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ORIGINAL ARTICLE

Aggregation, Counter Ion Binding and Adsorption Behaviors of Cetylpyridinium Chloride in Water/Glycerol Media at 25 °C

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Abstract The critical micelle concentrations (CMC) of cetylpyridinium chloride (CPC) in water/glycerol media and in the presence of sodium chloride were determined at 25 °C by surface tension and conductance methods. Variation in CMC follows the normal trend, i.e., it increases with increases in glycerol content and decreases on adding NaCl. Empirical analysis of the exponential increase in CMC of CPC with weight per cent of glycerol is indicative of CMC having two components; one component being dependent while the other independent of the glycerol amount. The counter ion binding constant was determined from both slope–ratio and Corrin-Harkins methods and showed no dependence on glycerol amount, thus confirming the unusual trend in the behavior of β in water/glycerol media. In a water/glycerol medium, the ratio of solvent surface tension to limiting surface tension at CMC is also independent of the glycerol amount, whereas the Gordon Parameter decreases with increasing glycerol content as in other aqueous organic solvents. The air–solution interface becomes saturated by the adsorption of CPC when the concentration of added NaCl is about 0.02 mol kg^{-1} irrespective of the glycerol amount.

Keywords Cetylpyridinium chloride · Critical micelle concentration · Counter ion binding constant · Free energy · Surface excess

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Introduction

Solvents play a decisive role in controlling the adsorption and micellization characteristics of surfactants. Mixing of solvents changes solvent properties, particularly polarity, and carrying out adsorption and aggregation studies of surfactants in mixed solvents provides a knowledge of fundamental and practical importance. For this reason, micellization characteristics of surfactants in various mixtures of solvents are being studied. Water/glycerol is one such mixed solvent medium in which micellization behaviors of a few surfactants have been studied [1–8]. In water/glycerol medium the counter ion binding constant (β) for the ionic surfactants is found to have no dependence on the glycerol amount while in all other mixed solvent media, the value of β decreases with increases in the organic solvent content. This is a striking feature observed only in water/glycerol media irrespective of the ionic surfactant. The values of β in water/glycerol media reported so far were determined from the conductance data by using the slope–ratio method except for one case where β was determined by the EMF method [6]. Another method commonly used for determining β is the Corrin–Harkins (CH) method [9], which has not been applied in water/glycerol media. Therefore in this paper we examine the unusual behavior of β in a water/glycerol medium by measuring the surface tension and conductance of CPC in the presence of NaCl.

Experimental Procedures

Glycerol (Aldrich, 99.5% assay), cetylpyridinium chloride CPC (Aldrich, 99.0% assay) and NaCl (Merck, 99.5% assay) were used as received. Millipore grade water was used in preparing the solutions. Surface tension was measured by the Wilhelmy plate method using a K11 Krüss Tensiometer. Conductance measurements were made at 1 kHz using a B905 Wayne Kerr Automatic Precision Bridge. A dip-type conductivity cell having platinized platinum electrodes was used. The cell constant was determined using standard KCl solution. Temperatures of the solutions were maintained at 25 °C by using a Haake DC10 circulation bath.

Results and Discussion

Surface Tension, Conductance and CMC

Surface tension (γ) and specific conductance (κ) values of CPC as functions of glycerol and NaCl amounts at 25 °C are shown in Figs. 1 and 2, respectively. The critical micelle concentration (CMC) values obtained from surface tension and conductance data are given in Table S1 (supplementary material). The dependence of CMC on glycerol content in the absence and presence of NaCl is shown in Fig. 3. The CMC of CPC increases with increasing glycerol content of the medium, which is a general trend in any water/polar organic solvent medium. To quantify the variation of CMC (c_0) with the amount of organic solvent, some groups [6, 8] have used an empirical equation of the form

