

THERMODYNAMICS OF MICELLIZATION OF HEXADECYLPYRIDINIUM BROMIDE IN AQUEOUS AND ALCOHOLIC (C₁-C₄) SOLUTIONS

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Dedicated to Professor Eudovít Treindl on the occasion of his 70th birthday.

In this work, we studied effects of temperature, alkyl chain, branching and increasing number of hydroxy groups of additives on the critical micelle concentration (CMC) and thermodynamics of micellization of 1-hexadecylpyridinium bromide (CPBr) using conductometric techniques in a series of solvents: water and C₁-C₄ alcohols (methyl (MeOH), ethyl (EtOH), n-propyl (n-PrOH), isopropyl (i-PrOH), n-butyl (n-BuOH), isobutyl (i-BuOH), *tert*-butyl alcohol (*t*-BuOH), 1,2-ethanediol (EtOH), 1,2-propanediol (PrOH) and 1,2,3-propanetriol (PrOH)). From the conductivity curves measured in water and alcohols in the temperature interval 20–50 °C, the CMC and concentrations of CPBr corresponding to a change of the micelle shape were calculated. For alcohols, the plots of the CMC vs temperature display U-shaped curves with minima at 30 °C, whereas in water, the CMC increases nonlinearly over the temperature interval studied. According to their effect on the CMC, the solvents can be arranged in the order H₂O < n-BuOH < i-BuOH < *t*-BuOH < PrOH < n-PrOH < i-PrOH < PrOH < EtOH < EtOH < MeOH. Degrees of counterion binding (β), as calculated from slopes of the conductivity curves, were found to decrease as the temperature increases. Thermodynamic functions of micellization – standard molar Gibbs energy, enthalpy and entropy – were analyzed in terms of the model of phase separation as well as the model based on the mass-action law. While the drop in the $\Delta_m G^0$ values over the given temperature interval is only 1–2 kJ mol⁻¹, the lowering of $\Delta_m H^0$ and $\Delta_m S^0$ is much more pronounced. Enthalpy-entropy compensation plots were used to calculate the compensation temperatures which characterise the solvent-solute interaction and lie in the range 289–313 K. The reference temperatures for $\Delta_m S^0$ converging to zero range from 318 to 344 K. The values of molar heat capacity $\Delta_m C_p$ were also calculated. In the mixed (water-alcohol-tenside) solutions with the volume alcohol-water ratios $\phi = 0-1.0$, the CMC were determined at 25 °C.

Key words: Quaternary ammonium salts; Pyridinium salts; Amphiphiles; Micelles; Micellization; Thermodynamics; Solvent effects; Alcohols.

The ability of a drug molecule to form aggregates in both aqueous and nonaqueous environments is of prime importance for its biological activity and practical application. Differences in the activity of drugs are related to their structure which determine adsorption of the drug through the cell membrane as well as specific interaction with proteins.

Quaternary ammonium salts (QAS) contain a positively charged quaternary ammonium nitrogen bonded to an alkyl or aryl group. The amphiphilic character of such compounds results in the formation of micelles which is a cooperative process demonstrated by critical micelle concentration (CMC). The CMC depends on various factors, such as the structure of the compound studied, temperature, pH, ionic strength and the presence of additives in the solution¹⁻³.

The most important forces contributing to the formation of micelles are hydrophobic interactions. A study of thermodynamics of micellization is indispensable for understanding the interactions that control the process of micellization and for predicting the behaviour of micellar solutions. The relevant thermodynamic parameters describing micellization are changes of standard molar Gibbs energy ($\Delta_m G^0$), standard molar enthalpy ($\Delta_m H^0$), standard molar entropy ($\Delta_m S^0$) and heat capacity of micellization ($\Delta_m C_p$). These parameters can be determined from the changes of the CMC with temperature by using the existing physicochemical methods⁴ and by fitting of these values to the chosen model of micellization. Based on this knowledge, the present work deals with micellar properties of a commercially available quaternary ammonium salt – hexadecylpyridinium bromide – in water, alcohols (methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, *tert*-butanol, 1,2-ethanediol, 1,2-propanediol and 1,2,3-propanetriol) and mixed (water–alcohol) solutions with the aims: (i) to examine the effect of temperature and the length of the alkyl chain (in alcohols) on the CMC, the degree of counterion binding and the thermodynamic parameters of micellization of the above compound in water and concentrated alcohols, (ii) to explore the effect of various concentrations of alcohols in the mixed solutions on the CMC, and (iii) to compare the calculated values of CMC, degrees of counterion binding and thermodynamic functions of micellization in order to find more general trends in their temperature dependence.

EXPERIMENTAL

Chemicals

The compound studied, 1-hexadecylpyridinium bromide monohydrate, analytical grade (Lachema Brno, Czech Republic), $M_r = 402.47$, m.p. 65–67 °C (hereafter designated as CPBr), was used without further purification.

Methanol (MeOH), ethanol (EtOH), n-propanol (PrOH), isopropanol (i-PrOH), n-butanol (n-BuOH), isobutanol (i-BuOH), *tert*-butanol (*t*-BuOH), 1,2-ethanediol (EtdOH), 1,2-propanediol (PrdOH) and 1,2,3-propanetriol (PrtOH), analytical grade (Lachema Brno, Czech Republic), were used as purchased.

Water, the conductivity of redistilled water used was below $1.2 \mu\text{S cm}^{-1}$.

Conductivity Measurements

The conductometric dependences in water and alcohols were measured in the temperature interval 20–50 °C (at 25 °C in the mixed alcohol–water solutions) by using a digital PHYWE conductometer (Germany) equipped with a double conductivity cell and a platine electrode (cell constant $K = 1.01 \text{ cm}^{-1}$); the precision of the measurements was $\pm 0.01 \mu\text{S cm}^{-1}$. The solutions were continually stirred and thermostatted with the precision of ± 0.05 °C. The measured conductivity values (κ) are given as means of repeated measurements.

Data Evaluation

CMC determination. The CMC values were determined from the dependence of specific conductivity changes against the QAS concentration, $\kappa = f(c_{\text{CPBr}})$ in aqueous, alcoholic and mixed solutions. The CMC was estimated from the intersection of two linear parts of the conductivity curve by a least-squares method.

