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Thermodynamic properties of aqueous micellar solutions of 1-methyl-4-octylpyridinium halides

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Abstract

Apparent and partial molar enthalpies at 298 K and Gibbs free energies at 313 K of aqueous solutions of the cationic surfactants 1-methyl-4-octylpyridinium chloride, bromide and iodide (OMPC, OMPB, OMPI, respectively) have been measured as a function of concentration. The changes in enthalpies upon micellization have been obtained from the experimental data by using a pseudo phase transition approach. The data reported here are a further contribution in defining the effect of the counter ion on the energetics of surfactant solutions and confirm the validity of the group contribution approach also for the counter ion. The effect of the counter ion on the trends of apparent and partial molar enthalpies is strong and inversely proportional to the radius of the hydrated counter ion.

The change in structure between the compounds in which the alkyl chain is bound directly to the pyridine nitrogen and those having the tail in position 4, significantly affects the value of the cmc, showing that the latter are more hydrophobic, but scarcely affects the enthalpic properties of the solutions.

Keywords: 1-Methyl-4-octyl-pyridinium halides; Micellization enthalpy; Cationic surfactants; Effect of the counter ion; Thermodynamics of surfactant solutions

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1. Introduction

In the past few years our research group has carefully characterized from a thermodynamic point of view the aqueous solutions of homologous series of cationic surfactants, in particular *N*-alkylpyridinium and *N*-alkylnicotinamide halide surfactants, both hydrogenated [1–4] and partially fluorinated [5–7], in which the hydrophobic tail is bound to the nitrogen carrying the positive charge. We have determined tensidic as well as thermodynamic properties as a function of concentration of the aqueous solutions of many members of the previously mentioned series. In particular, partial molar enthalpies, volumes, osmotic coefficients and heat capacities versus the concentration and the changes in these properties upon micellization have been obtained by means of direct experimental methods. Thermodynamic data have been interpreted and expressed in terms of group contribution of the methylene group, of the substituents and of the counter ion. Engberts and co-workers [8,12,13], Bijma [9], Nusselder and Engberts [10], Bijma and Engberts [11] in the University of Groningen has devoted a lot of attention to the synthesis and careful characterization of similar compounds, the 1-methyl-4-alkylpyridinium salts. Much interesting information have been reported about these

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compounds by the above research group. Further, they have undertaken microcalorimetric studies about the influence of counter ion and head group hydrophobicity on the enthalpies and heat capacities of micelle formation by 1-alkyl-4-dodecylpyridinium surfactants in aqueous solutions [11]. Nevertheless, a satisfactory description of the behavior of their aqueous solution in terms of solution thermodynamics is still missing.

It is, in our opinion, very interesting to study and quantify the effect on thermodynamic properties due to this structural change of the previously mentioned series of compounds.

Moreover, in our previous studies about hydrogenated and partially fluorinated cationic surfactants [2,14], we have outlined the strong effect of the counter ion in determining the energetics of the aqueous solutions. The present work, in which 1-methyl-4-octylpyridinium chloride, bromide and iodide (OMPC, OMPB and OMPI), respectively, are studied is also aimed to obtain a further experimental evidence on the possibility of applying the group contribution approach also to the counter ions.

2. Experimentals

2.1. Materials

The OMPI was prepared by us, as described in the literature [9,10]. The substitution of the counter ion, to obtain OMPC and OMPB, was achieved by ionic exchange. For this purpose, an aqueous solution of the iodide was loaded onto a column with Amberlite CG-400 (Merck) in suitable form (Cl^- and Br^-) and eluted with deionized water.

Purity was checked by TLC: eluent BAW (buthanol: acetic acid:water in the ratio of 4:1:5 in organic phase) on silica gel plate (Merck).

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}).

2.2. Measurements

The enthalpies of dilution were measured by means of the Thermometric TAM (flow mixing cell) microcalorimeter, equipped with 221 Nano Amplifier, at 298 K. The freshly prepared surfactant solutions, kept before injection at the experimental temperature by means of a Heto cryothermostatic bath, were diluted into the "mixing" measuring cell of the microcalorimeter in the ratio of 1:1 by using CO_2-free water. The injection of the solutions and of water into the calorimeter was done by means of a Gilson peristaltic pump, Minipuls 2, and their flows were determined by weight.

