

Adsorption of Tetradecylpyridinium Chloride on Aqueous Surfaces of Sodium Chloride Solutions

by

Katsuhiko FUJIO^{*1}, Koji HAYASHI^{*2} and Maki SUZUKI^{*1}

^{*1}*Department of Chemistry, School of Science, Tokai University*

4-1-1 Kitakaname, Hiratsuka-shi, Kanagawa, 259-1292, Japan

E-mail: kfujio@tokai-u.jp

^{*2}*Department of Chemistry, Faculty of Science, Shinshu University*

Matsumoto, Nagano, 390-8621, Japan

(Received on Sept. 27, 2013; accepted on Dec. 5, 2013)

Abstract

Surface tension of aqueous NaCl solutions of tetradecylpyridinium chloride (TPC) has been measured by the drop weight method at different NaCl concentrations from 0 to 1.000 mol dm⁻³ at 25°C. Surface excess densities of tetradecylpyridinium ion (TP⁺), Cl⁻ and Na⁺ have been obtained as functions of TPC concentration at different NaCl concentrations by applying the Gibbs adsorption isotherm to the surface tension data below the critical micelle concentration (CMC) of TPC. Surface excess densities of TP⁺ and Cl⁻ increased with increasing TPC concentration, and approached the saturated values at the CMC. On the other hand, the surface excess density of Na⁺ was nearly zero or slightly negative regardless of TPC concentration. Like common ionic surfactants, the molecular area of TPC on aqueous surface decreased with increasing NaCl concentration except for 0 mol dm⁻³ NaCl solution. The Corrin-Harkins plot was linear in NaCl concentration range studied.

1 Introduction

Surfactant molecules or ions are adsorbed on aqueous surface and thereby lower the surface tension of their aqueous solutions. The surface excess densities of nonionic surfactant molecule and concomitant salt can be obtained from the dependence of surface tension on concentrations of surfactant and salt by using the Gibbs adsorption isotherm, Eqns (2) – (4).

In the case of ionic surfactant in aqueous salt solution, only Eqns (2) – (4) are not sufficient to evaluate the surface excess densities of surfactant ion, counterion and constituent ions of salt, because these equations are the Gibbs adsorption isotherm for electrically neutral species. Ikeda and coworkers [1–7] derived the surface excess densities of surfactant ion and all other ionic species

as functions of concentrations of surfactant and concomitant salt in terms of the Gibbs adsorption isotherm for ionic species and applied them to some alkylammonium surfactant-sodium halide systems; dodecyldimethylammonium chloride (DDAC)-NaCl [2, 3], dodecyldimethylammonium bromide (DDAB)-NaBr [4], DDAC-NaBr [5], hexadecyltrimethylammonium bromide (CTAB)-NaBr [6], DDAB-NaCl [7] and dodecyltrimethylammonium bromide (DTAB)-NaBr [8].

In the previous work [9], we extended similar measurements of surface tension to aqueous NaCl solutions of dodecylpyridinium chloride (DPC) having an aromatic ring as a polar head group, and determined the surface excess densities of dodecylpyridinium ion (DP^+), Cl^- and Na^+ as functions of surfactant and NaCl concentrations by applying the Gibbs adsorption isotherm according to Ikeda and coworkers [1–7]. As observed for other cationic surfactant-simple salt systems, surface excess densities of DP^+ and Cl^- increased with increasing DPC concentration and approached the saturated values at the CMC, whereas the surface excess density of Na^+ was nearly zero or slightly negative. The molecular area of DPC on aqueous surface increased with increasing NaCl concentration up to $0.010 \text{ mol dm}^{-3}$ and then decreased to almost constant value.

In the present work we study the adsorption behavior of tetradecylpyridinium chloride (TPC), whose hydrophilic tail is the longer by two methylene groups than DPC, on aqueous surfaces of NaCl solutions in order to investigate the effect of aromatic ring in hydrophilic group on the adsorption behavior of cationic surfactant.

2 Experimental

TPC was synthesized by refluxing the mixture of pyridine and 1-chlorotetradecane at 120°C for 8 hours and recrystallized four times from ethanol-acetone mixture (25:1 v/v). Pyridine was obtained from Nacalai Tesque, Inc., and dried over molecular sieves 3A. 1-chlorotetradecane was purchased from Merck Ltd. and distilled at reduced pressure. NaCl of special grade reagent from Nacalai Tesque, Inc., was dried at 180°C for two hours. Water was redistilled from alkaline KMnO_4 solution.

