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Thermodynamic Properties of N-octyl-, N-decyl- and N-dodecylpyridinium Chlorides in Water

S. Causi,[1] R. De Lisi,[1] and S. Milioto[1]

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Densities, heat capacities and enthalpies of dilution at 25°C and osmotic coefficients at 37°C were measured for N-octyl-, N-decyl- and N-dodecylpyridinium chlorides in water over a wide concentration region. Conductivity measurements were performed in order to evaluate the cmc and the degree of counterion dissociation. Partial molar volumes, heat capacities, relative enthalpies and nonideal free energies and entropies at 25°C were derived from the experimental data as functions of the surfactant concentration. The changes with concentration of these properties are quite regular with the exception of the heat capacities which display anomalies at about 0.9, 0.25 and 0.12 mol-kg^{-1} for the octyl, decyl and dodecyl compounds, respectively. At these concentrations there were also changes in the slopes of the specific conductivity and of the product of the osmotic coefficients and the molality vs. concentration. These peculiarities can be ascribed to micelle structural transitions. The thermodynamic functions of micellization were graphically evaluated on the basis of the pseudo-phase transition model. These data have been compared to those for alkyltrimethylammonium bromides and alkylnicotinamide chlorides. It is shown that the introduction of the hydrophilic CONH$_2$ group lowers the hydrophilic character of the pyridinium ring.

KEY WORDS: N-octylpyridinium chloride; N-decylpyridinium chloride; N-dodecylpyridinium chloride; densities; heat capacities; enthalpies of dilution; osmotic coefficients; activity coefficients; partial molar volumes; partial molar heat capacities; partial molar relative enthalpies; nonideal free energies; nonideal entropies; thermodynamics of micellization

1. Introduction

The thermodynamic properties of ionic surfactants have been extensively studied as functions of the alkyl chain length(1-7) and of the nature of the head group.(7-11) In spite of the few complete sets of thermodynamic properties for homologous series of surfactants, there exists enough information about the effect of the nature of surfactants on the

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[1] Dipartimento di Chimica Fisica, Universite di Palermo, via Archirafi 26, 90123 Palermo, Italy.

surfactant concentration dependence of volume, heat capacity, enthalpy, entropy, free energy and compressibility. However, little attention has been given to the thermodynamic characterization of functionalized surfactants, *i.e.*, amphiphilic molecules whose polar moiety can participate in chemical reaction, despite their growing interest for industrial and fundamental research. Recently, we have carried out a complete thermodynamic study of alkylnicotinamide chlorides(12) whose head group is a pyridinium ring having an amidic group in the meta position. In this paper we examine the effect of introducing the amidic group in the pyridinium ring. For this reason, our attention has been devoted to the thermodynamic characterization of alkylpyridinium chlorides in water since, except for a few direct measurements,(13-15) our knowledge of them is generally confined to the critical micelle concentration (cmc) and surface tension determinations.(16-18) Here, we report specific conductivities, densities, heat capacities, osmotic coefficients and enthalpies of dilution of octyl-, decyl- and dodecylpyridinium chlorides. From these data partial molar thermodynamic properties (volumes, heat capacities, enthalpies, free energies and entropies) as a function of the surfactant concentration are derived.

2. Experimental

2.1. Materials

N-octyl- (OPC) and N-decylpyridinium (DePC) chlorides were synthesized by refluxing pyridine (Fluka product) for 36 h with the corresponding 1-alkyl chlorides (Merck) in the presence of 25% excess pyridine. The viscous oils obtained were solubilized in boiling acetone and white crystals of alkylpyridinium chlorides were obtained by cooling. They were crystallized four times from acetone and dried under vacuum for 48 h at room temperature. The two products have been checked by MS, NMR and IR and the results were consistent with their structure.

N-dodecylpyridinium chloride (DPC) (Aldrich) was crystallized three times from acetone and dried under vacuum for 48 h at room temperature. Analysis of water content of the surfactants, using both the K. Fischer method (Metrohm 655 Dosimat) and thermogravimetry (Mettler TA 3000 System), indicated the salts were monohydrates.

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

Table I. Equivalent Conductivities of Alkylpyridinium Chlorides in Water at 25°C[a]

C	Λ	C	Λ	C	Λ
OPC		DePC		DPC	
0.01491	95.00	0.01967	91.77	0.00248	90.02
0.02958	90.44	0.02769	90.16	0.00515	87.47
0.04536	86.57	0.05036	84.78	0.00773	86.26
0.05912	83.39	0.05890	82.53	0.01032	85.33
0.08946	77.76	0.06947	80.03	0.01285	84.55
0.1160	74.52	0.08661	73.88	0.01514	83.85
0.1431	71.63	0.1064	67.23	0.01773	81.91
0.1338	71.39	0.1236	63.15	0.02020	77.37
0.1878	66.54	0.1440	59.54	0.02322	71.96
0.2334	62.87	0.1665	56.46	0.02657	67.21
0.2603	59.76	0.1931	53.61	0.03017	63.15
0.2976	59.58	0.2327	50.54	0.03422	59.59
0.3152	57.91	0.2583	49.92	0.03982	55.85
0.3407	55.25	0.3080	47.28	0.04568	52.95
0.3760	53.15	0.3635	45.39	0.05143	50.78
0.4142	51.21	0.4356	43.62	0.05715	49.06
0.4569	50.90	0.5132	41.72	0.06266	47.73
0.5243	46.49			0.07041	46.25
0.5999	43.85			0.07913	44.93
0.6560	43.62				
0.7438	41.79				
0.8759	38.73				
1.0028	36.42				
1.1217	34.78				
1.2239	33.25				

[a] Units: C, mol-dm^{-3}; Λ, S-cm^{2}-mol^{-1}.

2.2. Equipment

Densities of the solutions were determined with a vibrating tube flow densimeter (Sodev Mod. 03D) sensitive to 3ppm or better. The instrument was calibrated with water and deuterium oxide. The following literature values were used for the densities: 0.997047 g-cm^{-3} for water(19) and 1.10445 g-cm^{-3} for deuterium oxide.(20) Care was taken to avoid H_2 contamination of deuterium oxide.(21) The temperature was kept constant at 25$\pm$0.001°C by using a closed loop temperature controller (Model CT-L, Sodev Inc.). The relative differences in heat

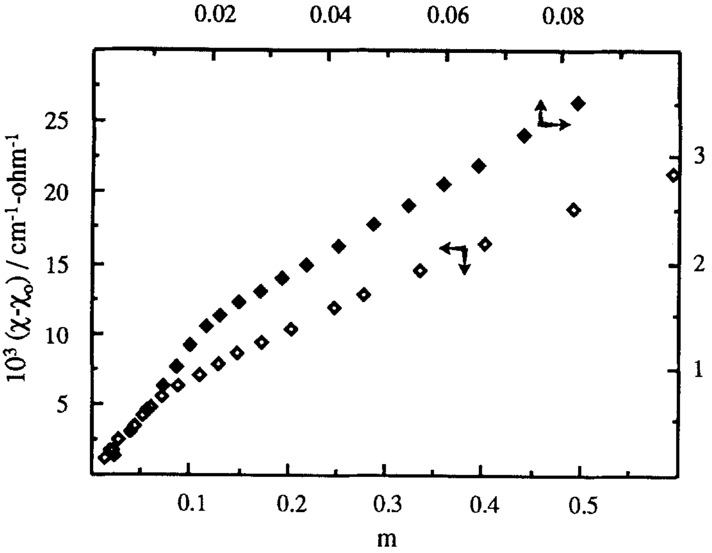

Fig. 1. Specific conductivities corrected for solvent *vs.* surfactant molality. Closed symbol, decylpyridinium chloride; open symbol, dodecylpyridinium chloride.

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). Using a flow rate of about 0.01 cm^3-sec^{-1} and a basic power of 21.2 mW, the temperature increment was approximately 0.5°C. 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_{po} and d_o are the specific heat capacity and density of water, respectively. The value of 4.1792 J-K^{-1}-g^{-1} was used for $c_{p,o}$.(22)

The enthalpies of dilution were measured at 25°C with a flow LKB 2107 microcalorimeter. The freshly prepared surfactant solutions were diluted in a ratio of 1:1 with water. The injection of these solutions into the microcalorimeter was made by means of a Gilson peristaltic pump (Minipuls 2) and the flow of both surfactant solutions and water were determined by weight.

