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General Theory of the Formation of Liquid Films

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Langmuir's theory of the formation of liquid films in narrow capillaries is developed for the general case of any electrolyte. The determination of the thicknesses of such films involves hyperelliptic integrals. By suitable transformations one can represent the integrand as the product of binomial series and Legendre's series. No attempt is made to evaluate the thicknesses of the film numerically, because of the complexity of the necessary computations.

INTRODUCTION

IN discussing the problem of measuring the surface tension of solutions of electrolytes in narrow capillaries, Langmuir¹ proposed a theory which has been extended by others.² Since the details have been discussed previously, they are not repeated here; only a brief mention is made here of the ideas involved. All adaptations of the theory so far published have been applicable only for 1-1 and 2-1 electrolytes; the presentation herein is an extension of the general theory given elsewhere by this author.³

Langmuir believes that the wetting film formed in the capillary can be large enough to decrease the effective diameter of the tube. Solutions will then rise to a greater height than corresponds to the measured diameter of the capillary. Hence the capillary would not be a measure of the surface tension alone. This film has varying thicknesses depending upon the solution studied. The experimental procedure of using narrow capillaries, according to Langmuir, corresponds to measuring surface tensions with tubes of different (unknown) diameters. The problem of Langmuir's theory is to calculate the wetting film thickness for different solutions so that there can be some basis for comparing the surface tensions in terms of the capillary rises observed. The thickness of the film depends upon the solution used, the height to which the liquid rises in the tube, the zeta-potential, and the potential at the air-solution interface.

In discussing the mathematics of the problem, Langmuir utilizes the Poisson-Boltzmann equation and does not introduce the usual Debye-Hueckel simplifying assumptions.

MATHEMATICAL FORMULATION

The Poisson-Boltzmann equation for the electrical potential in an electrolytic solution in the region of a charged plane is

$$\nabla^2\psi = -\frac{4\pi}{D} \sum_{i=1}^s n_i z_i e \exp\left(\frac{-z_i e\psi}{kT}\right). \quad (1)$$

$\nabla^2\psi = d^2\psi/dx^2$ in this case as the potential is assumed to vary only in the direction perpendicular to the planar interface. This equation can be applied to the capillary tube because the radius of the tube is so much larger than the thickness of the wetting film. The curvature of the tube is relatively slight, and the inside surface appears as a plane to the film.

A simplification of Eq. (1) is effected by using the following substitutions (generally adopted):

$$\left. \begin{aligned} \eta &\equiv e\psi/kT, \\ \theta &\equiv \kappa x, \\ \kappa &\equiv \left[(4\pi e^2/DkT) \sum_{i=1}^s n_i z_i^2 \right]^{1/2}, \\ 1/A &\equiv \sum_{i=1}^s n_i z_i^2, \\ p &\equiv d\eta/d\theta, \end{aligned} \right\} \quad (2)$$

Equation (1) becomes

$$p \frac{dp}{d\eta} = -A \sum_{i=1}^s n_i z_i \exp(-z_i \eta), \quad (3)$$

¹ I. Langmuir, *Science* **88**, 430 (1938); *J. Chem. Phys.* **6**, 894 (1938).

² G. Jones and L. D. Frizzell, *J. Chem. Phys.* **8**, 986 (1940); L. A. Wood and L. B. Robinson, *J. Chem. Phys.* **14**, 258 (1946).

³ L. B. Robinson, Ph.D. Thesis, Harvard University, Cambridge, Massachusetts, May 1946, pp. 193-195.

which, when integrated, yields

$$p^2 = \left(2A \sum_{i=1}^s n_i \exp(-z_i \eta) \right) + C. \quad (4)$$

The constant of integration is evaluated in the same manner as has been done by Langmuir, by assuming that at the air interface of the film, where $\theta=0$, the potential has a minimum. The minimum value of η is called m ; at this point $p=0$. Hence the value of C is given by

$$C = -2A \sum_{i=1}^s n_i \exp(-z_i m). \quad (5)$$

From (4) and (5) the following equation is obtained:

$$\frac{d\theta}{d\eta} = \frac{1}{\left[2A \sum_{i=1}^s n_i \{ \exp(-z_i \eta) - \exp(-z_i m) \} \right]^{\frac{1}{2}}}. \quad (6)$$

The solution of (6) may be written as

$$\Delta r = R(c_1, c_2, \dots; z_1, z_2, \dots; \psi_m, \zeta), \quad (7)$$

where the R function involves elliptic functions for the case that $-2 \leq z \leq +2$, but cannot be expressed in terms of known tabulated functions for the cases where $|z| \geq 3$. Δr is the thickness of the liquid film. ψ_m represents the minimum potential (at the air-solution interface according to Langmuir) and ζ is the zeta-potential. Equation (6) will be integrated for the general case.