Osmotic coefficients, Φ, were determined at 313 K by means of a vapor pressure osmometer, OSMOMAT 070-SA Gonotec, in which the molal decrease of vapor pressure of the used solvent is measured indirectly. The instrument was calibrated using an aqueous solution of NaCl (400 mOsmol kg^{-1}).

3. Results

The experimental data have been expressed in terms of the apparent and partial molar quantities of the solute, as usual in solution thermodynamics, assuming infinite dilution as the reference state. Apparent and partial molar quantities were obtained from the experimental data using methods in detail elsewhere [1–5,14,15].

For the sake of clarity, we recall that, with reference to the state of infinite dilution the molar enthalpy of dilution, ΔH_d, is given by:

$$\Delta H_d = \Phi_{L,f} - \Phi_{L,i} \quad (1)$$

where Φ_L is the apparent molar relative enthalpy and the indexes, f and i, stand for the final and initial concentrations, respectively.

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

$$\Phi_L = A_L m^{1/2} + B_L m + C_L m^{3/2} \quad (2)$$

where A_L is the limiting Debye-Huckel slope for relative enthalpies accounting for the long range electrostatic solute–solute interactions. Parameters B_L and C_L are obtained from the experimental points in the pre-micellar region by a least squares curve fitting.

In the micellar region, the apparent molar enthalpies are evaluated by means of Eq. (1) and by graphical interpolation, as described in detail in [3].

Table 1
Enthalpies of dilution, apparent and partial molar enthalpies of OMPC, in water at 298 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})
0.0200	0.0104	−117	333	212	583	345
0.0400	0.0207	−259	595	342	1140	601
0.0604	0.0310	−425	899	473	2080	881
0.0810	0.0412	−627	1242	612	2664	1191
0.1004	0.0510	−846	1598	754	3550	1514
0.1500	0.0760	−1800	2953	1150	7000	2500
0.2001	0.1008	−2490	4093	1595	7700	3550
0.2198	0.1000	−2715	4340	1593	7655	3550
0.2499	0.1245	−2513	4671	2158	7420	5770
0.3500	0.1666	−1927	5307	3380	6195	7415
0.5001	0.2369	−970	5495	4525	5435	7545
0.8023	0.3837	−113	5483	5370	5145	5895
1.0003	0.4579	173	5297	5470	4780	5465
1.2002	0.4928	357	5133	5490	4410	5440

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

The heats of dilution and apparent and partial molar enthalpies at 298 K, obtained by means of Eqs. (1) and (2), for the compounds under study are listed in Tables 1–3. In Fig. 1, the plots of the apparent molar enthalpies as a function of molality for the different counter ions for the compounds under study are shown. The same plot for the N-octylpyridinium halides can be found in [6]. In Fig. 2, the trends for OMPC and N-octylpyridinium chloride (C_8PC) are compared.

The osmotic coefficients were obtained as follows:

$$\Phi = \frac{N_{\text{osmotic}}}{\nu m} \qquad (4)$$

where N_{osmotic} is the osmolality of the solution, directly read from the instrument, and ν is the number of ions generated upon dissociation. Osmotic

Table 2
Enthalpies of dilution, apparent and partial molar enthalpies of OMPB, in water at 298 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})
0.0101	0.0051	−59	176	123	274	183
0.0200	0.0101	−93	270	176	459	274
0.0300	0.0151	−140	368	223	674	365
0.0400	0.0195	−211	474	265	920	450
0.0500	0.0250	−272	591	318	1198	563
0.0599	0.0298	−352	716	366	1500	670
0.1000	0.0496	−764	1350	586	3425	1184
0.1199	0.0587	−914	1614	701	2565	1462
0.1500	0.0725	−840	1729	888	1985	1922
0.2001	0.0964	−483	1748	1265	1590	3250
0.3504	0.1691	143	1602	1745	1220	1790
0.5016	0.2185	341	1399	1740	840	1525
0.7000	0.3003	526	1163	1690	370	1370
1.0003	0.4254	703	792	1495	−360	1020
1.2001	0.4764	886	554	1440	−735	900
1.4012	0.5772	848	462	1310	−940	633

