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APPARENT AND PARTIAL MOLAR ENTHALPIES OF POTASSIUM 4-((HEXYLCARBONYL)AMINO)-2-HYDROXYBENZOATE AQUEOUS MICELLAR SOLUTIONS

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)

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ABSTRACT

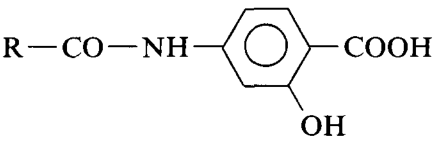
Enthalpies of dilution at 25 ° C of potassium 4-((hexylcarbonyl)amino)-2-hydroxybenzoate (KPAS-C_7) have been measured as a function of the pH and of the ionic strength using an LKB 2107 flow microcalorimeter. From the experimental data, apparent and partial molar relative enthalpies as a function of the molality of the surfactant have been derived. Enthalpic properties are strongly dependent on the pH, probably because the dissociation of the salicylic OH affects the hydrophilic–lipophilic balance of the molecule. Around a surfactant concentration of 0.13 mol kg^{-1}, the plot of apparent and partial molar enthalpies of the solutions in KOH (0.02 mol kg^{-1}) shows an abrupt change in slope: this is attributed to a transition in the micelle structure. The presence of maxima in the partial molar enthalpy versus molality curves at the highest KOH concentrations could confirm this hypothesis. An increase in the ionic strength in the KOH solutions (0.02 mol kg^{-1}) causes the transition to shift to a lower concentration, without a strong effect on the overall trend of the enthalpic curves. The thermodynamic functions of micellisation have been evaluated on the basis of the pseudo-phase-transition model by graphical extrapolation: in the limits of experimental error, they vary almost linearly with pH.

INTRODUCTION

Functionalised surfactants are defined as compounds containing reactive functions covalently bound to the molecular structure: amphiphilic ligands contain, in the polar head, a group able to coordinate metal ions. The use of these compounds and their aggregates in various analytical techniques, either in water or water–organic systems, has attracted increasing attention. Their practical applications in extraction methods, ion transport across lipophilic membranes and other analytical fields, including HPLC and membrane selective electrodes, are growing.

To our knowledge, there are only a few studies on the thermodynamic characterisation of these 'functionalised' surfactants, and the number of direct measurements is very limited [1–6].

A series of 'functionalised' surfactants containing the same chelating moiety, namely 4-((hexylcarbonyl)amino)-2-hydroxybenzoic acids (hereafter referred to as PAS-C_n where n is the number of carbon atoms in the alkylic chain plus 1), has been proposed as suitable micelle-forming ligands [6–8]. Their structure is as shown below.



$R = C_{n-1}H_{2n-1}$

The surface properties and micellar parameters of this series of compounds have been investigated for members with long tails ($8 \leq n \leq 16$) (sodium salts) by means of surface tension measurements and light scattering techniques [6]. Those with shorter tails have been studied as model ligands for metal ion extraction in aqueous micellar solutions of some polyoxyethylene-type surfactants; their acid–base properties and reactivity towards metal ions in the mixed micelles thus formed have also been examined [7].

These compounds can be solubilised in water and, in the case of sufficiently high values of n, aggregate only in basic environments, i.e. in conditions above the "critical micelle pH range" [9].

The system is complicated by the presence of the salicylic hydroxylic group: this group can be deprotonated either at high pH values, giving rise to a doubly charged polar head, or in the presence of a transition metal. The pK_a of the hydroxy group for the monomer below the critical micelle concentration (cmc) spectroscopically evaluated, lies around 13.0 ± 0.2 at 25 °C [6].

The present study is devoted to the thermodynamic characterisation of the binary system KOH solution–KPAS-C_7 and, in particular, to demonstrating how the enthalpic properties of the aqueous solutions are affected by the hydroxide concentration and the ionic strength. The enthalpic properties of the systems were obtained by measuring the enthalpies of dilution by means of flow microcalorimetric techniques.

EXPERIMENTAL

Reagents

4-((Hexylcarbonyl)amino)-2-hydroxybenzoic acid (PAS-C_7) was prepared as indicated in ref. 6 and purified by repeated crystallisation from ethanol. The purity was checked by TLC.

