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The Surface Tension of Debye-Hückel Electrolytes

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As has been shown by Wagner, the increase of the surface tension caused by the addition of a strong electrolyte to water is mainly due to the repulsion of ions from the surface by the electrostatic image force. Due to the shielding action of the "ionic atmospheres," of radius $1/\kappa$, the image force is appreciable only within distances of the order $1/\kappa$ from the surface. The computations become very complicated if, as Wagner did, one attempts to allow for the variation of κ with the depth in accordance with the decreased concentration of ions in the surface layers. Fortunately, a detailed analysis of the problem shows that this refinement may be dispensed with as a first approximation, and that the formulas thus derived will be accurate for not too high concentrations. The same analysis tends to show that Wagner's procedure supplies only a part of

the intended correction, so that the results will be applicable only over a slightly wider range of concentrations than the convenient explicit formulas which are derived from the simplified theory. In the limit of low concentrations, the increment of the surface tension is proportional to $c \log c$. The theory accounts reasonably well for the observed surface tensions up to 0.2 *N* concentration. The discrepancies, while partly due to mathematical approximations, may be of some physical significance and would mean that for small distances the repulsion from the surface is greater than expected from Coulomb's law. Nevertheless, the agreement obtained verifies Coulomb's law for univalent ions at distances greater than a molecular diameter from the surface.

INTRODUCTION

IT was first shown by Heydweiller and his co-workers¹ that the solutions of inorganic salts in water have greater surface tensions than that of the pure solvent. Thermodynamically interpreted, this result indicates a deficiency of solute in the interface region. Since different uni-univalent salts, added in equivalent amounts, cause about the same increment of the surface tension, the effect is apparently determined by the charges of the ions. Heydweiller sought an explanation in the electrostatic attraction between the ions. However, after Debye and Hückel had provided a workable basis for the computation of interionic forces, Wagner² was able to show that the principal effect is due to the "image force" near the boundary between two dielectrics, e.g., water and air. In this picture, the "ionic atmospheres" of Debye and Hückel are called upon to limit the depth of the layer in which the ions are repelled from the surface.

The mathematical problems involved are very difficult. Wagner was able to formulate differential equations comparable in accuracy to the

approximation of Debye and Hückel. After a further simplifying approximation, Wagner obtained by integration an implicit formula for the adsorption potential. From this stage, he had to proceed by laborious numerical integrations in order to compute the deficiency of solute in the interface region, and finally the surface tension.

In the present work, we shall not attempt to improve the accuracy of Wagner's computations. Instead, we shall adopt a further simplification which we believe not to impair greatly the accuracy, and which leads to explicit formulas that can be easily handled. Our main result is the following limiting law for the surface tension:

$$\sigma = \sigma_0 + \text{const.} \times c \log (\text{const.}/c). \quad (1)$$

Like Wagner, we shall limit ourselves to binary electrolytes, although our computations can be extended without much difficulty to asymmetric valence types as well.

THE STRUCTURE OF THE INTERFACE LAYER

According to general kinetic principles, the concentration $c(x)$ of solute at a distance x from the boundary depends on the work $W(x)$ required to bring a molecule of the solute—or an ion, as the case may be—from the interior of the solution to a point at the depth x . The connection between $c(x)$ and the *adsorption potential* $W(x)$

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¹ Heydweiller, *Ann. d. Physik* (4) **33**, 145 (1910).

² Wagner, *Phys. Zeits.* **25**, 474 (1924).

is given by the Maxwell-Boltzmann formula

$$c(x) = c \exp(-W(x)/kT), \quad (2)$$

where $c = c(\infty)$ denotes the concentration in the interior. In the case of an electrolyte, every species i of ions should be considered as a separate kind of molecule, which may possess its individual adsorption potential $W_i(x)$. Only for binary electrolytes, the adsorption potentials $W_1(x)$ and $W_2(x)$ of anions and cations are apt to be very nearly equal.

We now proceed to compute $W(x)$ from Wagner's picture. First, let us consider a single ion of charge e , in a medium of dielectric constant D , at a distance x from a plane boundary against another medium of dielectric constant $D' = 1$ (air). The electrostatic potential ψ in the medium containing the ion will be

$$\psi = \frac{e}{Dr_1} + \frac{(D-1)}{(D+1)} \frac{e}{Dr_2}, \quad (3)$$

where r_1 denotes the distance from the ion, and r_2 the distance from its image with regard to the boundary (see Fig. 1). The second term in (3) is due to the fictitious charge at the boundary, which exerts the force

$$-\frac{\partial W}{\partial x} = \left[\frac{(D-1)}{(D+1)} \frac{e^2}{Dr_2^2} \right]_{r_2=2x} = \frac{(D-1)}{(D+1)} \frac{e^2}{4Dx^2}$$

on the ion. The potential of this force equals

$$W(x) = \frac{(D-D')}{(D+D')} \frac{e^2}{4Dx} = \frac{(D-1)}{(D+1)} \frac{e^2}{4Dx}. \quad (4)$$

