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Comparison of the cosurfactant character of 1-butanol and phenol in sodium dodecylsulfate aqueous solutions from relative enthalpies of dilution at 298.15 K

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Abstract

Heats of dilution of 1-butanol and phenol in aqueous micellar solutions of sodium dodecylsulfate (SDS) have been measured at 298.15 K with a dynamic-flow Picker microcalorimeter and used for determining the relative apparent molar enthalpies of dilution ($L_{\phi,3}$) of solutes. The variation of $L_{\phi,3}$ for both solutes, at low concentrations, as a function of the surfactant concentration provides evidence of a postmicellar transition occurring at 0.2 mol kg^{-1} in SDS solutions. In each micellar domain, at concentrations below and above 0.2 mol kg^{-1}, the limiting apparent molar enthalpies of dilution of the solute (extrapolated to $1/m=0$ from the linear dependence of the inverse of surfactant concentration predicted by the pseudo-phase model), reflect various trends. For 1-butanol, both values are close to one another, whereas for phenol, where the sign of the linear slopes also changes, the limiting values are noticeably different. The latter indicates that a modification of the counterion binding, accompanying the postmicellar transition, occurred. For concentrated solute mixtures at fixed surfactant composition, an analysis of the variation of the abnormal, relative apparent molar enthalpies of dilution of 1-butanol with its unique concentration, shows that 1-butanol is strongly trapped in alcohol aggregates stabilized by the surfactant and, consequently, acts as a good cosurfactant capable of forming microemulsions. Alternatively, although phenol hydrophobicity is similar to that of 1-butanol, owing to its acid character, it is mostly solubilized in the aqueous layer of micelles and does not penetrate deeply towards the micellar interior and, hence, could not be considered as a very efficient cosurfactant. © 1997 Elsevier Science B.V.

Keywords: 1-Butanol; Heat of dilution; Phenol; Postmicellar transition; Pseudo-phase model; Relative apparent molar heat of dilution; Sodium dodecylsulfate

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1. Introduction

The usefulness of microemulsions for the solubilization of organic compounds and their applications in various fields of chemistry, pharmacology and industry, is related to the efficiency of the surfactant–cosurfactant combination. A good cosurfactant, generally assumed to be a short amphiphilic molecule which is able to interact with the surfactant by both hydrophobic and hydrophilic characters leading to mixed micelles, gave more favourable structures for the solubilization of strongly hydrophobic organic solutes [1,2]. Thus, depending on the surfactant, the

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choice of the cosurfactant is of great importance in allowing the formation of a large stable domain of a microemulsion.

As shown previously [3], the investigation of thermodynamic properties is well suited to detect structural changes and to predict the behaviour of surfactant solutions using classical thermodynamic relationships. For several years, we have undertaken thermodynamic studies of ternary systems (water+surfactant+alcohol) [4–6], in order to elucidate the role played by alcohol in micellar structures leading to microemulsions [7,8]. Furthermore, by setting up theoretical models to describe the properties of surfactant solutions [9], we would expect to predict the behaviour of micellar systems and microemulsions with temperature, pressure, and composition.

In the present work, enthalpies of dilution of 1-butanol and phenol in aqueous solutions of sodium dodecylsulfate at 298.15 K are reported. Our actual purpose is first to characterize, through enthalpies, the structural postmicellar transition clearly evidenced with heat capacities [4] and, secondly, to compare the site of solubilization of 1-butanol and phenol in relation with their chemical nature. These solutes have approximately the same hydrophobic character as asserted by their similar solubility (close to 1 m) in water. In addition to a different shape and size, phenol shows a slightly acid character. Large differences have been measured between standard enthalpies of transfer of these two solutes in SDS solutions [10,11]; positive values are observed with 1-butanol (4.8 [10] or 4.6 [11] kJ mol^{-1}), while negative values are obtained for phenol (−0.6 [10] or −6.4 [11] kJ mol^{-1}), showing the different interactions involved by phenol due to the presence of the aromatic group and the ionic character of the polar group. However, some discrepancy exists with regard to the values of the enthalpies of transfer of phenol from water to surfactant solutions because, as mentioned by Bury and Treiner [10], the deviations mainly result from the difficulty of extrapolating the property of the solute at infinite dilution in micellar phase. In spite of this uncertainty, the two solutes behave differently and these authors have suggested that the specific comportment of the aromatic compound compared to the linear alcohol is related to the presence of the benzene ring, but they also suggested that no specific interaction between π electrons and ionic head groups occurred. As a consequence, they confirmed the two-state model for solubilization proposed by Mukerjee and Cardinal [12]. The comparison of the enthalpies of transfer of phenol and benzene discussed by Causi et al. [11] led to a divergent conclusion. Nevertheless, various authors have insisted on the significant role of the chemical nature of the solute in the distribution process between aqueous and micellar phases.

