Radiotracer Studies on Adsorption of Surface Active Substance at Aqueous Surface. V. Effects of Additives on the Adsorption of Tritiated Nonionic Surfactant

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The effects of additives on the adsorption of tritiated hexaoxyethylene dodecyl monoether ($TD(EO)_6$) at the air-solution interfaces have been determined at 30 °C. The salting-out effect has been found to follow the Hofmeister series for the sodium salts of various anions, whereas a constant amount has been found for the adsorption increase due to the addition of various chlorides varying with the type of cation. The salting-in effect is observed for denaturants such as urea, urea nitrate and guanidine nitrate, but not for di- and tri-ethylene glycols.

It was reported[1] that the adsorbed amount of tritiated hexaoxyethylene dodecyl monoether ($TD(EO)_6$) at the air-solution interface is in good agreement with the surface excess based on the Gibbs adsorption isotherm for concentration dependence of the surface tension of its solution. The molecular area at the saturated adsorption has been found to be 60.8 Å^2, the value being slightly larger than that for sodium dodecyl sulfate.[2,3]

Several papers have dealt with the effects of additives in nonionic surfactant solutions upon their surface-chemical characters such as cloud point,[4] critical micelle concentration,[5] thinning of film,[6] and surface tension lowering.[7] All these phenomena were studied basically by means of adsorption, which, however, has never been determined directly. Another problem is how to make use of the Gibbs adsorption isotherm for calculation of the adsorbed amount in a mixed solution of a nonionic surfactant and a strong electrolyte. We have made an attempt to determine the adsorbed amounts of $TD(EO)_6$ at the interfaces between humidified nitrogen and its solutions containing strong electrolytes or denaturants frequently used for studying the mechanism of salting-in and salting-out of surfactants.

Experimental

Materials. The tritiated nonionic surfactant was the same as that used in the previous experiment.[1,3] All the additives were purified by appropriate procedures; distillation for di- and triethylene glycols and recrystallization for strong electrolytes, urea, urea and guanidine nitrates. All the crystalline additives were finally degreased by Soxhlet extraction.

Procedures. The surfactant solution was prepared by dissolving $TD(EO)_6$ in an aqueous solution of an additive. The adsorbed amount was determined by the same procedures as described previously.[1-3] The radioactivity was measured by sheet scintillation counting in an atmosphere of 98%-humidified nitrogen at 30±0.1 °C. The surface tension was measured by the Wilhelmy plate method under the same conditions as in the adsorption experiments. The concentration of the nonionic surfactant solution, throughout all experiments, was kept constant at 4.00×10^{-5} mol/l, at which the adsorption reached the saturated values, 2.73×10^{-10} mol/cm^2 for the salt-free solution.

Results and Discussion

Salt Effects. Ionic specificity does not appear to influence the adsorption of $TD(EO)_6$ at its solution/nitrogen interfaces for any of Li, Na, K, and Cs chlorides (Fig. 1). The peculiar behavior of Rb^+ probably comes from some impurity contained in the sample of RbCl. On the other hand, an order of $Cl^- > NO_3^- > I^- > SCN^-$ has been found for enhancement of the surfactant adsorption due to the addition of their sodium salt (Fig. 2). The order is in accord with the lyotropic series for hydration of various ions.[8] The same tendency has been found for the salt effects on the time required for formation of black film of polyoxyethylene nonylphenyl ether solution.[6] Malik and Jhamb[9] ob-

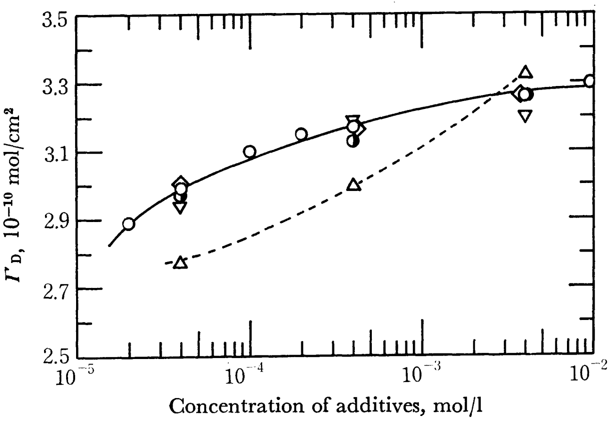

Fig. 1. Effects of various cations on the adsorbed amount of $TD(EO)_6$ at 30 °C.
The bulk concentration of $TD(EO)_6$ is 4.0×10^{-5} mol/l.
▽: LiCl, ○: NaCl, ◑: KCl, ◇: CsCl, △: RbCl.

