Equilibrium of counterion association in micellar systems: cetyltrimethylammoniumbromide♣

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Surface Complexation Model was applied for the analysis of counterion association in the micellar systems. The equilibrium in cetyltrimethylammoniumbromide (CtaBr) solution was examined. Thermodynamic equilibrium constant was calculated using experimental data obtained with ion-selective electrodes (silver/silver bromide and surfactant electrode).

1. INTRODUCTION

One of the most important features of surfactant systems lies in the ability of surfactant chains to form aggregates, *i.e.* the micelles. Theoretical interpretation of the formation of micellar species [1-3] is commonly based on the Mass Action Law concept (assuming micelles as molecules) or on the Pseudo-phase Separation Model (assuming micelles as a separate phase). In the case of ionic surfactants, both models consider formation of micelles composed of aggregated chains to which counterions are partially bound. Therefore, the equilibrium parameters characterizing formation of ionic micelles include mutual interaction of chains, as well as counterion association with oppositely charged heads [4-7]. These two effects are mutually dependent. For example, the higher extent of counterion association will reduce mutual repulsion of charged surfactant chains and thus will promote the micellization process. In order to characterize affinity

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of counterions towards association, and to distinguish different counterions, it is necessary to separate counterion association from the aggregation of chains. The common approach does not enable such an analysis. The association of counterions at micellar surface was analysed by Stigter by considering chemical potentials of counterions in the bulk of the solution and at the micellar interface [8].The detailed analysis of the electrostatic potentials at the interface was also provided [9,10].

Surface Complexation Model (SCM) [11,12] is a model developed for the analysis of surface charging and association of counterions with oppositely charged groups at the metal oxide aqueous interface. This model introduces some approximations defining different species at the interface, *e.g.* uncharged species, charged species and charged species associated with counterions. With respect to the metal oxides, the situation in the micellar systems is even simpler, since the surface charge is directly related to the density of charged surfactant chains. This article examines the application of Surface Complexation Model for interpretation of the association of counterions in micellar systems. The method will be demonstrated on the example of cetyltrimethylammoniumbromide micellar system [13].

2. THEORETICAL

Surface Complexation model, when applied to the ionic micellar system, assumes already aggregated ionic chains to which oppositely charged ions (counterions) associate to a certain degree. In the case of cationic surfactants association of anions may be represented by

$$\equiv L^+ + A^- \qquad \equiv L^+ \cdot A^- \tag{1}$$

where A^- denotes counterions in the bulk of the solution, $\equiv L^+$ charged chains at micellar surface, while $\equiv L^+ \cdot A^-$ stands for charged chains to which counterions are bound.

Applying the General Model of Electrical Interfacial Layer (G−EIL) [14] the interfacial positively charged groups $\equiv L^+$ are exposed to the inner surface potential Ψ_0, whereas the interfacial ion pairs $\equiv L^+ \cdot A^-$ are oriented, with one side $\equiv L^+ \cdot$ exposed to the inner potential Ψ_0 and the other side A^-, *i.e.* the associated counterions, to the lower, outer potential Ψ_β. According to the Surface Complexation Model, the equilibrium constant for an interfacial reaction is expressed in terms of relative surface concentrations denoted by curly braces and defined for *e.g.* surface species S by

$$\{S\} = \frac{\Gamma_S}{\Gamma^\circ} = \Gamma_S \,/\, \text{mol m}^{-2} \tag{2}$$

where Γ denotes surface concentration (amount of surface species per surface area), and $\Gamma^\circ = 1$ mol m^{-2} stands for standard value of the surface concentration. Introduction of the activity coefficients of interfacial species [15] gives the following expression for the thermodynamic equilibrium constant for association of counterions in micellar systems (Eq. 1)

$$K_{\text{ass}}^\circ = \frac{\exp\!\left(\left(\psi_0 - \psi_\beta\right) F \,/\, RT\right)\cdot\left\{\equiv\text{L}^+\!\cdot\text{A}^-\right\}}{\exp\!\left(\psi_0 F \,/\, RT\right)\cdot\left\{\equiv\text{L}^+\right\}\cdot a_{\text{A}^-}} = \exp\!\left(-\psi_\beta F \,/\, RT\right)\cdot\frac{\left\{\equiv\text{L}^+\!\cdot\text{A}^-\right\}}{\left\{\equiv\text{L}^+\right\}\cdot a_{\text{A}^-}} \tag{3}$$

where a_{A^-} denotes activity of counterions A$^-$ in the bulk of the solution, and R and T have their usual meaning.