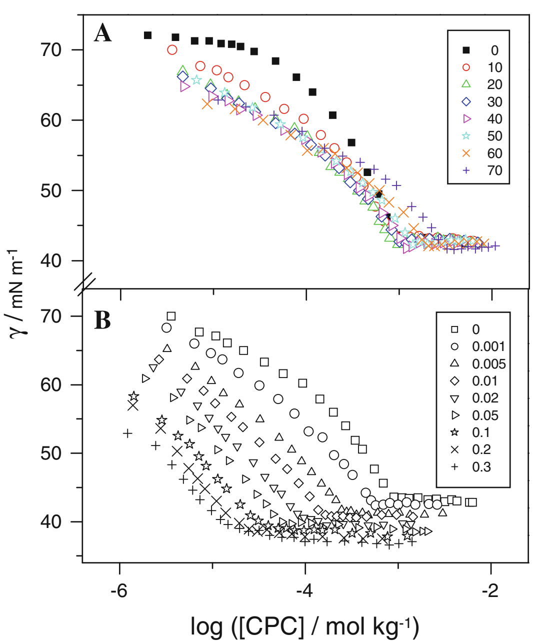


Fig. 1 Variation of surface tension with CPC concentration in **a** water/glycerol media and **b** 10 weight per cent glycerol in presence of NaCl at 25 °C. The values of wt% of glycerol in the medium (**a**) and of NaCl concentration in mol kg^{-1} (**b**) are given in the respective *insets*

$$c_0 = c_{00}\exp(bw) \tag{1}$$

where c_{00} is the CMC value in water, 'w' is the weight % of the organic solvent and 'b' is an empirical constant. In the present case Eq. 1 is not applicable as evident from the non-linearity of the plots of $\ln c_0$ versus w (Fig. 3). Instead, Eq. 2 is found to be applicable, which is given by

$$c_0 = y_0 + a\exp(bw) \tag{2}$$

The least-squares fitted values of the three constants y_0, 'a' and 'b' as a function of NaCl concentration are given in Table 1. The application of Eq. 2 implies that the CMC of

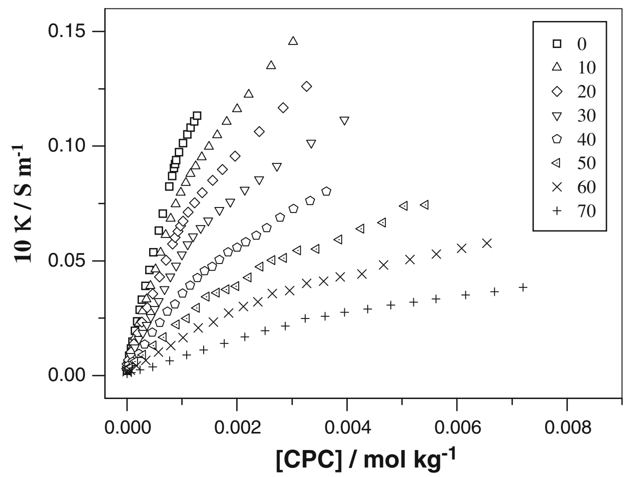


Fig. 2 Specific conductance plots of CPC in water/glycerol medium at 25 °C as a function of CPC concentration at fixed wt% values of glycerol (indicated in the *inset*)

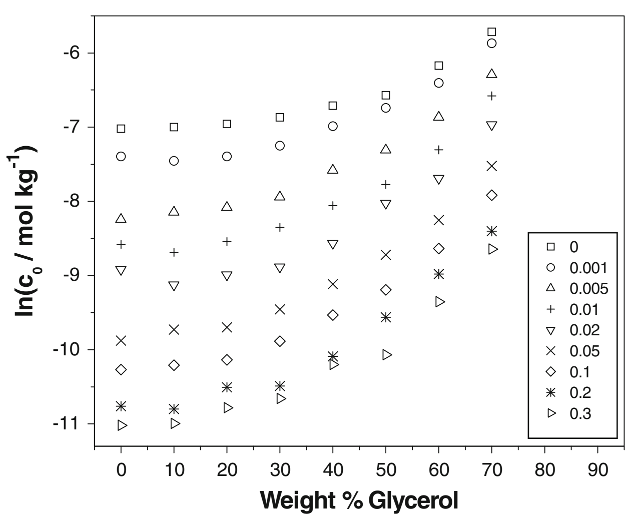


Fig. 3 Plots of logarithm of CMC of CPC in water/glycerol medium at 25 °C as a function of glycerol content at fixed concentrations of NaCl (indicated in the *inset*)