The surface tension of aqueous solutions was measured at $25 \pm 0.1^\circ\text{C}$ by the drop weight method. A capillary having a reservoir was kept perpendicular in a glass vessel immersed in a temperature-controlled bath and its upper end was connected to a micrometer syringe through a rubber tube. A drop of solution was suspended at the lower end of capillary in a state just before falling for 5 min or more, and then detached from the capillary tip. If a drop which falls from the capillary tip having outer radius r has a weight m , then the surface tension of the solution is given by

$$\gamma = (mg/r)F \quad (1)$$

where g is the gravitational acceleration and F is the Harkins-Brown correction factor determined by the drop volume V and the outer radius r of the tip. The drop volume V was obtained by dividing the drop weight m by the density of solvent, i.e., water or NaCl solution. The effective outer radius r of the capillary tip was determined by measuring the drop weight of redistilled water and assuming its surface tension to be 71.98 mN m^{-1} and found to be 3.457 mm . The capillary was cleaned by being immersed in chromic acid mixture after each measurement.

3 Results

Figure 1 shows the surface tension, γ , of aqueous NaCl solutions of TPC plotted against the logarithm of the molar concentration of TPC, $\log C$, at different NaCl concentrations, C_S . With increasing TPC concentration up to the critical micelle concentration (CMC), the surface tension decreases and its rate of decrease increases from about zero to a certain definite value. Above the CMC, the surface tension has an almost constant value at a given NaCl concentration. Surface tension is lower at the higher NaCl concentration except in the case of the lower TPC concentrations than $1 \times 10^{-5} \text{ mol dm}^{-3}$. The aspect of the surface tension-concentration relationship of the TPC-NaCl system is similar to that of DPC-NaCl system [9] and alkylammonium surfactant-sodium halide system [2–8]. Table 1 gives the CMC, C_0 , and the surface tension at the CMC, γ_0 . Both quantities decrease with increasing NaCl concentration.

According to the Gibbs adsorption isotherm, the surface tension depression can be represented by

$$-d\gamma = RT (\Gamma d \ln C + \Gamma_S d \ln C_S) \quad (2)$$

where R is the gas constant and T is the absolute temperature. Γ and Γ_S are the surface excess densities of TPC and NaCl, respectively, and defined by

$$\Gamma = -\frac{1}{RT} \left(\frac{\partial \gamma}{\partial \ln C} \right)_{C_S} \quad (3)$$

and

$$\Gamma_S = -\frac{1}{RT} \left(\frac{\partial \gamma}{\partial \ln C_S} \right)_C \quad (4)$$

Γ can be evaluated from the slope of curves shown in Fig. 1.

In order to estimate Γ_S , the surface tension is plotted afresh against the logarithm of the NaCl

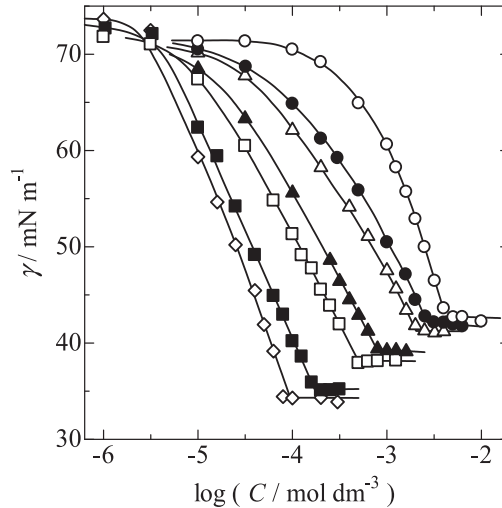


Figure 1: Dependence of surface tension of aqueous NaCl solutions of tetradecylpyridinium chloride on surfactant concentration at different NaCl concentrations. $C_S / \text{mol dm}^{-3}$: $\circ$, 0; $\bullet$, 0.005; $\triangle$, 0.010; $\blacktriangle$, 0.050; $\square$, 0.100; $\blacksquare$, 0.500; $\diamond$, 1.000.

concentration, $\log C_S$, at each TPC concentration, C , as shown in Fig. 2. The surface tension at the CMC, γ_0 , is also shown as a dashed line in Fig. 2.

