

The Thin Liquid Film between Glass and Mercury in An Aqueous Solution

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The equilibrium thickness of thin liquid film between glass and mercury electrode in an aqueous solution of inorganic electrolyte was measured interferometrically at various polarizations of the electrode. At the constant ionic strength, the thickness of the film increased with increasing magnitudes of the polarizations. At the constant polarization and ionic strength the film thickness decreased with increasing the squeezing pressure of thin liquid film as well. These results could be explained well by the DLVO force, and the effect of the Stern potential on the double layer force became experimentally evident.

I. INTRODUCTION

The DLVO theory^{1,2)} based on the double layer and van der Waals interactions is the inter-particle force as the function of the ionic strength, dielectric constant, Stern potential and Hamaker constant. The DLVO force increases with not only the increase of dielectric constant and Stern potential but also the decrease of ionic strength and Hamaker constant. Derjaguin *et al.*³⁾ and Scheludko *et al.*^{4,5)} initially exhibited the presence of the force, experimentally, using the free film made of the surfactant solution: the thickness of the film which becomes thin by the capillary pressure was measured interferometrically and the equilibrium thicknesses attained agreed well with the theoretical values of DLVO. Roberts *et al.*^{6,7)} extended the interferometrical method to the system of the thin liquid film between solid surfaces of rubber and glass, giving the experimental proof of the theory. Israelachvili *et al.*⁸⁾ and others^{9,10)} directly clarified the experimental dependence of the force and separation between two mica surfaces in solutions using the multi-beam interferometry, which gives the high accuracy of the thickness measurement. Their investigations were the most adequate proof for the DLVO theory as well as finding the presence of steric and hydration forces. The latter force which usually presents at the thickness less than 10 nm seems to be the origin of the exceptional colloid stabilization.

On the other hand, there seems to be very few experimental study of the influence of surface potential (Stern potential) on the DLVO force as the function of the inter-particle separation with well defined system of the potential. In the present investigation, the model experiment for the colloid stability is carried out to show how the equilibrium thickness of thin liquid film between glass and mercury electrode is influenced by the Stern potential, for mercury is one of the ideal electrode.

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II. EXPERIMENTS

II.1. Materials

An analar reagent of KCl was roasted for 6 hrs at about 700°C before use. Mercury used was distilled 3 times in vacuum after washing it by dilute nitric acid solutions. The common distilled water was further distilled 2 times in a Pyrex glass vessel. The aqueous solution prepared was passed through an activated charcoal column and then a milipore filter (pore size 220 nm) just before use. The TaFD-11 glass plate supplied by Hoya glass Ltd. was a dense Tantalum flint type having the refractive index 1.90 at the wavelength 633 nm. The optically flat plate carefully polished was used after ultra-sonication in the distilled water and then weeping treatment by acetone vapour in a Pyrex glass apparatus.

II.2. Method

II.2.1. Formation of the thin liquid film

The schematic diagram of experimental apparatus is depicted in Fig. 1. The glass plate A was placed and fixed in the inner compartment B of a Prexy glass cylinder cell of double wall types. Mercury for the counter electrode was added into the outer compartment C of the cell and subsequently the aqueous solution of $8 \times 10^{-4}M$ KCl was poured into the both compartments. The conductivity was thus made between the both. Mercury was gradually poured into the inner compartment by using a syringe D with a glass stop cock and maintained the level at about 1 mm below the glass plate. The cathodic polarization of $-5V$ was applied for about 5 minutes to the inner mercury electrode with reference to the outer one by using the potentiometer E. This pre-caution served to clean the surface of cathodic mercury electrode by the desorption of surface active impurities. After adjusting the polarization to $-\psi_1$ (Hg) mV against the counter mercury electrode (vs. ecm), the mercury level of the inner compartment was further raised by using the syringe, being maintained at 1 mm higher than the lower glass surface. This brings about the squeezing pressure F_s given by ρgl , where ρ is the density of mercury, g the gravitational acceleration and l the above mentioned value determined by the volume measurement of mercury added. The squeezing pressure thus obtained acts to thin the liquid film between glass and mercury, and the film thickness attains to the equilibrium at the position which is equal to the counter pressure in the film.

