

# Adsorption of Dodecylpyridinium Chloride on Aqueous Surfaces of Sodium Chloride Solutions

by

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## Abstract

Surface tension of aqueous NaCl solutions of dodecylpyridinium chloride (DPC) has been measured by the drop weight method at different NaCl concentrations from 0 to 1.000 mol dm<sup>-3</sup> at 25°C. Applying the Gibbs adsorption isotherm to the surface tension data at DPC concentrations below the critical micelle concentration (CMC), surface excess densities of dodecylpyridinium ion (DP<sup>+</sup>), Cl<sup>-</sup> and Na<sup>+</sup> have been obtained as functions of DPC concentration at different NaCl concentrations. Surface excess densities of DP<sup>+</sup> and Cl<sup>-</sup> increase with increasing DPC concentration, and approach the saturated values at the CMC. On the other hand, the surface excess density of Na<sup>+</sup> is nearly zero or slightly negative with respect to DPC concentration. Unlike common ionic surfactants, the molecular area of DPC on aqueous surface increases with increasing NaCl concentration up to 0.010 mol dm<sup>-3</sup>, and then decreases to almost constant value. The Corrin-Harkins plot is 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, these equations alone are not enough to evaluate the surface excess densities of surfactant ion, counterion and constituent ions of salt. S. 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 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 present work we extend similar measurements of surface tension to aqueous NaCl solutions of dodecylpyridinium chloride (DPC) having an aromatic ring as a polar head group, and determine 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]. The present results on DPC will be compared with those on the two kinds of cationic surfactants having a dodecyl chain as hydrophobic group, i.e., DDAB [4, 8] and DTAB [8].

## 2 Experimental

DPC was obtained from Sigma-Aldrich Co. and recrystallized three times from acetone. NaCl of special grade reagent from Nacalai Tesque, Inc., was dried at 200°C for two hours. Water was redistilled from alkaline  $KMnO_4$  solution.

The surface tension of aqueous solutions was measured at  $25 \pm 0.1^\circ C$  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

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

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 solutions. 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  $71.96 \text{ mN m}^{-1}$  and found to be  $3.459 \text{ mm}$ . The capillary was cleaned by being immersed in chromic acid mixture after each measurement.

### 3 Results

Figure 1 shows the surface tension,  $\gamma$ , of aqueous NaCl solutions of DPC plotted against the logarithm of the molar concentration of DPC,  $\log C$ , at different NaCl concentrations,  $C_S$ . With increasing DPC concentration up to the critical micelle concentration (CMC),  $C_0$ , 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 lowest DPC concentrations. The aspect of the surface tension-concentration relationship of the DPC-NaCl system is similar to that of alkylammonium surfactant-sodium halide system [2–8]. Table 1 gives the CMC,  $C_0$ , and the surface tension at the CMC,  $\gamma_0$ . 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 temperature.  $\Gamma$  and  $\Gamma_S$  are the surface excess densities of DPC and NaCl, respectively, and defined by

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

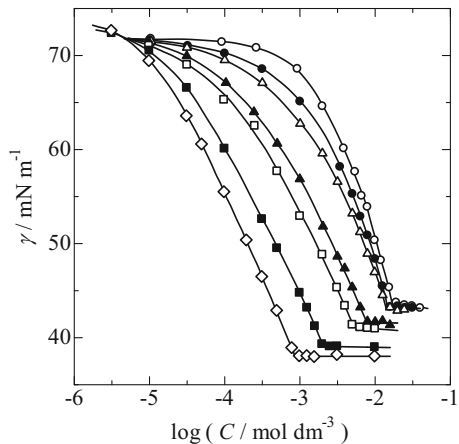


Fig. 1: Dependence of surface tension of aqueous NaCl solutions of dodecylpyridinium chloride on surfactant concentration at different NaCl concentrations.  $C_S / \text{mol dm}^{-3}$ :  $\circ$ , 0;  $\bullet$ , 0.005;  $\triangle$ , 0.010;  $\blacktriangle$ , 0.050;  $\square$ , 0.100;  $\blacksquare$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

Table 1: Adsorption properties of dodecylpyridinium 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	16.6	43.9	4.03	
0.005	14.5	43.4	5.25	0.12
0.010	14.1	43.1	3.67	0.73
0.050	7.73	41.7	2.99	2.11
0.100	5.26	41.1	3.03	2.09
0.500	2.08	39.1	2.86	2.59
1.000	0.857	38.0	3.19	4.47

and

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

$\Gamma$  can be evaluated from slopes of the curves shown in Fig. 1.