The osmotic coefficients ϕ were determined by means of an Osmomat 070 (Gonotec) vapor pressure osmometer equipped with an automatic control unit. The principles of operation have been described elsewhere.(3) Measurements were made at 37°C, the lowest operating temperature suggested for aqueous solutions. The instrument was

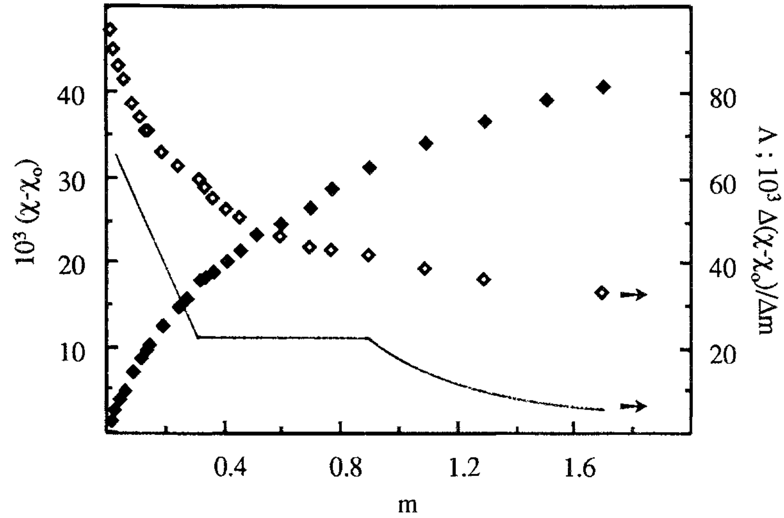

Fig. 2. Specific and equivalent conductivities *vs.* surfactant molality for octylpyridinium chloride. The line represents the differential plot of the specific conductivities.

calibrated using an aqueous NaCl solution 400*m* (mol-kg^{-1}). The accuracy of the osmotic coefficients is of the order of 1% at the lowest surfactant concentration analyzed and quickly improves to 0.2% when the surfactant concentration is increased.

The conductance measurements were performed using a 200 cm^3 Kraus type cell(23) for dodecylpyridinium solutions and a flow cell of about 2 cm^3 for octyl and decyl compounds; both cells contained unplatinized electrodes. The cell constants, respectively, were 2.834±0.001 and 10.49±0.01 cm^{-1} and were determined at 25°C using aqueous KCl and the equation of Lind *et al.*(24) The constant temperature oil-bath was controlled within 0.005°C by a Hewlett-Packard 2804 A Quartz thermometer. The electrical resistances were measured with a calibrated ac bridge(25) at a frequency of 2 kHz. All measured solution conductivities were correct for the solvent conductivities.

3. Results

Conductance measurements were used to estimate the values of the cmc and β, the degree of the counterions dissociation of the micellized surfactant. The cmc corresponds to the intersection point of the slopes, below and above the cmc, of the plot of specific κ or equivalent conductivity Λ *vs.* surfactant concentration whereas β can be estimated

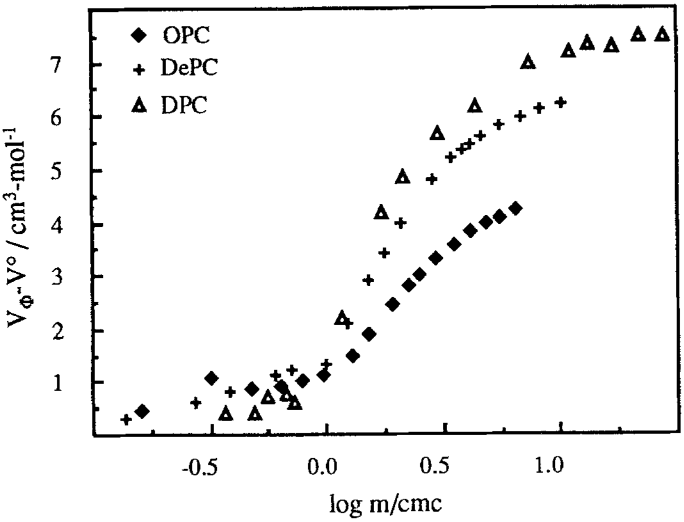

Fig. 3. Plots of excess apparent molar volumes for octyl- (OPC), decyl- (DePC) and dodecyl-pyridinium (DPC) chlorides against the logarithm of the reduced concentration.

as the ratio of the above slopes. Generally, κ *vs*. concentration plots are used since linear correlations are found at least for longer alkyl chain surfactants. The equivalent conductivities as functions of molarities are listed in Table I whereas the plots of κ *vs*. *m* are shown in Figs. 1 and 2. As can be seen in Fig. 1, for DePC and DPC straight lines were obtained and, hence, β and the cmc are easily calculated whereas it is not so for OPC (Fig. 2) because of the curvature of the κ *vs*. *m* plot. In this case, the cmc can only be estimated by plotting Δκ/Δ*m* *vs*. *m*. This plot is shown in Fig. 2 where also that of Λ *vs*. *m* is reported.

The cmc molalities m_{cmc} and β values are summarized in Table XI. A good exponential correlation was found between the present m_{cmc} values and the number of carbon atoms in the alkyl chain n_c. In addition, the m_{cmc} values agree with those obtained from partial molar volumes and heat capacities but are larger by about 20% than those obtained from enthalpies of dilution which in turn agree with those reported in the literature.(14,15,26)

It is worth noticing that, in addition to the cmc, another break was found in the plots of Figs. 1 and 2 for OPC and DePC but not for DPC. These breaks occur at about 0.9 and 0.25*m* for OPC and DePC, respectively. As it will be seen later, at the same concentrations anomalies were found in the plots of apparent and partial molar heat capacities *vs*. concentration.

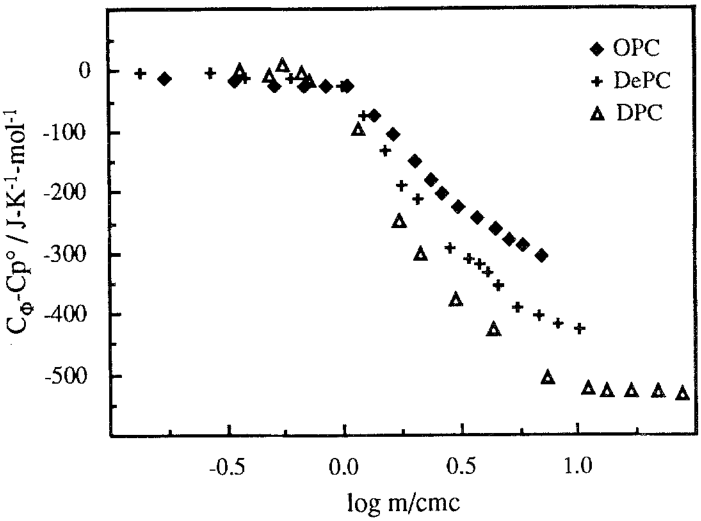

Fig. 4. Plots of excess apparent molar heat capacities for octyl- (OPC), decyl- (DePC) and dodecyl-pyridinium (DPC) chlorides against the logarithm of the reduced concentration.

As expected, the β value increases by shortening the alkyl chain. The present value of 0.40 for DPC is larger than that obtained by Maeda and Satake(26) from emf measurements; they found 0.31 on the basis of the pseudo-phase transition model for charged particles and 0.34 on the hypothesis that beyond the cmc the counterions activity coefficient and the unmicellized surfactant concentration are constant.(26)

The apparent molar volumes V_ϕ and heat capacities C_ϕ of surfactants have been calculated by means of

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

$$C_\phi = Mc_p + \frac{10^3(c_p - c_{p,o})}{m} \tag{3}$$

where m indicates the molality of solutions and M the molecular weight of the investigated 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 Tables II through IV. The plots of apparent molar volumes and heat capacities as functions of molality are shown in

Table II. Volumes and Heat Capacities of Octylpyridinium Chloride in Water at 25°C

m	$-10^3\Delta d$	V_ϕ	V_2	$-10^3\Delta\sigma/\sigma_o$	C_ϕ	$C_{p,2}$
0.04975	0.382	220.56	220.68	2.07	743.6	734
0.09984	0.720	221.16	221.00	4.34	735.4	722
0.1492	1.091	220.97	221.26	6.66	730.0	717
0.1981	1.428	221.00	221.48	8.71	727.0	719
0.2464	1.738	221.09	221.68	10.97	726.0	725
0.3000	2.055	221.22	221.88	14.00	726.8	680
0.3975	2.532	221.59	222.23	21.35	679.2	513
0.4747	2.804	222.00	224.26	28.62	646.6	456
0.5953	3.143	222.55	224.88	40.70	604.0	408
0.6946	3.400	222.88	225.00	51.61	570.3	389
0.7707	3.575	223.10	225.00	59.67	550.6	383
0.9075	3.880	223.39	225.00	72.57	529.1	384
1.0886	4.266	223.67	225.00	88.67	509.0	391
1.2971	4.652	223.91	225.00	106.6	490.1	386
1.5029	5.013	224.08	225.00	123.5	475.0	377
1.6937	5.342	224.19	225.00	138.4	463.1	373
2.0130	5.883	224.30	225.00	161.3	448.7	373

[a] Units: mol-kg^{-1} for m; g-cm^{-3} for d; cm^3-mol^{-1} for V_ϕ and V_2; J-K^{-1}-mol^{-1} for C_ϕ and $C_{p,2}$.

Figs. 3 and 4, where in order to compact the ordinate scale, the apparent molar properties are brought to the same origin by subtracting the corresponding standard properties while to scale the abscissa axis the logarithm of the reduced concentration, *i.e.*, the m/m_{cmc} ratio, was used.