Moreover, enthalpies are often recognized as properties more sensitive to ionic interactions than volumes or even heat capacities. They provide some direct information about the energetics of the solubilization of solutes into micelles and, consequently, reveal the cosurfactant ability of the solutes.

2. Experimental

Sodium dodecylsulfate (SDS) was a pure grade reagent (purity 99%) purchased from FLUKA. As only a shallow minimum was observed on the surface tension curve close to the critical micelle concentration (CMC), no further recrystallization was carried out and SDS was simply used after drying under vacuum for at least 48 h at room temperature. On account of their purity (FLUKA, purity 99%), 1-butanol (kept on molecular sieves) and phenol were used as received. All solutions were prepared by weight with deionized and distilled water, degassed prior to use.

Enthalpies of dilution of solutes in water as well as in different solutions of surfactant have been performed with a differential flow microcalorimeter, Picker (SODEV). The principle features and working conditions have been described in the literature [13,14]. However, to ensure liquid flow stability when relatively concentrated solutions were circulating in the calorimetric cells, push-syringe type of pumps (RAZEL A99) equipped with gas-chromatography glass syringes (HAMILTON) were installed to continuously fill solutions into the calorimeter. Previously calibrated by weighing water of well-known density values [15], the volumetric flows selected were converted into mass flows by means of densities determined with a Picker flow densimeter (SODEV) [16]. Further, the number of moles of solute by time unit, and the measured heat power dissipated during the dilution process, allowed the determination of the enthalpies of dilution ΔH_{dil} associated with the dilution between the initial and final concentrations, the latter being calculated from the flow rate.

Experimentally, the enthalpies of dilution of solutes (1-butanol and phenol) were determined by dilution of the ternary, water(1)+SDS(2)+solute(3), with the corresponding binary, water(1)+SDS(2) system, while maintaining the same molar ratio of surfactant relative to water. By changing the flow ratio of the ternary relative to the binary system, series of different enthalpies (ΔH_{dil}) associated with the final concentration of the solute were obtained. Such a procedure was repeated by using different initial concentrations of the solute(3) for a given binary system to ensure a good overlap of the final composition of solute between each experimental set where ΔH_{dil} was measured.

The relative apparent molar enthalpies of dilution of the solute ($L_{\phi,3}$) were calculated using a least-squares analysis of the experimental ΔH_{dil} data, obtained with each of the series of dilution from different initial molalities $m_{3,\mathrm{i}}$, leading to various final molalities $m_{3,\mathrm{f}}$ for solutions of fixed surfactant/water ratio according to the relation:

$$\Delta H(m_{3,\mathrm{i}} \rightarrow m_{3,\mathrm{f}}) = L_\phi(m_{3,\mathrm{i}}) - L_\phi(m_{3,\mathrm{f}})$$

The variation of L_ϕ vs. solute concentration was assumed to be represented by the general MacMillan–Meyer development in series (with molalities for neutral molecules or with the square root of molalities when ionic species are involved). The value at infinite dilution was conventionally equal to zero [17]:

$$L_\phi(m) = \sum_{i=1}^{n} A_i m^i \text{ or } L_\phi(m) = \sum_{i=1}^{n} A_i m^{i/2}$$

In case of associated solutions, it is generally more advantageous to use association models [18], to represent $L_\phi(m)$ accurately, with parameters having a significant physical meaning in spite of the uncertainties of the model approximations. However, for the purpose of relating structural changes of the micellar structure, the less sophisticated pseudo-phase model offers a convenient method of revealing transitions through a simple plot of L_ϕ as a function of $1/m_2$ (the inverse of SDS molality). The model implies a linear dependence while the structure of micelles remains unchanged [19].

3. Results and discussion

The nature and magnitude of the interactions involved between surfactant and cosurfactant are responsible for the localization of the solutes in the micellar aggregates. In the solutes studied, hydrophobic as well as hydrophilic interactions exist. In addition to phenol, the presence of the slightly acid –OH groups gives rise to repulsive electronic interactions with the negatively charged polar heads of SDS. Depending on surfactant concentration, the overall interactions can induce structural changes resulting in specific properties of the medium.

The relative apparent molar enthalpies of dilution of 1-butanol and phenol were determined as a function of the SDS concentration, when the solute was diluted sufficiently to reveal structural changes in the micellar solution, and as a function of the solute concentration for fixed SDS concentrations in order to characterize cosurfactant ability. The different experimental values of enthalpies of dilution of 1-butanol and phenol determined for several compositions of the SDS solutions are given, respectively, in Tables 1 and 2, where initial concentrations of solutes are close to 0.5 mol kg^{-1}, and in Tables 3 and 4 for higher concentrations.