Table 1 also includes values of Γ and Γ_S at the CMC. With increasing NaCl concentration the value of Γ at the CMC decreases, has a minimum value at $0.050 \text{ mol dm}^{-3}$ NaCl and then increases slightly. On the other hand, the value of Γ_S at the CMC monotonically increases as NaCl concentration increases. Such behavior of Γ and Γ_S at the CMC has been observed for DPC-NaCl system [9] and alkylammonium surfactant-sodium halide system [3–8].

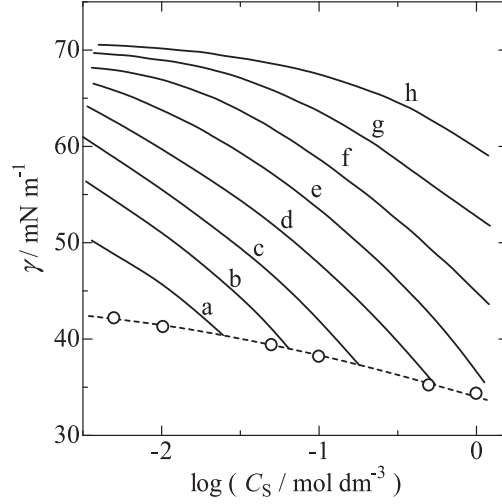


Figure 2: Dependence of surface tension of aqueous NaCl solutions of tetradecylpyridinium chloride on NaCl concentration at different surfactant concentrations. $-\log (C / \text{mol dm}^{-3})$: a, 2.9; b, 3.2; c, 3.5; d, 3.8; e, 4.1; f, 4.4; g, 4.7; h, 5.0. Dashed curve represents dependence of surface tension at the CMC, γ_0 , on NaCl concentration.

Table 1: Adsorption properties of tetradecylpyridinium chloride on the surface of aqueous NaCl solution at the critical micelle concentration.

$C_S / \text{mol dm}^{-3}$	$C_0 / \text{mmol dm}^{-3}$	$\gamma_0 / \text{mN m}^{-1}$	$\Gamma / 10^{-6} \text{ mol m}^{-2}$	$\Gamma_S / 10^{-6} \text{ mol m}^{-2}$
0	4.18	42.8	5.72	
0.005	2.67	42.2	3.88	2.00
0.010	2.04	41.2	3.62	2.09
0.050	0.782	39.4	3.24	3.39
0.100	0.497	38.2	3.34	3.44
0.500	0.172	35.2	3.94	3.49
1.000	0.095	34.3	4.87	4.11

4 Discussion

4.1 Surface excess densities of ions

According to Ikeda and coworkers [1–7], the Gibbs adsorption isotherm can be applied to the surface tension data at TPC concentrations below the CMC, shown in Figs.1 and 2, and the surface excess densities of tetradecylpyridinium ion (TP^+), Cl^- and Na^+ can be determined as functions of surfactant and NaCl concentrations. Furthermore, their works [2, 3] indicated that the substitution of activities of surfactant and salt by their concentrations causes no serious errors in calculations of surface excess densities for such systems containing a dilute ionic surfactant and a simple salt.

Representing the surface excess densities subject to the Gibbs convention of TP^+ , Cl^- and Na^+ by Γ_{TP^+} , Γ_{Cl^-} and Γ_{Na^+} , respectively, the coefficients, Γ and Γ_{S} , in the Gibbs adsorption isotherm, Eqn (2), can be represented by

$$\Gamma = \left(1 + \frac{C}{C + C_{\text{S}}}\right) \Gamma_{\text{TP}^+} + \frac{C}{C + C_{\text{S}}} \Gamma_{\text{Na}^+} \quad (5)$$

and

$$\Gamma_{\text{S}} = \frac{C_{\text{S}}}{C + C_{\text{S}}} \Gamma_{\text{TP}^+} + \left(1 + \frac{C_{\text{S}}}{C + C_{\text{S}}}\right) \Gamma_{\text{Na}^+} \quad (6)$$

respectively [2, 3]. Solving these equations for Γ_{TP^+} and Γ_{Na^+} , the following equations can be obtained.

$$\Gamma_{\text{TP}^+} = \frac{1}{2} \left\{ \left(1 + \frac{C_{\text{S}}}{C + C_{\text{S}}}\right) \Gamma - \frac{C}{C + C_{\text{S}}} \Gamma_{\text{S}} \right\} \quad (7)$$

$$\Gamma_{\text{Na}^+} = \frac{1}{2} \left\{ -\frac{C_{\text{S}}}{C + C_{\text{S}}} \Gamma + \left(1 + \frac{C}{C + C_{\text{S}}}\right) \Gamma_{\text{S}} \right\} \quad (8)$$

