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Effect of Counterion and Configurational Entropy on the Surface Tension of Aqueous Solutions of Ionic Surfactant and Electrolyte Mixtures

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Abstract: In order to clarify the adsorption behavior of cationic surfactants on the air/aqueous electrolyte solution surface, we derived the theoretical equation for the surface tension. The equation includes the electrical work required for charging the air/water surface and the work attributable to the configurational entropy in the adsorbed film. By fitting the equation to the experimental data, we determined the binding constant between adsorbed surfactant ion and counterion, and found that the bromide ions, rather than the chloride ions, are preferentially adsorbed by the air/water surface. Furthermore, it was suggested that the contribution of configurational entropy to the surface tension is predominant in the presence of electrolytes because of the increase in the surface density of surfactant molecules associated with decreasing the repulsive interaction between their hydrophilic groups.

Keywords: surface tension; Helmholtz free energy; configurational entropy; adsorption constant; binding constant

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List of Notations

γ	Surface tension of aqueous solution
γ^0	Surface tension of pure water
γ_{el}	Surface free energy attributable to electrical work
γ_{config}	Surface free energy attributable to configurational entropy
F^s	Helmholtz free energy of charged air/water surface
$F^{s,0}$	Helmholtz free energy of uncharged air/water surface
F_{el}	Electrical work required for charging air/water surface
F_{config}	Entropic term in Helmholtz free energy
S_{config}	Configurational entropy
A	Surface area
T	Absolute temperature
N_i	Number of ion i on air/water surface
N_{max}	Number of maximal adsorption sites on air/water surface
Ω_{config}	Number of all possible configurations of components on air/water surface
Ω_1	Number of possible configurations of surfactant ion on air/water surface
Ω_2	Number of possible configurations of counterions on air/water surface
κ	Debye-Hückel parameter
k	Boltzmann constant
ϵ_r	Relative dielectric constant of aqueous solution
ϵ_0	Dielectric constant of vacuum
e	Elementary charge
Z_i	Valence of ion i
N_{Av}	Avogadro's number
C_i	Molarity of aqueous solution of component i
σ	Surface charge density
$\psi(\sigma), \psi_0$	Surface potential
y_0	Reduced surface potential
μ_i^s	Electrochemical potential of ion i on air/water surface
$\mu_i^{s,0}$	Constant term in electrochemical potential of ion i on air/water surface
μ_i^{bulk}	Chemical potential of ion i in bulk phase
$\mu_i^{bulk,0}$	Standard chemical potential of ion i in bulk phase
K_A	Adsorption constant of surfactant ion
K_C, K_D	Binding constant between adsorbed surfactant ion and counterion
Γ_{max}	Maximal adsorption

1. Introduction

The surface tension of pure water increases by adding an electrolyte [1-5]. This phenomenon has been theoretically explained by the concept of image charge tentatively existing in the air phase and an ion-free layer due to the hydration of electrolyte ions [6,7]. In this case, the electrolyte ions are

repelled from the air/water surface, which is known as negative adsorption. The presence of an adsorbed film of ionic surfactant attracts the electrolyte ions toward the air/water surface, because the adsorbed film provides the charged surface. As a result, the concentration of electrolyte ions possessing the charge opposite to the hydrophilic group of surfactant molecule increases in the vicinity of air/water surface. Then, the weakened repulsive interaction between adsorbed surfactant molecules results in promoting the adsorption of ionic surfactant on the air/water surface. This implies that the addition of electrolytes lowers the surface tension of aqueous solution of ionic surfactant [8-11]. The surface properties of aqueous solution of ionic surfactant and electrolyte mixtures are significant for not only the fundamentals in surface chemistry, e.g., the stability of foam and emulsion, but also the technological processes such as detergency, tertiary oil recovery, froth flotation, *etc.*

Theoretical studies on the surface tension of aqueous solutions of ionic surfactants and electrolyte mixtures have been performed by many researchers [12-15]. There are some points on building up the theory. One needs to consider the contribution of configurational entropy, which is estimated by counting the number of possible configuration of surfactant ions and counterions on the two-dimensional plane of air/water surface. In the case of ionic surfactants, the work required for charging the air/water surface has to be taken into account. Moreover, the lateral interaction between adsorbed surfactant ions becomes important with increasing surface density at the air/water surface. In a previous study [16], we derived the theoretical equation for the surface tension of aqueous solutions of ionic surfactant and electrolyte mixtures, which have a common ion, and evaluated the configurational entropy, the adsorption constant of surfactant ion, and the binding constant of counterion, by applying the theoretical equation into the experimental results of surface tension measurement in a lower concentration region. These parameters made it possible for us to discuss the adsorption behavior on the air/water surface.

