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VISCOSITY OF BIMOLECULAR FILM OF CIS-9-OCTADECENYLAMINE (OLEYLAMINE) IN AQUEOUS SOLUTION

Tadayoshi YOSHIDA, Takahiro ITOH, and Masataka OKUYAMA
Department of Engineering Chemistry, Nagoya Institute of Technology,
Showa-ku, Nagoya 466

The viscosity of bimolecular film was estimated from the motion of an oil lens (diameter: ca. 0.2 mm) in film (thickness: ca. 5 nm). The oil lens consists of the bulk liquid remained as an island in large film (area: ca. 600 mm^2). For the film formed from oleylamine/n-decane (0.2/1, v/v) solution, the two-dimensional film viscosity was 5.6×10^{-8} N s/m at 22°C.

The fluidity of biological membranes is essentially associated with its functions. For example, the control of the fluidity of biological membranes by cholesterol has a significant effect on the multiplication of cells.$^{1)}$ Therefore, it seems that the study of fluidity of the black film (a model of biomembrane) is of importance. The viscosity of monolayers has been widely investigated by numerous investigators.$^{2)}$ The viscosity of soap films in air was also studied by Mysels et al.$^{3)}$ However, the viscosity of the black film in aqueous solution has not been reported so long as we have known. One of the causes probably is the difficulty of the formation of large black film.

From the motion of the oil lens in our large film (Fig.1), the viscosity of the black film can be estimated.

Large black film (area: ca. 600 mm^2) of oleylamine could be formed on the vertical frame in a $NiCl_2$ aqueous solution (Fig.2).$^{4)}$ The thinning process to the black film from the colored film is similar to that of soap film in air, but the oil lens (diameter: ca. 0.2 mm) of bulk liquid remains as an island in the black film. After many lenses float upward in a vertical black film, they coalesce to a Gibbs triangle (Plateau-Gibbs border) one after another.

The viscosity of black film can be estimated from the ascending motion of lens in the bilayer. The buoyant force, f, provides the driving force of the ascending motion of lens, while opposing force is provided by the film viscosity and by the viscosity of the adjacent aqueous solution. The balance between these forces should determine the steady state rate u of this motion. If the well-known Stokes' law can be applid to the motion of lens in the black film, we have

$$f = 6\pi \phi \eta u r \tag{1}$$

where η denotes the total viscosity, r the radius of lens, and ϕ a correction factor. In the case of a disk (thickness: infinitesimal) moving edgeways, we have $\phi = 0.566$.[5)]

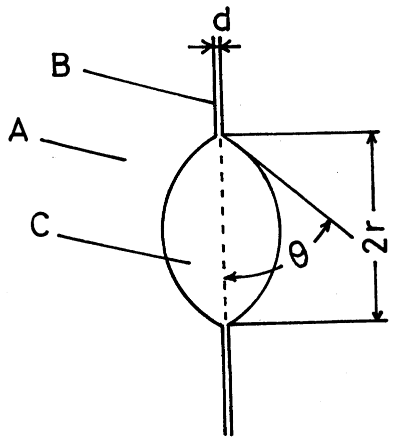

Fig.1. Oil lens in black film.
A: Aqueous solution, B: Black film (thickness $d \approx 5 \times 10^{-9}$m), C: Oil lens (radius $r \approx 1 \times 10^{-4}$m), θ : Contact angle.

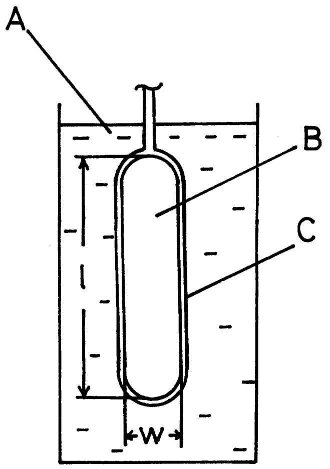

Fig.2. Large black film on a frame. A: Aqueous solution (30 mM $NiCl_2$), B: Large black film (width w = 12 mm, length l = 60 mm), C: Frame of Teflon-coated wire (diameter, 2 mm).