To estimate  $\Gamma_S$ , the surface tension is plotted afresh against the logarithm of the NaCl

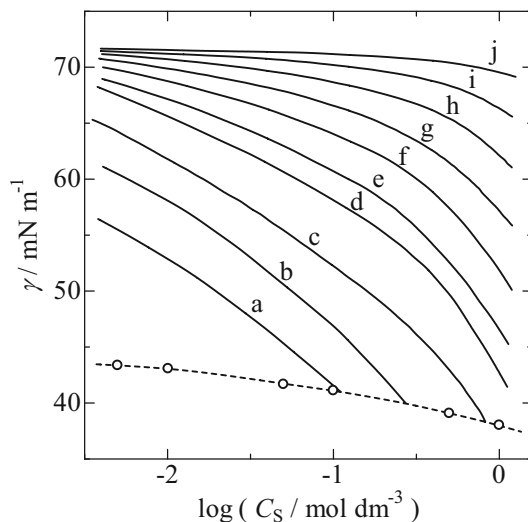


Fig. 2: Dependence of surface tension of aqueous NaCl solutions of dodecylpyridinium chloride on NaCl concentration at different surfactant concentrations.  $-\log(C / \text{mol dm}^{-3})$ : a, 2.3; b, 2.6; c, 2.9; d, 3.3; e, 3.5; f, 3.8; g, 4.1; h, 4.4; i, 4.7; j, 5.0. Dashed curve represents dependence of surface tension at the CMC,  $\gamma_0$ , on NaCl concentration.

concentration,  $\log C_S$ , at each DPC concentration,  $C$ , as shown in Fig. 2. The surface tension at the CMC,  $\gamma_0$ , is also shown in Fig. 2.

Table 1 also includes values of  $\Gamma$  and  $\Gamma_S$  at the CMC. With increasing NaCl concentration the value of  $\Gamma$  at the CMC decreases, has a minimum value at  $0.500 \text{ mol dm}^{-3}$  NaCl and then increases slightly. On the other hand, the value of  $\Gamma_S$  at the CMC monotonically increases as NaCl concentration increases. Such behavior of  $\Gamma$  and  $\Gamma_S$  at the CMC has been observed for alkylammonium surfactant-sodium halide system [3–8].

## 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 DPC concentrations below the CMC, shown in Figs. 1 and

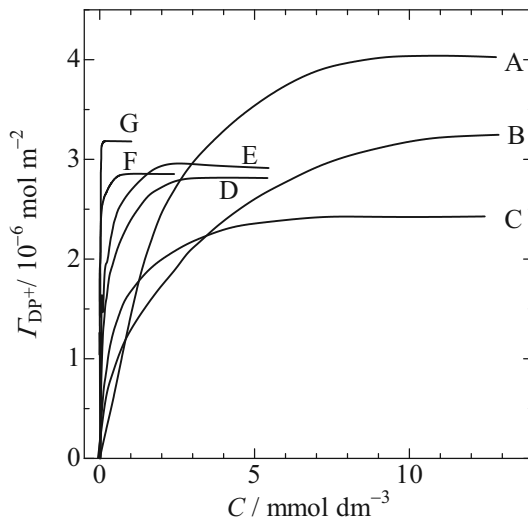


Fig. 3: Adsorption isotherm of dodecylpyridinium ion,  $\text{DP}^+$ , on aqueous surface at different NaCl concentrations.  $C_S / \text{mol dm}^{-3}$ : A, 0; B, 0.005; C, 0.010; D, 0.050; E, 0.100; F, 0.500; G, 1.000.

2, and the surface excess densities of dodecylpyridinium ion ( $\text{DP}^+$ ),  $\text{Cl}^-$  and  $\text{Na}^+$  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.