The purpose of this study is to extend the above theoretical equation so that it can be applied to the experimental system without a common ion. In the respect that two different kinds of counterion coexist in the aqueous solution, this makes it possible to discuss directly the preferential adsorption of counterion to the charged surface, as well as the contribution of configurational entropy to the surface tension.

2. Theory

An ionic surfactant (AC) and electrolyte (BD) dissociate into ions in an aqueous solution as follows:



For simplicity, we assume that both ionic surfactant and electrolyte are symmetrical and univalent. Namely, the valence Z_i of ion i is +1 for cation, and -1 for anion. In a similar manner as our previous paper [16], we can derive the equation for surface tension of aqueous solution of ionic surfactant and electrolyte mixtures even without common ions.

2.1. Helmholtz free energy

Previously, Ohshima has derived an equation for Helmholtz free energy of the interface between a charged colloidal particle and an electrolyte solution by considering the process that the uncharged particle surface gradually takes on a charge by the adsorption of electrolyte ions [17]. We start with the replacement of such an interface by a surface between the air phase and the aqueous solution of surfactant and electrolyte mixtures. According to this concept, a fundamental equation for Helmholtz free energy F^s in this system can be given as follows:

$$F^s = F^{s,0} + A \int_0^\sigma \psi(\sigma') d\sigma' + N_A \mu_A^{s,0} + N_C \mu_C^{s,0} + N_D \mu_D^{s,0} - TS_{config} \quad (3)$$

where $F^{s,0}$, N_i , and $\mu_i^{s,0}$ represent the Helmholtz free energy of uncharged air/water surface being equivalent to the product of surface tension γ^0 of pure water and surface area A , the number of adsorbed ions i , and the constant term in the electrochemical potential of adsorbed ion i on the air/water surface, respectively. The second term of right-hand side of Equation (3) denotes the electrical work F_{el} required for charging the air/water surface until its surface charge density goes up to σ .

$$F_{el} = A \int_0^\sigma \psi(\sigma') d\sigma' \quad (4)$$

Here, $\psi(\sigma')$ is the surface potential of air/water surface possessing the surface charge density σ' ($0 \leq \sigma' \leq \sigma$). In addition, the product of absolute temperature T and configurational entropy S_{config} in Equation (3) is the general entropic term F_{config} in the Helmholtz free energy:

$$F_{config} = -TS_{config} \quad (5)$$

2.2. Configurational entropy

The configurational entropy is defined by:

$$S_{config} = k \ln \Omega_{config} \quad (6)$$

where k is the Boltzmann constant. Ω_{config} means the number of all possible configurations of surfactants and electrolytes on the air/water surface and can be estimated as follows. First, supposing that N_{max} adsorption sites on the air/water surface are occupied by N_A ($\leq N_{max}$) surfactant ions (Figure 1), the number Ω_1 of possible configurations at the air/water surface is:

$$\Omega_1 = \frac{N_{max}!}{N_A!(N_{max} - N_A)!} \quad (7)$$

Second, assuming that N_C and N_D counterions, the sum of which is less than N_A , are bound to the adsorbed surfactant layer (Figure 2), the number Ω_2 of possible configurations at the air/water surface is:

$$\Omega_2 = \frac{N_A!}{N_C!N_D!(N_A - N_C - N_D)!} \quad (8)$$

Figure 1. Schematic illustration of surfactant adsorbed film (left) and adsorption model of surfactant ion on two-dimensional air/water surface with N_{max} adsorption sites (right).

