

Adsorption of Decylpyridinium Iodide on Aqueous Surfaces of Sodium Iodide Solutions

by

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Abstract

We have measured the surface tension of aqueous NaI solutions of decylpyridinium iodide (DePI) by the drop weight method at different NaI concentrations from 0 to 80 mmol dm⁻³ at 25°C and obtained surface excess densities of decylpyridinium ion (DeP⁺), I⁻ and Na⁺ as functions of DePI concentration at different NaI concentrations by applying the Gibbs adsorption isotherm to the surface tension data at DePI concentrations below the critical micelle concentration (CMC). Surface excess densities of DeP⁺ and I⁻ increase with increasing DePI concentration, and approach the saturated values at the CMC excluding the most concentrated NaI solution. On the other hand, the surface excess density of Na⁺ is nearly zero or slightly negative. The molecular area of DePI on aqueous surface increases with increasing NaI concentration up to 5 mmol dm⁻³ and then decreases, as associated with very small micelles of DePI in the absence of NaI. The Corrin-Harkins plot is linear in NaI concentration range studied, which suggests DePI forms only spherical micelles.

Keywords: decylpyridinium iodide; surface tension; Langmuir adsorption; critical micelle concentration

1 Introduction

Surfactant molecules or ions are adsorbed on aqueous surface and consequently lower the surface tension of their aqueous solutions. Using the Gibbs adsorption isotherm, Equations (2) – (4), we can obtain the surface excess densities of nonionic surfactant molecule and concomitant salt from the dependence of surface tension on concentrations of surfactant and salt.

In the case of ionic surfactant in aqueous salt solution, however, only these equations are not sufficient to evaluate the surface excess densities of surfactant ion, counterion and constituent ions of salt. 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].

Cationic surfactants with a quaternary ammonium head group are fully ionized over whole practical pH range and adsorbed onto most solid-water interface, which are usually negatively charged, so that they have special applications such as water-repellent and antistatic agents [9]. Furthermore, they exhibit good bactericidal action and hence for example hexadecylpyridinium bromide are used in mouthwashes [10]. Factors affecting these properties of cationic surfactants including alkylpyridinium halides are interesting. In the previous work [11, 12], therefore, we extended similar measurements of surface tension to aqueous NaCl solutions of dodecylpyridinium and tetradecylpyridinium chlorides (DPC and TPC) having an aromatic ring as a polar head group, and determined the surface excess densities of dodecylpyridinium and tetradecylpyridinium ions (DP^+ and TP^+), Cl^- and Na^+ as functions of surfactant and NaCl 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^+ , TP^+ and Cl^- increased with increasing surfactant concentration and approached the saturated values at the critical micelle concentration (CMC), whereas the surface excess density of Na^+ was nearly zero or slightly negative. 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. On the other hand, that of DPC increased with increasing NaCl concentration up to $0.010 \text{ mol dm}^{-3}$ and then decreased to almost constant value, as explained by the formation of very small micelles of DPC below 0.05 mol dm^{-3} NaCl.

In the present work we study the adsorption behavior of decylpyridinium iodide (DePI), whose hydrophilic tail is the shorter by two methylene groups than DPC and whose counterion is different from that of surfactants studied previously, on aqueous surfaces of NaI solutions in order to investigate the effect of alkyl chain length and the influence of the kind of counterion on the adsorption of alkylpyridinium halide on aqueous surfaces of sodium halide solutions.