If the surface excess densities subject to the Gibbs convention of  $\text{DP}^+$ ,  $\text{Cl}^-$  and  $\text{Na}^+$  are represented by  $\Gamma_{\text{DP}^+}$ ,  $\Gamma_{\text{Cl}^-}$  and  $\Gamma_{\text{Na}^+}$ , respectively, the coefficients,  $\Gamma$  and  $\Gamma_S$ , in the Gibbs adsorption isotherm, Eqn (2), can be represented by

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

and

$$\Gamma_S = \frac{C_S}{C + C_S} \Gamma_{\text{Na}^+} + \left(1 + \frac{C_S}{C + C_S}\right) \Gamma_{\text{DP}^+} \quad (6)$$

respectively [2, 3]. Solving these equations for  $\Gamma_{\text{DP}^+}$  and  $\Gamma_{\text{Na}^+}$ , the following equations can be obtained.

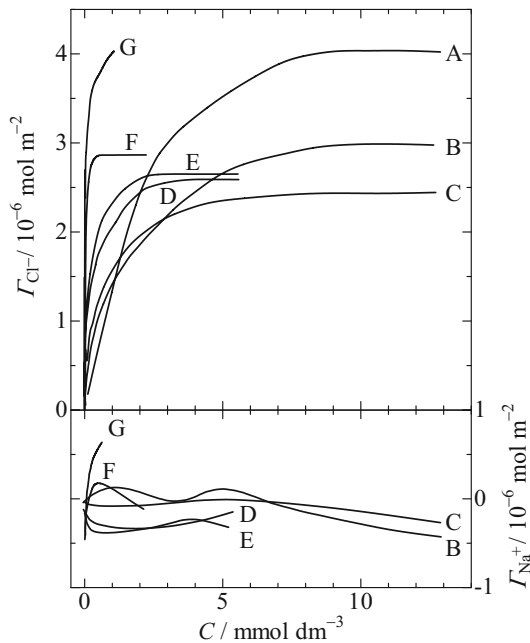


Fig. 4: Adsorption isotherms of chloride (upper) and sodium ions (bottom),  $\text{Cl}^-$  and  $\text{Na}^+$ , on aqueous surface at different  $\text{NaCl}$  concentrations.  $C_S / \text{mol dm}^{-3}$ : A, 0; B, 0.005; C, 0.010; D, 0.050; E, 0.100; F, 0.500; G, 1.000.

$$\Gamma_{\text{DP}^+} = \frac{1}{2} \left\{ \left( 1 + \frac{C_S}{C + C_S} \right) \Gamma - \frac{C}{C + C_S} \Gamma_S \right\} \quad (7)$$

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

The electroneutrality of the surface gives the surface excess density of  $\text{Cl}^-$  in the following form.

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

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  $\text{DP}^+$  and the ones of  $\text{Cl}^-$  and  $\text{Na}^+$ , respectively, at different  $\text{NaCl}$  concentrations as functions of DPC concentration.

With increasing DPC concentration, the value of  $\Gamma_{\text{DP}^+}$  increases towards a saturated value

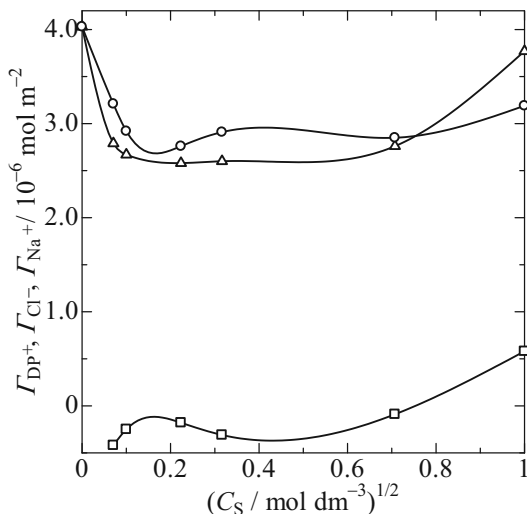


Fig. 5: Dependence of surface excess densities of ions at the CMC on NaCl concentration. ○,  $\Gamma_{\text{DP}^+}$ ; △,  $\Gamma_{\text{Cl}^-}$ ; □,  $\Gamma_{\text{Na}^+}$ .

and the rate of its increase sharpens except for the case in the absence of NaCl. At 1.000 mol dm<sup>-3</sup> NaCl the value of  $\Gamma_{\text{DP}^+}$  is already saturated at very low DPC concentrations.