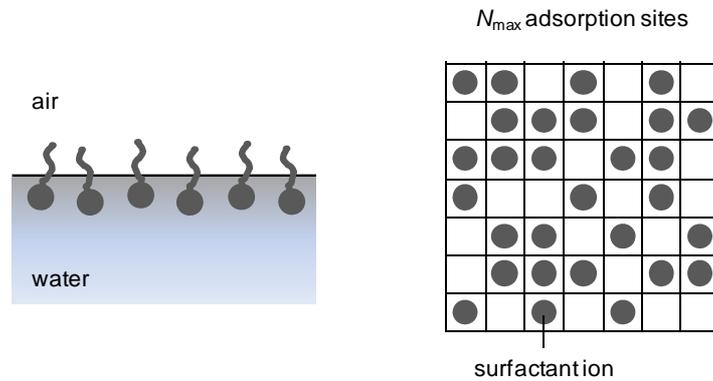
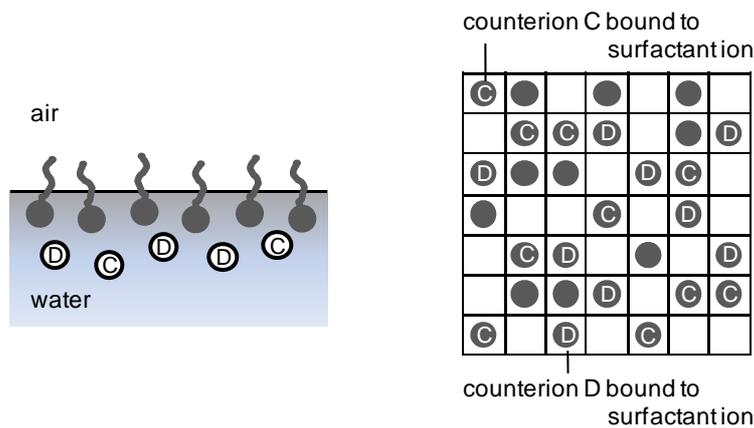


Figure 2. Schematic illustration of surfactant adsorbed film in the presence of counterions (left) and model of counterion bound to adsorbed surfactant layer with N_A surfactant ions (right).



Then, Ω_{config} is given by the following equation:

$$\Omega_{config} = \Omega_1 \times \Omega_2 = \frac{N_{max}!}{(N_{max} - N_A)! N_C! N_D! (N_A - N_C - N_D)!} \tag{9}$$

Substituting Equation (9) into Equation (6) and using the Stirling approximation, S_{config} is given by:

$$S_{config} = k [N_{max} \ln N_{max} - (N_{max} - N_A) \ln (N_{max} - N_A) - N_C \ln N_C - N_D \ln N_D - (N_A - N_C - N_D) \ln (N_A - N_C - N_D)] \tag{10}$$

2.3. Surface charge density

The surface charge density σ is related to the surface potential ψ_0 ($=\psi(\sigma)$) by the following Equation [18]:

$$\sigma = \frac{2\epsilon_r \epsilon_0 k T \kappa}{e} \sinh \frac{y_0}{2} \tag{11}$$

where ϵ_r , ϵ_0 , and e stand for the relative dielectric constant of aqueous solution, the dielectric constant of vacuum, and the elementary charge, respectively, and:

$$y_0 = \frac{e\psi_0}{kT} \tag{12}$$

The Debye-Hückel parameter κ is defined by:

$$\kappa = \sqrt{\frac{2000N_{Av}e^2}{\epsilon_r\epsilon_0kT}(C_{AC} + C_{BD})} \tag{13}$$

where N_{Av} and C_i represent the Avogadro's number and the molarity of aqueous solution of component i , respectively.

2.4. Surface tension

The differential of Helmholtz free energy F^s with reference to the surface area A yields the surface tension γ . By using Equations (3,10,11), and assuming that N_{max} is proportional to A , we can derive the equation for γ as follows:

$$\begin{aligned} \gamma &\equiv \left(\frac{\partial F^s}{\partial A}\right)_{T,V,N_A,N_C,N_D} = \left(\frac{\partial F^{s,0}}{\partial A}\right)_{T,V,N_A,N_C,N_D} + \left(\frac{\partial F_{el}}{\partial A}\right)_{T,V,N_A,N_C,N_D} + \left(\frac{\partial F_{config}}{\partial A}\right)_{T,V,N_A,N_C,N_D} \\ &= \gamma^0 + \gamma_{el} + \gamma_{config} = \gamma^0 - 8\epsilon_r\epsilon_0\kappa\left(\frac{kT}{e}\right)^2 \sinh^2\left(\frac{y_0}{4}\right) - \frac{kTN_{max}}{A} \ln \frac{N_{max}}{N_{max} - N_A} \end{aligned} \tag{14}$$