The electroneutrality of the surface gives the surface excess density of Cl^- in the following form.

$$\Gamma_{\text{Cl}^-} = \Gamma_{\text{TP}^+} + \Gamma_{\text{Na}^+} = \frac{1}{2} (\Gamma + \Gamma_{\text{S}}) \quad (9)$$

Applying Eqns (7) – (9) to the surface tension data given in Figs.1 and 2, the surface excess densities of three ionic species below the CMC can be obtained. Figures 3 and 4 show the surface excess density of TP^+ and the ones of Cl^- and Na^+ , respectively, at different NaCl concentrations as functions of TPC concentration.

With increasing TPC concentration, the value of Γ_{TP^+} increases towards a saturated value and the rate of its increase sharpens except for the case in the absence of NaCl. At the NaCl concentrations above $0.500 \text{ mol dm}^{-3}$, the value of Γ_{TP^+} is already saturated at very low TPC concentrations.

The value of Γ_{Na^+} is nearly zero or slightly negative. Consequently, the value of Γ_{Cl^-} is nearly equal to that of Γ_{TP^+} .

Table 2 gives Γ_{TP^+} , Γ_{Cl^-} and Γ_{Na^+} at the CMC for different NaCl concentrations and Fig. 5 shows them plotted against the square root of the NaCl concentration.

Figure 6 plots $1/\Gamma_{\text{TP}^+}$ smaller than $1.5 \times 10^6 \text{ m}^2 \text{ mol}^{-1}$, above which small values of Γ_{TP^+} cause significant errors in calculating $1/\Gamma_{\text{TP}^+}$, against $1/C$ and gives straight lines at each NaCl concentration. This indicates that the adsorption of tetradecylpyridinium ion obeys the Langmuir

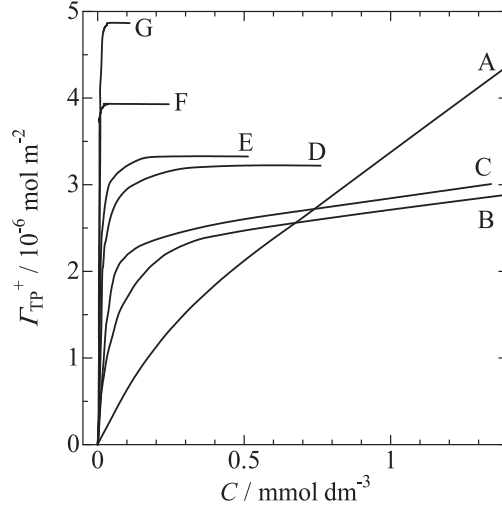


Figure 3: Adsorption isotherm of tetradecylpyridinium ion, TP^+ , on aqueous surface at different NaCl concentrations. $C_S / \text{mol dm}^{-3}$: A, 0; B, 0.005; C, 0.010; D, 0.050; E, 0.100; F, 0.500; G, 1.000.

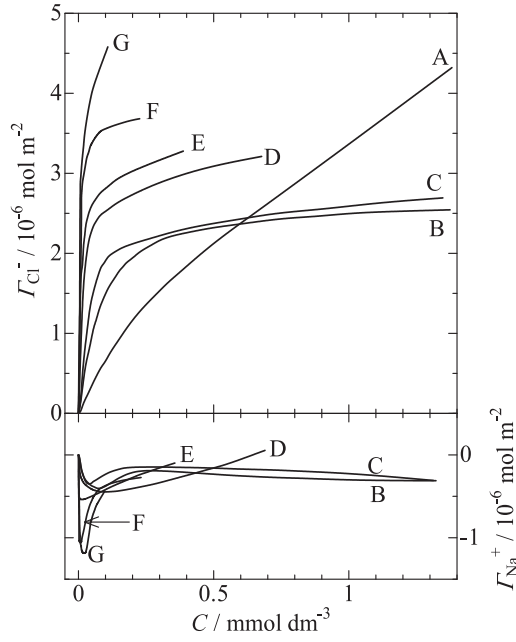


Figure 4: Adsorption isotherms of chloride (upper) and sodium ions (bottom), Cl^- and Na^+ , on aqueous surface at different NaCl concentrations. $C_S / \text{mol dm}^{-3}$: A, 0; B, 0.005; C, 0.010; D, 0.050; E, 0.100; F, 0.500; G, 1.000.

