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A general theory of the formation of liquid films is applied to the case of lanthanum chloride. The hyperelliptic integrals involved are approximated with elliptic integrals. The small values of the zeta-potentials make reliable assignments of the values of the "corrected surface tensions" difficult.

INTRODUCTION

LANGMUIR'S theory for the formation of liquid films of solutions of uni-univalent electrolytes in narrow capillaries was presented in a more general form by this writer.[1] It was shown that the thickness of such films could be represented as a hyperelliptic integral (Eq. (9) of reference 1):

$$\Delta r = K \int_{y_1}^{y_2} \frac{dy}{(a_n y^n + a_{n-1} y^{n-1} + \cdots + a_0)^{\frac{1}{2}}}. \qquad (1)$$

The numerical computations necessary to the evaluation of such an integral are in general prohibitive and hence none were attempted in the previous article. When the general theory is applied to the case of lanthanum chloride, a hyperelliptic integral results which can be shown to have values between two elliptic integrals. The maximum and minimum values as represented by the elliptic integrals can be made to approach each other as closely as one likes and, as such, the value of the hyperelliptic integral can be determined quite accurately. Some of the details of the necessary mathematical transformations as well as the numerical computations are given here. Such computations not only give the corrected surface tentions, but also have intrinsic interest in that they represent a method of approximating the value of a *hyperelliptic integral* by means of *elliptic integrals*.

An interpretation of the results is given at the end of this article.

MATHEMATICAL FORMULATION

Negative Zeta-Potentials

When Langmuir's theory is applied to the case of 3-1 electrolytes, hyperelliptic integrals become involved. All of the equations listed in reference 1 from (1) through (6) are valid and are not repeated here. It is known experimentally that some of the zeta-potentials are negative whereas those of the more concentrated solutions are positive.[2] According to the theory, the potential at the solution-air interface must have the same sign as that of the zeta-potential. In order to determine

the value of this potential, it is necessary to solve a fourth-degree equation. It is convenient to use different transformations for the positive and negative cases in order that the root of the equation which fixes the solution-air potential will be automatically selected. The method of selecting the proper root has been discussed in previous papers.

The transformation for the case of negative potentials follows immediately below. Take

La^{+++} as ionic species 1; $z_1 = +3$,
H$^+$ as ionic species 2; $z_2 = +1$,
OH$^-$ and Cl$^-$ as ionic species 3; $z_3 = -1$.

Let:

$$y = \exp(+\eta) \quad \text{and} \quad K = \exp(+m). \qquad (2)$$

The equation relating the film thickness to the potentials and concentrations of the ionic species becomes:

$$d\theta = \left[\frac{6c_1 + c_2}{c_3} \right]^{\frac{1}{2}} \times \frac{y^{\frac{1}{2}} dy}{\left[y^4 - \frac{c_1 K^{-3} + c_2 K^{-1} + c_3 K}{c_3} y^3 + c_2/c_3 y^2 + c_1/c_3 \right]^{\frac{1}{2}}}. \qquad (3)$$

The c's refer to the concentration of the various ionic species. In effecting a simplification of notation, Eq. (3) is written as

$$d\theta = L y^{\frac{1}{2}} Q^{-\frac{1}{2}} dy, \qquad (4)$$

where

$$Q \equiv y^4 + a_1 y^3 + a_2 y^2 + a_4,$$

$$L \equiv \left[\frac{6c_1 + c_2}{c_3} \right]^{\frac{1}{2}}; \quad a_1 \equiv -\frac{c_1 K^{-3} + c_2 K^{-1} + c_3 K}{c_3},$$

$$a_2 \equiv c_2/c_3; \quad a_4 \equiv c_1/c_3; \quad c_3 \equiv c_2 + 3c_1.$$

The constants a_2 and a_4 are determined from the concentration of the ionic species in the solution; a_1 depends on the concentrations and also K, which serves as the lower limit when the integration is performed. It is worth while to point out in some detail how both a_1 and K can be computed. When the film thickness is sufficiently large so that van der Waals' or other short range forces are of no consequence, there are three types

[1] L. B. Robinson, J. Chem. Phys. **16**, 734 (1948).
[2] L. A. Wood and L. B. Robinson, J. Am. Chem. Soc. **69**, 1862 (1947).