2 Experimental

DePC was synthesized by refluxing the mixture of pyridine and 1-iododecane at 120°C for 7 hours and recrystallized three times from acetone-diethyl ether mixture (1:2 v/v). Pyridine was obtained from Nacalai Tesque, Inc., and dried over molecular sieves 3A. 1-iododecane was purchased from ACROS ORGANICS and used without purification. NaI of special grade reagent from Nacalai Tesque, Inc., was dried at 120°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. We suspended a drop of solution at the lower end of capillary in a state just before falling for 5 min or more, and then detached it 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

$$\gamma = \frac{mg}{r} F \quad (1)$$

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 NaI 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 NaI solutions of DePI plotted against the logarithm of the molar concentration of DePI, $\log C$, at different NaI concentrations, C_S . As the DePI concentration increases up to the 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 NaI concentration. Surface tension is lower at the higher NaI concentration unless the DePI concentration is very low. The concentration dependence of surface tension of the DePI-NaI system is similar to that of DPC- and TPC-NaCl systems [11, 12] and alkylammonium surfactant-sodium halide systems [2–8]. Table 1 gives the CMC, C_0 , and the surface tension at the CMC, γ_0 . Both quantities decrease with increasing NaI 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

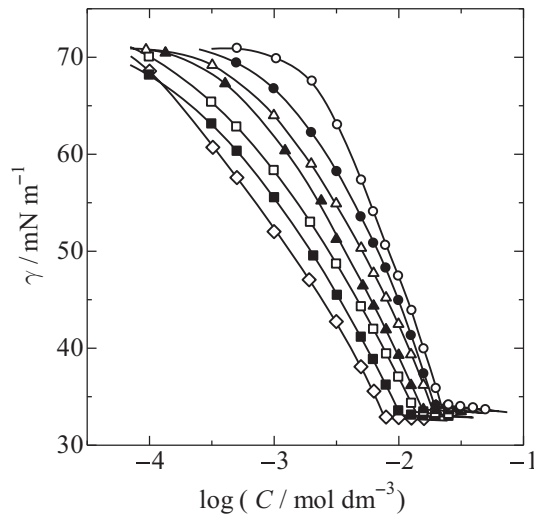


Fig. 1 Dependence of surface tension of aqueous NaI solutions of DePI on surfactant concentration at different NaI concentrations. $C_S / \text{mmol dm}^{-3}$: $\circ$, 0; $\bullet$, 5; $\triangle$, 10; $\blacktriangle$, 20; $\square$, 30; $\blacksquare$, 50; $\diamond$, 80.

Table 1 Adsorption properties of DePI on the surface of aqueous NaI solution at the CMC, C_0 .

$C_S / \text{mmol dm}^{-3}$	$C_0 / \text{mmol dm}^{-3}$	$\gamma_0 / \text{mN m}^{-1}$	$\Gamma / 10^{-6} \text{mol m}^{-2}$	$\Gamma_S / 10^{-6} \text{mol m}^{-2}$
0	21.8	34.2	7.76	
5.00	19.4	34.0	6.92	1.16
10.01	18.3	34.0	5.93	1.10
20.02	15.5	33.7	4.98	1.81
30.03	13.7	33.4	4.58	1.84
50.12	10.3	33.1	4.55	2.61
80.23	7.7	32.8	5.23	2.73

densities of DePI and NaI, respectively, 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 Figure 1.

In order to estimate Γ_S , the surface tension is plotted afresh against the logarithm of the NaI concentration, $\log C_S$, at each DePI concentration, C , as shown in Figure 2. This figure also indicates the NaI concentration dependence of surface tension at the CMC, γ_0 , by a dashed line.

