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Lloyd A. Wood and Lawrence B. Robinson

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A Test of Langmuir's Interpretation of the Jones-Ray Effect

LLOYD A. WOOD AND LAWRENCE B. ROBINSON

Department of Chemistry, Harvard University, Cambridge, Massachusetts

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Jones and Ray observed a minimum in the surface tension-concentration curve of electrolyte solutions at about 0.001*N*. Langmuir interpreted this as an instrumental effect rather than a real minimum, and advanced a quantitative theory by which the surface tension data could be corrected. To compute the Langmuir correction factor the zeta-potentials of vitreous silica in contact with the solutions measured by Jones and Ray in their capillarimeter are required. Since the zeta-potentials with barium chloride solutions have now been measured, the Langmuir theory has been tested to see whether it eliminated the minimum observed with this solute, and this paper presents the results of this test. It was found that Langmuir's interpretation was strikingly substantiated.

JONES and Ray¹ measured the capillary rise of water and of barium chloride solutions in their silica capillarimeter, and found, as with other electrolytes, that the first trace of added salt brought about an apparent decrease in the surface tension. The barium chloride surface tension-concentration curve appeared to have a minimum at about 0.0005 *M*, at which the surface tension was 99.982 percent of that of pure water. Langmuir² suggested that this minimum was not real but was the result of variation in the thickness of the wetting film on the capillary wall, and he advanced a quantitative theory by which the thickness could be calculated provided that the zeta-potential of the silica in contact with the various solutions was known. Jones and Frizzell³ have discussed the application of this theory to 1-1 electrolytes, and Jones and Wood⁴ made the first test of it with data on potassium chloride, in which it was found that application of the Langmuir correction eliminated the minimum. Another test⁵ was made with data on the same potassium chloride solutions but with 10⁻⁶ *M* thorium chloride added, but application of the correction only served to deepen the minimum. With the zeta-potential of silica in contact with various barium chloride solutions reported in the preceding paper, it is

possible to make another test of the Langmuir theory, and that is the purpose of this paper.

LANGMUIR'S METHOD FOR CALCULATING THE THICKNESS OF THE WETTING FILM APPLIED TO BARIUM CHLORIDE SOLUTIONS

The method by which Langmuir proposed that the wetting film thickness be calculated has been previously developed and applied^{2,3,5} to solutions of 1-1 electrolytes, but this treatment is not applicable directly to the barium chloride solutions. Therefore, the adaptation to this class of electrolytes is given below.

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

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

wherein ψ is the electrical potential, D is the dielectric constant of the solution, n_i is the number of ions per cc of species i , z_i is the charge on an ion of species i , and ϵ is the magnitude of the electronic charge. Integration of this equation yields

$$p^2 = [2A \sum_i n_i \exp(-z_i \eta)] + C, \quad (2)$$

wherein

$$\eta \equiv e\psi/kT, \quad 1/A \equiv \sum_i n_i z_i^2, \quad (3)$$

$$p \equiv d\eta/d\theta, \quad \theta \equiv \kappa x.$$

κ is the well-known Debye-Hückel parameter, and C is the constant of integration. The constant C is evaluated through use of the boundary condition that at the air surface, where $\theta = 0$,

¹ Grinnell Jones and W. A. Ray, *J. Am. Chem. Soc.* **63**, 288 (1941).

² I. Langmuir, *Science* **88**, 430 (1938); *J. Chem. Phys.* **6**, 894 (1938).

³ Grinnell Jones and L. D. Frizzell, *J. Chem. Phys.* **8**, 986 (1940).

⁴ Grinnell Jones and L. A. Wood, *J. Chem. Phys.* **13**, 106 (1945).

⁵ L. A. Wood, *J. Chem. Phys.* **13**, 429 (1945).

the potential is assumed to have its minimum magnitude ψ_m so that $\eta = m$ and $p = 0$. Thus

$$d\theta = d\eta / [2A \sum_i n_i \{ \exp(-z_i \eta) - \exp(-z_i m) \}]^{\frac{1}{2}} \quad (4)$$

Let

Ba⁺⁺ be species 1; $z_1 = +2$,
H⁺ be species 2; $z_2 = +1$,
Cl⁻ and OH⁻ be species 3; $z_3 = -1$.