As pointed out by Wagner, an adsorption potential of the type (4) would cause an infinite increment of the surface tension, because the adsorbed amount would be

$$\Lambda = c \int_{-\infty}^{\infty} (-1 + e^{-W/kT}) dx = -\infty.$$

The paradox readily resolves itself when we take into account the screening of the electrostatic force by the other ions. According to the theory developed by Gouy and by Debye and Hückel,³ the screening by an electrolytic conductor limits

³ Gouy, J. de Physique (4) 9, 457 (1910); Debye and Hückel, Phys. Zeits. 24, 185 (1923).

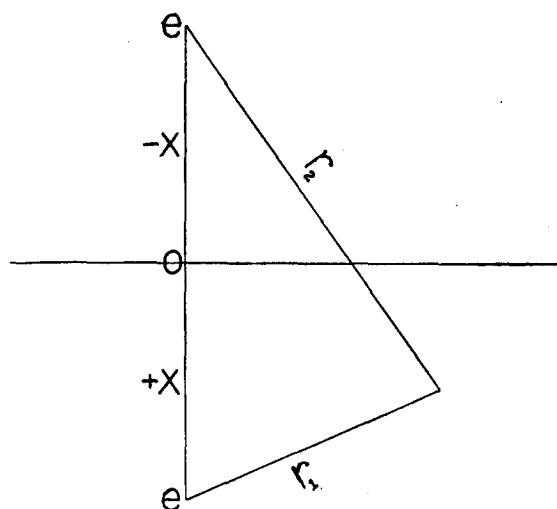


FIG. 1. Diagram for computing the electrostatic potential due to a point charge e and its image $[(D-1)/(D+1)]e \sim e$.

the effective range of electrostatic forces to a distance $1/\kappa$, where

$$\kappa^2 = (4\pi/DkT) \sum_i n_i e_i^2. \quad (5)$$

Here, n_1, n_2, \dots denote the numbers of ions with the charges e_1, e_2, \dots per unit volume. Instead of the Laplace equation

$$\Delta\psi = 0,$$

the electrostatic potential obeys the differential equation⁴

$$\Delta\psi - \kappa^2\psi = 0. \quad (6)$$

We must now remember that the concentration of electrolyte near the surface is less than that in the interior of the solution. In Eq. (6), therefore, the value of κ^2 at a given point depends on the distance ξ from the surface to this point according to Eqs. (5) and (2). In cylindrical coordinates (ξ, λ) we should write

$$\Delta\psi = \frac{\partial^2\psi}{\partial\xi^2} + \frac{1}{\lambda} \frac{\partial}{\partial\lambda} \left(\lambda \frac{\partial\psi}{\partial\lambda} \right) = \kappa^2(\xi)\psi. \quad (7)$$

We face the task of solving this equation for the case that an ion of charge e is present at the point $(\xi = x, \lambda = 0)$. For $\xi > 0$, $\kappa^2(\xi)$ is given by Eqs. (5) and (2), while for $\xi < 0$, $\kappa^2(\xi) = 0$. At the boundary $\xi = 0$, ψ is continuous and $\partial\psi/\partial\xi$ changes by the factor D .

⁴ Regarding the approximate nature of this equation, see Onsager, Chem. Rev. 13, 73 (1933).

In order to obtain an approximate solution of this problem, Wagner replaced the dielectric constant $D'=1$ of the adjoining air by

$$D'=0. \quad (8)$$

It can be shown that the relative error in W due to this approximation is less than $2/(D+1)$. If desired, the corrections to W due to the finite value of D' can be computed by expansion in integrals of cylinder functions.

