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Effects of the Tension and Viscosity on the Rate of Growth of Black Soap Films

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The additional tension and the rate of growth of black films formed from aqueous solutions of polyoxyethylated nonionic surfactants and sodium dodecylsulfate, which contain inorganic electrolytes in high concentrations, were measured for the large vertical films drawn from these solutions. It was found that the rate of growth of black films was proportional to the additional tension in both systems. The reciprocal of the slope of each line was concluded to be a viscosity parameter, since the additional tension acted as the driving force for the growth of black films, and the viscosity parameter, as the resistance. The effect of added glycerol on the rate of growth of black films was compared with that of electrolytes for the films of nonionic surfactants. The former affected both the viscosity parameter and the additional tension, while the latter showed an effect on only the additional tension.

The thinning of mobile films is considered to be caused mainly by gravity and capillary suction at the border when the films are thick. As the films become thinner, they exhibit a third type of thinning behavior, namely, the spontaneous appearance and growth of a thin black film from a much thicker silver film.[1] It is generally accepted that this thinning is due to van der Waals attraction acting between the molecules in the film.[2] In such a state, additional intermolecular forces come into action and give rise to a disjoining pressure, which results in additional film tension and a macroscopic contact angle between the thin film and the bulk liquid in contact with it.[3–5]

A previous paper has dealt with the thinning of large vertical films stabilized with nonionic surfactants.[6] The addition of the inorganic electrolytes did not show any appreciable effects on the rate of movement of the position of a definite thickness in the region of interference fringes, but the specific effects of anions did appear on the blackening time, namely, the time necessary for converting the total film area completely to the black film; these effects were explained in terms of lyotropy. Such a growth of black films plays an important role in the thinning of some soap films and is, therefore, of interest in connection with foam stability, for instance.[7,8]

In this paper, studies of the additional tension and the rate of growth of black films will be reported for large vertical films drawn from aqueous solutions of anionic and of nonionic surfactants containing varying amounts of inorganic electrolytes and glycerol.

Experimental

Materials. Heptaoxyethylene dodecyl ether (N7) of the Nikko Chemicals Co., Ltd., was used. Gas chromatography proved it to be homologously pure. The polyoxyethylene nonylphenyl ether (PNE) was obtained from commercially available PNE by molecular distillation. The average number of ethylene oxide groups was 11.4 per molecule.[6] The sodium dodecylsulfate (SDS) was synthesized by the usual method and was purified by recrystallization before use. Inorganic electrolytes commercially obtained were degreased with ether in a Soxhlet extractor. The sodium sulfate used for the viscosity measurements was also purified by recrystallization from water. Pure-grade glycerol was used without further purification. The surface tension of the 39.2 wt% aqueous glycerol solution was 69.1 dyn/cm; this value did not change with time. The water used was first distilled from an alkaline potassium permanganate solution and then distilled using a fused quartz vessel. All the solutions used were freshly prepared before use.

Measurement of the Rate of Growth of Black Films. The rate of growth of black films was measured for vertical large films supported on a rectangular glass frame. The apparatus was similar to that previously reported,[6] except for the following points. The frame used was made of a glass rod about 0.6 mm in diameter and 1 cm in width. It was supported vertically from the top of the vessel through a water seal and was withdrawn in 5 s from the surfactant solution by a motor operation so that the top of the film rose 3 cm above the solution surface. All the experiments were carried out by using film of the same size except for the study of the effects of film size on the rate of growth. The cell was submerged in a thermostated water bath of 30±0.1 °C, and the whole apparatus was set in a chamber of 30±0.5 °C for about 17 hr before measurement.

The border between the black and the thicker films was photographed to plot the displacement of it against the time, from which the rate was determined. The rate gradually changed in the case of a relatively long blackening time. In such cases, the constant rate appearing in the later stage (shown in Fig. 2) was taken in PNE systems, and the overall rate, in SDS systems.

Measurement of the Additional Tension of Black Films. The additional tension, $\overline{\Delta}$, is defined by:

$$\overline{\Delta} = 2\gamma - \sigma_f \tag{1}$$

where σ_f is the film tension, and γ, the surface tension of a solution.[9] It was measured by the microbalance technique[10,11] based on the Wilhelmy plate method. A rectangular vertical glass frame 4 cm in width was made of a glass rod about 0.4 mm in diameter. A thinner glass wire about 0.15 mm in diameter was attached horizontally across the frame at a position 1 cm below the top of frame; the wire limited the upper edge of the film formed on the frame. The frame was suspended from one arm of a recording microbalance (Cahn RG Electrobalance). The cell containing the solution and the frame were put in a glass jacket with double walls between which thermostated water was circulated to keep the temperature at 30±0.1 °C. All the apparatus was then placed in an air-thermostated chamber kept at 30±0.5 °C.