of forces in equilibrium at the level of the meniscus in the capillary tube, according to Langmuir's interpretation. One force results from the weight of the solution in the capillary, pulling down on the film (the film itself is also a part of solution in the capillary), tends to make the film thinner. The pressure is regarded here as negative, since it acts downward, and it is computed by the following relation:

$$p_1 = -(d-\beta)hg, \qquad (6)$$

where d and β are the density of the solution and air, respectively, h is the capillary vise, and g is the acceleration of gravity. The second force originates in the pressure resulting from the surface tension of the cylindrical surface and tends to make the film thicker; this pressure is determined by the formula given below:

$$p_2 = (d-\beta)(hg/2). \qquad (7)$$

The third force in equilibrium results from the difference between the osmotic pressure in the bulk solution and that at the air-solution interface of the wetting film. According to van't Hoff's simple law, the osmotic pressure is given by $p = nkT$, where n is the number of ions per cm³. It is also assumed that the ions at the air interface obey the Boltzmann distribution and hence:

$$n = \sum_{i=1}^{s} n_i \exp(-z_i \epsilon \psi / kT),$$

or

$$n = \sum_{i=1}^{s} n_i K^{z_i}; \qquad (8)$$

in the bulk solution the osmotic pressure is $p = \sum_i n_i kT$. Thus the difference in osmotic pressure tending to make the film thicker is:

$$p_3 = \sum_{i=1}^{s} n_i kT(K^{z_i} - 1). \qquad (9)$$

At equilibrium the sum of these three pressures is zero and therefore:

$$\sum_i n_i kT(K^{z_i} - 1) - (d-\beta)hg/2 = 0. \qquad (10)$$

Using $N_i = 10^{-3} C_i N$, where N is Avogadro's number, one can transform Eq. (10) into:

$$10^{-3} NkT[c_1 K^{-3} + c_2 K^{-1} + (c_2 + 3c_1)K \\ - (4c_1 + 2c_2)] = (d-\beta)hg/2. \qquad (11)$$

The above equation can be rewritten in the following form:

$$\frac{c_1 K^{-3} + c_2 K^{-1} + (c_2 + 3c_1)K}{c_2 + 3c_1} \\ = \frac{1}{c_2 + 3c_1}\left[4c_1 + 2c_2 + \frac{500(d-\beta)hg}{NkT}\right]. \qquad (12)$$

The left-hand side of Eq. (12) is identically the negative

of a_1 as defined by (5) and hence a_1 can be computed even through K is not known (every term on the right-hand side of (12) is known).

When the left-hand side of (12) is equated to a_1, the equation given below is obtained.

$$K^4 + a_1 K^3 + a_2 K^2 + a_4 = 0. \qquad (13)$$

It is apparent that the roots of (13) are identical with those of $Q = 0$ in Eq. (4). The proper value of K can be found and ψ_m, the potential at the air interface can be evaluated. Q has two real and two complex zeros. If K_1 and K_2 are taken as the real zeros, then Q becomes

$$Q = (y - K_1)(y - K_2)(y^2 + 2\lambda' y + \mu'), \qquad (14)$$

where $\lambda' = -(K_3 e^{i\theta_3} + K_3 e^{-i\theta_3})$; $\mu' = -K_3^2$, θ_3 is the argument of the complex roots, and $i^2 = -1$. Consequently (2) may be written as:

$$\Delta r = \frac{L}{K} \int_{y_1}^{y_2} \frac{y^{\frac{1}{2}}}{[(y - K_1)(y - K_2)(y^2 + 2\lambda' y + \mu')]^{\frac{1}{2}}} dy, \qquad (15)$$

where y_1 corresponds to ψ_m and y_2 to the measured ζ-potential. This equation is the hyperelliptic type as discussed in reference 1; the approximate solution is given below.

If the $y^{\frac{1}{2}}$ factor did not appear in the numerator, the solution of (15) could be had in terms of elliptic functions. Even as it stands, it can be seen that the integral has a value always between an elliptic integral multiplied by $y_1^{\frac{1}{2}}$ and $y_2^{\frac{1}{2}}$. The interval between y_1 and y_2 can be broken up into any number of smaller intervals; then one can find two numerical values between which Δr must always lie. Choosing the interval (over which the integration is performed) smaller and smaller makes these values approach each other more closely so that Δr may be determined quite accurately.

