Journal of Thermal Analysis and Calorimetry, Vol. 70 (2002) 229–234

THERMAL PARAMETERS ASSOCIATED TO MICELLIZATION OF DODECYLPYRIDINIUM BROMIDE AND CHLORIDE IN AQUEOUS SOLUTION

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Abstract

Electrical conductivity of aqueous solutions of dodecylpyridinium chloride and bromide have been determined. From these data the critical micelle concentration *(cmc*) was determined. The thermal properties as standard Gibbs free energy, enthalpy and entropy of micellization was estimated from a uncharged-phase separation model and enables to obtain another properties like heat capacity of micellization and the relevant parameters in the minimum of temperature dependence of *cmc*. The enthalpy-entropy compensation was shown for the studied compounds.

Keywords: conductivity, critical micelle concentration, dodecylpyridinium chloride and bromide, enthalpy, entropy and standard Gibbs free energy, temperature dependence

Introduction

Surfactants are molecular structures with amphiphilic behaviour. For this reason they can form structures called micelles over certain concentration range. The micelles are thermodynamically stables and reversibles. The knowledge of the thermodynamic parameters related to the processes of self-association of surfactants has been largely studied for the last 25 years [1]. These studies were made taking into account the alkyl chain length [2, 3] and the nature of the head group [4, 5].

Calorimetric techniques or analysis of temperature dependence of the thermodynamic parameters are suitable for clarifying the mechanism of the micellization process. We have carried out a thermodynamic study about alkylpyrininium halides. In this paper we present the results for two surfactants with the same chain length but with different counterion: dodecylpyridinium chloride (C12PyCl) and bromide (C12PyBr). Critical micelle concentrations (*cmc*) were obtained by conductivity measurements at several temperatures. Enthalpy, entropy and standard Gibbs free energy and heat capacity were estimated from the temperature dependence of cmc ap-

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1418–2874/2002/ $ 5.00

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Kluwer Academic Publishers, Dordrecht

plying the pseudo-phase separation model [6]. In addition, we report the existence of enthalpy-entropy compensation in both surfactants.

Experimental

C12PyCl was provided Merck with a purity of ≈95% and was used without further purification. This salt is monohydrated, according with potentiometric and thermogravimetric analysis. C12PyBr kindly donated by Czapkiewicz from the Jagiellonian University in Cracow, was synthesized following the next procedure: To a mixture of dodecyl bromide and pyridine, prepared in a 1:1.1 mol ratio, an equal volume of ethanol was added. The solution was then heated to boil and, while hot, the container was stoppered and transferred to an oven thermostated at 80±1°C. The reaction mixture was kept at that temperature for 3 days. Ethanol was then removed under vacuum in a rotary evaporator. An amount of butanone-2 was subsequently added to the oily material and evaporated under vacuum to remove traces of ethanol. The residue was then dissolved in acetone and the solution was kept overnight in the fridge. The copious and well-developed crystals were filtered off and recrystallized twice from acetone. Results of potentiometric and thermogravimetric analysis indicated that the air-dried crystals existed as a monohydrate.

All solutions were prepared by weigh using distilled water, with conductivity below 3 μS cm^{-1} at 25°C. The concentrations are expressed in molality.

The cductivity measurements were made with a Wheatstone bridge conductometer (CM-177 Kyoto Electronics and cell type K-212 Kyoto electronics). The cell constant was determined by calibration with several different concentrations of KCl solution, which conductance is very well known, using the procedure suggested by Monk [7]. All measurements were carried out in a thermostat bath (Polyscience 9010) maintaining the temperature constant to within ±0.05°C.

Results and discussion

From conductivity measurements *vs*. molality we study the isotherms in the range of 10 to 40°C for C12PyCl and from 15 to 40°C for C12PyBr. Conductivity *vs*. molality plots of C12PyBr and C12PyCl at 25°C are shown in Fig. 1.

At each temperature, from the two linear fragments in the conductivity *vs.* molality plots we can obtain the critical micelle concentration taken as the intersection of the apparently straight lines.