To measure $\overline{\Delta}$, the frame was manually withdrawn from the solution up to a fixed height of 1 or 2 cm. When the black/thicker film boundary reached the bulk liquid surface, a sudden decrease in the force exerted on the frame corresponding to the difference in tension between the black and the thicker films was recorded on a chart. The decrease divided by the width of the frame gives $\bar{\Delta}$.

The viscosity of the solutions was measured by an Ostwald viscometer at 30±0.1 °C.

Results and Discussion

The rate of growth of black films was measured for the films formed from 0.1 wt% aqueous PNE solutions containing varying amounts of Na_2SO_4, NaF, NaCl, and NaSCN. The same measurement was made for the films formed from 0.05 wt% (1.7×10^{-3} M) aqueous SDS solutions containing varying amounts of NaCl.

Figure 1 shows the effect of the concentration of Na_2SO_4 on the growth of the black films formed from 0.1 wt% PNE solutions. The vertical length of black film is plotted against the elapsed time. The plots in Fig. 1 give the straight lines except for the final stage of the boundary approaching the bulk liquid surface. The black film formed from a 0.1 wt% aqueous PNE solution containing 0.8 N NaF gave a similar linearity and a relatively short blackening time, as in the case of Na_2SO_4. The dependence of the total height and width of the films on the growth of black films of a short blackening time drawn from aqueous solutions of 0.1 wt% PNE containing 0.7 N Na_2SO_4 was studied by using films 1.5 and 3.0 cm in height and ranging from 1 to 4 cm in width. The effects of the size were found to be negligible.

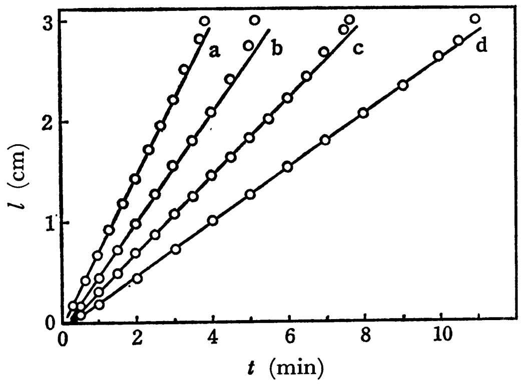

Fig. 1. Effect of the concentration of Na_2SO_4 on the rate of growth of black films formed from aqueous PNE solutions at 30 °C.
l: vertical length of black film
t: time elapsed after formation of liquid film
Composition of solutions: 0.1 wt% PNE+Na_2SO_4 (a) 0.8 N, (b) 0.7 N, (c) 0.6 N, (d) 0.5 N

Figure 2 shows the time dependence of the vertical length of the black film formed from a 0.1 wt% aqueous PNE solution containing 0.8 N NaCl. Plots a and b show the results for the films withdrawn 3.0 cm and 1.5 cm respectively above the liquid surface. As may be seen in Fig. 2, the b plot is linear, whereas the a plot exhibits a curve with a linear portion in the later stage which is nearly parallel to the b plot.[12] It is evident that the difference between the a and b plots is mainly due to the longer blackening time or the larger total height in the former film than in the latter. In the films 3 cm in total height, the black films formed from 0.1 wt% aqueous PNE solutions containing 0.5 N NaF, 0.5 N NaCl, 0.8 N NaCl, and 0.5 N NaSCN gave plots of the type of the a plot in Fig. 2. In the case of these films with a long blackening time, both the rate of film growth of the linear portion and the overall rate decreased to about four-tenths when the width of the film was changed from 1 to 4 cm, while the height was held constant at 3 cm.

Figure 3 shows the effect of the concentration of NaCl on the growth of the black films formed from 0.05 wt% SDS solutions. For the film formed from the solution containing 0.3 N NaCl, a transition from the first to the second black film was visually observed by the reflected light. A nucleation of the second black film appeared in the first black film already formed, and the former film grew rapidly at the ex-

