Thermochimica Acta, 168 (1990) 143–159
Elsevier Science Publishers B.V., Amsterdam

AQUEOUS MICELLAR SOLUTIONS OF SOME *N*-ALKYLNICOTINAMIDE AND *N*-ALKYLPYRIDINIUM HALIDE SURFACTANTS: APPARENT AND PARTIAL MOLAR ENTHALPIES

E. FISICARO *, E. PELIZZETTI and M. BARBIERI

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

P. SAVARINO and G. VISCARDI

*Dipartimento di Chimica Generale ed Organica Applicata, Università di Torino,
Corso M. D'Azeglio, 48, 10125 Torino (Italy)*

(Received 16 February 1990)

ABSTRACT

In order to acquire thermodynamic data for aqueous solutions of functionalized surfactants, and to study the effect of the amidic group in the polar head and of the counterion, the enthalpies of dilution at 25 ° C of *N*-alkylnicotinamide chlorides (alkyl chain length 7, 9 or 10 carbon atoms), *N*-alkylpyridinium chlorides (alkyl chain length 8, 10 or 12 carbon atoms), *N*-octylpyridinium bromide and *N*-decylpyridinium bromide have been measured by means of an LKB 2107 flow microcalorimeter. From the experimental data, apparent and partial molar relative enthalpies as a function of the molality of the surfactant have been derived. The amidic group in the nicotinamide compounds greatly enhances the hydrophobicity relative to the pyridinium compounds. For cationic surfactants with the same alkyl chain, the trends of the molar enthalpies vs. concentration can be explained in terms of charge localization on the polar head. For the compounds under investigation, enthalpic data are not able to show phase transitions in the micellar region, but they confirm the role of the counterion in the energetics of micellar solution.

The thermodynamic functions of micellization have been evaluated on the basis of the pseudo-phase transition model by graphical extrapolation.

INTRODUCTION

Functionalized surfactants are defined as compounds containing reactive functions covalently bound to the molecular structure. They can exhibit simultaneously properties of both aggregation and chemical or biochemical reactivity, because the polar moiety can take part in such chemical reactions as complexation, redox, hydrolysis, etc. In recent years the number of

---

* Author to whom correspondence should be addressed.

studies has been growing for this very interesting class of surfactants and their applications, especially in the fields of analytical chemistry and biomimetic chemistry. In the former field the use of organized molecular assemblies has led to the development of new procedures, particularly in chemical separations, and to the improvement of methods already existing [1,2]; in the latter, studies on synthesis, physico-chemical characterization and reactivity of functionalized surfactants, mimicking enzymes, have achieved a significant refinement of biochemical models [3,4]. Despite that, only a few thermodynamic studies have been carried out [5–8].

Recently some of us have been interested in studying aggregation, spectroscopic, photoredox [9,10] and thermodynamic [8] properties of *N*-alkylnicotinamide derivatives, because, owing to their structure, these molecules can be used as model compounds of nicotinamide–adenine dinucleotide (NAD^+), which is an important cofactor taking part in numerous cellular processes, particularly in intermediary metabolism and in energy conversion reactions. Although the synthesis of *N*-alkylnicotinamide has been known for quite some time [11–14], no systematic study of this important class of compounds has so far been carried out.

Densities, heat capacities and enthalpies of dilution at 25 °C and osmotic coefficients at 37 °C have been measured for *N*-octyl- and *N*-dodecyl-nicotinamide chlorides over a wide range of concentrations [8]. From the experimental data, partial molar volumes, heat capacities, relative enthalpies and non-ideal free energies and entropies at 25 °C have been derived as a function of the surfactant concentration. In order to understand the effect of the amidic group on the pyridinium ring, it would be very interesting to compare the thermodynamic properties of this class of compounds with those of alkylpyridinium surfactants. Unfortunately only a few data are available in the literature [7]. It is the goal of this work to begin to collect directly measured thermodynamic data, particularly enthalpic data, for studying the role played by the amidic group and by the counterion.

EXPERIMENTAL

Materials

N-Alkylnicotinamide surfactants were synthesized by the reaction of nicotinamide with a series of 1-alkyl halides in solvents such as xylene or DMF, as described in the literature [9–14]. The products were crystallized in the form of shiny white powders from ethanol.

N-Alkylpyridinium halides were prepared by reaction of an excess of pyridine with the alkyl halides (reactant ratio 1.5 : 1) for 24 h, according to the general procedure indicated in refs. 15 and 16. The unreacted pyridine was removed by vacuum distillation. The residue was repeatedly extracted with a boiling mixture of petroleum ether (b.p. 80 ° C) and ethyl ether (1 : 0.25).

All solutions were prepared using freshly boiled doubly distilled water stored under nitrogen.

Measurements

The enthalpies of dilution at 25 ° C were measured by an LKB 2107 flow microcalorimeter. The freshly prepared surfactant solutions in the mixing measuring cell of the microcalorimeter were diluted in ratio 1 : 1 by using CO_2-free water. 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.

RESULTS

The method of obtaining apparent and partial molar enthalpies from heats of dilution has already been described in detail [5,8,17–21].