isotherm

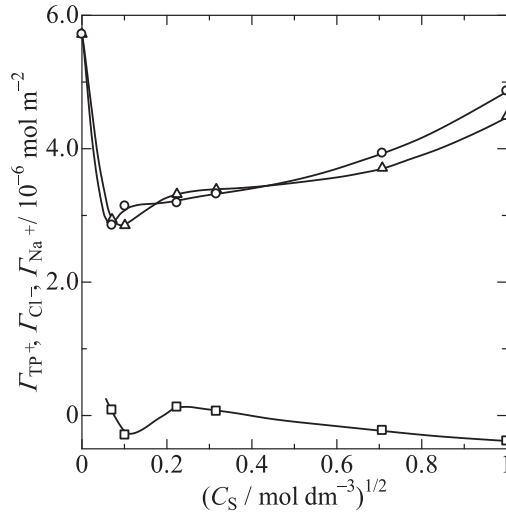
$$\Gamma_{\text{TP}^+} = \Gamma_{\text{TP}^+}^{\infty} \frac{KC}{1 + KC} \quad (10)$$

where $\Gamma_{\text{TP}^+}^{\infty}$ is the saturated adsorption density of TP^+ and K is the adsorption coefficient. Table 3 gives values of $\Gamma_{\text{TP}^+}^{\infty}$ and K at different NaCl concentrations.

The molecular area, A_0 , corresponding to $\Gamma_{\text{TP}^+}^{\infty}$ is obtained in $\text{\AA}^2$ by

Table 2: Surface excess densities of tetradecylpyridinium ion, Cl^- and Na^+ at the critical micelle concentration.

$C_S/\text{mol dm}^{-3}$	$\Gamma_{\text{TP}^+}/10^{-6} \text{ mol m}^{-2}$	$\Gamma_{\text{Cl}^-}/10^{-6} \text{ mol m}^{-2}$	$\Gamma_{\text{Na}^+}/10^{-6} \text{ mol m}^{-2}$
0	5.72	5.72	
0.005	2.86	2.94	0.08
0.010	3.14	2.85	-0.29
0.050	3.19	3.32	0.13
0.100	3.32	3.39	0.07
0.500	3.93	3.71	-0.22
1.000	4.87	4.49	-0.38


 Figure 5: Dependence of surface excess densities of ions at the CMC on NaCl concentration. $\circ$, Γ_{TP^+} ; $\triangle$, Γ_{Cl^-} ; $\square$, Γ_{Na^+} .

$$A_0 = \frac{10^{20}}{N_A \Gamma_{\text{TP}^+}^\infty} \quad (11)$$

where N_A is the Avogadro constant, and its values are also given in Table 3. For common ionic surfactant such as DTAB, the molecular area decreases with increasing salt concentration due to the electrostatic shielding effect of salt on the adsorbed surfactant ions [8]. With increasing NaCl concentration, however, the molecular area of TPC increases from $18.5 \text{ \AA}^2$ in the absence of NaCl to $58.6 \text{ \AA}^2$ at $0.005 \text{ mol dm}^{-3}$ NaCl, and then decreases to $32.3 \text{ \AA}^2$ at $1.000 \text{ mol dm}^{-3}$ NaCl. Similar dependence of molecular area on NaCl concentration was observed for DPC-NaCl system: with increasing NaCl concentration, the molecular area of DPC increased from $28.9 \text{ \AA}^2$ in the absence of NaCl to $63.5 \text{ \AA}^2$ at $0.010 \text{ mol dm}^{-3}$ NaCl, and then decreased to almost constant value of $55 \text{ \AA}^2$ above $0.050 \text{ mol dm}^{-3}$ NaCl [9]. This dependence of molecular area of DPC on NaCl concentration was inferred to be associated with very small micelles of DPC in aqueous NaCl solution below 0.05 mol dm^{-3} [10]. In the case of TPC the cause would be the same.