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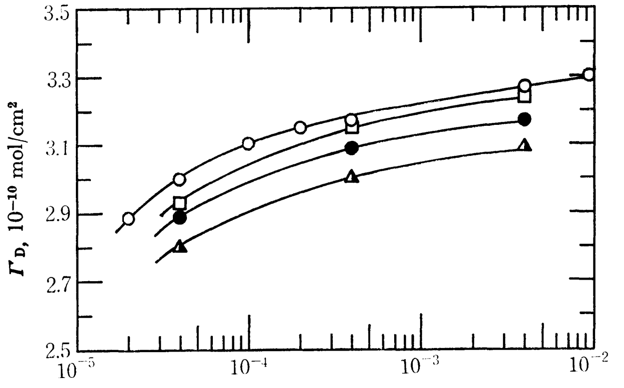

Fig. 2. Effects of various anions on the absorbed anmout of TD(EO)$_6$ at 30 °C.
The bulk concentration of TD(EO)$_6$ is 4.0×10^{-5} mol/l.
○: NaCl, □: NaNO$_3$, ●: NaI, ▲: NaSCN.

served similar effects with electrolytic additives on the lowering of cmc for Tween 20, 40, and 80 in their solutions. All these phenomena are explicable by almost the same co-ordination number, *i.e.*, 3.8 for Li$^+$, 3.7 for Na$^+$, 3.8 for K$^+$, and 3.5 for Cs$^+$, for relatively small cations surrounded by common anions (chloride) of larger size.[10] On the other hand, the result (Fig. 2) probably reflects the different charge density due to the variation of ionic radius.

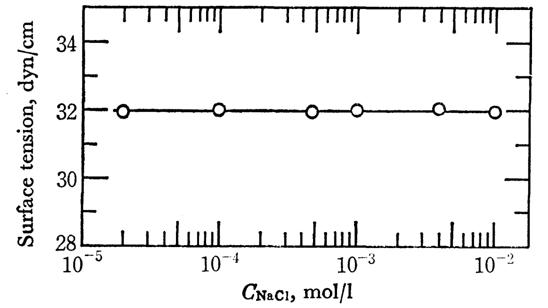

Fig. 3. Surface tension as a function of concentration of NaCl added to the solution of TD(EO)$_6$ ($C_D=4.0\times10^{-5}$ mol/l) at 30 °C.

The surface tension given as a function of NaCl added to TD(EO)$_6$ in solution is shown in Fig. 3. For such a system, the surface tension γ is expressed as

$$-d\gamma = RT\Gamma_D d\ln a_D + RT\Gamma_{Na^+} d\ln a_{Na^+} + RT\Gamma_{Cl^-} d\ln a_{Cl^-} \qquad (1)$$

in terms of surface excess Γ, activity a of individual components in the solution, gas constant R, and absolute temperature T. Subscripts D, Na$^+$, and Cl$^-$ denote surfactant, sodium and chloride ions, respectively. From the constancy of surfactant concentration and the electrical neutrality in surface and bulk phases, it follows that $dC_D=0$, $\Gamma_{Na^+}=\Gamma_{Cl^-}=\Gamma_{NaCl}$, and $C_{Na^+}=C_{Cl^-}=C_{NaCl}$. Thus Eq. (1) can be rewritten as follows,

$$-\frac{d\gamma}{RT d\ln C_{NaCl}} = \Gamma_D \frac{d\ln f_D}{d\ln C_{NaCl}} + 2\Gamma_{NaCl}\left(1+\frac{d\ln f_\pm^{NaCl}}{d\ln C_{NaCl}}\right) \qquad (2)$$

where $f_\pm^{NaCl}$ is the mean activity coefficient of NaCl in the solution. Because of the small value of C_D ($=4.0\times10^{-5}$ mol/l) in comparison with C_{NaCl}($=10^{-2}\sim10^{-5}$ mol/l), the Debye-Hückel limiting law can be applied. Thus

$$-\frac{d\ln f_\pm^{NaCl}}{d\ln C_{NaCl}} = \frac{A}{2}C_{NaCl}^{1/2} \qquad (3)$$

