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SOLUBILIZATION OF BUTANOL/PENTANOL/HEXANOL IN DODECYLPYRIDINIUM CHLORIDE
Estimation of thermal parameters

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The specific conductivities of dodecylpyridinium chloride have been determinated in water-butanol/pentanol/hexanol solutions in the temperature range of 10 to 35°C, and butanol, pentanol and hexanol concentrations up to 0.05 mol kg^{-1}.

From these data the temperature dependence of the critical micelle concentration, (cmc), was determined. The molar fraction of alcohol in the micelle was estimated using the theory suggested by Motomura *et al.* for surfactant binary mixtures. The standard Gibbs free energy of solubilization of alcohols in the micelles was worked out using the phase separation model.

Keywords: *conductivity, critical micelle concentration, dodecylpyridinium chloride, standard Gibbs free energy, temperature dependence*

Introduction

Surfactants are molecular structures with amphilic behaviour. These kinds of molecules have been recently studied by several techniques [1–3]. The nature of surfactants molecules is responsible for their tendency to form aggregates or micelles.

A micelle can be considered as a little drop inside of which some organic substances can be easily solubilizated [4–5].

The phenomena make it possible to be called solubilization, and the organic material is the solubilizate [6].

Of course, the solubilization phenomena is not only for insoluble materials, but also for little soluble ones, but their solubility grows largely in presence of micelles. The monomeric material hardly produces some effect upon solubility. In consequence, the solubilization is a good method for estimation of critical micelle concentration (cmc) of the surfactant.

A very interesting case of solubilization system are the microemulsions, they are made up by water, surfactant, cosurfactant (alcohol) and oil. These four components behave as an only one phase system, stable and transparent (slightly translucid). Microemulsions have a great interest in researching activities due to applications as a tertiary oil recovery [7]. In this case, the alcohols play a very important role because viscosity decreases in their presence [8] growing down the adsorption of surfactants materials in the porosity of the rocks, in consequence the efficiency of the process grows and the cost decreases.

All these facts explain the importance of the comprehension of the mechanisms of the alcohol effect in the micellar system process and why they are present in most of current researches [7]. Studies on the effect of alcohols on micellar properties of surfactants were initiated by Ward in 1940 [9], who found that the critical micelle concentration, (cmc), of SDS passes through a minimum on the addition of ethanol. Papers on related phenomena, which appeared during the following decade, were review by Herzfeld [10]. Extensive studies on the effect of the linear alcohols (ethanol to hexanol) on the cmc, micellar molecular weight and ionization degree of the micelles of homologous alkyltrimethylammonium bromides were reported by Zana *et al.* [11–15].

In a previous paper [16] we reported the behaviour of dodecyldimethylbenzylammonium bromide in water-butanol and water-benzyl alcohol solutions. In the present work we studied another surfactant, dodecylpyridinium chloride (C12PCl) in presence of water-butanol, water-pentanol and water-hexanol system. C12PCl was already studied in aqueous solutions by our group [17].

Experimental

C12PCl was provided by Merck with a purity of 95% and was used without further purification. This salt is

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monohydrated, according with potentiometric and thermogravimetric analysis [17]. Butanol (BuOH), pentanol (PeOH) and hexanol (HexOH) were provided by Merck (assay>99%). All solutions are prepared by mass using distilled water with conductivity below 3 μS cm^{-1} at 25°C. The concentrations are expressed in molalities.

The conductivity measurements were made with a Wheatstone bridge conductometer (CM-177 Kyoto Electronics) and a cell (type K-121 Kyoto Electronics). The cell constant was determined by calibration with several different concentration of KCl solution using the procedure suggested by Monk [18]. All measurements were carried out in a thermostat bath (Polyscience 9010) maintaining the temperature constant within ±0.05°C.

Results and discussion

C12PCl+water+butanol system

We have selected six concentrations of butanol in water, 0.05, 0.097, 0.151, 0.205, 0.249 and 0.310 M. The measurements are made in a temperature range of 10 to 35°C at 5°C intervals.

In Fig. 1, we show the plots of specific conductivity *vs.* molality. In order to favour the visualization only three concentrations and one temperature have been used.

In this figure, breaks in the specific conductivity *vs.* molality plots can be observed, these breaks are generally attributed to the beginning of formation of micelles, i.e., to critical micelle concentration, cmc. In order to estimate the values of critical micelle molality, we fit these fragments, above and below the breaks, with a linear function each one. Solving the two obtained equation systems, the values of cmc were found. Ionization degree, β, has been calculated as the ratio of the slopes of the two straight lines.

