1720
0.09818	0.04717	1152	−1281	−130	−2650	−2020
0.14876	0.06961	1066	−1835	−770	−2990	−2420

TABLE 2

Enthalpies of dilution, apparent and partial molar enthalpies of DMeMC at 313 K

m_i (mol kg^{-1})	m_f (mol kg^{-1})	ΔH_d (J mol^{-1})	Φ_{Li} (J mol^{-1})	Φ_{Lf} (J mol^{-1})	L_{2i} (J mol^{-1})	L_{2f} (J mol^{-1})
0.01174	0.00589	−151	353	175	690	335
0.01663	0.00831	−261	510	252	1090	470
0.01956	0.00963	−313	605	290	1235	555
0.02151	0.01059	−303	660	320	1240	615
0.02297	0.01127	−351	690	345	1180	665
0.02444	0.01204	−368	722	370	1045	723
0.02936	0.01449	−265	690	450	−10	920
0.03908	0.01919	330	275	585	−1565	1225
0.04888	0.02310	856	−143	718	−1955	1095
0.05871	0.02832	1164	−455	713	−2200	225
0.07826	0.03825	1227	−925	323	−2570	−1500
0.09779	0.04833	1198	−1290	−110	−2815	−1945
0.14668	0.07155	1052	−1820	−770	−3030	−2455

enthalpies as a function of molality are also shown in Figs. 2 and 3. From these plots the effect on enthalpic behavior of the different groups on the polar heads can be calculated, because the surfactants studied have the

TABLE 3

Enthalpies of dilution, apparent and partial molar enthalpies of DBeMC at 313 K

m_i (mol kg^{-1})	m_f (mol kg^{-1})	ΔH_d (J mol^{-1})	Φ_{Li} (J mol^{-1})	Φ_{Lf} (J mol^{-1})	L_{2i} (J mol^{-1})	L_{2f} (J mol^{-1})
0.00295	0.00146	−112	231	109	508	211
0.00344	0.00173	−169	279	129	628	257
0.00393	0.00190	−187	331	141	757	288
0.00394	0.00198	−178	331	147	758	303
0.00494	0.00245	−193	379	186	770	397
0.00591	0.00302	−196	434	238	780	525
0.00688	0.00343	−238	516	278	700	626
0.00885	0.00443	−227	562	356	−900	740
0.01081	0.00569	326	114	440	−3300	780
0.01180	0.00587	696	−246	450	−4450	780
0.01720	0.00856	2306	−1746	560	−5940	−670
0.01975	0.00987	2794	−2504	290	−6215	−2450
0.02457	0.01213	2884	−3254	−370	−6495	−4055
0.02976	0.01486	2659	−3828	−1170	−6715	−5575
0.03440	0.01689	2469	−4189	−1720	−6815	−5880
0.05894	0.02849	1595	−5285	−3690	−7280	−6670
0.09833	0.04889	1361	−6280	−4920	−7925	−7070
0.14746	0.07215	1169	−6824	−5655	−8240	−7500
0.19570	0.09467	1077	−7286	−6210	−8550	−7880

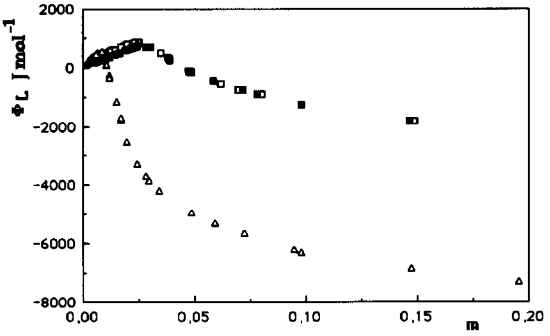

Fig. 2. Apparent molar relative enthalpies of DTCA (□), DMeMC (■) and DBeMC (△) as a function of surfactant concentration at 313 K.

same hydrophobic chain. It follows that Φ_L and L_2 values are very similar in the premicellar region for all compounds studied. However, it can be noted that, in comparison with DTAC, the values are a little higher for DBeMC and a little lower for DMeMC. DMeMC differs from DTAC by the replacement of two methyl groups attached to nitrogen by a morpholinium group. So, due to the presence of electronegative oxygen, the repulsion between charged nitrogens is lowered in comparison to DTAC. The higher values in the case of DBeMC may be attributed to the steric effect of the benzyl group.