In Fig. 2 we show the dependence of the *cmc* with temperature for C12PyBr and C12PyCl.

The temperature dependence of *cmc* reveals a typical U-shaped curve. The results of *cmc* are in good agreement with the data published for other authors [8–12]. In order to obtain the thermal information of the micellization process we must apply the uncharged-phase separation model [6] extracting information from the *cmc*. According to this model, the micelle is treated as a separate phase and the *cmc* as a saturation concen-

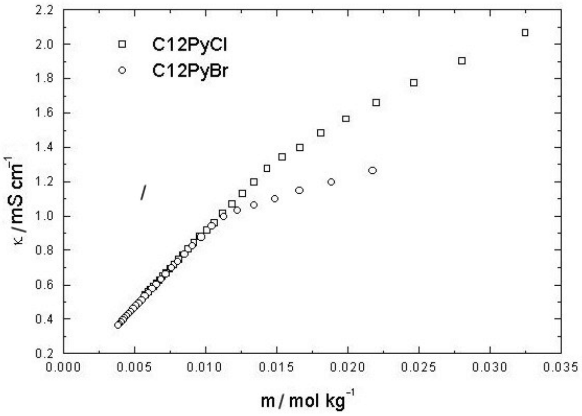

Fig. 1 Specific conductivity *vs*. molality of C12PyCl and C12PyBr at 25°C

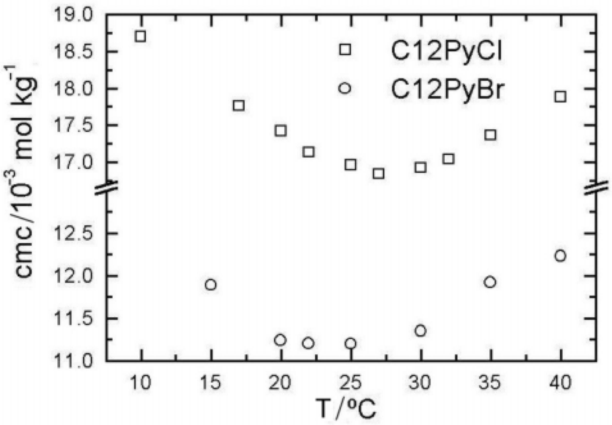

Fig. 2 Temperature dependence of *cmc* of C12PyCl and C12PyBr

tration which, if exceeded leads to the production of a new phase. It should be noted, however, that the micellar phase comprises both the poly-ion and the counterions in the diffuse double layer, so the micelar phase, defined in this way, has zero net charge. In this case, the standard free energy of micellization, ΔG_m^0 is given by:

$$\Delta G_m^0 = RT \ln x_{cmc} \tag{1}$$

where x_{cmc} is the *cmc* of the surfactant expressed in mole fraction. From the temperature dependence of *cmc* of surfactants it can be estimate the enthalpy, ΔH_m^0 and entropy, ΔS_m^0, of micellization as well as the difference in heat capacities, ΔC_{Pm}^0, of the surfactants in the monomeric and micellar forms. They can be extracted from the following relations:

$$\Delta H^0_{\mathrm{m}} = -RT^2 \left[\frac{\partial \ln x_{\mathrm{cmc}}}{\partial T}\right]_{\mathrm{P}} \tag{2}$$

$$\Delta S^0_{\mathrm{m}} = \frac{\Delta H^0_{\mathrm{m}} - \Delta G^0_{\mathrm{m}}}{T} \tag{3}$$

$$\Delta C^0_{\mathrm{Pm}} = \left[\frac{\partial \Delta H^0_{\mathrm{m}}}{\partial T}\right]_{\mathrm{P}} \tag{4}$$

The $\ln x_{\mathrm{cmc}}$ was fitted to a second order polynomial curve in order to use the Eqs (1)–(4). The temperature dependence of ΔG^0_{m}, ΔH^0_{m}, and $T\Delta S^0_{\mathrm{m}}$ for C12PyCl and C12PyBr are shown in Figs 3 and 4 respectively.

