

**THERMODYNAMICS OF MICELLIZATION OF
HEXADECYLTRIMETHYLAMMONIUM BROMIDE
IN PROPYLENE GLYCOL–WATER MIXTURE:
A CONDUCTIVITY STUDY**

UDC [544.3 : 532.74] : 544.62

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Abstract. *Micellization of hexadecyltrimethylammonium bromide (syn. cetyltrimethylammonium bromide, CTAB) in propylene glycol–water (30% v/v) binary mixture, as well as the thermodynamic properties of the resulting micelles, were investigated by electrical conductivity measurements. The conductivity data were used to determine both the critical micellar concentration (CMC) and the micellar ionization degree (α) of CTAB in the temperature range 298.2–310.2 K. The equilibrium model of micelle formation was applied in order to obtain the thermodynamic parameters (the standard molar Gibbs free energy, ΔG_m^0 , enthalpy, ΔH_m^0 and entropy, ΔS_m^0) of the micellization process. The values of ΔG_m^0 and ΔH_m^0 were found to be negative at all investigated temperatures, while the values of ΔS_m^0 were positive and became more positive as temperature increased. A linear dependence between ΔS_m^0 and ΔH_m^0 , i.e. an enthalpy–entropy compensation effect, was observed.*

Key words: *hexadecyltrimethylammonium bromide, critical micellar concentration, propylene glycol–water mixture, thermodynamics of micellization, enthalpy–entropy compensation*

1. INTRODUCTION

Surfactants are amphiphile molecules composed of two parts, one (polar; hydrophilic headgroup or liophobic segment) which is soluble in a specific polar solvent and the other (nonpolar; hydrophobic organic segment or lipophilic tail) that is insoluble. Based on the nature of their hydrophilic group—this is scientifically broadly accepted classification—surfactants may be divided into three main groups: ionic (anionic and cationic), amphoteric and

Received March 06th, 2014; revised May 21st, 2014; accepted July 09th, 2014

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nonionic [1, 2]. In this work, we investigated cationic surfactant, hexadecyltrimethylammonium bromide (*syn.* cetyltrimethylammonium bromide, CTAB) (Fig. 1), which dissociated in water into cation of surfactant and bromide counterion. This surfactant is widely used as antiseptic, solubilizing agent for pharmaceuticals, in electrophoresis of proteins (for extraction of DNA), in hair conditioning products, and so forth.

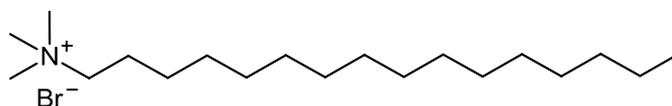


Fig. 1 Chemical structure of cetyltrimethylammonium bromide (CTAB)

Upon dispersion in water, and above the concentration known as the critical micelle concentration (CMC), the surfactants hydrophobic segment tend to minimize its exposure to solvent; due to this, molecules of surfactant self-associate to form aggregates (called micelles). Besides temperature, pH and pressure, the surfactant micelle formation in an aqueous solution is highly depend on presence of additives such as cosolvent, co-surfactants and electrolytes [2, 3]. Thus, much effort has been devoted to exploring nature of micellization and surfactant behavior in binary mixtures of organic solvent with water as well as in polar organic solvents (nonaqueous polar medium) [4-16].

Interfacial and micelle properties of surfactants in the presence of polar organic solvents, as cosolvents added to water, are modified due to both, cosolvent specific interactions with surfactant molecules, and modification of water-surfactant interaction (because of the changing of the bulk solvent properties) [4-6]. Considering significant application of surfactants in nonaqueous media (as lubricants or cleaners), the investigation of cosolvent influence on micellar and physicochemical properties of surfactants has wide interests in both the fundamental as well as in the applied research [7, 8]. Because of their water-resembling like properties (high dielectric constant, a high cohesive energy and a significant hydrogen bonding ability), polar organic solvents such as formamide, ethylene glycol, glycerol, *etc.*, have been studied extensively. The most common methodology used for studying micellization of various surfactants in water-organic solvent mixtures is based on gradual exchange of water for another (polar) solvent [5-14]. This methodology allows a simple characterization of the examined system (determination of structural properties of aggregates formed in those media, as well as revealing which properties the solvent should have in order to form micelle). On the other hand, in view of the fact that the micellar properties of surfactant sensitive to temperature changes, a lot of information on the strength and the nature of solvent-surfactant and solvent-solvent interactions can be obtained from the thermodynamic properties of micellization. These are also useful for uncovering (possible) relationship between solvophobic or hydrophobic effects [4, 15] and tendency of surfactant tails to minimize their contact with the bulk phase (water or organic solvent-water mixture) and aggregate.