where γ_{el} and γ_{config} are the surface free energy attributable to the electrical work and configurational entropy, respectively. In order to take advantage of the experimental variables for the calculation of γ , furthermore, the third term of right-hand side of Equation (14) needs to be rewritten by the molarity of surfactant and electrolyte. For this purpose, let us derive the chemical potential of surfactant ion (A) and counterions (C and D) at the air/water surface:

$$\mu_A^s \equiv \left(\frac{\partial F^s}{\partial N_A}\right)_{T,V,N_C,N_D,A} = \mu_A^{s,0} + Z_A e\psi_0 + kT \ln \frac{N_A - N_C - N_D}{N_{max} - N_A} \tag{15}$$

$$\mu_C^s \equiv \left(\frac{\partial F^s}{\partial N_C}\right)_{T,V,N_A,N_D,A} = \mu_C^{s,0} + Z_C e\psi_0 + kT \ln \frac{N_C}{N_A - N_C - N_D} \tag{16}$$

and:

$$\mu_D^s \equiv \left(\frac{\partial F^s}{\partial N_D}\right)_{T,V,N_A,N_C,A} = \mu_D^{s,0} + Z_D e\psi_0 + kT \ln \frac{N_D}{N_A - N_C - N_D} \tag{17}$$

Similarly, the chemical potential of each ion in the bulk phase is given by:

$$\mu_A^{bulk} = \mu_A^{bulk,\theta} + kT \ln C_A = \mu_A^{bulk,\theta} + kT \ln C_{AC} \tag{18}$$

$$\mu_C^{bulk} = \mu_C^{bulk,\theta} + kT \ln C_C = \mu_C^{bulk,\theta} + kT \ln C_{AC} \tag{19}$$

and:

$$\mu_D^{bulk} = \mu_D^{bulk,\theta} + kT \ln C_D = \mu_D^{bulk,\theta} + kT \ln C_{BD} \tag{20}$$

where $\mu_i^{bulk,\theta}$ represents the standard chemical potential of ion i in the bulk phase. Taking into consideration that the chemical potential of each component in the surface and bulk phase becomes equal to each other, the following relations can be obtained:

$$\frac{N_A - N_C - N_D}{N_{max} - N_A} = C_{AC} K_A \exp(-Z_A y_0) \tag{21}$$

$$\frac{N_C}{N_A - N_C - N_D} = C_{AC} K_C \exp(-Z_C y_0) \tag{22}$$

and:

$$\frac{N_D}{N_A - N_C - N_D} = C_{BD} K_D \exp(-Z_D y_0) \tag{23}$$

Here, we defined the adsorption constant K_A of surfactant ion to the air/water surface and the binding constant K_C and K_D between the adsorbed surfactant ion and counterion as follows:

$$K_A \equiv \exp\left(\frac{\mu_A^{bulk,\theta} - \mu_A^{s,0}}{kT}\right) \tag{24}$$

$$K_C \equiv \exp\left(\frac{\mu_C^{bulk,\theta} - \mu_C^{s,0}}{kT}\right) \tag{25}$$

and:

$$K_D \equiv \exp\left(\frac{\mu_D^{bulk,\theta} - \mu_D^{s,0}}{kT}\right) \tag{26}$$

Arranging Equations (21–23) and substituting them into Equation (14), we can finally obtain the equation for surface tension:

$$\gamma = \gamma^0 - 8\varepsilon_r \varepsilon_0 \kappa \left(\frac{kT}{e}\right)^2 \sinh^2\left(\frac{y_0}{4}\right) - kT\Gamma_{max} \ln\{1 + C_{AC} K_A \exp(-Z_A y_0) [1 + C_{AC} K_C \exp(-Z_C y_0) + C_{BD} K_D \exp(-Z_D y_0)]\} \tag{27}$$

where the maximal adsorption Γ_{max} is defined by:

$$\Gamma_{max} = \frac{N_{max}}{A} \tag{28}$$

From Equation (27), we obtain the following relations:

$$\gamma_{el} = -8\varepsilon_r \varepsilon_0 \kappa \left(\frac{kT}{e}\right)^2 \sinh^2\left(\frac{y_0}{4}\right) \tag{29}$$

and:

$$\gamma_{config} = -kT\Gamma_{max} \ln\{1 + C_{AC} K_A \exp(-Z_A y_0) [1 + C_{AC} K_C \exp(-Z_C y_0) + C_{BD} K_D \exp(-Z_D y_0)]\} \tag{30}$$

2.5. Surface potential

Once the values of K_A , K_C , and K_D are fixed, the surface tension can be estimated from Equation (27). However, it must be kept in mind that a restriction is imposed on the surface potential.