Freshly boiled doubly distilled water, stored under nitrogen, was used throughout. Potassium hydroxide solutions (approximately 2 and 0.2 mol l^{-1}) were prepared by diluting the contents of Merck Titrisol ampoules with the proper quantity of water and standardised with potassium hydrogen phthalate (C. Erba; dried at 120 ° C).

The surfactant solutions were prepared under nitrogen by adding to the acid the quantity of KOH needed both to neutralise the carboxylate group and to reach the required excess of hydroxide ion in the final solution.

The basic solutions of surfactant must be prepared just before use, because during long storage oxidation occurs, resulting in a yellowing of the solution.

Measurements

The enthalpies of dilution at 25 ° C were measured by an LKB 2107 flow microcalorimeter. The freshly prepared surfactant solutions were diluted into the mixing measuring cell of the microcalorimeter in a 1 : 1 ratio using a KOH solution of the same molality as the excess KOH in the surfactant solutions, so that no correction for the heat of dilution of KOH is needed. Injection of these solutions into the calorimeter was by means of a Gilson peristaltic pump, Minipuls 2, and their flows were determined by weight.

The critical micelle concentrations were determined by means of a Dognon–Abribat tensiometer with a platinum blade: during the measurement, at 25 ± 1 ° C, the chamber was flushed with nitrogen to avoid CO_2 absorption from the atmosphere.

RESULTS

The calculation of apparent and partial molar enthalpies from heats of dilution has been described before [3,10–14]: however the most important aspects are summarised below for clarity.

The apparent and partial molar relative enthalpies, Φ_L and L_2 respectively, are the best functions to express the changes in enthalpy of micellar solutions: they can be derived from the enthalpies of dilution ΔH_{id}, with infinite dilution being assumed as the reference state

$$\Delta H_{id} = \Phi_{L,f} - \Phi_{L,i} \qquad (1)$$

where subscripts f and i refer to the final and initial concentrations, respectively.

For an ionic surfactant in the pre-micellar region, the apparent relative molar enthalpy can be expressed as a polynomial of the square root of the molality m. Stopping the serial expansion at the third term gives

$$\Phi_L = Am^{1/2} + Bm + Cm^{3/2} \qquad (2)$$

where $A = 1973$ is the limiting Debye–Hückel slope for relative enthalpies accounting for the long-range solute–solute interactions, and the parameters B and C are averaged on the experimental points in the pre-micellar region by a least-squares curve fitting

$$\Delta H_{\mathrm{id}} - 1973\left(m_{\mathrm{f}}^{1/2} - m_{\mathrm{i}}^{1/2}\right) = B\left(m_{\mathrm{f}} - m_{\mathrm{i}}\right) + C\left(m_{\mathrm{f}}^{3/2} - m_{\mathrm{i}}^{3/2}\right) \tag{3}$$

When the final concentration of the dilution process is above the cmc, $\Phi_{\mathrm{L,f}}$ is evaluated by means of eqn. (2) and $\Phi_{\mathrm{L,i}}$ by eqn (1). At higher surfactant concentrations, one of the values of the second member of eqn. (1) is graphically interpolated, and the other is evaluated by means of the same equation.

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

DISCUSSION

As the experimental data will show, the enthalpic properties of the KPAS-C$_7$ solutions are strongly affected by the hydroxide ion concentration and, in a different way, by the value of the ionic strength. The principal features of each system under investigation will be discussed below in an attempt to understand the role played by the dissociation of the salicylic OH and by the increase in the salt concentration.

Solutions in 0.02 mol kg^{-1} KOH

The results obtained from the calorimetric dilution experiments are reported in Table 1 and are shown in Fig. 1.

The cmc, evaluated by means of surface tension measurements, is 0.021 mol kg^{-1}, in accordance with the cmc values for *p*-*n*-octylbenzoic acid [14] (0.013 mol dm^{-3}) and for octylbenzenesulfonate [15] (0.014 mol dm^{-3}), and also in agreement with the value obtained by extrapolation of the data in ref. 6.

In the pre-micellar region, the trend of the apparent molar enthalpies was evaluated by means of eqn. (2). Parameters B and C, obtained by least-squares curve fitting, are reported in Table 2.