As shown in Table 3, the adsorption coefficient K increases with increasing NaCl concentration

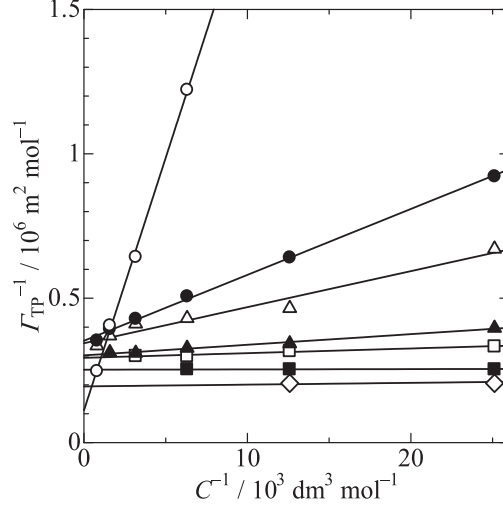


Figure 6: Langmuir isotherm of tetradecylpyridinium ion, TP^+ , at different NaCl concentrations. $C_S / \text{mol dm}^{-3}$: $\circ$, 0; $\bullet$, 0.005; $\triangle$, 0.010; $\blacktriangle$, 0.050; $\square$, 0.100; $\blacksquare$, 0.500; $\diamond$, 1.000.

Table 3: Saturated adsorption density, molecular area, adsorption coefficient and free energy of adsorption of tetradecylpyridinium chloride.

$C_S / \text{mol dm}^{-3}$	$\Gamma_{\text{TP}^+}^\infty / 10^{-6} \text{ mol m}^{-2}$	$A_0 / \text{\AA}^2$	$K / \text{dm}^3 \text{ mol}^{-1}$	$\Delta G_{\text{ad}} / \text{kJ mol}^{-1}$
0	8.96	18.5	6.40×10^2	-16.0
0.005	2.84	58.6	1.54×10^4	-23.9
0.010	2.91	57.2	2.76×10^4	-25.3
0.050	3.31	50.2	8.22×10^4	-28.1
0.100	3.41	48.8	1.81×10^5	-30.0
0.500	3.96	41.9	2.43×10^6	-36.5
1.000	5.14	32.3	3.16×10^5	-31.4

up to $0.500 \text{ mol dm}^{-3}$, which suggests the electrostatic shielding effect of NaCl on the adsorption of surfactant ions. Smaller value of K in $0.500 \text{ mol dm}^{-3}$ NaCl might be attributed to such micellar shape transition as a sphere-rod transition.

Table 3 also includes values of the free energy of adsorption evaluated from K by

$$\Delta G_{\text{ad}} = -RT \ln K \quad (12)$$

Corresponding to the increase in K , ΔG_{ad} decreases with NaCl concentration up to $0.500 \text{ mol dm}^{-3}$.

K and ΔG_{ad} for the TPC-NaCl system are compared with those for DPC-NaCl system at the same salt concentrations in Table 4. The free energy of adsorption of TPC is smaller than that of DPC, which would reflect the dominant role of the hydrophobic effect of the alkyl chain in the adsorption of surfactant ions.

Table 4: Adsorption coefficient and free energy of adsorption of TPC and DPC.

$C_S/\text{mol dm}^{-3}$		TPC	DPC [9]
0	$K / \text{dm}^3 \text{mol}^{-1}$	638	350
	$\Delta G_{\text{ad}} / \text{kJ mol}^{-1}$	-16.0	-14.5
0.01	$K / \text{dm}^3 \text{mol}^{-1}$	27600	1900
	$\Delta G_{\text{ad}} / \text{kJ mol}^{-1}$	-25.3	-18.7
0.05	$K / \text{dm}^3 \text{mol}^{-1}$	82200	3800
	$\Delta G_{\text{ad}} / \text{kJ mol}^{-1}$	-28.1	-20.4

4.2 Critical micelle concentration

The CMC of TPC decreases with increasing NaCl concentration, as given in Table 1. It follows the Corrin-Harkins equation

$$\log(C_0/\text{mol dm}^{-3}) = -0.679 \log\{(C_0 + C_S)/\text{mol dm}^{-3}\} - 3.99 \quad (13)$$

as shown in Fig.7. The absolute value of slope of this Corrin-Harkins plot means the degree of counterion binding for ionic micelle [11].