Degree of counterion binding (β). The β values were calculated from slopes of the two linear parts of the conductivity curves, according to the relation⁵

$$\beta = 1 - (S_2/S_1), \quad (1)$$

where S_1 and S_2 are slopes of the above dependence below and above the CMC (in $\text{S m}^2 \text{ mol}^{-1}$).

For the aqueous solutions for which the slopes above the CMC (S_2), molar conductivities at infinity dilution of the counterion⁶ ($\Lambda_{0\text{Br}}$), viscosity of water at various temperatures⁷ and the radius of a micelle (r_m) are known, the degrees of counterion binding were also calculated according to Evans⁸

$$S_2 = \left[\frac{F^2}{6\pi\eta_0 r_m N_A} + \Lambda_{0\text{Br}} \right] \alpha \quad (2)$$

$$\beta = 1 - \alpha, \quad (3)$$

where S_2 is the slope of the dependence $\kappa = f(c_{\text{CPBr}})$ above the CMC (in $\text{S m}^2 \text{mol}^{-1}$), F is the Faraday constant (in C mol^{-1}), N_A is the Avogadro number (in mol^{-1}), η_0 is the viscosity of water (in Pa s), r_m is the radius of a micelle for 16-membered chain⁹ (in m), $\Lambda_{0\text{Br}^-}$ is the molar conductivity of Br^- anion at infinity dilution (in $\text{S m}^2 \text{mol}^{-1}$) and α is the degree of ionization.

Calculation of Thermodynamic Parameters of Micellization

Standard molar Gibbs energy, $\Delta_m G^0$, standard molar enthalpy, $\Delta_m H^0$ and standard molar entropy, $\Delta_m S^0$ of micellization were calculated from changes of the CMC with temperature. Changes of these parameters are usually analyzed in terms of two models: 1) a model of phase separation (PS) and 2) a model based on the mass-action law (MA). For both models, the following equations were used to calculate the thermodynamic functions of micellization^{10,11}.

$$\Delta_m G^0 = \gamma RT \ln \text{CMC} \quad (4)$$

By applying the Gibbs–Helmholtz equation in the form

$$\left[\frac{\partial(\Delta_m G^0/T)}{\partial T} \right]_p - \frac{\Delta_m H^0}{T^2}, \quad (5)$$

the following relation was derived for calculation of the standard molar enthalpy changes

$$\Delta_m H^0 = -\gamma RT^2 \frac{\partial(\ln \text{CMC})}{\partial T} = -\gamma RT^2 (B + 2CT), \quad (6)$$

where B , C are parameters of the polynomial

$$\ln \text{CMC} = f(T) = A + BT + CT^2. \quad (7)$$

Finally, the molar entropy changes were calculated according to the equation

$$\Delta_m S^0 = \frac{\Delta_m H^0 - \Delta_m G^0}{T}. \quad (8)$$

The parameter γ in Eqs (4) and (6) is model-dependent and for models PS_1 and PS_2 it takes the value of 1 (when the counterions are fully ionized) or 2 (all counterions are bound in the micelle) and for model MA the value of $(1 + \beta)$.

Calculation of the Compensation Temperature

According to some authors^{12,13}, the dependence $\Delta_m H^0 = f(\Delta_m S^0)$ is usually linear and known as compensation (enthalpy–entropy) dependence. The slope of the compensation depend-

ence is expressed in temperature units and called compensation temperature (T_c). The latter is a characteristic of the solvent-solute interaction¹⁰.

Calculation of the Molar Heat Capacity Changes

Molar heat capacity of micellization can be calculated from the relation

$$\Delta_m S^0 = \Delta_m S^* + \Delta_m C_p [\ln(T/T^*)], \quad (9)$$

where $\Delta_m S^*$ is the molar entropy change at $T = T^*$, T^* is the reference temperature at which $\Delta_m S^0$ converges to zero and $\Delta_m C_p$ is the change of molar heat capacity (slope of linear dependence)

RESULTS AND DISCUSSION

Although 1-hexadecylpyridinium bromide is well soluble in water and alcohols, a turbidity is observed in aqueous solutions at temperatures below 20 °C; the quenching (Kraft) temperature was 15.5 °C. For this reason the conductivity curves for CPBr solutions in water and alcohols were measured in the temperature interval 20–50 °C in appropriately chosen concentration ranges comprising the CMC (Fig. 1). The CMC values given in Table I and

TABLE I

Calculated CMC values (in 10^{-3} mol dm⁻³) for CPBr in water and alcohols

| Solvent | <i>t</i> , °C | | | | | | |
|------------------|---------------|-------|-------|-------|-------|-------|-------|
| | 20 | 25 | 30 | 35 | 40 | 45 | 50 |
| H ₂ O | 0.637 | 0.645 | 0.676 | 0.692 | 0.740 | 0.786 | 0.870 |
| MeOH | 44.60 | 43.82 | 43.42 | 43.62 | 44.50 | 46.14 | 49.50 |
| EtOH | 31.65 | 31.40 | 30.99 | 31.37 | 31.88 | 33.22 | 34.30 |
| EtdOH | 34.80 | 34.68 | 34.60 | 34.87 | 35.25 | 35.96 | 36.88 |
| n-PrOH | 19.41 | 19.30 | 19.25 | 19.37 | 19.66 | 20.01 | 20.72 |
| i-PrOH | 20.60 | 20.40 | 20.30 | 20.60 | 21.00 | 21.60 | 22.50 |
| PrdOH | 21.45 | 21.17 | 21.01 | 21.24 | 21.77 | 22.58 | 23.43 |
| n-BuOH | 7.00 | 6.80 | 6.75 | 6.90 | 7.15 | 7.60 | 8.10 |
| i-BuOH | 8.99 | 8.89 | 8.86 | 8.91 | 9.17 | 9.61 | 10.12 |
| <i>t</i> -BuOH | 10.00 | 9.81 | 9.75 | 9.90 | 10.26 | 10.64 | 11.20 |
| PrtOH | – | – | 18.55 | 18.81 | 19.39 | 19.56 | 20.04 |

Figs 2, 3 are the means of repeated (at least 3) measurements and standard deviations fall in the range $(0.1-0.5) \cdot 10^{-5} \text{ mol dm}^{-3}$.