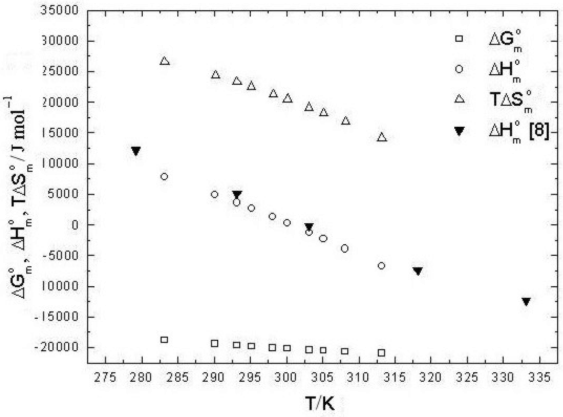

Fig. 3 Temperature dependence of ΔG^0_{m}, ΔH^0_{m} and $T\Delta S^0_{\mathrm{m}}$ for C12PyCl and data extracted from reference [8]

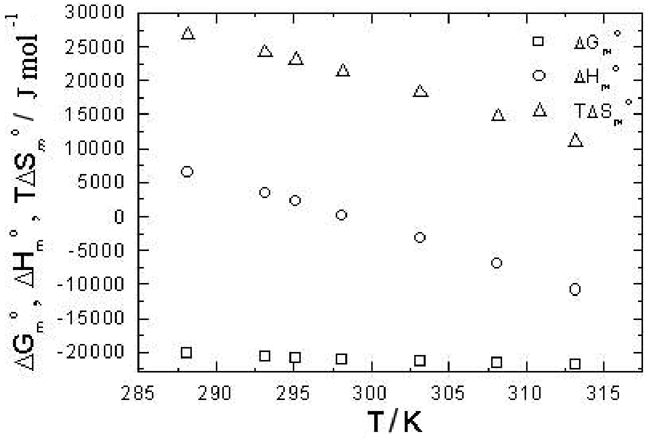

Fig. 4 Temperature dependence of ΔG^0_{m}, ΔH^0_{m} and $T\Delta S^0_{\mathrm{m}}$ for C12PyBr

The results are in good agreement with the data obtained with calorimetric technique by Mehrian *et al.* [8]; these data were inserted in Fig. 3. The most relevant quality of the enthalpy of micellization is its strong dependence with temperature. The heat capacity associated to the process of micellization, ΔC^0_{Pm}, was estimated form the temperature dependence of enthalpy of micellization. The result for C12PyCl was –58.52 J mol^{-1} K^{-1} in good agreement with the result of –55.6 J mol^{-1} K^{-1} obtained by Mehrian *et al.* [8]. In the case of C12PyBr we obtain a result of –83.59 J mol^{-1} K^{-1}.

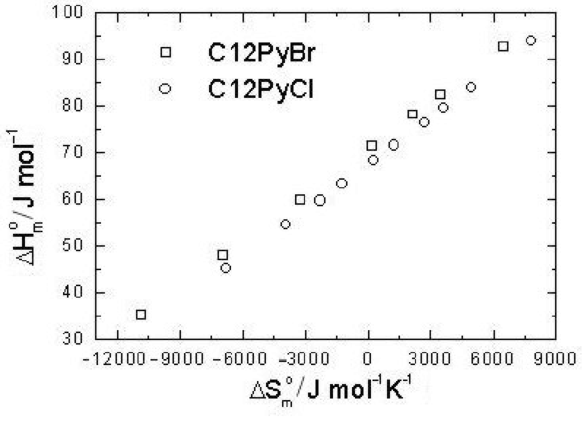

Fig. 5 Enthalpy–entropy compensation plots for C12PyCl and C12PyBr

A great amount of chemical process, like oxidation-reduction, hydrolysis and so on, has a linear relationship between ΔH^0_{m} and ΔS^0_{m}, this phenomena is known as enthalpy–entropy compensation [13–14]. This process is shown in Fig. 5 for the C12PyCl and C12PyBr.

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