Assuming infinite dilution as the reference state, the enthalpies of dilution, ΔH_{id}, are given by

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

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

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

$$\Phi_L = Am^{\frac{1}{2}} + Bm + Cm^{\frac{3}{2}} \tag{2}$$

where $A = 1973$ J mol$^{-3/2}$ is the limiting Debye–Hückel slope for relative enthalpies accounting for the long range solute–solute interactions. B and C are averaged on the experimental points in the premicellar region by least squares curve fitting

$$\Delta H_{id} - 1973\left(m_f^{\frac{1}{2}} - m_i^{\frac{1}{2}}\right) = B(m_f - m_i) + C\left(m_f^{\frac{3}{2}} - m_i^{\frac{3}{2}}\right) \tag{3}$$

When the final concentration of the dilution process is above the critical micelle concentration (cmc), $\Phi_{L,f}$ is evaluated by means of eqn. (2) and $\Phi_{L,i}$ by eqn. (1); below the cmc, one of the quantities in the second term of eqn. (1) is interpolated graphically, and the other is evaluated by means of the same equation.

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

DISCUSSION

N-Alkylnicotinamide chlorides

The heats of dilution and the apparent and partial molar quantities, obtained by means of eqns. (1)–(3), for the *N*-alkylnicotinamide chlorides (NAC) under investigation are reported in Tables 1–3. Figures 1 and 2, in which the data for the compounds with 8 and 12 carbon atoms from Ref. 8 are also reported by way of comparison, show in a more direct way the trends of these quantities as the length of the hydrophobic chain increases.

The parameters B and C in eqn. (3), obtained by a least squares linear regression in the premicellar region, are reported in Table 9 below. If the values for the dodecyl compound are overlooked, because they are obtained from a very few experimental points and are therefore subject to error, these parameters can be empirically correlated with the number of carbon atoms n by simple functions [B (J mol^{-2}) $= -1840 - 290\ n$ and C (J mol$^{-5/2}$) $= 23.6 \times 10^{0.35n}$], as Fig. 3 shows.

Trends like those reported in the figures are typical of ionic surfactants [5,8,21–30].

TABLE 1

Enthalpies of dilution and apparent and partial molar enthalpies of C_7NAC

m_i (mol kg^{-1})	m_f (mol kg^{-1})	ΔH_{id} (J mol^{-1})	Φ_{Li} (J mol^{-1})	Φ_{Lf} (J mol^{-1})	L_{2i} (J mol^{-1})	L_{2f} (J mol^{-1})
0.06972	0.03448	−67.1	327	247	465	310
0.09946	0.04903	−108.1	389	282	583	370
0.14923	0.07241	−179.5	504	332	800	480
0.17898	0.08746	−221.3	582	364	950	540
0.19910	0.09731	−258.1	640	385	1080	580
0.24871	0.12058	−354.9	797	436	1400	670
0.30150	0.14542	−452.4	954	502	1800	830
0.34799	0.16519	−555.2	1095	540	2230	870
0.39795	0.18981	−658.6	1278	619	2760	970
0.49732	0.23484	−866.0	1611	745	3360	1300
0.59685	0.27875	−1054.9	1930	875	3685	1615
0.69601	0.32225	−1191.6	2192	1000	3860	2020
0.79541	0.36395	−1270.0	2400	1130	3900	2380
0.89479	0.40537	−1280.1	2535	1255	3685	2820
0.99480	0.44677	−1237.1	2657	1420	3330	3130
1.18496	0.52356	−1060.9	2710	1700	2830	3480
1.67944	0.70652	−384.6	2570	2210	1550	3890
2.18863	0.86544	293.4	2197	2490	390	3800
2.68644	1.03467	864.2	1801	2670	−150	3250
4.47515	1.48116	2087.9	582	2670	−450	1990

Table 2

Enthalpies of dilution and apparent and partial molar enthalpies of C_9NAC

m_i (mol kg^{-1})	m_f (mol kg^{-1})	ΔH_{id} (J mol^{-1})	Φ_{Li} (J mol^{-1})	Φ_{Lf} (J mol^{-1})	L_{2i} (J mol^{-1})	L_{2f} (J mol^{-1})
0.01150	0.00555	−62.7	201	136	315	160
0.02300	0.01114	−120.2	311	197	520	310
0.02875	0.01397	−121.5	367	225	610	340
0.03449	0.01672	−189.6	423	251	750	420
0.04022	0.01951	−203.7	482	278	870	460
0.05748	0.02782	−311.8	671	358	1280	600
0.08618	0.04157	−531.6	1012	480	2170	890
0.11454	0.05506	−825.0	1475	650	3250	1220
0.14941	0.07152	−1199.0	2024	825	3750	1700
0.18386	0.08763	−1253.1	2300	1035	3220	2220
0.23007	0.10891	−1025.5	2415	1340	2775	3010
0.28748	0.13548	−631.3	2480	1850	2390	3830
0.34497	0.16157	−289.7	2440	2155	2050	3540
0.40248	0.18811	−48.3	2363	2315	1735	3130
0.57485	0.26227	389.4	2080	2465	1078	2555
0.80492	0.35766	711.7	1710	2430	395	2005
1.03486	0.44860	930.9	1359	2290	−220	1505
1.38054	0.57125	1196.3	889	2090	−1000	1085

TABLE 3

Enthalpies of dilution and apparent and partial molar enthalpies of $C_{10}NAC$

m_i (mol kg^{-1})	m_f (mol kg^{-1})	ΔH_{id} (J mol^{-1})	Φ_{Li} (J mol^{-1})	Φ_{Lf} (J mol^{-1})	L_{2i} (J mol^{-1})	L_{2f} (J mol^{-1})
0.00995	0.00530	−79.5	222	147	390	285
0.01990	0.01059	−137.3	389	232	700	392
0.02489	0.01321	−230.2	480	275	940	475
0.02985	0.01585	−248.1	576	319	1205	540
0.03482	0.01848	−300.8	671	370	1490	650
0.04977	0.02638	−512.0	1027	515	2400	1010
0.07463	0.03948	−771.4	1530	770	2125	1750
0.09954	0.05249	−498.5	1592	1070	1600	2550
0.11953	0.06284	−242.0	1570	1330	1363	2575
0.15916	0.07692	26.0	1479	1535	1000	2060
0.17918	0.08640	146.1	1415	1580	850	1840
0.19907	0.09590	207.0	1342	1595	715	1650
0.24887	0.11920	403.0	1175	1572	400	1365
0.29872	0.14283	481.8	1018	1520	135	1145
0.34842	0.17099	530.1	885	1430	−75	910
0.39791	0.19144	594.8	768	1365	−270	760
0.49726	0.22333	707.8	550	1265	−575	560
0.59693	0.26610	799.3	322	1112	−810	300

