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Effects of Electrolytes on Properties on Black Films and Foam Stability of Aqueous Nonionic Surfactant Solutions

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The properties of black film, the surface tension of solution and the foam stability in the aqueous solutions of polyoxyethylene-type nonionic surfactants containing various electrolytes were studied. The additional tension $\overline{\Delta}$ of black films showed a maximum and a minimum in the concentration range of electrolytes of 1×10^{-5}—1 N. The concentration at this minimum shifted in accordance with the lyotropic series of anions. The surface tension was unaffected by the electrolyte of the concentration less than about 1×10^{-2} N, whereas $\overline{\Delta}$ exhibited a maximum in this range. The overall rate of growth of the black film was found to be proportional to $\overline{\Delta}$ over a wide range of electrolyte concentration. The effects of electrolytes on the foam stability were discussed being based upon the properties of the black films.

Single liquid film is easily formed on a frame and provides a geometrically well-defined model system for investigating the stability of foams consisting of thin liquid films. Most studies of such films have been made for ionic surfactants, while studies using nonionic surfactants have been rather few.[1,2] The films stabilized with nonionic surfactants are of particular interest in discussing the repulsive forces acting between two surfaces of the thin films consisting of non-ionic molecules.

In the previous papers, [3,4] the dependence of the rate of growth of black films formed from aqueous nonionic surfactant solutions on the added electrolytes was reported, and the phenomena were interpreted in terms of the lyotropic effect of anions. Further, a proportionality was observed between the rate of growth of the black film and the additional tension, regardless of the electrolytes used.

In the present paper, the effects of added electrolytes on the properties of black films, on the surface tension of the solutions, and on the foam stability are studied for the aqueous solutions of the polyoxyethylene-type nonionic surfactants. The effects of electrolytes on the foam stability are discussed on the basis of the properties of the black films.

Experimental

Materials. Heptaoxyethylene dodecyl ether (N7) of Nikko Chemicals Co., Ltd. was used without purification, while polyoxyethylene nonylphenyl ether (PNE) of Kao Soap Co., Ltd. was used after being purified by molecular distillation.[3,4] Inorganic reagents were recrystallized twice from water, and it was confirmed that they showed no time dependence in the surface tension of 1 M aqueous solutions. Water was first distilled from alkaline potassium permanganate solution and then distilled using fused quartz vessel. All the solutions were freshly prepared before the experiment.

Properties of Thin Liquid Films and Surface of Solutions. The additional tension, $\overline{\Delta}$, is defined by the formula:

$$\overline{\Delta} = 2\gamma - \sigma_f = 2\gamma(1-\cos\theta) \qquad (1)$$

where σ_f is the film tension, γ the surface tension of the bulk solution, and θ the contact angle formed by the black film and the bulk liquid surface.[5] The method used for $\overline{\Delta}$ measurements consists essentially of the Wilhelmy plate method, and the liquid film was formed on a rectangular vertical glass frame 4 cm in width. The difference in tension between the black and the thicker films was measured by using a electro-microbalance, details of which were described in the previous papers.[4,6] The surface tension was measured by the Wilhelmy plate method using the electro-microbalance. The contact angle was calculated from the experimental results of $\overline{\Delta}$ and γ according to Eq. (1). The overall rate, v, of growth of the black film was obtained as the reciprocal of blackening time recorded on the chart of $\overline{\Delta}$ measurement. Here the blackening time was taken as the time required for converting total film area into the black film. All the measurements were performed at 30±0.1 °C.

Foam Stability. In a cylinder of 2 cm in diameter, a foam column 30 cm in height was produced by passing nitrogen gas saturated with water vapor through the solution from a single orifice under a constant pressure. After the gas flow was cut off, the height, H, of the foam column was measured as a function of time for about an hour.