The standard (infinite dilution) partial molar volume and heat capacity correspond to the intercept of the plot of the corresponding apparent molar properties in the pre-micellar region against concentration according to

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

where A_Y is the Debye-Hückel long-range interaction parameter and B_Y, C_Y, *etc.* are curve fitting parameters which account for solute-solute interactions. The C_Y contribution was included for OPC only. The values used for A_Y at 25°C are 1.865 cm^3-mol$^{-3/2}$-kg$^{1/2}$ and 28.95 J-K^{-1}-mol$^{-3/2}$-kg$^{1/2}$ for volumes and heat capacities, respectively.(27)

The apparent molar relative enthalpies L_ϕ, using infinite dilution as the reference state, were derived from the enthalpies of dilution ΔH_{id}

Table III. Volumes and Heat Capacities of Decylpyridinium Chloride in Water at 25°C

m	$-10^3\Delta d$	V_ϕ	V_2	$-10^3\Delta\sigma/\sigma_o$	C_ϕ	$C_{p,2}$
0.00999	-0.043	252.35	252.60	0.28	934.3	932
0.01983	-0.078	252.68	253.00	0.56	934.6	925
0.02794	-0.105	252.85	253.40	0.84	927.4	919
0.04393	-0.151	253.16	254.00	1.34	926.0	906
0.05116	-0.170	253.26	254.30	1.67	916.7	901
0.07093	-0.225	253.39	255.75	2.37	913.6	885
0.08882	-0.214	254.17	257.63	4.05	864.4	600
0.1096	-0.181	254.94	258.58	6.59	804.1	520
0.1275	-0.144	255.47	258.85	9.40	746.4	498
0.1499	-0.090	256.02	259.15	11.75	726.6	475
0.2038	0.035	256.83	259.15	19.78	643.4	482
0.2482	0.145	257.27	259.15	24.84	625.1	562
0.2775	0.201	257.43	259.15	28.09	619.5	546
0.3001	0.238	257.51	259.15	31.15	605.7	448
0.3355	0.319	257.69	259.15	36.46	580.4	381
0.4023	0.441	257.87	259.12	45.89	548.4	420
0.4984	0.597	258.01	259.10	57.06	535.3	474
0.5933	0.775	258.16	259.09	68.31	521.1	472
0.7282	0.994	258.28	259.05	82.78	512.1	474

[a] For units see Table II.

by means of

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

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

In the pre-micellar region, where the surfactant behaves like a normal ionic hydrophobic solute, Eq. (4) can be applied to the apparent molar relative enthalpy so that by taking into account Eq. (5), we obtain the following linear relation

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

where $A_L = 1973$ J-kg$^{1/2}$-mol$^{-3/2}$ is the Debye-Hückel limiting slope for apparent molar relative enthalpy at 25°C.(27) The B_L and C_L values, summarized in Table XI, correspond to the intercept and slope of the plot of the quantity at the left hand side of Eq. (6) against ($m_f^{3/2}$ –

Table IV. Volumes and Heat Capacities of Dodecylpyridinium Chloride in Water at 25°C

m	$-10^3\Delta d$	V_ϕ	V_2	$-10^3\Delta\sigma/\sigma_o$	C_ϕ	$C_{p,2}$
0.00662	0	284.73	285.00	0.10	1123	1117
0.00867	0	284.73	285.18	0.15	1114	1115
0.01008	0.003	285.03	285.31	0.14	1130	1114
0.01209	0.004	285.06	285.48	0.20	1119	1113
0.01300	0.004	284.89	285.55	0.26	1104	1112
0.02079	0.036	286.48	287.00	0.85	1022	718
0.03084	0.114	288.48	291.00	2.40	874.1	650
0.03849	0.167	289.14	291.24	3.53	817.4	620
0.05359	0.275	289.97	291.54	5.87	743.4	580
0.07814	0.435	290.46	291.90	9.46	692.9	540
0.1334	0.836	291.28	292.05	18.42	614.4	530
0.1977	1.254	291.48	292.04	27.39	595.8	582
0.2370	1.518	291.62	292.02	32.98	593.5	594
0.2991	1.882	291.61	292.00	41.02	592.1	595
0.3955	2.484	291.77	291.96	52.91	592.4	595
0.5035	3.078	291.78	291.94	66.14	586.5	595
0.5914	3.557	291.82	291.90	76.57	581.8	593

[a] For units see Table II.

$m_i^{3/2})/(m_f - m_i)$. For the present surfactants, Eq. (6) holds up to the cmc. For molalities lower than m_{cmc}, L_ϕ values have been calculated by means of Eq. (4) and B_L and C_L values. For the dilution processes whose final concentration is smaller than the cmc, $L_{\phi,f}$ can still be calculated by means of Eq. (4) while $L_{\phi,i}$ can be calculated by means of Eq. (5) and $L_{\phi,f}$; so, L_ϕ values at higher surfactant concentrations can been obtained and plotted against the molality. Using this procedure L_ϕ over the complete concentration range have been obtained.

The enthalpies of dilution and the apparent molar relative enthalpies at the initial and final concentrations are summarized in Tables V - VII whereas the plots of apparent molar relative enthalpies as functions of concentration are shown in Fig. 5. In the same figure literature data$^{(15)}$ are also reported. The agreement between the two sets of data is good for DePC (not shown) and OPC whereas a difference of about 1 kJ-mol^{-1} is observed for DPC in the post-micellar region. This difference is essentially due to the fact that the literature L_ϕ values have been calculated by neglecting the C_L parameter. When the comparison is made between purely experimental data, our results agree well with

Table V. Enthalpies of Dilution, Apparent and Partial Molar Relative Enthalpies of Octylpyridinium Chloride in Water at 25°C

m_i	m_f	$L_{\phi,i}$	$L_{\phi,f}$	ΔH_{id}	$L_{2,i}$	$L_{2,f}$
0.04975	0.02619	467	310	-156	795	492
0.09984	0.05211	813	483	-342	1543	827
0.1492	0.07737	1197	653	-506	2432	1188
0.1965	0.09287	1611	737	-880	3417	1429
0.1981	0.1021	1625	829	-817	3452	1580
0.3000	0.1529	2707	1228	-1479	5973	2506
0.3975	0.1998	3760	1641	-2130	7430	3489
0.4747	0.2248	4360	1878	-2492	7400	4062
0.5953	0.2772	4960	2410	-2534	7040	5365
0.6946	0.3199	5290	2940	-2352	6740	6521
0.7707	0.3537	5430	3290	-2123	6520	7240
0.9075	0.4248	5580	3950	-1637	6170	7440
1.0886	0.4892	5660	4460	-1307	5730	7340
1.2971	0.5652	5660	4830	-840	5660	7150
1.5029	0.6571	5660	5180	-491	5660	6850
1.6937	0.6542	5660	5170	-480	5660	6880
2.0130	0.8400	5500	5520	18		6350

[a] Units: mol-kg^{-1} for m; J-mol^{-1} for ΔH_{id}, L_ϕ and L_2.

the literature data. This is shown in Fig. 6 where the quantity at the left hand side of Eq. (7) is plotted *vs.* $(m_f^{3/2} - m_i^{3/2})/(m_f - m_i)$.

The partial molar properties Y_2 were determined by drawing the best curve for the corresponding apparent molar quantities *vs.* molality and then by calculating them from points interpolated at regular narrow intervals according to

$$Y_2 = Y_\phi + m\left(\frac{\partial Y_\phi}{\partial m}\right) = \frac{\partial (Y_\phi m)}{\partial m} \approx \frac{\Delta Y_\phi m}{\Delta m} \qquad (7)$$

In the pre-micellar region, the partial molar properties have been calculated by means of Eqs. (4, 7) and the known A_Y, B_Y and C_Y parameters. Partial molar volumes, heat capacities and relative enthalpies are given in Tables II through VII.

Osmotic coefficients were measured in order to calculate the nonideal free energies. They were carried out at 37°C. Since other thermodynamic properties have been measured at 25°C, osmotic coefficients were calculated at this temperature by means of[(28)]

Table VI. Enthalpies of Dilution, Apparent and Partial Molar Relative Enthalpies of Decylpyridinium Chloride in Water at 25°C

m_i	m_f	$L_{\phi,i}$	$L_{\phi,f}$	ΔH_{id}	$L_{2,i}$	$L_{2,f}$
0.00999	0.00504	283	179	-143	483	293
0.01442	0.00750	370	233	-162	647	389
0.01983	0.01000	474	284	-222	848	483
0.02012	0.00871	479	258	-216	859	435
0.02214	0.01160	517	315	-221	935	542
0.02794	0.01410	628	364	-276	1158	635
0.02979	0.01289	663	340	-322	1230	590
0.03207	0.01676	707	415	-320	1320	734
0.04394	0.02210	939	517	-415	1803	934
0.05116	0.02565	1080	584	-576	2110	1069
0.07093	0.03557	1880	773	-1104	5600	1460
0.08882	0.04448	2700	950	-1819	6080	1826
0.1096	0.05664	3320	1199	-2103	6150	2380
0.1275	0.06661	3710	1650	-1990	6070	5270
0.1499	0.07494	4060	2090	-1964	5880	5760
0.2038	0.1012	4480	3090	-1363	5360	6150
0.2482	0.1228	4600	3630	-917	5020	6080
0.3355	0.1643	4630	4220	-445	4530	5720
0.4023	0.1973	4600	4450	-173	4070	5440
0.4984	0.2422	4540	4590	46	3870	5070
0.5933	0.2910	4420	4630	212	3580	4720
0.7282	0.3006	4220	4630	409	2850	4700

[a] For units see Table V.

$$\phi_{25} = \phi_{37} + \frac{310 - 298}{2R \times 298 \times 310}\left((L_2 - L_\phi) - 298(C_{p,2} - C_\phi)\right) - \frac{(C_{p,2} - C_\phi)}{2R}\ln\frac{298}{310} \qquad (8)$$

where $(L_2 - L_\phi)$ and $(C_{p2} - C_\phi)$ are at 25°C. Equation (8) was recovered by assuming partial and apparent molar heat capacities to be temperature independent in the temperature range considered. The mean activity coefficients were calculated by means of(28)