Micellar properties and thermodynamic parameters of micelization of CTAB were investigated, both in aqueous media [12, 16-18], and in mixtures of water and various organic solvents such as *N*-methylacetamide, *N*-methylpropionamide, dimethyl sulfoxide, formamide, *N*-methylformamide, *N,N*-dimethylformamide [5, 16, 19], ethanol [12], propanol [20], butanol [20], glycerol [21, 22] and ethylene glycol [12, 15, 23]. A lot of effort has been made to investigate the effect of various glycols (e.g. propylene glycol, PG) on the

surfactant aggregation and micellar properties since these solvents are widely used in different products (foods, pharmaceuticals, cosmetics and personal care products, *etc.*), whereby most of these products also contain surfactants. Recently, Rodríguez et al. [9], investigated the effects of various glycols on aggregation of tetradecyltrimethylammonium bromide. To our knowledge, however, no previous studies of the role of propylene glycol on the micellar characteristics of CTAB were carried out.

The aim of this work was to investigate the influence of temperature on the micellization process of CTAB in PG–water (30% *v/v*) binary mixture. For this reason, we have carried out a series of conductivity measurements, in the temperature range 298.2–310.2 K. The CMC values and degree of micellar ionization (α) corresponding to each temperature were obtained from the conductivity data, and all were determined from inflections in plots of conductivity against surfactant concentration (William's method [24]). Also, to get more precise values of CMC and α we have applied method of Carpena et al. [25]. From the temperature dependence on CMC acquired by this method, and considering the equilibrium model for micelle formation, we have obtained the corresponding thermodynamic parameters of micellization (the standard molar Gibbs free energy (ΔG_m^0), enthalpy (ΔH_m^0) and entropy (ΔS_m^0)).

2. MATERIALS AND METHODS

2.1. Chemicals

The cationic surfactant, hexadecyltrimethylammonium (*syn.* cetyltrimethyl-ammonium bromide, CTAB; purity $\geq 97\%$) was obtained by Merck (Germany) and was used without any pretreatment. Propylene glycol, PG (1,2-propylene glycol, purity $> 99.5\%$) was obtained by Carlo Erba (Italy). Deionized water ($\rho = 18 \text{ M}\Omega \text{ cm}$, Milli-Q, Millipore, Bedford, MA, USA) was used for all solutions preparing.

Fresh solutions of CTAB in PG–water (30% *v/v*) binary mixtures were prepared in the following way. The accurately weighed (Mettler electronic balance with a precession of 0.0001 g) mass of CTAB was quantitatively transferred into a 100 mL volumetric beaker, and dissolved in 90 mL of 30% (*v/v*) PG; the mixture was gently stirred with a glass rod in order to avoid the foam formation. Then, the solution was transferred into 100 mL volumetric flask and made up to volume with 30% (*v/v*) PG.

2.2. Apparatus

The conductivity measurements were carried out with digital conductivity meter HI8820N (Hanna instruments, Portugal) with the accuracy $\pm 0.5\%$, and with the matching HI7684W probe that uses the 4–ring method. Specific conductivity values of each set containing 18 different CTAB concentrations at a fixed solvent composition were taken at different working temperatures (298.2, 302.2, 306.2 and 310.2 K). A circulating water bath (Series U, MLW, Frital, Germany) was used for maintaining the constant temperature within uncertainties of $\pm 0.1 \text{ K}$.

All measurements were conducted in glass vessel, $V \approx 100 \text{ mL}$ (Metrohm Model 876–20) wrapped in the water recirculation jacket connected to thermostat and equipped with the magnetic stirrer (IKA–COMBIMAG RET, Staufen, Germany).

2.3. Procedure

The 90 mL solution of CTAB of different concentrations was introduced into the glass vessel that was capped with openings through which thermometer and conductometric cell are always put in the same place. Then, CTAB solution was thermostated (20 min) at some of the examined temperatures (298.2, 302.2, 306.2 and 310.2 K) along with stirring (300 rpm), and equilibrated until the conductivity value becomes constant. For each of the examined solution CTAB, the specific conductivity measurements were repeated three times.

