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Thinning of Nonionic Detergent Films

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The effect of added electrolytes on the thinning of single vertical film formed from nonionic detergent solution has been studied. Addition of the electrolytes did not show an appreciable effect on the thinning of the film in the region of interference fringes. Specific effects of anions upon the "blackening time" (the time necessary for turning the total film area completely into a black film) were observed similarly to those on the cloud point. The order of magnitude of these effects followed the lyotropic series, which may be explained qualitatively by the effects on the dehydration of detergent molecules and on the electrical double layer of the film. The effect of the electrolytes on aqueous ionic detergent film was also examined. It was mainly explained by their influence on the electrical double layer.

Single liquid film is considered to be a very simple colloid system, and is useful in elucidating various colloidal and interfacial phenomena. Interest has been shown by many investigators,[1–4] particularly the kinetic study of single liquid film stabilized by ionic detergent for its influence on the drainage of the film. However, there are few reports on nonionic detergent films.[5,6]

It has been confirmed that the effects of the addition of electrolytes on the foam stability and on the cloud point of aqueous solutions of nonionic detergent are similar.[7] They are both specific for anion and follow the lyotropic series.

The purpose of this work is to study the effect of the addition of electrolytes upon the thinning of single liquid film formed from aqueous nonionic detergent solutions, in connection with the investigation of foaming. In observing the thinning process of liquid film, special attention was paid to the rate of formation of an ultra-thin film, the so called "black film", which always appears in the last stage of the draining process of the liquid film.

Experimental

Materials. Polyoxyethylene nonylphenyl ether (PNP) was obtained from commercially available PNP by molecular distillation. The average chain length of the ethylene oxide adducts obtained by distillation was determined from their hydroxyl values to be 11.4 in ethylene oxide units. The aqueous solutions of this compound exhibited a sharp break in the plots of surface tension against logarithm of concentration, so it is considered to be sufficiently homogeneous. Sodium dodecylsulphate (SDS) was prepared by the reaction of $C_{12}H_{25}OH$ with $ClSO_3H$ and purified by the ordinary procedure. Inorganic electrolytes were of analytical reagent grade and were purified by using a soxhlet extractor with ether as a solvent, except for HCl and NaOH which were used without further purification. Water was distilled first in a hard glass apparatus from potassium permanganate solution to remove organic impurities and then was redistilled in a quartz glass apparatus. All solutions were freshly prepared before use.

Apparatus and Procedure. The method used for these measurements is similar to that discribed by Miles and co-workers[8] and by Lyklema and co-workers.[9] The apparatus consists essentially of a square cell 4× 4 cm containing the solution and a rectangular frame supported from above. The rectangular frame is made from a glass rod of about 1 mm in diameter, and is 2.3 cm wide for PNP solutions and 1.4 cm wide for SDS solutions.

After standing the solution in the closed cell for about 17 hr, the frame was vertically withdrawn in about 5 sec

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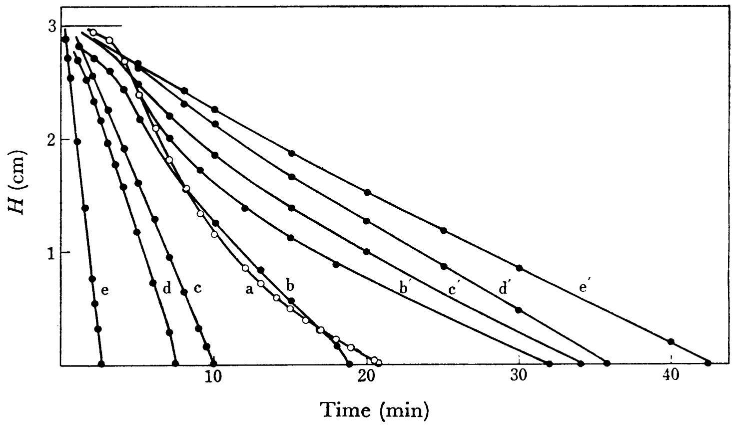

Fig. 1. Effect of increasing concentrations of NaCl and Na_2CO_3 on the rate of formation of black film in liquid films at 30°C.
H: distance between black-silver boundary and solution surface.
Time: time elapsed after formation of liquid film.
Aqueous solutions: 0.1% PNP (a), 0.1% PNP+Na_2CO_3 [0.1N (b) 0.5N (c) 0.8N (d) 1N (e)], 0.1% PNP+NaCl [0.1N (b′) 0.5N (c′) 1N (d′) 2N (e′)]

from the solution by manual opperation so that the top of the frame was 3 cm above the solution surface (2.5 cm in the case of SDS solutions). Xenon lamp was used for illuminating the film. By using optical filters, wave length was limited to 400—450 mμ with the maximum at about 417.5 mμ. The positions of interference fringes and boundary between black and silver film were measured and expressed as the distance from the solution surface on the photograph properly enlarged. All the measurements were carried out in a thermostated room of 30 ± 1°C.