3.1. *Enthalpies of dilution of 'low concentration solutions' of 1-butanol and phenol vs. SDS concentration*

When the solute concentration is kept low (m_3<0.5 m), the thermodynamic properties provide information about the micellar solubilization, reflected from the dependence of the apparent relative molar enthalpies (L_ϕ) on concentration. For different surfactant concentrations, the dilution processes of ternary solutions (water+SDS+solute) with the associated binary solutions (water+SDS) lead to a similar variation of the solute concentration ($m_{3,\mathrm{i}} \rightarrow m_{3,\mathrm{f}}$) giving a set of curves which represents the variations of $L_{\phi,3}$ ($m_{3,\mathrm{f}}$) with m_2 (SDS concentration), where each curve corresponds to a different final concentration ($m_{3,\mathrm{f}}$) of the solute [20].

The variation of $L_{\phi,3}$ for 1-butanol and phenol, shown in Figs. 1 and 2 when the 'pseudo-phase model' representation [19] is applied, is plotted

Table 1
Enthalpies of dilution of butanol for low initial butanol molality (0.5 mol kg^{-1}) in SDS solutions at different concentrations at 25°C

$m_{3,i}$ (mol kg^{-1})	$m_{3,f}$ (mol kg^{-1})	ΔH_{dil} (J mol^{-1})	$m_{3,i}$ (mol kg^{-1})	$m_{3,f}$ (mol kg^{-1})	ΔH_{dil} (J mol^{-1})	$m_{3,i}$ (mol kg^{-1})	$m_{3,f}$ (mol kg^{-1})	ΔH_{dil}/
	$m_2 = 0.04006$			$m_2 = 0.04997$			$m_2 = 0.5992$	
0.4995	0.393	−178	0.5032	0.396	−185	0.5004	0.394	−183
	0.342	−268		0.344	−269		0.342	−264
	0.288	−342		0.293	−346		0.291	−338
	0.239	−411		0.243	−418		0.241	−407
	0.190	−484		0.193	−486		0.192	−473
	0.142	−565		0.143	−555		0.143	−540
	$m_2 = 0.06998$			$m_2 = 0.08547$			$m_2 = 0.1001$	
0.4969	0.391	−179	0.5087	0.400	−176	0.4919	0.387	−164
	0.340	−258		0.348	−255		0.336	−245
	0.289	−332		0.296	−329		0.286	−317
	0.240	−403		0.245	−401		0.237	−383
	0.191	−472		0.195	−470		0.189	−452
	0.142	−543		0.145	−538		0.141	−524
	0.0944	−622					0.0934	−589
	$m_2 = 0.1198$			$m_2 = 0.1600$			$m_2 = 0.2004$	
0.5000	0.393	−165	0.5039	0.396	−152	0.5118	0.402	−156
	0.342	−241		0.344	−229		0.350	−234
	0.291	−314		0.293	−300		0.298	−308
	0.241	−385		0.243	−371		0.247	−378
	0.192	−456		0.193	−444		0.196	−448
	0.143	−529		0.144	−523		0.146	−523
				0.0956	−608		0.0970	−613
	$m_2 = 0.2497$			$m_2 = 0.2999$			$m_2 = 0.3499$	
0.4949	0.389	−152	0.5001	0.393	−137	0.4959	0.390	−145
	0.338	−228		0.342	−213		0.339	−214
	0.288	−298		0.291	−282		0.289	−281
	0.239	−362		0.241	−348		0.239	−347
	0.188	−424		0.192	−416		0.190	−410
	0.141	−490		0.143	−491		0.142	−471
				0.0949	−570		0.0941	−530
	$m_2 = 0.4000$			$m_2 = 0.4492$				
0.4930	0.389	−133	0.4965	0.391	−149			
	0.337	−205		0.339	−218			
	0.287	−274		0.290	−282			
	0.238	−335		0.239	−342			
	0.189	−389		0.190	−399			
	0.141	−444		0.142	−449			
	0.0936	−526		0.0942	−495			

against the inverse of SDS molality in the micellar domain beyond the CMC. Often related to the sphere-to-cylinder transition of micellar shape, the transition occurring at 0.2 m in SDS solutions [4] is clearly observed with both solutes through a variation of the slope between each linear segment characterizing two microstructural domains, domain α (from CMC to 0.2 m) and domain β (beyond 0.2 m). The slopes S in α and β domains are always positive with 1-butanol ($S_\alpha < S_\beta$), whereas for phenol S_α is negative and S_β is positive. The extrapolated limiting values of $L_{\phi,3}$ ($1/m_2 \rightarrow 0$) for the linear segments associated to each domain (L_α and L_β) are representative of the relative molar enthalpy of the solute in the microphase under consideration. The variation of these quantities, L_α and L_β, vs. the solute molality (in the $m_3 < 0.5$ con-

Table 2
Enthalpies of dilution of phenol for low initial phenol molality (0.5 mol kg^{-1}) in SDS solutions at different concentrations at 25°C