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

Table VII. Enthalpies of Dilution, Apparent and Partial Molar Relative Enthalpies of Dodecylpyridinium Chloride in Water at 25°C

m_i	m_f	$L_{\phi,i}$	$L_{\phi,f}$	ΔH_{id}	$L_{2,i}$	$L_{2,f}$
0.00797	0.00396	253	100	-157	633	212
0.01028	0.00520	374	139	-246	963	319
0.01209	0.00555	484	144	-326	1260	354
0.01359	0.00673	585	198	-382	1531	480
0.01596	0.00798	870	254	-637	2001	634
0.01807	0.00903	1220	306	-958	3180	777
0.02079	0.00956	1530	334	-1133	3290	853
0.02246	0.01109	1660	422	-1267	3280	1092
0.02755	0.01378	1925	598	-1178	3150	1567
0.03518	0.01753	2150	1110	-998	2925	2900
0.03849	0.01791	2210	1175	-1148	2850	2900
0.04483	0.02231	2295	1650	-688	2715	3280
0.05998	0.02975	2370	2005	-360	2420	3080
0.07814	0.03623	2350	2175	-199	2160	2900
0.09911	0.04881	2285	2330	103	1925	2625
0.1335	0.06138	2150	2370	237	1640	2400
0.1977	0.08856	1910	2320	426	1250	2040
0.2371	0.1065	1780	2255	476	1070	1860
0.2991	0.1333	1610	2150	537	840	1640
0.3955	0.1733	1370	2000	604	515	1380
0.5035	0.2240	1150	1830	710	190	1130
0.5914	0.2623	980	1710	720	-70	970

[a] For units see Table V.

where $A_\phi = -0.39\ \mathrm{kg}^{1/2}\text{-}\mathrm{mol}^{-1/2}$ is the Debye-Hückel limiting slope(27) and m_o the concentration at which the plots of the experimental and the calculated (by using the D-H limiting law) ϕ values tend to converge. The m_o values used are 0.07, 0.02 and 0.006*m* for OPC, DePC and DPC, respectively. The integral at the right hand side of Eq. (9) was solved graphically from the plot of $(\phi - 1)/m$ *vs.* m.

The nonideal free energies for the 1:1 ionic surfactants investigated can be easily calculated as

$$G_2^{ni} = 2RT\ln\gamma_\pm \qquad (10)$$

and the nonideal contribution to the partial molar entropies as

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

Table VIII. Osmotic Coefficients at 37 and 25°C, Activity Coefficients, Nonideal Free Energies, Enthalpies and Entropies at 25°C for Octylpyridinium Chloride in Water

m	ϕ_{37}	ϕ_{25}	$-\ln\gamma_\pm$	$-G_2^{\mathrm{ni}}$	L_2	TS_2^{ni}
0.01500	0.956	0.956	0.138	0.68	0.35	1.03
0.02986	0.936	0.937	0.194	0.96	0.54	1.50
0.04975	0.906	0.908	0.262	1.30	0.80	2.09
0.06008	0.886	0.889	0.284	1.41	0.94	2.34
0.1383	0.900	0.908	0.368	1.82	2.22	4.04
0.1482	0.887	0.896	0.386	1.92	2.41	4.33
0.1808	0.888	0.900	0.403	2.00	3.07	5.07
0.1965	0.869	0.882	0.430	2.13	3.42	5.55
0.2188	0.823	0.839	0.488	2.42	3.92	6.34
0.2468	0.799	0.818	0.529	2.62	4.59	7.21
0.2771	0.779	0.802	0.567	2.81	5.36	8.17
0.3398	0.706	0.734	0.682	3.38	7.30	10.68
0.3961	0.644	0.666	0.796	3.95	7.43	11.38
0.4575	0.615	0.631	0.881	4.37	7.46	11.83
0.4747	0.617	0.632	0.895	4.44	7.40	11.84
0.5100	0.584	0.597	0.957	4.75	7.32	12.07
0.5953	0.544	0.551	1.069	5.30	7.04	12.34
0.6946	0.510	0.513	1.179	5.84	6.74	12.58
0.7707	0.472	0.473	1.272	6.31	6.52	12.83
0.8947	0.441	0.438	1.388	6.88	6.12	13.00
1.0925	0.411	0.407	1.535	7.61	5.72	13.33
1.2971	0.377	0.372	1.674	8.30	5.66	13.96

[a] Units are: kJ-mol^{-1} for G_2^{ni}, L_2 and TS_2^{ni}; mol-kg^{-1} for m.

whereas the excess standard partial molar free energies and entropies were calculated from the nonideal and ideal contributions by means of

$$G_2 - G_2^{\circ} = G_2^{\mathrm{ni}} + 2RT\ln m \qquad (12)$$

$$S_2 - S_2^{\circ} = S_2^{\mathrm{ni}} - 2R\ln m \qquad (13)$$

The experimental osmotic coefficients at 37°C are reported in Table VIII whereas those at 25°C together with the mean activity coefficients and the nonideal free energies, enthalpies and entropies are given in Tables VIII - X.

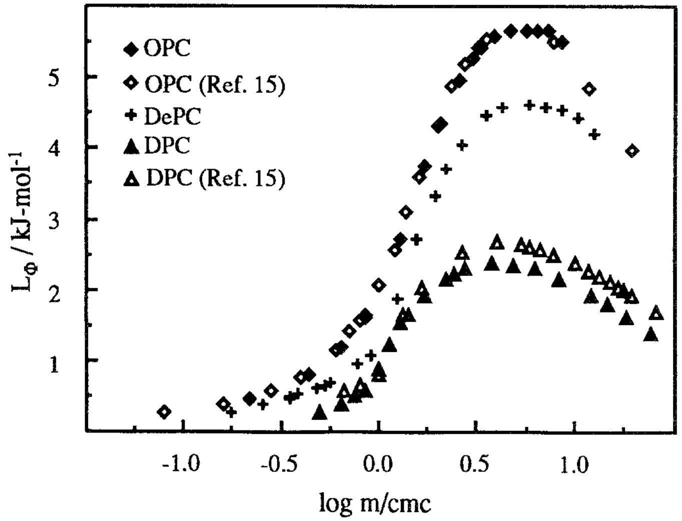

Fig. 5. Plots of excess apparent molar relative enthalpies for octyl- (OPC), decyl- (DePC) and dodecyl-pyridinium (DPC) chlorides against the logarithm of the reduced concentration.

4. Discussion

4.1. Premicellar Region

From the V_2^o and $C_{p,2}^o$ values reported in Table XI, the CH_2 group contribution to the partial molar volume and heat capacity is 16.0 cm^3-mol^{-1} and 92 J-K^{-1}-mol^{-1}, respectively, which agree with those currently accepted$^{(29)}$ of 15.9 cm^3-mol^{-1} and 89 J-K^{-1}-mol^{-1}. As it will be seen later, this is important in view of the difficulties in explaining the micellization properties of DePC. No comparison can be made with literature data since, to the best of our knowledge, the only standard partial molar property reported in the literature is the $C_{p,2}^o$ value of DePC,$^{(13)}$ whose value estimated from data representation is clearly higher that the present result for DPC.

Recently, we investigated octyl- (ONAC) and dodecylnicotinamide (DNAC) chlorides and the values of 238.0 and 301.8 cm^3-mol^{-1} have been reported for V_2^o of ONAC and DNAC, respectively, and the values of 760 and 1115 J-K^{-1}-mol^{-1} for $C_{p,2}^o$ of ONAC and DNAC, respectively. Since alkylnicotinamide chlorides correspond to alkylpyridine chlorides in which the hydrogen atom in the meta position is substituted by a $CONH_2$ group, on the basis of the additivity rule their standard properties can be calculated from those of the corresponding

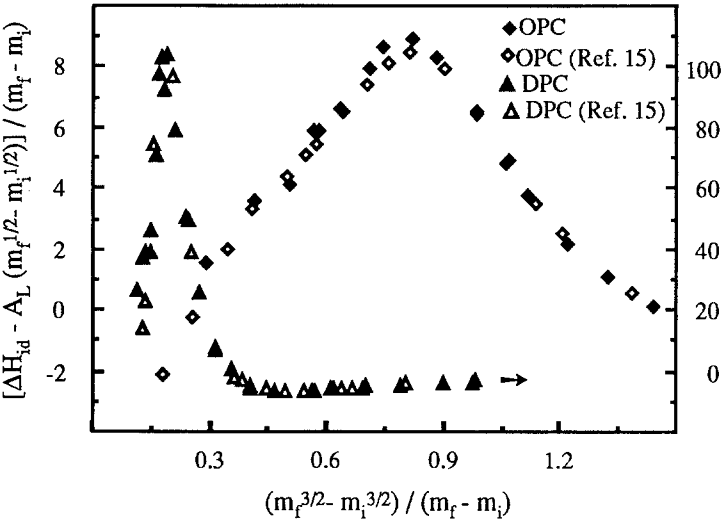

Fig. 6. Comparison between the present and literature data for the enthalpies of dilution according to Eq. (8).

alkylpyridinium by subtracting the contribution of the H atom attached to an aromatic (or heteroaromatic) ring and by adding the contribution of the amidic group.