By introducing the degree of counterion association (α_{ass}) [16] defined by

$$\alpha_{\text{ass}} = \frac{\left\{\equiv\text{L}^+\!\cdot\text{A}^-\right\}}{\left\{\equiv\text{L}^+\right\} + \left\{\equiv\text{L}^+\!\cdot\text{A}^-\right\}} \tag{4}$$

one obtains

$$K_{\text{ass}}^\circ = \exp\!\left(-\psi_\beta F \,/\, RT\right)\cdot\frac{\alpha_{\text{ass}}}{\left(1 - \alpha_{\text{ass}}\right)\cdot a_{\text{A}^-}} \tag{5}$$

According to the Gouy-Chapman theory for spheres of radius r, the effective surface charge density σ_s is related to the potential at the onset of the diffuse layer Ψ_d by

$$\psi_d = \frac{\sigma_s r}{\varepsilon\left(1 + r\kappa_{\text{DH}}\right)} \tag{6}$$

where the reciprocal Debye-Hückel distance κ_{DH} is related to the relative permittivity ε_r and the ionic strength I_c by

$$\kappa_{\text{DH}} \,/\, \text{nm}^{-1} = \left(\frac{2.6215}{\varepsilon_r \cdot (T\,/\,\text{K})}\right)^{1/2} \cdot \left(I_c \,/\, \text{mol dm}^{-3}\right)^{1/2} \tag{7}$$

In the Double Layer (DL) approximation [17] the outer surface potential Ψ_β may be taken to be approximately equal to Ψ_d.

Effective surface charge density is related to the surface concentration of chains by

$$\sigma_s = F \cdot \{\equiv L^+\} = F \cdot (1 - \alpha_{ass}) \cdot (\{\equiv L^+\} + \{\equiv L^+ \cdot A^-\}) \tag{8}$$

and could be obtained from

$$\sigma_s = (1 - \alpha_{ass}) \cdot \frac{n e_0}{4 r^2 \pi} \tag{9}$$

where e_0 is the elementary charge, while n and r are micellar aggregation number and their radius, respectively.

3. RESULTS AND DISCUSSION

By using ion selective electrodes one is able to measure activities of Br^- counterions and of surfactant L^+ chains in the cetyltrimethylammoniumbromide micellar system [13]. By knowing the total surfactant concentration c_{tot} one calculates the degree of bromide ion association from

$$\alpha_{ass} = \frac{c_{tot} - c_{Br^-}}{c_{tot} - c_{Cta^+}} \tag{10}$$

Figure 1 presents the bulk activities of Cta^+ and Br^- ions, as well as the degree of association of Br counterions, as a function of the total CtaBr concentration above the critical micellization concentration of 10^{-3} mol dm^{-3}. In the calculations the data from reference [13] were used.

