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Thermodynamic study of the process of micellization of long chain alkyl pyridinium salts in aqueous solution

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Abstract The molality dependence of specific conductivity of pentadecyl bromide, cetylpyridinium bromide and cetylpiridinium chloride in aqueous solutions has been studied in the temperature range of 30–45 °C. The critical micelle concentration (cmc) and ionization degree of the micelles, β, were determined directly from the experimental data. Thermal parameters, such as standard Gibbs free energy ΔG_m^0, enthalpy ΔH_m^0 and entropy ΔS_m^0, of micellization were estimated by assuming that the system conforms to the pseudo-phase separation model. The change in heat capacity on micellization ΔC_p, was estimated from the temperature dependence of ΔH_m^0. An enthalpy–entropy compensation phenomenon for the studied system has been found.

Keywords Pentadecylpyridinim bromide · Cetylpyridinium bromide · Cetylpyridinium chloride · Conductivity · Critical micelle concentration · Enthalpy, entropy and standard Gibbs free energy of micellization · Heat capacity · Temperature dependence

Introduction

The formation of micelles by surfactants is a cooperative process. This process occurs above a certain concentration, the critical micelle concentration (cmc). Cmc value can be modified by ionic and non-ionic additives, changing the temperature or pH of the solution [1]. In previous papers we have estimated the thermal parameters related to the self-association process of several pyridinium salts with different counterions [2, 3]. In the present work we report the results of our conductivity measurements of pentadecylpyridinium bromide (C15PBr), cetylpyridinium bromide (C16PBr) and cetylpyridinium chloride (C16PCl) in aqueous solutions at different temperatures, in order to characterize these systems thermodynamically.

The importance of cationic surfactants is due, among other reasons, to their bacteriostatic properties, and so they have been introduced into several commodities, such as cosmetics and germicides [4]. More recently, they have been applied in such diverse fields as phase transfer catalysis [5] and the production of silica-based mesoporous materials [6]. They are being used in systems with nucleic acid [7] and biological system [8].

In particular, long chain pyridinium-based surfactants are involved in semiconductor techniques in order to obtain materials with high cubic pore order [9]. They also are used in medical research because pyridinium compounds were found to be essentially non-toxic towards cells [10]. Some pyridinium aggregates are useful as dyes, such as styryl pyridinium for example, these cationic dyes interacting with membranes and they can be used as membrane probes [11].

The three pyridinium salts chosen can play an important role in research as mentioned above. However, it is necessary to know their fundamental properties on micellization. For that purpose, thermal parameters associated with

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micellization were estimated, because they thus enable us to know the principles governing the formation of micelles [12] and so to know the suitable application of each one. Thermodynamic functions were estimated taking into account the dependence with temperature of cmc, as well as the degree of ionization of the micelles, β, by assuming a pseudo phase separation model.

Experimental

Pentadecypyridinium bromide was synthesized, personally, by Dr Czapkiewiecz from Jagiellonian University, Krakow, Poland in the following way:

A mixture of pentadecyl bromide (0.1 mole), provided by Koch-Light Ltd., and pyridine (0.15 mole) in 100 cm^3 of ethanol (99.5%) was boiled off in a 250 cm^3 flask. The vessel was then stopped and transferred to a thermostat set at a temperature of 78 °C. The mixture was kept in the thermostat for three days. The solvent was removed in a rotatory vacuum evaporator, the residue being then treated with 50 cm^3 of butanone-2, which was subsequently evaporated off thus enabling the removal of traces of ethanol and pyridine. The residue was dissolved in acetone and the solution kept in a refrigerator. The crystalline crop was filtered off and purified by repeated recrystallization from acetone-diethyl ethyl ether mixtures. The product was dried in air and then in a vacuum pistol over P_2O_5.

C16PBr and C16PCl were provided as a monohydrate by Aldrich with 98% purity and used without further purification. All solutions were prepared by mass, using distilled and de-gassed water with conductivity below 3 μScm^{-1}. The concentrations are expressed as moles of solute per kg of solvent, that is, molality.

Conductivity measurements were carried out 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 concentrations of KCl solutions, using the procedure suggested by Monk [13]. All measurements were carried out in a thermostat bath (Polysciencie 9010) maintaining the temperature constant to within ±0.05 °C.