Table 3
Enthalpies of dilution, apparent and partial molar enthalpies of OMPI, in water at 298 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})
0.0102	0.0047	−23	141	101	211	142
0.0150	0.0072	−48	174	121	274	174
0.0200	0.0102	−83	208	141	350	210
0.0300	0.0143	−122	284	169	532	264
0.0380	0.0182	−165	355	195	709	320
0.0401	0.0193	−160	374	202	758	337
0.0451	0.0215	95	123	219	−5250	374
0.0504	0.0256	730	−481	249	−5480	445
0.0602	0.0302	1619	−1333	286	−5710	536
0.0700	0.0333	2369	−2057	312	−5880	602
0.0801	0.0380	2811	−2456	35	−6040	709
0.0900	0.0428	2961	−2790	240	−6180	−4970
0.0998	0.0498	2670	−3120	−450	−6300	−5470
0.1301	0.0619	2524	−3950	−1490	−6560	−5750
0.1501	0.0742	2146	−4320	−2230	−6665	−5950
0.1504	0.0720	2253	−4325	−2130	−6670	−5915
0.1699	0.0806	2108	−4563	−2455	−6750	−6050
0.2002	0.0984	1739	−4865	−3090	−6845	−6280
0.2507	0.1216	1529	−5230	−3730	−6960	−6500
0.5017	0.2206	1213	−6213	−5020	−7430	−6890
0.7004	0.3124	1044	−6624	−5580	−7675	−7100
1.0052	0.4207	1008	−6998	−5990	−8030	−7320
1.2004	0.5046	938	−7148	−6210	−8170	−7430

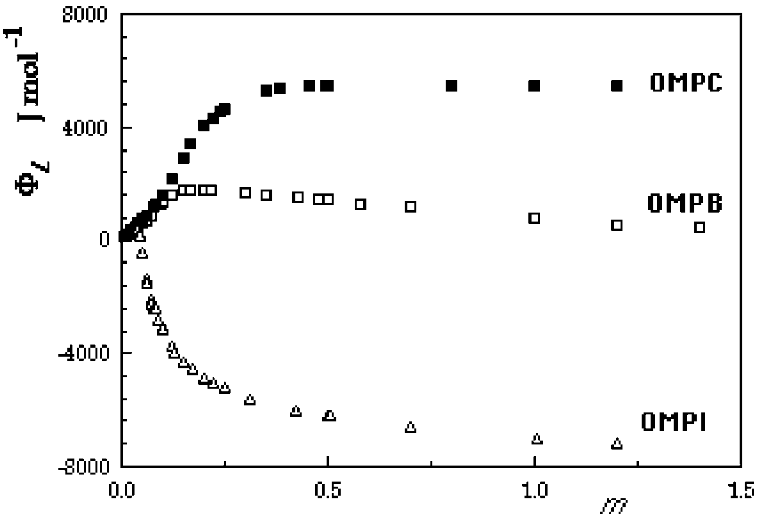

Fig. 1. Apparent molar relative enthalpies of OMPC (full squares), OMPB (empty squares) and OMPI (empty triangles) as a function of surfactant molality, *m*.

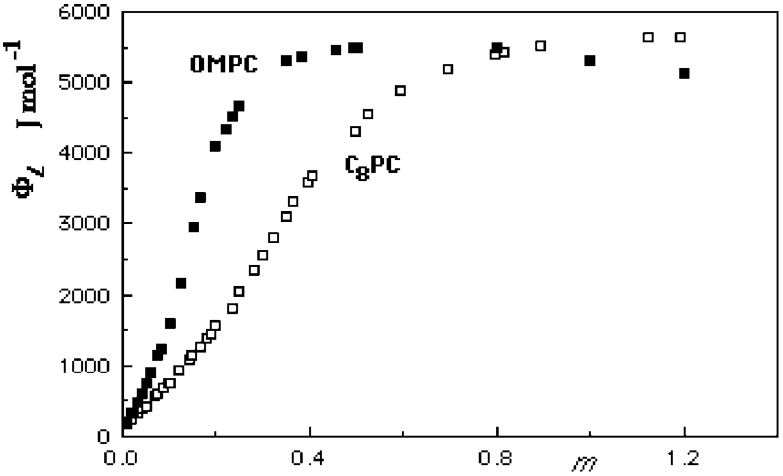

Fig. 2. Apparent molar relative enthalpies of C_8PC (empty squares) [6] and OMPC (full squares) as a function of surfactant molality, *m*.

coefficients are related to activity coefficients by:

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

where A_{γ} is the Debye-Huckel limiting slope and m_o is the molality at which the experimental and limiting values of Φ converge.

