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Thermodynamic study in aqueous micellar solutions at 298.15 K: comparison of the interactions between ionic surfactants (SDS and CTAB) and 1-alcohols or phenol[☆]

K. Busserolles [*], G. Roux-Desgranges, A.H. Roux

Laboratoire de Thermodynamique et Génie Chimique, URA CNRS 434
Université Blaise Pascal, 63177 Aubière Cedex, France

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Abstract

Densities and heat capacities of the ternary systems water + surfactants (SDS or CTAB) + alcohols (C_4–C_6) or phenol have been measured in the aqueous domain at 298.15 K. Transfer molar volumes and transfer molar heat capacities of alcohols or phenol from water to water + SDS or water + CTAB were deduced therefrom. In both surfactants, the variations of the transfer quantities of alcohols are typical of the partition of an amphiphilic solute between aqueous and micellar phases, depending on its hydrophobicity, and moreover, they reveal postmicellar transitions. In contrast, phenol behaves differently. In SDS solutions, the variations of transfer properties are similar to what is observed with alcohols, but in CTAB solutions, particularly large variations are observed for a phenol/CTAB ratio of between 1 and 2. At the same time, the viscosity of these solutions increases, and viscoelasticity appears. The formation of a strong complex between the positive quaternary ammonium polar heads of the surfactant and phenol resulting from the weak acidic character of phenol, is certainly responsible for the evolution of the transfer properties and for the viscosity of CTAB solutions in the presence of phenol.

Keywords: Butanol; Cetyltrimethylammonium bromide; Gel-like solutions; Hexanol; Pentanol; Phenol; Sodium dodecylsulphate; Surfactants; Transfer molar heat capacities; Transfer molar volumes; Viscoelasticity

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[*] Corresponding author.

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1. Introduction

Aqueous solutions of surfactants are known to form micelles which are able to dissolve hydrophobic molecules. Depending on the surfactant concentration, the aggregation pattern undergoes changes going from spherical micelles to ellipsoidal, rod-like, or even lamellae, structures. Amphiphilic molecules often play the role of co-surfactant. Partitioned between aqueous and micellar phases, they act upon micellar structures and increase considerably the solubilization power for oils [1,2]. In the presence of various solutes, the micellar structural transitions observed with many surfactants in aqueous solutions would lead to viscoelastic properties or to gels ("ringing gels" having highly elastic properties) or even to liquid crystalline phases having optically active properties [3]. With amphiphilic long molecules (long-chain alcohols or hydrosoluble polymers), the viscosity increases progressively with increasing concentration or decreasing temperature. With particular amphiphilic solutes, the viscosity reveals a great sensitivity to a small variation of solute concentration or to a weak temperature change. In this case, strong interactions between the polar head groups of the surfactant and the solute promote the formation of worm-like micelles [4]. A large number of industrial processes exploit this ability: oil recovery, lubricants, paints and varnish, cosmetics, pharmaceutical preparations, etc.

In previous works concerning anionic surfactant solutions [5–7], attention was specially focused on structural transitions and on the co-surfactant role of alchohols. The study of some thermodynamic properties, like volumes and mainly heat capacities, proved to be a good way to investigate such complex systems. The present objective is to evidence, by similar techniques, the more complex role of specific interactions between solute and surfactant leading to gel formation.

To study the specificity of interactions with a particular amphiphilic molecule like phenol, the comparison between two classes of ionic surfactants has been investigated. An anionic surfactant, sodium dodecylsulphate (SDS), and a cationic one, cetyltrimethylammonium bromide (CTAB), have been selected as reference surfactants. They have been previously investigated extensively by various techniques [4,8]; furthermore they have a similar aggregation number. In order to refer to specific interactions in comparison to simple hydrophobic effects, 1-alcohols (C4, C5 and C6) have also been studied. Phenol and 1-butanol which have a similar hydrophilic character as asserted by their solubility in water (close to 1 mol kg^{-1}) are suitable for this comparative study [9].

