

## **THE SOLUBILIZATION OF ALCOHOLS IN MICELLAR SOLUTIONS**

### **Estimation of thermal parameters**

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### **Abstract**

The specific conductivities of dodecyldimethylbenzylammonium bromide (C12BBr) have been determined in aqueous butanol and aqueous benzyl alcohol solutions in the temperature range of 5–40°C. From these data the temperature dependent 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 thermal properties such as standard Gibbs free energy, enthalpy and entropy of solubilization of alcohols in the micelles were estimated for the phase separation model. The change in heat capacity upon solubilization of alcohol in the micelle has been estimated from the above properties.

**Keywords:** conductivity, critical micelle concentration, dodecyldimethylbenzylammonium bromide, enthalpy, entropy and standard Gibbs free energy, heat capacity, temperature dependence

### **Introduction**

The addition of alcohols to aqueous surfactant solutions can significantly influence the phase behaviour of the systems. Alcohols play an important role as a cosurfactant in the formation of microemulsions, which have been used in ternary oil recovery [1]. The effect of alcohols on micellar properties of surfactant systems have been reviewed recently by Zana [2]. A monography devoted to such systems was edited by Christian and Scamehorn [3]. In particular, the effect of alcohols on the micellar properties of aqueous solutions of alkyltrimethylammonium bromides have been studied by Zana and co-workers [4–6], Attwood *et al.* [7] and Del Castillo *et al.* [8].

In previous papers we have reported the temperature dependence of critical micelle concentration, *cmc*, and of some thermodynamic properties associated with the process of micellization such as changes in apparent molar volumes for a series of homologous alkyldimethylbenzylammonium chlorides and bromides [9–13].

The aim of this work is to study the thermal parameters related to the solubilization of alcohols into the micelles. For this purpose we measured the conductivity of

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dodecyldimethylbenzylammonium bromide in the water–butanol and water–benzyl alcohol solutions at various temperatures. Butanol was chosen as representative of the mean alkyl chain length alcohol and benzyl alcohol because of its structural correspondence with the head group of the studied surfactant. The partition coefficient of the alcohols between the micelle and the bulk aqueous phase was estimated from the thermodynamic model of mixed surfactants developed by Motomura [14]. The thermal parameters such as standard Gibbs free energy, enthalpy, entropy and heat capacity associated with the process of solubilization were estimated.

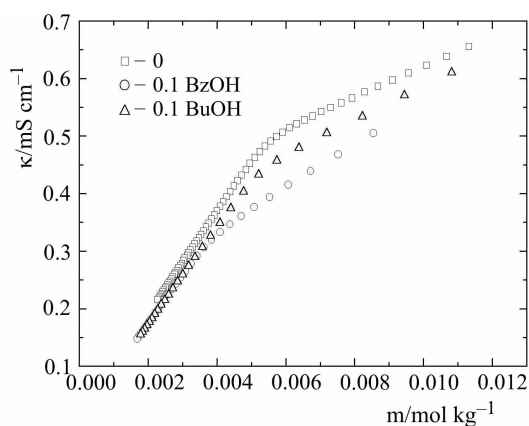
## Experimental

C12BBr was provided by Fluka with a purity of 99% and was used without further purification. This salt is monohydrated according to previous analysis [15]. Butanol (BuOH), and benzyl alcohol, (BzOH), were from Merck (assay>99.5%) and Fluka (assay>99%) respectively. All solutions were prepared by mass using distilled water with a conductivity below  $3 \mu\text{S cm}^{-1}$  at 25°C. The concentrations are expressed in molalities.

The conductivity measurements were made with a Wheatstone bridge conductometer (CM-177 Kyoto Electronics) and cell (type K-121 Kyoto Electronics). The cell constant was determined by calibration with several different concentrations of KCl solution using the procedure suggested by Monk [16]. All measurements were carried out in a thermostat bath (Polyscience 9010) maintaining the temperature constant to within  $\pm 0.05^\circ\text{C}$ .

