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SHORT COMMUNICATIONS

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Effect of counterion on thermodynamic micellar properties of tetradecylpyridinium in aqueous solutions

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Abstract Electrical conductivity of aqueous solutions of tetradecylpyridinium bromide and chloride has been measured as a function of surfactant molal concentration and temperature. From the molal dependence of conductivity, the critical micelle concentration and the micellar ionization degree were estimated. The temperature dependence of these parameters has been used for calculating the thermodynamic parameters related with the micellization process by using the classical charged pseudophase separation model. The effect of the counterion on the conventional thermodynamic potentials of micellization such as standard Gibbs free energy, enthalpy and entropy has also been a matter of study. Finally, the occurrence of the enthalpy–entropy compensation phenomenon was verified and the relevant parameters discussed.

Keywords Tetradecylpyridinium bromide and chloride · Critical micelle concentration · Ionization degree of the micelles · Thermodynamic magnitudes

Introduction

The micellar properties of cationic surfactant in aqueous solutions have been extensively studied during the last decades. This extensive work was justified not only by its theoretical interest but also by the large number of industrial applications of these compounds. The germicidal activity of different kinds of quaternary ammonium salts is well known, and their ability to form microemulsions has attracted attention due to the potential use as in tertiary oil recovery. Another application arises from the combination with other compounds as electrolytes and non electrolyte moieties as well as other surfactants that opens the door to, for example, noticeable applications in the field of mesoporous materials [1].

Since the earlier works of Adderson and Taylor [2], who reported the thermodynamic properties of dodecylpyridinium bromide, a remarkable number of papers on micellar properties have appeared in the literature. Among the most important are the works of Skerjanc et al. [3] on the equilibrium and transport properties of alkylpyridinium bromides using conductimetry, osmometry and densitometry. Relevant contributions on thermodynamics of micellization of alkylpyridinium chlorides have also been reported by

Mehrian et al. [4] using calorimetric measurements. A systematic study of the dependence of different thermodynamic parameters of alkylpyridinium chlorides on the alkyl chain length has been carried out by Causi et al. [5]. More recently, the effect of counterion on micellization of dodecylpyridinium halides has been analyzed by Galán et al. [6], and additional contributions on dye solubilization in micellar solutions of alkylpyridinium bromides–sodium bromide have been recently developed by Fujio et al. [7].

In order to obtain a deeper understanding of the effect of the counterions on the micellar properties of alkylpyridinium halides, we have measured the temperature dependence on critical micelle concentration (cmc) and ionization degree of the micelles, α, by means of conductivimetric measurements. To determine the cmc and α, conductivity isotherms in the pre and postmicellar regime of tetradecylpyridinium bromide and chloride have been measured. The thermodynamic functions of micellization for both components have been estimated by means of the charged pseudophase separation model, and the obtained results were compared and discussed as a function of the counterion and the chain length, taking into account previous results.

Experimental

Materials

Tetradecylpyridinium chloride (C14PyCl) was synthesized [8] treating chlorotetradecane with a large excess (nine equivalent) of pyridine at reflux for 100 h. The reaction mixture was concentrated under vacuum and the residue recrystallized from acetone (82% yield). Tetradecylpyridinium bromide (C14PyBr) was obtained as described elsewhere [9]. The purity of both compounds was established by spectroscopic analysis, and an elemental analysis indicated that the two products were in their monohydrate form.

Distilled water with a conductivity lower than 3 μS cm^{-1} at 25 °C was used in all solutions, and the concentration was calculated by means of weigh techniques.

Methods

The molal dependence of conductivity was obtained at each temperature by continuous dilution. After a known amount of concentrated solution was placed in the cell, an identical amount of pure water was repetitively added to the cell using an automatic dispenser with an accuracy of (0.7 ± 0.1)%. The conductivities were measured with a Kyoto Electronics Conductometer Model CM-117, with a cell, Model K-121. The cell constant was determined at the beginning of the experiment by using KCl solutions according to the procedure suggested by Monk [10]. The temperature control was achieved by means of a Julabo F25 thermostat with a precision better than 0.01 K.

Results and discussion

The molal dependence of specific conductivity for C14PyCl and C14PyBr has been determined at 15, 20, 25, 30, 35 and 40 °C. As an example, in Fig. 1 we represent the isotherms of specific conductivity against molality, for C14PyBr and C14PyCl at 25 °C.

The critical micelle concentration, cmc, has been estimated from the intercepts of the linear fits above and below the critical point in Fig. 1 according to the Williams method [11]. The values of cmc obtained for C14PyBr and C14PyCl at 25 °C are 0.0027 and 0.0043 mol kg^{-1}, respectively. These values are in accordance with the values previously reported by Fujio et al. [12], 0.00282 mol dm^{-3}, Skerjanc et al. [3], 0.0027 mol dm^{-3}, for C14PyBr, and 0.0035 mol dm^{-3} for C14PyCl reported by Mehrian et al. [4]. Table 1 shows the cmc of alkylpyridinium chlorides and bromides at 25 °C reported in the literature together with the present results.