where A is a constant. From the empirical relationship, $-[d\gamma/(RT\ d\ln C_{NaCl})]_D=0$ (see Fig. 3), Eq. (2) becomes

$$\Gamma_D = \frac{A\Gamma_{NaCl}}{\Delta_{NaCl}}C_{NaCl}^{1/2} - \frac{2\Gamma_{NaCl}}{\Delta_{NaCl}} \qquad (4)$$

where $\Delta_{NaCl}=d\ln f_D/d\ln C_{NaCl}$. In the $\Gamma_D\sim C_{NaCl}^{1/2}$ relationship (Fig. 4), a value of 1×10^{-10} mol/cm^2/(mol/l)$^{1/2}$ is obtained for $A\Gamma_{NaCl}/\Delta_{NaCl}$ from the linear portion at $C_{NaCl}>1\times10^{-4}$ mol/l. If we assume the empirical relationship,[11]

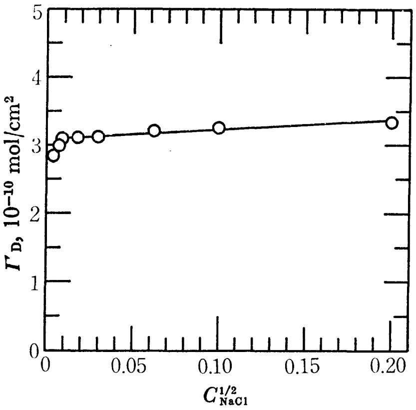

Fig. 4. Γ_D *vs.* $C_{NaCl}^{1/2}$

$$\gamma_{NaCl} = 1.92C_{NaCl} + \gamma_{H_2O} \qquad (5)$$

for explaining a surface tension increase from γ_{H_2O} to γ_{NaCl} due to the addition of NaCl to water, the result $-0.762\ C_{NaCl}\times10^{-10}$ mol/cm^2 is obtained for the adsorbed amount of NaCl at its solution surface. If we further assume that the Γ_{NaCl} value remains unchanged by addition of TD(EO)$_6$ and A is 1.14 (l/mol)$^{1/2}$ at 30 °C, we obtain

$$-\ln f_D = 0.869C_{NaCl} \qquad (6)$$

The relationship is essentially the same as the equation proposed by McDevit and Long[12] for a solution of benzene in aqueous salt solution. Mukerjee[13] derived a similar relationship for the activity coefficient for nonionic amphiphiles dissolved in aqueous salt solutions of various concentrations. It is natural to find a negative value of Δ_{NaCl} so as to give a smaller f_D value corresponding to a larger C_{NaCl} value.

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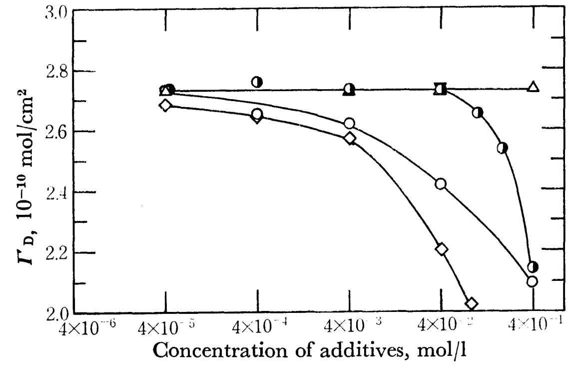

Fig. 5. Effects of various denaturants on the adsorbed amount of TD(EO)$_6$ at 30 °C.
The bulk concentration of TD(EO)$_6$ is 4.0×10^{-5} mol/l.
○: urea, ◑: urea nitrate, ▼: diethylene glycol, △: triethylene glycol, ◇: guanidine nitrate.

Denaturant Effects. Figure 5 shows the effects of urea, urea nitrate, guanidine nitrate, di- and triethylene glycols on the adsorbed amounts of the surfactant. Addition of the denaturants causes a decrease in the adsorbed amount in the order guanidine nitrate> urea>urea nitrate>glycols, the tendency being in parallel with the effect of similar additives on the cmc elevation of Triton X-100 in its solutions[14] and on the denaturation of proteins.[15] A marked lowering of Γ_D at a concentration of urea nitrate higher than 4.0×10^{-2} mol/l might indicate a decrease in activity of ionic species. In fact, the conductivity~concentration relationship for urea nitrate (Fig. 6) gives a distinct deviation from a linear portion in log-log scale. The rather weak effect of glycols on the adsorption of TD(EO)$_6$ is understandable when we consider their weak action as denaturants.