The non-ideal (or excess) Gibbs free energies [15] are related to the activity coefficients by:

$$G_2^{ni} = \nu RT \ln \gamma_{\pm} \qquad (6)$$

Table 4
Osmotic coefficients and related thermodynamic quantities for OMPC in water at 313 K

m (mol kg^{-1})	Φ	$\ln \gamma_{\pm}$	G_2^{ni} (kJ mol^{-1})
0.0100	0.650	−0.430	−2.24
0.0201	0.956	−0.310	−1.62
0.0300	0.981	−0.299	−1.56
0.0400	1.130	−0.137	−0.71
0.0601	0.958	−0.284	−1.48
0.0800	0.848	−0.420	−2.19
0.1000	0.760	−0.550	−2.86
0.2198	0.545	−1.033	−5.37
0.3499	0.391	−1.434	−7.46
0.5001	0.319	−1.740	−9.05
0.7498	0.271	−2.079	−10.82
0.9988	0.262	−2.301	−11.98
1.2002	0.259	−2.441	−12.70

Table 5
Osmotic coefficients and related thermodynamic quantities for OMPB in water at 313 K

m (mol kg^{-1})	Φ	$\ln \gamma_{\pm}$	G_2^{ni} (kJ mol^{-1})
0.0101	0.863	−0.218	−1.13
0.0200	0.891	−0.285	−1.48
0.0300	0.868	−0.363	−1.89
0.0400	0.834	−0.439	−2.29
0.0500	0.831	−0.480	−2.50
0.0600	0.843	−0.498	−2.59
0.1000	0.739	−0.706	−3.68
0.1199	0.647	−0.853	−4.44
0.1500	0.550	−1.041	−5.42
0.2001	0.443	−1.292	−6.72
0.2004	0.465	−1.271	−6.61
0.2499	0.378	−1.486	−7.73

In Tables 4–6, the values obtained for the excess Gibbs free energies versus *m* are reported.

4. Discussion

The data presented in this work are further evidence of the role played by the counter ion in determining the energetics of micellar solutions and allow one to quantify it in terms of group contribution, at least in the case of halides. Moreover, it is very interesting to rationalize the effect of the position of the alkyl chain with respect to the charged pyridinium nitrogen.

Table 6
Osmotic coefficients and related thermodynamic quantities for OMPI in water at 313 K

m (mol kg^{-1})	Φ	$\ln \gamma_\pm$	G_2^{ni} (kJ mol^{-1})
0.0100	0.692	−0.389	−2.02
0.0200	0.797	−0.488	−2.54
0.0300	0.793	−0.578	−3.01
0.0400	0.798	−0.633	−3.29
0.0600	0.654	−0.884	−4.60
0.0800	0.507	−1.151	−5.99
0.1000	0.412	−1.366	−7.11
0.1000	0.415	−1.364	−7.10
0.1300	0.334	−1.610	−8.38
0.1498	0.289	−1.752	−9.12
0.1700	0.265	−1.867	−9.72
0.1999	0.230	−2.025	−10.54
0.2501	0.190	−2.242	−11.67
0.4999	0.117	−2.940	−15.30
0.7001	0.095	−3.269	−17.01
1.0015	0.081	−3.616	−18.82
1.2009	0.074	−3.791	−19.73