The counterion interfacial association equilibrium constant was calculated on the basis of Eq (5) and for the calculation of outer surface potential ($\Psi_\beta \approx \Psi_d$) Eqs (6-9) were used. For that purpose, the micellar radius was taken from the literature [19] as 3.14 nm. The micellar aggregation number was calculated from conductometric and potentiometric experimental data [13]. The results of calculations are presented in Figure 2 as a function of the total CtaBr concentration.
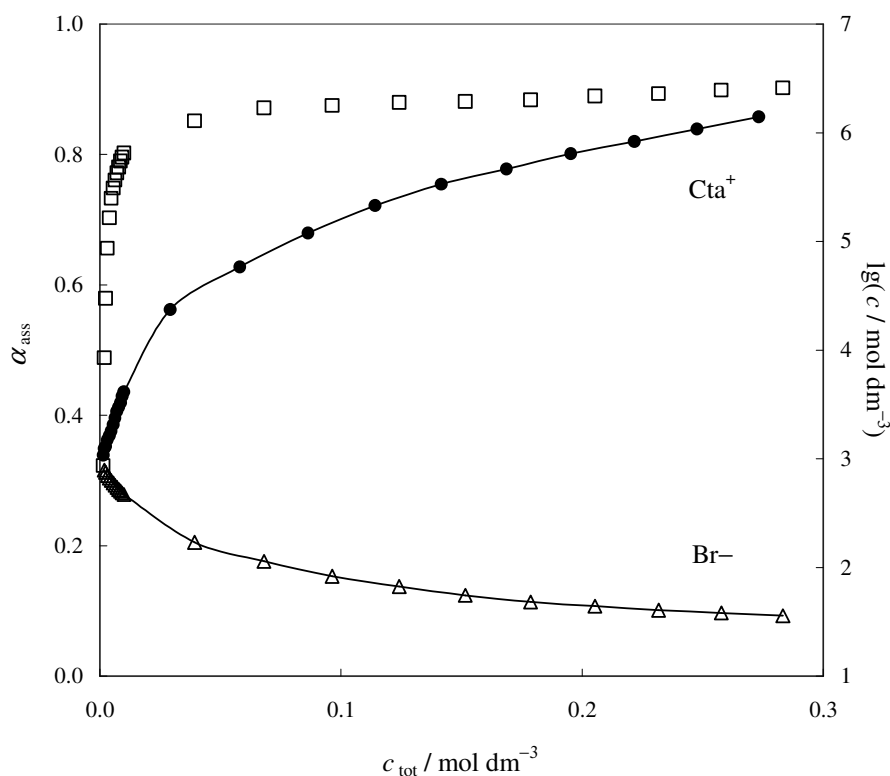
Fig. 1. The bulk concentration, c, of Cta^+ ($\bullet$) and Br^- (Δ) ions, and the degree of association, α_{ass}, of Br^- counterions ($\square$), as a function of the total CtaBr concentration at 30 °C above the critical micellization concentration of 1×10^{-3} mol dm^{-3}. The data were taken from reference [13].

As it could be concluded from Figure 2, the counterion association equilibrium constant significantly decreased with total surfactant concentration. The main reason is probably the increase in the degree of counterion association. As it can be concluded from Figure 1, the saturation of the surface with associated counterions is at $\alpha_{ass} = 0.85$. It may be speculated that the size of hydrated counterions does not allow their higher density, so that further association is somehow prevented and the association affinity is reduced. At low density of associated counterions enough space is available and the equilibrium constant is thus relatively high. Also the effect the aggregation number and the structure and shape of micelles may play an important role. The Surface Complexation Model is an approximation which does not take into account the penetration of counterions into micelles as proposed by Warszynski [20] and Ivanov [21].
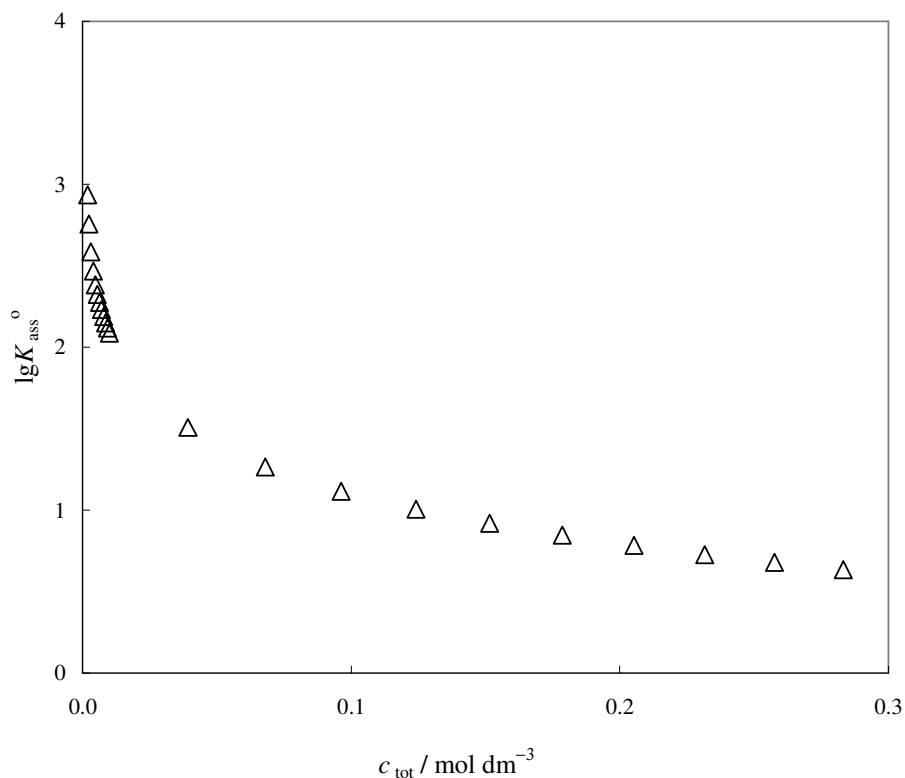
Fig. 2. The thermodynamic equilibrium constant for association of Br^- ions at the CtaBr micellar interface, K^o_{ass}, as a function of the total CtaBr concentration at 30 °C above the critical micellization concentration of 1 mmol dm^{-3}. The experimental data were taken from reference [13].