The value of  $\Gamma_{\text{Na}^+}$  is nearly zero or slightly negative except for the case of 1.000 mol dm<sup>-3</sup> NaCl, where its value is positive. Consequently, the value of  $\Gamma_{\text{Cl}^-}$  is nearly equal to that of  $\Gamma_{\text{DP}^+}$  except for the highest NaCl concentration.

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

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

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

where  $\Gamma_{\text{DP}^+}^{\infty}$  is the saturated adsorption density of DP<sup>+</sup> and  $K$  is the adsorption coefficient. Table 3 gives values of  $\Gamma_{\text{DP}^+}^{\infty}$  and  $K$  at different NaCl concentrations. The molecular area,  $A_0$ , corresponding to  $\Gamma_{\text{DP}^+}^{\infty}$  is obtained in Å<sup>2</sup> by



Table 2: Surface excess densities of dodecylpyridinium ion,  $\text{Cl}^-$  and  $\text{Na}^+$  at the critical micelle concentration.

$C_S / \text{mol dm}^{-3}$	$\Gamma_{\text{DP}^+} / 10^{-6} \text{mol m}^{-2}$	$\Gamma_{\text{Cl}^-} / 10^{-6} \text{mol m}^{-2}$	$\Gamma_{\text{Na}^+} / 10^{-6} \text{mol m}^{-2}$
0	4.03	4.03	
0.005	3.21	2.79	-0.42
0.010	2.92	2.67	-0.25
0.050	2.76	2.58	-0.18
0.100	2.91	2.60	-0.31
0.500	2.85	2.76	-0.09
1.000	3.19	3.77	0.58

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

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 DPC increases 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 decreases to almost constant value of  $55 \text{ \AA}^2$  above  $0.050 \text{ mol dm}^{-3}$  NaCl. This dependence of molecular area on NaCl concentration might be associated with very small micelles of DPC in aqueous NaCl solution below  $0.05 \text{ mol dm}^{-3}$  [9], although its cause remains unsolved.

As shown in Table 3, the adsorption coefficient  $K$  increases with increasing NaCl concentration, which suggests the electrostatic shielding effect of NaCl on the adsorption of surfactant ions. 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  $K$ ,  $\Delta G_{\text{ad}}$  decreases with NaCl concentration.

$K$  and  $\Delta G_{\text{ad}}$  for the DPC-NaCl system are compared with those for DDAB-NaBr and DTAB-NaBr systems at the same salt concentrations in Table 4. The free energy of adsorption of DPC is nearly the same as those of DDAB and DTAB in water, which would

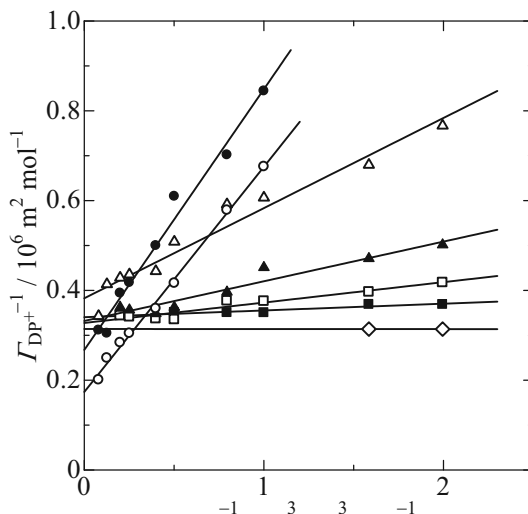


Fig. 6: Langmuir isotherm of dodecylpyridinium ion,  $\text{DP}^+$ , at different NaCl concentrations.  $C_S / \text{mol dm}^{-3}$ :  $\circ$ , 0;  $\bullet$ , 0.005;  $\triangle$ , 0.010;  $\blacktriangle$ , 0.050;  $\square$ , 0.100;  $\blacksquare$ , 0.500;  $\diamond$ , 1.000.