Besides Equation (11), the surface charge density can be described as:

$$\begin{aligned} \sigma &= \pm \frac{e}{A} (N_A - N_C - N_D) \\ &= \pm \frac{e\Gamma_{\max} C_{AC} K_A \exp(-Z_A y_0)}{1 + C_{AC} K_A \exp(-Z_A y_0) [1 + C_{AC} K_C \exp(-Z_C y_0) + C_{BD} K_D \exp(-Z_D y_0)]} \end{aligned} \quad (31)$$

using Equations (21–23), where the positive and negative sign are available for the cationic and anionic surfactant system, respectively. Equating Equations (11,31), the following relation is obtained:

$$\begin{aligned} G(y_0) &= \frac{2\varepsilon_r \varepsilon_0 k T \kappa}{e} \sinh \frac{y_0}{2} \\ &\mp \frac{e\Gamma_{\max} C_{AC} K_A \exp(-Z_A y_0)}{1 + C_{AC} K_A \exp(-Z_A y_0) [1 + C_{AC} K_C \exp(-Z_C y_0) + C_{BD} K_D \exp(-Z_D y_0)]} = 0 \end{aligned} \quad (32)$$

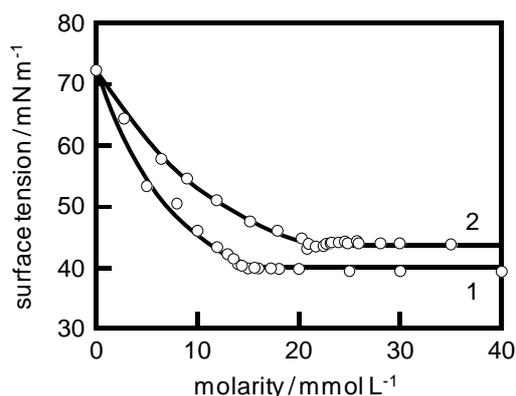
The y_0 value of satisfying the transcendental equation $G(y_0) = 0$ yields the surface potential ψ_0 . Thus, we can determine the values of K_A , K_C , K_D , and ψ_0 by fitting Equation (27) to the results of surface tension measurement under the condition $G(y_0) = 0$.

3. Experimental Section

3.1. Materials

Cationic surfactants, dodecyltrimethylammonium bromide (DTAB, Wako Pure Chemical Industries, Ltd.) and dodecyltrimethylammonium chloride (DTAC, Tokyo Chemical Industry Co., Ltd.) were purified by recrystallization from a mixture of acetone and ethanol, and further extraction of organic impurities using hexane when necessary. The purity of surfactants was checked by observing no minimum around a critical micelle concentration (cmc) on the surface tension *versus* molarity of aqueous solution of surfactant curve (Figure 3).

Figure 3. Surface tension *versus* molarity of aqueous solution of (1) DTAB and (2) DTAC curves.



Sodium chloride (NaCl) and sodium bromide (NaBr) were purchased from Wako Pure Chemical Industries, Ltd. and used without further purification.