4.1. *Effect of the counter ions*

Many papers have been published in the past few years about the role of the counter ion on the energetics of surfactant solutions. Some of us, in fact, have shown that in the case of dodecyltrimethylammonium chloride (DTAC) and dodecyltrimethylammonium bromide (DTAB) [14], the substitution of chloride ion by bromide ion leads to a significant change in the thermodynamic properties of solutions, comparable with that obtained by increasing the surfactant chain length by about three methylene groups. In the case of enthalpic properties, this effect has been confirmed by the behaviour of *N*-alkylpyridinium halides [2,6,7], we have carefully studied previously. Bijma et al. [8] have studied a series of 1-methyl-4-alkylpyridinium halide surfactants at 303 K and have observed that the standard enthalpy of micellization becomes more exothermic with increasing size of the halide counter ion. Structural parameters of micelles, such as degree of counter ion binding, β [14,16,17] and aggregation number, n [18], are also strongly dependent on the effective size of the hydrated counter ion, both decreasing with the increasing radius. In fact, because the smallest ions are more strongly hydrated than the largest ones, the effective radius in aqueous solution is inversely proportional to the size of the bare ion [19,20]. The values 72.9, 61.9, and 37.1 cm^3 mol^{-1} of the volumes of the hydrated ions at infinite dilution (corresponding to the radii of 0.3069, 0.2906 and 0.245 nm) have been proposed [20] for Cl^-, Br^- and I^-, respectively.

The data reported here confirm the above observations also in the case of the compounds under study, as it is easily seen from the comparison of Figs. 1 and 2. The apparent and partial molar enthalpy curves, after increasing in the pre-micellar region, tend to level-off at concentrations above the cmc. The curves are lowered in micellar region of an amount increasing with increasing the size of the counter ion. Taking Cl^- as the reference, the curves of Φ_L are lowered by −5.1 and −12.8 kJ mol^{-1} for Br^- and I^-, respectively, in the plateau region. Our previous studies have shown that, in the case of the compounds having the hydrophobic tail bound to the charged nitrogen, the corresponding values are −5.4 and −12.7 kJ mol^{-1} [6]. It means that the strong effect of the counter ion agrees qualitatively and quantitatively in both the cases, confirming the validity of the group contribution approach also for the counter ion.

In Fig. 3, the trends of the non-ideal molar Gibbs free energies as a function of molality for the compounds under study are reported. The trends, monotonically decreasing in the micellar region, as usually observed, agree with the observation that the structural parameters of the micelles related with the number of particles in solution, in particular, β, the degree of counter ion binding [14,16,17] and n, the aggregation number [18] decrease with the increasing size of the hydrated counter ion (i.e. in the order of $I^- < Br^- < Cl^-$). As a consequence, the number of particle in solution increases. Similar trends have been reported for *N*-octylpyridinium and 1-(3,3,4,4,5,5,6,6,6-nonafluorohexyl)pyridinium halides [6,7,21]. According to the pseudo-phase transition model, the micelle formation take place at equilibrium, at which $\Delta G_m = 0$. The curves, in Fig. 3, show that no discontinuity is present at the cmc for excess Gibbs free energies, confirming the validity of the pseudo-phase transition approach.

4.2. *Effect of the chemical structure*

Little information is available in the literature about the effect on thermodynamic properties due to the different position of the hydrophobic chain with respect

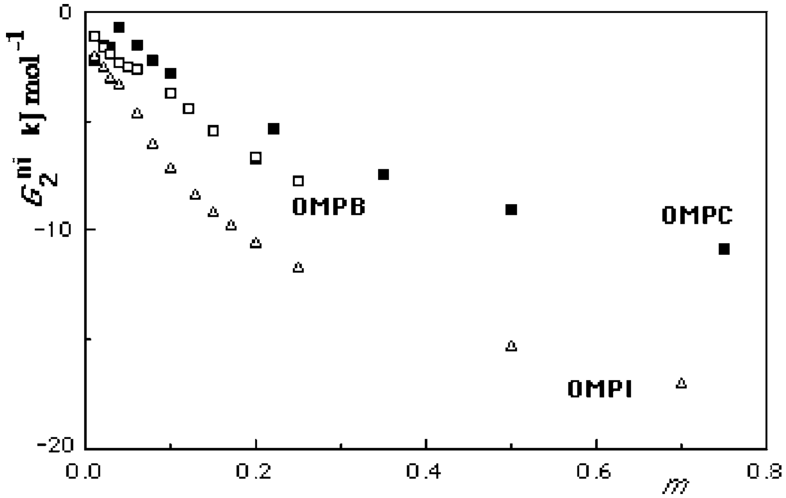

Fig. 3. Non-ideal Gibbs free energies of OMPC (full squares), OMPB (empty squares) and OMPI (empty triangles) as a function of surfactant molality, *m*.