The CMC values in the aqueous solutions increase (though not linearly) with temperature in the interval 20–50 °C. By contrast, the dependences $\text{CMC} = f(T)$ display U-shaped curves with minima at 30 °C in alcohols, the only exception is 1,2,3-propanetriol, most likely due to its high density which lowers the solubility of CPBr at lower temperatures and hence causes imprecisions of the measurements. As it is seen from Fig. 2, butanols, according to their effect on the CMC value, can be arranged in the descending order *tert*-butanol (curve 4) > isobutanol (curve 3) > n-butanol (curve 2).

From comparison of the CMC values in ethanol and 1,2-ethanediol (Table I; Fig. 3, curves 5, 6) and those in n-propanol, isopropanol and 1,2-propanediol (Table I; Fig. 3, curves 1–3) it is obvious that increasing the number of hydroxyl groups as well as branching of the alkyl chain suppresses

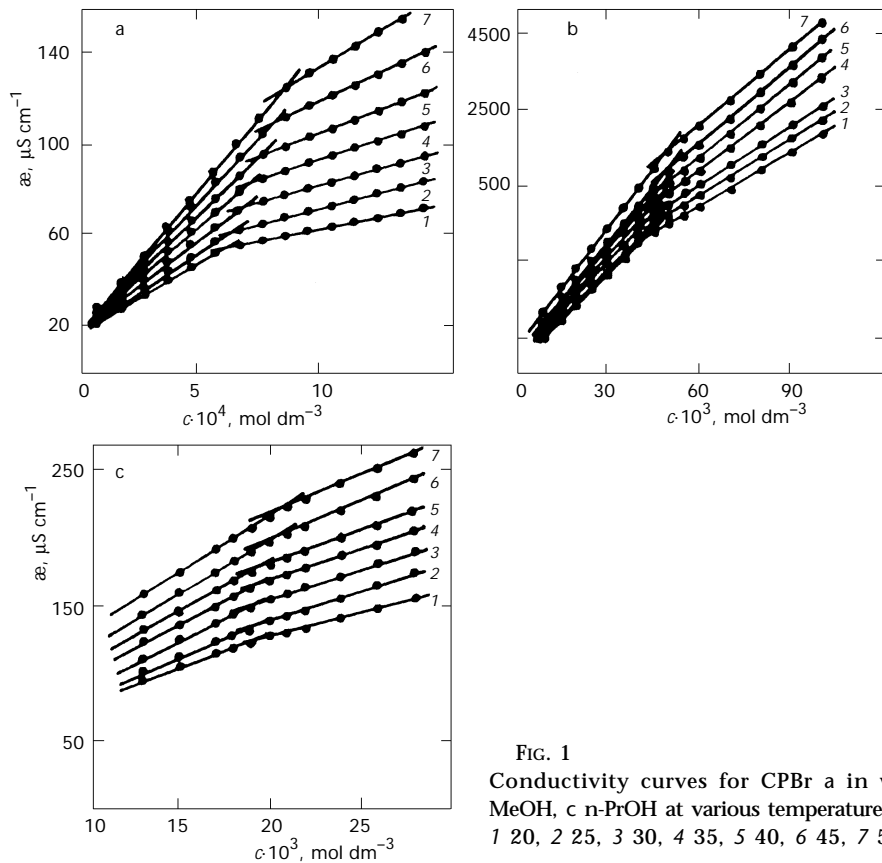


FIG. 1

Conductivity curves for CPBr a in water, b MeOH, c n-ProOH at various temperatures (in °C): 1 20, 2 25, 3 30, 4 35, 5 40, 6 45, 7 50

micellization, *i.e.*, the CMC increases in the order EtOH < EtdOH and PrtOH < *n*-PrOH < *i*-PrOH < PrdOH.

As shown in Table I, water and alcohols increase the CMC of CPBr in the order H₂O < *n*-BuOH < *i*-BuOH < *t*-BuOH < PrtOH < *n*-PrOH < *i*-PrOH < PrdOH < EtOH < EtdOH < MeOH.

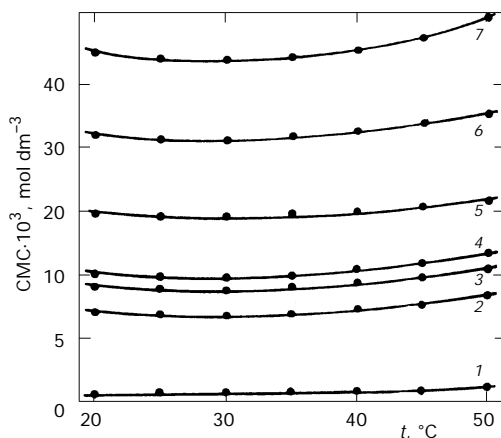


FIG. 2

Plots of CMC vs temperature for CPBr in the following solvents: water (1), *n*-BuOH (2), *i*-BuOH (3), *t*-BuOH (4), *n*-PrOH (5), EtOH (6) and MeOH (7)

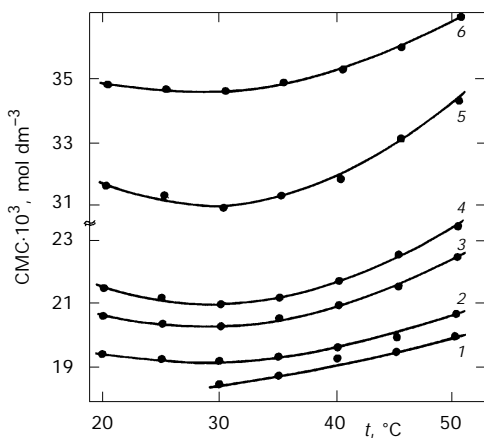


FIG. 3

Plots of the CMC for CPBr vs temperature in PrtOH (1), *n*-PrOH (2), *i*-PrOH (3), PrdOH (4), EtOH (5) and EtdOH (6)

Similar results were obtained by Emerson and Holtzer¹⁴ who examined the effect of alcohols on sodium dodecylsulphate and dodecyltrimethylammonium bromide micellization as well as by Chung^{15,16} who studied the effect of methanol, ethanol and propanol on hexadecylpyridinium chloride and bromide by spectrophotometric techniques. The effect of alcohols containing short hydrophobic chains on micellization of ionic tensides is usually explained by lowering the surface charge density caused by entering the alcohols into the outermost layer of the micelle, *i.e.*, by solubilization of alcohols in micelles (system tenside–alcohol) or by alcohol-induced changes in water structure (mixed solutions water–alcohol–tenside); free energy of micellization could also be affected by the dielectric constant of alcohols.