In the postmicellar region the curves for DTAC and DMeMC are almost the same whereas the calorimetric titration curves for adding micellar solutions (above the critical micellar concentration (c.m.c.)) of these compounds into water at 25°C are different [3]. Specifically, the enthalpies of dilution are lower for DTAC than for DMeMC. This effect was ascribed to the interaction between oxygen of one molecule and nitrogen of another. With increasing temperature, this interaction should get weaker due to the thermal motion. In consequence, with increasing temperature the curve for

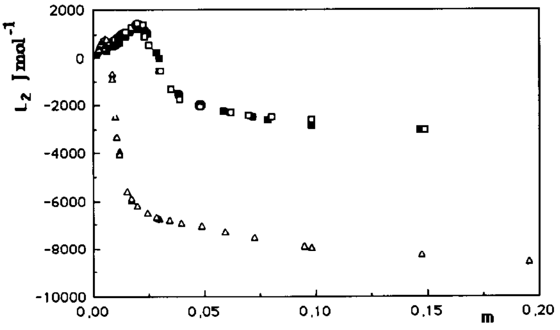

Fig. 3. Partial molar relative enthalpies of DTAC (□), DMeMC (■) and DBeMC (△) as a function of surfactant concentration at 313 K.

TABLE 4

Osmotic coefficients and related thermodynamic quantities for DTAC in water at 313 K

m (mol kg^{-1})	Φ	$\ln \gamma_\pm$	L_2 (J mol^{-1})	G_2^{ni} (J mol^{-1})	TS_2^{ni} (J mol^{-1})	S_2^{ni} (J mol^{-1} K^{-1})
0.00989	0.962	−0.119	810	−618	1428	4.6
0.01193	0.956	−0.132	930	−684	1614	5.2
0.01248	0.950	−0.140	960	−728	1688	5.4
0.01292	0.944	−0.148	1060	−766	1826	5.8
0.01342	0.942	−0.151	1040	−786	1826	5.8
0.01896	0.939	−0.176	1400	−913	2313	7.4
0.01989	0.930	−0.187	1450	−974	2424	7.7
0.02242	0.892	−0.236	1400	−1227	2626	8.4
0.02487	0.824	−0.318	530	−1657	2187	7.0
0.02984	0.704	−0.481	−550	−2502	1952	6.2
0.03485	0.631	−0.605	−1320	−3147	1827	5.8
0.04807	0.489	−0.887	−2000	−4618	2618	8.4
0.06157	0.406	−1.107	−2300	−5762	3462	11.1
0.08001	0.331	−1.348	−2450	−7015	4565	14.6
0.09818	0.285	−1.536	−2600	−7994	5394	17.2
0.14876	0.215	−1.924	−3000	−10012	7012	22.4

DMeMC should be shifted towards lower enthalpy values, i.e. in the direction of the curve for DTAC. So at a certain temperature it may happen that the curve for DMeMC overlaps that for DTAC. This occurs at 40°C as shown in Figs. 2 and 3.

The curve for DBeMC is quite different from that for DMeMC and DTAC. Values of Φ_L and L_2 for DBeMC are much lower than those for DMeMC and DTAC. This means that the hydrophobic interactions in the case of DBeMC are much greater than in the case of the other surfactants. Such a decrease is typical for increasing hydrophobicity of an amphiphilic compound [5–7,9].

Similar conclusions can be drawn from the trends of osmotic coefficients and of the related thermodynamic quantities from eqns. (4)–(9), reported in Tables 4–6. The trends vs. m are shown in Figs. 4–7. The osmotic coefficients of DTAC have already been measured in a broader range of concentrations by means of the same experimental method at 310 K. Results, obtained with different instruments, different batch of samples and at different times, agree very well with those reported here, confirming the reliability of the technique [4]. However, it should be noted that the precision of the experimental method used is not very high (±1 mOsmole), so, especially at low concentrations, the experimental data could be affected by a significant error. Again DTAC and DMeMC behave in a similar way, but the values of osmotic coefficients of DMeMC are always a

TABLE 5

Osmotic coefficients and related thermodynamic quantities for DMeMC in water at 313 K

m (mol kg^{-1})	Φ	$\ln \gamma_{\pm}$	L_2 (J mol^{-1})	G_2^{ni} (J mol^{-1})	TS_2^{ni} (J mol^{-1})	S_2^{ni} (J mol^{-1} K^{-1})
0.01174	0.971	−0.116	690	−601	1291	4.1
0.01468	0.964	−0.130	935	−676	1611	5.1
0.01664	0.956	−0.143	1090	−746	1836	5.9
0.01761	0.951	−0.150	1160	−782	1942	6.2
0.01956	0.946	−0.161	1235	−838	2073	6.6
0.02151	0.907	−0.207	1240	−1079	2319	7.4
0.02298	0.892	−0.228	1180	−1189	2369	7.6
0.02444	0.859	−0.269	1045	−1399	2444	7.8
0.02936	0.800	−0.359	−10	−1866	1856	5.9
0.03909	0.652	−0.583	−1565	−3034	1469	4.7
0.04890	0.552	−0.772	−1955	−4016	2061	6.6
0.05874	0.494	−0.918	−2200	−4776	2576	8.2
0.07828	0.390	−1.182	−2570	−6152	3582	11.4
0.09775	0.327	−1.387	−2815	−7219	4404	14.1
0.14670	0.256	−1.752	−3030	−9116	6086	19.4