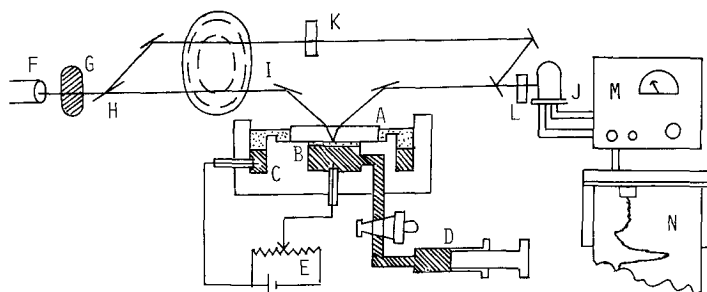


Fig. 1. The schematic diagram of experimental apparatus.

II.2.2. Measurement of the film thickness

The thickness of thin liquid film was calculated from the reflectance measurement by using the optical interference method, see Fig. 1. The 632.8 nm beam from a 2 mW He-Ne laser F was polarized with the electric vector normal to the incidence plane by the polarizer G. The beam was then divided into the reference and sample beams at the half mirror H. Both beams were chopped at 180 Hz by the sector I. The reference beam was led to the photomultiplier J after passing through the attenuator K and slit L. The sample beam was incident from air on the glass plate with the angle of 52° . The sample beam reflected from the lower glass surface and aqueous-mercury interface was interfered and focused on the same photomultiplier plane as the reference beam. The intensity change of the interference beam with respect to the reference beam was recorded at M after amplification at N. The applied working voltage to the photomultiplier was 400 V d. c. with the fluctuation less than 1%. The whole experimental apparatus was placed on double vibration free mountings on a stone table. The experiment was carried out at a room temperature.

II.2.3. Measurement of the electrokinetic potential

The Stern potential of mercury electrode could be controlled by applying the potential from the outer circuit. On the other hand, the Stern potential of glass plate was approximated by the electrokinetic potential. For this measurement, a small piece of cleaned TaFD-11 glass block ground to fine powders in air and then in aqueous solution of 8×10^{-4} M KCl was allowed to stand for about one hour. The turbid supernatant was further diluted by the same solution and then filled in the micro-electrophoretic cell. The electrokinetic potential was calculated with the aid of the Henry's equation¹¹⁾ from the measurement of electrophoretic mobilities. In the case of no correction of particle size dependence on the mobility, the potential was in the range of -15 to -25 mV.

III. RESULTS AND DISCUSSION

Intensity of the reflected light from glass plate and mercury indicates the periodical oscillation with the decrease in the thickness of thin liquid film. Fig. 2 shows the final part of the oscillation in the relation of the squeezing time, where the KCl concentration of aqueous solution is 8×10^{-4} M, the squeezing pressure is 1441 dyne/cm² and the polarized potential of mercury electrode is approximated to be the Stern potential ϕ_1 (Hg) = -100 mV vs. ecm. The light intensity attains to the equilibrium at about 25 minutes after the maximum intensity.

Denoting the maximum, minimum and equilibrium intensities by the symbols of I_{\max}/I_0 , I_{\min}/I_0 and I/I_0 , respectively, we can calculate the thickness of thin liquid film between glass and mercury by the following equation¹²⁾.

$$\frac{(I/I_0) - (I_{\min}/I_0)}{(I_{\max}/I_0) - (I_{\min}/I_0)} = \frac{[\{ r^2 + r_1^2 + 2rr_1 \cos(x-\delta) \} / \{ 1 + r^2r_1^2 + 2rr_1 \cos(x-\delta) \}] - 0.811}{0.112} \quad (1)$$

where r and r_1 are the amplitudes of reflected light at the glass-thin liquid film and