When the conductometric measurements were carried out in a broader concentration range (in order to find the concentration range necessary to detect the CMC), two break-points were clearly seen on the conductivity curves. According to ref.¹⁷, the two break-points, 1 and 2, were assigned to the CMC and the concentration (c), corresponding to a change of the micelle shape, respectively (Fig. 4). The c values (curve 1, Fig. 5) and the CMC (curve 2) for CPBr in alcohols at 25 °C are summarized in Table II. It is obvious that both dependences have a linear trend and the c values are roughly two times higher than the CMC.

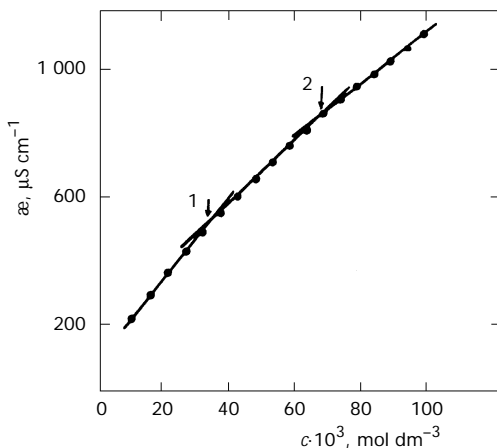


FIG. 4

Conductivity curve for CPBr in ethanol at 25 °C with two break-points corresponding to CMC (1) and concentration corresponding to a change of the micelle shape (2)

Slopes of the dependence $\kappa = f(c_{\text{CPBr}})$ were used to calculate the degrees of counterion binding (β), according to Eq. (1) (as well as Eqs (2) and (3) in the case of aqueous solutions) (Table III and Figs 6, 7). The β values calculated by using the two equations in the aqueous environment are in good agreement. In all solutions, the degrees of counterion binding decrease

TABLE II
Calculated values of the concentrations (c) of CPBr corresponding to a change of the micelle shape and the CMCs in alcohols at 25 °C

| Alcohol | $c \cdot 10^3, \text{ mol dm}^{-3}$ | CMC $\cdot 10^3, \text{ mol dm}^{-3}$ |
|---------|-------------------------------------|---------------------------------------|
| MeOH | 87.94 | 43.82 |
| EtOH | 64.94 | 31.40 |
| EtdOH | 69.00 | 34.68 |
| n-PrOH | 39.03 | 19.30 |
| i-PrOH | 41.00 | 20.40 |
| PrdOH | 42.00 | 21.17 |
| n-BuOH | 14.05 | 6.80 |
| i-BuOH | 17.00 | 8.89 |
| t-BuOH | 20.01 | 9.81 |

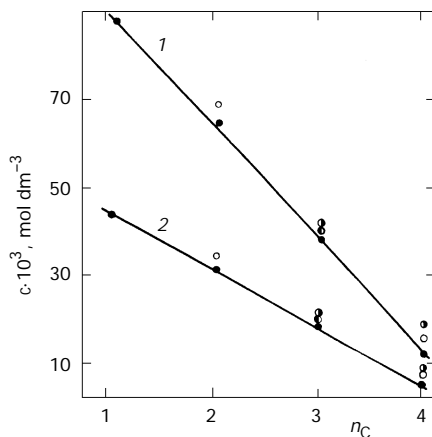


FIG. 5
Plots of concentrations (1) and CMC (2) for CPBr vs the number of carbons in the alkyl chain of alcohols at 25 °C; ● n-alcohols, ○ isobutanol, ● t-butanol

TABLE III
Degrees of counterion binding (β) for CPBr in water and alcohols

| Solvent | $t, ^\circ\text{C}$ | | | | | | |
|----------------------------|---------------------|-------|-------|-------|-------|-------|-------|
| | 20 | 25 | 30 | 35 | 40 | 45 | 50 |
| H ₂ O (Eq.(1)) | 0.695 | 0.692 | 0.674 | 0.653 | 0.631 | 0.611 | 0.590 |
| H ₂ O(Eq.(2,3)) | 0.697 | 0.690 | 0.674 | 0.653 | 0.623 | 0.608 | 0.575 |
| MeOH | 0.350 | 0.347 | 0.341 | 0.338 | 0.330 | 0.326 | 0.312 |
| EtOH | 0.320 | 0.318 | 0.316 | 0.313 | 0.304 | 0.292 | 0.277 |
| EtdOH | 0.337 | 0.335 | 0.333 | 0.330 | 0.327 | 0.321 | 0.310 |
| n-PrOH | 0.280 | 0.278 | 0.273 | 0.267 | 0.259 | 0.251 | 0.239 |
| i-PrOH | 0.307 | 0.305 | 0.301 | 0.294 | 0.287 | 0.276 | 0.260 |
| PrdOH | 0.319 | 0.317 | 0.314 | 0.310 | 0.301 | 0.290 | 0.277 |
| n-BuOH | 0.243 | 0.241 | 0.236 | 0.230 | 0.221 | 0.212 | 0.201 |
| i-BuOH | 0.254 | 0.252 | 0.250 | 0.247 | 0.238 | 0.227 | 0.215 |
| <i>t</i> -BuOH | 0.262 | 0.258 | 0.257 | 0.253 | 0.246 | 0.237 | 0.225 |
| PrtOH | - | - | 0.356 | 0.352 | 0.342 | 0.334 | 0.320 |

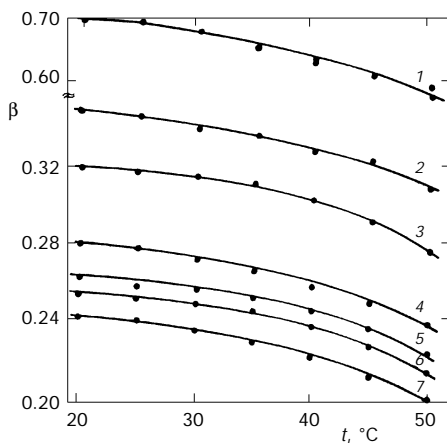


FIG. 6
Dependence $\beta = f(t)$ for CPBr in water (1), MeOH (2), EtOH (3), n-PrOH (4), *t*-BuOH (5), i-BuOH (6) and n-BuOH (7)

with temperature but in alcohols they increase in the order $n\text{-BuOH} < i\text{-BuOH} < t\text{-BuOH} < n\text{-PrOH} < i\text{-PrOH} < \text{PrdOH} = \text{EtOH} < \text{EtdOH} < \text{MeOH} < \text{PrtOH} < \text{H}_2\text{O}$.