The total viscosity η consists of the contributions from the film (film viscosity η_f) and from the aqueous solution (solution viscosity η_a). Therefore, as a first approximation, we have

$$\eta = \frac{S_f}{S_f + S_l}\eta_f + \frac{S_l}{S_f + S_l}\eta_a \tag{2}$$

where S_f denotes the area of an image in horizontal plane resulting from the projection of the interface between the film and the oil lens (i.e. $S_f = 2rd$) and S_l that of the interface between the oil lens and the adjacent aqueous solution. Since $S_f \ll S_l$, Eq.2 can be approximated by Eq.3.

$$\eta = \frac{S_f}{S_l}\eta_f + \eta_a \qquad (3)$$

Therefore the two-dimensional film viscosity η_f^s can be obtained as follows,

$$\begin{aligned}\eta_f^s &= \eta_f\, d \\ &= \frac{S_l\, d}{S_f}(\eta - \eta_a) \qquad (4)\end{aligned}$$

where d denotes the thickness of film.

The buoyancy is directly proportional to the difference in density between the aqueous solution and lens, viz.

$$f = v\,(\rho_a - \rho_l)g \qquad (5)$$

where ρ_a denotes the density of the aqueous solution, ρ_l the density of the lens, and v the volume of the lens. Assuming the lens consists of two spherical segments,

$$v = \frac{2\pi r^3}{3\sin^3\theta}(2 - 3\cos\theta - \cos^3\theta) \qquad (6)$$

where θ is the contact angle between the black film and the lens in Fig.1. Assuming the correction factor ϕ for the lens to be equal to that of a disk (thickness: infinitesimal) moving edgeways, i.e. $\phi = 0.566$, η_f^s is obtained from Eqs.1, 4, 5, and 6.

$$\eta_f^s = \frac{S_l\, d}{S_f}\left\{\frac{r^2(2 - 3\cos\theta - \cos^3\theta)}{4.53\, u \sin^3\theta}(\rho_a - \rho_l)g - \eta_a\right\} \qquad (7)$$

The radius r and rate of ascent u of the lens can be estimated from successive photographs. Most of the lenses had radii somewhat under 0.1 mm. Typical velocities were $(1 - 2) \times 10^{-4}$ m/s. It is possible, in principle, to deduce the contact angle from measurement of the spacing of Newton's rings in the lens.$^{6)}$ Owing to the large contact angle in our case, however, the observation of the spacing of Newton's rings was difficult. Therefore, we estimated photographically the contact angle by the following procedure (Fig.3). A small volume (ca. 0.2 cm^3) of the oleylamine/n-decane solution (sample solution, 0.2/1, v/v) was delivered onto the upper rim of a small Teflon cup, with the help of a Teflon tube (c) attached to a syringe. The cup was lowered slowly into the $NiCl_2$ solution [Fig.3(c)～(f)]. A slight convex film was formed on the upper rim of the cup [Fig.3(f)]. The film (E) showed the interference. The thinning process [Fig.3(f) to (g)] that leads to the black film from the colored film usually begins at the lower part (F) of the film, as the excess oil is extruded to the top of the convex film. A small lens (G) is formed at the top of the convex film. If a capillary comes into contact with the lens, the diameter of lens becomes smaller because of the migration of oil into the capillary, i.e. the capillarity.