It is necessary to verify that the results reported in Table 1 follow the well-known Stauff–Klevens rule [13, 14] that relates the number of carbon atoms in the alkyl chain length, n_c, with the cmc as follows

$$\log \mathrm{cmc} = A + Bn_c \qquad (1)$$

The results given by the data reported in Table 1 lead to similar slopes in the interval -0.71 ± 0.01 for both counterions. The calculated decrease of log cmc associ-

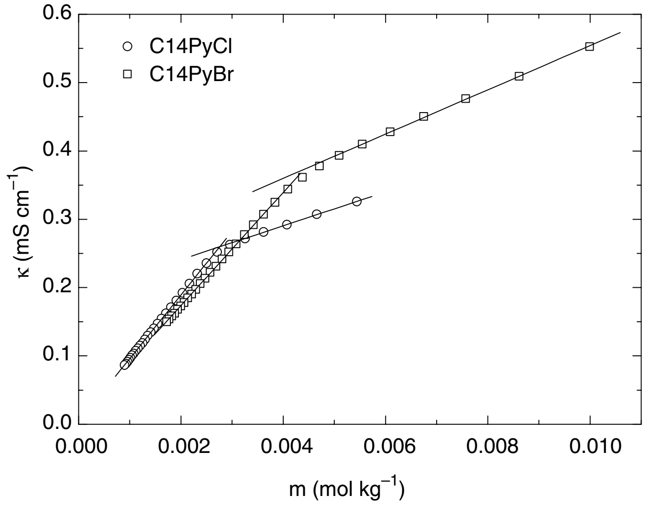

Fig. 1 Plot of the specific conductivity of C14PyCl and C14PyBr in water at 25 °C as a function of molality

Table 1 Critical micelle concentration of alkylpyridinium chlorides and bromides at 25 °C

Alkylchain	Counterion	
	Br	Cl
C8Py		0.30 [5]
C10Py	0.0513 [13] 0.0516 [32] 0.044 [3]	0.073 [5]
C11Py	0.021 [3]	
C12Py	0.012 [13] 0.0121 [31] 0.01 [3] 0.0112 [6]	0.01696 [6] 0.018 [5]
C13Py	0.0053 [3]	
C14Py	0.0027 [3] 0.00275 (Present result)	0.00434 (Present result)
C15Py	0.0013 [3]	
C16Py	0.00064 [3]	

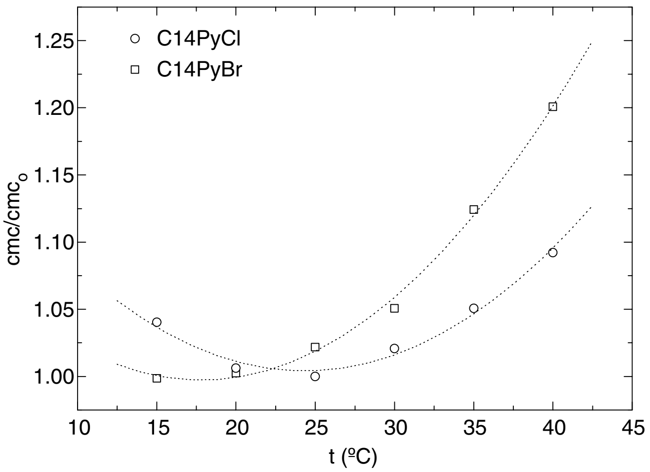

Fig. 2 Temperature dependence of cmc/cmc_o for C14PyBr and C14PyCl

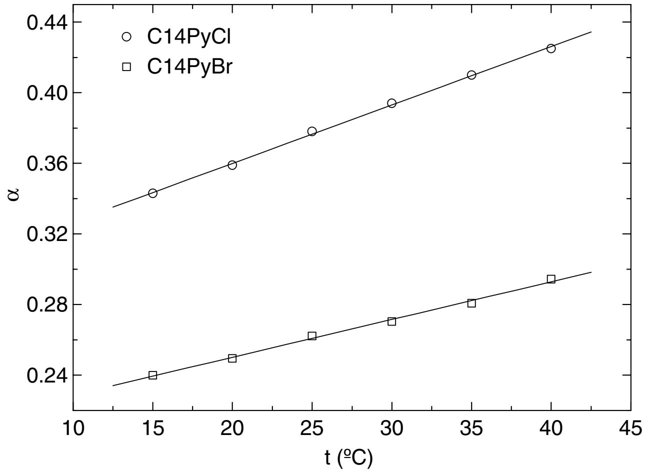

Fig. 3 Temperature dependence of the ionization degree α of the micelles for C14PyBr and C14PyCl

ated to the replacement of Cl^- by Br^- is 0.44 ± 0.05. This apparent independence of the Stauff–Klevens slope on the counterion is a common feature in other quaternary ammonium salts, as can be inferred from Refs. [15] and [16] for homologous alkyldimethylbenzylammonium chloride and bromide, respectively.