Branching, lengthening of the alkyl chain in alcohols and increasing the number of the hydroxy groups suppresses micellization and increase the β values.

Values of the thermodynamic functions of micellization were calculated for models PS_1 , PS_2 and MA. The values of standard molar Gibbs energy for all three models are given in Table IV and for model PS_1 also in Fig. 8. As it is seen, in the case of model PS_1 and in the given temperature interval the $\Delta_m G^0$ values decrease by about 1 kJ mol^{-1} and in the methanolic solution they pass through a shallow minimum at 318.15 K. For the PS_2 model the $\Delta_m G^0$ values are two times lower and hence their drop amounts to 2 kJ mol^{-1} , while for the MA model the $\Delta_m G^0$ values are intermediate between those for PS_1 and PS_2 and due to variations in the degrees of counterion binding all dependences $\Delta_m G^0 = f(T)$ pass through a minimum at 313.15 (or 318.15) K.

The standard molar enthalpy changes ($\Delta_m H^0$) calculated according to Eq. (6) are summarized in Table V. As shown in the table, the drop in $\Delta_m H^0$ is remarkable; in aqueous media $\Delta_m H^0$ takes only negative values, in alcohols a switch from positive to negative values is observed, the overall drop in the temperature interval studied being as much as 40 kJ mol^{-1} , the switch to negative values occurs at 303.15 and 308.15 K for methanol and ethanol,

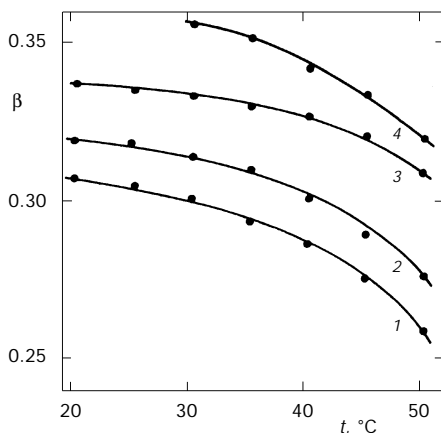


FIG. 7

Degrees of counterion binding β of CPBr as a function of temperature in alcoholic solutions: EtdOH (1), $i\text{-PrOH}$ (2), PrdOH (3) and PrtOH (4)

TABLE IV
Standard molar Gibbs energies ($\Delta_m G^0$, kJ mol⁻¹) of micellization for CPBr in water and alcohols

| Solvent | | $\Delta_m G^0$, kJ mol ⁻¹ | | | | | | |
|------------------|-----------------|---------------------------------------|--------|--------|--------|--------|--------|--------|
| | | 293.15 | 298.15 | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 |
| H ₂ O | PS ₁ | -17.94 | -18.21 | -18.40 | -18.64 | -18.77 | -18.91 | -18.93 |
| | PS ₂ | -35.88 | -36.42 | -36.80 | -37.28 | -37.54 | -37.82 | -37.86 |
| | MA | -30.41 | -30.77 | -30.80 | -30.81 | -30.61 | -30.46 | -30.10 |
| MeOH | PS ₁ | -7.61 | -7.75 | -7.91 | -8.02 | -8.10 | -8.14 | -8.08 |
| | PS ₂ | -15.22 | -15.50 | -15.82 | -16.04 | -16.20 | -16.28 | -16.16 |
| | MA | -10.27 | -10.44 | -10.61 | -10.73 | -10.77 | -10.79 | -10.60 |
| EtOH | PS ₁ | -8.42 | -8.58 | -8.76 | -8.85 | -8.97 | -9.01 | -9.06 |
| | PS ₂ | -16.84 | -17.16 | -17.52 | -17.70 | -17.94 | -18.02 | -18.12 |
| | MA | -11.11 | -11.31 | -11.53 | -11.62 | -11.70 | -11.64 | -11.57 |
| EtdOH | PS ₁ | -8.19 | -8.33 | -8.48 | -8.60 | -8.71 | -8.80 | -8.87 |
| | PS ₂ | -16.38 | -16.66 | -16.96 | -17.20 | -17.42 | -17.60 | -17.74 |
| | MA | -10.95 | -11.12 | -11.30 | -11.44 | -11.56 | -11.62 | -11.62 |
| n-PrOH | PS ₁ | -9.61 | -9.79 | -9.96 | -10.11 | -10.23 | -10.35 | -10.42 |
| | PS ₂ | -19.22 | -19.58 | -19.92 | -20.22 | -20.46 | -20.70 | -20.84 |
| | MA | -12.30 | -12.51 | -12.68 | -12.81 | -12.88 | -12.95 | -12.92 |
| i-PrOH | PS ₁ | -9.46 | -9.65 | -9.82 | -9.95 | -10.06 | -10.14 | -10.19 |
| | PS ₂ | -18.92 | -19.30 | -19.64 | -19.90 | -20.12 | -20.28 | -20.38 |
| | MA | -12.36 | -12.59 | -12.78 | -12.88 | -12.95 | -12.94 | -12.87 |
| PrdOH | PS ₁ | -9.36 | -9.56 | -9.74 | -9.87 | -9.96 | -10.03 | -10.09 |
| | PS ₂ | -18.72 | -19.12 | -19.48 | -19.74 | -19.92 | -20.06 | -20.18 |
| | MA | -12.34 | -12.59 | -12.80 | -12.93 | -12.96 | -12.94 | -12.88 |
| n-BuOH | PS ₁ | -12.09 | -12.37 | -12.56 | -12.73 | -12.86 | -12.91 | -12.94 |
| | PS ₂ | -24.18 | -24.74 | -25.12 | -25.46 | -25.72 | -25.82 | -25.88 |
| | MA | -15.03 | -15.35 | -15.52 | -15.65 | -15.70 | -15.65 | -15.54 |
| i-BuOH | PS ₁ | -11.48 | -11.71 | -11.91 | -12.09 | -12.22 | -12.29 | -12.34 |
| | PS ₂ | -22.96 | -23.42 | -23.82 | -24.18 | -24.44 | -24.58 | -24.68 |
| | MA | -14.40 | -14.66 | -14.89 | -15.08 | -15.13 | -15.08 | -15.00 |
| t-BuOH | PS ₁ | -11.22 | -11.46 | -11.67 | -11.82 | -11.92 | -12.02 | -12.07 |
| | PS ₂ | -22.44 | -22.92 | -23.34 | -23.64 | -23.84 | -24.04 | -24.14 |
| | MA | -14.16 | -14.42 | -14.67 | -14.81 | -14.85 | -14.87 | -14.79 |
| PrtOH | PS ₁ | - | - | -10.05 | -10.18 | -10.27 | -10.41 | -10.51 |
| | PS ₂ | - | - | -20.10 | -20.36 | -20.54 | -20.82 | -21.02 |
| | MA | - | - | -13.63 | -13.76 | -13.78 | -13.89 | -13.87 |