to the pyridine nitrogen. Thermodynamics of micelle formation by 1-methyl-4-alkylpyridinium halides at 303.2 K, as a function of the counter ion and of the degree of branching of the alkyl chain has been discussed in [8]. At the same temperature, a very interesting comparison between 1-methyl-4-dodecylpyridinium bromide (DMPB) and the *N*-dodecylpicolinium bromide (DPB), as for cmc and β-values are concerned, is reported in [9,22]. The values of cmc and β result 4.95×10^{-3} m and 71% for DMPB and 9.7×10^{-3} m and 72% for DPB. This means that the hydrophobicity of DMPB is greater than that of DPB, because the cmc of the latter is about twice than that of DMPB. On the contrary, β is about unaffected. As shown by the comparison between the trends of the apparent molar enthalpies versus *m* between, for instance, *N*-octyl pyridinium chloride (C_8PC) and OMPC (Fig. 2), the difference in the structure affects more strongly the value of the cmc (Table 7) than the enthalpic properties. In fact, the plateau values of the two curves differ by a quantity comparable with the group contribution determined by the adding of a methylene group in the alkyl chain. It must be kept in mind that C_8PC is missing the $-CH_3$ group in the position 4. One of us [14] has already shown that in the series dodecylamine hydrocloride (DAC), dodecyldimethyl-

Table 7
Micellization enthalpy changes (ΔH_m) for the surfactants under study

	OMPC	OMPB	OMPI	C_8PI	C_8PC	C_8PB
Cmc (mol kg^{-1} for 298 K)	0.102[a]	0.080[a]	0.040[a]	0.094[a]	0.3[b], 0.25[c]	0.19[d]
Cmc (mol kg^{-1} for 313 K[e])	0.109	0.088	0.049	0.118		
$L_{2,m}$ (kJ mol^{-1})	8.0	2.5	−5.8	−4.8	8.8[b], 9.8[c]	4.2[c]
$L_{2,s}$ (kJ mol^{-1})	3.5	2.0	0.7	0.7	3.3[b], 4.7[c]	2.8[c]
ΔH_m (kJ mol^{-1})	4.5	0.5	−6.5	−5.5	5.4[b], 5.1[c]	1.3[c]

Indices *s* and *m* stand for the properties of the surfactants in micelles and as monomer, respectively.

[a] from [6].

[b] from [21].

[c] from [2].

[d] from [24,25].

[e] from [7].

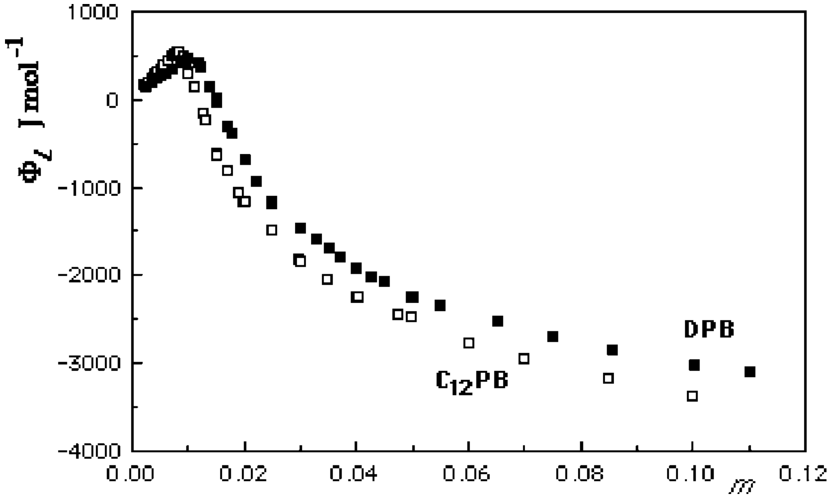

Fig. 4. Apparent molar relative enthalpies of C_{12}PB (empty squares) and DPB (full squares) as a function of surfactant molality, *m*, [23].

ammonium chloride (DDAC) and DTAC, 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 that for the removal of a $–CH_2–$ group in the hydrophobic tail. The effect of adding this group to the aromatic ring of the polar head seems to be in the same direction, but more limited quantitatively as shown in Fig. 4, in which the trends of *N*-dodecylpyridinium bromide (C_{12}PB) and DPB are compared [23].