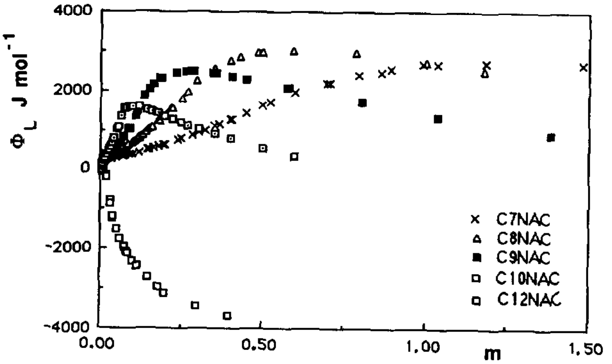

Fig. 1. Apparent molar relative enthalpies of *N*-alkylnicotinamide chlorides (alkyl chain length 7, 8, 9, 10 or 12 carbon atoms) as a function of surfactant concentration. The data for the octyl and dodecyl compounds are reported in ref. 8.

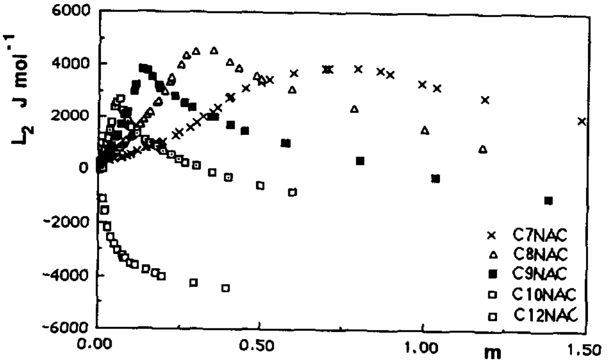

Fig. 2. Partial molar enthalpies (closed symbols) of *N*-alkylnicotinamide chlorides (alkyl chain length 7, 8, 9, 10 or 12 carbon atoms) as a function of surfactant concentration. The data for the octyl and dodecyl compounds are reported in ref. 8.

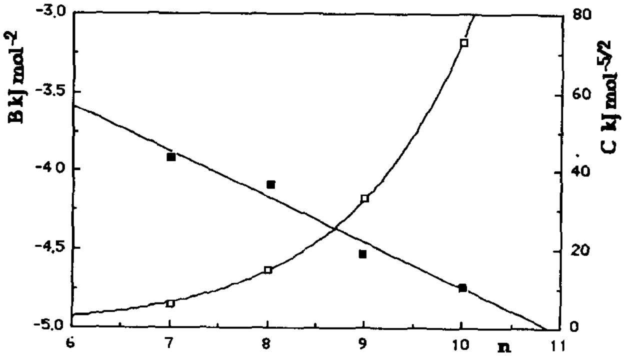

Fig. 3. Empirical correlation by means of simple functions (see text) between the number of carbon atoms *n* and the parameters *B* and *C* in eqn. (3) for *N*-alkylnicotinamide chloride surfactants.

For the compounds with chain length up to ten carbon atoms, the plots of Φ_L against m do not show any sudden change in slope around the cmc but only an inflexion point, as already observed for the octyl derivative [8]. The curves present a maximum around a concentration twice the cmc, then at higher concentration tend to level off, owing to the effect of hydrophilic interactions. The partial molar quantities present the same general trend, but with the difference, as is usual, of a steeper increase before the maximum and a steeper decrease at higher concentrations. In this region the curves become nearly parallel, with a difference of ca. -1.7 kJ mol^{-1} per $-CH_2$ added.

In the case of the dodecyl compounds previously studied [8], the apparent molar heat capacity curves have shown a drop, not only at the cmc but also at ca. 0.8 and 0.1 mol kg^{-1}, respectively. These drops, ascribed to a rearrangement of the micellar structure, have no corresponding feature in the enthalpic curves, probably because the thermal effect involved in the micellar transition is very low. There is no reason why compounds of intermediate chain length do not show this kind of transition at the appropriate value of m, but it is not possible to prove this by means of enthalpic measurements alone. If this fact is due to the accuracy of calorimetric measurements or to the graphical elaboration of the experimental data resulting in a smoothing of the curve is an open question.

N-Alkylpyridinium halide surfactants

The enthalpic data obtained in the case of *N*-alkylpyridinium compounds are reported in Tables 4–8 and shown in Figs. 4 and 5. The values of the parameters B and C of eqn. (3), used to describe the premicellar region, are reported in Table 9. In the case of this class of compounds it is hard to say whether there is a correlation between the values of B and C and the number of carbon atoms in the alkyl chain, because of the low number of compounds examined and because the dodecyl compound suffers the same limitations as described in the case of *N*-dodecylnicotinamide chloride. Moreover, in the case of *N*-dodecylpyridinium chloride, a better fit is obtained by using only the B parameter.

The shapes of the curves describing the enthalpic properties of this class of surfactant are comparable with those for nicotinamide derivatives, but quantitatively they differ greatly.