$m_{3,i}$ (mol kg^{-1})	$m_{3,f}$ (mol kg^{-1})	ΔH_{dil} (J mol^{-1})	$m_{3,i}$ (mol kg^{-1})	$m_{3,f}$ (mol kg^{-1})	ΔH_{dil} (J mol^{-1})	$m_{3,i}$ (mol kg^{-1})	$m_{3,f}$ (mol kg^{-1})	ΔH_{dil} (J mol^{-1})
	$m_2 = 0.03961$			$m_2 = 0.05979$			$m_2 = 0.07992$	
0.500	0.446	-83.6	0.4916	0.438	-106	0.4985	0.444	-132
	0.393	-169		0.387	-220		0.392	-266
	0.342	-261		0.336	-343		0.341	-412
	0.291	-359		0.286	-481		0.290	-572
	0.241	-463		0.237	-636		0.240	-752
	0.192	-578		0.188	-817		0.191	-955
	0.143	-715		0.140	-1031		0.142	-1191
	0.0949	-896		0.0932	-1285		0.0944	-1480
	0.0475	-1141		0.0465	-1586		0.0472	-1843
	$m_2 = 0.09992$			$m_2 = 0.1541$			$m_2 = 0.2000$	
0.4962	0.442	-136	0.5001	0.445	-138	0.5000	0.445	-154
	0.390	-287		0.393	-307		0.393	-336
	0.339	-450		0.342	-497		0.342	-537
	0.289	-629		0.291	-699		0.291	-751
	0.239	-826		0.241	-914		0.241	-980
	0.190	-1052		0.191	-1149		0.191	-1230
	0.142	-1315		0.143	-1417		0.143	-1513
	0.0940	-1628		0.0947	-1736		0.0947	-1847
	0.0470	-2003						
	$m_2 = 0.2499$			$m_2 = 0.2989$			$m_2 = 0.3493$	
0.5001	0.445	-186	0.5001	0.445	-171	0.5002	0.446	-187
	0.393	-380		0.393	-354		0.393	-386
	0.342	-582		0.291	-753		0.342	-594
	0.291	-787		0.241	-969		0.291	-795
	0.241	-998		0.191	-1197		0.241	-974
	0.191	-1220		0.143	-1435		0.191	-1129
	0.143	-1465		0.0947	-1683		0.143	-1289
	0.0947	-1755					0.0947	-1523
	0.0473	-2115					0.0473	-1950
	$m_2 = 0.3998$			$m_2 = 0.4500$			$m_2 = 0.5000$	
0.4931	0.439	-166	0.5003	0.446	-195	0.4997	0.445	-181
	0.388	-363		0.394	-381		0.393	-341
	0.337	-562		0.342	-570		0.342	-513
	0.287	-747		0.291	-752		0.291	-671
	0.237	-918		0.241	-909		0.241	-793
	0.189	-1087		0.192	-1036		0.192	-892
	0.141	-1280		0.143	-1162		0.143	-1020
	0.0934	-1539		0.0949	-1363		0.0948	-1241
				0.0475	-1777		0.0474	-1576

centration range) is given in Fig. 3(a) for 1-butanol and in Fig. 3(b) for phenol. In the case of 1-butanol, L_α and L_β vary linearly with the concentration m_3, and their values are very close to one another. In contrast, for phenol the curvature of L_β is convex while that of L_α is concave, and the values at a given molality m_3 are quite different.

These results show that the interactions and, consequently, the sites of solubilization of 1-butanol and phenol into micelles are different in the two microstructural domains. In case of 1-butanol, the linear variation of L_α and L_β and their relatively close values suggest that 1-butanol is distributed similarly between aqueous and each micellar microphase. Small varia-

Table 3
Enthalpies of dilution of butanol with higher initial butanol concentrations in different SDS solutions at 25°C