Wagner made one more approximation, which served to remedy the most inconvenient feature of Eq. (7), that is the variation of κ^2 with ξ . For this purpose, he replaced $\kappa^2(\xi)$ throughout by $\kappa^2(x)$. The resulting approximate equation can be readily integrated, but leads to an implicit equation for $W(x)$. Substantially simpler results can be obtained by the more drastic approximation⁵

$$\kappa^2(\xi) \sim \kappa^2(\infty) = \kappa^2. \quad (9)$$

Let us try to estimate the errors involved by the two approximations. First, we note that Eq. (4), where the shielding is entirely neglected, must give us an overestimate of W , and therefore an underestimate of $\kappa^2(\xi)$. It makes no important difference if we adopt Wagner's first approximation $D'=0$, whereby Eq. (4) becomes

$$W(x) = e^2/4Dx.$$

We shall write

$$q = e^2/2DkT. \quad (10)$$

For univalent ions in water, the length q equals 3.5×10^{-8} cm. If the concentration of the electrolyte in the interior is c , then at a distance ξ from the surface it will be at least

$$c \exp(-q/2\xi) \leq c(\xi). \quad (11)$$

Therefore, as soon as $\xi \geq q$, $\kappa^2(\xi)$ is certainly comparable to $\kappa^2(\infty)$. It also follows that, if

$$\kappa q < 1,$$

the shielding range near the surface will be of the same order of magnitude as that in the interior of the solution. In conjunction with Eq. (11), this observation provides a basis for estimating the

total deficiency ($-\Lambda$) of electrolyte per unit surface area. On account of the shielding, we need only consider a layer of the depth m/κ , where m is some constant comparable to unity. For $x < m/\kappa$, we apply the estimate (11), and obtain

$$-\Lambda \sim c \int_0^{m/\kappa} [1 - \exp(-q/2x)] dx \\ \sim \frac{1}{2}cq \log(m/\kappa q).$$

This deficiency is equivalent to a layer of the thickness

$$\delta \sim \frac{1}{2}q \log(m/\kappa q), \quad (12)$$

entirely depleted of solute. With very little actual computation, we have thus, in effect, demonstrated the general form of the limiting law (1) for low concentrations. It is important that although δ increases logarithmically when κq approaches zero, still δ increases much less rapidly than $1/\kappa$, so that

$$\kappa\delta \ll 1 \quad \text{when} \quad \kappa q \ll 1. \quad (13)$$

We now have to consider how the decreased concentration of electrolyte near the surface will affect the shielding of the electrostatic force between an ion and its image. An exact solution of the problem is very difficult; but it can be shown that the shielding depends mainly on the concentrations in the layers between the ion and the surface. In case of a constant "shielding coefficient" κ , the absorption of the force-lines introduces a factor

$$\exp(-\kappa r)$$

in the potential of a point source. An ion at the distance x from the surface is at the distance $2x$ from its image, so that the corresponding shielding factor would be

$$\exp(-2\kappa x). \quad (14)$$

Now if a layer of the thickness δ contributes nothing to the shielding, then the exponent in Eq. (14) will be changed (at the worst) to $2(x-\delta)\kappa$; so that the relative error involved by the approximation (9) is not greater than

$$e^{2\kappa\delta} - 1 \sim 2\kappa\delta \sim \Delta\Lambda/\Lambda. \quad (15)$$

We have shown already (formulas (12) and (13)) that an error of this order of magnitude may be neglected for sufficiently low concentrations of electrolyte.

⁵ Oka (Proc. Phys.-Math. Soc. Japan 14, 649 (1932); ibid. 15, 407 (1933)) adopted this equation as a starting point for his computation. Due to an oversight on his part, he obtained twice our value for the adsorption potential.

This analysis throws light on Wagner's approximation as well. In his computation he replaces $\kappa^2(\xi)$ throughout by $\kappa^2(x)$. It seems probable that this approximation still involves an overestimate of the "effective" κ , considering that the shielding is mainly effected by the region $0 < \xi < x$, where $c(\xi) < c(x)$. We therefore believe that Wagner's error, although smaller than ours, is still of the same order of magnitude, given by (15), and in the same direction. Both computations lead to overestimates of κ , with consequent underestimates of W , Λ , and finally of the increment of the surface tension. Both computations are correct in the limit of low concentrations.

We now compute the adsorption potential with the aid of the approximations

$$D' = 0, \quad \kappa^2(\xi) = \kappa^2(\infty) = \kappa^2.$$

With these assumptions, and for the case of point ions with charges e , e present at $(\xi = x, \lambda = 0)$ and $(\xi = -x, \lambda = 0)$, the solution of the differential Eq. (6),

$$\Delta\psi - \kappa^2\psi = 0,$$

assumes the simple form

$$\psi = ee^{-\kappa r_1}/Dr_1 + ee^{-\kappa r_2}/Dr_2. \quad (16)$$

Here, ψ is the electrostatic potential in the medium containing the ion, and the second term arises from the fictitious surface charge, which exerts the force

$$-\frac{\partial W}{\partial x} = -\frac{\partial}{\partial r_2} \left(\frac{e^2 e^{-\kappa r_2}}{Dr_2} \right)_{r_2=2x} = -\frac{\partial}{\partial x} \left(\frac{e^2 e^{-2\kappa x}}{4Dx} \right)$$