## Results and discussion

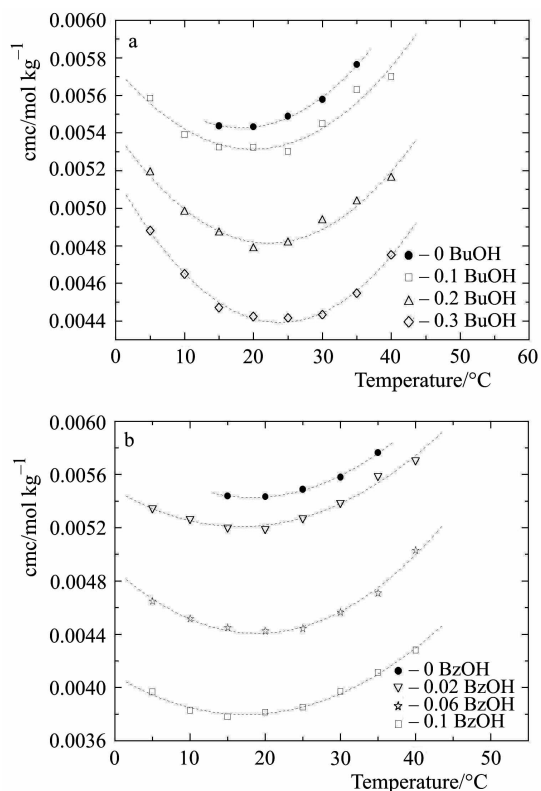
The *cmc* values and the degree of ionization of the micelles,  $\beta$ , were estimated from the molality dependence of specific conductivity at different temperatures and alcohol concentrations. Figure 1 exemplifies the typical behavior of the conductivity vs. molality for C12BBr in water, water–butanol, and water–benzyl alcohol at 0.1 mol kg<sup>-1</sup> of alcohol and 25°C.



**Fig. 1** Specific conductivity vs. molality of C12BBr at 25°C in water and 0.1 BuOH and BzOH concentration

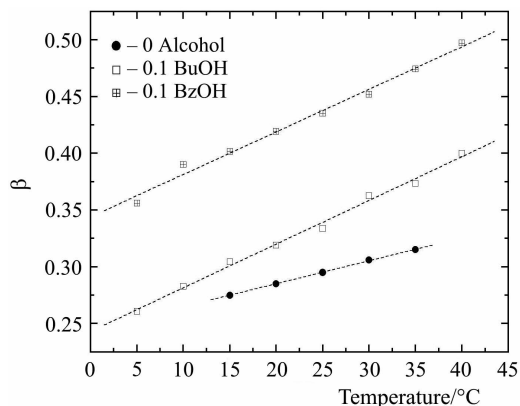
Fitting the two linear fragments, the intercept of both is assumed to be the *cmc* and the ratio of the slopes above and below the critical point is the ionization degree of the micelle. In Fig. 2 we represent the temperature dependence of *cmc* for C12BBr–BuOH (a) and C12BBr–BzOH (b) at different alcohol molalities.

Figures 2a and 2b show a typical U-shaped dependence of *cmc* on temperature and the expected decrease in the *cmc* as the amount of alcohol increases. Being the *cmc* the intersection point of two straight lines, the transmitted error to the intersection point of the two fitted slopes and intercepts errors, can be taken as the uncertainty of the so determined value. The relative errors obtained for the *cmc* oscillates at different temperatures and alcohol concentrations between 1 and 2% for butanol and between 2 and 4% for benzyl alcohol. This higher observed error for the last case may be probably due to its tendency to stacking [17].



**Fig. 2** Temperature dependence of *cmc* of a – C12BBr–BuOH and b – C12BBr–BzOH

A linear temperature dependence of the ionization degree of the micelles in the C12BBr–BuOH and C12BBr–BzOH systems was found as exemplified in Fig. 3 for both systems at 0.1 mol kg<sup>-1</sup>. From the increase of the slope of  $\beta$  against alcohol concentration it is concluded that the space between the ionogenic group increases as a consequence of the solubilization of alcohol by the micelle. This phenomena is more



**Fig. 3** Ionization degree of the micelles  $\beta$ , in function of temperature for the C12BBR–BuOH and C12BBR–BzOH at 0.1 mol kg<sup>-1</sup> systems

relevant for the benzyl alcohol. This fact suggest that the benzylic group of the alcohol interacts with the corresponding head group of the surfactant, increasing the area per molecule at the interface and shifting counter-ions out of the micelle. The relative error of  $\beta$ , obtained as the addition of the relative errors in the slopes of the two linear segments of the conductivity vs. surfactant molality plots, oscillates between 1 and 2% irrespective of the alcohol.