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

$C_S / \text{mol dm}^{-3}$	$\Gamma_{\text{DP}^+}^\infty / 10^{-6} \text{mol m}^{-2}$	$A_0 / \text{\AA}^2$	$K / \text{dm}^3 \text{mol}^{-1}$	$\Delta G_{\text{ad}} / \text{kJ mol}^{-1}$
0	5.75	28.9	350	-14.5
0.005	3.74	44.4	460	-15.2
0.010	2.61	63.5	1900	-18.7
0.050	3.01	55.1	3800	-20.4
0.100	3.05	54.4	7200	-22.0
0.500	2.94	56.5	23000	-24.9
1.000	3.18	52.1	-	-

reflect the dominant role of the hydrophobic effect of the alkyl chain in the adsorption of surfactant ions. In aqueous salt solutions, however,  $\Delta G_{\text{ad}}$  of DPC is slightly higher than those of other surfactants. This would be responsible for the effect of counterion binding on

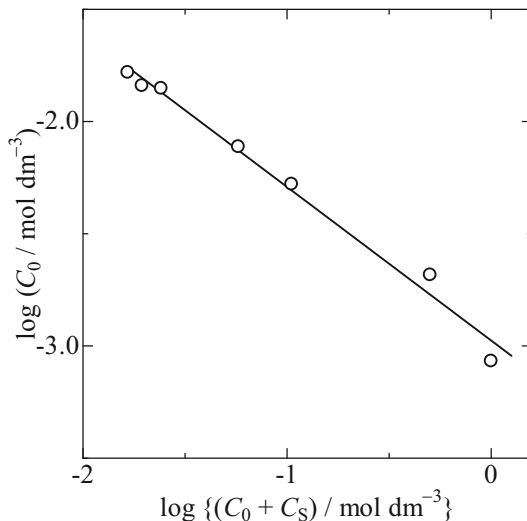


Fig. 7: The Corrin-Harkins plot of dodecylpyridinium chloride in aqueous NaCl solutions.

Table 4: Adsorption coefficient and free energy of adsorption of three surfactant ions.

$C_S / \text{mol dm}^{-3}$		DPC	DDAB [8]	DTAB[8]
0	$K / \text{dm}^3 \text{mol}^{-1}$	350	355	510
	$\Delta G_{\text{ad}} / \text{kJ mol}^{-1}$	-14.5	-14.5	-15.4
0.01	$K / \text{dm}^3 \text{mol}^{-1}$	1900	2410	2600
	$\Delta G_{\text{ad}} / \text{kJ mol}^{-1}$	-18.7	-19.3	-19.5
0.05	$K / \text{dm}^3 \text{mol}^{-1}$	3800	10000	7800
	$\Delta G_{\text{ad}} / \text{kJ mol}^{-1}$	-20.4	-22.8	-22.2

the adsorbed surfactant ions.

#### 4.2 Critical micelle concentration

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

$$\log(C_0/\text{mol dm}^{-3}) = -0.684 \log\{(C_0 + C_S)/\text{mol dm}^{-3}\} - 2.98 \quad (13)$$

as shown in Fig. 7. The coefficient of  $\log(C_0 + C_S)$  and the constant in the above equation

are slightly smaller than those obtained by light scattering measurements, -0.593 and -2.845, respectively [9]. This would be caused by light scattering measurement detecting micelles formed.

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 [10, 11]. Because DPC forms only spherical micelles in aqueous NaCl solutions [9], the Corrin-Harkins equation for DPC 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

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

As the CMC is a good measure of stability of the micellar state relative to the monomeric state, Eqns (13) – (15) indicates that the stability of DPC micelles is nearly equal to that of DTAB micelles and higher than that of DDAB micelles.

## 5 Conclusion

By applying the Gibbs adsorption isotherm to the surface tension of aqueous NaCl solutions of DPC at 25°C, surface excess densities of DP<sup>+</sup>, Cl<sup>-</sup> and Na<sup>+</sup> have been derived as functions of DPC concentration at different NaCl concentrations. As observed for other cationic surfactant-simple salt systems, surface excess densities of DP<sup>+</sup> and Cl<sup>-</sup> increase with increasing DPC concentration and approach the saturated values at the CMC, whereas the surface excess density of Na<sup>+</sup> is nearly zero or slightly negative. The molecular area of DPC on aqueous surface increases with increasing NaCl concentration up to 0.010 mol dm<sup>-3</sup> and then decreases to almost constant value. This might be associated with very small micelles of DPC at NaCl concentrations below 0.05 mol dm<sup>-3</sup>. The Corrin-Harkins plot is linear in NaCl concentration range studied, which consists with DPC forming only spherical micelles.

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