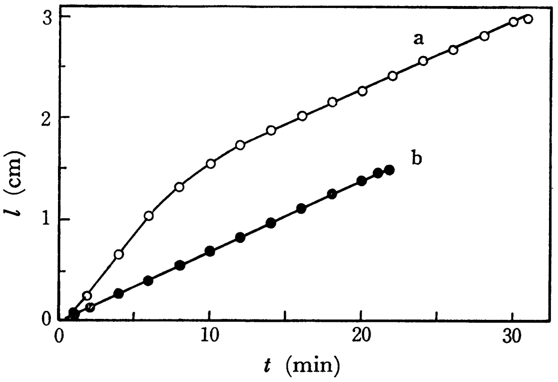

Fig. 2. Dependence of total height of film on the rate of growth of black film formed from aqueous (PNE+NaCl) solution at 30 °C.
l and t: the same as in Fig. 1
Total height of films: (a) 3 cm, (b) 1.5 cm
Width of film: (a) and (b) 1 cm
Composition of solution: 0.1 wt% PNE+0.8 N NaCl

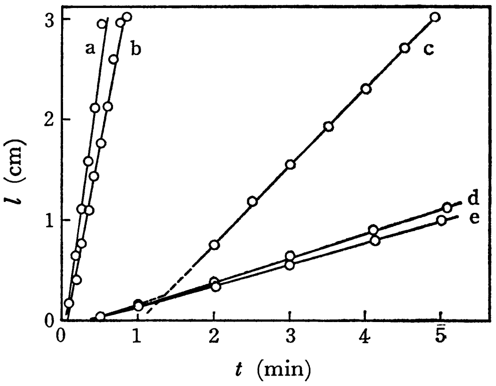

Fig. 3. Effect of the concentration of NaCl on the rate of growth of black films formed from aqueous SDS solutions at 30 °C.
l and t: the same as in Fig. 1
Composition of solutions: 0.05 wt% SDS+NaCl (a) 0.5 N, (b) 0.4 N, (c) 0.3 N, (d) 0.2 N, (e) 0.1 N

pense of the latter and any remaining thicker films. The second black film was easily distinguished from the first one because the former was darker than the latter and a sharp boundary could be observed between the two films.13) From another study14) it may be deduced that the first black film is exclusively formed at concentrations lower than 0.3 N, whereas above 0.3 N the second black film is exclusively formed. As is shown in Fig. 3, the second black film of SDS grows at a constant rate and faster than the first black film, which shows a gradual decrease in the rate of growth.

The values of $\bar{\Delta}$ were measured for the black films formed from the same solutions as those used for the measurements of the growth rate of black films. First, to check the reliability of the measurement, the contact angle, θ, between the black film and the bulk liquid was calculated for a 0.05 wt% aqueous SDS solution containing 0.5 N NaCl. For the calculation, the following relation was used:5,9)

$$\bar{\Delta} = 2\gamma(1-\cos\theta) \tag{2}$$

using the additional tension, $\bar{\Delta}$, and the surface tension, γ, separately obtained. The calculated value of 9°25′ (30.0 °C) is considered to be reasonable in comparison with the reported values of 9°54′ (28.5 °C),11) 10°52′ (25.0 °C),10) and 11°28′ (24.3 °C),15) considering the temperatures.

Figures 4 and 5 show the plots of the rate of growth of black films, dl/dt, against $\bar{\Delta}$ for the black films formed from aqueous PNE and SDS solutions containing varying amounts of electrolytes. The values of $\bar{\Delta}$ and dl/dt depend strongly on the kind of surfactant, on the added electrolytes, and on the kind or the thickness of the black films. However, dl/dt is proportional to $\bar{\Delta}$, regardless of the kind and the amount of added electrolytes as well as the kind of surfactants. The reciprocals of the slope of the lines in these figures, $\bar{\Delta}/(dl/dt)$, considered as a viscosity parameter, are about 8.6 and 8.3 g/(cm·s) for PNE and SDS films respectively.

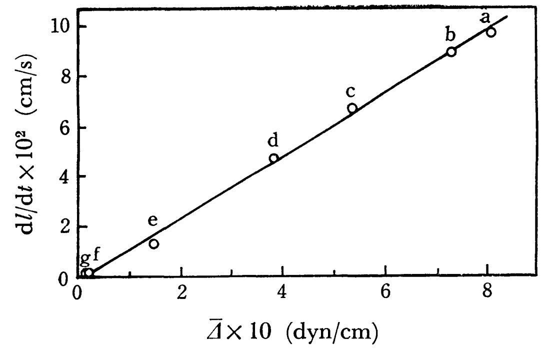

Fig. 5. Dependence of the additional tension on the rate of growth of black films formed from aqueous (SDS+NaCl) solutions at 30 °C.
dl/dt and $\bar{\Delta}$: the same as in Fig. 4
Composition of solutions: 0.05 wt% SDS+NaCl (a) 0.5 N, (b) 0.45 N, (c) 0.4 N, (d) 0.35 N, (e) 0.3 N, (f) 0.2 N, (g) 0.1 N