Using the procedure developed by Castedo *et al.* [18] we can obtain the molar fraction of alcohol in the micellar phase by applying the following equation

$$X_2^M = \frac{\left\{ \alpha_1 \left[ \frac{1}{m_1} - \frac{\alpha_1}{\mu} \right] \left( \frac{\partial m_1}{\partial m_2} \right)_{TP} - \frac{\alpha_1 \alpha_2}{\mu} \right\}}{\left\{ \frac{\alpha_2 - \alpha_1}{\mu} \left[ \alpha_2 + \alpha_1 \left( \frac{\partial m_1}{\partial m_2} \right)_{TP} \right] + \frac{\alpha_1}{m_1} \left( \frac{\partial m_1}{\partial m_2} \right)_{TP} - \frac{\alpha_2}{m_2} \right\}} \quad (1)$$

where  $\alpha_i$  ( $i=1, 2$ ) is the dissociation number of the surfactant in the theory of Motomura (in the actual application  $\alpha_1=2$  and  $\alpha_2=1$  for the ionic 1:1 surfactant and alcohol respectively),  $m_1$  and  $m_2$  are the molalities of the surfactant and alcohol correspondingly, and  $\mu = \alpha_1 m_1 + \alpha_2 m_2 + (1000/M_w)$ ,  $M_w$  being the molecular mass of water [18].

Thus calculated values of the molar fraction of alcohol in the micelle  $X_2^M$  are presented in Table 1. An estimation of the error associated to this magnitude can be obtained by calculating the difference between its value for the *cmc* and its value for the *cmc* increased in the corresponding quota of error. Relative errors so calculated for  $X_2^M$  are around 1% for both butylic and benzylic alcohols.

**Table 1** Molar fraction of alcohol in the micelle for different amounts of alcohol in the systems C12BBR–BuOH and C12BBR–BzOH at different temperatures

$T/^\circ\text{C}$	BuOH/mol kg <sup>-1</sup>		
	0.1	0.2	0.3
	$X_\alpha^M$		
5	0.074	0.206	0.355
10	0.083	0.230	0.392
15	0.092	0.250	0.421
20	0.099	0.266	0.442
25	0.105	0.278	0.455
30	0.110	0.284	0.461
35	0.113	0.286	0.460
40	0.115	0.284	0.453

$T/^\circ\text{C}$	BzOH/mol kg <sup>-1</sup>		
	0.02	0.06	0.1
	$X_\alpha^M$		
5	0.105	0.320	0.519
10	0.110	0.324	0.512
15	0.113	0.326	0.506
20	0.114	0.326	0.502
25	0.113	0.324	0.499
30	0.110	0.320	0.498
35	0.105	0.315	0.499
40	0.099	0.308	0.501

To obtain more information about the stability of our system when the alcohol is solubilized into the micelle we can estimate the standard free energy of solubilization,  $\Delta G_s^0$ , from the relation [18]