Results and Discussion

The additional tension, $\overline{\Delta}$, is of importance for the studies of thin films, since it expresses the difference of free energies, ΔF_e, between the black film and the bulk liquid, and is associated with a disjoining pressure, π, by the formula:

$$\overline{\Delta} = -\int_h^\infty \pi \mathrm{d}h - \pi h \qquad (2)$$

where h is the film thickness.[5] Figure 1 shows $\overline{\Delta}$ of the N7 stabilized films over a wide range of concentration of the added electrolytes. It is seen that each curve gives a maximum and a minimum in $\overline{\Delta}$. The concentrations at the minimum are found to be about 2×10^{-1}, 1×10^{-1}, 5×10^{-2}, and 1×10^{-2} N for Na_2SO_4, NaCl, NaBr, and NaSCN respectively.

Recently, Clunie *et al.* and Ingram measured the thickness and the additional tension of the black films formed from aqueous solutions of nonionic surfactant *n*-decyl methyl sulfoxide (DMS) as a function of the concentration of NaCl and NaBr.[7,8] They reported that the thickness of the films formed in the lower concentrations of electrolytes was not changed, but when increased the concentration it abruptly increased, where the films were transformed from the second

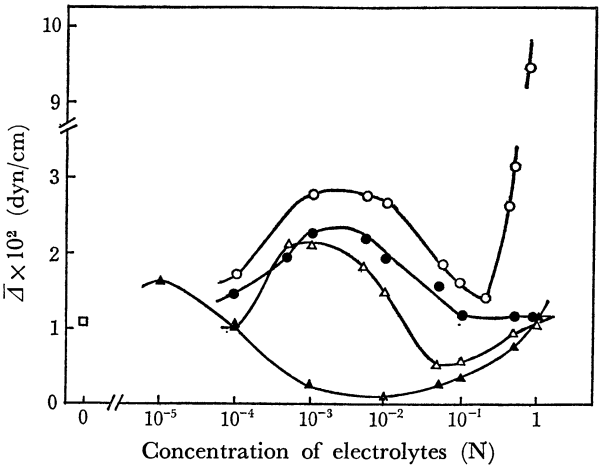

Fig. 1. Effect of electrolytes on additional tension ($\bar{\varDelta}$) of black films formed from aqueous N7 solutions at 30 °C.
Concentration of N7: 5×10^{-4} M
Added electrolytes: ○ Na_2SO_4, ● NaCl, △ NaBr, ▲ NaSCN, □ None

black film to the first one. They also reported that the curve of the additional tension *vs.* electrolyte concentration showed a minimum at this transition concentration. Although the thickness of the films was not measured in the present experiment, the respective minima appeared in the curves of Fig. 1 are considered to reveal the same kind of transition in the films, because of the similarity in the shape of the curves to that of DMS, despite the difference in hydrophilic groups between both systems.

The transition from the second to the first black films with increasing concentration of electrolytes was interpreted to be due to the formation of diffuse electrical double layer resulting from a specific adsorption of the respective anions at the film surfaces.[7,8] This effect is more marked for weakly hydrated ions than strongly hydrated ones. The concentrations at the minimum in the curves of Fig. 1 increase in the order of

$$\text{NaSCN} < \text{NaBr} < \text{NaCl} < 1/2\text{Na}_2\text{SO}_4.$$

Thus, the present results obtained with various anions having different adsorption tendency are in agreement with those reported[7,8] and the anions also follow the lyotropic series.

As seen in Fig. 1, the additional tensions of first black films formed from N7–Na_2SO_4 solutions remarkably increase with increasing concentration of Na_2SO_4, whereas in the other electrolytes they are all smaller than the former even at 1 M solutions. In the concentration range above the minima, that is, in the first black films, the order of $\bar{\varDelta}$ for different electrolytes still obeys the lyotropic series though not so distinct. This fact is further stressed in the systems including F^- as seen in Fig. 2. It was reported that the variation of additional tension of the first black films with electrolyte concentration was in excellent agreement with the predictions of DLVO theory of colloid stability.[8] The contribution of electrical double layer to the additional tension must become much smaller than that of dispersion force, as the concentration of electrolytes