Results and discussion

As expected, it was not easy to find data about C15PBr. Apart from the results at 25 °C provided by Skerjanc et al. [14], other data were unavailable, so we estimated the Krafft temperature in regard to this compound. For this purpose; an oversaturated water solution of C15PBr was prepared at <4 °C; afterwards, the specific conductivity of this solution was measured as against temperature, maintaining constant the concentration of C15PBr into the water solution. An inflection point was found around 16 °C. This result can be seen more clearly by representing conductivity derivative as against temperature. Figure 1 shows both. According to this result, we decided to start measurement of specific conductivity measurements as against molality for this salt solution at 17 °C.

Cmc was determined by the usual conductivity method from the intersection of two linear fits above and below the critical point in the specific conductivity against molality plots. Figure 2 shows the molar conductivity against the root square of concentration of C15PBr in water at 25 °C. For this temperature, cmc reaches a value of 1.36 mmolal, which is in concordance with 0.0013 mol L^{-1} by Skerjanc et al. [14].

All values of cmc vs temperature for C15PBr and C16Br are shown in Fig. 3a and b, respectively; as for other cationic surfactants, a typical U-shaped curve appeared in the plot. In the present case only one branch can be appreciated because of the high Krafft temperature value for both of them.

The same procedure was followed for C16PBr solutions, this salt has low solubility in water at room temperature; Krafft point was located above 25 °C. Skerjank et al. [14], Fujio et al. [15], Gharibi et al. [16] and Ghosh and Roy [12] reported data on cmc values at different temperatures. In Table 1 we compare our results with bibliographical data.

From data in Table 1, two important facts must be pointed out: the first aspect is that Skerjank et al. obtain results at 25 °C while the rest of the authors give values at higher temperatures, in better concordance with our findings about Krafft temperatures above 25 °C; the second is the lack of agreement between data of the cmc for C16PBr reported by Ghosh and Roy [12] and rest values reported by others for the same parameter and compound.

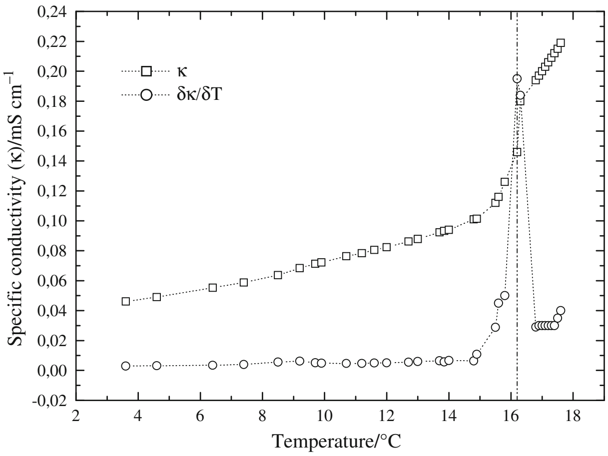

Fig. 1 Specific conductivity and its derivative versus temperature for C15PBr

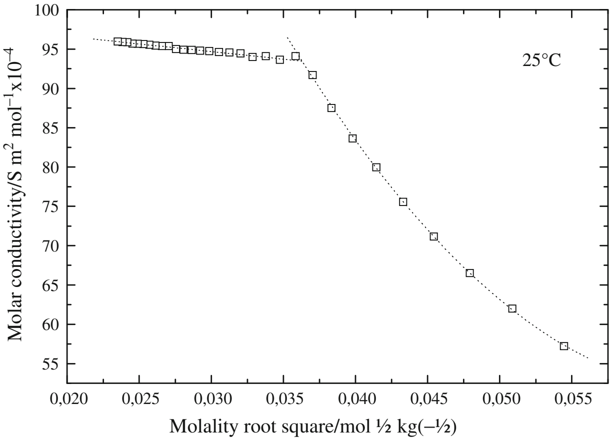

Fig. 2 Molar conductivity versus square root of molality for C15PBr

CMC values for C16PCl in water solutions in the range of 15–40 °C were obtained using the same procedure. The results can be observed in Fig. 4.