By taking for the standard properties of H atom the difference between the reported values for CH and C groups in an aromatic or heteroaromatic ring,(30) *i.e.*, the values of 3.2 cm^3-mol^{-1} and 46.2 J-K^{-1}-mol^{-1} for V_2° and $C_{p,2}^{\circ}$, respectively, and for those of CONH$_2$ group the values(30) of 23.1 cm^3-mol^{-1} and −24.4 J-K^{-1}-mol^{-1} for V_2° and $C_{p,2}^{\circ}$, respectively, from data reported in Table XI for the corresponding alkylpyridinium chlorides, the values of 240.0 and 304.2 cm^3-mol^{-1} for V_2° (ONAC) and V_2° (DNAC), respectively, and the values of 682 and 1049 J-K^{-1}-mol^{-1} for $C_{p,2}^{\circ}$ (ONAC) and $C_{p,2}^{\circ}$ (DNAC), respectively, can be calculated. These calculated values are higher than the experimental values by 2.0 (ONAC) and 2.5 (DNAC) cm^3-mol^{-1} for volumes and smaller by 80 (ONAC) and 65 (DNAC) J-K^{-1}-mol^{-1} for heat capacity indicating that the hydrophilic character of the nicotinamide ring is larger than that predicted on the basis of the additivity rule. Actually, it is to be stressed that the CONH$_2$ group contribution to V_2° and $C_{p,2}^{\circ}$ reported in the literature refers to the group contribution when it is attached to an aliphatic frame and that it is different from that of the group attached to an aromatic or heteroaromatic frame because of the interaction effects in the bifunctional molecule. Obviously, the difference is not related to a

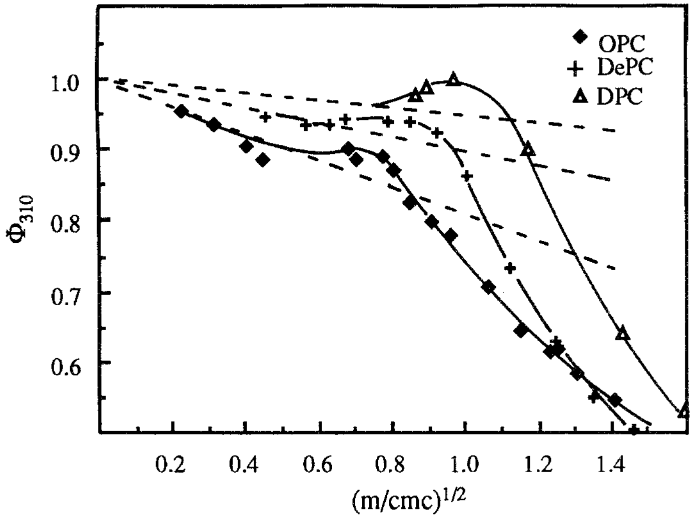

Fig. 7. Experimental osmotic coefficients of octyl- (OPC), decyl- (DePC) and dodecylpyridinium (DPC) chlorides as a function of the square root of the reduced concentration. Dashed lines indicate the Debye-Hückel limiting law for the three surfactants (see text).

change of the geometrical contribution but rather to a modification of the hydrophilic solvation when the hydrated group is introduced in an hydrated aliphatic or aromatic framework. For example, in our case it is possible that the main factor leading to a smaller than predicted hydrophilicity of the nicotinamide group is due to the fact that the pyridinium ring and amidic group are placed in different planes or, as suggested by Fisicaro *et al.*,(15) that the amidic group affects the charge localization on the polar head.

As expected, since the hydrophobicity increases with the alkyl chain length n_c of the alkylpyridinium chlorides, the interaction parameter B_V increases and B_C decreases. No reliable information can be obtained on the effect of the introduction of the amidic group in the pyridinium ring since B_V and B_C are available only for ONAC. The comparison between ONAC and OPC shows that, according to the increase of the hydrophilicity of the nicotinamide ring with respect to the pyridinium ring, the introduction of the amidic group causes a decrease of B_V from 0.6 to -2.1 cm^3-kg-mol^{-2} and an increase of B_C from -441 to -239 J-kg-K^{-1}-mol^{-2}.

As far as the B_L parameter is concerned, its contribution to the relative apparent and partial molar enthalpy is larger for nicotinamide than for pyridinium compounds. Also, in contrast to other homologous

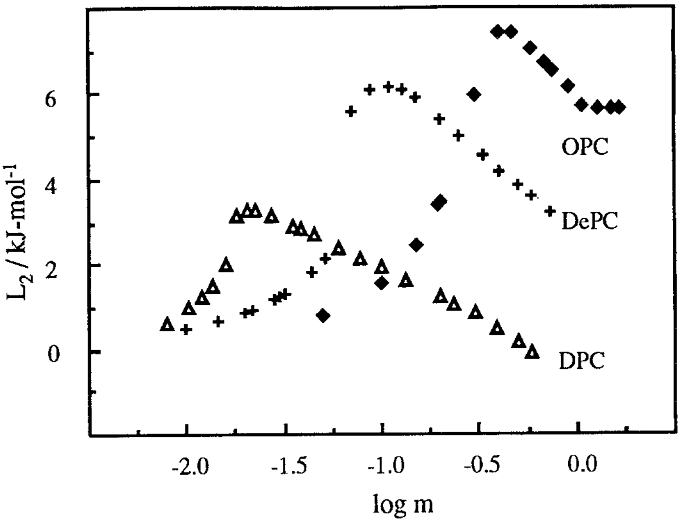

Fig. 8. Plots of the relative partial molar enthalpies of octyl- (OPC), decyl- (DePC) and dodecyl-pyridinium (DPC) chlorides as a function of the surfactant concentration.

series, for alkylpyridinium chlorides the B_L parameter does not monotonically change with n_c whereas C_L does. The large uncertainty with which it can be evaluated does not substantiate the peculiar trend of B_L. In fact, OPC and DePC, B_L and C_L, are in good agreement with those reported in the literature(15) whereas for DPC there is a large difference between the two sets of B_L and C_L values because the C_L literature value was assumed to be zero.

The concentration dependence of the osmotic coefficients at 37°C are quite peculiar, showing positive deviations from the Debye-Hückel limiting law that start at almost the same concentration but progressively decrease in magnitude with increasing n_c. Furthermore, the deviations are almost independent of the nature of the alkyl group. This is shown in Fig. 7 where ϕ is plotted against the reduced concentration $(m/m_{cmc})^{1/2}$. The dashed lines indicate the limiting law for the three surfactants. It is to be noted that using $(m/m_{cmc})^{1/2}$ as ordinate scale there is a limiting law for each surfactant in that the slope is given by $A_\phi \, m_{cmc}^{1/2}$ Even if the uncertainty of the experimental data is large at lower concentrations, the observed positive deviations must be considered real since positive second virial coefficients have been observed at low temperatures for the nonionic alkyldimethylamine oxides surfactants(31) and for the interactions of alkanes(32) and alcohols(33) with tetraalkylammonium halides in water.

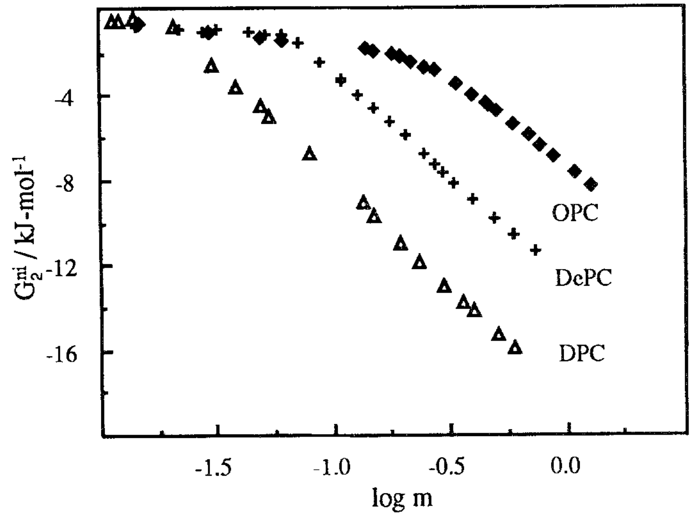

Fig. 9. Nonideal free energies of octyl- (OPC), decyl- (DePC) and dodecylpyridinium (DPC) chlorides as a function of the surfactant concentration.

4.2. Micellar Solutions

The dependence of V_ϕ and C_ϕ on molality are shown in Figs. 3 and 4. As can be seen, the V_ϕ *vs.* m profiles do not differ from those of other surfactants. By increasing the surfactant concentration just beyond the cmc, V_ϕ abruptly increases and approaches a constant value which can be seen if the partial molar volumes are plotted *vs.* the surfactant concentration (not shown). The longer the alkyl chain the sharper is the increase of the slope of V_ϕ *vs.* m as a result of the increase of the micellization equilibrium constant and because of the increase of the volume of the surfactant in the micellized form.