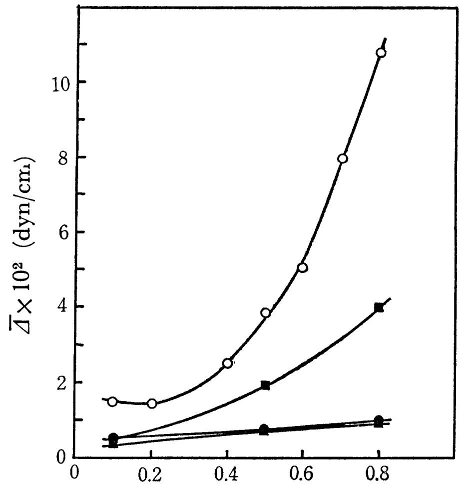

Fig. 2. Effect of electrolytes on additional tension ($\bar{\varDelta}$) of black films formed from aqueous PNE solutions at 30 °C.
Concentration of PNE: 0.1 wt%
Added electrolytes: ○ Na_2SO_4, ■ NaF, ● NaCl, ▲ NaSCN

increases. This effect together with the dehydration effect of electrolytes causes the formation of the thinner first black film, which leads to the significant increase of the additional tension of N7 and PNE films at high concentrations of Na_2SO_4.

It is interesting to compare the effects of electrolytes upon $\bar{\varDelta}$ of the black film with those upon the surface tension of the solution. The effects of electrolytes upon the surface tension were studied for the same series of solutions used for the measurements of $\bar{\varDelta}$. The results are shown in Fig. 3. The surface tension decreases with the increase in concentration of electrolytes, except for NaSCN in the concentration range above 10^{-2} N. Observed change of surface tension is in accordance with the lyotropic series of anions. This effect is analogous to that appearing on the cloud points of surfactant solutions.[9] On the other hand, in the range of electrolyte concentration less than about 1×10^{-2} N, the surface tension is unaffected by

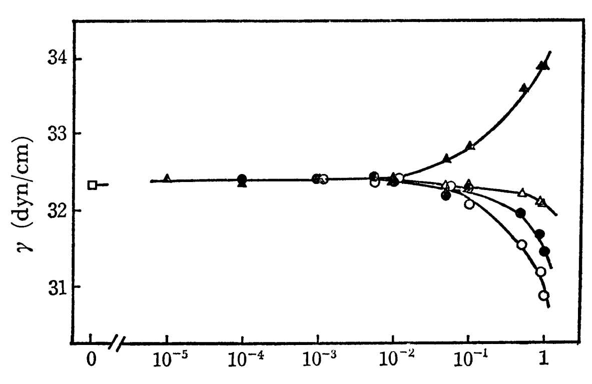

Fig. 3. Effect of electrolytes on surface tension (γ) of aqueous N7 solutions at 30 °C.
Concentration of N7 and added electrolytes: The same as in Fig. 1

Table 1. Effect of electrolytes on film contact angle (θ) of black film for aqueous 5×10^{-4} M N7 solutions at 30 °C

Electrolyte	Na_2SO_4	NaCl	NaBr	NaSCN
1×10^{-4}N	1°20′	1°13′	1° 2′	1°19′
1×10^{-3}	1 42	1 30	1 28	32
1×10^{-2}	1 38	1 24	1 14	24
1×10^{-1}	1 17	1 6	46	38
5×10^{-1}		1 6	57	54
8×10^{-1}	3 24	1 6	1 7	1 4
1	4 39	1 7	1 4	1 5

the electrolytes and is equal to that of pure nonionic surfactant solution. The corresponding contact angles were calculated from the experimental results of $\bar{\Delta}$ and γ according to Eq. (1), a part of which are shown in Table 1.