Figure 6 shows the effects of the change in bulk viscosity upon the addition of glycerol on the relationship between dl/dt and the $\bar{\Delta}$ of the black films, which is formed from aqueous solutions of 5×10^{-4} M (2.5×10^{-2} wt%) N7 containing varying amounts of Na_2SO_4. The solid lines indicate the systems containing varying amounts of Na_2SO_4 while keeping the amounts of N7 and glycerol constant, and the broken lines indicate the systems in which the amounts

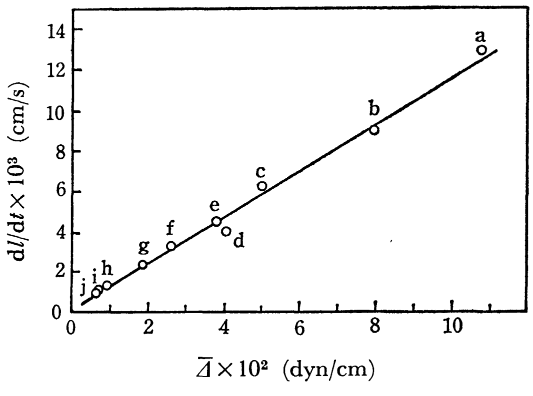

Fig. 4. Dependence of the additional tension on the rate of growth of black films formed from aqueous (PNE+electrolyte) solutions at 30 °C.
dl/dt: rate of growth of black film
$\bar{\Delta}$: additional tension of black film
Composition of solutions: 0.1 wt% PNE + (a) 0.8 N Na_2SO_4, (b) 0.7 N Na_2SO_4, (c) 0.6 N Na_2SO_4, (d) 0.8 N NaF, (e) 0.5 N Na_2SO_4, (f) 0.4 N Na_2SO_4, (g) 0.5 N NaF, (h) 0.8 N NaCl, (i) 0.5 N NaCl, (j) 0.5 N NaSCN

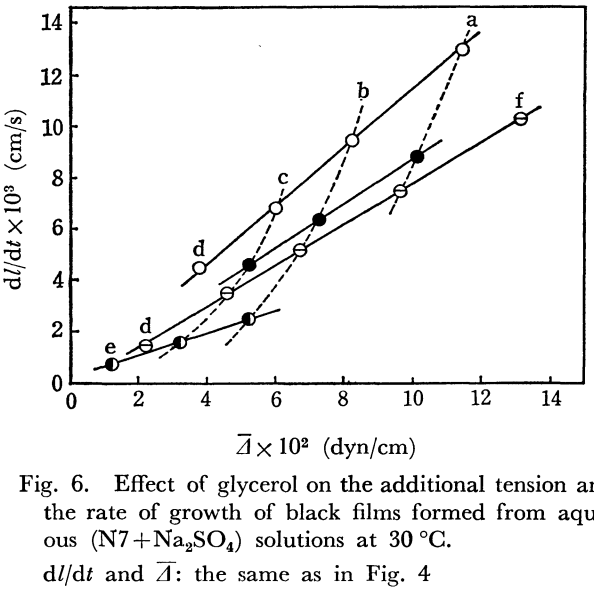

Fig. 6. Effect of glycerol on the additional tension and the rate of growth of black films formed from aqueous ($N7+Na_2SO_4$) solutions at 30 °C.
dl/dt and $\bar{\Delta}$: the same as in Fig. 4
Composition of solutions:
solid line, glycerol, ○ 0 wt%, ● 10 wt%, ⊖ 15wt%, ◐ 30 wt%
broken line, Na_2SO_4, (a) 0.8 N, (b) 0.7 N, (c) 0.6 N
other points, Na_2SO_4, (d) 0.5 N, (e) 0.4 N, (f) 0.9 N
N7: 5×10^{-4} M for all solutions

of glycerol are varied while N7 and Na_2SO_4 are kept constant.