little higher. This fact could be attributed either to a lower aggregation number (in agreement with the higher value of c.m.c.) or to a higher degree of dissociation of micelles, due to the presence on the surface of the oxygen of the morpholinium ring.

TABLE 6

Osmotic coefficients and related thermodynamic quantities for DBeMC in water at 313 K

m (mol kg^{-1})	Φ	$\ln \gamma_{\pm}$	L_2 (J mol^{-1})	G_2^{ni} (J mol^{-1})	TS_2^{ni} (J mol^{-1})	S_2^{ni} (J mol^{-1} K^{-1})
0.00295	0.949	−0.097	508	−502	1010	3.2
0.00344	0.945	−0.109	628	−568	1196	3.8
0.00393	0.891	−0.174	757	−906	1662	5.3
0.00492	0.833	−0.262	770	−1363	2133	6.8
0.00591	0.804	−0.325	780	−1689	2469	7.9
0.00639	0.798	−0.346	740	−1780	2539	8.1
0.00689	0.784	−0.376	700	−1956	2656	8.5
0.00885	0.734	−0.485	−900	−2526	1626	5.2
0.01180	0.678	−0.626	−3900	−3260	−640	−2.0
0.01476	0.644	−0.737	−5550	−3835	−1715	−5.5
0.02457	0.549	−1.039	−6495	−5409	−1086	−3.5
0.02976	0.504	−1.176	−6715	−6118	−597	−1.9
0.03441	0.480	−1.274	−6815	−6630	−185	−0.6
0.03930	0.445	−1.380	−6910	−7181	271	0.9
0.05895	0.382	−1.685	−7280	−8770	1490	4.8
0.09835	0.315	−2.095	−7925	−10905	2980	9.5
0.14748	0.244	−2.463	−8240	−12820	4580	14.6
0.19569	0.212	−2.716	−8550	−14135	5585	17.8

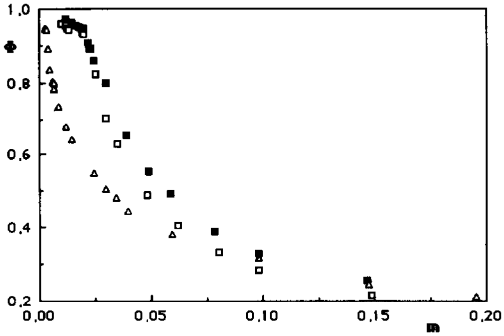

Fig. 4. Osmotic coefficients vs. *m* at 313 K for DTAC (□), DMeMC (■) and DBeMC (△).

In order to extract micellization parameters from the trends of thermodynamic quantities, a physical model for the micellization process must be assumed. The simplest one is the pseudo-phase transition model [4–9] in which the transition from monomer to aggregate pseudo-phase is considered as a two-state process taking place at equilibrium. Therefore, a discontinuity in the trend of thermodynamic quantities vs. *m*, except for free energies, is generally expected at the c.m.c., due to the formation of micelles. The reliability of this assumption can be checked by the trends of non-ideal quantities, vs. *m*, shown in Figs. 5–7 for the compounds DTAC, DMeMC and DBeMC, respectively, as obtained from eqns. (4)–(7). In fact, whereas no discontinuity or sudden change is present in the case of non-ideal free energies, rather sharp changes in enthalpies and entropies take place around the c.m.c. The non-ideal free energy curves become nearly parallel at concentrations higher than 0.05 M, those of DBeMC being lower by about 5 kJ mol^{-1} with respect to DTAC and DMeMC.

Although an actual break in the property at c.m.c. is generally never found, especially for shorter alkyl chain surfactants, nevertheless, a thermodynamic value of c.m.c. can be derived. By using the pseudo-phase transi-

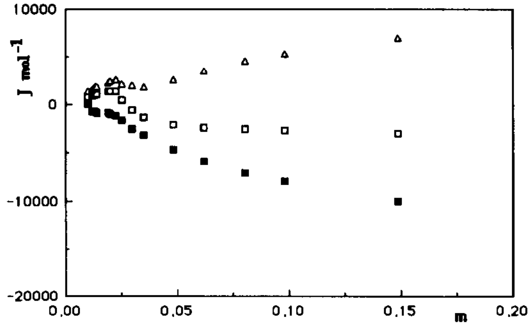

Fig. 5. Non-ideal thermodynamic properties of DTAC as a function of molality at 313 K: L_2 (□), G_2^{ni} (■) and TS_2^{ni} (△).