Let the interval between y_1 and y_2 be broken up into subintervals, the end points of which are y_i and y_j ($y_j > y_i$ and $y_j < 1$) for each interval. It follows that

$$y_j^{\frac{1}{2}} \int_{y_i}^{y_j} Q^{-\frac{1}{2}} dy > \int_{y_i}^{y_j} y^{\frac{1}{2}} Q^{-\frac{1}{2}} dy > y_i^{\frac{1}{2}} \int_{y_i}^{y_j} Q^{-\frac{1}{2}} dy. \qquad (16)$$

The integral $\int Q^{-\frac{1}{2}} dy$ can be evaluated readily if it is reduced to the Lagrangian form. Q is factored into two quadratic forms with real coefficients and is written:

$$Q = (y^2 + 2\lambda y + \mu)(y^2 + 2\lambda' y + \mu'). \qquad (17)$$

Then, as usual, let y become $(p + qt)/(1 + t)$, from which

$$y^2 + 2\lambda y + \mu = H(t^2 + 2ft + b^2)/(1 + t)^2, \qquad (18)$$

where

$$\left.\begin{array}{l} H = q^2 + 2\lambda q + \mu. \\ b^2 = (p^2 + 2\lambda p + \mu)/(q^2 + 2\lambda q + \mu). \end{array}\right\} \qquad (19)$$

Likewise:

$$y^2 + 2\lambda' y + \mu' = H'(t^2 + 2f't + b'^2)/(1 + t)^2, \qquad (20)$$

where H' and f', and b'^2 are the same functions of p, q, λ', and μ' as H, f, and b^2 are of p, q, λ, and μ. Equations (18) and (20) hold for any arbitrary values of p and q. However, f and f' can be made to equal zero simultaneously by choosing p and q such that:

$$\left.\begin{array}{c} p \equiv \dfrac{(\mu-\mu')+W}{2(\lambda'-\lambda)}, \\[2mm] q \equiv \dfrac{(\mu-\mu')-W}{2(\lambda'-\lambda)}, \end{array}\right\} \quad (21)$$

and

$$W^2 \equiv (\mu+\mu'-2\lambda\lambda')^2 - 4(\mu-\lambda^2)(\mu'-\lambda'^2). \quad (22)$$

It can be shown that W^2 is always positive for all values of λ, λ', μ, and μ' and hence p and q are always real. After the substitutions are made, the elliptic integral can be written as

$$\int_{y_1}^{y_2} Q^{-\frac{1}{2}} dy = \frac{q-p}{(HH')^{\frac{1}{2}}} \int_{t_1}^{t_2} \frac{dt}{[-(t^2-b^2)(t^2-b'^2)]^{\frac{1}{2}}}. \quad (23)$$

The other transformations which are made in order that the integral be evaluated depend upon the numerical values of t_1, t_2, b, and b'. One can see from an examination of Table I and also the relation $t=(p-y)/(y-q)$ that $b'>t>b$; consequently the integrand in (23) is real. The following transformations are necessary to convert (23) in a form so that it can be evaluated from tables:

$$\left.\begin{array}{c} t^2 = b'^2 - (b'^2-b^2)\sin^2\phi, \\[1mm] b'^2 \sin^2\alpha = b'^2 - b^2. \end{array}\right\} \quad (24)$$

When Eq. (24) is substituted in (23), the integral given by Eq. (25) is used to compute the thicknesses of the films.

$$I = \int_{\phi_1}^{\phi_2} \frac{d\phi}{(1-\sin^2\alpha \sin^2\phi)^{\frac{1}{2}}}. \quad (25)$$

The film thicknesses are calculated by using the inequality (16). The limits ϕ_1 and ϕ_2 (corresponding to y_1 and y_2, respectively) are selected sufficiently close to each other so that

$$y_2^{\frac{1}{2}} \int_{\phi_1}^{\phi_2} \frac{d\phi}{(1-\sin^2\alpha \sin^2\phi)^{\frac{1}{2}}}$$

is almost equal to $\qquad\qquad\qquad\qquad\qquad (6)$

$$y_1^{\frac{1}{2}} \int_{\phi_1}^{\phi_2} \frac{d\phi}{(1-\sin^2\alpha \sin^2\phi)^{\frac{1}{2}}}.$$