4.3. Changes in thermodynamic properties upon micelle formation

In order to obtain the changes in thermodynamic properties upon micellization, we have applied a pseudo-phase transition model, in which the aggregation process is considered like a phase transition, taking place at equilibrium. By means of this model, assuming that at the cmc, the partial molar properties present a discontinuity due to the formation of a pseudo-phase, the micellization parameters are obtained by extrapolating at the cmc, the trends of partial molar properties before and after cmc [1–5,14,23]. In fact, rather sharp changes occur around the cmc, but they are never discontinuous, especially for surfactants with short hydrophobic chain. It is, therefore, important to know the value of the cmc: we have assumed as cmc of the compounds under investigation, the value at the abscissa of the intersection of the two straight lines, experimentally obtained from plotting the milliosmolality (mOsmol), measured at 313 K, versus *m* in the pre- and post-micellar regions, as shown in Fig. 5. In fact, it has be shown [1,4,14] that according to pseudo-phase transition model, the plot versus *m* of the quantity *Φ* times *m*, which represents the concentration of the particles in solution divided by *n*, in the post-micellar region should be linear:

$$\Phi m = \mathrm{cmc} + [(1 + n - \beta n)/2n](m - \mathrm{cmc}) \qquad (7)$$

where *n* is the aggregation number and *β* is the degree of counter ion binding. This model is an oversimplified one. In spite of the fact that the predicted linear trend is generally experimentally obtained, meaningless values of *n* are obtained from the slope, probably because the polydispersity of the system must be adequately taken into account.

The values at 298 K have been guessed by considering that the effect of the temperature on the cmc is quite small and taking into account the ratio between the values at 313 and 298 K, reported in the case of C_8PC [6,7]. The values so obtained for the cmc and the micellization enthalpies, obtained by extrapolating at the cmc the trends of partial molar enthalpies versus molality before and after the cmc, are reported in Table 7.

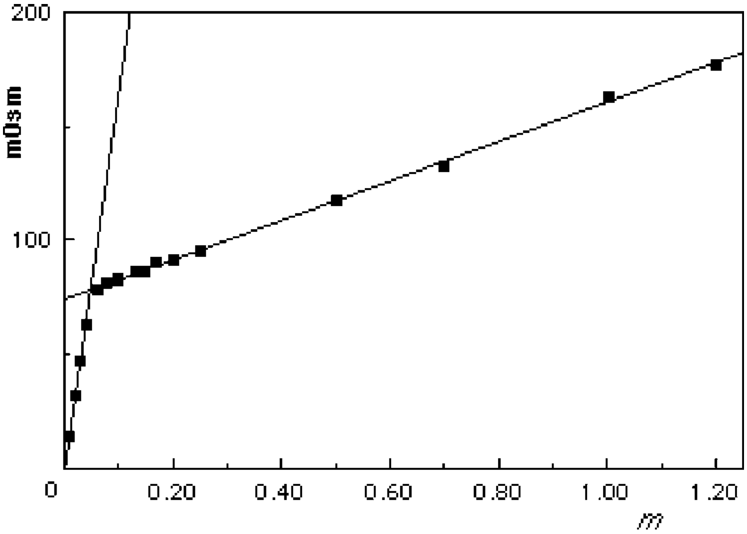

Fig. 5. Evaluation of the cmc from the curves of milliosmolality (mOsmol) vs. function of surfactant molality, *m*, for OMPI at 313 K.

Qualitatively, the enthalpies of micellization decrease with the decreasing in the size of the hydrated counter ion, as it has been found for *N*-alkylpyridinium surfactants [2,6,8,14]. This trend has been rationalized by taking into account the positive enthalpy for the partial dehydration of the counter ion in the process of micelle formation [8].

Quantitatively, the values of micellization enthalpies confirm the additivity of the group contribution of the counter ion, as far as the compounds reported in Table 1 are concerned. The enthalpies of micellization of DTAC and DTAB [14] at 298 K differed by 5.1 kJ mol^{-1}, a value slightly greater than that reported in Table 7 for the pyridinium halides.