Then substituting $K = \exp(m)$ and $y = \exp(\eta)$,

$$d\theta = \frac{dy}{y[2A(n_1 y^{-2} + n_2 y^{-1} + n_3 y - n_1 K^{-2} - n_2 K^{-1} - n_3 K)]^{\frac{1}{2}}} \quad (5)$$

Since $n_i = c_i N \times 10^{-3}$, where c_i is the molar concentration of species i and N is Avogadro's number, Eq. (5) becomes

$$d\theta = \frac{(3c_1 + c_2)^{\frac{1}{2}} dy}{[a_1 y^3 + a_2 y^2 + a_3 y + a_4]^{\frac{1}{2}}} \quad (6)$$

wherein

$$\begin{aligned} a_1 &\equiv c_3 = 2c_1 + c_2; \\ a_2 &\equiv -[c_1 K^{-2} + c_2 K^{-1} + (c_2 + 2c_1)K]; \\ a_3 &\equiv c_2; \quad a_4 \equiv c_1. \end{aligned} \quad (7)$$

The constant m introduced into Eq. (4) must be evaluated, so that K and a_2 may be known. According to Langmuir, if the film is thick enough so that van der Waals and other short range forces may be neglected, there are then the following three forces in equilibrium at the air surface of the film: (1) the pressure $-(d-\beta)hg$, owing to the pull of gravity, which tends to make the film thinner (d is the density of the solution; β , the density of air; h , the height above the surface of the main body of the liquid; and g , the acceleration of gravity); (2) the pressure $(d-\beta)hg/2$, resulting from the surface tension of the cylindrical surface which tends to make the film thicker; and (3) the difference between the osmotic pressure in the bulk solution and in the air interface of the wetting film. From van't Hoff's simple law and the Maxwell-Boltzmann equation, this difference in osmotic pressure is

$$\sum_i n_i kT(K^{-z_i} - 1)$$

tending to make the film thicker. At equilibrium, the sum of these pressures is zero, and therefore:

$$\sum_i n_i kT(K^{-z_i} - 1) - (d-\beta)hg/2 = 0. \quad (8)$$

Substituting $n_i = c_i N \times 10^{-3}$:

$$\begin{aligned} c_1 K^{-2} + c_2 K^{-1} + (c_2 + 2c_1)K \\ = \frac{500(d-\beta)hg}{NkT} + 3c_1 + 2c_2 = -a_2. \end{aligned} \quad (9)$$

This equation may be solved for K to give the value of ψ_m . Because the potentials to be considered are negative and m is therefore negative, and since $K = e^m$, the root of Eq. (9) between 0 and +1 is the only possible value of K .

The thickness of the wetting film, Δr , is given by

$$\kappa \cdot \Delta r = \int_{y_0}^{y_1} d\theta = (3c_1 + c_2)^{\frac{1}{2}} \int_{y_0}^{y_1} \frac{dy}{Q^{\frac{1}{2}}}, \quad (10)$$

wherein $Q = a_1 y^3 + a_2 y^2 + a_3 y + a_4$, $y_0 = K$, and y_1 is the value of y at the solid surface where $\psi = \zeta$. For numerical evaluation of Δr , Eq. (10) must be transformed into the Legendrian form of an elliptic integral. Let Q be factored such that $e_1 > e_2 > e_3$:⁶

$$Q = a_1(y - e_1)(y - e_2)(y - e_3). \quad (11)$$

Substituting

$$y = (p + qt)/(1 + t),$$

wherein

$$\begin{aligned} p &= e_1 + ((e_1 - e_2)(e_1 - e_3))^{\frac{1}{2}}, \\ q &= e_1 - ((e_1 - e_2)(e_1 - e_3))^{\frac{1}{2}}; \end{aligned}$$

then

$$\Delta r = -M \int_{t_0}^{t_1} \frac{dt}{[(t^2 - 1)(t^2 - b^2)]^{\frac{1}{2}}}, \quad (12)$$

wherein

$$\begin{aligned} b^2 &\equiv -\frac{(p - e_2)(p - e_3)}{(q - e_2)(q - e_3)}, \\ M &\equiv \frac{(p - q)}{\kappa} \left[\frac{3c_1 + c_2}{a_1(q - e_1)(q - e_2)(q - e_3)} \right]^{\frac{1}{2}}. \end{aligned}$$

Substituting $\sin \phi = b/t$, $\sin \alpha = 1/b$,

$$\begin{aligned} \Delta r &= (M/b) \int_{\phi_0}^{\phi_1} \frac{d\phi}{[1 - \sin^2 \alpha \sin^2 \phi]^{\frac{1}{2}}}, \\ &= -(M/b)[F(\alpha, \phi_0) - F(\alpha, \phi_1)], \end{aligned} \quad (13)$$

wherein $F(\alpha, \phi)$ denotes an elliptic integral of the first kind. Although it is not immediately apparent, it is true that $\phi_0 = \pi/2$. Thus

$$\Delta r = -(M/b)[F(\alpha, \pi/2) - F(\alpha, \phi_1)], \quad (14)$$

⁶ e_1, e_2, e_3 are numerically equal to the roots of Eq. (9), and $e_2 = K$ for the systems to be considered.