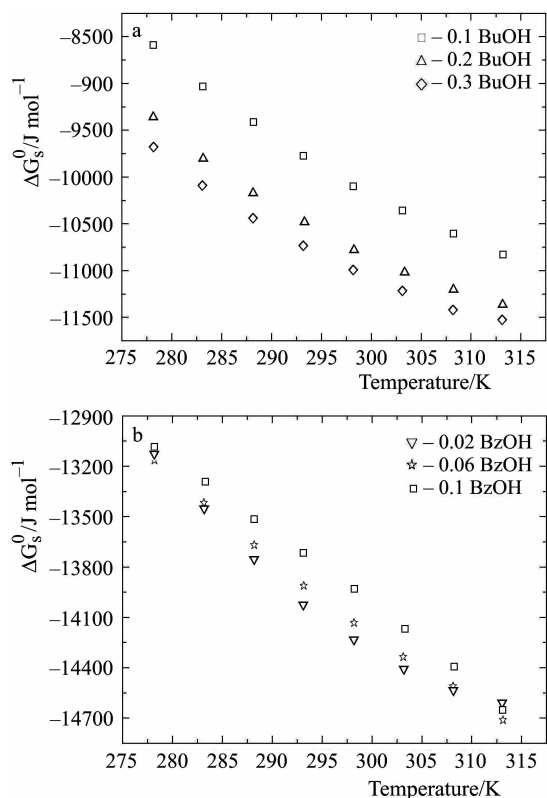
$$\Delta G_s^0 = -RT \ln \frac{X_2^M}{X_2} \quad (2)$$

where  $X_2$  is the molar fraction of alcohol in the aqueous phase.

In Fig. 4 we represent the temperature dependence of for  $\Delta G_s^0$  C12BBR–BuOH (a) and C12BBR–BzOH (b) systems.

The values of  $\Delta G_s^0$  decrease with temperature and show weak dependence on alcohol concentration. Castedo *et al.* [18] studied the tetradecyltrimethylammonium bromide–BuOH system and reported lower values of  $\Delta G_s^0$  and a negligible dependence on alcohol concentration.

Plots show a decrease of  $\Delta G_s^0$  when temperature is increased, as pointed out by Castedo *et al.* [18]. Solubilization is favoured at higher temperatures due to the increase of thermal agitation, which rises to more space available for the solubilization of alcohol in the core of the micelles. The hydrophobicity of BzOH appears to be comparable to that of pentanol [17].



**Fig. 4** Temperature dependence of  $\Delta G_s^0$  for a – C12BBR–BuOH and b – C12BBR–BzOH

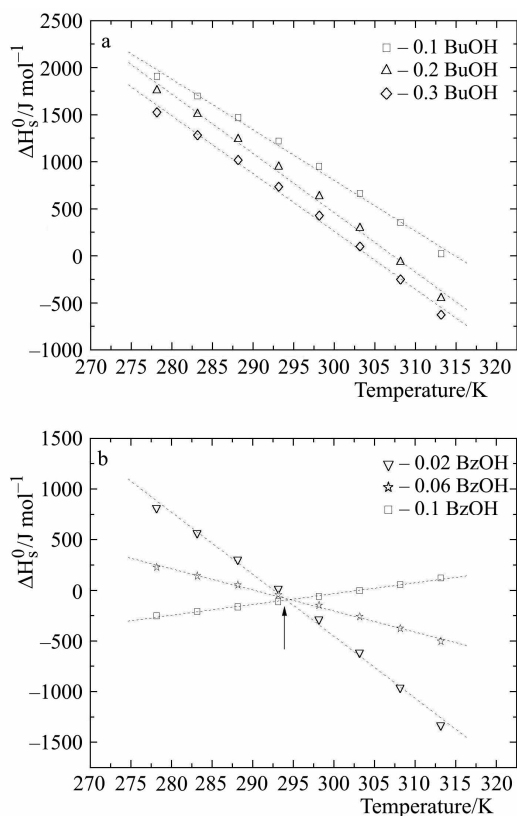
The  $\Delta G_s^0$  values are more negative for BzOH than for BuOH. From the energetic point of view, this result indicates that solubilization is reached more easily with the BzOH. Previous results on interactions of BuOH with surfactants suggest that the alcohol goes to the palisade zone inside the micelle, meanwhile the BzOH probably interacts at the interface of the micelle. A phenomenon of stacking appears between the head group of the surfactant and the phenyl group of the BzOH.

We can estimate the  $\Delta H_s^0$  and the  $\Delta S_s^0$  from the following equations

$$\Delta H_s^0 = RT^2 \frac{\partial \ln(X_2^M/X_2)}{\partial T} \quad (3)$$

$$\Delta S_s^0 = \frac{\Delta H_s^0 - \Delta G_s^0}{T} \quad (4)$$

The results for  $\Delta H_s^0$  are shown in Fig. 5 for C12BBR–BuOH (a) and C12BBR–BzOH (b).