These integrals are multiplied by

$$M \equiv \frac{L}{K} \frac{q-p}{b'(HH')^{\frac{1}{2}}}. \quad (27)$$

This multiplicative factor comes from (3), (23), and (25); from Eq. (3), $\Delta\theta = K\Delta r$. In calculating the values

for the curve in Fig. 1, the two integrals in (26) were usually selected so that the two extremes differed by not more than about 1 or 2 angstrom units; in the most extreme cases, the difference was never more than 6 angstrom units.

Positive Zeta-Potentials

In the solutions in which the zeta-potentials are positive, it is convenient that

$$y \equiv \exp(-\eta) \quad \text{and} \quad K \equiv \exp(-m), \quad (28)$$

instead of Eq. (2). The ionic species 1, 2, and 3 are the same as in the first transformation.

Equation (29) then replaces Eq. (3).

$$d\theta = -\left[\frac{6c_1+c_2}{c_1}\right]^{\frac{1}{2}}$$

$$\times \frac{y^{-\frac{1}{2}} dy}{\left[y^4 + \dfrac{c_2}{c_1} y^2 - \dfrac{c_1 K^3 + c_2 K + c_3 K^{-1}}{c_1} y + \dfrac{c_3}{c_1}\right]^{\frac{1}{2}}}. \quad (29)$$

This equation may be rewritten as

$$\Delta r = -\frac{L}{K} \int_{y_1}^{y_2} \frac{y^{-\frac{1}{2}}}{(y^4 + a_1 y^2 + a_2 y + a_3)^{\frac{1}{2}}} dy, \quad (30)$$

where

$$\left.\begin{array}{c} L \equiv \left[\dfrac{6c_1+c_2}{c_1}\right]^{\frac{1}{2}}; \quad a_1 = c_2/c_1; \\[3mm] a_2 \equiv -\dfrac{c_1 K^3 + c_2 K + c_3 K^{-1}}{c_1}; \\[3mm] a_3 \equiv c_3/c_1 \equiv \dfrac{3c_1+c_2}{c_1} = a_1 + 3. \end{array}\right\} \quad (31)$$
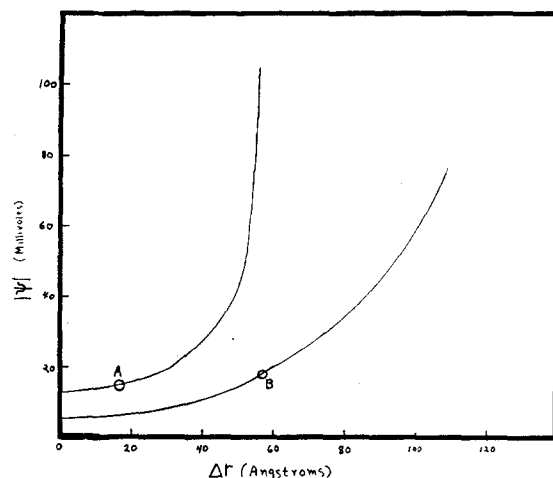

FIG. 1. Zeta-potential vs. film thickness.

TABLE I. Parameters for the evaluation of film thicknesses.