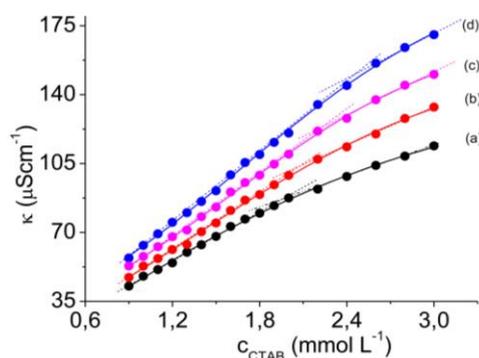


Fig. 2 Plots of specific conductivity (κ) versus total concentration of CTAB (c_{CTAB}) in PG–water mixture (30% (v/v) at different temperatures: 298.2 K (a), 302.2 K (b), 306.2 K (c) and 310.2 K (d). At each temperature, the solid line corresponds to the Carpena's fitting

The data points above and below the inflection were fit by the least square method (correlation coefficients were greater than 0.999 in all cases) to two equations of the form: $\kappa = A + S \times c_{\text{CTAB}}$, and by two equation solving, the point of intersection (CMC) was obtained [23, 24, 26]. The obtained values of the CMC of CTAB as well as slopes below (S_1) and above (S_2) the CMC in the conductivity–concentration plots at different temperatures, are all summarized in Table 1.

3. RESULTS AND DISCUSSION

3.1. Critical micellar concentration (CMC) and micelle ionization degree (α)

The CMC value of CTAB in PG–water (30% v/v) binary mixture was determined from inflection in plot of specific conductivity, κ against concentration of CTAB, c_{CTAB} . Representative plots, $\kappa = f(c_{\text{CTAB}})$ at different temperatures, 298.2 K, 302.2 K, 306.2 K and 310.2 K are shown in Figure 2. The obtained graphical dependence is a curve which consists of two segments (premicellar and postmicellar); each plot shows the single break point at a certain temperature.

Table 1 Critical micellar concentration (CMC), slopes of lines in both premicellar (S_1) and posmicellar (S_2) region and micellar ionization degrees of CTAB in mixture propylene glycol-water (30% (v/v) at different temperatures. The values given in parentheses obtained by method of Carpena et al. [25].

T (K)	CMC (mmol L ⁻¹)	S_1 ($\mu\text{S dm}^2 \text{mol}^{-1}$)	S_2 ($\mu\text{S dm}^2 \text{mol}^{-1}$)	α
298.2	1.91 (1.85)	41.336 (43.069)	26.928 (27.145)	0.651 (0.630)
302.2	2.03 (2.09)	48.164 (48.795)	35.400 (31.472)	0.735 (0.645)
306.2	2.21 (2.38)	52.450 (51.536)	42.000 (32.519)	0.801 (0.631)
310.2	2.43 (2.63)	58.300 (57.318)	49.700 (35.480)	0.852 (0.619)

The micellar ionization degree (α) was estimated from the ratio of the slopes of the linear segments above and below CMC: $\alpha = S_2/S_1$ [27]. The values of α at various temperatures are summarized in Table 1.

Besides the above-described "conventional procedure" (William's method [24]) for the CMC and α determination, in order to find out precise CMC values from conductivity data, different fitting procedures to the experimental data have also been applied [25, 26]. Thus, in order to improve quality of the calculated CMC and α , the method proposed by Carpena et al. [25] was used. This method is based on the fit of the experimental raw data to a simple nonlinear function obtained by direct integration of Boltzmann type sigmoid function. Fitting to the data was carried out by Origin software (Origin version 8.0.). The solid lines (Fig. 2) correspond to the Carpena's fitting. The values of the CMC and α obtained by this approach are listed in Table 1. Obviously, these values, as well as the values of the CMC and α , obtained by "conventional procedure" appear to be in good agreement at temperatures 298.2 K and 302.2 K, that cannot be said for the other two temperatures. For thermodynamic calculations, temperature dependences of the CMC and α obtained by Carpena's method were used.

The attained values of CMC of CTAB in PG-water mixture (Table 1) are higher than those obtained for CTAB in water [12, 16-18], at a constant temperature. Previously, an increase in the CMC values of different surfactants upon the addition of various solvents [5, 10-12, 14, 16, 19, 22] was acquired. This behavior was found for organic solvents whose presence either increases or decreases the permittivity of the bulk phase, and can only be explained if one takes into account a number of factors that affect the micellization process, such as solvent polarity, solvent interaction, solvophobic forces, *etc.*

For the examined system in selected temperature range, the values of CMC increased with temperature, while values of α slightly changed (Table 1). Generally, the effect of temperature on CMC in aqueous solution may be explained by temperature influence on the degree of hydration of the hydrophilic groups, which decreases with an increase of temperature (this favors micellization). The opposite effect (unfavorable for micellization) is disruption of water structure surrounding the hydrophobic surfactant group, which occurs at higher temperatures [5, 11, 12]. From the obtained results (Table 1) it seems that this second effect is predominant in the studied temperature range.