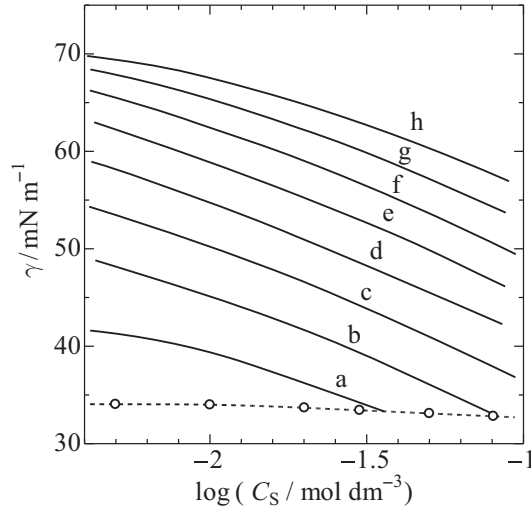


Fig. 2 Dependence of surface tension of aqueous NaI solutions of DePI on NaI concentration at different DePI concentrations. $-\log (C / \text{mol dm}^{-3})$: a, 1.9; b, 2.1; c, 2.3; d, 2.5; e, 2.7; f, 2.9; g, 3.1; h, 3.3. Dashed curve represents dependence of surface tension at the CMC, γ_0 , on NaI concentration.

Table 1 also includes values of Γ and Γ_S at the CMC. With increasing NaI concentration the value of Γ at the CMC decreases, has a minimum value at 50.12 mmol dm⁻³ NaI and then increases. The value of Γ_S at the CMC also exhibits the similar NaI concentration dependence with a minimum at 10.01 mmol dm⁻³ NaI. Excluding the decrease in Γ_S at low NaI concentration, such behavior of Γ and Γ_S at the CMC has been observed for DPC- and TPC-NaCl systems [11, 12] and alkylammonium surfactant-sodium halide systems [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 DePI concentrations below the CMC, shown in Figures 1 and 2, and the surface excess densities of decylpyridinium ion (DeP^+), I^- and Na^+ can be determined as functions of DePI and NaI concentrations. Furthermore, their works [2, 3] indicated that the substitution of activities of surfactant and salt by their molar 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 DeP^+ , I^- and Na^+ by Γ_{DeP^+} , Γ_{I^-} and Γ_{Na^+} , respectively, the coefficients, Γ and Γ_{S} , in the Gibbs adsorption isotherm, Equation (2), can be represented by

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

and

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

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

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

and

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

The electroneutrality of the surface gives the surface excess density of I^- in the following form:

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

Applying Equations (7) – (9) to the surface tension data given in Figures 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 DeP^+ and those of I^- and Na^+ , respectively, at different NaI concentrations as functions of DePI concentration.

With increasing DePI concentration, the value of Γ_{DeP^+} increases towards a saturated value except for the most concentrated NaI solution. It appears that above $20.02 \text{ mmol dm}^{-3}$ NaI the value of Γ_{DeP^+} is already saturated at the low DePI concentrations.

The value of Γ_{Na^+} is nearly zero or slightly negative except the case of $5.00 \text{ mmol dm}^{-3}$ NaI, where it is slightly positive. Consequently, the value of Γ_{I^-} is nearly equal to that of Γ_{DeP^+} .

Table 2 gives Γ_{DeP^+} , Γ_{I^-} and Γ_{Na^+} at the CMC for different NaI concentrations and Figure 5 shows them plotted against the square root of the NaI concentration.

Figure 6 plots $1/\Gamma_{\text{DeP}^+}$ smaller than $0.6 \times 10^6 \text{ m}^2 \text{ mol}^{-1}$, above which small values of Γ_{DeP^+} cause significant errors in calculating $1/\Gamma_{\text{DeP}^+}$, against $1/C$ and gives straight lines at each NaI concentration. This indicates that the adsorption of DeP^+ obeys the Langmuir isotherm

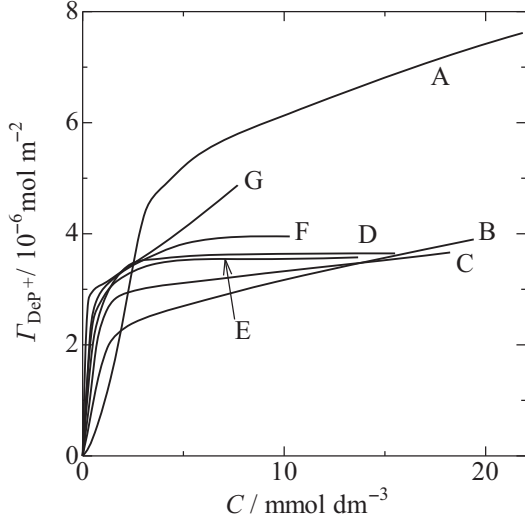


Fig. 3 Adsorption isotherm of decylpyridinium ion, DeP^+ , on aqueous surface at different NaI concentrations. $C_S / \text{mmol dm}^{-3}$: A, 0; B, 5; C, 10; D, 20; E, 30; F, 50; G, 80.