| | Concentration of lanthanum chloride solutions | | | |
	1.00×10	2.50×10	1.00×10	5.00×10
$c_1(\times10^6)$	1000	250	100	50
$c_2(\times10^6)$	1	1	1	1
$c_3(\times10^6)$	3001	751	301	151
$(\times10^8)$	39.28		124.1	
K	0.8184	0.6562	0.6155	0.5301
K'	1.1936	1.3926	2.0114	2.7380
$d-\beta$	0.9973	0.9971	0.9971	0.9971
λ	−1.0060	−1.0244	−1.3085	−1.6340
μ	0.9768	0.9138	1.2320	1.4514
λ'	1.0060	1.0244	0.2855	0.2569
μ'	3.0732	3.2917	0.2688	0.2281
$\psi_{m(mv)}$	5.15	10.8	12.5	16.3
$\zeta_{(mv)}$	16.4	2.0	14.5	15.0
W	6.0979		2.3264	
p	0.9944		1.0320	
q	−2.0364		−0.4276	
H	9.2209		2.5339	
H'	3.1229		0.2075	
b	0.0617		0.3991	
b'	1.9414		9.2677	
t_1	0.0617		0.3991	
α(degrees)	87.53		88.18	
$M(\times10^8)$	27.994		−38.09	
η	−0.6385		−0.5646	
y_2	0.5281		0.5686	
$y_1(=K)$	0.8184		0.6156	
t_2	0.1818		0.4651	
ϕ_1(degrees)	84.95		88.52	
Δr(angstroms)	56	0	18	0

From equilibrium conditions, one sees that

$$K^4 + a_1K^2 + a_2K + a_3 = 0, \qquad (32)$$

from which the different values of K and also a_1 are formed by using a procedure similar to that following Eq. (5). One then treats Eq. (30) in the same fashion as (3) and (16) were treated with p, q, and all other parameters defined exactly as in the first case.

As before, the integral is evaluated by computing several small increments and subsequently adding all of the successive increments to those which have been previously calculated. Since $y = \exp(-\eta)$, and $y^{-\frac{1}{2}} = \exp(+\eta/2)$, it follows that $y^{-\frac{1}{2}}\int Q^{-\frac{1}{2}}dy$ goes to infinity as the potential does. This, however, presents no difficulty in evaluating the increments for $y^{-\frac{1}{2}}\int Q^{-\frac{1}{2}}dy$; in the region where $y^{-\frac{1}{2}}$ begins to become large so that the difference between y_i and y_j to be considered must be very small, the increment of the elliptic integral in this corresponding region approaches zero. Actually, the elliptic integral attains its full value, very nearly, at about 80 millivolts so that all of the many increments to be added between 80 mv and infinity are practically negligible. The curve showing the variation of the film thickness with potential for this case is also shown in Fig. 1.

INTERPRETATION OF COMPUTATIONS

The values of the zeta-potential listed in Table I have been used to compute the wetting film thicknesses for lanthanum chloride solutions of concentrations 10^{-3} and

TABLE II. Corrected surface tensions for lanthanum chloride solutions.

Concen- tration	Δr (ang- stroms)	Langmuir correction factor	Apparent relative surface tension	Corrected relative surface tension
Reference water: ionic concentration 4.2×10^{-6} mole/liter				
Water	548	(1.000,00)	(1.000,00)	(1.000,00)
0.00005	0	1.000,40	0.999,85	1.000,25
0.00010	18	1.000,39	0.999,84	1.000,23
0.00025	0	1.000,40	0.999,81	1.000,21
0.00100	56	1.000,36	0.999,87	1.000,23
Reference water: ionic concentration 2.0×10^{-6} mole/liter				
Water	508	(1.000,00)	(1.000,00)	(1.000,00)
0.00005	0	1.000,37	0.999,85	1.000,22
0.00010	18	1.000,36	0.999,84	1.000,20
0.00025	0	1.000,37	0.999,81	1.000,18
0.00100	56	1.000,33	0.999,87	1.000,20
Reference water: ionic concentraotin 0.95×10^{-6} mole/liter				
Water	442	(1.000,00)	(1.000,00)	(1.000,00)
0.00005	0	1.000,32	0.999,85	1.000,17
0.00010	18	1.000,31	0.999,84	1.000,15
0.00025	0	1.000,32	0.999,81	1.000,13
0.00100	56	1.000,28	0.999,87	1.000,15

10^{-4} mole/liter. When the minimum potential in the film, at the air-solution interface, is larger than the zeta-potential, no film of any significant size can form according to Langmuir's theory. Any film which would form would be controlled by van der Waals' and other short range forces. Because of this consideration, the value of the wetting film is taken as zero for the 2.50×10^{-4} and the 5.0×10^{-5} mole/liter solutions as in both cases the ζ-potentials were less than the air-solution potentials. Table I is not completely filled out for these solutions since many of the entries were not required as no computations were made. Table I shows all of the necessary parameters used to evaluate Δr (the film thickness) as well as the computed values of Δr. Table II shows the "corrected surface tensions" when three samples of water with varying ionic concentrations are taken as having surface tension equal to unity. The minimum is eliminated in the case of lanathum chloride as predicted by Langmuir.