on the ion. Consequently, the adsorption potential $W(x)$ is

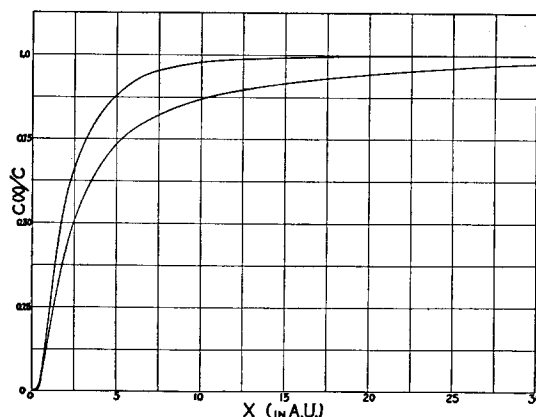


FIG. 2. Density distribution in the interface region for uni-univalent electrolytes. The concentrations are 0.1 mol./l. (upper curve) and 0.001 mol./l.

$$W(x) = \int_{\infty}^x \frac{\partial W}{\partial x} dx = \frac{e^2 e^{-2\kappa x}}{4Dx}. \quad (17)$$

Combining expressions (2) and (17) we obtain

$$c(x)/c = e^{-e^2 e^{-2\kappa x}/4DkTx} = e^{-qe^{-2\kappa x}/2x}. \quad (18)$$

This density distribution is shown in Fig. 2, for uni-univalent electrolytes and for concentrations of 0.1 (upper curve) and 0.001 mol./l.; the corresponding values of the shielding range $1/\kappa$ are 10A and 100A, respectively.

If we consider the size of the ions as well, and introduce the Debye-Hückel "mean distance of approach" a which we may take, with Wagner, as small compared to x , formula (17) is modified as follows:

$$W(x) = \frac{e^{\kappa a}}{1 + \kappa a} \frac{e^2}{4Dx} e^{-2\kappa x}. \quad (19)$$

COMPUTATION OF THE SURFACE TENSION INCREASE

The total amount "negatively" adsorbed per unit change in surface area is thus given by

$$\Lambda = c \int_0^{\infty} (e^{-(e\kappa a/(1+\kappa a)) (e^2/4DkTx)} e^{-2\kappa x} - 1) dx. \quad (20)$$

If, for convenience, we substitute

$$q = e^2/2DkT; \quad h = [e^{\kappa a}/(1+\kappa a)]\kappa q; \quad u = 2\kappa x, \quad (21)$$

expression (20) becomes

$$\Lambda = (c/2\kappa) \int_0^\infty (e^{-he^{-u}/u} - 1) du = (c/2\kappa) I. \quad (22)$$

First, we proceed to evaluate I by integration in the complex plane.⁶ Let $z = -u$; then,

$$I = \int_{-\infty}^{-0} (e^{he^z/z} - 1) dz. \quad (23)$$

Consider the integral

$$\Phi = (1/2\pi i) \int_{-\infty}^{(0+)} (e^{he^z/z} - 1) (e^z/z)^\beta dz, \quad (24)$$

where $-1 < \beta < 1$, and $|\arg(z)| \leq \pi$; the path of integration runs from $-\infty$ counterclockwise around the origin and back to $-\infty$. In analogy with Hankel's treatment of the gamma function,⁷ the contour integral (24) may be broken up as follows:

$$\begin{aligned} \Phi = (1/2\pi i) \int_{-\infty}^{-0} (e^{he^z/z} - 1) e^{\beta z} \{ (-z)^{-\beta} e^{\pi i \beta} - (-z)^{-\beta} e^{-\pi i \beta} \} dz \\ + (1/2\pi i) \int_{-0}^{(0+)} (e^{he^z/z} - 1) e^{\beta z} z^{-\beta} dz = \Phi_1 + \Phi_2. \end{aligned} \quad (25)$$

Since

$$\Phi_1 = (\sin \pi \beta / \pi) \int_{-\infty}^{-0} (e^{he^z/z} - 1) e^{\beta z} (-z)^{-\beta} dz,$$

it can be easily seen that

$$\left[\frac{\partial \Phi_1(\beta)}{\partial \beta} \right]_{\beta=0} = \lim_{\beta \rightarrow 0} \frac{1}{\beta} \Phi_1(\beta) = \int_{-\infty}^{-0} (e^{he^z/z} - 1) dz = I, \quad \text{or} \quad I = \lim_{\beta \rightarrow 0} \frac{1}{\beta} (\Phi - \Phi_2) = \left[\frac{\partial}{\partial \beta} (\Phi - \Phi_2) \right]_{\beta=0} \quad (26)$$