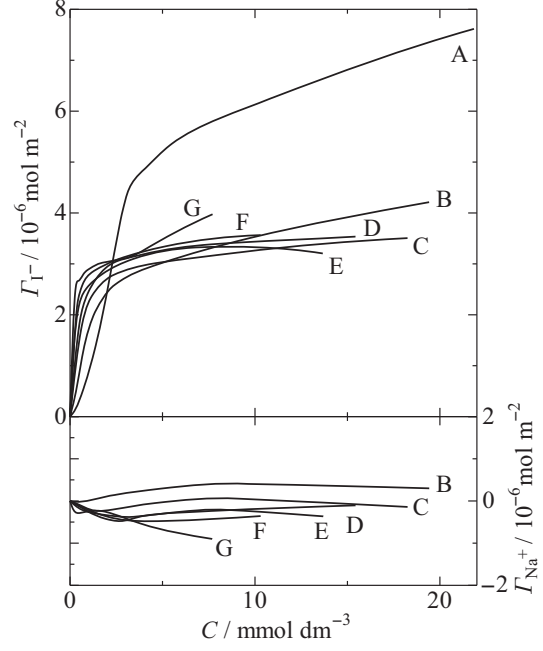


Fig. 4 Adsorption isotherms of I^- (upper) and Na^+ (bottom) on aqueous surface at different NaI concentrations. $C_S / \text{mmol dm}^{-3}$: A, 0; B, 5; C, 10; D, 20; E, 30; F, 50; G, 80.

Table 2 Surface excess densities of decylpyridinium ion, I^- and Na^+ at the CMC.

$C_S / \text{mmol dm}^{-3}$	$\Gamma_{\text{DeP}^+} / 10^{-6} \text{ mol m}^{-2}$	$\Gamma_{\text{I}^-} / 10^{-6} \text{ mol m}^{-2}$	$\Gamma_{\text{Na}^+} / 10^{-6} \text{ mol m}^{-2}$
0	7.76	7.76	
5.00	3.71	4.04	0.33
10.01	3.66	3.51	-0.14
20.02	3.50	3.39	-0.10
30.03	3.57	3.21	-0.36
50.12	3.94	3.58	-0.36
80.23	4.88	3.98	-0.90

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

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

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

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

where N_A is the Avogadro constant, and its values are also given in Table 3. The molecular area of common ionic surfactant such as DTAB decreases with increasing salt concentration because the electrostatic shielding effect of salt weakens the electrostatic repulsion between the charged head groups of the adsorbed surfactant ions [8]. With increasing NaI concentration, however, the molecular area of DePI increases from $21.7 \text{ \AA}^2$ in the absence of NaI to $51.9 \text{ \AA}^2$ at $5.00 \text{ mmol dm}^{-3}$

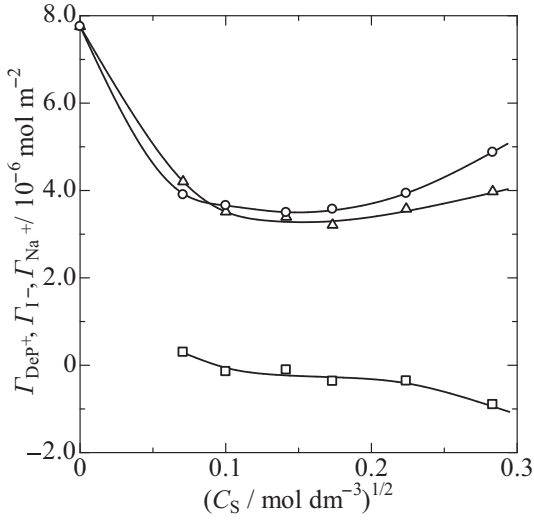


Fig. 5 Dependence of surface excess densities of decylpyridinium ion, I^- and Na^+ at the CMC on NaI concentration. $\circ$, Γ_{DeP^+} ; $\triangle$, Γ_{I^-} ; $\square$, Γ_{Na^+} .