**Fig. 5** Temperature dependence of  $\Delta H_s^0$  for a – C12BBR–BuOH and b – C12BBR–BzOH

Figure 5a shows a linear decrease of  $\Delta H_s^0$  with growth of temperature at the studied concentrations of BuOH. With the increase in concentration of BuOH  $\Delta H_s^0$  decreases and becomes negative at the high temperature range studied. Figure 5b illustrates the changes in the enthalpy of solubilization of BzOH in function of temperature and concentration of the alcohol. The slopes of the  $\Delta H_s^0$  vs.  $T$  plots change progressively with concentration of BzOH. At the highest concentration of BzOH the slope is positive. It is worth noting that the three plots intersect at a critical temperature of 294 K when  $\Delta H_s^0$  is zero for the three systems studied. The change in the sign of the slope at the high concentration of BzOH may be related to the formation of clusters of alcohol molecules of BzOH in the aqueous phase as suggested earlier on the basis of results of studies of the tetradecyltrimethylammonium bromide–BzOH and tetradecyldimethylbenzylammonium chloride–BzOH systems [17].

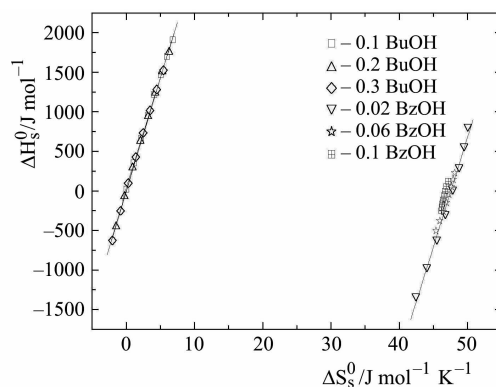
From the data of  $\Delta H_s^0$  we can estimate the change in heat capacity associated with the process of solubilization of the alcohol into the micelle using the equation

$$\Delta C_{Ps}^0 = \left( \frac{\partial \Delta H_s^0}{\partial T} \right)_p \quad (5)$$

The results obtained for the C12BBr–BuOH system are  $-53.8$ ,  $-63.0$  and  $-61.4 \text{ J mol}^{-1} \text{ K}^{-1}$  at  $0.1$ ,  $0.2$  and  $0.3 \text{ mol kg}^{-1}$  BuOH concentration respectively. For the C12BBr–BzOH system the results are  $-61.2$ ,  $-20.8$  and  $10.7 \text{ J mol}^{-1} \text{ K}^{-1}$  at  $0.02$ ,  $0.06$  and  $0.1 \text{ mol kg}^{-1}$  BzOH concentration, respectively.

In the calculation of the previous related thermodynamical quantities, only measured values of  $T$ ,  $X_2$ , and  $X_2^M$  appears. If we note that the experimental errors of the two first are obviously much less than the corresponding error of the third, only the error of  $\ln X_2^M$  must be taken into account significantly in order to estimate the errors in the thermodynamical magnitudes. If we note that the absolute value of  $\ln X_2^M \sim 2$ , the relative error of Gibbs free energy as well as enthalpy and heat capacity of solubilization are approximately half of the corresponding to  $X_2^M$ , that is,  $0.5\%$ . The entropy of solubilization accumulates the errors of both magnitudes, enthalpy and Gibbs free energy of solubilization.

The enthalpy–entropy compensation phenomenon [19–20] associated with the process of solubilization of the alcohol into the micelle is shown in Fig. 6.



**Fig. 6** Enthalpy-entropy compensation plots for C12BBr–BuOH and C12BBr–BzOH

The figure exhibits the classical linear relation for the enthalpy–entropy compensation and reveals that the effect does not depend on the concentration of alcohol in the system. Fitting the values we obtain the temperature of compensation which amounts to  $284 \pm 6$  and  $267 \pm 11 \text{ K}$  for the C12BBr–BuOH and C12BBr–BzOH systems, respectively [21].

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