At a total surfactant concentration of about 0.01 mol kg^{-1}, lower than the measured cmc, a sharp decrease to negative values begins, indicating that aggregation is occurring. Hydrophilic and, particularly, micelle–counterion interactions seem to play a very important role in this region.

The behaviour up to a surfactant concentration of 0.14 mol kg^{-1} is quite similar to that of other anionic dodecyl surfactants, e.g. sodium dodecyl-

TABLE 1

Enthalpies of dilution, apparent and partial molar enthalpies of potassium 4-((hexylcarbonyl)amino)-2-hydroxybenzoate in 0.02 mol kg^{-1} KOH

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})
0.00394	0.00203	−72	265	185	385	270
0.00499	0.00255	−78	293	212	492	330
0.00679	0.00350	−81	318	251	365	360
0.00799	0.00411	-52	322	270	315	390
0.00955	0.00494	−18	315	291	260	490
0.01817	0.00938	55	261	316	90	265
0.03304	0.01684	142	138	280	−221	140
0.05786	0.02884	270	−96	174	−477	−153
0.07169	0.03683	282	−169	85	−536	−275
0.09420	0.04814	244	−260	−16	−555	−403
0.11917	0.06044	217	−321	−104	−544	−492
0.13732	0.07003	191	−351	−160	−580	−531
0.15883	0.07962	173	−390	−206	−802	−551
0.16862	0.08631	185	−420	−233	−975	−556
0.17797	0.09023	207	−455	−247	−1080	−556
0.21584	0.10958	289	−590	−301	−1390	−547
0.23727	0.11879	344	−664	−320	−1540	−544
0.28792	0.14480	494	−858	−364	−1840	−625

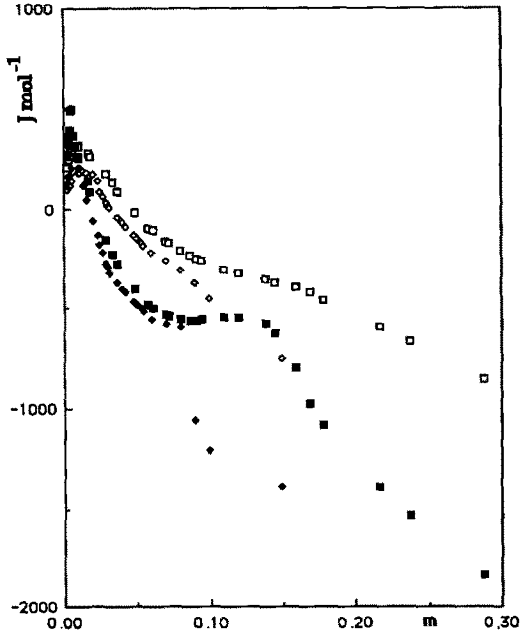


Fig. 1. Apparent molar relative enthalpies (open symbols) and partial molar enthalpies (filled symbols) of potassium 4-((hexylcarbonyl)amino)-2-hydroxybenzoate in 0.02 mol kg^{-1} KOH (squares) and in 0.02 mol kg^{-1} KOH + 0.10 mol kg^{-1} KCl (diamonds) as a function of surfactant concentration.

TABLE 2

Critical micelle concentration, 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 micellisation ΔH_m for potassium 4-((hexylcarbonyl)amino)-2-hydroxybenzoate at the different KOH excess concentrations

KOH excess conc. (mol kg^{-1})	cmc (mol kg^{-1})	B (kJ mol^{-2})	C (kJ mol$^{-5/2}$)	$L_{2,\mathrm{m}}$ (kJ mol^{-1})	$L_{2,\mathrm{s}}$ (kJ mol^{-1})	ΔH_m (kJ mol^{-1})
0.02	0.021	77.5	−662.4	1.31	−0.47	−1.36
0.02 +0.10 KCl	0.0075	1.4	−28.2	0.25	−0.40	−0.65
0.05	0.019	−19.0	116.3	0.26	1.40	1.14
0.10	0.0175	−42.0	522.5	0.95	3.96	3.01

sulphate [16–18], at the same temperature, despite the shorter alkyl chain. In fact, in these working conditions, KPAS-C_7 can be considered a 1 : 1 anionic surfactant because at this pH the degree of dissociation of the hydroxyl group is about 0.16 for the monomer: when the monomeric units are closely packed, as in a micellar structure, the combined electrostatic effects caused by the proximity of the hydrophilic heads, considerably increase the apparent pK_a of the acidic groups. It can therefore be assumed that the salicylic OH in the micelles is practically undissociated and probably engaged in intramolecular and/or intermolecular hydrogen bonding. The intramolecular hydrogen-bond formation causes delocalization of the negative charge on the six-membered ring formed between the carboxylic and hydroxylic parts of the molecule, the aromatic ring contributing to the hydrophobic character of the surfactant.