TABLE I. Calculation of wetting film thicknesses.

c	0.0025	0.001	0.0005	0.0001
e_1	1.1895	1.3200	1.4880	2.4840
$e_2(=K)$	0.84865	0.77546	0.70345	0.49077
e_3	-0.49522	-0.48824	-0.47721	-0.40810
m	-0.16411	-0.25430	-0.35175	-0.71177
b	2.6349	3.4321	4.4322	10.7772
α	22.304°	16.939°	13.039°	5.324°
$\psi_m(\text{mv})$	-4.21	-6.53	-9.03	-18.28
$\zeta(\text{mv})$ (experimental)	-35	-34	-55	-70
y_1	0.25596	0.26612	0.11749	0.065517
t_1	-9.6622	-33.226	-20.277	-275.05
$\sin \phi_1$	-0.27384	-0.10330	-0.21859	-0.039182
ϕ_1	-15.893°	-5.929°	-12.626°	-2.242°
$F(\alpha, \pi/2) - F(\alpha, \phi_1)$	1.9103	1.7093	1.8118	1.6129
$1/\kappa(\times 10^8)$	35.13	55.54	78.54	175.4
$M(\text{\AA})$	120.5	224.2	372.7	1487
$\Delta r(\text{\AA})$	87	112	152	223

and the integral is now in a form suitable for computation. In some instances the angle ϕ_1 is negative, and it should be noted that

$$F(\alpha, -\phi_1) = -F(\alpha, \phi_1).$$

The negative sign of Δr is a result of the fact that the potential is negative. This means that although $|\zeta| > |\psi_m|$, $\zeta < \psi_m$, so that the integration must be regarded as performed in the negative direction.

COMPUTATION OF Δr

The surface tensions of the 2.5×10^{-3} , 1×10^{-3} , 5×10^{-4} , and $1 \times 10^{-4} M$ BaCl_2 solutions were measured by Jones and Ray,¹ and with the reliable values of the zeta-potentials reported in the preceding paper, their surface tension data can be corrected in accordance with Langmuir's suggestion. The Langmuir correction requires the thickness of the wetting film at the meniscus in the capillary of the surface tension capillimeter. The capillary radius was 0.0136 cm, and the meniscus was 10.862 cm above the surface of the main body of the liquid. In Table I is given an outline with numerical values of the computation of Δr . With each solution it was assumed, although the effect was negligible, that the concentration of the ions from the water was $1 \times 10^{-6} M$. The values for the fundamental physical constants are those of Birge;⁷ the other required data are found in the paper of Jones and Ray.¹ The experimental values of the zeta-potential were used, rather than those given by

a smoothed curve. The ψ_m values are given to show that the condition is fulfilled that these are the minimum values, being in each instance less than the zeta-potential (in absolute value). In Fig. 1 is shown the variation of Δr with different values of the zeta-potential. It is evident that had smoothed values for the zeta-potentials been used, the Δr 's then obtained would have differed at most by 5 angstroms from the values in Table I.

THE REFERENCE LIQUID

The differential method of Jones and Ray yields the surface tension values which are relative to the surface tension of the reference liquid, water, and this observed surface tension is called the "apparent relative surface tension." The "corrected relative surface tension" is obtained by multiplying the apparent relative surface tension by the Langmuir correction factor, $(r - \Delta r_c)/(r - \Delta r_0)$, wherein Δr_c is the wetting film thickness of a solution at the meniscus in the capillary, and Δr_0 is the wetting film thickness with the reference water. According to Langmuir, because the value of Δr_0 depends on the concentration of ions in the reference water, it seems probable that the wetting film thickness with water should have varied somewhat with the purity of the water. However, Jones and Frizzell found that there was no variation in capillary rise with various samples of water with specific conductivities from 0.37×10^{-6} to 1.67×10^{-6} . If the equivalent conductances of the ions in the water (presumably H^+ , HCO_3^- , OH^-) are assumed to total about 400, this range corresponds

⁷ R. T. Birge, Rev. Mod. Phys. **13**, 233 (1941); Am. J. Phys. **13**, 63 (1945).