respectively. As shown in Fig. 9, the dependences $\Delta_m H^0 = f(T)$ for methanol, ethanol and propanol intersect at 305 K. The decrease of $\Delta_m H^0$ indicates that the process of micellization becomes more exothermic as the temperature increases. The standard molar entropy changes decreased (Table VI).

From compensation dependences $\Delta_m H^0 = f(\Delta_m S^0)$ for all models, the compensation temperatures (T_c) were calculated and the mean values are given in Table VII. Except for ethanol and n-butanol, the T_c values range from 302 to 307 K which is close to the temperature at which the enthalpic dependences of alcohols intersect. The correlation coefficient of all dependences was at least 0.999.

Another parameter derived from the thermodynamic functions concerns the reference temperature T^* , their mean values are also given in Table VII. The reference temperatures fall in the range 318–344 K and the highest value corresponds to propanol. The $\Delta_m S^*$ values as calculated according to the Eq. (9) as well as dependences $\Delta_m C_p$ are summarized in Table VIII.

In the last part of the work, we studied the effect of alcohols in the mixed (alcohol–water) solutions on the CMC of CPBr. The measurements were made at a single temperature (25 °C) and the volume ratio of alcohol–water was $\varphi = 0, 0.1, 0.3, 0.5, 0.7, 0.9, 1.0$. Based on the conductivity curves, the CMC values were calculated and are given in Table IX and Figs 10, 11.

Comparing the variations in the CMC caused by increasing the temperature and the volume ratio of alcohols it can be concluded that the effect of

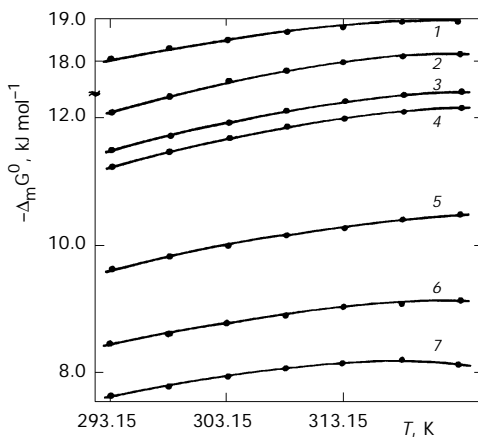


FIG. 8

Plots of $\Delta_m G^0$ vs temperature for CPBr in water (1), n-BuOH (2), i-BuOH (3), t-BuOH (4), n-PrOH (5), EtOH (6) and MeOH (7) for model PS₁

TABLE V
Standard molar enthalpies ($\Delta_m H^0$, kJ mol⁻¹) of micellization for CPBr in water and alcohols

| Solvent | | $\Delta_m H^0$, kJ mol ⁻¹ | | | | | | |
|------------------|-----------------|---------------------------------------|--------|--------|--------|--------|--------|--------|
| | | 293.15 | 298.15 | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 |
| H ₂ O | PS ₁ | -0.95 | -3.08 | -5.37 | -7.80 | -10.37 | -13.13 | -16.00 |
| | PS ₂ | -1.90 | -6.16 | -10.74 | -15.60 | -20.74 | -26.26 | -32.00 |
| | MA | -1.61 | -5.21 | -8.99 | -12.89 | -16.91 | -17.93 | -25.44 |
| MeOH | PS ₁ | 6.07 | 3.52 | 0.78 | -2.15 | -5.27 | -8.58 | -12.10 |
| | PS ₂ | 12.14 | 7.54 | 1.56 | -4.30 | -10.54 | -17.16 | -24.20 |
| | MA | 8.19 | 4.74 | 1.05 | -2.88 | -7.00 | -11.38 | -15.87 |
| EtOH | PS ₁ | 3.65 | 1.92 | 0.065 | -1.91 | -4.02 | -6.27 | -8.64 |
| | PS ₂ | 7.30 | 3.84 | 0.13 | -3.82 | -8.04 | -12.54 | -17.28 |
| | MA | 4.82 | 2.53 | 0.086 | -2.51 | -5.24 | -8.10 | -11.03 |
| EtdOH | PS ₁ | 1.43 | 0.53 | -0.44 | -1.47 | -2.57 | -3.74 | -4.98 |
| | PS ₂ | 2.86 | 1.06 | -0.88 | -2.94 | -5.14 | -7.48 | -9.96 |
| | MA | 1.91 | 0.71 | -0.59 | -1.96 | -3.41 | -4.94 | -6.52 |
| n-PrOH | PS ₁ | 1.94 | 0.89 | -0.23 | -1.43 | -2.71 | -4.07 | -5.51 |
| | PS ₂ | 3.88 | 1.78 | -0.46 | -2.86 | -5.42 | -8.14 | -11.02 |
| | MA | 2.48 | 1.14 | -0.29 | -1.81 | -3.41 | -5.09 | -6.83 |
| i-PrOH | PS ₁ | 2.06 | 0.63 | -0.91 | -2.55 | -4.30 | -6.15 | -8.12 |
| | PS ₂ | 4.14 | 1.26 | -1.82 | -5.10 | -8.60 | -12.30 | -16.24 |
| | MA | 3.40 | 0.82 | -1.18 | -3.30 | -5.53 | -7.85 | -10.23 |
| PrdOH | PS ₁ | 2.91 | 1.25 | -0.52 | -2.41 | -4.42 | -6.57 | -8.84 |
| | PS ₂ | 5.82 | 2.50 | -1.04 | -4.82 | -8.84 | -13.14 | -17.68 |
| | MA | 3.84 | 1.65 | -0.68 | -3.16 | -5.75 | -8.48 | -11.29 |
| n-BuOH | PS ₁ | 3.42 | 0.58 | -2.46 | -5.70 | -9.15 | -12.81 | -16.69 |
| | PS ₂ | 6.84 | 1.16 | -4.92 | -11.40 | -18.30 | -25.62 | -33.38 |
| | MA | 4.25 | 0.72 | -3.04 | -7.01 | -11.17 | -15.53 | -19.96 |
| i-BuOH | PS ₁ | 3.31 | 1.26 | -0.92 | -3.26 | -5.75 | -8.39 | -11.19 |
| | PS ₂ | 6.62 | 2.52 | -1.84 | -6.52 | -11.50 | -16.78 | -22.38 |
| | MA | 4.15 | 1.58 | -1.15 | -4.06 | -7.12 | -10.29 | -13.60 |
| t-BuOH | PS ₁ | 3.72 | 1.63 | -0.60 | -2.99 | -5.54 | -8.24 | -11.10 |
| | PS ₂ | 7.44 | 3.26 | -1.20 | -5.98 | -11.08 | -16.48 | -22.20 |
| | MA | 4.69 | 2.05 | -0.75 | -3.75 | -6.90 | -10.19 | -13.60 |
| PrtOH | PS ₁ | - | - | -2.88 | -2.95 | -3.01 | -3.08 | -3.14 |
| | PS ₂ | - | - | -5.76 | -5.90 | -6.02 | -6.16 | -6.28 |
| | MA | - | - | -3.91 | -3.99 | -4.04 | -4.11 | -4.14 |