The excess apparent molar heat capacities $(C_\phi$-$C^{\circ}_{p,2})$ *vs.* m curves differ from those of the apparent molar volumes in that, as expected, in the micellization region C_ϕ decreases and in the post-micellar region a second break is found. This is more evident if the partial molar heat capacities (not shown) are considered. This break is shifted towards lower concentrations by increasing the alkyl chain length such as occurs for other homologous series of surfactants.(3) In fact, it is localized at 0.9m for OPC, at 0.25 for DePC and at 0.12 for DPC. According to the literature,(3,12,34,35) a rearrangement of the micellar shape from a spherical to a rod-like structure can account for these breaks. Since micellar rearrangements should involve changes of the aggregation number and/or of the degree of the counterion binding β,(10) changes in the profile of

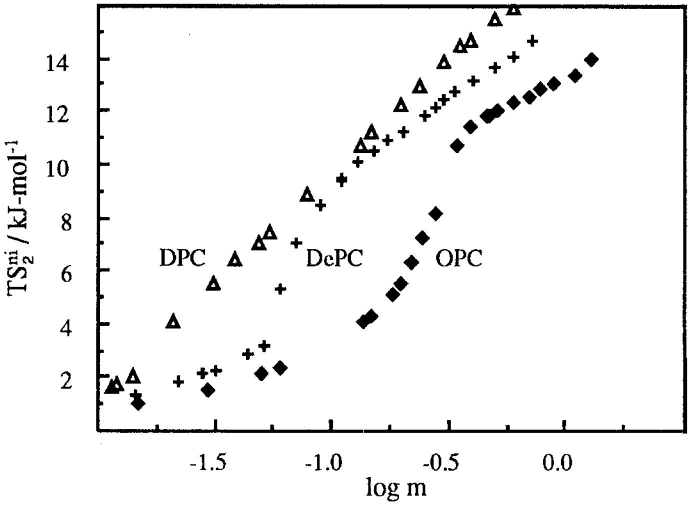

Fig. 10. Nonideal entropies of octyl- (OPC), decyl- (DePC) and dodecylpyridinium (DPC) chlorides as a function of the surfactant concentration.

physico-chemical properties as a function of the surfactant concentration should be observed whenever the property is sensitive to these properties. As it is shown in Figs. 1 and 2, a change in the profile of the specific/equivalent conductivity *vs.* concentration is evident for OPC and DePC at the same concentration as that for heat capacity. The lack of a break in the plot of χ *vs.* m for DPC is due to the narrow concentration interval analyzed. It must be stressed that the post-micellar transitions for the alkylpyridinium compounds investigated here occur at nearly the same concentration as the corresponding nicotinamide compounds indicating that the amidic group does not play a relevant role in this transition whereas the opposite is the case for the pyridinium ring. In fact, the location of the transition for DPC occurs at a 50% lower concentration than that for dodecyltrimethylammonium chloride, dodecyldimethylammonium chloride and dodecylammonium chloride.

No peculiarities have been observed in the profile of L_ϕ *vs.* m (see Fig. 5). Although in the post-micellar region L_ϕ of ionic surfactants often decreases with increasing surfactant molality because of hydrophilic interactions, for the present systems the decrease starts at a concentration close to that where the transition occurs. Consequently, the L_ϕ *vs.* m curves are quite regular showing a more or less sharp increase at the cmc and decrease at higher surfactant concentration. The longer the alkyl chain the sharper are both the increase in the micelliza-

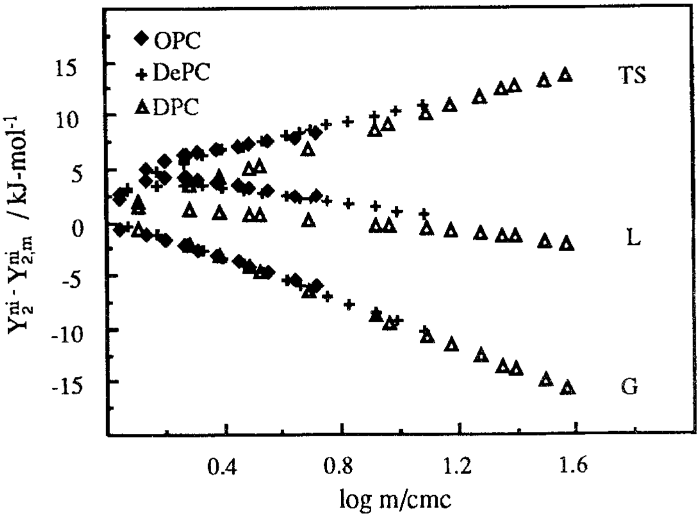

Fig. 11. Relative partial molar enthalpies, entropies and free energies of octyl- (OPC), decyl- (DePC) and dodecyl-pyridinium (DPC) chlorides in micellar solutions as a function of the logarithm of the reduced surfactant concentration.

tion region and the decrease in the post micellar region.

Plots of the nonideal partial molar free energies, enthalpies and entropies *vs.* log$m$ are shown in Figs. 8-10. As can be seen, regardless of the n_c, beyond the cmc the three properties change exponentially with m. In addition, by increasing n_c and/or m, the free energy and enthalpy decrease while entropy increases. If the logarithm of the reduced concentration is used as the abscissa scale, the effect of the n_c on the above profiles shows a different result. In fact, at a given m/m_{cmc} ratio, by increasing n_c the free energy increases while enthalpy and entropy decrease. For example, for $\log m/m_{cmc} = 0.4$, G_2^{ni} is −5.3, −4.6 and −4.0 kJ-mol^{-1}, L_2 is 7.0, 5.9 and 2.7 kJ-mol^{-1} and TS_2^{ni} is 12.6, 10.5 and 6.5 kJ-mol^{-1} for OPC, DePC and DPC, respectively. It seems that different abscissa scales lead to different conclusions about the effect of n_c.

Actually, the Y_2 *vs.* m plot clearly shows the role of the stoichiometric surfactant concentration; by contrast, the profile of Y_2 *vs.* $\log m/m_{cmc}$ is ambiguous in that it seems to be a scaled function normalizing the concentration in terms of that of the micellized surfactant. For this reason, to show the energetics of the micellized surfactant solutions it is useful to compare the plots of Y_2 corrected for the corresponding property of surfactant in the unmicellized form $Y_{2,m}^{ni}$ *vs.* $\log m/m_{cmc}$. $Y_{2,m}^{ni}$ corresponds to the Y_2^{ni}value at the cmc because on the basis of the

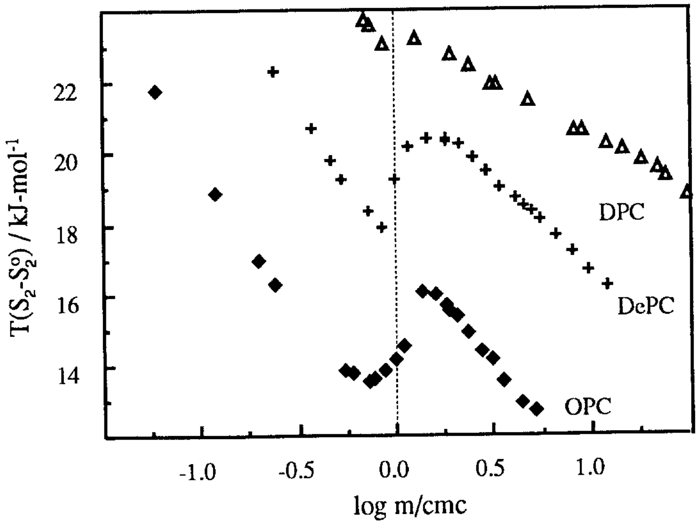

Fig. 12. Plots of excess partial molar entropies of octyl- (OPC), decyl- (DePC) and dodecylpyridinium (DPC) chlorides in micellar solutions as a function of the logarithm of the reduced surfactant concentration.

pseudo-phase transition model beyond the cmc the thermodynamic properties of the unmicellized surfactant can be assumed to be constant.

As Fig. 11 shows, $G_2^{ni} - G_{2,m}^{ni}$ starts from zero and decreases linearly by increasing logm/m_{cmc}; a single straight line with a slope of about −10.5 kJ-mol^{-1} fits the data for the three surfactants. This is not surprising since it has been observed that data of other surfactants having different n_c and different head groups and counterions$^{(12)}$ can be fitted by a single straight line. This behavior was ascribed to a constant activity of surfactants in the micellized form; for a real constant activity the theoretical slope for 1:1 ionic surfactants is $2(2.3RT) = -11.4$ kJ-mol^{-1}. Figure 11 also shows that, with the exception of the points near the cmc, the enthalpy and entropy of the micellized surfactant depend linearly on the logarithm of the reduced concentration and that data for OPC superimpose essentially on those for DePC.