Results

The effect of the addition of electrolytes on the thinning process of single liquid film was measured for 0.1% PNP aqueous solutions. For comparison, the observation was made with 1×10^{-2}M SDS solutions in the presence of NaCl and Na_2SO_4.

Freshly formed films quickly drain and the horizontal interference fringes are produced. The film drains further and a silver film appears at the top of the film and spreads downward. Finally a black film develops and its area gradually increases at the expense of silver film. The boundary between black and silver films is very sharp and horizontal except for the place near the frame. Black films so formed are fairly stable, with the exception of those formed from pure SDS solution. Their average life is more than 2 hr.

Aqueous PNP Solutions. Figure 1 shows typical effects of concentration of some electrolytes upon the rate of descent of the black-silver boundary. The positions of the black-silver boundary are plotted against time elapsed after complete formation of the liquid film. The time necessary for turning the whole film area into a black film, which is taken as the standard of the rate of formation of a black film, was also measured in all solutions. For brevity, this is called "blackening time" in this paper.

Curves of the descent of black-silver boundary in liquid films formed from aqueous solutions of PNP with and without added electrolytes can be classified into three types. Type 1 curve shows that the rate of descent of the black-silver boundary is faster in the early period and slower in the later stage, except for the first stage. This type appears in the case of relatively long blackening time. Type 2 curve shows a nearly constant rate of descent. Each instance is shown by (a) and (c) in Fig. 1. In the same electrolytes, curves of the descent tend to change into type 2 from type 1 with increasing concentrations, and the tendency is marked in the case of shorter blackening time. Type 3 curve, which shows a slow rate of descent in the early stage and a fast one in the final stage, only appears in the case of addition of 1N NaOH.

Contrary to these behaviors, the drainage of the film in the region of interference fringes is not affected by the addition of electrolytes.

Figure 2 shows the effect of added electrolytes and their concentrations upon the blackening time. Evidently, blackening time of liquid films formed from PNP solutions is greatly affected by the nature and concentration of the added electrolytes. The effect is classified into two types; namely electrolytes which decrease and those which increase blackening time with increasing concentration. The electrolytes can be arranged in the following series according to the order of magnitude of blackening time.
$Na_3PO_4 < Na_2CO_3 \simeq Na_2SO_4 < NaF \simeq NaOH \ll NaCl \simeq KCl \simeq LiCl \simeq NaSCN \simeq HCl$.

Ions such as SCN^- and Cl^- act as an inhibitor whereas PO_4^{3-}, SO_4^{2-}, CO_3^{2-}, F^- and OH^- ions act as a promoter for the black film formation. It is evident that the effect is not so sensitive to the

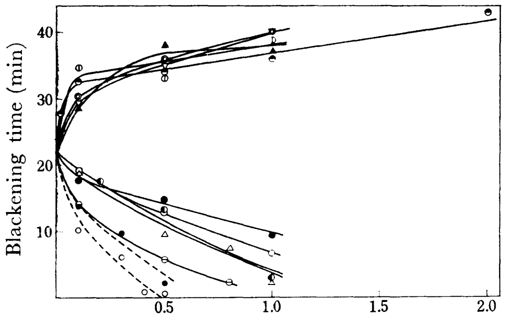

Fig. 2. Effect of added electrolytes on the blackening time of liquid films at 30°C. (average of five films)

Aqueous solutions: 0.1% PNP+electrolyte (◎ NaSCN, ▲ HCl, ▽ LiCl, ⦶ KCl, ◓ NaCl, ● NaOH, ○ NaF, ◐ 1/2Na_2SO_4, △ 1/2Na_2CO_3, ⊖ 1/3Na_3PO_4), 1×10^{-2} mol/l SDS+electrolyte (---●--- 1/2Na_2SO_4, ---○--- NaCl)

nature of cation, but is specific to the nature of anion, and the series is similar as a whole to the lyotropic series of anions.

With regard to the region of the interference fringes, the change of the film thickness with time at its center is almost independent of the nature and concentration of the electrolytes added as shown in Fig. 3. The film thickness is calculated from the order of interference fringes.