5. Conclusions

The data here reported are a further contribution in defining the effect of the counter ion on the energetics of the surfactant solutions and confirm the validity of the group contribution approach also for the counter ion. The effect of the counter ion on the trends of apparent and partial molar enthalpies is strong and inversely proportional to the radius of the hydrated counter ion.

The change in structure between the compounds in which the alkyl chain is bound directly to the pyridine nitrogen and those having the tail in position 4, significantly affects the value of the cmc, showing that the latter are more hydrophobic, but scarcely affects the enthalpic properties of the solutions.

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References

[1] R. De Lisi, E. Fisicaro, S. Milioto, E. Pelizzetti, P. Savarino, J. Solution Chem. 19 (1990) 247.
[2] E. Fisicaro, E. Pelizzetti, M. Barbieri, P. Savarino, G. Viscardi, Thermochim. Acta 168 (1990) 143.
[3] E. Fisicaro, M. Barbieri, E. Pelizzetti, P. Savarino, J. Chem. Soc., Faraday Trans. 87 (1991) 2983.
[4] E. Fisicaro, E. Pelizzetti, E. Lanfredi, P. Savarino, Prog. Colloid Polym. Sci. 84 (1991) 474.
[5] E. Fisicaro, E. Pelizzetti, G. Viscardi, P.L. Quagliotto, L. Trossarelli, J. Colloids Surf. Part A: Physicochem. Eng. Aspects 84 (1994) 59.
[6] E. Fisicaro, A. Ghiozzi, E. Pelizzetti, G. Viscardi, P.L. Quagliotto, J. Colloid Interface Sci. 182 (1996) 549–557.

[7] E. Fisicaro, A. Ghiozzi, E. Pelizzetti, G. Viscardi, P.L. Quagliotto, J. Colloid Interface Sci. 184 (1996) 147–154.

[8] K. Bijma, J.B.F.N. Engberts, G. Haandrikman, N. van Os, M.J. Blandamer, M.D. Butt, P.M. Cullis, Langmuir 10 (1994) 2578.

[9] K. Bijma, Ph.D. thesis, University of Groningen, 1995.

[10] J.J.H. Nusselder, J.B.F.N. Engberts, Langmuir 7 (1991) 2089.

[11] K. Bijma, J.B.F.N. Engberts, Langmuir 13 (1997) 4843–4849.

[12] K. Bijma, M.J. Blandamer, J.B.F.N. Engberts, Langmuir 14 (1998) 79–83.

[13] K. Bijma, E. Rank, J.B.F.N. Engberts, J. Colloid Interface Sci. 205 (1998) 245–256.

[14] R. De Lisi, E. Fisicaro, S. Milioto, J. Solution Chem. 17 (1988) 1015.

[15] J.E. Desnoyers, G. Perron, Surfactant Solutions—New Methods of Investigation, in: R. Zana (Ed.), Marcel Dekker, New York, 1987, p. 1 and references therein.

[16] W.P.J. Ford, R.H. Ottewill, H.C. Parreira, J. Colloid Interface Sci. 21 (1966) 522.

[17] A.L. Underwood, E.W. Anacker, J. Colloid Interface Sci. 44 (1973) 505.

[18] A.L. Underwood, E.W. Anacker, J. Colloid Interface Sci. 117 (1987) 242.

[19] J.N. Israelachvili, Intermolecular and Surface Forces, 2nd Edition, Academic Press, London, 1991.

[20] Y. Marcus, Ion Solvation, Wiley, New York, 1985.

[21] S. Causi, R. De Lisi, S. Milioto, J. Solution Chem. 20 (1991) 1031.

[22] G. Viscardi, P. Quagliotto, C. Barolo, P. Savarino, E. Barni, E. Fisicaro, J. Org. Chem. 65 (2000) 8197.

[23] E. Fisicaro, C. Compari, G. Viscardi, P.L. Quagliotto, in preparation.

[24] K. Kalyanasundaram, T. Colassis, R. Humphry-Baker, P. Savarino, E. Barni, E. Pelizzetti, M. Grätzel, J. Am. Chem. Soc. 111 (1989) 3300.

[25] N.M. van Os, J.R. Haak, L.A.M. Rupert, Physico-chemical Properties of Selected Anionic, Cationic and Nonionic Surfactants, Elsevier, Amsterdam, 1993.