Table 1 Least-squares fitted values of the parameters of Eq. 2

[NaCl]/ mol kg^{-1}	$y_0 \times 10^4$/ mol kg^{-1}	$a \times 10^5$/ mol kg^{-1}	b	R^2 (R = correlation coefficient)
0	8.85	1.65	0.071	0.998
0.001	5.69	1.98	0.067	0.997
0.005	2.61	1.38	0.068	0.999
0.01	1.86	0.33	0.084	0.997
0.02	1.15	0.33	0.079	0.994
0.05	0.59	0.17	0.081	0.998
0.10	0.37	0.11	0.081	0.999
0.20	0.16	0.19	0.067	0.999
0.30	0.18	0.04	0.085	0.996

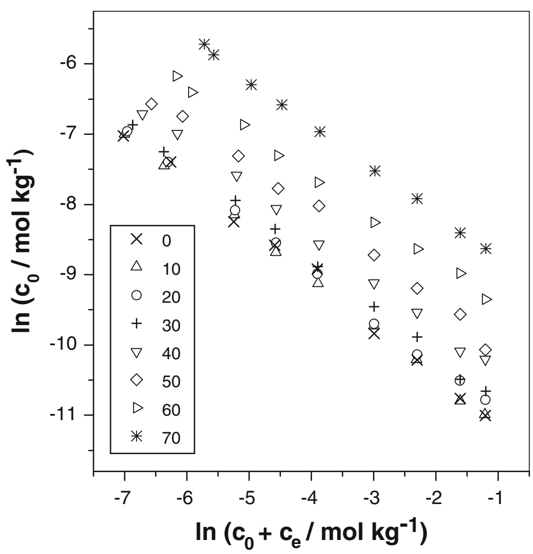


Fig. 4 CH plots for CPC in a water/glycerol medium at 25 °C. The wt% values of glycerol are given in the inset

CPC has two components; one component (exponential part) is dependent on the glycerol content while the other component (y_0) is independent of the glycerol amount.

Counter ion Binding Constant

The counter ion binding constant, β, was calculated using the Corrin-Harkins (CH) equation [9]

$$\ln c_0 = A - \beta_{CH} \ln(c_0 + c_e) \quad (3)$$

The terms c_0 and c_e represent the CMC and the concentration of added electrolyte, respectively, and A is a constant related to the standard free energy of micellization. The term $c_0 + c_e$ gives the total concentration of free counter ion. β_{CH} represents the counter ion binding constant determined from the slope of the CH equation. The CH plots are shown in Fig. 4 and the values of β_{CH} are given in Table 2. The counter ion binding constant was also calculated from the slope–ratio method which is denoted by β_κ and its values are also listed in Table 2. The striking feature of β_{CH} or β_κ in a water/glycerol medium is its negligible dependence on glycerol content. A similar observation was made by others [1–3, 6, 8] for different ionic surfactants in water/glycerol media including CPC at 40 °C using the slope–ratio method. Generally, in an aqueous organic solvent medium β_{CH} or β_κ decreases with increase in the amount of organic solvent. Thus, water/glycerol media behave differently from other mixed solvents with respect to the binding of counter ions to ionic micelles. A water-like environment around micellar surfaces may exist in a water/glycerol medium as shown in Fig. 5 and that could be the probable reason for the unexpected constancy of β_{CH} or β_κ as viewed by Palepu et al. [6] also.

Free Energy of Micellization

The free energy of micellization per mole of surfactant, ΔG^0_m, was calculated using the relation

$$\Delta G^0_m = RT(1 + \beta) \ln X_{cmc} \quad (4)$$

Table 2 Values of counterion binding constant for CPC in water/glycerol media at 25 °C derived from the CH plots (β_{CH}) and the slope–ratio method (β_κ)