$m_{3,i}$ (mol kg^{-1})	$m_{3,f}$ (mol kg^{-1})	ΔH_{dil} (J mol^{-1})	$m_{3,i}$ (mol kg^{-1})	$m_{3,f}$ (mol kg^{-1})	ΔH_{dil} (J mol^{-1})	$m_{3,i}$ (mol kg^{-1})	$m_{3,f}$ (mol kg^{-1})	ΔH_{dil} (J mol^{-1})
	$m_2 = 0.08510$			$m_2 = 0.08508$			$m_2 = 0.08515$	
0.6982	0.620	−136	1.1805	1.042	−311	1.9969	1.748	−478
	0.546	−266		0.912	−592		1.517	−976
	0.473	−388		0.787	−847		1.298	−1480
	0.402	−500		0.664	−1080		1.088	−1976
	0.332	−605		0.546	−1293		0.887	−2452
	0.263	−702		0.431	−1489		0.695	−2894
	0.195	−795		0.319	−1671			
	0.129	−889		0.210	−1842			
	0.0645	−986		0.104	−1996			
	$m_2 = 0.1500$			$m_2 = 0.1499$			$m_2 = 0.1501$	
0.7051	0.626	−127	1.1960	1.056	−266	2.1950	1.917	−437
	0.551	−249		0.925	−512		1.660	−869
	0.477	−364		0.797	−740		1.417	−1298
	0.405	−471		0.673	−953		1.185	−1721
	0.335	−572		0.553	−1153		0.965	−2139
	0.265	−670		0.436	−1344		0.754	−2552
	0.197	−769		0.323	−1530		0.554	−2959
	0.131	−877		0.213	−1710		0.362	−3356
	0.0651	−997		0.106	−1881		0.178	−3731
	$m_2 = 0.1499$			$m_2 = 0.2999$			$m_2 = 0.2999$	
3.9946	3.416	−349	0.7990	0.710	−123	1.2477	1.104	−221
	2.904	−747		0.625	−245		0.968	−430
	2.435	−1202		0.542	−356		0.836	−624
	2.003	−1668		0.460	−456		0.707	−802
	1.605	−2125		0.380	−554		0.582	−969
	1.237	−2611		0.302	−656		0.460	−1131
	0.896	−3228		0.224	−765		0.341	−1298
	0.578	−4425		0.149	−882		0.225	−1480
	0.281	−5289		0.0741	−1014		0.112	−1989
	$m_2 = 0.3015$			$m_2 = 0.2988$			$m_2 = 0.2999$	
2.0131	1.769	−317	3.5024	3.035	−334	5.9925	5.074	−250
	1.541	−632		2.610	−632		4.277	−525
	1.322	−987		2.213	−987		3.558	−879
	1.112	−1307		1.839	−1307		2.907	−1288
	0.909	−1572		1.488	−1572		2.315	−1709
	0.714	−1833		1.157	−1833		1.773	−2125
	0.527	−2148		0.845	−2148		1.276	−2605
	0.346	−2496		0.549	−2496		0.819	−3350
	0.171	−2712		0.269	−2712		0.397	−4730

tions of the hydrophilic interactions of the –OH group with water, which orients and maintains the polar group in the aqueous micellar layer, are emphasized. As a consequence, the variation of the binding of the micellar counterion accompanying the change of the micellar shape [21,22] at 0.2 m simply influences the linear dependence of L_α and L_β. With phenol, the curved trends of the variation of L_α and L_β should mean that the microphase α tends to be saturated, whereas in the microphase β more phenol could be solubilized by cooperative effects. The acid character of phenol is certainly responsible for the observed differences. On one hand, in domain α, the large values of L_α are due to the ionic repulsions between

Table 4
Enthalpies of dilution of phenol with higher initial phenol concentrations in different SDS solutions at 25°C

$m_{3,i}$ (mol kg^{-1})	$m_{3,f}$ (mol kg^{-1})	ΔH_{dil} (J mol^{-1})	$m_{3,i}$ (mol kg^{-1})	$m_{3,f}$ (mol kg^{-1})	ΔH_{dil} (J mol^{-1})	$m_{3,i}$ (mol kg^{-1})	$m_{3,f}$ (mol kg^{-1})	ΔH_{dil} (J mol^{-1})
	$m_2 = 0.1500$		$m_2 = 0.1500$				$m_2 = 0.1500$	
0.7996	0.753	−75	1.4001	1.316	−62.9	2.4979	2.335	−22.7
	0.710	−145		1.237	−129		2.185	−53.6
	0.668	−235		1.160	−204		2.039	−93.8
	0.625	−315		1.083	−280		1.896	−139
	0.584	−407		1.008	−365		1.757	−187
	0.542	−493		0.939	−454		1.620	−249
	0.501	−496		0.861	−549		1.488	−316
	0.460	−700		0.790	−655		1.358	−393
	0.420	−817		0.719	−766		1.231	−486
	0.380	−943		0.649	−895		1.106	−589
	0.341	−1080		0.580	−1041		0.985	−705
	0.301	−1227		0.512	−1188		0.866	−841
	0.263	−1383		0.445	−1353		0.750	−990
	0.224	−1558		0.379	−1549		0.636	−1182
	0.186	−1748		0.314	−1780		0.310	−2080
	0.148	−1986		0.250	−2025			
	0.111	−2226		0.186	−2382			
	0.074	−2493		0.124	−2790			
				0.0623	−3266			
	$m_2 = 0.1500$		$m_2 = 0.3000$				$m_2 = 0.3000$	
3.9991	3.712	−4.6	0.8482	0.799	−83.2	1.4003	1.316	−91.3
	3.451	−17.6		0.753	−184		1.237	−186
	3.200	−31.4		0.708	−284		1.160	−279
	2.958	−49.9		0.663	−384		1.083	−385
	2.724	−72.8		0.618	−484		1.008	−495
	2.499	−103		0.574	−589		0.934	−613
	2.281	−137		0.531	−721		0.861	−735
	2.071	−181		0.487	−853		0.789	−866
	1.867	−240		0.445	−996		0.718	−1018
	1.670	−315		0.402	−1140		0.649	−1174
	1.479	−398		0.360	−1294		0.580	−1341
	1.295	−481		0.319	−1457		0.512	−1522
	1.116	−591		0.278	−1639		0.445	−1733
	0.942	−725		0.237	−1841		0.379	−1968
	0.298	−2241		0.197	−2060		0.314	−2233
	0.149	−2892		0.157	−2284		0.250	−2533
				0.117	−2520		0.186	−2860
				0.0781	−2746		0.124	−3208
							0.0622	−3690
	$m_2 = 0.3000$		m$_2$ = 0.3000				$m_2 = 0.3000$	
2.5000	2.337	−60.2	3.9991	3.712	−32.9	6.0037	5.088	−39.0
	2.187	−130		3.451	−74.4		4.292	−100
	2.040	−200		3.199	−123		3.573	−187
	1.897	−285		2.957	−172		2.921	−298
	1.757	−367		2.723	−234		2.327	−460
	1.621	−467		2.497	−299		1.783	−682
	1.488	−572		2.280	−377		1.284	−1024
	1.358	−696		2.069	−460		0.824	−1500
	1.231	−830		1.866	−563		0.607	−1979
	1.107	−975		1.669	−676		0.399	−2639
	0.985	−1142		1.478	−804			