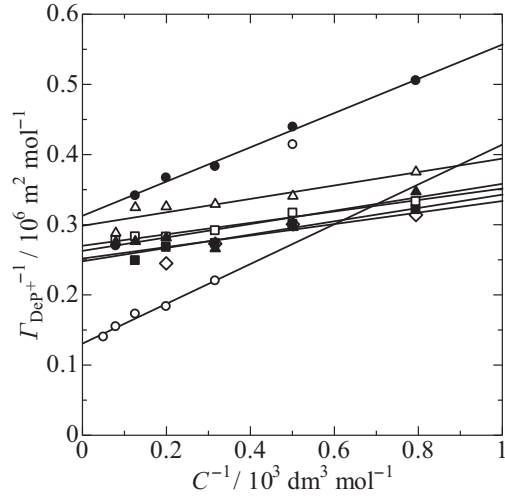


Fig. 6 Langmuir isotherm of decylpyridinium ion at different NaI concentrations. C_S / mmol dm^{-3} : $\circ$, 0; $\bullet$, 5; $\triangle$, 10; $\blacktriangle$, 20; $\square$, 30; $\blacksquare$, 50; $\diamond$, 80.

Table 3 Saturated adsorption density, molecular area, adsorption coefficient and free energy of adsorption of DePI.

C_S / mmol dm^{-3}	$\Gamma_{DeP^+}^\infty$ / $10^{-6} \text{ mol m}^{-2}$	A_0 / $\text{\AA}^2$	K / $10^3 \text{ dm}^3 \text{ mol}^{-1}$	ΔG_{ad} / kJ mol^{-1}
0	7.66	21.7	0.46	-15.2
5.00	3.20	51.9	1.28	-17.7
10.01	3.35	49.6	3.12	-19.9
20.02	3.84	43.2	2.46	-19.4
30.03	3.70	44.8	3.29	-20.1
50.12	3.84	43.2	3.92	-20.5
80.23	3.76	44.1	5.02	-21.1

NaI, and then decreases to about $44 \text{ \AA}^2$ at $20.02 \text{ mmol dm}^{-3}$ NaI, above which the molecular area remains almost constant. Similar dependence of molecular area on salt 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 [11]. 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} [13]. The NaI concentration dependence of molecular area of DePI also would be interpreted in the same manner.

Table 3 shows that the adsorption coefficient K increases with increasing NaI concentration, which suggests the electrostatic shielding effect of NaI on the adsorption of DeP^+ , except for $20.02 \text{ mol dm}^{-3}$ NaI. This exception would be attributed to a large error in K due to a deviation of the $1/\Gamma_{DeP^+}$ vs. $1/C$ plot from a straight line expected by the Langmuir isotherm.

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

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

Corresponding to the increase in K , ΔG_{ad} decreases with NaI concentration except for the case of 20.02 mmol dm⁻³ NaI.

K and ΔG_{ad} for the DePI-NaI system are compared with those for DPC- and TPC-NaCl systems at the same salt concentrations in Table 4. The free energy of adsorption is the smallest for TPC and is almost same for DePI and DPC, but slightly smaller for DePI than for DPC. In the previous study the smaller free energy of adsorption of TPC than DPC was explained by the dominant role of the hydrophobic effect of the alkyl chain in the adsorption of surfactant ions [12]. In this case the higher counterion binding of I⁻ to a charged self-assembly such as micelle than Cl⁻ [14] also would have to be considered. The higher counterion binding results in the smaller free energy of adsorption because the electrostatic repulsion between head groups of adsorbed surfactants is weakened.