However, despite the approximation included in the model, SCM provides information on the affinity of counterions towards the association at the micellar interface. Considering the obtained values, it may be concluded that the governing forces are of the Coulombic nature as in the case of metal oxide aqueous interfaces [12].

4. REFERENCES

[1] Y. Moroi, *Micelles, Theoretical and Applied Aspects*; Plenum Press: New York and London, 1992.

[2] D. F. Evans; H. Wennerström, *The Colloidal Domain: Where Physics, Chemistry, Biology and Technology Meet*, 2nd ed.; Wiley-VCH, New York, 1999.

[3] Y. Moroi, N. Yoshida, *Langmuir* 13, 3909-3912 (1997).

[4] E. B. Abuin, E. Lissi, *J. Colloid Interface Sci.,* 93, 562-564 (1983).

[5] N. Kallay, V. Tomišić, V. Hrust, R. Pieri, A. Chittofrati, *Colloids Surf. A,* 222, 95-101. (2003).

[6] G. Para, E. Jarek, P. Warszynski, Z. Adamczyk, *Colloids Surf. A,* 222, 213-222. (2003).

[7] P. Koelsch, P.Viswanath, H.Motschmann, V. L. Shapovalov, G. Brezesinski, H. Möhwald, D. Horinek, R. R. Netz, K. Giewekemeyer, T. Salditt, H. Schollmeyer, R. von Klitzing, J. Daillant, P. Guenoun, *Colloids Surf. A,* 303, 110-136, (2007).

[8] D. Stigter, *J. Phys. Chem.,* 68, 3603-3611 (1964).

[9] D. Stigter, *J. Phys. Chem.,* 79, 1008-1014 (1975).

[10] D. Stigter, *J. Phys. Chem.,* 79, 1015-1022 (1975).

[11] W. Stumm, C. P. Huang, S. R. Jenkins, *Croat. Chem. Acta,* 42, 223-245. (1970).

[12] N. Kallay, S. Žalac, D. Kovačević, *Thermodynamics of the Solid/Liquid Interface. Its Application to Adsorption and Colloid Stability* in *Surface Complexation Modelling* (J. Lützenkirchen, Ed.) in the series *Interface Science and Technology*, Elsevier, 2006.

[13] T. Glušac, *Equilibrium of Association of Bromide Ions with Cetyltrimethylammonium-bromide micelles (in Croatian),* Diploma Thesis, Department of Chemistry, Faculty of Science, University of Zagreb, 2005.

[14] A. V. Delgado, F. Gonzalez-Caballero, R. J. Hunter, L. K. Koopal, H. Lyklema, *Pure Appl. Chem.,* 77, 1753-1805 (2005).

[15] N. Kallay, T. Preočanin, S. Žalac, *Langmuir,* 20, 2986- 2988 (2004).

[16] L. Sepulveda, J. Cortes, *J. Phys. Chem.,* 89, 5322-5324 (1985).

[17] D. Kovačević, T. Preočanin, S. Žalac and A. Čop, *Croat. Chem. Acta,* 80, 287-301 (2007).

[18] P. C. Shanks, E. I. Franses, *J. Phys. Chem.,* 96, 1794-1805 (1992).

[19] R. Dorshow, J. Briggs, C. A. Bunton, D. F. Nicoli, *J. Phys. Chem.,* 86, 2388-2395 (1982).

[20] G. Para, E. Jarek, P. Warszynski, *Adv. Colloid Interface Sci.,* 122, 39-55 (2006).

[21] I. B. Ivanov, K. G. Marinova, K. D. Danov, D. Dimitrova, K. P. Ananthapadmanabhan, A. Lips, *Adv. Colloid Interface Sci.,* 134-135, 105-124 (2007).