As shown in Fig. 1, $\bar{\Delta}$ shows a maximum in the range of second black film for all electrolytes added, which is also observed in the DMS system.[7,8] The concentrations at maximum are 1×10^{-3}, 1×10^{-3}, 5×10^{-4}, and 1×10^{-5} N for Na_2SO_4, NaCl, NaBr, and NaSCN respectively, the values of which depend upon the kinds of anions. Since the surface tensions of the solutions are nearly constant at low electrolyte concentrations, the increase of $\bar{\Delta}$ in such a dilute electrolyte range may indicate the decrease of tension of the second black film involving a minimum. Such a behavior could be explained by the additional intermolecular forces arising from the change in the orientation of the solvent molecules and specific adsorption of ions and so on, besides the van der Waals attraction and a steric repulsion acting within the films, as appeared in the literature.[7,8]

Figure 4 shows the dependence of the blackening time on the concentration of added electrolyte, and Fig. 5 gives a plot of the overall rate of growth of the black film as a function of $\bar{\Delta}$. As seen in Fig. 5, the overall rate of growth of the black film is proportional to $\bar{\Delta}$, regardless of the amounts and kinds of added electrolytes.

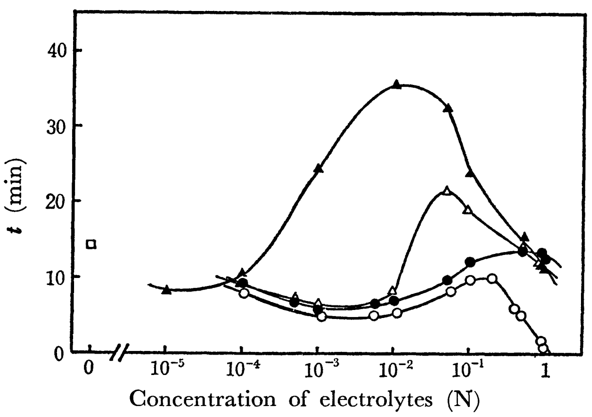

Fig. 4. Effect of electrolytes on blackening time (t) of liquid films formed from aqueous N7 solutions at 30 °C.
Concentration of N7 and added electrolytes: The same as in Fig. 1

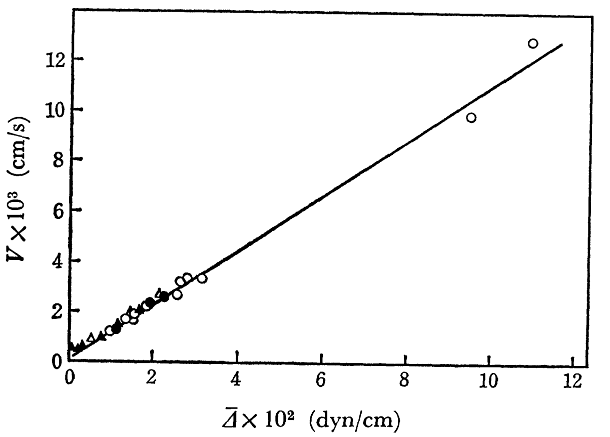

Fig. 5. Dependence of additional tension ($\bar{\Delta}$) on overall rate (v) of growth of black films formed from aqueous N7 solutions containing varying amounts of electrolytes at 30 °C.
Concentration of N7 and added electrolytes: The same as in Fig. 1

The rate of growth of the black film was previously found to be proportional to $\bar{\Delta}$ in the systems of sodium dodecylsulfate (SDS), PNE, and N7 at high concentrations of added electrolytes, and it is mentioned that a_f in the equation $\bar{\Delta}=a_f\cdot v$ may be taken as a viscosity parameter which is found to be proportional to the bulk viscosity.[4] The straight lines showing the proportionality in our preceding paper[4] fall on the same straight line together with the line of Fig. 5, except for the systems containing glycerol, irrespective of the types of the surfactants as well as the amounts and kinds of the electrolytes. This may indicate that the viscosity parameter a_f is independent of the amounts and kinds of added electrolytes, and of the types of the surfactants used at least.