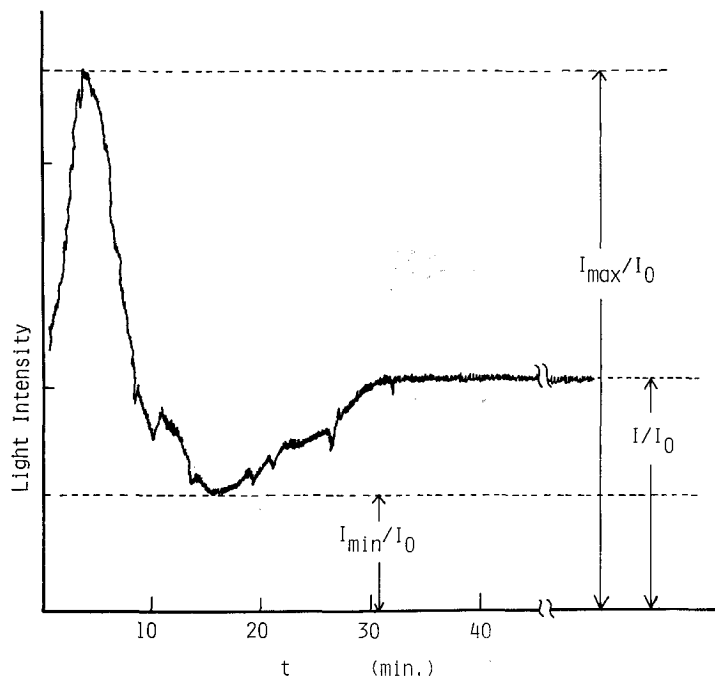


Fig. 2. The intensity variation of reflected light with the squeezing time: 8×10^{-4} M KCl, ϕ_1 (Hg) = -100 mV and ϕ_2 (glass) = -15 to -25 mV.

thin liquid film-mercury interfaces, respectively, x the phase difference due to the optical path in the film and δ the phase of reflected light at the film-mercury interface:

$$r = (n_0 \cos \phi_0 - n_1 \cos \phi_1) / (n_0 \cos \phi_0 + n_1 \cos \phi_1),$$

$$r_1^2 = \{(n_1 \cos \phi_1 - n_2 \cos \phi_2)^2 + n_2^2 k^2\} / \{(n_1 \cos \phi_1 + n_2 \cos \phi_2)^2 + n_2^2 k^2\},$$

$$x = 4\pi n_1 h \cos \phi_1 / \lambda$$

and

$$\tan \delta = 2n_1 n_2 k \cos \phi_1 / (n_1^2 \cos^2 \phi_1 - n_2^2 \cos^2 \phi_2 - n_2^2 k^2).$$

Here, n_0 , n_1 and n_2 are the refractive indexes of glass (1.90), thin liquid film (1.33) and mercury (1.69), respectively, ϕ_0 , ϕ_1 and ϕ_2 are the incidence angle from glass to thin liquid film ($24^\circ 30'$), the refraction angles in the film ($36^\circ 20'$) and in mercury ($27^\circ 43'$), respectively, k is the absorption index of mercury (4.02), λ is the wavelength of light in air and h is the thickness of thin liquid film. All parameters of the right hand side in equation 1 have been known except the film thickness h , so that the measurement of the left hand side allows the calculation of h .

The equilibrium thickness thus obtained from the result of Fig. 2 is 49.3 nm. At the same condition of salt concentration and squeezing pressure the equilibrium thickness h_e increases with increasing the magnitude of Stern potentials: $h_e = 53.8$ and 57.1 nm at ϕ_1 (Hg) = -150 and -200 mV, respectively.

According to the DLVO theory, the inter-particle force of colloid is given by the summation of electrical double layer F_e and van der Waals forces F_a which are the function of the inter-particle separation. Provided the same force acts in the thin liquid film between glass and mercury, the equilibrium thickness h_e of the film

is considered to be maintained by the force relation $F_s = F_e + F_a$. Derjaguin,¹³⁾ Devereux-de Bruyn¹⁴⁾ and Hogg-Healy-Fuerstenau's¹⁵⁾ equations are available for the unsymmetrical double layer force such as the present case. The van der Waals force is expressed as the function of relative permittivities of bodies and continuous liquid medium. But the force at the large separation takes the very close value with the Hamaker's equation¹⁶⁾ given by the summation of inter-molecular attraction assuming the uniform density of molecules in the bodies and medium. The squeezing pressure is given experimentally. Hence the theoretical calculation of the equilibrium h_e can be made if the parameters such as the ionic strength, dielectric constant, Stern potentials and Hamaker constant A included in F_e and F_a terms*¹⁾ were known. The former two parameters are defined from that the concentration of electrolyte in the aqueous phase is kept constant throughout the experiment. The Stern potentials are also known from the electrokinetic potential and the double layer potential in the absence of specific adsorption of ions. The Hamaker constant A is cited from the literature value of 1.5×10^{-13} erg.¹⁷⁾ The theoretical and experimental values of h_e thus obtained are shown in the relation of the ratio of Stern potentials ψ_1 (Hg)/ ψ_2 (glass), see Fig. 3. As precedently mentioned ψ_2 (glass) had some distributions of the values ranging -15 to -25 mV. In the theoretical calculation of h_e ψ_2 (glass) was assumed to be -15 mV, for the value gave the closest h_e values with the experimental ones. An agreement between the theoretical and experimental h_e values are not always excellent, but the experimental ones are slightly smaller than those