The values of the bulk viscosity of 5×10^{-4} M aqueous N7 solutions containing 0.8 N Na_2SO_4 and glycerol of different concentrations, that is, 0, 10, and 15 wt%, were 0.89, 1.13, and 1.29 centipoise respectively; also, the bulk viscosity of a 5×10^{-4} M N7 solution containing 0.7 N Na_2SO_4 and 30 wt% glycerol was 1.98 centipoise. On the other hand, the bulk viscosity increased only slightly with the concentration of Na_2SO_4; that is, the bulk viscosity of the aqueous N7 solutions varying from 0.5 N to 0.8 N Na_2SO_4 increased from 0.86 to 0.89 centipoise. All the films formed from these solutions were found to be simple mobile films.[16] The reciprocals of the slope of the straight lines, $\overline{\Delta}/(\mathrm{d}l/\mathrm{d}t)$, shown in Fig. 6 are 8.7, 11.6, 12.4, and 21.9 g/(cm·s) for solutions of 0, 10, 15, and 30 wt% glycerol respectively. It was also found, when $\overline{\Delta}/(\mathrm{d}l/\mathrm{d}t)$ was plotted against the bulk viscosity from the results in Fig. 6, that $\overline{\Delta}/(\mathrm{d}l/\mathrm{d}t)$ was proportional to the bulk viscosity of the solution used.

As is shown in Figs. 1—3, the growth rate of the black film becomes nearly constant after arriving at the stationary state. Since the values of $\mathrm{d}l/\mathrm{d}t$ in Figs. 4—6 are those in the stationary state, and since a proportionality is observed between $\overline{\Delta}$ and $\mathrm{d}l/\mathrm{d}t$, the following relation is obtained by using a proportionality constant, a_f:

$$\overline{\Delta} = a_f(\mathrm{d}l/\mathrm{d}t) \tag{3}$$

In this equation, it may be inferred that a_f gives a friction coefficient and that $\overline{\Delta}$ is a dominant factor in the driving force in the growing process of the black film, considering that the friction force is equal to the external force.

As Scheludko indicated,[9] $\overline{\Delta}$ is related to the disjoining pressure, π, in the expression:

$$\overline{\Delta} = -\int_h^\infty \pi \mathrm{d}h - \pi h \tag{4}$$

where h is the film thickness. Furthermore, at a sufficiently high concentration of added electrolytes, the diffuse electrical double layer is highly compressed and $\overline{\Delta}$ is almost entirely determined by the van der Waals component of the disjoining pressure, expressed by:

$$\overline{\Delta} \approx -\int_{h_e}^\infty \pi_{vw} \mathrm{d}h \tag{5}$$

where π_{vw} is the van der Waals component of the disjoining pressure, and h_e, the equilibrium thickness of the film. Kolarov *et al.* observed the same relationship as in this report between the growth rate of black film in the initial stage and $\overline{\Delta}$ for the micro-horizontal circular films; that is, $(\mathrm{d}r/\mathrm{d}t)_{t_0}=a_{t_0}\overline{\Delta}$, where r represents the radius of the black film.[17]

Here, as a_f is considered to be the friction coefficient for the growing process of black film, various kinds of factors affecting the rate of drainage, such as the bulk viscosity and the surface dilational or shear viscosity, must be included in this coefficient. However, since a_f is proportional to the bulk viscosity of the solution, as has been described above, it may be inferred that the growth rate of the black film is predominantly determined by a flow controlled by the bulk viscosity, and that the contribution of the other factors to the growth rate is negligibly small.

From this point of view, if the black film grows at an invariable thickness, its growth will be determined by the outflow of the excess liquid in the silver film. In most cases in this experiment, however, $\mathrm{d}l/\mathrm{d}t$ is nearly constant, regardless of the length of the thicker film between the black/thicker film boundary and the solution surface. Therefore, if $\overline{\Delta}$ is invariable, a_f must be constant, irrespective of the length of the thicker film. It thus seems reasonable to assume that the flow of bulk solution in the whole thicker film does not determine the growth rate of the black film, but that only a certain local flow in the thicker film dominates this. It is considered that the flow of liquid between surface layers in the vicinity of the black/thicker film boundary has a high resistance to the film growth. In addition to this, the contribution of dilational surface viscosity must also be considered to some extent, but it must be small, because the relationship between a_f and the bulk viscosity of solution passes near the point of origin. In this context, it is concluded that the flow resistance resulting from the bulk viscosity in the thin film regulates the growth rate of the black film, though the precise mechanism of the growth of black films based on hydrodynamics has not yet been made clear because of its complexity.

As may be seen in Figs. 4 and 5, the effects of added electrolytes on the rate of growth of black films are mainly due to the increase in the additional tension operating as a driving force, and the magnitude of the increase of this tension depends on the nature and amounts of electrolytes, whereas glycerol is found to show the two effects shown in Fig. 6. Glycerol, as far as has been observed in the presence of the electrolytes, decreases the additional tension, as seen in the broken lines in this figure, and simultaneously reduces the slope of the straight lines. For the former, further study is still awaited.

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