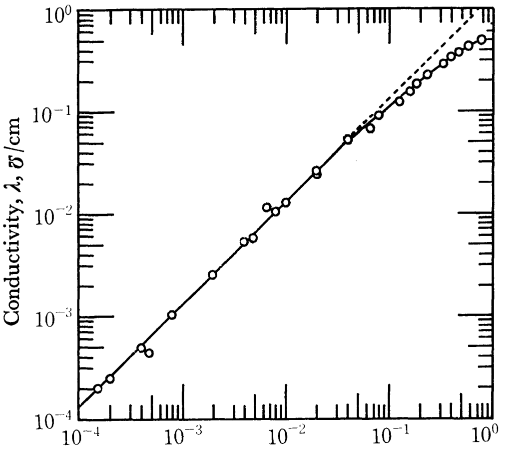

Fig. 6. Conductivity of aqueous solution of urea nitrate at 30 °C.

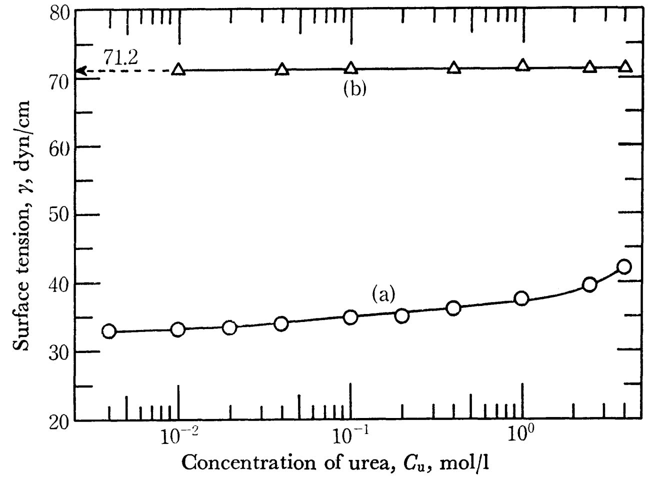

Fig. 7. Surface tension of urea solution with (a) and without (b) TD(EO)$_6$ ($C_D=4.0\times10^{-5}$ mol/l) at 30 °C.

The surface tensions of urea solution with and without the nonionic surfactant are shown in Fig. 7. As in the derivation of Eq. (2), we obtain

$$-\left[\frac{d\gamma}{RTd\ln C_U}\right]_D=\Gamma_D\frac{d\ln f_D}{d\ln C_U}+\Gamma_U\left(1+\frac{d\ln f_U}{d\ln C_U}\right)\quad(7)$$

for surface tension γ as a function of the concentration C_U and the activity coefficient f_U of urea in the solution. The left side term in Eq. (7) is given empirically by

$$\left(\frac{d\gamma}{RTd\ln C_U}\right)_D=4.5\times10^{-11}C_U{}^{0.15}\quad(8)$$

in the region below 0.4 mol/l of urea solution. Assuming $\Gamma_U=0$ from the inclination of curve (b) in Fig. 7, we can rewrite Eq. (7) as follows.

$$\Gamma_D=-\frac{4.5\times10^{-11}}{\Delta_U}C_U{}^{0.15}\quad(9)$$

where $\Delta_D=d\ln f_U/d\ln C_U$, which is obtainable as the inclination of the linear portion of $\Gamma_U\sim C^{0.15}$ relationship. It is obvious that $\Delta_U>0$ shows a salting-in effect of urea on surfactant. Sears[16] reported a marked expansion of the monolayer of stearic acid when it is spread on an aqueous urea solution, unless the surface pressure is too high. It is likely that the urea molecules are anchored on the ethoxyl groups of the surfactant.

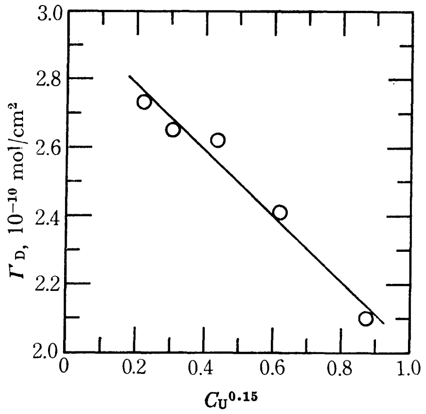

Fig. 8. Test of Eq. (9).

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