3.2. Thermodynamic properties

In order to quantify how addition of PG affects the micellization of CTAB, the standard molar Gibbs free energy, enthalpy and entropy of micellization were calculated by means of the equilibrium model for the micelle formation [28], and temperature dependence of CMC.

The change of the standard molar Gibbs free energy, ΔG_m^0 was calculated by using the following equation:

$$\Delta G_m^0 = (2 - \alpha)RT \ln X_{\text{CMC}} \quad (1)$$

where α is the micellar ionization degree, R is the gas constant, T is the Kelvin temperature, and X is the value of CMC expressed in the mole fraction unit [2]. For this calculations, values of the CMC and α obtained by Carpena's method were used.

The corresponding standard molar enthalpy, ΔH_m^0 is given by [2]:

$$\Delta H_m^0 = -RT^2 \left[(2 - \alpha) \left(\frac{\partial \ln X_{\text{CMC}}}{\partial T} \right)_p - \ln X_{\text{CMC}} \left(\frac{\partial \alpha}{\partial T} \right)_p \right] \quad (2)$$

The changes of standard molar enthalpy of micellization, ΔH_m^0 may be obtained from equation (2), if the dependences of the $\ln X_{\text{CMC}}$ as well as α on temperature are known. With this purpose, $\ln X_{\text{CMC}}$ was plotted against T, and the slope at each temperature was taken as $\left(\frac{\partial \ln X_{\text{CMC}}}{\partial T} \right)_p$. The obtained dependence, $\ln X_{\text{CMC}} = f(T)$, is polynomial ($r^2 = 0.9989$). Note

that second term in equation (2) can be neglected due to the fact that values of α vary slightly with temperature.

The change of the standard molar entropy, ΔS_m^0 was calculated from equation:

$$\Delta S_m^0 = \frac{\Delta H_m^0 - \Delta G_m^0}{T} \quad (3)$$

Thermodynamic parameters of CTAB micellization (ΔG_m^0 , ΔH_m^0 and ΔS_m^0) at different temperatures (298.2 K, 302.2 K, 306.2 K and 310.2 K) obtained from equations (1)–(3), are listed in Table 2.

Table 2 Thermodynamic parameters of micellization of CTAB in mixture propylene glycol–water (30% (v/v)) at different temperatures

Thermodynamic parameter	Temperature (K)			
	298.2	302.2	306.2	310.2
ΔG_m^0 (kJ mol ⁻¹)	-35.02	-34.68	-35.06	-35.47
ΔH_m^0 (kJ mol ⁻¹)	-34.44	-32.10	-30.42	-28.39
ΔS_m^0 (kJ mol ⁻¹ K ⁻¹)	0.0019	0.0086	0.0151	0.0228
$T\Delta S_m^0$ (kJ mol ⁻¹)	0.578	2.585	4.639	7.072

The value of ΔG_m^0 was negative at all the considered temperatures (the micellization process is spontaneous), and slightly changes (Table 2) in the investigated temperature range. The value of ΔH_m^0 was negative at all temperatures (the micellization process is exothermic), and becomes less negative as the temperature increases.

In the micellar process of different surfactants, the so-called enthalpy-entropy compensation was obtained [11, 29-31]. This phenomenon reflects a linear correlation between enthalpy and entropy change. For CTAB, such enthalpy-entropy compensation effect was reported for micellization of this surfactant in polar nonaqueous solvents (*N*-methylacetamide, *N,N*-dimethylformamide, formamide and dimethyl sulfoxide) [16]. The slope of compensation line is termed as compensation temperature, T_c [29]. The compensation plot obtained for CTAB in studied PG-water binary mixture is shown in Fig. 3. This curve obeys the following linear regression equation: $\Delta H_m^0 = -34.8 + 286.0 \times \Delta S_m^0$ ($r^2 = 0.997$). At around ΔS_m^0 value of 0.12 $\text{kJ mol}^{-1} \text{K}^{-1}$, ΔH_m^0 becomes zero, and CTAB interaction in this condition is favored only by entropy change. The obtained T_c is 286.05 K. At this temperature the micellization of CTAB is totally independent of structure changes of the system and it depends on the enthalpic forces.