2. Experimental

2.1. Materials

Sodium dodecylsulphate (purity > 99% +) was purchased from Merck; cetyltrimethylammonium bromide (purum) and 1-alcohols (puriss) were from Fluka; and phenol (99%) was from Aldrich. Due to their stated purity, all compounds were used without further purification. All solutions were prepared by mass with deionized, filtered and freshly degassed water.

2.2. Instruments

The volumic masses (ρ) of solutions were measured at low flow rate with a Picker vibrating-tube densimeter type 03D [10]. The volumic heat capacities (ρc_p) were determined using a Picker flow differential micro calorimeter [11]. The working operations, calibrations and precisions obtained have been previously reported [7]. Microcomputers were used on-line for collection and treatment of the data. The densities and the volumic heat capacities of the solutions were obtained relative to water for the binary systems and to the related binaries for the ternary mixtures. All measurements were made at 298.15 K.

2.3. Thermodynamic properties

The apparent molar properties ($Y_{\Phi,3}$) of a solute (3) were calculated from ρ and c_p values using the classical formulae [7].

The transfer molar properties of the solute (3) from water to the micellar solutions (1 + 2) are very convenient to investigate in order to evaluate the interactions between the solute and the surfactant because the solute concentration m_3 is kept at the same low value in both binary (1 + 3) and ternary (1 + 2 + 3) systems.

The transfer property $\Delta Y_3(H_2O \rightarrow H_2O + \text{Surf.})$ is then related to the apparent quantities by the following relation

$$\Delta Y_3(H_2O \rightarrow H_2O + \text{Surf.}) = Y_{\Phi,3}(H_2O + \text{Surf.}) - Y_{\Phi,3}(H_2O)$$

The solute concentrations were 0.05 *m* with butanol, pentanol and phenol, and 0.04 *m* with hexanol, respectively.

3. Results and discussion

3.1. Anionic surfactant (SDS)

In Figs. 1 and 2, respectively, volumes and heat capacities of transfer of phenol from water to water + SDS, plotted versus the surfactant concentration, are compared to those previously obtained with 1-alcohols [7]. For both properties, the magnitude of the transfer values of phenol is less important than for 1-butanol which has a similar hydrophobicity. ΔV_3 increases rapidly after the CMC (8×10^{-3} *m*) and then levels off. The variation in ΔC_3 appears more complex and presents close similarities for all solutes. A sharp decrease follows immediately after the CMC, and a maximum appears between 0.2 and 0.3 *m*, depending on the solute. This maximum is related to a change in the micellar aggregation as previously evidenced from heat capacity measurements on binary systems and on ternary mixtures containing alcohols [5–7]. This has to be attributed to the rather complex shift of the equilibrium between the two micellar

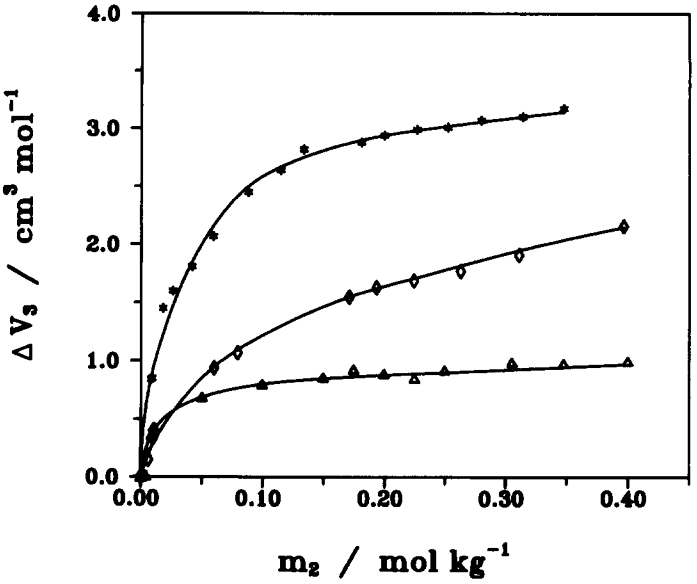

Fig. 1. Transfer molar volumes of solutes from water to water + SDS solutions at 298.15 K, as a function of the concentration of SDS: △, phenol; ◇, butanol (Ref. [7]); *, pentanol (Ref. [7]).