We obtained a value of 9.6×10^{-4} mol kg^{-1} at 25 °C, which is in agreement with bibliographical data: Malsch and Hartley [17] reported 9×10^{-4} mol dm^{-3} and Molinero et al. [18] 1×10^{-3} mol L^{-1} for the same temperature. The values of cmc vs temperature for the water solutions for C16PCl also have a U-shaped plot, with a minimum at $T = T_m$. This means that the pyridinic head group has no influence on the behaviour of the cationic surfactants. According to Chen et al. [19], the minimum, T_m, is a consequence of two opposite effects:

(a) The decrease in the hydratation of the ionic head group with temperature which leads to growth of hydrophobicity of the surfactant and hence lowering of cmc, and
(b) The breakdown of the structure of the water, which leads to a decrease in hydrophobic interactions and hence to an increase in cmc value.

Comparing our results for C16PBr and C16PCl water solutions, it can be observed that the substitution of the bromide anion by the more hydrophilic chloride leads to an increase in cmc by a factor of approximately 1.3.

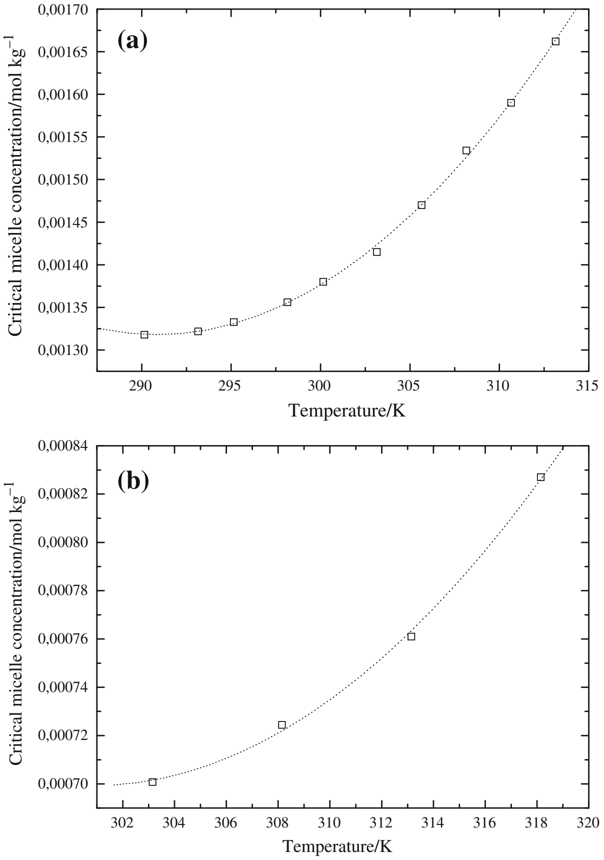

Fig. 3 **a** Temperature dependence of cmc for C15PBr. **b** Temperature dependence of cmc for C16PBr

In previous papers, we reported values of cmc for the C12PCl and C14PCl in water solutions [2, 20]. We plotted the ratio of cmc and cmc$_m$, that is, the minimum value of cmc for each salt, for all of them in Fig. 5.

T_m seems to fall with the growth of hydrophobic chain length: this behaviour was observed by Zielinsky et al. [21] for alkyltrimethyl ammonium bromide, by Chen et al. [19] for some non ionic surfactants and by González-Pérez et al. [22] for alkyldimethyl-benzylammonium bromide.

The ionization degree, β, of the micelles has been calculated as the ratio of the slopes of two intersecting lines on the conductivity versus molality plots. The values obtained for β for C15PBr and C16PBr at 35 °C amount to 0.32 and 0.33 respectively, and 0.49 for C16PCl at the same temperature. The expected linear dependence between the ionization degree of the micelles and the temperature is

Table 1 Comparative values of cmc for C16PBr

Author	CMC (C16PBr)
Skerjanc et al. [14] (25 °C) (mol L^{-1})	6.4×10^{-4}
Fujio et al. [15] (35°) (mol L^{-1})	8.15×10^{-4}
Gharibi et al. [16] (30, 35 °C) (mol L^{-1})	7.0×10^{-4}; 7.6×10^{-4}
Ghosh and Roy [12] (35, 45, 55, 65 °C) (mol L^{-1})	1.74×10^{-3}; 1.40×10^{-3}; 1.35×10^{-3}; 1.20×10^{-3}
Current work (30, 35, 40, 45 °C) (mol kg^{-1})	7.00×10^{-4}; 7.24×10^{-4}; 7.6×10^{-4}; 8.27×10^{-4}