Again, the curves of Φ_L and L_2 vs. m increase up to a maximum related to the value of the cmc, then they decrease and level off at high concentration, at which they become nearly parallel. In this region, the values of the partial molar relative enthalpies decrease by ca. 1.5 kJ mol^{-1} per $-CH_2$ added, irrespective of the counterion, a value similar to that for the above family of compounds.

TABLE 4

Enthalpies of dilution and apparent and partial molar enthalpies of C_8PC

m_i (mol kg^{-1})	m_f (mol kg^{-1})	ΔH_{id} (J mol^{-1})	Φ_{Li} (J mol^{-1})	Φ_{Lf} (J mol^{-1})	L_{2i} (J mol^{-1})	L_{2f} (J mol^{-1})
0.01991	0.00991	−60.4	252	177	425	310
0.03981	0.01988	−109.8	378	252	590	420
0.06961	0.03449	−222.3	564	345	900	550
0.09948	0.04914	−345.2	765	435	1220	730
0.14924	0.07358	−555.8	1145	590	2120	920
0.17913	0.08791	−716.7	1400	685	2820	1130
0.19891	0.09718	−823.4	1579	749	3250	1200
0.24869	0.12064	−1131.3	2061	930	5070	1500
0.29829	0.14405	−1473.9	2574	1100	5870	2050
0.34771	0.16693	−1834.0	3114	1280	6820	2650
0.39746	0.18988	−2147.6	3598	1450	7065	3060
0.49662	0.23469	−2508.5	4308	1800	7045	3970
0.59628	0.27882	−2547.8	4898	2350	6810	5410
0.69579	0.32230	−2374.7	5185	2810	6595	6390
0.79518	0.36523	−2080.6	5411	3330	6395	7010
0.89434	0.40651	−1837.5	5527	3690	6205	7070
1.19247	0.52696	−1106.1	5646	4540	5695	6970
1.98740	0.81584	−49.6	5485	5435	4545	6360
2.98225	1.12246	794.1	4851	5645	3270	5810
4.97367	1.59393	1635.9	3971	5605	1885	5115

TABLE 5

Enthalpies of dilution and apparent and partial molar enthalpies of $C_{10}PC$

m_i (mol kg^{-1})	m_f (mol kg^{-1})	ΔH_{id} (J mol^{-1})	Φ_{Li} (J mol^{-1})	Φ_{Lf} (J mol^{-1})	L_{2i} (J mol^{-1})	L_{2f} (J mol^{-1})
0.00499	0.00244	−57.7	185	118	305	130
0.00748	0.00366	−76.9	242	152	410	180
0.00998	0.00489	−135.0	296	183	500	300
0.01198	0.00586	−141.0	338	206	510	350
0.01494	0.00730	−154.8	398	238	710	400
0.01996	0.00976	−193.5	500	292	1060	490
0.02496	0.01219	−267.8	600	343	1300	520
0.03993	0.01945	−409.5	901	490	2200	1050
0.06990	0.03393	−1041.1	1819	778	3850	1825
0.09984	0.04828	−2052.3	3162	1110	5660	2680
0.14981	0.07203	−2186.9	4047	1860	5807	3990
0.29923	0.14136	−643.8	4589	3945	4670	5885
0.50004	0.23070	64.5	4437	4465	3831	5105
0.69961	0.31514	394.3	4201	4595	3311	4532
0.99828	0.43474	658.0	3857	4515	2681	4032
1.49685	0.61601	997.6	3292	4290	1850	3521

TABLE 6

Enthalpies of dilution and apparent and partial molar enthalpies of $C_{12}PC$

m_i (mol kg^{-1})	m_f (mol kg^{-1})	ΔH_{id} (J mol^{-1})	Φ_{Li} (J mol^{-1})	Φ_{Lf} (J mol^{-1})	L_{2i} (J mol^{-1})	L_{2f} (J mol^{-1})
0.00994	0.00495	−128.8	566	323	1010	420
0.01192	0.00593	−201.3	658	372	1270	520
0.01491	0.00741	−628.3	795	445	2000	670
0.01988	0.00976	−1126.3	1656	530	3235	1000
0.02485	0.01238	−1299.7	2020	700	3280	1390
0.03978	0.01976	−885.8	2536	1650	3105	3230
0.05967	0.02955	−376.9	2677	2300	2720	3265
0.07952	0.03928	−92.4	2620	2510	2390	3115
0.08962	0.04411	−33.7	2588	2528	2250	3015
0.09947	0.04897	72.4	2550	2630	2149	2925
0.11930	0.05838	147.4	2475	2670	1980	2740
0.14917	0.07268	279.1	2359	2640	1778	2498
0.17894	0.08695	347.6	2247	2595	1610	2288
0.19894	0.09670	379.4	2181	2560	1518	2176
0.22868	0.11021	407.5	2090	2510	1390	2054
0.24865	0.11957	425.2	2030	2470	1312	1978
0.26846	0.13073	449.8	1980	2430	1240	1900
0.29806	0.14228	480.1	1908	2388	1140	1825
0.39754	0.18694	530.2	1683	2221	835	1570
0.49715	0.23031	576.4	1509	2085	610	1380
0.59665	0.27588	613.4	1347	1960	410	1214