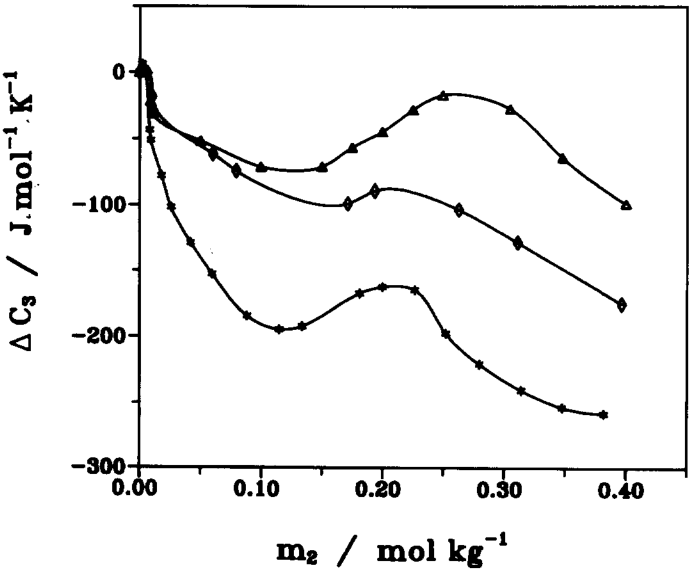

Fig. 2. Transfer molar heat capacities of solutes from water to water+SDS solutions at 298.15 K, as a function of the concentration of SDS: △, phenol; ◇, butanol (Ref. [7]); *, pentanol (Ref. [7]).

structures due to the temperature change and the presence of the solute. This effect is similar to what is observed close to the CMC of the surfactant when a solute is added, a phenomenon for which a theoretical approach has been developed by Hetu et al. [12]. Except for phenol, the greater effect is observed with the more hydrophobic alcohol due to a larger solubilization into the micellar phase [7].

In the case of phenol, the effect is less important due to the weak acidic character of the molecule, the electrostatic negative charge on the oxygen atom being of the same sign as that of the anionic head group of the surfactant, repulsive interactions occur which reduce the partition of phenol toward the micellar phase. These electrostatic interactions have been associated with the relatively large heats of dilution of phenol in SDS aqueous solutions obtained by Khadir et al. [9].

3.2 Cationic surfactant (CTAB)

The transfer volumes of 1-alcohols, given in Fig. 3 as a function of the CTAB concentration, behave similarly to what was observed with SDS: a rapid increase follows the CMC ($8.5 \times 10^{-4}\, m$) and then the curves level off. A large ΔV_3 is also observed, larger with the more hydrophobic alcohols. With phenol (Fig. 3), ΔV_3 behaves quite differently: a slight positive maximum is observed at low concentration, followed by a smooth decrease toward negative values beyond 0.05 *m*. This different shape reflects strong interactions occurring between CTAB and phenol.

The heat capacities of transfer of alcohols, represented in Fig. 4, are a little different in the case of CTAB as compared to SDS. With 1-butanol, the variation is