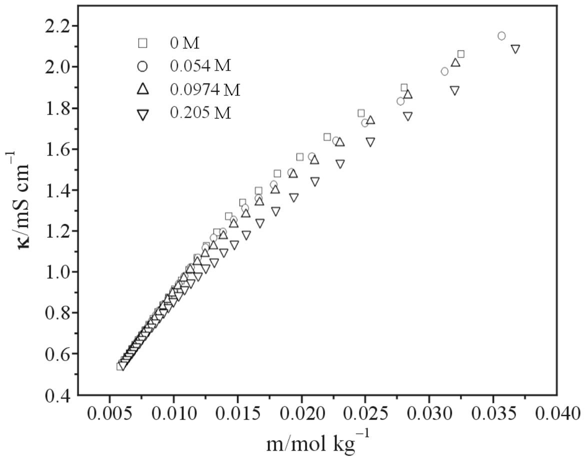

Fig. 1 Specific conductivity *vs.*C12PCl molality at different butanol concentration

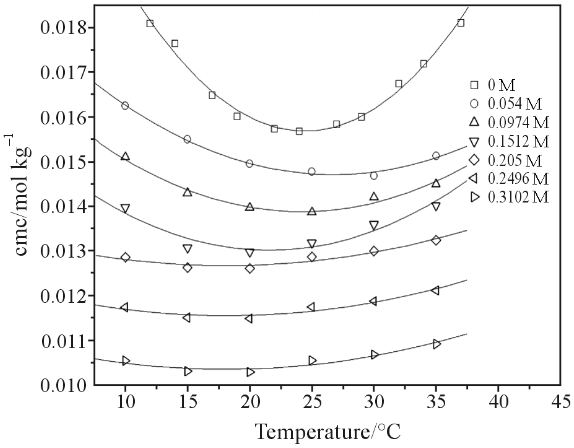

Fig. 2 Influence of temperature and molality of BuOH on cmc values

Upon increasing the molality of the alcohol in the aqueous system, the slopes of conductivity *vs.* molality plots in the premicellar concentration range gradually decrease. On the other hand, the corresponding slopes in the postmicellar range strongly increase.

The first of these facts is due to the increase of the viscosity of the solvent, so the mobility of the ions of the surfactant goes down. In the postmicellar region the increase of the slopes is originated by the ionization degree grows [19, 20].

The results of the cmc as a temperature function are shown in Fig. 2 for all concentrations.

We can observe that cmc decreases when butanol concentration grows. The plot of cmc of the system *vs.* temperature keeps the typical U-shaped observed in aqueous solution system. The highest concentration of alcohol corresponds to the flattest plot of cmc *vs.* temperature. Besides, the minimum of the curve does not seem be seriously affected by the presence of alcohol, as Castedo *et al.* [21] reported.

As far as β is concerned, its behaviour is in the same way as in aqueous solutions, i.e., growing with temperature. In addition, β grows with butanol concentration as we said before. This behaviour is well known in other cationic surfactants as tetradecyltrimethylammonium bromide [22] and tetradecyldimethylbenzylammonium chloride [23].

These effects can be seen in Fig. 3, where β *vs. T* for several concentrations of butanol are plotted.

Motomura model [24, 25] is used, in order to obtain relevant information about the distribution of alcohols between aqueous and micellar phases. The model can be utilized in our system if we consider the alcohol as a cosurfactant.

Molar fraction of alcohol into the micelle as a function of concentration of alcohol in the solution can be calculated by the expression [21].

$$X_2^{\mathrm{M}}=\frac{\left\{\alpha_1\left[\frac{1}{m_1}-\frac{\alpha_1}{\mu}\right]\left(\frac{\partial m_1}{\partial m_2}\right)_{\mathrm{T,P}}-\frac{\alpha_1\alpha_2}{\mu}\right\}}{\frac{\alpha_2-\alpha_1}{\mu}\left[\alpha_2-\alpha_1\left(\frac{\partial m_1}{\partial m_2}\right)_{\mathrm{T,P}}\right]+\frac{\alpha_1}{m_1}\left(\frac{\partial m_1}{\partial m_2}\right)_{\mathrm{T,P}}-\frac{\alpha_2}{m_2}} \qquad (1)$$

where the subscripts 1 and 2 are referred to the surfactant and alcohol respectively, m_1 is the molality of surfactant in the cmc, m_2 is the molality of alcohol in the solution, α_i are the number of ions dissociated of the component i, then $\alpha_1=2$ and $\alpha_2=1$, finally $\mu=\alpha_1 m_1+\alpha_2 m_2+(1000/M_w)$ [21], where M_w is the molecular mass of the water.

The results for the C12PCl+water+butanol system are shown in Table 1.