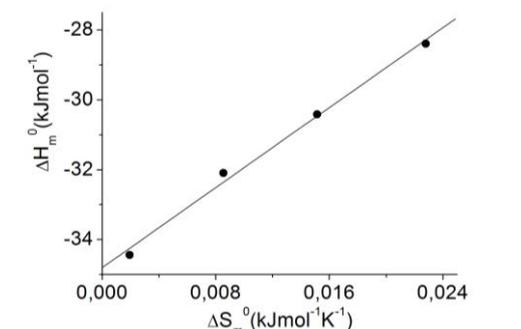


Fig. 3 Enthalpy–entropy compensation plot

In addition, the effect of PG on CTAB micellization can be also discussed through so-called free energy of transfer, $\Delta G_T^0 = (\Delta G_m^0)_{\text{PG}+\text{H}_2\text{O}} - (\Delta G_m^0)_{\text{H}_2\text{O}}$ [32], where $(\Delta G_m^0)_{\text{PG}+\text{H}_2\text{O}}$ and $(\Delta G_m^0)_{\text{H}_2\text{O}}$ are changes of standard molar Gibbs free energy of CTAB micellization in PG–water mixture and water, respectively. For this calculation, values of $(\Delta G_m^0)_{\text{H}_2\text{O}}$ are taken from literature [12]. At certain temperature, $(\Delta G_m^0)_{\text{PG}+\text{H}_2\text{O}}$ is: 12.48 kJ mol^{-1} (298.2 K), 12.82 kJ mol^{-1} (302.2 K), 12.41 kJ mol^{-1} (306.2) and 12.22 kJ mol^{-1} (310.2 K). The obtained values are positive at all investigated temperatures. Rodríguez et al. [5] have pointed out that organic solvent addition results in the bulk phase that is becoming a better solvent for the surfactant molecules. This would make the hydrophobic tail transfer from the bulk phase into the micelle less favorable. As a result of this increase in the solubility of hydrophobic tails, there is also an increase in the CMC. This fact can explain the obtained experimental results in a qualitative way. Thus, the positive values of the obtained ΔG_T^0 , in the presence of PG in the solvent system, indicate that the presence of PG causes increasing of CTAB hydrocarbon tails solubility, and decreasing of the solvophobic effect. Similar behavior has been obtained previously for micellization of tetradecyltrimethylammonium bromide in ethylene glycol–water binary mixture [11].

4. CONCLUSIONS

From the obtained results it is possible to reach the following conclusions:

a) The obtained values of CMC of CTAB in the examined system (PG–water (30% v/v) binary mixture) are higher than the values obtained in water [12, 16-18]. So, the micellization was inhibited by this additive.

b) The values of CMC of CTAB in the examined system increase with temperature. It seems clear that the effect of breaking the water structure surrounding the hydrophobic groups is dominant in the studied temperature range.

c) The micellization process is spontaneous ($\Delta G_m^0 < 0$) and exothermic ($\Delta H_m^0 < 0$) at all the examined temperatures.

d) At the temperature 286.05 K, micellization of CTAB in presence of 30% PG in binary mixture (with water) is totally independent of structure changes of the system and it depends on the enthalpic forces.

e) The calculated ΔG_T^0 values are positive at all temperatures. This implies that addition of PG causes the increase of CTAB hydrocarbon tails solubility as well as decrease of the solvophobic effect, and consequently an increase of the CMC.

Acknowledgement. *The present investigations were partially supported by The Ministry of Education, Science and Technological Development of Serbia, under Project 172015.*

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**TERMODINAMIKA MICELIZACIJE
HEKSADECILTRIMETILAMONIJUM-BROMIDA
U SMEŠI PROPILEN-GLIKOL-VODA:
KONDUKTOMETRIJSKO ISPITIVANJE**

Konduktometrijski je ispitivana micelizacija heksadeciltrimetilamonijum-bromida (sinonim cetiltrimetilamonijum-bromid, CTAB) u binarnoj smeši propilen-glikol-voda (30%, v/v), kao i termodinamičke osobine nastalih micela. Merenjem specifične provodljivosti određeni su kritična micelarna koncentracija (KMK) i stepen jonizacije micela (α) CTAB u opsegu temperatura 298,2–310,2 K određeni su. Primenom ravnotežnog modela za proces micelizacije izračunati su termodinamički parametri: promena standardne molarne Džibsove slobodne energije, (ΔG_m^0), entalpije (ΔH_m^0) i entropije (ΔS_m^0) micelizacije. Vrednosti ΔG_m^0 i ΔH_m^0 su bile negativne na svakoj od ispitivanih temperatura, dok su vrednosti ΔS_m^0 bile pozitivne i povećavale su se sa porastom temperature. Na osnovu linearne zavisnosti između ΔH_m^0 i ΔS_m^0 utvrđen je tzv. entalpijsko-entropijski kompenzacioni efekat.

Ključne reči: *heksadeciltrimetilamonijum-bromid, smeša propilen-glikol-voda, termodinamika micelizacije, kritična micelarna koncentracija, termodinamika micelizacije, entalpijsko-entropijska kompenzacija*