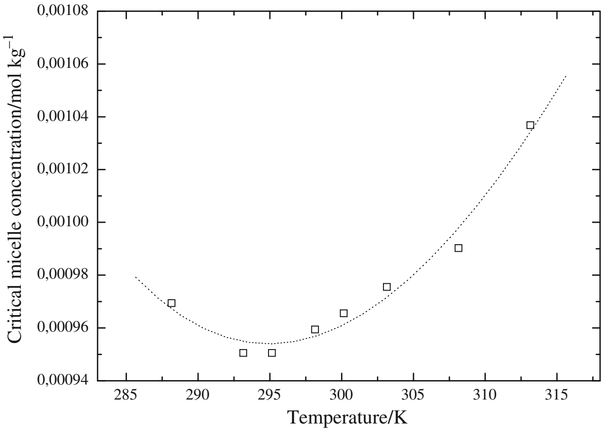

Fig. 4 Temperature dependence of cmc for C16PCl

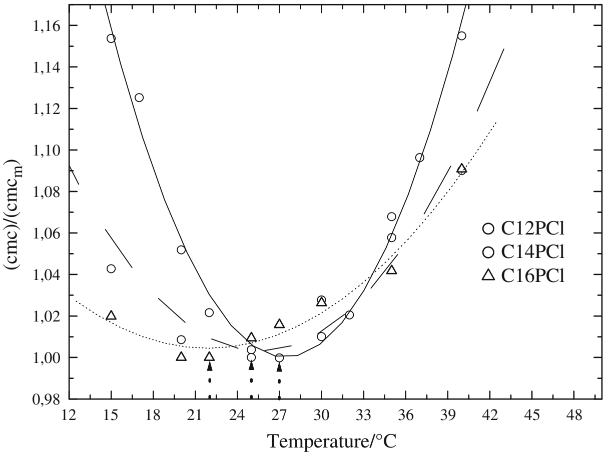

Fig. 5 Temperature dependence of cmc for C12, C14 and C16PCl

shown in Fig. 6 for C15PBr, C16PBr and C16PCl solutions. This behaviour is to be expected, because the higher temperature is the higher thermical agitation is and the counter ion is easily dissociated from the micelle.

Thermodynamic quantities of micellization such as Gibbs free energy ΔG_m^0, enthalpy ΔH_m^0, and entropy ΔS_m^0, can be derived from the temperature dependence of cmc, and β on basis of the pseudo-phase separation model [23]. According to this model the relationships between thermal functions and micellization parameters are as follows:

$$\Delta G_m^0 = (2-\beta)RT\ln\chi_{cmc} \tag{1}$$

$$\Delta H_m^0 = \left[\frac{\partial\left(\Delta G_m^0\right)}{\partial(1/T)}\right] \tag{2}$$

$$\Delta S_m^0 = \frac{\Delta H_m^0 - \Delta G_m^0}{T} \tag{3}$$

where χ_{cmc} is the molar fraction of the surfactant solution at cmc. The temperature dependence of β and ln χ_{cmc} were