The present system behaves in a consonant way with the behaviour of tetradecyltrimethylammonium bromides found by Mosquera *et al.* [26].

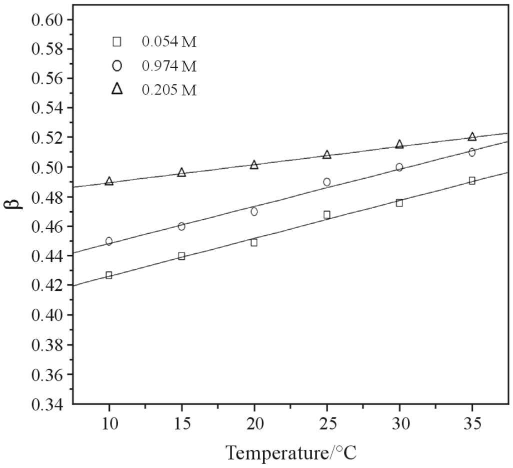

Fig. 3 Dependence of ionization degree, β, of the micelles on the temperature at different butanol molalities

Once the molar fraction of alcohol into the micelle was determined, the standard Gibbs free energy of solubilization can be obtained by:

$$\Delta G_s^0=-RT\ln\frac{X_2^{\mathrm{M}}}{X_2} \qquad (2)$$

The obtained results are shown in Fig. 4. The plots show a decrease of the standard Gibbs free energy of solubilization with increase in temperature and indicate, as pointed out by Shinoda [19], that solubilization is favoured at higher temperatures due to increase of thermal agitation which gives rise to more space available for the solubilization of alcohols in the interior of the micelles. On the other hand, the results reveal an increase of the amount of alcohol acts against the process of solubilization.

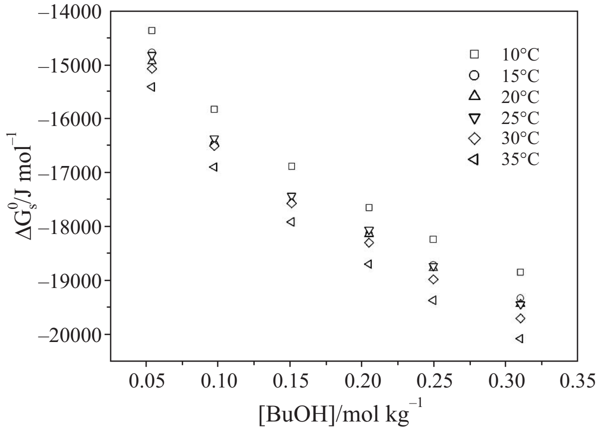

Fig. 4 Standard Gibbs free energy of solubilization *vs.* butanol molality plots

C12PCl+water+pentanol system

Five solutions of pentanol in water were prepared 0.021, 0.035, 0.047, 0.065 and 0.080 M. The measurements were made in a range of temperatures of 10 to 35°C at 5°C.

Table 1 Butanol molality dependence of X_2^{M} for C12PCl–BuOH system

[BuOH]/mol kg^{-1}	X_2^{M}					
	10°C	15°C	20°C	25°C	30°C	35°C
0	–	–	–	–	–	–
0.054	0.131	0.145	0.124	0.105	0.105	0.112
0.097	0.226	0.249	0.214	0.184	0.179	0.191
0.151	0.329	0.360	0.312	0.270	0.261	0.275
0.205	0.419	0.441	0.388	0.339	0.334	0.353
0.249	0.491	0.514	0.459	0.406	0.400	0.420
0.310	0.571	0.594	0.541	0.486	0.480	0.500