Figure 6 shows the effect of electrolytes on the decay constant, k, of foams formed from 0.1 wt% aqueous PNE solutions containing varying amounts of electro-

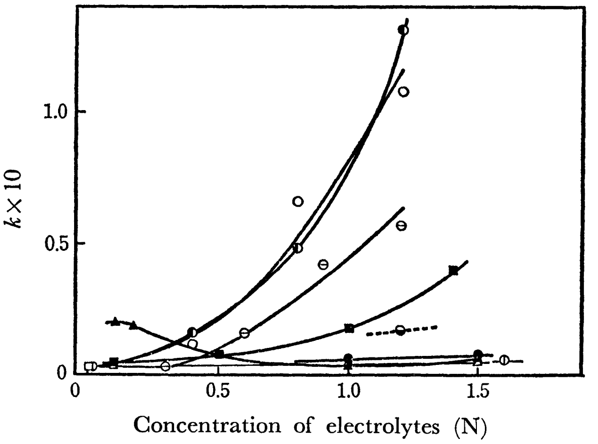

Fig. 6. Effect of electrolytes on decay constant (k) of foams formed from aqueous PNE solutions at 30 °C.
Concentration of PNE: 0.1 wt%
Added electrolytes: ◐ Na_2CO_3, ○ Na_2SO_4, ⊖ Na_3PO_4, ■ NaOH, ◒ $AlCl_3$, ● NaCl, ▲ NaSCN, ⦶ $CaCl_2$, △ HCl, □ None

lytes.[9] Foam stability was conventionally expressed by a decay constant $k=-\mathrm{d}\log H/\mathrm{d}t$, since H was found to decrease as a whole exponentially with time. Foam stability decreases with increasing concentration of electrolyte. The values of k are in the following order; $HCl \simeq 1/2\ CaCl_2 \simeq NaSCN \simeq NaCl < 1/3\ AlCl_3 < NaOH < 1/3\ Na_3PO_4 < 1/2\ Na_2SO_4 \simeq 1/2\ Na_2CO_3$.

The order for sodium salts is in agreement with the lyotropic series of anions excepting minor detail.

Figure 7 shows the plot of $\bar{\Delta}$ *vs*. k for varying concentrations of inorganic electrolytes added. It is seen that k is proportional to $\bar{\Delta}$, which indicates that the rate of collapse of foam is proportional to the additional tension and therefore to the rate of growth of the black film as seen in Fig. 5. Thus, the stability of foam is mainly determined by the rate of growth of the black film, that is, the rate of thinning or the thickness of black film, because $\bar{\Delta}$ is reported to vary with the reciprocal of the square of film thickness in the first black film.[8] This is consistent with the view proposed by de Vries.[10] No appreciable influence of the electrolytes on the thinning of films in the range of colored film was observed,[3] which indicates less influence of the drainage in the thick films on the stability of foams. Eventually, it may be concluded that the rupture of the foams under consideration does not occur until the colored foam film has given way to the black film, and the thickness and the expansion of the black of film dominates the rupture.

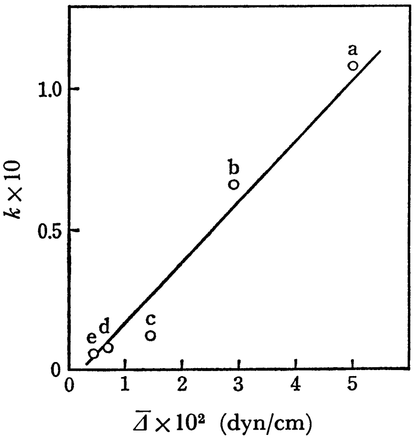

Fig. 7. Dependence of additional tension ($\bar{\Delta}$) on decay constant (k) of foams formed from aqueous PNE solutions containing varying amounts of electrolytes at 30 °C.

Composition of solutions: 0.1 wt% PNE+(a) 0.6 N Na_2SO_4, (b) 0.4 N Na_2SO_4, (c) 0.2 N Na_2SO_4, (d) 0.5 N NaSCN· (e) 0.1 N NaCl.

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