Table 4
(Continued)

$m_{3,i}$ (mol kg^{-1})	$m_{3,f}$ (mol kg^{-1})	ΔH_{dil} (J mol^{-1})	$m_{3,i}$ (mol kg^{-1})	$m_{3,f}$ (mol kg^{-1})	ΔH_{dil} (J mol^{-1})	$m_{3,i}$ (mol kg^{-1})	$m_{3,f}$ (mol kg^{-1})	ΔH_{dil} (J mol^{-1})
	0.866	−1313		1.294	−940			
	0.750	−1517		1.115	−1096			
	0.636	−1760		0.941	−1301			
	0.525	−2065		0.773	−1564			
	0.416	−2436		0.452	−2425			
	0.309	−2896		0.298	−2986			
	0.205	−3379						

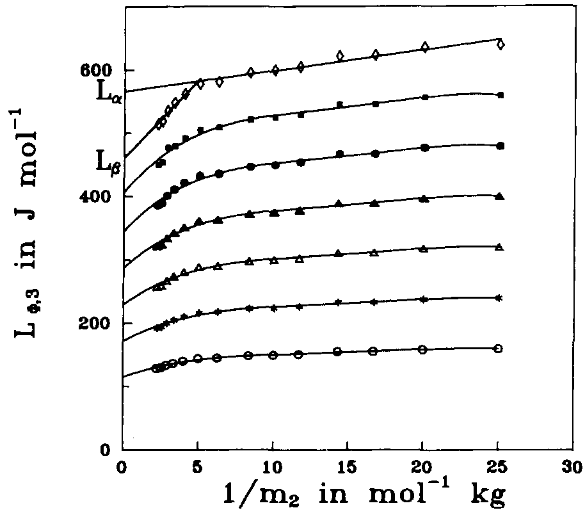

Fig. 1. Relative apparent molar enthalpies of dilution of 1-butanol vs. the inverse of SDS molality at 298.15 K, for different initial concentrations of 1-butanol: (○) – 0.10; (*) – 0.15; (△) – 0.20; (▲) – 0.25; (●) – 0.30; (■) – 0.35; and (◇) – 0.40 m.

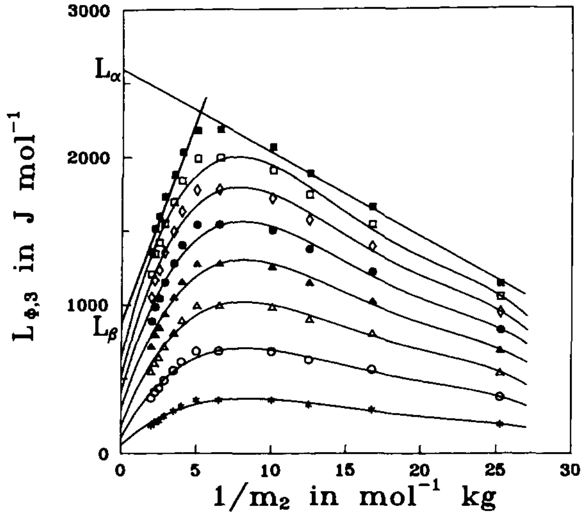

Fig. 2. Relative apparent molar enthalpies of dilution of phenol vs. the inverse of SDS molality at 298.15 K, for different initial concentrations of phenol: (*) – 0.05; (○) – 0.10; (△) – 0.15; (▲) – 0.20; (●) – 0.25; (◇) – 0.30; (□) – 0.35; and (■) – 0.40 m.