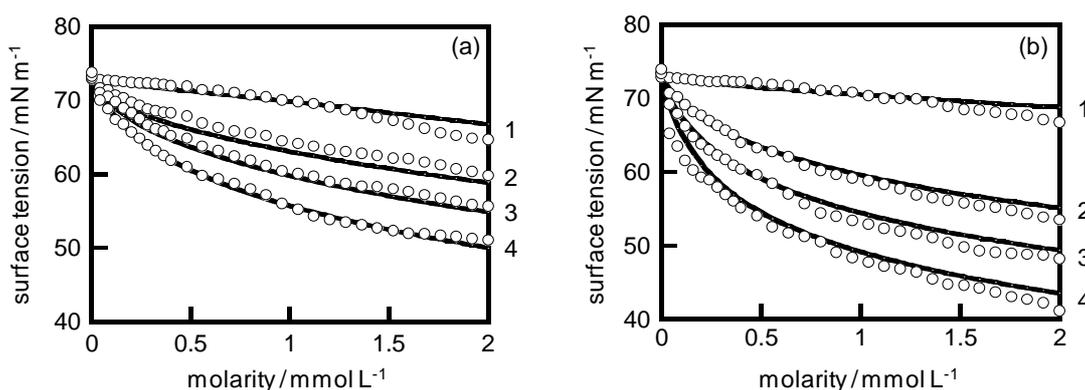
3.2. Measurements

Surface tension of an aqueous solution of the mixture of surfactant and electrolyte was measured as a function of surfactant concentration at constant electrolyte concentration under atmospheric pressure by the Wilhelmy plate method (KRÜSS surface tensiometer K12). The rectangular plate with dimensions of 2.0 cm × 1.0 cm was thoroughly washed by Milli-Q water from Millipore, and then, immersed in acetone to remove organic impurities. The temperature was kept constant at 298.15 ± 0.1 K by circulating thermostated water during measurement. The surface tension measurement was repeated three times at each concentration, and its experimental error was ± 0.5 mN m⁻¹ at most.

4. Results and Discussion

The results of surface tension measurement are shown in Figure 4. The surface tension monotonously decreases with increasing both surfactant and electrolyte concentration. At the same electrolyte concentration, the values of surface tension in the DTAC-NaBr system are lower than that in the DTAB-NaCl system. It is speculated from this fact that the bromide ions, rather than the chloride ions, affect the adsorbed surfactant film. This is explained more clearly using the binding constant of electrolyte ions.

Figure 4. Plots of experimental surface tension (open circle) of (a) DTAB-NaCl and (b) DTAC-NaBr system against molarity of aqueous solution of surfactant at constant electrolyte concentration: (1) 0, (2) 25, (3) 50, and (4) 100 mmol L⁻¹. The solid lines show the curves calculated from Equation (27).



The solid lines in Figure 4 show the curves calculated from Equation (27), and the estimated parameters are tabulated in Table 1. These parameters were determined as follows: (1) a tentative value is put into K_A , K_C , and K_D . (2) Substituting the values of K_A , K_C , and K_D into Equation (32), the surface potential ψ_0 of satisfying $G(y_0) = 0$ is determined at a certain concentration of surfactant C_{AC} and electrolyte C_{BD} . (3) From the estimated surface potential and Equation (27), the theoretical surface

tension $\gamma_{\text{the}}(C_{\text{AC}}, C_{\text{BD}})$ can be obtained. (4) For all the concentration measured in both systems, the $\gamma_{\text{the}}(C_{\text{AC}}, C_{\text{BD}})$ values are estimated and compared with the experimental surface tension $\gamma_{\text{exp}}(C_{\text{AC}}, C_{\text{BD}})$:

$$f(K_A, K_C, K_D) = \sum_{\text{all } C_{\text{AC}}, C_{\text{BD}}} [\gamma_{\text{the}}(C_{\text{AC}}, C_{\text{BD}}) - \gamma_{\text{exp}}(C_{\text{AC}}, C_{\text{BD}})]^2 \quad (33)$$

Thus, we determined the parameters by choosing the values of K_A , K_C , and K_D so that $f(K_A, K_C, K_D)$ yields a minimum value.

Table 1. Values of adsorption constant and binding constant determined from Equations (27,32).

System	$K_A/10^4$	K_C	K_D
DTAB-NaCl	3.7	3.1	0.7
DTAC-NaBr	3.7	0.7	3.1

It is found that the theoretical curves in the presence of electrolytes are in good agreement with the experimental surface tensions within an error of $\pm 1.0 \text{ mN m}^{-1}$. The deviation over 1.0 mN m^{-1} at a higher concentration in the absence of electrolytes (curve 1) is attributable to the phase transition of adsorbed film from the gaseous (lower surface density) to the expanded (higher surface density) film, which is caused by the lateral interaction between adsorbed surfactant molecules [19,20]. From Table 1, we found that the binding constants of bromide and chloride ions are 3.1 and 0.7, respectively. This indicates that compared to the chloride ones, the bromide ions are preferentially adsorbed by charged surfaces. The adsorption of counterions reduces the repulsive interaction between hydrophilic groups of adsorbed surfactant molecules due to the shielding effect of electric field, and as a result, increases the surface density of surfactant on the air/water surface. Therefore, the preferential adsorption of bromide ion promotes effectively the decrease in the surface tension of DTAC aqueous solution (Figure 4b), while the effect of chloride ion on the surface tension of DTAB aqueous solution is less than that of bromide ion (Figure 4a), even at the same ionic strength.