At a surfactant concentration of about 0.14 mol kg^{-1}, a sudden change in slope suggests a structural transition. The trend of partial molar enthalpies, reported in Table 1 and in Fig. 1, confirms this kind of behaviour.

The occurrence of a phase transition in aqueous solutions of surfactants containing a polar group attached to an aromatic ring has already been reported in the literature. In particular, Porte and Poggi [15], examining octyl benzene sulfonate solutions by measuring the changes in the orientational order induced by a magnetic field, have demonstrated that "first and second critical micellar concentrations" occur. They have attributed the second cmc to the transition from spherical to cylindrical micelles. The subsequent thermodynamic studies of Caron et al. [19] on the same surfactants are not in conflict with this interpretation. In our opinion hydrogen bonding as well as the benzene ring are influential in determining the structure of the micelles. An intramicellar rearrangement from intramolecular to intermolecular hydrogen bonding with the consequent modification of the hydration sphere could be one of the possible origins of the transition. Such an intramicellar rearrangement has already been proposed to explain the behaviour of phosphate dialkyl esters, the pH-dependence of the fusion of didodecyl phosphate vesicles [20] and of the phase transition temperature of dimyristoylalkylphosphatidic acids [21,22]. The fact that the transition is clearly detectable at the lowest pH examined, at which the OH is dissociated to the lowest extent, provides further evidence to support this hypothesis, see below.

Moreover, it must be noted that the homologues of higher molecular weight in the PAS-C_n series form gels in aqueous solution below a transition temperature which considerably increases with n and with the amphiphile concentration, and decreases with hydroxide concentration [6]. Preliminary light-scattering data on the system under investigation suggest the idea of the presence of small cylindrical particles over the entire concentration range examined: in this case the phase transition could arise either from a change in the micelle–counterion interactions [23], or in the hydrogen-bonding structure, or from a form of association between the cylindrical particles. In any case, it must be stressed that this transition must be important because enthalpy data are not, in general, as sensitive to structural transitions as other second-derivative thermodynamic properties.

Solutions in 0.10 mol kg^{-1} KOH

At higher pH, the KPAS-C_7–KOH solution system is complicated by the presence of divalent anionic species. In 0.10 mol kg^{-1} KOH excess solutions, the salicylic hydroxyl group of the monomer is dissociated by one half and also, bearing in mind the increase in the apparent pK_a of the associated molecules, the concentration of dissociated OH in the micellar phase is probably not negligible, resulting in a strong influence on the thermodynamic properties.

In fact, the apparent and partial molar enthalpies in 0.10 mol kg^{-1} KOH reported in Table 3 and shown in Fig. 2, show a completely different trend with respect to the solutions in 0.02 mol kg^{-1} KOH: in the concentration range examined, they are always positive and, below the cmc, of the order of a few kJ mol^{-1}. The data in the pre-micellar region were obtained in the same way as described above for the lower pH, and the values of the parameters obtained are reported in Table 2.

No change in slope can be seen around the cmc: the idea that at this hydroxide concentration the aggregation occurs at higher amphiphile concentration was rejected because of the surface tension measurements, which gave the cmc of KPAS-C_7 in 0.10 mol kg^{-1} KOH as 0.0175 mol kg^{-1}, in very good agreement with the value obtained by extrapolating surface tension versus log m data using the same conditions as in ref. 6. Moreover, from the same work, the aggregation number, extrapolated from the plot of the logarithm of the aggregation number obtained from light-scattering data versus the number of carbon atoms of the alkyl chain is found to be 22.