phenol and the polar heads of the surfactant molecules, indicating a solubilization of phenol mainly in the polar layer of the micelles. On the other hand, in domain β, where the sphere-to-rod transition is followed by an enhancement of the counterion binding to micelles [21], some ionic repulsive interactions are replaced by more favourable dipole–ion interactions acting cooperatively with stronger aliphatic–aromatic as opposed to aliphatic–aliphatic interactions [10], thereby favouring solubilization of phenol. Besides, a large increase in the solubility of phenol was observed, between 0.15 and 0.2 m, in the concentration range corresponding to the postmicellar transition [20].

3.2. Enthalpies of dilution of 'concentrated' solutions of 1-butanol and phenol in micellar SDS solutions

The calorimetric study of ternary micellar systems, in which the amount of solute may be significant, gives information on the ability of the structures to solubilize large amounts of organic solutes.

3.2.1. Enthalpies of dilution of 1-butanol

Some examples of the variations of $L_{\phi,3}$ as a function of the 1-butanol molality, resulting from the dilution of several initial 1-butanol concentrations ($m_{3,i}$) by the corresponding binary SDS solutions at

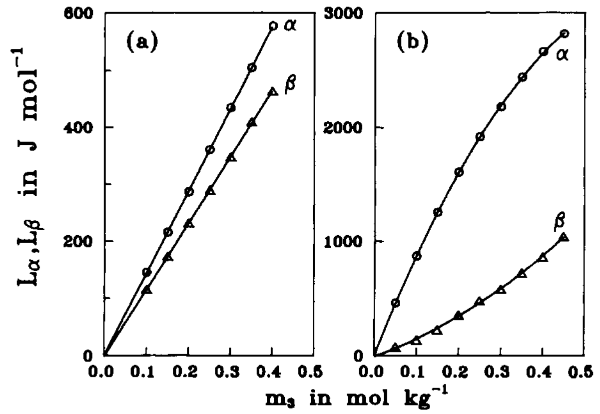

Fig. 3. Variation of the relative molar enthalpies (○) – L_α and (△) – L_β extrapolated for $1/m_2$ tending to zero in the two microphases α and β, as a function of the solute molality. (a) – 1-butanol; and (b) – phenol.

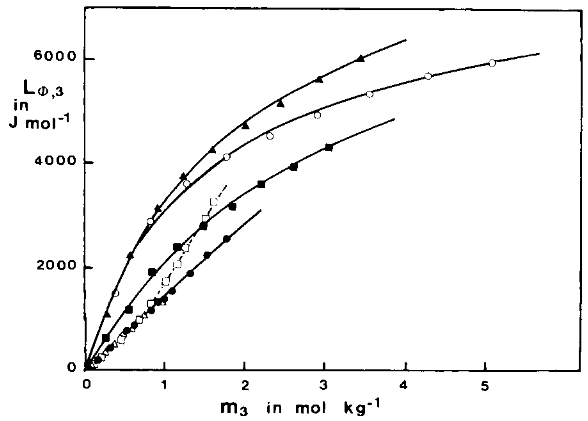

Fig. 4. Variation of the relative apparent molar enthalpies of dilution of solutions of 1-butanol as a function of the 1-butanol molality, in different SDS solutions at given concentrations with different initial molalities of 1-butanol: (△) – $m_2 = 0$, $m_3 = 1$; (□) – $m_2 = 0.085$, $m_3 = 2$; (▲) – $m_2 = 0.15$, $m_3 = 4$; (●) – $m_2 = 0.30$, $m_3 = 2$; (■) – $m_2 = 0.30$, $m_3 = 4$; and (○) – $m_2 = 0.30$, $m_3 = 6$ m.