TABLE VI
Standard molar entropies ($\Delta_m S^0$, kJ mol⁻¹ K⁻¹) of micellization for CPBr in water and alcohols

| Solvent | | $\Delta_m S^0$, kJ mol ⁻¹ K ⁻¹ | | | | | | |
|------------------|-----------------|---|--------|--------|--------|--------|---------|--------|
| | | 293.15 | 298.15 | 303.15 | 308.15 | 313.15 | 318.15 | 323.15 |
| H ₂ O | PS ₁ | 0.058 | 0.051 | 0.043 | 0.035 | 0.027 | 0.018 | 0.009 |
| | PS ₂ | 0.116 | 0.102 | 0.086 | 0.070 | 0.054 | 0.036 | 0.018 |
| | MA | 0.098 | 0.086 | 0.072 | 0.058 | 0.044 | 0.029 | 0.014 |
| MeOH | PS ₁ | 0.047 | 0.038 | 0.029 | 0.019 | 0.009 | -0.0014 | -0.012 |
| | PS ₂ | 0.094 | 0.076 | 0.058 | 0.038 | 0.018 | -0.0028 | -0.024 |
| | MA | 0.063 | 0.051 | 0.039 | 0.025 | 0.012 | -0.0019 | -0.016 |
| EtOH | PS ₁ | 0.045 | 0.035 | 0.029 | 0.023 | 0.016 | 0.008 | 0.0013 |
| | PS ₂ | 0.090 | 0.070 | 0.058 | 0.046 | 0.032 | 0.016 | 0.0026 |
| | MA | 0.059 | 0.046 | 0.038 | 0.030 | 0.021 | 0.010 | 0.0017 |
| EtdOH | PS ₁ | 0.033 | 0.030 | 0.026 | 0.023 | 0.020 | 0.016 | 0.012 |
| | PS ₂ | 0.066 | 0.060 | 0.052 | 0.046 | 0.040 | 0.032 | 0.024 |
| | MA | 0.044 | 0.040 | 0.035 | 0.031 | 0.026 | 0.021 | 0.016 |
| n-PrOH | PS ₁ | 0.039 | 0.036 | 0.032 | 0.028 | 0.024 | 0.020 | 0.015 |
| | PS ₂ | 0.078 | 0.072 | 0.064 | 0.056 | 0.048 | 0.040 | 0.030 |
| | MA | 0.032 | 0.050 | 0.041 | 0.036 | 0.030 | 0.025 | 0.019 |
| i-PrOH | PS ₁ | 0.039 | 0.034 | 0.029 | 0.024 | 0.018 | 0.012 | 0.006 |
| | PS ₂ | 0.078 | 0.068 | 0.058 | 0.048 | 0.036 | 0.024 | 0.013 |
| | MA | 0.051 | 0.044 | 0.038 | 0.031 | 0.023 | 0.015 | 0.008 |
| PrdOH | PS ₁ | 0.042 | 0.036 | 0.030 | 0.024 | 0.018 | 0.011 | 0.004 |
| | PS ₂ | 0.084 | 0.072 | 0.060 | 0.048 | 0.036 | 0.022 | 0.008 |
| | MA | 0.055 | 0.047 | 0.039 | 0.031 | 0.023 | 0.014 | 0.005 |
| n-BuOH | PS ₁ | 0.053 | 0.043 | 0.033 | 0.023 | 0.012 | 0.003 | -0.012 |
| | PS ₂ | 0.106 | 0.086 | 0.066 | 0.046 | 0.024 | 0.006 | -0.024 |
| | MA | 0.066 | 0.053 | 0.041 | 0.028 | 0.015 | 0.004 | -0.014 |
| i-BuOH | PS ₁ | 0.050 | 0.044 | 0.036 | 0.029 | 0.021 | 0.012 | 0.004 |
| | PS ₂ | 0.100 | 0.088 | 0.072 | 0.058 | 0.042 | 0.024 | 0.008 |
| | MA | 0.063 | 0.055 | 0.045 | 0.036 | 0.026 | 0.015 | 0.005 |
| t-BuOH | PS ₁ | 0.051 | 0.044 | 0.037 | 0.029 | 0.020 | 0.012 | 0.003 |
| | PS ₂ | 0.102 | 0.088 | 0.074 | 0.058 | 0.040 | 0.024 | 0.006 |
| | MA | 0.064 | 0.055 | 0.047 | 0.036 | 0.025 | 0.015 | 0.004 |
| PrtOH | PS ₁ | - | - | 0.0237 | 0.0234 | 0.0232 | 0.0230 | 0.0228 |
| | PS ₂ | - | - | 0.0474 | 0.0468 | 0.0464 | 0.0460 | 0.0456 |
| | MA | - | - | 0.0321 | 0.0316 | 0.0311 | 0.0307 | 0.0300 |