Wt% glycerol	β_{CH}	β_k							
		[NaCl]/mol kg^{-1}	wt% glycerol						
			10	20	30	40	50	60	70
0[a]	0.66	0	0.60	0.58	0.58	0.50	0.52	0.57	0.58
10	0.69	0.001	0.61	0.61	0.62	0.51	0.50	0.58	0.56
20	0.67	0.005	0.66	0.60	0.61	0.58	0.54	0.50	0.55
30	0.67	0.01	0.65	0.66	0.62	0.46	0.45	0.43	0.51
40	0.65	0.02	0.66	0.60	0.65	0.62	0.47	0.50	0.53
50	0.65								
60	0.62								
70	0.64								

[a] Data from Ref. [15]

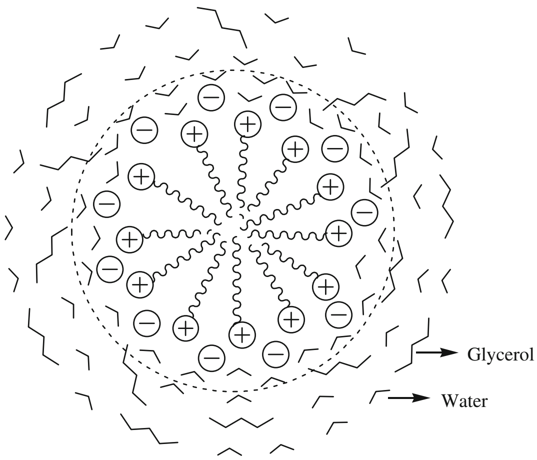


Fig. 5 A schematic representation of the micellar surface with water-like stern layer. Most of the hydrogen-bonded glycerol molecules are in the diffuse layer

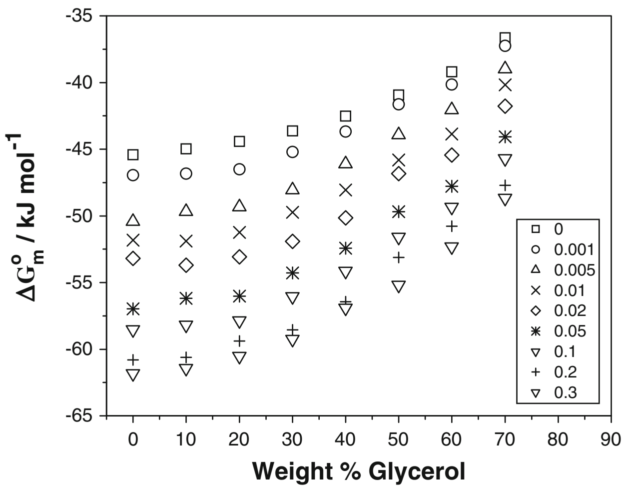


Fig. 6 Plots of standard free energy of micellization of CPC in a water/glycerol medium at 25 °C as a function of glycerol content at fixed concentrations of NaCl (indicated in the *inset*)