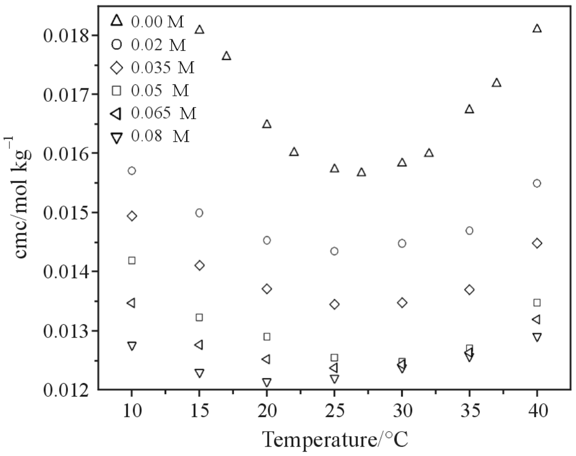

Fig. 5 Dependence of cmc on the temperature and pentanol molality

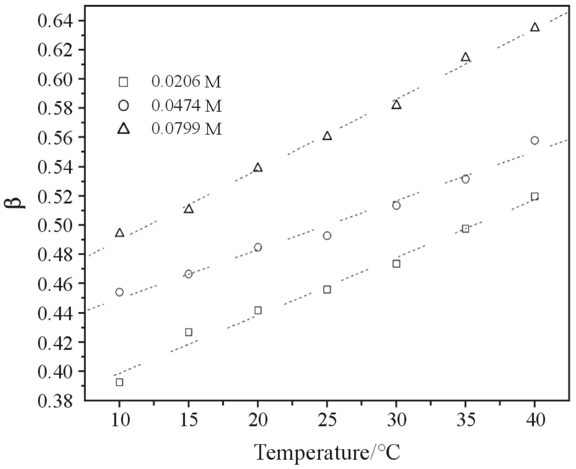

Fig. 6 Ionization degree of the micelle, β, in function of temperature for the C12PCl–PeOH system

In Fig. 5 the curve of cmc *vs.* temperature for the whole range of concentration of pentanol is shown. In Fig. 6 we represent the ionization degree *vs.* temperature and in Fig. 7 the standard Gibbs free energy *vs.* temperature is plotted.

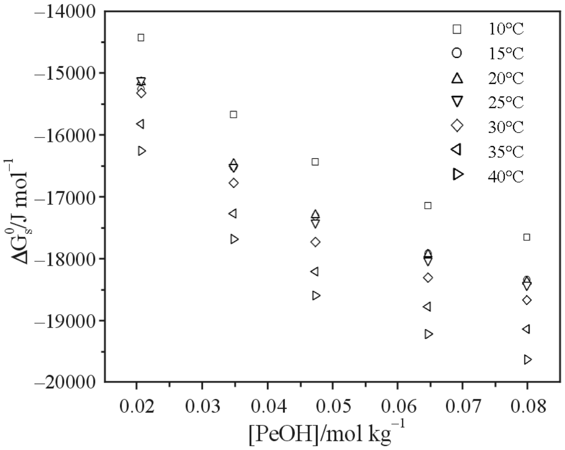

Fig. 7 Standard Gibbs free energy of solubilization *vs.* pentanol molality plots

C12PCl+water+hexanol system

The studied concentrations of hexanol in water were 0.013, 0.017, 0.020, 0.035 and 0.049 M, for the range of temperatures of 10 to 40°C at 5°C

The results for cmc and ionization degree show a similar behaviour as pentanol and butanol cases.

The variation of standard free energy of solubilization can see in Table 2.

Conclusions

The three alcohol+water+surfactant systems which have been studied have a common behaviour, whose characteristics are exposed below:

- The critical micelle concentration, cmc, has an U-shaped dependence with temperature, in the whole range of studied concentration. This feature is regular in systems with surfactants in solution. It is due to the competition effect between the thermal agitation, avoiding the micellization process and the re-structuring of the water molecules.
- The minimum of the curve between cmc *vs.* temperature hardly depends on the length of the alcohol's chain.

Table 2 Standard Gibbs free energy of solubilization at different temperatures and alcohol molalities for C12PCl–HexOH system

[HexOH]/mol kg^{-1}	ΔG_s^0/J mol^{-1}						
	10°C	15°C	20°C	25°C	30°C	35°C	40°C
0	–	–	–	–	–	–	–
0.013	–14880	–15630	–15550	–15520	–15730	–16110	–16600
0.017	–15540	–16310	–16280	–16280	–16500	–16860	–17310
0.020	–16100	–16910	–16930	–16970	–17180	–17500	–17920
0.035	–17210	–17960	–18010	–18050	–18270	–18580	–18990
0.049	–17880	–18580	–18650	–18660	–18880	–19180	–19590

- The cmc abruptly decreases when alcohol is added. This fact is a very common behaviour in surfactant+ alcohol system. It can be explained for the affinity of hydrocarbon chain for non-polar medium.
- The effect of the length of the chain of alcohol is clearly appreciated; the cmc decreases when the length of the chain increases, because the hydrophobicity of alcohol grows.
- The ionization degree increases with temperature in a quasi-linear way for the three alcohols in the whole range of studied concentrations. The origin of this fact is the increase of the thermal agitation, which produces an enlargement in the polar head area.
- It is not so clear that molar fraction of alcohol in the micelle depends on temperature, at least in the uncertainty of experimental data.
- The proportion of alcohol/surfactant into the micelles increases with the length of the chain of alcohol, because the hydrophobicity of it grows with hydrocarbon chain, so the molecules of alcohol tend to gather in a non-polar region.

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