TABLE 7

Enthalpies of dilution and apparent and partial molar enthalpies of C_8PB

m_i (mol kg^{-1})	m_f (mol kg^{-1})	ΔH_{id} (J mol^{-1})	Φ_{Li} (J mol^{-1})	Φ_{Lf} (J mol^{-1})	L_{2i} (J mol^{-1})	L_{2f} (J mol^{-1})
0.00966	0.00487	−14.1	128	101	140	130
0.01991	0.01003	−21.0	164	130	190	141
0.03974	0.01995	−50.0	223	165	340	191
0.06966	0.03505	−125.1	332	208	620	280
0.09940	0.04953	−236.8	479	255	1000	420
0.14911	0.07391	−463.7	807	351	2160	660
0.17905	0.08807	−624.5	1053	419	2660	870
0.19884	0.09770	−744.7	1199	454	2900	970
0.24845	0.12150	−1067.5	1668	600	3270	1500
0.29840	0.14495	−1179.1	1939	760	3450	2100
0.34788	0.17049	−1176.3	2146	970	2810	2500
0.39786	0.19121	−1063.1	2203	1140	2410	2770
0.49722	0.23658	−665.1	2175	1510	1990	3150
0.59644	0.28046	−253.1	2123	1870	1620	3400
0.69633	0.32507	13.7	2056	2070	1310	3300
0.89556	0.40970	386.5	1814	2200	730	2400
1.19366	0.52891	715.3	1450	2165	60	1900
1.98840	0.81739	1200.4	725	1890	−1060	940
2.98318	1.12403	1621.2	−106	1535	−2160	180
4.97211	1.68658	2065.2	−1080	985	−2960	−700

TABLE 8

Enthalpies of dilution and apparent and partial molar enthalpies of $C_{10}PB$

m_i (mol kg^{-1})	m_f (mol kg^{-1})	ΔH_{id} (J mol^{-1})	Φ_{Li} (J mol^{-1})	Φ_{Lf} (J mol^{-1})	L_{2i} (J mol^{-1})	L_{2f} (J mol^{-1})
0.01491	0.00743	−102.6	286	178	441	280
0.01986	0.00989	−149.9	360	214	600	325
0.02485	0.01235	−192.7	437	249	965	385
0.02982	0.01484	−227.1	517	285	1000	440
0.03479	0.01736	−266.1	586	320	1230	515
0.04966	0.02463	−470.1	900	430	1610	960
0.06165	0.03079	−448.7	960	525	960	1040
0.07451	0.03685	−252.4	889	637	510	1340
0.08950	0.04465	−12.5	808	795	240	1540
0.09941	0.04902	113.5	772	885	120	1600
0.14905	0.07306	426.1	470	895	−270	550
0.17896	0.08708	489.7	325	815	−460	280
0.19885	0.09692	515.2	265	780	−570	155
0.24857	0.12074	556.0	64	620	−780	−110
0.29824	0.14437	578.4	−82	496	−945	−240
0.39763	0.19042	615.6	−325	291	−1235	−525
0.54657	0.25702	660.1	−637	23	−1615	−810

Effect of the counterion and of the polar head

It is interesting to discuss the effect of the counterion and of the amidic group on the enthalpic properties.

The present results confirm also for surfactants with a different polar head and a shorter alkyl chain what has already been shown in the case of dodecyltrimethylammonium chloride (DTAC) and bromide (DTAB) [19]:

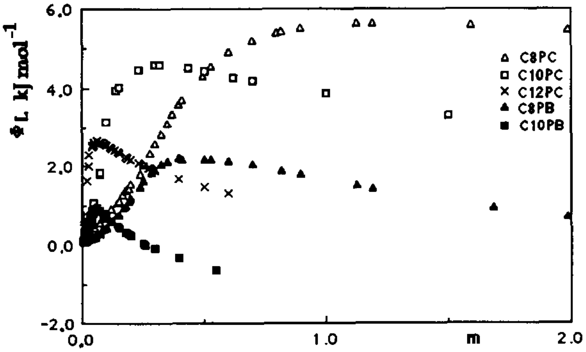

Fig. 4. Apparent molar relative enthalpies of N-alkylpyridinium chlorides (alkyl chain length 8, 10 or 12 carbon atoms), N-octylpyridinium bromide and N-decylpyridinium bromide as a function of surfactant concentration.

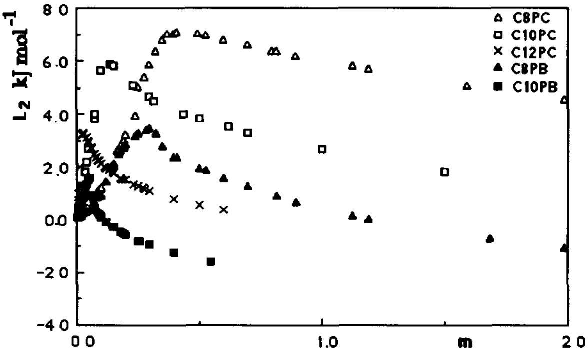

Fig. 5. Partial molar enthalpies of *N*-alkylpyridinium chlorides (alkyl chain length 8, 10 or 12 carbon atoms), *N*-octylpyridinium bromide and *N*-decylpyridinium bromide as a function of surfactant concentration.

the substitution of chloride ion by bromide ion leads to a significant lowering of the enthalpic quantities in the micellar region, comparable with that obtained by increasing the surfactant chain length by about three methylene groups. In fact, in the case of both octyl- and decyl-pyridinium compounds, as Figs. 6 and 7 show, the value of L_2 at high concentration is lowered by ca. 5.4 kJ mol^{-1} in the presence of Br$^-$ counterions. Once more, the experimental data outline the role played by the counterion in determining the energetics of micellar solutions.

A similar effect of slightly lower magnitude is brought about by the addition of the amidic group on the pyridinium ring. The amidic group seems to greatly affect the hydrophobicity of the polar head, as recently outlined [8].