TABLE 3

Enthalpies of dilution, apparent and partial molar enthalpies of potassium 4-((hexylcarbonyl)amino)-2-hydroxybenzoate in 0.10 mol kg^{-1} KOH

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	0.00253	−60	114	58	397	243
0.00700	0.00358	−88	177	79	520	309
0.00848	0.00431	−140	233	96	611	355
0.00998	0.00512	−182	298	117	700	405
0.02005	0.01027	−343	680	312	1177	717
0.02514	0.01288	−368	770	390	1552	872
0.03489	0.01779	−457	1010	570	1848	1152
0.03604	0.01834	−417	1040	572	2101	1183
0.04006	0.02047	−429	1120	695	2290	1300
0.04995	0.02535	−553	1365	775	2726	1563
0.05012	0.02443	−657	1367	760	2733	1514
0.06002	0.03065	−639	1540	915	3127	1836
0.08016	0.03954	−808	1960	1115	3801	2266
0.08022	0.04066	−828	1962	1125	3803	2318
0.10004	0.05060	−1014	2374	1370	4307	2753
0.10027	0.04929	−1010	2375	1360	4312	2698
0.12062	0.06043	−1178	2742	1545	4668	3142
0.13059	0.06719	−1221	2880	1695	4786	3386
0.14260	0.07188	−1237	3030	1790	4880	3544
0.15084	0.07569	−1242	3132	1890	4812	3666
0.16107	0.07855	−1242	3162	1920	4757	3753
0.16112	0.08100	−1244	3165	1980	4756	3826
0.17095	0.08563	−1228	3310	2075	4692	3956
0.18109	0.09088	−1218	3387	2170	4620	4093
0.20142	0.10096	−1124	3488	2365	4476	4326
0.22093	0.10986	−1013	3560	2540	4358	4499
0.22189	0.11105	−967	3562	2555	4353	4520
0.23197	0.11400	−966	3581	2615	4303	4569
0.24217	0.11813	−908	3610	2690	4267	4633
0.24324	0.12061	−897	3615	2740	4264	4668
0.28306	0.14009	−683	3665	3000	4195	4864
0.28318	0.13894	−693	3666	2985	4194	4857
0.29304	0.14570	−599	3675	3060	4185	4834
0.30456	0.15185	−548	3682	3135	4180	4806
0.31348	0.15344	−542	3692	3150	4178	4800
0.32458	0.15888	−515	3709	3195	4175	4769
0.34477	0.16934	−435	3715	3300	4165	4703
0.35610	0.17598	−414	3720	3355	4150	4657
0.38589	0.18990	−336	3730	3435	4141	4557
0.40761	0.19755	−269	3735	3480	4135	4502

The plot of L_2 as a function of surfactant concentration, Fig. 2, shows a sharp increase up to about 0.14 mol kg^{-1}, a value comparable with that of the transition observed in 0.02 mol kg^{-1} KOH, where the function is a

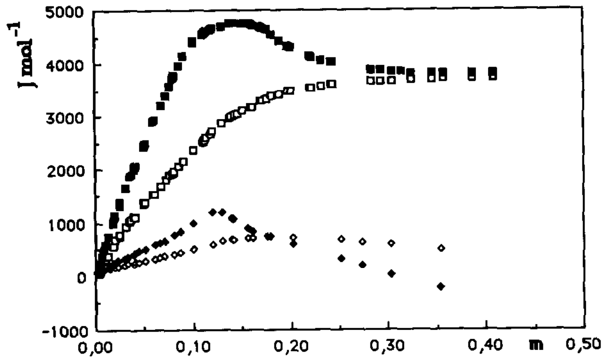


Fig. 2. Apparent molar relative enthalpies (open symbols) and partial molar enthalpies (filled symbols) of potassium 4-((hexylcarbonyl)amino)-2-hydroxybenzoate in 0.10 mol kg^{-1} KOH (squares) and in 0.05 mol kg^{-1} KOH (diamonds) as a function of surfactant concentration.

maximum: this fact confirms the structural transition even if the evidence is not so convincing as at the lower pH. After a KPAS-C$_7$ concentration of 0.25 mol kg^{-1}, both the apparent and partial molar enthalpies become practically constant at around 3.5–4.0 kJ mol^{-1}.

A similar behaviour can be seen when the number of carbon atoms in a homologous series of surfactants is decreased [3]. The trend at higher pH could be due to a decrease in the hydrophobicity of the surfactant, determined both by the dissociation of the OH group, and by the delocalization of the negative charge of the OH on the benzene ring. The overall situation is complicated by the coexistence of singly and doubly charged species, probably giving rise to a mixed-micelle type of formation.