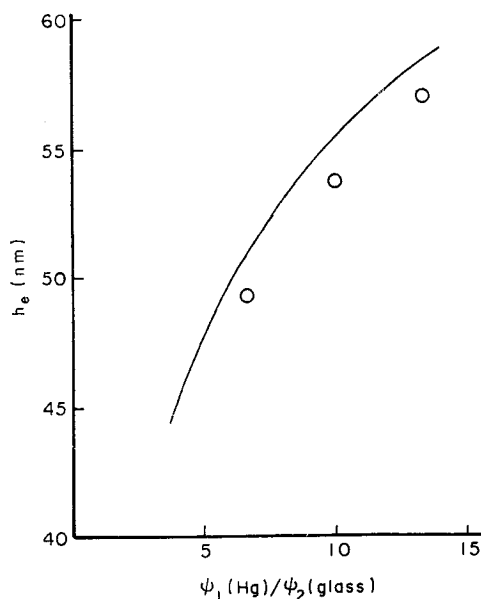


Fig. 3. The dependence of Stern potential of mercury on the equilibrium thickness h_e of thin liquid film: —, theoretical curve; ○, experimental values. ψ_1 (glass) was taken as -15 mV.

*1) The equations for F_a and F_e applied here were the Hamaker's equation and Hogg-Healy-Fuerstenau's one derived by using the Debye-Hückel approximation, respectively.

of theoretical h_e values. This can be explained by that the theoretical equation of F_e used includes the Debye-Hückel approximation, the Stern potential of mercury was assumed to be the same as apparent polarizations and the capillary pressure was neglected: the Stern potential will slightly decrease by a trace of impurities or the specific adsorption of ions, which results in the decrease of the theoretical h_e with the capillary pressure. However, here is a clear dependence of the Stern potential on the equilibrium thickness of thin liquid film suggesting the effect of the Stern potential on the double layer force in the film.

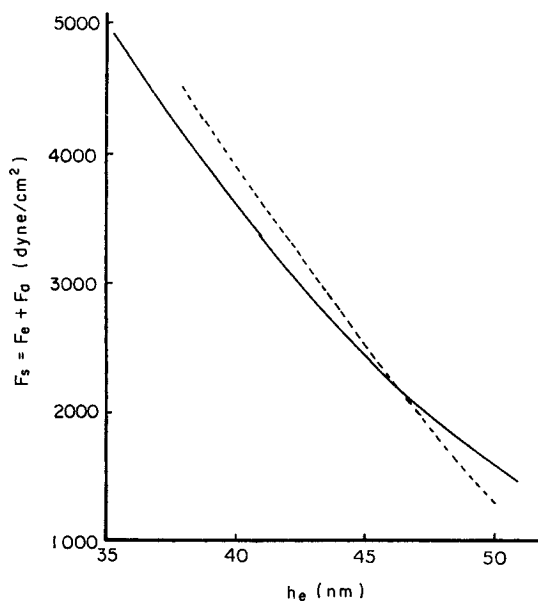


Fig. 4. The relation between squeezing pressures F_s and equilibrium thickness h_e of thin liquid film: 8×10^{-4} M KCl, ψ_1 (Hg) = -100 mV and ψ_2 (glass) = -15 mV. Solid line, theoretical curve; broken line, experimental curve.

The further investigation is the direct measurement of relation between the force and equilibrium thickness in the thin liquid film. This can be attained by changing the magnitude of squeezing pressure, maintaining the electrolyte concentration (8×10^{-4} M KCl) and Stern potential (ψ_1 (Hg) = -100 mV *vs.* ecm) constant. Fig. 4 indicates the variation of the squeezing pressure F_s with the equilibrium thickness h_e of thin liquid film between glass and mercury. Here the solid line is the theoretical curve given by the relation of $F_e + F_0$ using the same equation as before and the broken line is the experimental curve. Both curves agree fairly well. This result suggests that the force acting in the thin liquid film is essentially the same as the inter-particle force of colloid. In other words, the stability and drainage of thin liquid film in the present system are mainly governed by the electrical double layer interaction and van der Waals force.

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