That no regularity in the corrected data is observed is not surprising. The corrected surface tensions have the following sources of error inherent in them: (a) the experimental error in determining the streaming potentials (used to compute the zeta-potentials); and (b) the unknown value of the ratio of the dielectric constant of the electric double layer to its viscosity which is necessary to convert streaming potential data to zeta-potentials. In case the potentials were as large as 80 millivolts, it is quite apparent from the graph that errors of these types might be quite insignificant. But such small potential values as are obtained experimentally make it possible that an error of from two to three millivolts (especially in the case of the 10^{-4} and 5×10^{-5} solutions) in the zeta-potential could make a difference of from 0 to 30

angstroms in the film thickness. This difference in turn would cause significant changes in the calculated "corrected surface tensions." Actually the zeta-potential is not reproducible to more than two or three millivolts. No significant error results from the mathematical approximations.

It seems apparent that the original capillary rise data of Jones and Ray can be interpreted without assuming that a minimum exists in the surface tension-concentration curve. In order to compare the corrected values with the theory one needs to know the zeta-potentials with a higher degree of accuracy. The curves given in Fig. 1 will still be valid, but points A and B will have different locations on the curves.

On the Non-Equilibrium Theory of Absolute Reaction Rates

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The ensemble of point masses representing reaction complexes in configuration space is treated as an ideal gas by methods of exact kinetic theory. Hydrodynamic equations for the mean motion of the ensemble are derived. The theory of compressible flow is used to show that under a very wide range of conditions, the energy distribution characteristic of the reactants in a chemical reaction is maintained in the reaction complex at least until it passes through the activated state.

THE current theory of reaction rates[1] is limited in its rigorous application to reversible reactions proceeding at dynamic equilibrium. Ever since its proposal, the theoretical applicability of this theory to irreversible reactions or to the rate of approach to equilibrium has been a subject of discussion.[2] Recently two attempts have been made to make more precise the limits of its applicability. Kramers[3] has extended the classical theory of Brownian motion to calculate, in terms of an empirical "friction factor," the rate at which point masses diffuse over a one-dimensional potential energy barrier under conditions that the mean flow is nearly zero, and the energy distribution of the masses consequently nearly that of equilibrium. This implies that the energy barrier is relatively high ($>20kT$). Eyring and Zwolinski[4] verify Kramer's general conclusions by a different type of calculation in which a specific rate of reaction is assigned to each quantum state of the reaction complex. Over-all rates are calculated for different sets of assumptions concerning the magnitudes of these specific reaction rates. Making spot checks supposed to cover the extremes likely to be encountered, they find that the non-equilibrium rate for a unimolecular reaction may deviate by no more than 20 percent from its equilibrium value, in general agreement with Kramer's estimates.

It is the purpose of this paper to present a third approach to the theory of the rate of an irreversible reaction which is not restricted to slow reactions and which leads to some immediate qualitative conclusions concerning the rate of approach to equilibrium.

We proceed from the view that a chemical reaction can be represented by the motion of a mass-point in the configuration space of the reacting complex. In the interests of clarity, we list the principle restrictions and assumptions which this involves:

1. We suppose the reaction complex to remain in the same electronic quantum state throughout its motion. Reactions involving excited reactants or products will need special consideration.

2. We suppose the point-mass to obey the classical Hamilton's equations of motion.

Previous considerations[5,6] have shown that, except possibly for reactions of atomic hydrogen and its isotopes, this assumption introduces no serious error as long as the rate of reaction must be averaged over a normal distribution of reactant energies.

When each possible reaction complex is represented by a point mass in configuration space, the macroscopic course of the reaction will be represented by a distribution of such point-masses with varying density in space and moving with varying velocities. For such a distribution it is possible to derive macroscopic differential equations governing the average density, average momentum and average energy of the fluid system. These are the hydrodynamic equations of the system. Chapman and Cowling[7] give the derivation for a real mon-

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