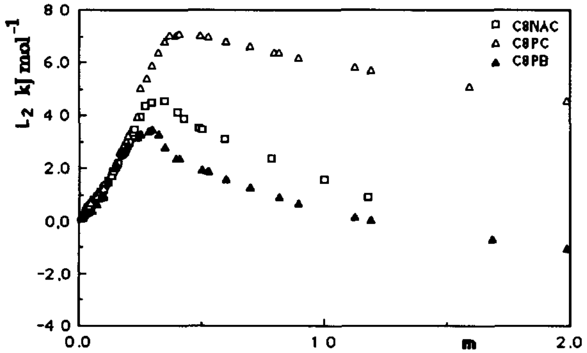

Fig. 6. Effect of the amidic group on the polar head and of the counterion on the trends of the apparent molar relative enthalpies vs. surfactant concentration for *N*-octylnicotinamide chloride, *N*-octylpyridinium chloride and *N*-octylpyridinium bromide.

TABLE 9

Critical micelle concentration (cmc), Krafft temperatures, fitting parameters B and C of eqn. (3), partial molar enthalpies at cmc in aqueous phase, $L_{2,\mathrm{m}}$ and in micellar phase, $L_{2,\mathrm{s}}$, and enthalpy of micellization ΔH_m for the surfactants under investigation and from ref. 8

Surfactant	cmc [a] (mol kg^{-1})	Krafft [a] temperature (°C)	B (kJ mol^{-2})	C (kJ mol$^{-5/2}$)	$\Phi_{\mathrm{L,m}}$ (kJ mol^{-1})	$\Phi_{\mathrm{L,s}}$ (kJ mol^{-1})	ΔH_m (kJ mol^{-1})
C_7NAC	0.45	< 0	−3.92	6.56	3.13	6.29	3.16
C_8NAC [b]	0.22	< 0	−4.06	14.71	3.37	5.81	2.44
C_9NAC	0.09	< 0	−4.53	33.28	2.33	4.74	2.41
$C_{10}NAC$	0.034	5.0	−4.73	73.03	1.49	3.08	1.59
$C_{12}NAC$ [b]	0.0117	17.0	−127.0	1.3×10^3	1.67	−0.85	−2.52
C_8PC	0.25	< 0	−3.57	15.88	4.69	9.83	5.14
C_8PB	0.19	< 0	−9.203	24.62	2.83	4.15	1.32
$C_{10}PC$	0.060 [c]	< 0	7.23	27.28	3.25	7.14	4.08
$C_{10}PB$	0.03	< 0	−3.83	56.34	1.00	1.31	0.31
$C_{12}PC$	0.015	< 0	37.16	–	1.60	4.04	2.44

[a] Refs. 9 and 10.

[b] Ref. 8.

[c] Ref. 7.

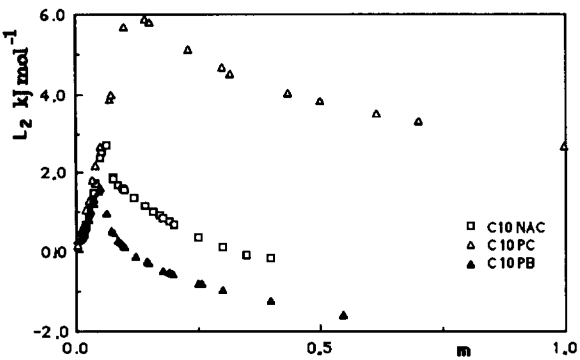

Fig. 7. Effect of the amidic group on the polar head and of the counterion on the trends of the apparent molar relative enthalpies vs. surfactant concentration for *N*-decylnicotinamide chloride, *N*-decylpyridinium chloride and *N*-decylpyridinium bromide.

However, the experimental results can give further information if we compare the behaviour of different surfactants with the same lipophilic chain, in order to rationalize the effect of the polar head. Figure 8 shows the curves of the apparent molar enthalpies vs. *m* for an interesting series of dodecyl cationic surfactants from refs. 8 and 19 from this work. If the counterion is kept constant, a sort of "charge localization scale" for the polar head could be obtained. The more delocalized is the charge, the more similar is the behaviour to that of a non-ionic surfactant. This fact agrees with what we know about the effect of methyl groups in stabilizing the positive charge of aminic nitrogen, and about the destabilization of the positive charge of the pyridinium ring due to the electron attracting power

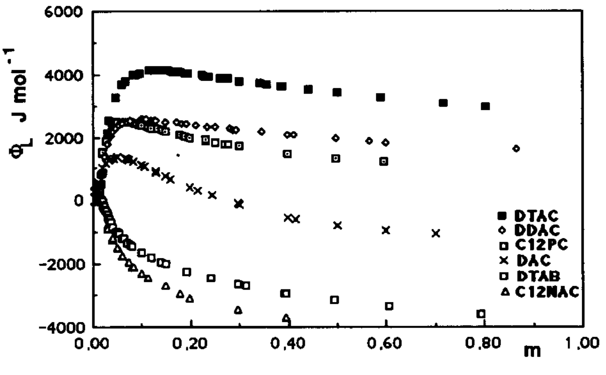

Fig. 8. Comparison of the trends of the apparent molar enthalpies vs. concentration for a series of dodecyl cationic surfactants: dodecyltrimethylammonium chloride (DTAC) [19], dodecyldimethylammonium chloride (DDAC) [19], *N*-dodecylpyridinium chloride (C12PC), dodecylamine hydrochloride (DAC) [19], dodecyltrimethylammonium bromide (DTAB) [20] and *N*-dodecylnicotinamide chloride (C12NAC) [8].

of the amidic substituent. It should be noted that the pyridinium ring behaves in a similar way to dodecyldimethylammonium chloride (DDAC), with slightly stronger hydrophilic interactions in the micellar region, as might reasonably be expected.