The effectiveness of preferential adsorption of bromide ion as shown in Table 1 was also confirmed by comparing the experimental surface tensions of this study with those of previous one [16]. Figure 5a shows the results of surface tension measurement in the DTAB-NaCl (open circle) and DTAC-NaCl (filled circle) systems. There is a difference in the surface tensions at a lower NaCl concentration (root mean square deviation $\sigma_{\text{rms}} = 1.42 \text{ mN m}^{-1}$ in curve 1), but the difference shrinks as the NaCl concentration increases ($\sigma_{\text{rms}} = 0.77$ and 0.53 mN m^{-1} in curves 2 and 3, respectively). As shown in Figure 5b, on the other hand, the surface tensions in the DTAC-NaBr (open circle) and DTAB-NaBr (filled circle) systems are almost equal to each other over all the electrolyte concentration ($\sigma_{\text{rms}} = 0.34, 0.47, \text{ and } 1.15 \text{ mN m}^{-1}$ in curves 1, 2, and 3, respectively). Consequently, Figure 5 suggests qualitatively that the vicinity of adsorbed film on the air/water surface is richer in the bromide ions than the chloride ions.

Next, let us examine the contribution of electrical work, γ_{el} , and configurational entropy, γ_{config} , to the surface tension. The concentration dependence of γ_{el} is given in Figure 6. We noted that irrespective of electrolyte concentration, γ_{el} shows a similar behavior in the presence of electrolyte. It

follows from Equation (13) that the addition of electrolyte leads to the increase in κ . On the one hand, the surface potential decreases with increasing the electrolyte concentration. Figure 6 is the result of compensation of these two effects (Equation (29)). From the phenomenological point of view, we can say that the ionic atmosphere near the air/water surface is virtually same in the presence of electrolyte because the electrical double-layer is sufficiently compressed as shown by the extremely small Debye length ($1/\kappa \sim 2$ nm).

Figure 5. Plots of experimental surface tension of (a) DTAB-NaCl (open circle) and DTAC-NaCl (filled circle), and (b) DTAC-NaBr (open circle) and DTAB-NaBr (filled circle) system against molarity of aqueous solution of surfactant at constant electrolyte concentration: (1) 25, (2) 50, and (3) 100 mmol L⁻¹.

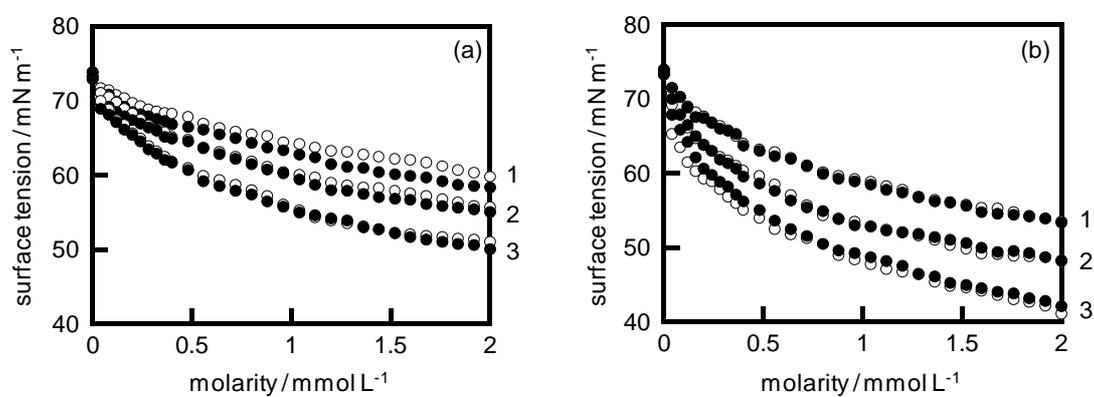


Figure 6. Contribution of electrical work to surface tension of (a) DTAB-NaCl and (b) DTAC-NaBr system at constant electrolyte concentration: (1) 0, (2) 25, (3) 50, and (4) 100 mmol L⁻¹.