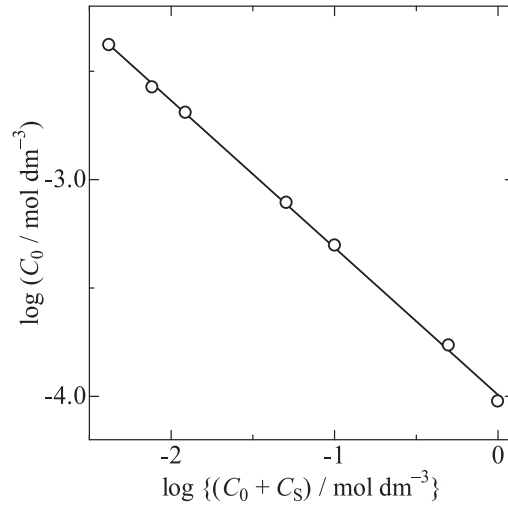


Figure 7: The Corrin-Harkins plot of tetradecylpyridinium chloride in aqueous NaCl solutions.

For DDAB-NaBr and DTAB-NaBr systems, the Corrin-Harkins plot consists of two linear plots at low and high NaBr concentrations owing to salt-induced sphere-rod transition of their micelles [12, 13]. The slope of Corrin-Harkins plot for TPC can be compared with those for DDAB [4] and DTAB [8] at low NaBr concentrations, where spherical micelles are formed:

$$\log(C_0/\text{mol dm}^{-3}) = -0.452 \log\{(C_0 + C_S)/\text{mol dm}^{-3}\} - 2.83 \quad (14)$$

and

$$\log(C_0/\text{mol dm}^{-3}) = -0.674 \log\{(C_0 + C_S)/\text{mol dm}^{-3}\} - 3.04 \quad (15)$$

and that for DPC [9], where only spherical micelle is formed [10]:

$$\log (C_0/\text{mol dm}^{-3}) = -0.684 \log \{(C_0 + C_S)/\text{mol dm}^{-3}\} - 2.98 \quad (16)$$

As the CMC is a good measure of stability of the micellar state relative to the monomeric state, Eqns (13) – (16) indicates that the stability of TPC micelles is higher than those of DDAB, DTAB and DPC micelles.

5 Conclusion

By applying the Gibbs adsorption isotherm to the surface tension of aqueous NaCl solutions of TPC at 25°C, surface excess densities of TP^+ , Cl^- and Na^+ have been derived as functions of TPC concentration at different NaCl concentrations. As observed for other cationic surfactant-simple salt systems, surface excess densities of TP^+ and Cl^- increase with increasing TPC concentration and approach the saturated values at the CMC, whereas the surface excess density of Na^+ is nearly zero or slightly negative. The molecular area of TPC on aqueous surface increases with increasing NaCl concentration up to 0.005 mol dm⁻³ and then decreases. This might be associated with very small micelles of TPC in the absence of NaCl. The Corrin-Harkins plot is linear in NaCl concentration range studied, which suggests TPC forms only spherical micelles.

References

- [1] S. Ikeda, *Hyomen*, **15**, 592 (1977).
- [2] S. Ozeki, M. Tsunoda and S. Ikeda, *J. Colloid Interface Sci.*, **64**, 28 (1978).
- [3] S. Ozeki and S. Ikeda, *Bull. Chem. Soc. Jpn.*, **53**, 1832 (1980).
- [4] H. Okuda, S. Ozeki and S. Ikeda, *Bull. Chem. Soc. Jpn.*, **57**, 1321 (1984).
- [5] H. Okuda, S. Ozeki and S. Ikeda, *J. Colloid Interface Sci.*, **115**, 155 (1987).
- [6] H. Okuda, T. Imae and S. Ikeda, *Colloids Surf.*, **27**, 187 (1987).
- [7] H. Okuda and S. Ikeda, *J. Colloid Interface Sci.*, **131**, 333 (1989).
- [8] A. Tanaka and S. Ikeda, *Colloids Surf.*, **56**, 217 (1991).
- [9] K. Fujio, K. Takeuchi and M. Suzuki, *Proc. Sch. Sci. Tokai Univ.*, **47**, 35 (2012).
- [10] K. Fujio and S. Ikeda, *Bull. Chem. Soc. Jpn.*, **65**, 1406 (1992).
- [11] K. Fujio and S. Ozeki, *Nihon Yukagakukaishi*, **49**, 221 (2000).
- [12] S. Ozeki and S. Ikeda, *Colloid Polym. Sci.*, **262**, 409 (1984).
- [13] S. Ozeki and S. Ikeda, *J. Colloid Interface Sci.*, **87**, 424 (1982).