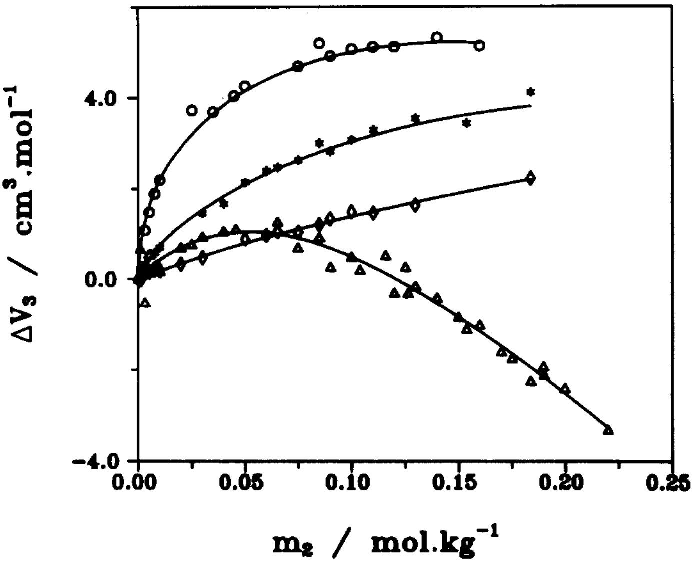

Fig. 3. Transfer molar volumes of solutes from water to water + CTAB solutions at 298.15 K, as a function of the concentration of CTAB: ◇, butanol; *, pentanol; ○, hexanol; △, phenol.

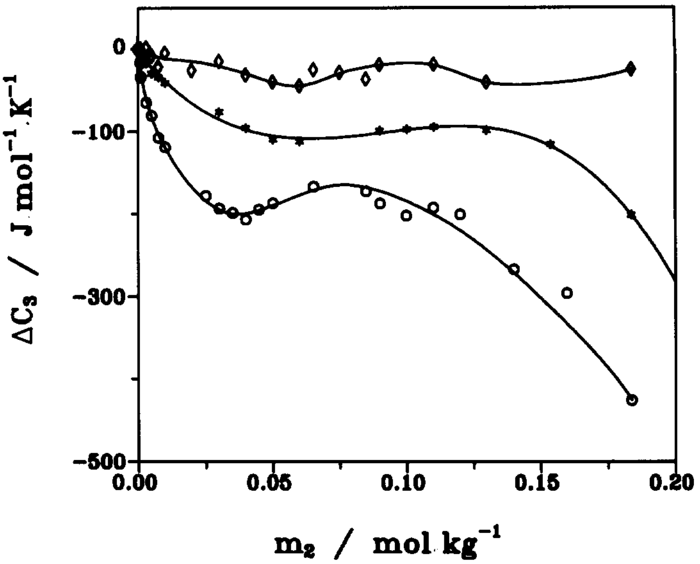

Fig. 4. Transfer molar heat capacities of solutes from water to water+CTAB solutions at 298.15 K, as a function of the concentration of CTAB: ◇,butanol; *, pentanol; ○, hexanol.

almost linear, whereas with 1-pentanol, ΔC_3, which initially decreases, remains almost constant up to 0.15 *m* in CTAB and then decreases slowly for higher concentrations. Our results in the domain between 0.05 and 0.15 *m* depart from those obtained by De Lisi et al. [13]. These authors observed a minimum following by a broad maximum, the larger deviation from our values being about 40 $J\,K^{-1}\,mol^{-1}$. These differences are probably due to an increase in the viscosity of the solutions which alters the flow rate, thus affecting the experimental measurements. With 1-hexanol, beyond the CMC, ΔC_3 shows a marked decrease which precedes a pronounced maximum before the large decrease observed at higher concentrations. Similar to what is observed in SDS solutions, the present maximum is presumably related to a change in the micellar organization. The sphere-to-rod micellar transition has been shown to exist; nevertheless, Backlund et al. [14] have indicated that the transition concentration at 298.15 K in binary solution may be found over a large range of concentration, from 0.21 to 0.45 *m*, depending on the measurement techniques used. De Lisi et al. [13] have even mentioned the existence of two micellar transitions respectively at 0.13 and 0.25 *m*. With hexanol, the sphere-to-rod transition leads to a less pronounced maximum of transfer heat capacity as with the corresponding transition in SDS solutions [7]. At $m_{\mathrm{CTAB}} > 0.05$ *m*, Vikholm et al. [15] have shown that a narrow maximum of viscosity occurs for a 1-hexanol/CTAB ratio of between 1 and 2, the amplitude of the maximum largely depending on the CTAB concentration. In fact, in the presence of many other solutes [16], CTAB solutions become viscous and gel-like, with a marked dependence on temperature.