The ionization degree of the tetradecylpyridinium halide micelles was estimated from the ratio of the slopes above and below cmc as was suggested by Hoffmann and Ulbright [17]. The obtained ionization degrees of the micelles at 25 °C were 0.26 and 0.38 for C14PyBr and C14PyCl, respectively. Skerjank et al. [3] reported a value of 0.31 ± 0.03 for C14PyBr at 25 °C that is in good agreement with our result. A slightly more sophisticated calculation of the ionization degree proposed by Van Nieuwkoop [18] takes into account the contribution of the micelles and the monomers to the conductivity as described in Ref. [19]. This approach gives for the ionization degree of our C14PyBr at 25 °C data, a value of 0.30, that does not differ much from that obtained by the somewhat simpler procedure used in this work.

In Fig. 2 we show the temperature dependence of cmc/cmc_o ratio, where cmc_o represents the cmc at the minimum of the cmc versus temperature curve. The classical U-shaped curve, characteristic of the dependence of cmc with temperature, can be observed in this representation. The Br^- counterion shifts the minimum towards lower temperatures, so the replacement of Cl^- by Br^- is equivalent to increasing the alkyl chain length, enhancing the hydrophobicity of the system [15, 20–25].

In Fig. 3 we represent the temperature dependence of the ionization degree, α, of the micelles for C14PyCl and C14PyBr.

The increase of ionization degree with temperature has been found in cationic surfactant micellar systems. The lower values found for C14PyBr denotes that the bromide ion neutralizes the charge of the micelle in a more effective way due to the lower hydration degree of Br^- associated to its lower electronegativity. The hydration of chlorides is less negative than that of bromides [26]. This effect is also present, among others, in the dodecyldimethylbenzylammonium chloride and bromide [25, 27].

In order to estimate the thermodynamic magnitudes associated to the micellization process, when the aggregation number of the micelles is sufficiently large, we can apply the classical charged pseudophase separation model [28], which predicts a standard Gibbs free energy of micellization:

$$\Delta G_m^o = (2-\alpha)RT\ln\chi_{cmc} \tag{2}$$

where χ_{cmc} is the surfactant molar fraction at cmc. From the temperature dependence of $\Delta G_m{}^o$, we can estimate other thermodynamic quantities of micellization such as the enthalpy ($\Delta H_m{}^o$) and entropy ($\Delta S_m{}^o$) using conventional thermodynamic relations:

$$\Delta H_m^o = \left[\frac{\partial(\Delta G_m^o/T)}{\partial(1/T)}\right]_P \tag{3}$$

$$\Delta S_m^o = \frac{\Delta H_m^o - \Delta G_m^o}{T} \tag{4}$$

Values for $\Delta G_m{}^o$ have been obtained from Eq. 2, with α and $\ln \chi_{cmc}$ fitted to a straight line and a second degree polynomial function respectively with temperature. Figure 4 shows the standard Gibbs free energy of micellization, $\Delta G_m{}^o$, as a function of temperature.

As expected, the usual decrease of $\Delta G_m{}^o$ with temperature associated to exothermic entropically driven processes was found. Additionally, the lower value observed on the bromide compound confirms that the introduction of a Br^- ion in the place of Cl^- further promotes the micellization process. This behavior follows the Hoffmaister series depending on the hydrophobicity of the counterions. A similar behavior was found on the dodecyl homologues [6].

Figure 5 shows the temperature dependence of $\Delta H_m{}^o$ and $T\Delta S_m{}^o$ for C14PyBr and C14PyCl.

It can be seen in this figure that the enthalpic contribution to $\Delta G_m{}^o$ is almost the same for both studied surfactants. However, the entropic contribution is more pronounced for Cl^- ion; results that are similar to those previously reported by Galan et al. [6] for C12PyBr and C12PyCl.

It is well known that several chemical processes exhibit a linear relation between $\Delta H_m{}^o$ and $\Delta S_m{}^o$. This phenomenon is called enthalpy–entropy compensation [15, 20, 29, 30]. The enthalpy–entropy compensation is also present in the compounds studied in this paper, and it is shown in Fig. 6.