to a variation in concentration of 0.9×10^{-6} to $4.2 \times 10^{-6} M$. Actually Jones and Frizzell⁸ gave a value for the capillary rise of the $0.9 \times 10^{-6} M$ water which was 0.003 percent lower than that of the less pure samples, but they apparently did not consider this a significant difference, the probable error having been about the same magnitude. Since the work of Jones and Frizzell, it has been learned that the zeta-potential of vitreous silica in contact with water of $\kappa = 0.2 \times 10^{-6}$ to 0.4×10^{-6} is about -177 millivolt.⁹ With this knowledge it is possible to reexamine the question of whether the Langmuir theory would predict a variation for these samples of water. Although it is improbable that the zeta-potential is -177 millivolt over the entire range, it is not likely that the variation is large, since it has been shown that the addition of $10^{-5} M$ KCl lowers it only to -148 millivolt. It seems justifiable to assume a value of -177 millivolt over this range as an approximation.

On this basis the wetting film corrections for the surface tension data of Jones and Frizzell have been calculated as a function of the ion concentration of the water. In Table II are given the wetting film corrections for four different samples of water, including three samples measured by Jones and Frizzell, and a fourth of lower ion concentration than those. The Langmuir correction is given with reference

TABLE II. Wetting film thicknesses and surface tensions for various water samples.

c	$\Delta r(A)$	Langmuir correction	Apparent relative s.t.	Corrected relative s.t.
0.54×10^{-6}	366	1.000,11	^a	
0.95×10^{-6}	442	1.000,05	0.999,97 ^c	1.000,02
2×10^{-6}	508	(1.000,000 ^b)	(1.000,000)	(1.000,000)
4.2×10^{-6}	543	0.999,97	1.000,00	0.999,97

^a Surface tension not available for this sample.

^b This sample is considered the reference liquid for the purposes of these calculations. Had any other sample been chosen as reference, the same relative values would have been held by all the numbers.

^c It has been considered preferable to take this value literally from Table VI of Jones and Frizzell (reference 5) and to reserve considerations of significance for the "corrected relative surface tensions."

to the $2 \times 10^{-6} M$ water. It is evident that the 0.003 percent difference given by Jones and Frizzell is in the direction predicted by the Langmuir theory, whether or not any significance

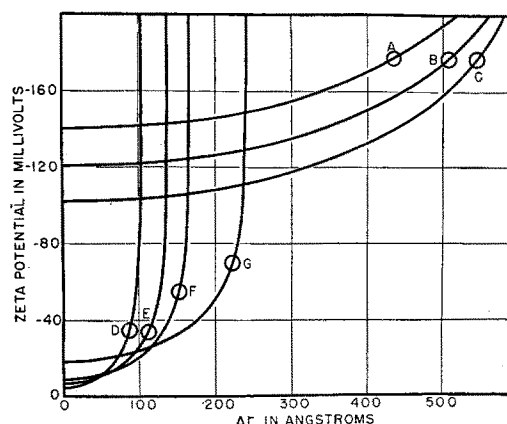


FIG. 1. Variation of the wetting film thickness in the Jones-Ray capillarmeter as a function of the zeta-potentials.

Water: A: $c = 0.95 \times 10^{-6}$; B: $c = 2 \times 10^{-6}$; C: $c = 4.2 \times 10^{-6}$.
Barium chloride solutions: D: $c = 0.0025$; E: $c = 0.001$;
F: $c = 0.0005$; G: $c = 0.0001$.

may be attached to it. From the column of "corrected relative surface tensions" it may be concluded that no significant variation should have been observed by Jones and Frizzell with the various water samples measured. It is also evident that had they measured water of the lowest ion concentration given, they would have detected a significant variation as a result of the wetting film, according to the Langmuir theory, because the correction factor is large enough to indicate that there should have been an observable difference, 0.011 percent, easily detectable within the precision of their method, in the apparent relative surface tensions. These arguments are of course all based upon the predicate that the true surface tension of the various samples of water is the same. It may be pointed out that if the zeta-potential decreases somewhat with increasing concentration, as it probably does, the evidence becomes still more favorable to the Langmuir theory, because the Δr 's would then be somewhat smaller for the 2×10^{-6} and $4.2 \times 10^{-6} M$ samples. It is apparent from these considerations that the observations of Jones and Frizzell with the various water samples do not offer any contradiction to the Langmuir theory. It is also apparent that the choice of the reference water with which to compare the BaCl_2 surface tensions does not matter greatly, provided it is chosen from the range measured by Jones and Frizzell.

⁸ See Table VI, p. 996 in reference 3.

⁹ L. A. Wood, J. Am. Chem. Soc. 68, 437 (1946).