It is apparent that the general solution of (6) will involve hyperelliptic functions. If one makes the transformation,

$$y = \exp(-\eta), \quad K = \exp(-m), \quad (8)$$

assuming positive potentials, Eq. (6) becomes

$$d\theta = \kappa dx = \frac{b dy}{(a_n y^n + a_{n-1} y^{n-1} + \dots + a_0)^{\frac{1}{2}}}, \quad (9)$$

where one or more of the a 's may be zero. Let the radicand in the denominator be written $Q(y)$ and let it be factored as

$$Q(y) = (y - K_1)(y - K_2) \dots (y - K_r) Q_0(y), \quad (10)$$

where $Q_0(y)$ is the term containing the part of the expression with whatever complex roots that

may result. Let the root between zero and positive unity be called K_1 . It is apparent that this root fixes the value of the minimum potential. This point is discussed elsewhere in connection with the specific examples of Jones-Frizzell and Wood-Robinson.

F. R. Moulton⁴ provided a general method whereby hyperelliptic integrals can be evaluated and E. G. Keller⁵ has applied this method to non-linear circuit problems. The question of the periods of the integral does not need to be discussed here in that the problem herein is different from those of Moulton and Keller. They were interested in the inverse problem, namely, the equivalent of finding y as a function of Δr .

The transformation given immediately below is made so as to put $Q(y)$ in a form more suitable for integration. Let

$$y = \frac{K_1 + K_2}{2} + \frac{K_2 - K_1}{2} t. \quad (11)$$

K_1 is the lower limit of the integration sign. Equation (10) now becomes

$$Q(y) = \frac{(K_2 - K_1)^2}{4} (1 - t^2) \prod_{j=1}^m b_j \left[1 + \frac{K_2 - K_1}{2b_j} t \right], \quad (12)$$

where

$$\frac{K_2 - K_1}{2b_j} = \frac{g}{b_j} = \left| \frac{K_2 - K_1}{K_2 + K_1 - 2K_j} \right| < 1. \quad (13)$$

If

$$b_j \left(1 + \frac{g}{b_j} t \right)$$

is a complex root, then its complex conjugate

$$b_{j+1} \left(1 + \frac{g}{b_{j+1}} t \right)$$

is, of course, also a root. Then

$$b_j b_{j+1} \left(1 + \frac{g}{b_j} t \right) \left(1 + \frac{g}{b_{j+1}} t \right) = B^2 (1 + \alpha_j t + \beta_j t^2), \quad (14)$$

where α_j and β_j are real and $B^2 > 0$.

⁴ F. R. Moulton, Am. J. Math. **34**, 177 (1912).

⁵ E. G. Keller, J. Frank. Inst. **225**, 561 (1938); **228**, 319 (1939); *Mathematics of Modern Engineering* (John Wiley and Sons, Inc., New York, 1942), Vol. II, pp. 264-284.

The use of t instead of y transforms (9) into

$$\Delta r = M \int_{-1}^{t_1} \frac{dt}{[(1-t^2)(1+f_1t) \cdots (1+f_qt) \cdots \times (1+\alpha_1t+\beta_1t^2) \cdots l(t)]^{\frac{1}{2}}}, \quad (15)$$

where all symbols, other than l and t , represent constants. The integration must be performed for many values of the upper limit in order to obtain sufficient points to insure a smooth curve representing Δr as a function of the potentials. It is convenient also to make a transformation so that the upper limit will become plus one. The transformation is

$$t = [(\lambda-1)/2] + [(\lambda+1)/2]\omega, \quad (16)$$

or

$$\omega = (2t - \lambda + 1)/(\lambda + 1).$$

It is apparent that a different value of the parameter λ must be selected to equal each value of the upper limit t_1 . This transformation is made in order to assist in the study of the convergence conditions of the series generated by the terms in the denominator of (15). Actually, no worry need exist concerning this point since the physical nature of the problem will make it so that the series involved will be suitable. The maximum value which can assume is given by the zeta-potential.

The transformation (16) is an interesting one in that the lower limit retains the value -1 for every value of λ . This is because the t representing the lower limit is -1 .