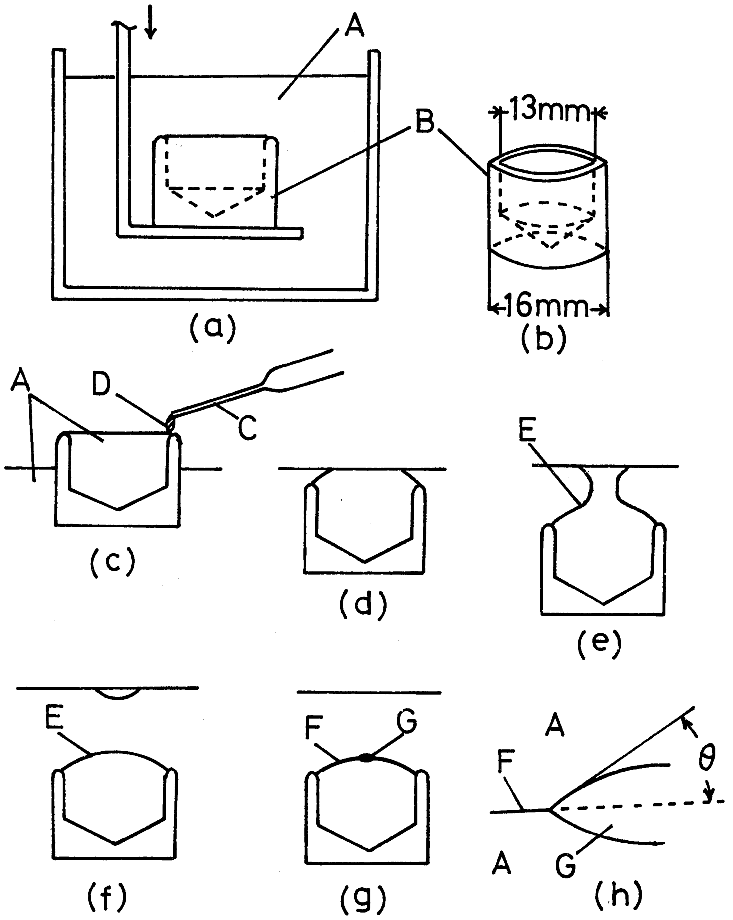

Fig.3. Preparation of the oil lens for the contact angle measurements. A small lens (G) is formed at the top of the convex black film (F) via the process (c) to (g). A: Aqueous solution (30 mM $NiCl_2$), B: Small Teflon cup, C: Teflon tube attached to a syringe, D: A drop of oleylamine/n-decane solution, E: Colored film, F: Convex black film, G: A oil lens (diameter, ca. 0.5 mm).

In order to estimate the contact angle, the small lens was observed by a microscope in the horizontal direction. When the diameter of lens was less than 0.5 mm, no significant dependence of the size of lens on contact angle was found. The contact angle θ in Fig.3 (h) was measured to be $17 \pm 0.5^{\circ}$. When n-octane (C_8) or n-dodecane (C_{12}) was used instead of n-decane, the contact angle remained to be the same within the experimental error.

The viscosity η_a and density ρ_a of the $NiCl_2$ solution (30 mM at 22°C) were taken to be 9.9×10^{-4} N s/m^2 and 1.01×10^{-3} kg/m^3, respectively. Assuming the density ρ_ℓ of the lens to be equal to that of the sample solution, the densities for C_8, C_{10} and C_{12} solvents were taken to be 0.722×10^{-3}, 0.741×10^{-3} and 0.757×10^{-3} kg/m^3, respectively.

On the other hand, assuming the black film to be a parallel plate condenser, we find from the observed value of the static capacitance that the thickness of film depends on the kind of solvent of the sample solution.4) That is to say, the thickness d for C_8, C_{10} and C_{12} solvent was 3.3, 4.6 and 3.8 nm, respectively.

When above values are substituted in Eq.7, η_f^s can be obtained. The mean value of η_f^s for 35 lenses in the film formed from oleylamine/n-decane solution was 5.6×10^{-8} N s/m (5.6×10^{-5} surface poise) at 22°C, while the mean values of η_f^s for C_8 and C_{12} solvents were 7.4×10^{-8} and 8.5×10^{-8} N s/m, respectively. These values of η_f^s for three films are comparable to the three-dimensional viscosities of 12, 22 and 22 N s/m^2, respectively. The viscosity of the film formed from oleylamine/n-decane solution is smaller than that of the film from oleylamine/n-octane or from oleylamine/n-tetradecane. The film viscosity consists of the contributions from the two surfaces and from the intralamellar liquid. If the solvent of sample solution remains appreciably among the oleyl chains, the viscosity of the intralamellar liquid should become smaller. From the influence of the solvent of sample solution on the thickness of black film, it is obvious that n-decane tends to remain among the oleyl chains rather than other n-alkanes.4) Therefore, we presume that the viscosity of the film formed from oleylamine/n-decane solution becomes smaller owing to the larger quantities of solvent in the film.

The viscosity of the soap film formed in air from the solution of sodium dodecyl sulfate is ca. 10 times larger than that of our black films.3) Joly7) and Jarvis8) reported viscosity measurements on expanded monolayer.

Its surface viscosity had smaller value (10^{-7} to 10^{-8} N s/m) than typical value (10^{-6} to 10^{-4} N s/m) for a condensed monolayer of the saturated straight-chain acids. Since the oleylamine formed an expanded monolayer on $NiCl_2$ solution, the small viscosity of our oleylamine black film is attributable to the expansile property of oleyl chains.

From the facts presented above, it is concluded that the viscosity of black film can be estimated by our new technique.

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