An increase in the pH also increases the ionic strength of the system. In order to distinguish between the effect of the pH and the effect of the ionic strength, we have carried out measurements at an intermediate pH, adding an electrolyte to the solutions at the lowest pH.

Solutions in 0.05 mol kg^{-1} KOH

In order to determine if the enthalpic properties of the systems change gradually as a function of OH concentration or if a sharp variation occurs, measurements at 0.05 mol kg^{-1} excess KOH were performed. The results, shown in Table 4 and Fig. 2, indicate an intermediate behaviour for the system at this pH: over all the concentration range examined, the apparent and partial molar enthalpies are always positive, the maximum value being around 1 kJ mol^{-1}.

Difficulties arise in the evaluation of the trend in the pre-micellar region, the very low values of the enthalpies of dilution being near the limits of the instrumental sensitivity. Because the possible uncertainties in this region

TABLE 4

Enthalpies of dilution, apparent and partial molar enthalpies of potassium 4-((hexylcarbonyl)amino)-2-hydroxybenzoate in 0.05 mol kg^{-1} KOH

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})
0.00399	0.00202	−18	78	61	112	86
0.00649	0.00328	−22	98	72	140	104
0.00800	0.00420	−29	110	80	156	118
0.01500	0.00758	−35	142	105	215	152
0.03000	0.01510	−54	209	143	338	216
0.04000	0.02020	−61	251	167	421	258
0.04511	0.02302	−79	272	181	463	284
0.06536	0.03340	−112	356	224	628	367
0.07988	0.04158	−146	415	256	764	434
0.10013	0.05033	−216	502	293	981	507
0.12070	0.06051	−303	601	335	1194	590
0.14064	0.07023	−337	689	375	1095	670
0.16135	0.08047	−333	728	417	852	766
0.17617	0.08756	−314	734	446	751	838
0.20188	0.10016	−235	727	503	605	982
0.25175	0.13042	−37	674	646	321	1207
0.27232	0.13930	43	641	687	203	1093
0.30331	0.15653	118	589	724	30	897
0.35307	0.17882	228	508	736	−210	738

could cause a systematic error of a few tens of joules in the absolute values of the enthalpic quantities, the general trend should not be affected and the comparison is meaningful.

The apparent molar enthalpies increase up to a concentration of 0.17 mol kg^{-1}, after which they slowly decrease; the partial molar enthalpies show a maximum, once again at about 0.13 mol kg^{-1}, the value of the supposed phase transition. No change in slope can be seen around the cmc.

Effect of the ionic strength

The effect of the ionic strength was studied by measuring the enthalpies of dilution of KPAS-C_7 solutions in 0.02 mol kg^{-1} KOH with 0.10 mol kg^{-1} KCl as background electrolyte (Table 5).

The cmc (0.0075 mol kg^{-1} from surface tension measurements) was affected by the added electrolyte in the expected direction.

In the region below 0.08 mol kg^{-1}, the enthalpic behaviour is very similar in shape and in extent to that of solutions without background electrolyte. Around this concentration, there is a sudden change in slope of the curves of Φ_L and L_2 versus m, very similar to that observed in the trend of the solutions without KCl. This could be interpreted as the same phase transi-

TABLE 5

Enthalpies of dilution, apparent and partial molar enthalpies of potassium 4-((hexylcarbonyl)amino)-2-hydroxybenzoate in 0.02 mol kg^{-1} KOH and 0.10 mol kg^{-1} KCl

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})
0.00396	0.00215	−41	123	92	174	130
0.00594	0.00316	−26	148	110	212	160
0.00991	0.00527	−45	183	140	212	204
0.01982	0.01052	8	176	184	−54	211
0.02476	0.01308	97	91	188	−174	118
0.02973	0.01577	172	13	185	−292	52
0.03964	0.02290	205	−60	145	−400	−127
0.04959	0.02622	203	−143	60	−480	−215
0.05454	0.02878	216	−181	35	−515	−270
0.05949	0.03131	227	−217	10	−553	−317
0.06947	0.03665	213	−256	−43	−576	−372
0.07945	0.04229	212	−303	−91	−590	−420
0.08932	0.04709	237	−367	−130	−1052	−460
0.09937	0.05274	274	−444	−170	−1206	−496
0.14936	0.07913	450	−752	−302	−1390	−589

tion, occurring at a lower surfactant concentration because of the presence of the added electrolyte. According to the observations of Quirion and Desnoyers [23], the dependence on counterion concentration could also be explained by a change in the counterion binding involved in the transition.