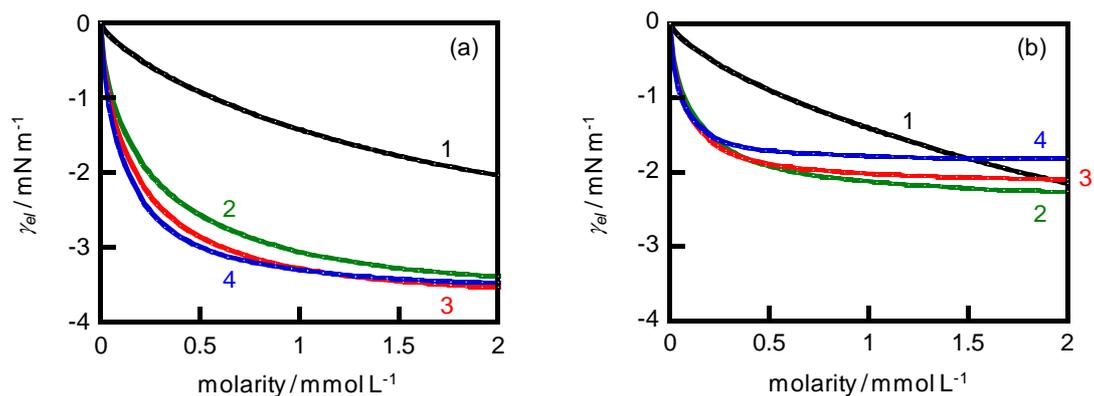
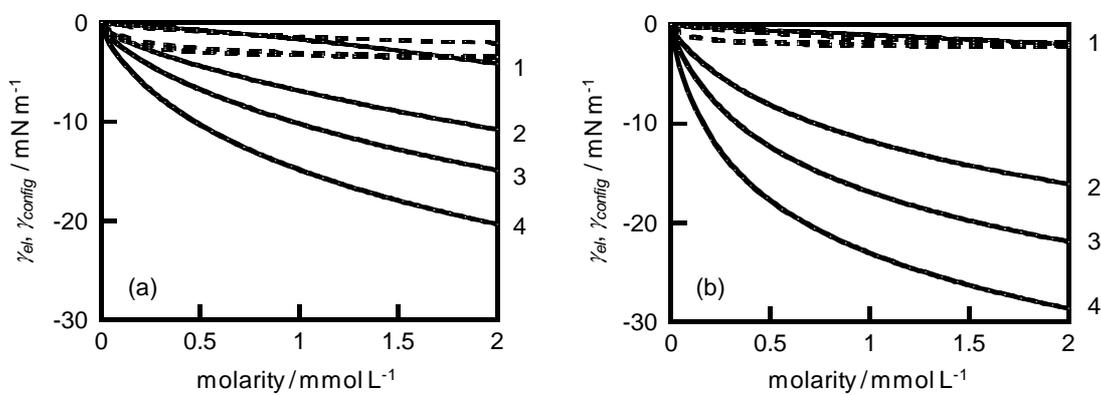


Figure 7 shows the concentration dependence of γ_{config} (solid line) and γ_{el} (broken line). In the case of no electrolytes, the magnitude of γ_{config} is in competition with that of γ_{el} . Therefore, it is significant to consider simultaneously the effect of electrical work and configurational entropy to the surface tension of aqueous solution of ionic surfactant. Once the electrolytes are added into the solution, the values of γ_{config} becomes much larger than that of γ_{el} . As mentioned above, the effects of the addition of electrolytes on γ_{el} are compensated. From Equation (30), on the other hand, the increase in the magnitude of γ_{config} is supported by the increase in the surface density of surfactant molecules Γ_{max}

and the configurational entropy (the logarithmic term) associated with increasing Γ_{\max} . Such a synergistic effect results in the remarkable change of γ_{config} . Summarizing this consideration, it is suggested that a predominant role of configurational entropy for the surface tension of aqueous surfactant solution in the presence of electrolytes is caused by the increase in the number of adsorbed surfactant molecules on the air/water surface due to the reduction of repulsive interaction between the hydrophilic groups.

Figure 7. Contribution of configurational entropy (solid line) to surface tension of (a) DTAB-NaCl and (b) DTAC-NaBr system at constant electrolyte concentration: (1) 0, (2) 25, (3) 50, and (4) 100 mmol L⁻¹. The broken lines show the contribution of electrical work to surface tension (Figure 6).



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