The transfer heat capacities of phenol, shown in Fig. 5, present a particular evolution. In dilute CTAB solutions, ΔC_3 is almost identical to ΔC_3 of pentanol; beyond

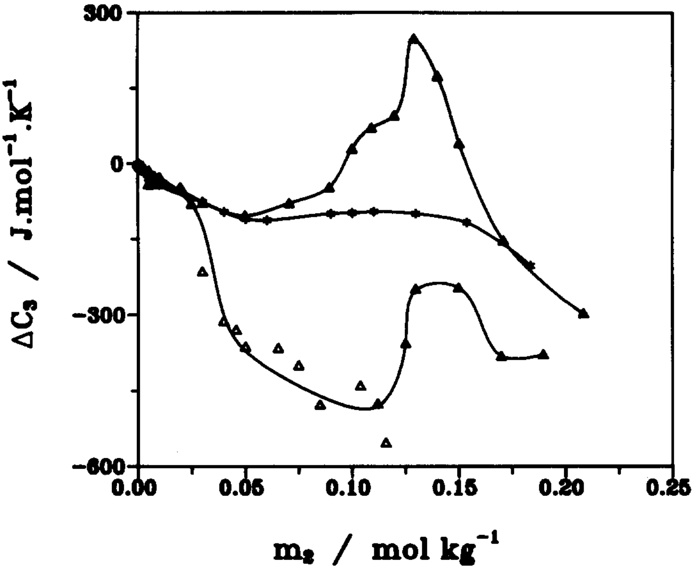

Fig. 5. Transfer molar heat capacities of solutes from water to water+CTAB solutions at 298.15 K, as a function of the concentration of CTAB: △, phenol; *, pentanol; ▲, benzene (Ref. [17]).

0.02 *m* a marked decrease occurs which levels off; then a broad maximum appears between 0.1 and 0.15 *m*. This maximum should be related to the post-micellar transition mentioned before. The ΔC_3 value of phenol at 0.1 *m* is close to $-500\,\mathrm{J\,K^{-1}\,mol^{-1}}$ with CTAB and is only $-80\,\mathrm{J\,K^{-1}\,mol^{-1}}$ with SDS. This unexpected large difference in the transfer heat capacities of phenol confirms the selective interaction between CTAB and phenol which has been suggested from the analysis of transfer volumes. When $m_{\mathrm{CTAB}} > 0.02\,m$, phenol tends to be partitioned more favourably toward the micellar phase. As with 1-hexanol, large viscosity starts to increase rapidly with CTAB concentration up to 0.05 *m*; between 0.05 and 0.1 *m*, solutions present viscoelastic properties, and in the domain where ΔC_3 is maximum, solutions are gel-like. The apparent maximum in viscosity, corresponding approximately to a phenol/CTAB ratio of 1, coincides with the maximum observed in the case of transfer volumes (Fig. 3). The formation of a phenol/CTAB complex is assumed to be responsible for the change in the molecular arrangement; rod-like micelles are formed, and on becoming longer and more flexible, they lead to worm-like micelles. When the phenol/CTAB ratio is sufficient, the increase in the surfactant concentration favours the formation of such micelles which get entangled with each other to reduce intermicellar creeping, yielding stable gels.

The specific interactions responsible for the formation of the above molecular aggregation should be found in the following hypotheses:

(i) An amphiphilic molecule shields the polar head groups of the surfactant at the micellar interface which diminishes the repulsive interactions between charged heads. But if a large increase in viscosity appears with 1-hexanol [15], the less hydrophobic phenol would behave as 1-butanol for which gel formation was not observed with CTAB micelles.