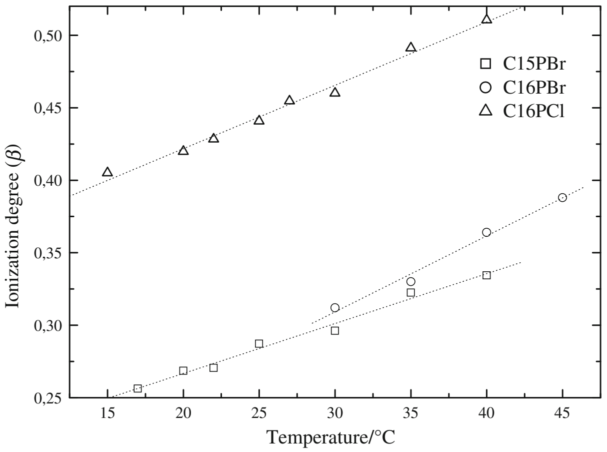

Fig. 6 Ionization degree versus temperature for C15PBr, C16PBr and C16PCl

fitted to a first and second order polynomial curve, respectively, to obtain relevant values from Eqs. 1, 2 and 3. Figure 7a, b, c shows the plots of the thermal functions versus temperature for the solutions of C15PBr, C16PBr and C16PCl, respectively. As can be seen, ΔG_m^0 is negative in the whole temperature and concentrations range studied for the three surfactants considered, which means that micellization is a spontaneous process in this temperature range and for the concentrations studied.

Using the results for alkylpyridinium bromides and chlorides reported by us [2, 3, 20], a variation of ΔG_m^0 with the carbon number can be estimated (Fig. 8).

The slopes have values of –2,100 J mol^{-1} for chlorides halides and –2,500 J mol^{-1} for bromides halides, which suggest that the counter ion fails to have a significant influence on ΔG_m^0 per CH$_2$ group.

According to the data of the variation of standard enthalpy of micellization showed in Fig. 7a–c micellization is an exothermic process in the whole range of temperature studied, and the more exothermic it is, the longer the hydrocarbon chain.

The change in heat capacity of the surfactant upon micellization can be estimated from data of $\Delta C_{p,m}^0$, using the following relationship:

$$\Delta C_{p,m}^0 = \left(\frac{\partial \Delta H_m^\circ}{\partial T}\right)_p \tag{4}$$

The results yield a value of −1,330 and −1,620 J mol^{-1}K^{-1} for C15PBr and C16PBr respectively and −810 J mol^{-1}K^{-1} for C16PCl. Some authors [24–26] prefer not to take into account the ionization degree of the micelles, because the results give a better agreement with calorimetric data. In our case, such an approach leads to $\Delta C_{p,m}^0$ value of −690, −1110 and −380 J mol^{-1} K^{-1} respectively. From the values of ΔS_m^0 listed in Fig. 7a–c, we