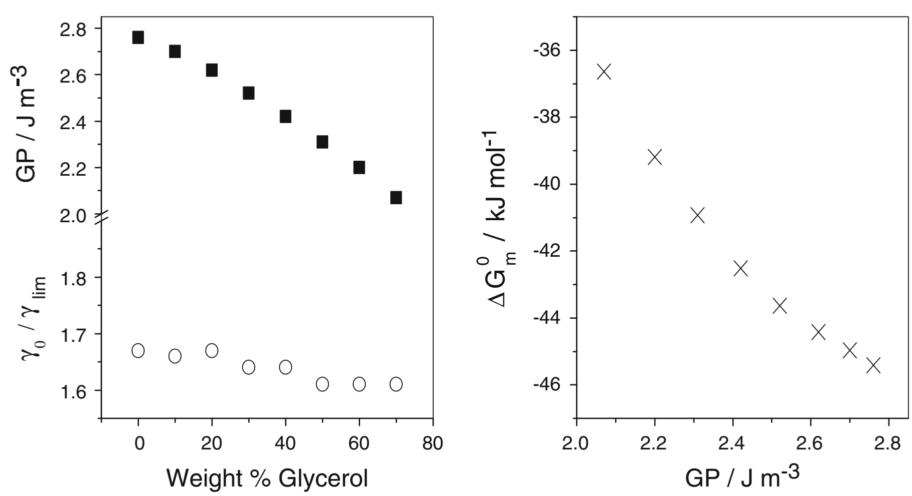
X_{cmc} is the CMC in the mole fraction unit. In Eq. (4), for β we substituted the average of β_{CH} values in water/glycerol media, which was found to be 0.66. The values of ΔG_m^0 are shown in Fig. 6. The rate of decrease of ΔG_m^0 with addition of NaCl is almost the same in water and in water/glycerol media. The addition of glycerol does not favor micellization, which is attributed to the decrease in solvophobicity of CPC. Quantification of solvophobicity is a difficult problem and still remains unsolved. Therefore, some empirical parameters are used to express the solvophobic effect of a solvent medium. The Gordon parameter (GP) is one such term and it is defined as GP $= \gamma_0/\mathrm{V}^{1/3}$, where γ_0 and V refer to surface tension and molar volume of the solvent, respectively. Decrease in GP reflects a decrease in solvophobicity of a medium. Moya and coworkers [1, 3] assessed the solvophobic effect of a variety of aqueous organic solvents with respect to different surfactants by using GP term. The correlation between ΔG_m^0 and GP is illustrated in Fig. 7. We recently proposed that the ratio of the solvent surface tension to the limiting surface tension at the CMC, $\gamma_0/\gamma_{\mathrm{lim}}$, can be used as a probable new scale to describe the solvophobic effect [10] and applied it in water/formamide and water/propylene carbonate media [11, 12]. However, in a water/glycerol medium, like β_{CH}, $\gamma_0/\gamma_{\mathrm{lim}}$ also remains almost constant with increasing glycerol amounts (Fig. 7) thereby rendering the $\gamma_0/\gamma_{\mathrm{lim}}$ term not suitable for expressing solvophobicity.

Surface Excess and Free Energy of Adsorption

The values of the surface excess for CPC at the air–water interface near its CMC (Γ_{cmc}) were calculated from the respective surface tension data using the expression [13, 14]

$$\Gamma_{\mathrm{cmc}} = -\frac{1}{\mathrm{RT}}\left[\frac{1}{1+\frac{c_0}{c_0+c_e}}\right]\left(\frac{\mathrm{d}\gamma}{\mathrm{d}\ln c}\right)_{\mathrm{cmc}} \quad (5)$$

Fig. 7 Variation of the Gordon parameter and the ratio of solvent surface tension to limiting surface tension with weight per cent of glycerol, and of ΔG_m^0 with Gordon parameter



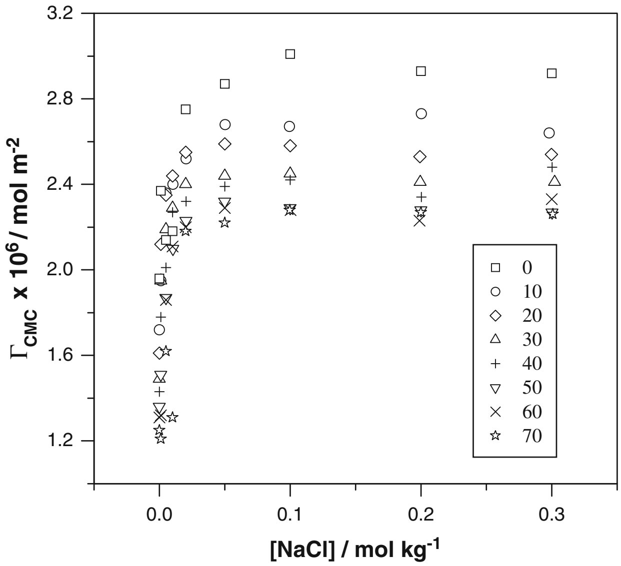


Fig. 8 Variation of surface excess of CPC at CMC in water/glycerol media at 25 °C with NaCl concentration. wt% values of glycerol are given in the *inset*