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

C_S / mol dm ⁻³		DePI	DPC [11]	TPC [12]
0	K / dm ³ mol ⁻¹	461	350	638
	ΔG_{ad} / kJ mol ⁻¹	-15.2	-14.5	-16.0
0.01	K / dm ³ mol ⁻¹	3120	1900	27600
	ΔG_{ad} / kJ mol ⁻¹	-19.9	-18.7	-25.3
0.05	K / dm ³ mol ⁻¹	3920	3800	82200
	ΔG_{ad} / kJ mol ⁻¹	-20.5	-20.4	-28.1

4.2 Critical micelle concentration

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

$$\log(C_0/\text{mol dm}^{-3}) = -0.734 \log\{(C_0 + C_S)/\text{mol dm}^{-3}\} - 2.88 \quad (13)$$

as shown in Figure 7.

For DDAB-NaBr and DTAB-NaBr systems, the Corrin-Harkins plot consists of two linear plots

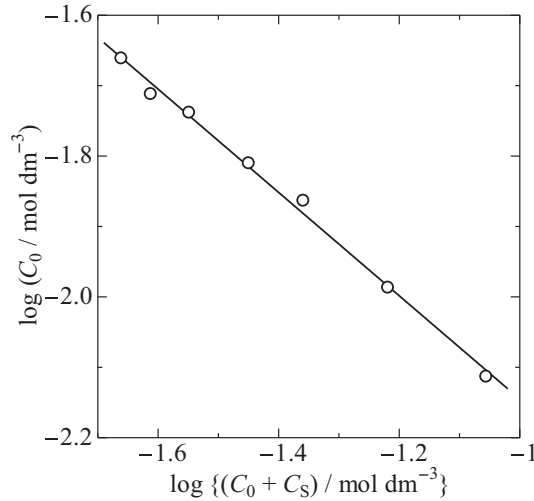


Fig. 7 The Corrin-Harkins plot of DePI in aqueous NaI solutions.

at low and high NaBr concentrations owing to the salt-induced sphere-rod transition of their micelles [15, 16]. The slope of Corrin-Harkins plot for DePI 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 those for DPC [11], where only spherical micelle is formed [13], and TPC [12]:

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

and

$$\log (C_0/\text{mol dm}^{-3}) = -0.679 \log \{(C_0 + C_S)/\text{mol dm}^{-3}\} - 3.99 \quad (17)$$

Consequently, the Corrin-Harkins plot suggests DePI forms only spherical micelles.

As the CMC is a good measure of stability of the micellar state relative to the monomeric state, Equations (13) – (17) indicates that the stability of DePI micelles is lower than that of DDAB, DTAB, DPC and TPC micelles.

5 Conclusion

By applying the Gibbs adsorption isotherm to the surface tension of aqueous NaI solutions of DePI at 25°C, surface excess densities of DeP^+ , I^- and Na^+ have been derived as functions of DePI concentration at different NaI concentrations. As observed for other cationic surfactant-simple salt systems, surface excess densities of DeP^+ and I^- increase with increasing DePI concentration and approach the saturated values at the CMC except for the most concentrated NaI solution, whereas the surface excess density of Na^+ is nearly zero or slightly negative. The molecular area of DePI on aqueous surface increases with increasing NaI concentration up to 5.00 mmol dm⁻³ and then decreases. This might be associated with very small micelles of DePI in the absence of NaI. The Corrin-Harkins plot is linear in NaI concentration range studied, which suggests DePI forms only spherical micelles. The free energy of adsorption for DePI-NaI system is slightly smaller than that for DPC-NaCl system, as explained by competition between the hydrophobic effect of alkyl chain and the counterion binding to adsorbed surfactant film.

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