4.3. Micellization Properties

A closer inspection of Fig. 11 shows that the slope of $L_2 - L_{2,m}$ and $T(S_{ni,2} - S_{2,m}^{ni})$ *vs.* logm/m_{cmc} for OPC and DePC differ slightly so that the extrapolated values at $m = m_{cmc}$ are also different. This is important because the intercepts of Fig. 11 correspond to the thermodynamic properties of micellization ΔY_m. In fact, on the basis of the

Table IX. Osmotic Coefficients at 37 and 25°C, Activity Coefficients, Nonideal Free Energies, Enthalpies and Entropies at 25°C for Decylpyridinium Chloride in Water

m	ϕ_{37}	ϕ_{25}	$-\ln \gamma_\pm$	$-G_2^{ni}$	L_2	TS_2^{ni}
0.01441	0.946	0.948	0.146	0.72	0.65	1.37
0.02214	0.935	0.938	0.181	0.90	0.94	1.84
0.02794	0.936	0.940	0.193	0.96	1.16	2.12
0.03207	0.944	0.948	0.192	0.95	1.32	2.27
0.04394	0.940	0.946	0.211	1.05	1.80	2.85
0.05116	0.937	0.945	0.221	1.10	2.11	3.21
0.06005	0.922	0.943	0.231	1.15	4.20	5.35
0.07093	0.863	0.891	0.297	1.47	5.60	7.07
0.08882	0.733	0.747	0.480	2.38	6.08	8.46
0.1096	0.629	0.638	0.653	3.24	6.15	9.39
0.1097	0.622	0.615	0.676	3.35	6.15	9.50
0.1280	0.547	0.553	0.802	3.98	6.08	10.06
0.1499	0.505	0.507	0.923	4.58	5.88	10.46
0.1744	0.451	0.451	1.057	5.24	5.63	10.87
0.2038	0.419	0.420	1.176	5.83	5.36	11.19
0.2482	0.350	0.350	1.368	6.78	5.02	11.80
0.2775	0.320	0.318	1.474	7.31	4.85	12.16
0.3001	0.300	0.293	1.553	7.70	4.71	12.41
0.3355	0.285	0.275	1.651	8.19	4.53	12.72
0.4023	0.268	0.258	1.802	8.93	4.20	13.13
0.4924	0.246	0.238	1.975	9.79	3.89	13.68
0.5933	0.236	0.234	2.122	10.52	3.58	14.10
0.7282	0.217	0.215	2.301	11.40	3.23	14.63

pseudo-phase transition model, ΔY_m is given by the difference between the extrapolated values at the cmc of the trend of the partial molar properties as functions of concentration above ($Y_{2,S}$) and below ($Y_{2,m}$) the cmc. Consequently, Fig. 11 shows that, since at the cmc micelles are forming, the extrapolated values for the free energy is zero whereas it is not so for enthalpy and entropy, nor for volume and heat capacity. The ΔY_m, $Y_{2,S}$ and $Y_{2,m}$ are summarized in Table XI together with the literature data. Note that the value of -460 J-K^{-1}-mol^{-1} for $\Delta C_{p,m}$ for DPC, reported in Table XI as a literature value, was calculated by us from the value of -425 J-K^{-1}-mol^{-1} that we have estimated from data$^{(13)}$ for the corresponding bromide compound and from the value of -35 J-K^{-1}-mol^{-1} which is the contribution to the micellization process for the replacement of bromide with chloride ion calculated from DTAC and

Table X. Osmotic Coefficients at 37 and 25°C, Activity Coefficients, Nonideal Free Energies, Enthalpies and Entropies at 25°C for Dodecylpyridinium Chloride in Water

m	ϕ_{37}	ϕ_{25}	$-\ln \gamma_{\pm}$	$-G_2^{ni}$	L_2	TS_2^{ni}
0.01134	0.977	0.982	0.103	0.51	1.14	1.65
0.01192	0.988	0.994	0.092	0.46	1.23	1.69
0.01405	1.000	1.008	0.078	0.39	1.62	2.01
0.02079	0.901	0.901	0.161	0.80	3.29	4.09
0.03084	0.642	0.640	0.505	2.50	3.04	5.54
0.03849	0.530	0.526	0.710	3.52	2.85	6.37
0.04936	0.469	0.463	0.903	4.48	2.60	7.08
0.05359	0.410	0.403	1.005	4.98	2.51	7.49
0.07814	0.313	0.304	1.350	6.69	2.16	8.85
0.1334	0.241	0.233	1.826	9.05	1.64	10.69
0.1484	0.198	0.191	1.953	9.68	1.53	11.21
0.1977	0.174	0.168	2.213	10.97	1.25	12.22
0.2370	0.142	0.137	2.399	11.89	1.07	12.96
0.2991	0.130	0.124	2.615	12.97	0.84	13.81
0.3575	0.117	0.111	2.786	13.81	0.68	14.49
0.3955	0.131	0.124	2.862	14.19	0.52	14.71
0.5035	0.132	0.125	3.075	15.25	0.19	15.44
0.5914	0.133	0.126	3.216	15.94	-0.07	15.87

DTAB.(10)

In order to test the self-consistency of the data, $T\Delta S_m$ was evaluated by graphical extrapolation from both the plot of TS_2^{ni} and of $T(S_2 - S_2^{\circ})$, calculated according to Eq. (13), against $\log m/m_{cmc}$. Despite using the latter plot which seems to be a more reliable method, shown in Fig. 12, the $T\Delta S_m$ values are the same. However, they are smaller by about 0.2, 0.3 and 0.7 kJ-mol^{-1} for OPC, DePC and DPC, respectively, than the ΔH_m values obtained from the partial molar enthalpies by using the same procedure. While the disagreement observed for OPC and DePC can be considered within the uncertainties involved in the procedure, it is not so for DPC. To determine which value is to be considered the best, we recall that at the cmc $\Delta G_m = 0$. Therefore, it follows that

$$G_{2,m}^{ni} = G_{2,S}^{ni} = L_{2,m} - TS_{2,m}^{ni} = L_{2,S} - TS_{2,S}^{ni} \qquad (15)$$

By plotting G_2^{ni} *vs.* $\log m$, we can obtain $G_{2,m}^{ni}$ as the cross point of the straight lines through the experimental points above and below the cmc. The $G_{2,m}^{ni}$ values are -2.2, -1.2 and -0.25 kJ-mol^{-1} for OPC, DePC and DPC, respectively. By comparing these data with those calculated from enthalpies and entropies data reported in Table XI and Eq. (15), a good self-consistency of data results for OPC and DePC in both the micellized and unmicellized forms and for DPC in the unmicellized form. Therefore, the difference between ΔH_m and $T\Delta S_m$ for DPC is to ascribe to a lack of self-consistency between $L_{2,s}$ and $TS^{ni}_{2,s}$. The reason of this disagreement is not clear. However, probably the incorrect value is that of $TS^{ni}_{2,s}$ since the ΔH_m value of 1.7 kJ-mol^{-1} for DPC is closer to the literature values of 1.9 and 2.4 kJ-mol^{-1} reported by Kresheck and Hardgraves(14) and Fisicaro *et al.*,(15) respectively.

In addition, data in Table XI show that our data and those from the literature(15) for $L_{2,m}$, $L_{2,s}$ and ΔH_m for the three surfactants analyzed in this paper are not in good agreement despite, as shown in Fig. 6, the good agreement between the experimental data, *i.e.*, the enthalpies of dilution. This demonstrates that the evaluation of the micellization properties, especially for ionic surfactants, by graphical procedure results in a larger uncertainty than one estimates.

Thermodynamic data for the micellization process shown in Table XI qualitatively agree with the results for other classes of surfactants, *i.e.*, by increasing the n_c the micellization volume increases while heat capacity, enthalpy and entropy decrease. However, from a quantitative point of view, the data show that the additivity rule for micellization does not hold with the exception of volume. The CH_2 group contribution to the micellization volume (0.75 cm^3-mol^{-1}) is 1.5 times larger than that calculated from alkyltrimethylammonium bromides(3) but it is half of that obtained from ONAC and DNAC. For heat capacity, enthalpy and entropy we can try to calculate the following values from OPC and DePC: $\Delta C_{p,m}(CH_2) = -32$ J-K^{-1}-mol^{-1}; $\Delta H_m(CH_2) = -0.5$ kJ-mol^{-1}; $\Delta S_m(CH_2) = -1.7$ J-K^{-1}-mol^{-1} and the following values from OPC and DPC: $\Delta C_{p,m}(CH_2) = -55$; $\Delta H_m(CH_2) = -0.9$; $\Delta S_m(CH_2) = -3.5$. The latter series of values can be considered to be in agreement with those calculated from ONAC and DNAC, *i.e.*, $\Delta C_{p,m}(CH_2) = -61$; $\Delta H_m(CH_2) = -1.3$; $\Delta S_m(CH_2) = -4.3$; and with those reported in the literature from alkyltrimethylammonium bromides, *i.e.*, $\Delta C_{p,m}(CH_2) = -52$; $\Delta H_m(CH_2) = -1.1$; $\Delta S_m(CH_2) = -3.7$.