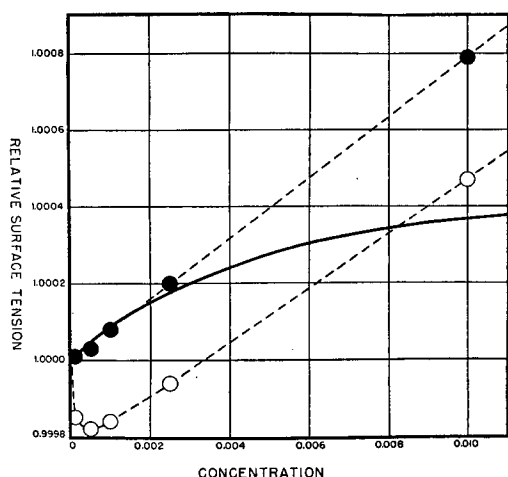


FIG. 2. Apparent and corrected relative surface tensions. Open circles are the measurements of Jones and Ray. Solid circles are the same measurements after application of the Langmuir correction. Solid line is given by the limiting law of Onsager and Samaras.

APPLICATION OF THE LANGMUIR CORRECTION TO THE BaCl_2 SURFACE TENSIONS

Whether or not it is proper to place much weight on the above considerations as a test of the Langmuir theory, a far more impressive substantiation can be observed with the barium chloride data. In Table III are given the corrected relative surface tensions of the barium chloride solutions with reference to the three samples of water. Since the Langmuir correction factor depends on the wetting film thickness for the reference water, the magnitudes of the factors are slightly different, depending on which Δr_0 is used. It is assumed in accord with the observations of Jones and Frizzell that the values for the observed apparent relative surface tensions are independent of the reference water, provided it is within the range discussed. It is clear from Table III that application of the Langmuir correction serves to eliminate the minimum from the surface tension curve no matter which reference Δr_0 is used. The effect of the Langmuir correction is shown graphically in Fig. 2, wherein the dashed curve with open circles represents the observed apparent relative surface tensions, and the dashed line with solid circles represents the corrected relative surface tensions with reference to the $0.95 \times 10^{-6} M$ water. The radius of each circle is 0.001 percent, and it is seen that

the corrected surface tensions fall almost exactly on a straight line. Had the corrected surface tensions with reference to the other water samples been plotted, the corresponding points for each concentration would have been 0.000,05 and 0.000,08 units above the given ones, for the 2×10^{-6} and $4.2 \times 10^{-6} M$ samples, respectively. For the general interest, the relative surface tensions of these solutions have been computed according to the limiting law of Onsager and Samaras¹⁰ and are given by the solid line. In these computations, the distance of approach of the ions was neglected, but the Y_c and Y_f series of Onsager and Samaras were evaluated to enough terms so that no approximation was introduced from that source. It may be observed that the limiting law curve appears to approach tangentially the line described by the corrected surface tensions. It is thus apparent that the Langmuir correction not only eliminates the

TABLE III. Corrected surface tensions for BaCl_2 solutions.

Conc.	Δr (angstroms)	Correction factor	Apparent relative s.t.	Corrected relative s.t.
Reference water: $4.2 \times 10^{-6} M$				
Water	548	(1.000,00)	(1.000,00)	(1.000,00)
0.0001	223	1.000,24	0.999,85	1.000,09
0.0005	152	1.000,29	0.999,82	1.000,11
0.0010	112	1.000,32	0.999,84	1.000,16
0.0025	87	1.000,34	0.999,94	1.000,28
0.0100	0	1.000,40	1.000,47	1.000,87
Reference water: $2.0 \times 10^{-6} M$				
Water	508	(1.000,00)	(1.000,00)	(1.000,00)
0.0001	223	1.000,21	0.999,85	1.000,06
0.0005	152	1.000,26	0.999,82	1.000,08
0.0010	112	1.000,29	0.999,84	1.000,13
0.0025	87	1.000,31	0.999,94	1.000,25
0.0100	0	1.000,37	1.000,47	1.000,84
Reference water: $0.95 \times 10^{-6} M$				
Water	442	(1.000,00)	(1.000,00)	(1.000,00)
0.0001	223	1.000,16	0.999,85	1.000,01
0.0005	152	1.000,21	0.999,82	1.000,03
0.0010	112	1.000,24	0.999,84	1.000,08
0.0025	87	1.000,26	0.999,94	1.000,20
0.0100	0	1.000,32	1.000,47	1.000,79

minimum in the surface tension curve, but yields surface tensions which approach infinite dilution with a slope in agreement with the limiting law of Onsager and Samaras.

¹⁰ L. Onsager and N. N. T. Samaras, J. Chem. Phys. 2, 528 (1934).