When this transformation is made, Eq. (15) becomes

$$\Delta r = M' \int_{-1}^{+1} \prod_{i=1}^n (1+h_i\omega)^{-\frac{1}{2}} (1+\omega)^{-\frac{1}{2}} \times \prod_{j=1}^m \left\{ \sum_{l=0}^{\infty} P_l(\mu\gamma^{\frac{1}{2}})(\gamma^{\frac{1}{2}}\omega)^l \right\} d\omega, \quad (17)$$

where the source of the various terms is explained below. The term $(1-t^2)^{\frac{1}{2}}$ transforms⁶ as

$$(1-t^2)^{\frac{1}{2}} = C(1+\omega)^{\frac{1}{2}}(1+h\omega)^{\frac{1}{2}}. \quad (18)$$

The terms in (15) of the general nature $(1+\alpha t+\beta t^2)^{-\frac{1}{2}}$ retain the corresponding powers of ω in the transformation, and the values of the coefficients of ω and ω^2 are such that each ex-

pression can be represented by a Legendre series, which converges rapidly.

$$(1+\alpha t+\beta t^2)^{-\frac{1}{2}} = E(1-2\mu\gamma^{\frac{1}{2}}\omega+\gamma\omega^2)^{-\frac{1}{2}}, \quad (19)$$

and

$$(1-2\mu\gamma^{\frac{1}{2}}\omega+\gamma\omega^2)^{-\frac{1}{2}} = \sum_{l=0}^{\infty} P_l(\mu\gamma^{\frac{1}{2}})(\gamma^{\frac{1}{2}}\omega)^l, \quad (20)$$

where $P_l(x)$, the Legendre polynomial, is given by

$$P_l(x) = \frac{(2l)!}{2^l(l!)^2} \left\{ x^l - \frac{l(l-1)}{2(2l-1)} x^{l-2} + \frac{l(l-1)(l-2)(l-3)}{2 \cdot 4(2l-1)(2l-3)} x^{l-4} - \dots \right\}. \quad (21)$$

It is apparent now that (17) will be an integral involving powers of the variable ω which can be evaluated at once. However, numerical computations are too difficult to make.

REMARKS

A general theory of the formation of liquid films consistent with Langmuir's ideas is developed. This theory involves hyperelliptic integrals, and a method of evaluating these integrals is given. For the case of 1-1 and 2-1 electrolytes, the integrals become elliptic integrals.

APPENDIX

All of the mathematical transformations given in this paper are more or less immediately apparent with the exception of Eq. (18). The details of this transformation are given here.

$$\begin{aligned} (1-t^2)^{\frac{1}{2}} &= \left[1 - \frac{(\lambda-1)^2}{4} - \frac{2(\lambda^2-1)}{4}\omega - \frac{(\lambda+1)^2}{4}\omega^2 \right]^{\frac{1}{2}} \\ &= - \left[\frac{(\lambda^2-2\lambda-3)+2(\lambda^2-1)\omega+(\lambda+1)^2\omega^2}{4} \right]^{\frac{1}{2}} \\ &= -\frac{1}{2}[(\lambda-3)(\lambda+1)]^{\frac{1}{2}} \left[1 + \frac{2(\lambda-1)}{(\lambda-3)}\omega + \frac{(\lambda+1)}{(\lambda-3)}\omega^2 \right]^{\frac{1}{2}} \\ &= -\frac{1}{2}[(\lambda-3)(\lambda+1)]^{\frac{1}{2}} \\ &\quad \times \left[1 + \left\{ \frac{(\lambda+1)+(\lambda-3)}{(\lambda-3)} \right\} \omega + \frac{(\lambda+1)}{(\lambda-3)}\omega^2 \right]^{\frac{1}{2}} \\ &= -\frac{1}{2}[(\lambda-3)(\lambda+1)]^{\frac{1}{2}} \\ &\quad \times \left[1 + \left\{ \frac{(\lambda+1)}{(\lambda-3)} + 1 \right\} \omega + \frac{(\lambda+1)}{(\lambda-3)}\omega^2 \right]^{\frac{1}{2}} \\ &= -\frac{1}{2}[(\lambda-3)(\lambda+1)]^{\frac{1}{2}} \left[1 + \frac{(\lambda+1)}{(\lambda-3)}\omega \right]^{\frac{1}{2}} (1+\omega)^{\frac{1}{2}} \\ &= C(1+\omega)^{\frac{1}{2}}(1+h\omega)^{\frac{1}{2}}. \end{aligned}$$

⁶ See appendix.