The above comparisons seem to indicate that the additivity rule failure for the surfactants is to be ascribed to the decyl compound whose micellization properties (with exception of volume) seem to be incorrect. However, the self-consistency of the enthalpy and entropy of micellization, the procedure used to evaluate these properties, which is the same as that used for the other surfactants, seem to exclude uncer-

Table XI. Thermodynamic Properties of Various Phases and of Micellization (ΔY_m) for Octylpyridinium, Decylpyridinium and Dodecylpyridinium Chlorides[a]

	OPC	DePC	DPC
m_{cmc} (mol-kg^{-1})	0.30,[b] 0.23,[c] 0.25[e]	0.073,[b] 0.057,[c] 0.06[e]	0.018,[b] 0.016,[c,d] 0.015,[e] 0.014[f]
β		0.47	0.40, 0.31,[d] 0.34[d]
V_W (cm^3-mol^{-1})	220.09 ± 0.07	252.06 ± 0.05	284.3 ± 0.2
B_V (cm^3-kg-mol^{-2})	0.59 ± 0.3	16 ± 2	36 ± 27
V_m (cm^3-mol^{-1})	222.1	254.9	286.0
V_S (cm^3-mol^{-1})	225.0	259.4	292.0
ΔV_m (cm^3-mol^{-1})	3.0	4.5	6.0
$C^o_{p,W}$ (J-K^{-1}-mol^{-1})	753 ± 3	937 ± 2	1120 ± 5
B_C (J-kg-K^{-1}-mol^{-2})	-441 ± 78	-451 ± 57	-500 ± 50
C_C (J-kg$^{3/2}$-K^{-1}-mol$^{-5/2}$)		548 ± 157	
$C_{p,m}$ (J-K^{-1}-mol^{-1})	734	884	1108
$C_{p,S}$ (J-K^{-1}-mol^{-1})	380	460	540
$\Delta C_{p,m}$ (J-K^{-1}-mol^{-1})	-350	-425	-570, −460,[g] -490[f]
B_L (kJ-kg-mol^{-2})	- 2.7 ± 0.50, -3.57[e]	5.6 ± 2.5, 7.23[e]	-44 ± 14, 37.16[e]
C_L (kJ-kg$^{3/2}$-mol$^{-5/2}$)	14.5 ± 0.9,15.88[e]	30 ± 11, 27.28[e]	602 ± 100
L_2,m (kJ-mol^{-1})	3.3, 4.7[e]	2.6, 3.3[e]	2.0, 1.6[e]
$L_{2,S}$ (kJ-mol^{-1})	8.8, 9.8[e]	7.1, 7.1[e]	3.7, 4.0[e]
ΔH_m (kJ-mol^{-1})	5.4, 5.1[e]	4.5, 3.8[e]	1.7, 2.4[e], 1.9[f]
$T(S_2\text{-}S^o_2)_m$ (J-K^{-1}-mol^{-1})	12.5	17.7	22.7
$T(S_2\text{-}S^o_2)_S$ (J-K^{-1}-mol^{-1})	17.7	21.9	23.7
$T\Delta S_m$ (J-K^{-1}-mol^{-1})	5.2	4.2	1.0
$T(S^{ni}_2)_m$ (kJ-mol^{-1})	5.6	3.8	2.2
$T(S^{ni}_2)_S$ (kJ-mol^{-1})	10.8	8.0	3.2
$T\Delta S_m$ (kJ-mol^{-1})	5.2	4.2	1.0

[a] The phases are: water (subscript W), aqueous phase (subscript m), micellar phase (subscript s). [b] Averaged values from conductivity, heat capacity and volume measurements. [c] From enthalpies of dilution. [d] From Ref. 26. [e] From Ref. 15. [f] From Ref. 14. [g] From Refs. 10 and 13 (see text).

tainties larger than those for the other surfactants. Also, experimental enthalpies of dilution, as said above, are in good agreement with literature data. On the other hand, the additivity rule verified in at infinite dilution for volume and heat capacity seems to exclude ascribing the peculiar behavior of DePC to impurities in the compound. We can conclude that the additivity rule for micellization does not always hold. This is not unexpected since, except for compensative effects, the additivity rule for a given micellization property implies that this rule is verified for the corresponding property of the surfactant in both the micellized and unmicellized form. Since the additivity rule in the standard state involves its failure in the aqueous phase, where surfactant-additive interactions are also present, the observed additivity rule for micellization is system specific and can be considered to be fortuitous in that it is verified only when some contributions are negligible.

Finally, in order to understand the role of the $CONH_2$ group in the pyridinium ring, the thermodynamic properties of micellization of OPC and DPC can be compared with those of ONAC and DNAC, respectively. The comparison between the data reported in Table XI and in the literature(12) shows that the $CONH_2$ group allows an increase of ΔV_m (2.9 and 5.7 cm^3-mol^{-1}, for C_8 and C_{12} compounds, respectively) and of $\Delta C_{p,m}$ (95 and 80 J-K^{-1}-mol^{-1}) and a decrease of ΔH_m (3.0 and 4.2 kJ-mol^{-1}) and of ΔS_m (8.4 and 17.5 J-K^{-1}-mol^{-1}). With the exception of the heat capacity for which the presence of structural transitions could mask the real $\Delta C_{p,m}$ values, the change of micellization properties seems to indicate that the introduction of the amidic group lowers the hydrophilic character of the pyridinium ring. This is probably due to the loss of hydrophilic hydration during micellization which is more important for nicotinamide than for the pyridinium ring.

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References

1. M. T. Bashford and E. M. Woolley, *J. Phys. Chem.* **89**, 3173 (1985).
2. E. Vikingstad, A. Skauge, and H. Høiland, *J. Colloid Interface Sci.* **66**, 240 (1978).
3. R. De Lisi, S. Milioto, and R. Triolo, *J. Solution Chem.* **17**, 673 (1988).
4. J. E. Desnoyers, G. Caron, R. De Lisi, D. Roberts, A. H. Roux, and G. Perron, *J. Phys. Chem.* **87**, 1397 (1983).

5. M. Tanaka, S. Kaneshina, K. Shin-No, T. Okajima, and T. Tomida, *J. Colloid Interface Sci.* **46**, 132 (1974).
6. G. M. Musbally, G. Perron, and J. E. Desnoyers, *J. Colloid Interface Sci.* **48**, 494 (1974).
7. J. M. Corkill, J. F. Goodman, and T. Walker, *Trans. Faraday Soc.* **63**, 768 (1967)
8. D. M. Bloor, J. Gormally, and E. Wynne-Jones, *J. Chem. Soc., Faraday Trans. I* **80**, 1915 (1984).
9. L. Benjamin, *J. Phys. Chem.* **70**, 3790 (1966).
10. R. De Lisi, E. Fisicaro, and S. Milioto, *J. Solution Chem.* **17**, 1015 (1988).
11. Y. Moroi, N. Nishihido, H. Uehara, and R. Matuura, *J. Colloid Interface Sci.* **50**, 254 (1975).
12. R. De Lisi, E. Fisicaro, S. Milioto, E. Pelizzetti, and P. Savarino, *J. Solution Chem.* **19**, 247 (1990).
13. E. M. Woolley, private communication.
14. G. C. Kresheck and W. A. Hardgraves, *J. Colloid Interface Sci.* **48**, 481 (1974).
15. E. Fisicaro, E. Pelizzetti, M. Barbieri, P. Savarino, and G. Viscardi, *Thermochim. Acta* **168**, 143 (1990).
16. E. Pelizzetti, E. Pramauro, E. Barni, P. Savarino, M. Corti, and V. Degiorgio, *Ber. Bunsenges. Phys. Chem.* **86**, 529 (1982).
17. K. Kalyanasundaram, T. Colassis, R. Humphry-Baker, P. Savarino, E. Barni, E. Pelizzetti, and M. Gratzel, *J. Am. Chem. Soc.* **111**, 3300 (1989).
18. K. Kalyanasundaram, T. Colassis, R. Humphry-Baker, P. Savarino, E. Barni, E. Pelizzetti, and M. Gratzel, *J. Coll. Interface Sci.* (in press).
19. G. S. Kell, *J. Chem. Eng. Data* **12**, 66 (1967).
20. *Handbook of Chemistry and Physics*, 67th edn., (CRC Press, Boca Rotan, 1986).
21. R. De Lisi, S. Milioto, M. Castagnolo, and A. Inglese, *J. Solution Chem.* **19**, 000 (1990).
22. M. F. Stimson, *Am. J. Phys.* **23**, 614 (1955).
23. H. N. Daggett, E. S. Bair, and C. A. Kraus, *J. Am. Chem. Soc.* **73**, 799 (1951).
24. J. E. Lind Jr., J. J. Zwolenick, and R. M. Fuoss, *J. Am. Chem. Soc.* **81**, 1557 (1959).
25. G. J. Janz and J. D. E. McIntyre, *J. Electrochem. Soc.* **108**, 72, (1961).
26. T. Maeda and I. Satake, *Bull. Chem. Soc. Jpn.* **57**, 2396 (1984).
27. R. De Lisi, C. Ostiguy, G. Perron, and J. E. Desnoyers, *J. Colloid Interface Sci.* **71**, 147 (1979).
28. J. E. Desnoyers, R. De Lisi, C. Ostiguy, and G. Perron, in *Solution Chemistry of Surfactants*, Vol. 1, K. L. Mittal, ed., (Plenum Press, New York, 1979).
29. C. Jolicoeur and G. Lacroix, *Can. J. Chem.* **54**, 624 (1976).
30. S. Cabani, P. Gianni, V. Mollica, and L. Lepori, *J. Solution Chem.* **10**, 563 (1981).
31. J. E. Desnoyers, G. Caron, R. De Lisi, D. Roberts, A. Roux, and G. Perron, *J. Phys. Chem.* **87**, 1397 (1983).
32. W.-Y. Wen and J. H. Hung, *J. Phys. Chem.* **74**, 170 (1970).
33. J. E. Desnoyers, G. Perron, S. Leger, B. Y. Okamoto, T. H. Hill, and R. H. Wood, *J. Solution Chem.* **7**, 165 (1978).
34. G. Roux-Desgranges, A. H. Roux and A. Viallard, *J. Chim. Phys.* **82**, 441 (1985).
35. F. Quirion and J. E. Desnoyers, *J. Colloid Interface Sci.* **112**, 565 (1986).