Enthalpy changes for the micellisation process

The complexity of the system under investigation and the multiple equilibria involved, enable the phase transition model [12] to be used for extracting the thermodynamic parameters of the micellisation process. Moreover, the low cmc values justify this choice; in fact it has been shown [24] that changes in thermodynamic properties for a given 1 : 1 ionic surfactant calculated by graphical extrapolation of partial molar quantities to the cmc, agree with changes calculated from the mass-action model.

Using a pseudo-phase-transition model, the enthalpy change for the micellisation process is evaluated from the difference between the two values obtained by extrapolating, at the cmc, the trends of the partial molar enthalpies, above and below the cmc. Table 2 reports the enthalpic parameters thus obtained for the micellisation process in all the conditions under study.

At 0.02 mol kg^{-1} KOH, the ΔH_m value is -1.36 kJ mol^{-1}; for solutions in 0.10 and 0.05 mol kg^{-1} KOH, ΔH_m is not so easily evaluated: if the hypothesis of a second structural transition is assumed, it is not correct to

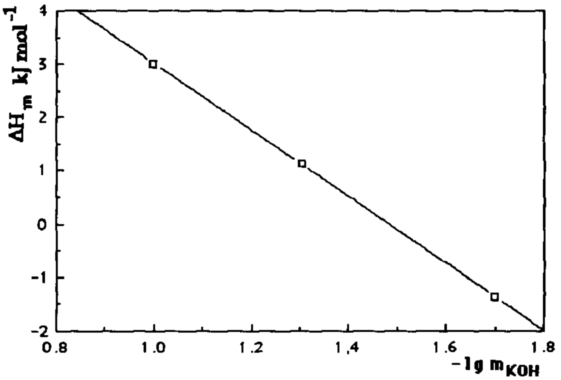


Fig. 3. Enthalpy change for the micellisation process of potassium 4-((hexylcarbonyl)amino)-2-hydroxybenzoate as a function of the logarithm of the KOH concentration.

evaluate ΔH_m from the plateau at high surfactant concentration. If the second transition is overlooked, ΔH_m is positive (3.01 and 1.14 kJ mol^{-1}, respectively).

In any case, for the system under investigation the enthalpy change for the micellisation process is strongly dependent on the hydroxide concentration and, to a first approximation, could be considered linearly dependent on the pH, as shown in Fig. 3.

Adding the electrolyte halves the ΔH_m of the system containing 0.10 mol kg^{-1} KCl and 0.02 mol kg^{-1} KOH compared to the same system without KCl, the resulting enthalpy change being around -0.65 kJ mol^{-1}.

CONCLUSIONS

Enthalpic properties of aqueous solutions of potassium 4-((hexylcarbonyl)amino)-2-hydroxybenzoate are strongly dependent on the pH because the dissociation of the salicylic OH affects the hydrophilic–lipophilic balance of the molecule.

To our knowledge, there are no current literature studies on the effect of pH on the thermodynamic properties of bifunctional weak acid surfactants, nor have models been proposed to predict these trends. Mass-action models [23–30] have been obtained for a 1 : 1 ionic surfactant and the effect of the ionic strength has been considered [28,29]. These models have to be modified to account for the behaviour of a doubly-charged polar head, and the dependence of the degree of dissociation both on the aggregation and on the pH. Nevertheless, the pseudo-phase-transition model does make it possible to obtain the micellisation parameters.

The possibility of demonstrating a structural transition in the micellar system by means of enthalpy measurements is unusual, because, in general, only second-derivative thermodynamic properties, in particular the heat capacities, are able to confirm phase transitions in micellar solutions [3,10,19,23]. It would be very interesting to perform structural studies to better explain the thermodynamic data in terms of microscopic interactions, and to understand the influence of intra- and/or intermolecular hydrogen bonding on the structure.

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