In general, the compensation effect can be described by relation $\Delta H_m{}^o = \Delta H_m{}^* + T_c\, \Delta S_m{}^o$ where T_c is the so-called compensation temperature and $\Delta H_m{}^*$ is the intercept at the origin. The intercept observed for the present compounds amounts to −38.3 kJ mol^{-1} and −43.0 kJ mol^{-1} for C14PyCl and C14PyBr, respectively. The values reported by Galan et al. [6] for C12PyCl and C12PyBr are −20.2 and −21.4 kJ mol^{-1}, respectively. We have also obtained the same value $T_c = 301 \pm 1$ K for both C14PyCl and C14PyBr. From previous data reported by Galan et al. [6], the same value of 300 ± 1 K has been found for C12PyBr and C12PyCl. It was found by Sugihara et al. [29] that the value obtained for

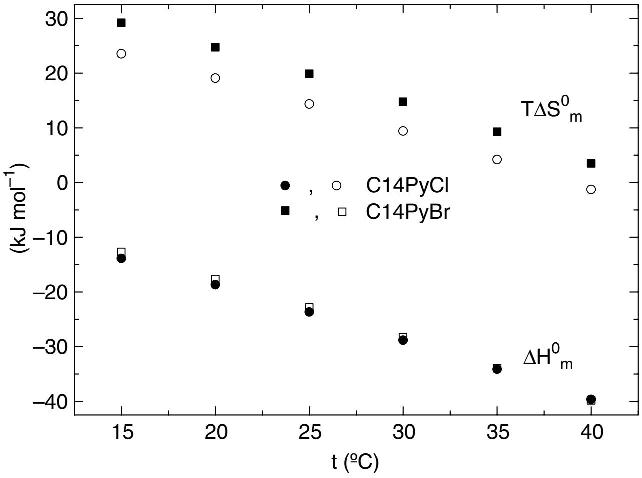

Fig. 5 $\Delta H_m{}^o$ and $T\Delta S_m{}^o$ values for C14PyCl and C14PyBr as a function of temperature

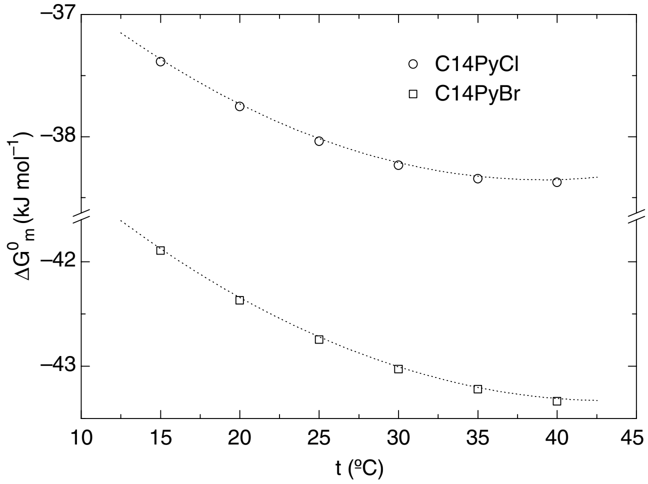

Fig. 4 $\Delta G_m{}^o$, values for C14PyCl and C14PyBr as a function of temperature

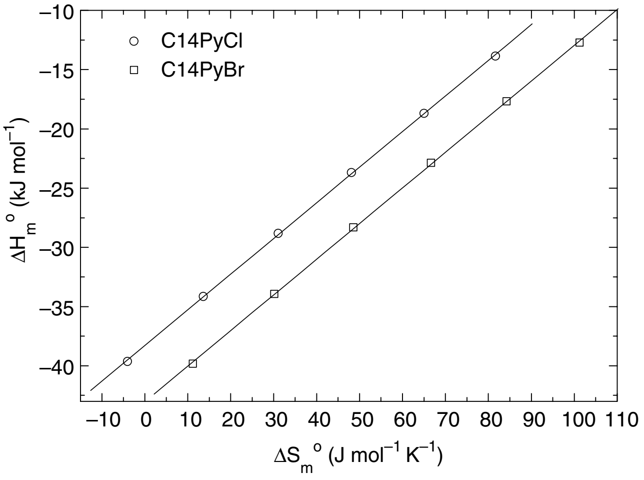

Fig. 6 Enthalpy–entropy compensation plot for C14PyCl and C14PyBr

alkyltrimethylammonium bromides is around 308 ± 4 K, and more recently Rodríguez et al. [15] found a value approximately 10 K lower for alkyldimethylbenzylammonium chlorides. These results fit well in the general framework proposed by Chen et al. [20] in which all ionic surfactants should be included in the interval 308 ± 4 K.

Conclusions

The temperature dependence of the critical micelle concentration and the micellar ionization degree have been determined for C14PyCl and C14PyBr by measuring the molal dependence of the conductivity at different temperatures. These data have been used to estimate the thermodynamic magnitudes of micellization, and the results have been discussed as a function of counterion and, comparing with previous data reported in the literature, of alkyl chain length. The behavior of the relevant thermodynamic magnitudes has also been discussed.

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