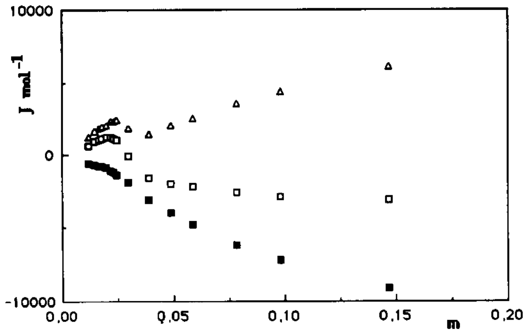

Fig. 6. Non-ideal thermodynamic properties of DMeMC as a function of molality at 313 K: L_2 (□), G_2^{ni} (■) and TS_2^{ni} (△).

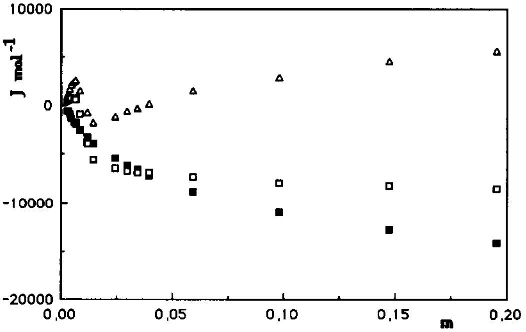

Fig. 7. Non-ideal thermodynamic properties of DBeMC as a function of molality at 313 K: L_2 (□), G_2^{ni} (■) and TS_2^{ni} (△).

tion model, the micellization parameters can be obtained by graphic extrapolation at the c.m.c. of the trends of the partial molar properties above and below the c.m.c. The values of c.m.c. and enthalpy of micellization for the compounds under investigation, listed in Table 7, have been obtained in this way. From the differences of the enthalpies of micellization reported here and the values at 25°C (see ref. 3), on the assumption that heat capacities are constant in the above mentioned temperature

TABLE 7

Critical micelle concentration (c.m.c.), enthalpy (ΔH_m) and heat capacity (ΔC_m) change for the micellization process of the surfactants studied at 313 K

Surfactant	c.m.c. (mol kg^{-1})	ΔH_{mic} (kJ mol^{-1})	$\Delta C_{p,mic}$ (J K^{-1} mol^{-1})
DTAC	0.020	−3.7	−420
DMeMC	0.025	−4.2	−440
DBeMC	0.008	−8.2	−630

range, the change in heat capacities for the micellization process was obtained by

$$\Delta C_{p,\mathrm{mic}} = [\Delta H_{\mathrm{mic}}(40°\mathrm{C}) - \Delta H_{\mathrm{mic}}(25°\mathrm{C})]/15$$

The values obtained are listed in Table 7. All the values for DTAC and DMeMC are very similar whereas those for DBeMC are significantly different. The enthalpy of micellization and heat capacity are much lower than for DMeMC.

The difference in heat capacities (-190 J K^{-1} mol^{-1}) between DBeMC and DMeMC can be attributed to the phenyl group since DBeMC differs from DMeMC by the replacement of one hydrogen of the methyl group by the phenyl group. Assuming that the $-\mathrm{CH}_2-$ group contribution to the heat capacity of micellization of DBeMC and DMeMC has the same value as for other quaternary ammonium salts, such as alkyltrimethyl ammonium bromides (i.e. $\Delta C_p(-\mathrm{CH}_2-) = -52$ J K^{-1} mol^{-1} [6,9,12]), the phenyl group contribution may be estimated as equivalent to about four methylene groups.

Following the additivity rule proposed by Tanford [13] for evaluating the volume of a surfactant monomer

$$V = m(27.4 + 26.9n')$$

where m is the number of chains and n' is the number of carbon atoms of the chain minus one, and taking into account the different lengths of the chains, we have $V = 2(27.4 + 26.9 \times 4) + 26.9 \times 7 = 458$ Å^3.

If we assume the same maximum chain length ($l = 17$ Å) and head group area ($a = 64$ Å^2) as for dodecyltrimethylammonium salts [14,15], the dimensionless packing parameter, introduced by Israelachvili et al. [16], $P = V/(la)$, works out at about 0.42.