Micellization properties

Changes in enthalpic properties for micelle formation can be evaluated by means of direct methods, i.e. from the trend of data on partial or apparent molar properties [5,8,17–30] or from the temperature dependence of the cmc [17,18,31,32]. Moreover, in order to extract the micellization parameters, a physical model to interpret the experimental data must be chosen. The differences in techniques and models, together with the problems of purity and stability of chemicals, often do not allow valid comparisons. It has been observed, however, how the use of the single-step mass action model of Woolley and Burchfield generally leads to results comparable with those from the pseudo-phase transition model [27]. The model assumes that the micelle formation is a two state process, e.g. like a fusion, in which the transition from unmicellized to aggregate pseudo-phase takes place at equilibrium. This very simple model implies that at the cmc the partial molar properties present a discontinuity due to formation of the pseudo-phase, and this is not generally the case. Generally, rather sharp changes in partial molar properties occur around the cmc, but they are never discontinuous, especially for surfactants with a short hydrophobic chain. The model therefore can be applied successfully when the transition is sharp, i.e. when the value of the cmc is very low and the concentration of the monomers in equilibrium with the aggregate solutions can be disregarded: the overall heat involved in the transition is equivalent to the entropy change. In this approximation the micellization parameters can be extracted graphically by extrapolating at the cmc the trends of the partial molar properties above and below the cmc. This graphical method could allow a relative uncertainty in the evaluation of the micellization quantity, especially in the extrapolation of the behaviour below the cmc. Recently it has been shown how the value can be obtained more precisely if the plot of the molar quantity vs. the logarithm of the reduced concentration (i.e. the ratio between the molality and the cmc) is used [8]. The above method has been used in evaluating the micellization enthalpies of the compounds under investigation, reported in Table 9.

It would be interesting to establish and compare the contribution to the micellization enthalpy of each $-CH_2-$ group for the different classes of compound shown in Table 9. However, in the case of nicotinamide surfactants, it is not easy to establish the contribution for each methylene group in the range of chain length examined. In fact, the relation between the number of carbon atoms in the tail and the value of the enthalpy of micellization

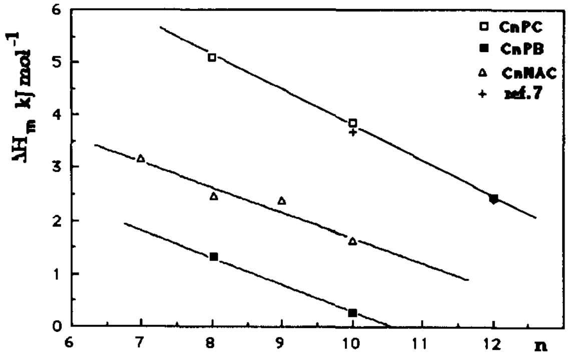

Fig. 9. Enthalpy changes for the micellization process of *N*-alkylnicotinamide chlorides and *N*-alkylpyridinium chlorides and bromides as a function of the number *n* of carbon atoms in the alkyl chain.

shows a deviation from linearity, probably because the high cmc values of the shortest chain surfactants make the pseudo-phase transition model unsuitable. Nevertheless, considering all the data in Table 9, a value of -1.1 kJ mol^{-1} for the $-CH_2-$ group contribution to the enthalpy change in the micellization process can be obtained, in good agreement with the data reported in the literature [8,31,32] for the alkyltrimethylammonium bromides. In the case of pyridinium compounds, the contribution is about half that for the nicotinamide surfactants and is independent of the counterion. This surprisingly low value could be somewhat unreliable because it suffers the same limitations as indicated above, and it is obtained from a very low number of points. It must be pointed out, however, that if the term with twelve carbon atoms is neglected in the linear regression, a similar contribution could be obtained also in the case of nicotinamide surfactants, as Fig. 9 shows.

Woolley [7] has measured the enthalpic properties of some alkylpyridinium chlorides (PC) with an even number of carbon atoms from ten to sixteen in the hydrophobic tail and has interpreted the data by means of his mass action model; the enthalpies of micellization for the decyl and the dodecyl compounds related at the cmc agree very well with the results shown in Table 9 (see Fig. 9), confirming what has already been observed [27] about the consistency of the two methods. The data of Woolley also present a deviation from linearity of the plot of ΔH_m vs. n between the twelve and fourteen carbon atoms terms so that a different contribution for the $-CH_2-$ group could be evaluated depending on the chain length.

It seems that the addivity rule, at least as far as the enthalpies of micellization are concerned, is an oversimplification not applicable in the overall range of chain length, apart from the model used for extracting the data.

CONCLUSIONS

The previous thermodynamic study of aqueous solutions of C_8NAC and $C_{12}NAC$ showed some interesting features, such as the presence of a phase transition in the micellar region, and stressed the opportunity for comparing the properties of alkylnicotinamide and alkylpyridinium derivatives in order to understand the role played by the amidic group on the polar head [8]. The present work is a contribution in this direction.

Again enthalpic curves alone are not able to show any kind of transition, apart from the aggregation process at the cmc, probably because (as mentioned above) the very small thermal effects involved are smoothed by the graphical method used to obtain the molar quantities from the heats of dilution. Even if the enthalpic data are uninformative in this respect, they nevertheless give a further insight on the effects of the counterion and the polar head. Our present results confirm the role of the counterion on the energetics of micellar solution: the substitution of bromide for chloride ions has a dramatic effect in lowering the enthalpic curves below the cmc.