R and T represent the gas constant and absolute temperature, respectively. The value of the slope (dγ/dlnc) at the CMC was determined by least-squares fitting the γ vs lnc data near the CMC to a linear equation. The values of Γ_{cmc} as a function of NaCl concentration at a fixed weight percentage of glycerol are shown in Fig. 8. Γ_{cmc} increases on adding NaCl up to about 0.02 mol kg^{-1} and thereafter remains almost constant. By the addition of glycerol Γ_{cmc} decreases due to decrease in the solvophobicity or GP, but the saturation point of adsorption remains almost same at 0.02 mol kg^{-1} NaCl. Therefore, the electrolyte concentration required for saturating the air–solution interface by the adsorption of CPC is independent of the glycerol amount. The surface area, $A_0 = 1/(N_A\Gamma_{cmc})$, where N_A is the Avogadro number, of the adsorbed CPC molecule attains a minimum value of 0.62 ± 0.01 nm^2 near the adsorption saturation.

The standard free energy of adsorption (ΔG^0_{ad}) at the air–solution interface was calculated using the relation

$$\Delta G^0_{ad} = RT\ln X_{cmc} - \frac{\pi_{cmc}}{\Gamma_{cmc}} \qquad (6)$$

The surface pressure, $\pi_{cmc} = \gamma_o - \gamma_{cmc} \cdot \gamma_o$ and γ_{cmc} refer to the surface tensions of solvent and the surfactant solution at the CMC. The computed values of ΔG^0_{ad} are given in Table S2 (supplementary material). The value of ΔG^0_{ad} for CPC decreases on addition of electrolyte and increases on addition of glycerol.

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References

1. Rodriguez A, MdM Graciani, Moya ML (2008) Effects of addition of polar organic solvents on micellization. Langmuir 24:12785–12792
2. Ruiz CC, Díaz-López L, Aguiar J (2008) Micellization of sodium dodecyl sulfate in glycerol aqueous mixtures. J Disp Sci Technol 29:266–273
3. Moya ML, Rodriguez A, MdM Graciani, Fernandez G (2007) Role of the solvophobic effect on micellization. J Colloid Interface Sci 316:787–795
4. Ruiz CC, Diaz-Lopez L, Aguiar J (2007) Self-assembly of tetradecyltrimethyl ammonium bromide in glycerol aqueous mixtures: a thermodynamic and structural study. J Colloid Interface Sci 305:293–300
5. Dai S, Tam KC (2006) Effect of cosolvents on the binding interaction between poly(ethylene oxide) and sodium dodecyl sulfate. J Phys Chem B 110:20794–20800
6. Palepu R, Gharibi H, Bloor DM, Wyn-Jones E (1993) Electrochemical studies associated with the micellization of cationic surfactants in aqueous mixtures of ethylene glycol and glycerol. Langmuir 9:110–112
7. D'Errico G, Ciccarelli D, Ortona O (2005) Effect of glycerol on micelle formation by ionic and nonionic surfactants at 25 °C. J Colloid Interface Sci 286:747–754
8. Rafati AA, Gharibi H, Iloukhani H (2001) Micellization of cetylpyridinium chloride using conductometric technique. Phys Chem Liq 39:521–532
9. Corrin ML, Harkins WD (1947) The effect of salts on the critical concentration for the formation of micelles in colloidal electrolytes. J Am Chem Soc 69:684–688
10. Das D, Ismail K (2008) Aggregation and adsorption properties of sodium dodecyl sulfate in water-acetamide mixtures. J Colloid Interface Sci 327:198–203
11. Das J, Ismail K (2009) Aggregation, adsorption, and clouding behaviors of triton X-100 in formamide. J Colloid Interface Sci 337:227–233
12. Das J, Ismail K (2010) Effect of propylene carbonate on the adsorption and aggregation of surfactants. Colloid Polym Sci 288:527–533
13. Prosser A, Franses E (2001) Adsorption and surface tension of ionic surfactants at the air-water interface: review and evaluation of equilibrium models. Colloids Surf A 178:1–40
14. Umlong IM, Ismail K (2007) Micellization behaviour of sodium dodecyl sulfate in different electrolyte media. Colloids Surf A 299:8–14
15. Mukhim T, Ismail K (2005) Micellization of cetylpyridinium chloride in aqueous lithium chloride, sodium chloride and potassium chloride media. J Surface Sci Technol 21:113–127

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