(ii) Specific interactions exist between the quaternary ammonium cation and the π-electrons of the aromatic ring of phenol. The transfer volumes and transfer heat capacities of benzene, from water to micellar CTAB solutions, have been determined by Quirion and Desnoyers [17]. With respect to volumes, benzene has the typical behaviour of a simple hydrophobic molecule. As shown in Fig. 5, the trends of the ΔC_3 variation of benzene are less typical: a sharp peak is observed near 0.13 m revealing the previously noticed post-micellar transition. But, in contrast to phenol, no large decrease in ΔC_3 and no high viscosity or viscoelasticity are observed in the domain before the maximum.

(iii) A specific complex is formed at the micellar interface due to the strong electrostatic interactions between the cationic head groups of surfactant and the phenoxide ions resulting in the weak acidic character of phenol, as suggested by Treiner et al. [18] to explain the large negative values of the enthalpy of transfer of phenol in CTAB solutions. This strong interaction leads to the formation of a 1:1 complex between phenol and CTAB; the repulsive interactions between polar head groups are then decreased, which favours the stability and furthermore the elongation of micelles. The decrease in the superficial charges on the worm-like micelles also reduces the repulsive interactions between micelles and the entanglement of micelles is more easily realized, promoting gel formation.

References

[1] A.H Roux, G. Roux-Desgranges, J.-P.E. Grolier and A. Viallard, J. Colloid Interface Sci., 84 (1981) 250.

[2] G. Roux-Desgranges, A.H. Roux, J-P.E. Grolier and A. Viallard, J. Colloid Interface Sci., 84 (1981) 536.

[3] H. Hoffman and W. Ulbricht, J. Colloid Interface Sci., 129 (1989) 388.

[4] R. Zana, in D.N. Rubingh and P.M. Holland (Eds.), Cationic Surfactants, Dekker, New York, 1991, p. 41.

[5] G. Roux-Desgranges, A.H. Roux, J-P.E. Grolier and A. Viallard, J. Solution Chem., 11 (1982) 357.

[6] V. Majer, G. Roux-Desgranges, A.H. Roux and A. Viallard, Can. J. Chem., 87 (1983) 1397.

[7] G. Roux-Desgranges, A.H. Roux and A. Viallard, J. Chim. Phys., 82 (1985) 441.

[8] J.E. Desnoyers, G. Perron and A.H. Roux, in R. Zana (Ed.), Surfactant Solutions: New Methods of Investigation, Dekker, New York, 1987, p. 1.

[9] A. Khadir, C. Aucouturier, K. Busserolles, G. Roux-Desgranges and A.H. Roux, Cal. Anal. Therm., 23 (1992) 79.

[10] P. Picker, E. Tremblay and C. Jolicoeur, J. Solution Chem., 3 (1974) 377.

[11] P. Picker, P.A. Leduc, P.R. Philip and J.E. Desnoyers, J. Chem. Thermodyn., 3 (1971) 631.

[12] D. Hetu, A.H. Roux and J.E. Desnoyers, J. Solution Chem., 16 (1987) 529; J. Colloid Interface Sci., 122 (1988) 418.

[13] R. De Lisi, S. Milioto and R. Triolo, J. Solution Chem., 17 (1988) 673.

[14] S. Backlund, H. Høiland, O.J. Kvammen and E. Ljosland, Acta Chem. Scand., A36 (1982) 698.

[15] I. Vikholm, G. Douhéret, S. Backlund and H. Høiland, J. Colloid Interface Sci., 116 (1987) 582.

[16] T. Wolff and K.J. Kerperin, J. Colloid Interface Sci., 157 (1993) 185.

[17] F. Quirion and J.E. Desnoyers, J. Colloid Interface Sci., 112 (1986) 565.

[18] C. Treiner, A.K. Chappopadhyay and R. Bury, J. Colloid Interface Sci., 104 (1985) 569.