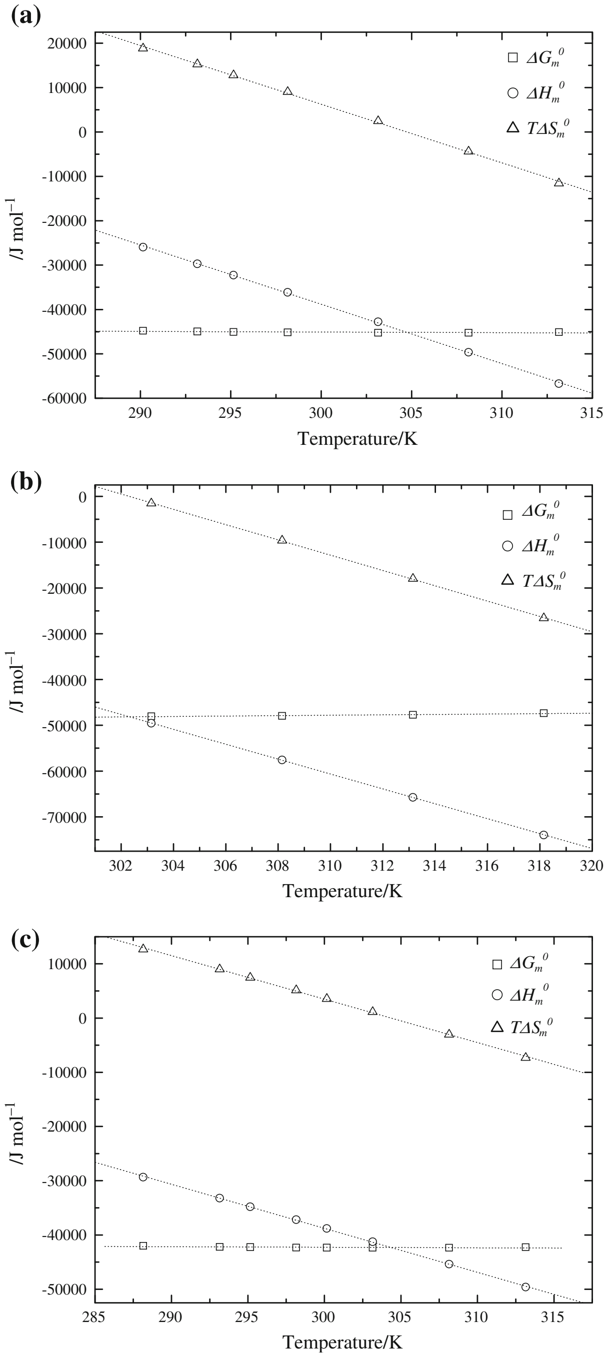

Fig. 7 **a** Temperature dependence of ΔG_m^0, ΔH_m^0 and ΔS_m^0 for C15PBr. **b** Temperature dependence of ΔG_m^0, ΔH_m^0 and ΔS_m^0 for C16PBr. **c** Temperature dependence of ΔG_m^0, ΔH_m^0 and ΔS_m^0 for C16PCl

can assert that in the micellization process the order increases with temperature.

Several chemical processes show a linear relationship between ΔH_m^0 and ΔS_m^0.

This phenomenon is known as enthalpy–entropy compensation [19–26] and, in general, the compensation effect can be described by the relationship:

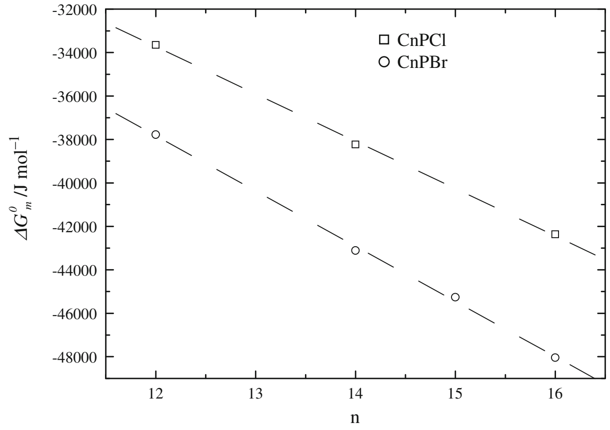

Fig. 8 ΔG_m^0 versus number of carbons for C_nPBr and C_nPCl

$$\Delta H_m^\circ = \Delta H_m^* + T_c \Delta S_m^\circ \tag{5}$$

where Tc is the so-called compensation temperature and its value is a measure of desolvatation of the chain of surfactant molecule and ΔH_m^* is the intercept and a measure of the aggregation of the chains to make up the micelle.

In Fig. 9, ΔH_m^0 versus ΔS_m^0 was plotted for the C15PBr, C16PBr and C16PCl water solutions systems. The parallelism among the linear fitted straights for C15PBr and C16PBr, implies that the slope, T_c, is independent of the length of the hydrophobic chain of the surfactant.

The above-mentioned fact is in agreement with the literature, and both non-ionic and ionic systems, such as octylphenoxiethanols [27]. An increase of ΔH_m^* causes a diminution in the stability of the micelle, because ΔG_m^0 increases in the same ratio.

The values of ΔH_m^* for the compounds studied are –45383, –47940 and –42429 J mol^{-1} for C15PBr, C16PBr and C16PCl respectively.

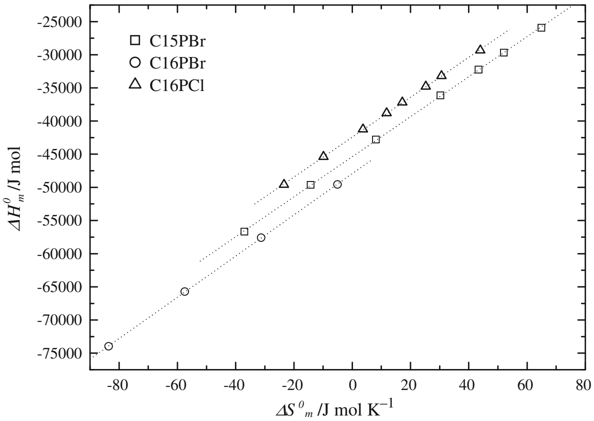

Fig. 9 Enthalpy–entropy compensation plots for C15PBr, C16PBr and C16PCl

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