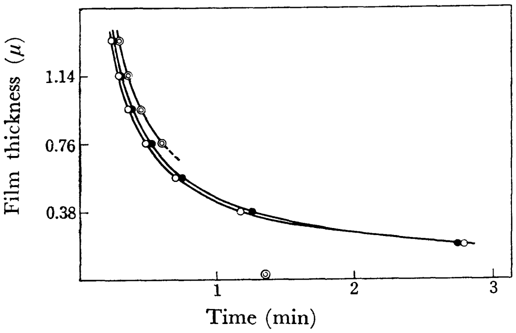

Fig. 3. Time dependence of film thickness at center of films at 30°C.

Aqueous solutions: 0.1% PNP+electrolyte (○ 0, ● 0.5N Na_2CO_3, ◎ 0.8N Na_3PO_4)

Aqueous SDS Solutions. Measurements of the SDS solutions were performed for a smaller film area (width 1.4 cm, height 2.5 cm), because the instability of the liquid film of pure SDS solution prevented the use of a larger frame employed in the measurement of PNP solutions.

The broken lines in Fig. 2 show the effect of added electrolyte upon the blackening time of films formed from 1×10^{-2}M SDS solutions. It is evident that the effect of electrolytes is quite different for the films formed from SDS and PNP solutions. Addition of NaCl prolongs blackening time in the case of PNP solutions, whereas in the case of SDS solutions blackening time is shortened.

Discussion

Thinning of vertical thin film is caused mainly by gravity and the border suction when the film is thick. However, the van der Waals force and electrostatic repulsion become important as the thinning advances by drainage to such an extent that the formation of a black film begins.[10]

Overbeek explained the mechanism of the formation of balck film as follows.[2] The welt at the boundary between black and colored films is a kind of border and sucks the colored film (a thicker film) by border suction to form more black film (a thinner film). An excess liquid accumulates at the welt and later flows down as a two-dimensional droplet. The rate of formation of a black film depends upon the electrostatic repulsion between detergent ions adsorbed on both surfaces of the film, the van der Waals force acting among all the molecules in the film and the viscous resistance in the film.[2] However, a precise interpretation of this kinetic process is not clear.

On the other hand, it has been proved experimentally that the thin film has a sandwich structure, consisting of two surface layers and inner core of solutions.[11] Of the forces acting on the thin film, the force between water molecules gathered around the polar heads of the detergent molecules assumes considerable importance in films of an aqueous nonionic detergent. However, in the case of aqueous ionic detergent film, the electrostatic repulsion between the charged surface layers on both sides of the film becomes important as well.

Thus the influence of electrolyte on black films may be explained as follows.

For nonionic detergent, added electrolytes affect the stability and so the rate of drainage of the film through their influence on the amount of hydration and on the formation of the diffuse double layer.

It is recognized that the solubility of polyoxyethylated detergents is closely related to the hydration of ethylene oxide. The effect of added electrolyte on black film is considered to cause dehydration of the ethylene oxide chains and this results in the decrease of steric repulsion against the thinning of the film. Thus, small or polyvalent and strongly hydrated ions are expected to be more effective in decreasing stability and increasing the rate of drainage than large and weakly hydrated ions. However, to elucidate the increase in stability and the retardation of film drainage produced by some electrolytes the possibility of electrostatic repulsion of surface film should be also taken into account,

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[10] A. Scheludko, "Colloid Chemistry," Elsevier Pub. Co., Amsterdam, London, N. Y. (1966), p. 173.

[11] J. M. Corkill, J. F. Goodman, D. R. Haisman and S. P. Harrold, *Trans. Faraday Soc.*, **57**, 821 (1961).

since the added electrolytes are expected to be adsorbed at the film surface to form a diffuse electrical double layer. This effect would be stronger for weakly hydrated large ions than strongly hydrated small ions.

It may be expected that large ions such as SCN^- and Cl^- increase while small or polyvalent ions such as OH^-, F^-, CO_3^{2-}, SO_4^{2-} and PO_4^{3-} decrease the stability of the film. The results shown in Fig. 2 are in line with this explanation. It should be inferred that such an explanation is in accord with the lyotropic effect of anions. A similar effect of electrolytes on the cloud point of nonionic detergent could be observed.[7)]

As regards the effect of electrolyte on the ionic detergent, increase in the rate of black film formation with increasing concentration of electrolyte may be explained by the contraction of the diffuse electrical double layer and the resulting decrease of the repulsion between two surface layers. The minor difference observed in the effect between Na_2SO_4 and NaCl requires further study. It should be noted that the mutually opposite effect of NaCl for ionic and nonionic detergent films can also be understood from the opposite effect of ions on the electrical double layer of the film.

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