TABLE VII
 Compensation (T_c) and reference (T^*) temperatures for CPBr in the solvents used

| Solvent | T_c , K | T^* , K |
|------------------|-----------|-----------|
| H ₂ O | 289.10 | 328.90 |
| MeOH | 307.00 | 318.10 |
| EtOH | 289.00 | 325.80 |
| EtdOH | 305.70 | 338.04 |
| n-PrOH | 305.20 | 343.40 |
| i-PrOH | 306.70 | 327.80 |
| PrdOH | 302.61 | 327.00 |
| n-BuOH | 312.60 | 316.10 |
| i-BuOH | 307.40 | 326.00 |
| <i>t</i> -BuOH | 306.60 | 325.30 |
| PrtOH | 307.20 | – |

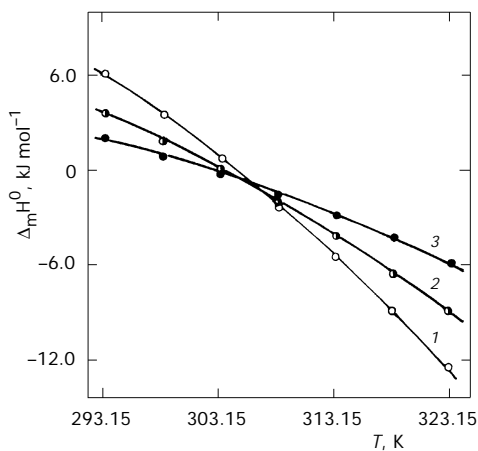


FIG. 9
 Plots of $\Delta_m H^0$ vs temperature for CPBr in MeOH (1), EtOH (2) and n-PrOH (3)

TABLE VIII
Calculated values of $\Delta_m S^*$ and $\Delta_m C_p$ for CPBr in the solvents

| Solvent | $\Delta_m C_p$, J mol ⁻¹ K ⁻¹ | $\Delta_m S^*$ J mol ⁻¹ K ⁻¹ |
|------------------|--|--|
| H ₂ O | -865.5 | 18.7 |
| MeOH | -810.0 | 10.7 |
| EtOH | -576.2 | 2.3 |
| EtdOH | -285.7 | 2.8 |
| n-PrOH | -338.7 | 1.6 |
| i-PrOH | -441.0 | 3.6 |
| PrdOH | -507.9 | 0.7 |
| n-BuOH | -863.7 | 0.7 |
| i-BuOH | -617.9 | 0.8 |
| t-BuOH | -619.5 | 1.1 |

TABLE IX
CMC values (in 10⁻³ mol dm⁻³) for CPBr in mixed alcohol-water solvents at 25 °C (ϕ is the alcohol volume fraction)

| Solvent | ϕ | | | | | | |
|---------|--------|------|------|-------|-------|-------|-------|
| | 0 | 0.1 | 0.3 | 0.5 | 0.7 | 0.9 | 1.0 |
| MeOH | 0.645 | 1.20 | 3.90 | 12.20 | 20.60 | 32.86 | 43.82 |
| EtOH | 0.645 | 1.11 | 2.37 | 6.80 | 11.18 | 23.00 | 31.40 |
| EdtOH | 0.645 | 0.82 | 3.32 | 6.93 | 15.07 | 28.20 | 34.68 |
| n-PrOH | 0.645 | 0.78 | 1.43 | 2.67 | 5.98 | 12.23 | 19.30 |
| i-PrOH | 0.645 | 0.81 | 1.50 | 2.83 | 7.58 | 18.98 | 22.50 |
| PrdOH | 0.645 | 0.76 | 3.10 | 7.93 | 12.66 | 18.00 | 21.17 |
| t-BuOH | 0.645 | 1.03 | 1.69 | 2.88 | 5.66 | 8.14 | 9.81 |
| PrtOH | 0.645 | 0.73 | 0.97 | 1.53 | 2.54 | - | - |

temperature on the CMC is much less pronounced relative to the concentration of the alcohol.

In conclusion, as shown above, a study of thermodynamics of micellization becomes more and more important to understand the forces controlling the process of micellization as well as to predict the micellar properties and their

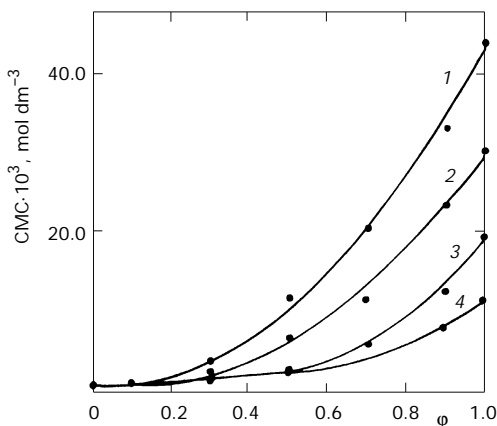


FIG. 10

Dependence $\text{CMC} = f(\phi)$ for CPBr in mixed aqueous solvents with MeOH (1), EtOH (2), PrOH (3) and *t*-BuOH (4)

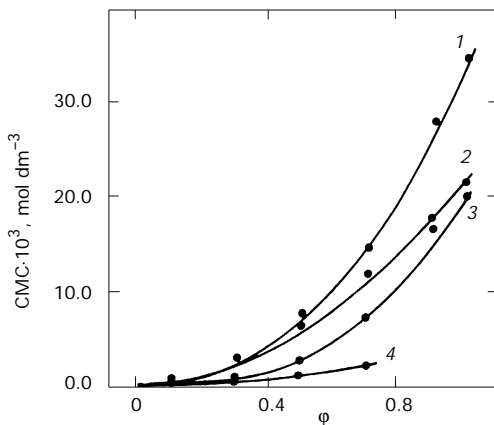


FIG. 11

Plots of the CMC vs the volume ratio at CPBr in mixed (alcohol-water) solutions: EtdOH (1), *i*-PrOH (2), PrdOH (3) and PrtOH (4) at 25 °C

changes due to a variety of factors, such as temperature, the length of the alkyl chain in the tenside molecule, presence of additives, ionic strength, etc.

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