This value suggests the hypothesis that micelles are rod-like, so the aggregation number should be greater compared to spherical micelles, formed by the other compounds. This hypothesis, based only on geometrical considerations, explains why the electrostatic repulsion in the micellar region must be greater in the case of DBeMC. Therefore, the thermodynamic behavior suggests that the aggregates formed by DBeMC are non-spherical: what the shape really is should be investigated by means of light-scattering techniques.

Since the phenyl group can be treated as equivalent to four methylene groups, so the benzyl group probably can be treated as equivalent to an alkyl chain of five carbon atoms. This conclusion is supported also by the lower c.m.c. value of DBeMC compared to that of DMeMC, and similar to the c.m.c. value expected by adding two more methylene groups to DMeMC. In fact, adding two more methylene groups corresponds to an increment of about -5.85 kJ mol^{-1} in $\mu^{\ominus}_{\mathrm{mic}} - \mu^{\ominus}_{\mathrm{w}}$ [13]. Approximately the same increase is observed for double-chain surfactants due to a minor chain of five carbon atoms [13].

CONCLUSIONS

Thermodynamic data at 40°C for *N*-dodecyl-*N*-benzylmorpholinium chloride, *N*-dodecyl-*N*-methylmorpholinium chloride and dodecyltrimethylammonium chloride are reported for the first time. On the basis of the pseudo-phase separation model, the values of c.m.c. and enthalpy of micellization are graphically evaluated and, from micellization enthalpy changes evaluated at 25°C by means of titration calorimetry, micellization heat capacities are also evaluated.

The studies carried out not only support the suggestion that the benzyl group can be treated as a second chain but also allow us to estimate its length as equivalent to five methylene groups. From these results, the estimated packing parameter of DBeMC suggests the formation of non-spherical aggregates by this surfactant.

ACKNOWLEDGEMENTS

The authors thank Professor Stanislaw Witek of the Technical University of Wrocław for the free gift of the compounds studied and Professor Ezio Pelizzetti for useful discussions. They also are grateful to the Italian Ministry for the University and the Scientific and Technological Research (MURST), to ENI Ricerche and to National Research Council (CNR-Progetto Finalizzato Chimica Fine) for financial support.

REFERENCES

1 S. Witek, D. Grobelny, J. Ptaszkowska, A. Bielecki, E. Bakuniak, S. Fulde and J. Gorska-Poczopko, Belgium Patent No. 864782, 1978.
2 J. Kuczera, J. Gabrielska, R. Zylka, S. Przestalski, S. Witek and D. Grobelny, Studia Biophys., 96 (1983) 203.
3 B. Różycka-Roszak, J. Colloid Interface Sci., 140 (1990) 538.
4 R. De Lisi, E. Fisicaro and S. Milioto, J. Solution Chem., 17 (1988) 1015.
5 E. Fisicaro, E. Pelizzetti, M. Barbieri, P. Savarino and G. Viscardi, Thermochim. Acta, 168 (1990) 143.
6 R. De Lisi, E. Fisicaro, S. Milioto, E. Pelizzetti and P. Savarino, J. Solution Chem., 19 (1990) 247.
7 J.E. Desnoyers and G. Perron, in R. Zana (Ed.), Surfactant Solutions — New Methods of Investigation, Marcel Dekker, New York, 1987, p. 1 and references cited therein.
8 R. De Lisi, S. Milioto, M. Castagnolo and A. Inglese, J. Solution Chem., 16 (1987) 373.
9 E. Fisicaro, M. Barbieri, E. Pelizzetti and P. Savarino, J. Chem. Soc., Faraday Trans., 87 (1991) 2983.
10 R. De Lisi, C. Ostiguy, G. Perron and J.E. Desnoyers, J. Colloid Interface Sci., 71 (1979) 147.

11 E. Fisicaro, E. Pelizzetti, E. Lanfredi and P. Savarino, Prog. Colloid Polym. Sci., 84 (1991) 474.
12 M.T. Bashford and E.M. Woolley, J. Phys. Chem., 89 (1985) 3173.
13 C. Tanford, The Hydrophobic Effect — Formation of Micelles and Biological Membranes, Wiley-Interscience, New York, 1980, Chapter 7.
14 R. De Lisi, S. Milioto and R. Triolo, J. Solution Chem., 17 (1988) 673.
15 C. Tanford, J. Phys. Chem., 76 (1972) 3020.
16 J.N. Israelachvili, D.J. Mitchel and B.W. Ninham, J. Chem. Soc. Faraday Trans. 2, 72 (1976) 1525.