the following fixed concentrations $m_2 = 0.085$, 0.15 and 0.3 m, are reported in Fig. 4. When $m_3 < 0.5$ m, $L_{\phi,3}$ varied linearly for the different SDS solutions and remained close to the values obtained in pure water. With an increase in the initial 1-butanol content ($m_{3,i} < 2$ m), the different $L_{\phi,3}$ curves diverge, depending on the SDS concentration. Such effects are related to the different interactions of 1-butanol, with both kinds of micelles, in a manner similar to that observed with volumes and heat capacities [4]. In the case of higher 1-butanol concentrations (up to 6 m), the results obtained from ΔH data, corresponding to different dilution experiments ($m_{3,\mathrm{i}} \rightarrow m_{3,\mathrm{f}}$) for a given surfactant composition m_2 cannot be simultaneously treated to lead to a unique $L_{\phi,3}$ ($m_{3,\mathrm{f}}$) curve. This is in contrast to the results obtained for the less concentrated 1-butanol ternary systems. The examples shown in Fig. 4 demonstrate that the different dilution curves do not overlap, and moreover, the deviations of $L_{\phi,3}$ became larger as the initial concentration of 1-butanol increases. For these higher alcohol contents, the mixed micelles formed were transformed into alcohol aggregates stabilized by the surfactant, according to the observed noticeable variations of the apparent (or partial) molar volumes and heat capacities of 1-butanol in these concentration ranges [4]. The observed results mean that the exchange kinetics of 1-butanol between the phases, constituted by the 'swollen core' of micelles and the 'free alcohol' micelles, was too slow to reach a true thermodynamic equilibrium during the residence time (<1 min) of the solutions in the active part of the cells after mixing in the calorimeter. Thus, 1-butanol is strongly trapped in stable aggregates constituting an almost 'pure' organic phase. It is well known that these alcohol microphases, stabilized by surfactants, favour a large solubilization of oils and, as a consequence, 1-butanol is often considered to be, and used as a powerful cosurfactant.

3.2.2. *Enthalpies of dilution of phenol*

In contrast to 1-butanol, for a given SDS solution, even at the highest initial phenol concentration, all dilution experiments can be simultaneously computer-treated to lead to a unique curve $L_{\phi,3}$ (m_3). Fig. 5 illustrates the variation of $L_{\phi,3}$ as a function of the square root of m_3, at two SDS concentrations, corresponding to each previously defined microstructural domain. Even at low phenol concentrations, the curves behave very differently in surfactant solutions compared to pure water. This is mainly a manifestation of the peculiar ionic interactions between phenol and the polar heads of the surfactant, and is confirmed by the almost linear dependence of $L_{\phi,3}$ with the square root of m_3. For higher phenol concentrations, the curves

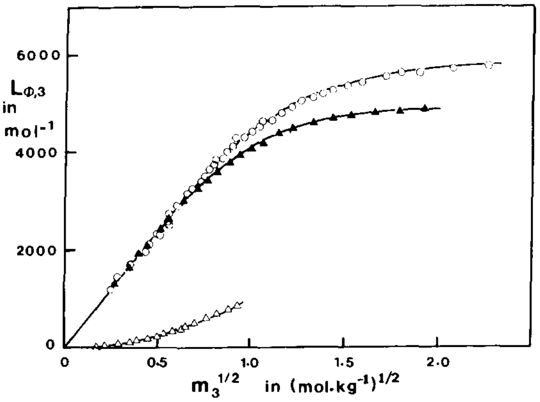

Fig. 5. Variation of the relative apparent molar enthalpies of dilution of concentrated solutions of phenol as a function of the square root of the phenol molality, in different solutions of SDS at given concentrations with different initial molalities of phenol: (△) – $m_2 = 0$; (▲) – $m_2 = 0.15$; (○) – $m_2 = 0.30$ m.

bend and the values of $L_{\phi,3}$ tend towards a plateau. Due to its acid character, phenol remains mainly in the aqueous layer of the micelles, where its ionization is favoured by the electronic field between the ionic head group and the counterion of the surfactant. Furthermore, as the phenol concentration is increased, the water micellar interfaces may be saturated and phenol becomes less dissociated, penetrating deeper into the micellar core as indicated by the plateau. The overlap of the different dilution curves means that the exchange of phenol during the dilution process is fast enough to reach equilibrium during the residence time in the apparatus. As opposed to the case of 1-butanol, the formation of some stable 'phenolic microphases' is not expected and thus phenol cannot behave as a good cosurfactant in systems containing SDS as the surfactant. As a confirmation of this hypothesis, it has been observed that the solubilization of phenol reaches a relatively low saturation limit [20] even in concentrated SDS solutions, whereas the saturation of 1-butanol is considerably enhanced in the same micellar domain [6].

4. Conclusions

Just like heat capacities, apparent molar relative enthalpies of dilution of 1-butanol and phenol, at low concentrations in micellar SDS solutions, show a clearly postmicellar transition around 0.2 mol kg^{-1} owing to the different limiting molar enthalpies of the solutes in each micellar structure. In case of 1-butanol, the difference remains small with the environment surrounding the solute being only slightly modified by the sphere-to-rod transition. In the case of phenol, however, the limiting enthalpy differences reflect the influence of ionic interactions on the solubilization at the micellar interface.

When solutes are in large excess, 1-butanol can penetrate deeply in the micellar core and form alcohol aggregates (swollen micelles), thus being able to facilitate the solubilization of hydrophobic organic solutes, especially when surfactant concentrations are >0.2 m. These latter micellar structures appear more appropriate to enhance microemulsion formation. Phenol, remaining mainly located in the aqueous palisade layer, saturates micelles in spite of the change of structure which favours a large increase of its solubility. Consequently, phenol cannot be considered as an efficient cosurfactant.

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