In the case of cationic surfactants, the effect of the polar head can be put in evidence by comparing the behaviour of surfactants with the same alkyl chain: the trends of the molar enthalpies vs. concentration can be explained in terms of charge localization on the polar head.

The amidic group in the nicotinamide compounds greatly enhances the hydrophobicity in respect to the pyridinium compounds.

The enthalpy changes for the micellization process, obtained from the pseudo-phase transition approach, allow one to evaluate, for the class of compounds examined and within the limits of experimental error, a similar contribution for each $-CH_2-$ group if short chain surfactants, with a number of carbon atoms less than twelve, are considered. The reason why the additivity rule seems not to hold for longer chain lengths is open to discussion.

ACKNOWLEDGEMENTS

The authors are grateful to the Italian Ministry for University and Scientific and Technological Research (MURST), to ENI Ricerche and to the National Research Council (CNR) for financial support. They would also like to thank Prof. E.M. Woolley, of Brigham Young University, Provo, Utah, U.S.A. for making available his so far unpublished results about some of the systems under investigation, and Prof. R. De Lisi, University of Palermo, Italy, for useful discussions.

REFERENCES

1 E. Pramauro, C. Minero and E. Pelizzetti, in W.L. Hinze and D.W. Armstrong (Eds.), Ordered Media in Chemical Separations, ACS Symp. Ser., (342) 152.

2 E. Pramauro, E. Pelizzetti, C. Minero, E. Barni, P. Savarino and G. Viscardi, in E. Barni and E. Pelizzetti (Eds.) Colloids and Surfactants: Fundamentals and Applications, Soc. Chim. It., Ann. Chim. (Rome), 77 (1987) 209.

3 U. Tonellato, Colloids Surf., 35 (1989) 121 and references therein.

4 R. Fornasier, P. Scrimin, P. Tecilla and U. Tonellato, J. Am. Chem. Soc., 111 (1989) 224.

5 E. Fisicaro, E. Pelizzetti, M. Barbieri, P. Savarino and G. Viscardi, Thermochim. Acta, 162 (1990) 277.

6 G.C. Kresheck and W.A. Hardgraves, J. Colloid Interface Sci., 48 (1974) 481.

7 E.M. Woolley, personal communication.

8 R. De Lisi, E. Fisicaro, S. Milioto, E. Pelizzetti and P. Savarino, J. Solution Chem., 19 (1990) 247.

9 K. Kalyanasundaram, T. Colassis, R. Humphry-Baker, P. Savarino, E. Barni, E. Pelizzetti and M. Gratzel, J. Am. Chem. Soc., 11 (1989) 3300.

10 K. Kalyanasundaram, T. Colassis, R. Humphry-Baker, P. Savarino, E. Barni, E. Pelizzetti and M. Gratzel, J. Colloid Interface Sci., 132 (1989) 469.

11 P. Karrer, G. Schwarzenbach, F. Benz and U. Solmssen, Helv. Chim. Acta, 19 (1936) 81.

12 P. Karrer and F. Blumer, Helv. Chim. Acta, 30 (1947) 1157.

13 S. Zehani and G. Gelbard, Nouv. J. Chim., 10 (1986) 511.

14 D.M. Stout and A.I. Meyers, Chem. Rev., 82 (1982) 223.

15 R.S. Shelton, M.G. Van Campen, C.H. Tilford, H.C. Lang, L. Nisonger, F.J. Bandelin and H.L. Rubenkoenig. J. Am. Chem. Soc., 68 (1946) 757.

16 J.C. Locicero, D.E.H. Frear and H.J. Miller, J. Biol. Chem., 172 (1948) 689.

17 J.E. Desnoyers, R. De Lisi, C. Ostiguy, and G. Perron, in K.L. Mittal (Ed.), Solution Chemistry of Surfactants, Plenum, New York, NY, (1979) Vol. 1, p. 221 and references therein.

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

19 R. De Lisi, E. Fisicaro and S. Milioto J. Solution Chem., 17 (1988) 1015.

20 R. De Lisi, S. Milioto, M. Castagnolo and A. Inglese, J. Solution Chem., 16 (1987) 373.

21 E. Fisicaro, E. Pelizzetti, R. Bongiovanni and E. Borgarello, Colloids Surf., (1990), in press.

22 R. De Lisi, G. Perron and J.E. Desnoyers, Can. J. Chem., 58 (1980) 959.

23 J.E. Desnoyers, R. De Lisi and G. Perron, Pure Appl. Chem., 52 (1980) 433.

24 D.G. Archer, J. Solution Chem., 16 (1987) 347.

25 E.M. Woolley and T.E. Burchfield, J. Phys. Chem., 88 (1984) 2149.

26 E.M. Woolley and T.E. Burchfield, J. Phys. Chem., 88 (1984) 2155.

27 E.M. Woolley and T.E. Burchfield, Fluid Phase Equilibria, 20 (1985) 207.

28 E.M. Woolley and T.E. Burchfield, in K.L. Mittal and P. Bothorel (Eds.), Surfactants in Solution, Vol. 4, Plenum, New York, NY, 1987, p. 5.

29 E.M. Woolley and T.E. Burchfield, Fluid Phase Equilibria, 20 (1985) 225.

30 E.M. Woolley and T.E. Burchfield, in K.L. Mittal and P. Bothorel (Eds.), Surfactants in Solution, Vol. 4, Plenum, New York, NY, 1987, p. 69.

31 K. Shinoda, and E. Hutchinson, J. Phys. Chem., 66 (1962) 577.

32 K. Shinoda, T. Nakagawa, B. Tamamushi and T. Isemura, Colloidal Surfactants, Academic Press, New York, NY, 1963, p. 37.