Now, with the aid of Hankel's formula⁷ for the gamma function,

$$\begin{aligned} \Phi &= (1/2\pi i) \int_{-\infty}^{(0+)} (e^{he^z/z} - 1) (e^z/z)^\beta dz \\ &= \sum_{n=1}^{\infty} \frac{h^n (n+\beta)^{n+\beta-1}}{n!} \cdot \frac{1}{2\pi i} \int_{-\infty}^{(0+)} e^{z(n+\beta)} (z(n+\beta))^{-(n+\beta)} dz (z(n+\beta)) \\ &= \sum_{n=1}^{\infty} \frac{h^n (n+\beta)^{n+\beta-1}}{n! \Gamma(n+\beta)} = \sum_{n=1}^{\infty} \frac{h^n (n+\beta)^{n+\beta}}{n! \Gamma(n+\beta+1)}. \end{aligned} \quad (27)$$

To handle the integral

$$\Phi_2 = (1/2\pi i) \int_{-0}^{(0+)} (e^{he^z/z} - 1) e^{\beta z} z^{-\beta} dz$$

we may substitute $e^z/z = 1/t$, and by Lagrange's theorem⁸ expand z in the following power series in t :

$$z = \sum_{n=1}^{\infty} (n^{n-1}/n!) t^n.$$

⁶ This integration can also be carried out by expanding in modified Bessel functions of the second kind—a more laborious method.

⁷ Whittaker and Watson, *A Course of Modern Analysis*, p. 244, §12.22, Cambridge University Press, 1927.

⁸ Whittaker and Watson, reference 7, p. 132, §7.32.

By common criteria, the expansion is valid within the circle of convergence, $|t| \leq e^{-1}$. Hence,

$$\Phi_2 = \sum_{n=1}^{\infty} \frac{n^n}{n!} \frac{1}{2\pi i} \int_{-\infty}^{(0+)} (e^{h/t} - 1) t^{n-\beta-1} dt$$

or, taking $1/t = v$,

$$\begin{aligned} \Phi_2 &= \sum_{n=1}^{\infty} \frac{n^n}{n!} \frac{1}{2\pi i} \int_{-\infty}^{(0-)} (e^{hv} - 1) v^{\beta-n-1} (-dv) = \sum_{n=1}^{\infty} \frac{n^n h^{n-\beta}}{n!} \frac{1}{2\pi i} \int_{-\infty}^{(0+)} (e^{hv} - 1) (hv)^{\beta-n-1} d(hv) \\ &= \sum_{n=1}^{\infty} \frac{n^n h^{n-\beta}}{n!} \frac{1}{2\pi i} \int_{-\infty}^{(0+)} e^{hv} (hv)^{\beta-n-1} d(hv) = \sum_{n=1}^{\infty} \frac{n^n h^{n-\beta}}{n! \Gamma(n-\beta+1)}. \end{aligned} \quad (28)$$

From Eqs. (27) and (28)

$$\left(\frac{\partial \Phi}{\partial \beta} \right)_{\beta=0} = \sum_{n=1}^{\infty} \frac{h^n}{n!} \frac{\partial}{\partial n} \left(\frac{n^n}{\Gamma(n+1)} \right); \quad \left(\frac{\partial \Phi_2}{\partial \beta} \right)_{\beta=0} = - \sum_{n=1}^{\infty} \frac{n^n}{n!} \frac{\partial}{\partial n} \left(\frac{h^n}{\Gamma(n+1)} \right).$$

Therefore, expression (26) gives

$$\begin{aligned} \int_0^{\infty} (e^{-h e^{-u/u}} - 1) du &= I = \lim_{\beta \rightarrow 0} \frac{1}{\beta} (\Phi - \Phi_2) = \sum_{n=1}^{\infty} \left\{ \frac{h^n}{\Gamma(n+1)} \frac{\partial}{\partial n} \left(\frac{n^n}{\Gamma(n+1)} \right) + \frac{n^n}{\Gamma(n+1)} \frac{\partial}{\partial n} \left(\frac{h^n}{\Gamma(n+1)} \right) \right\} \\ &= \sum_{n=1}^{\infty} \frac{\partial}{\partial n} \left\{ \frac{n^n h^n}{\Gamma(n+1) \Gamma(n+1)} \right\} = \sum_{n=1}^{\infty} \frac{n^n h^n}{n! n!} \left\{ \log_e (nh) + 1 - 2 \frac{\Gamma'(n+1)}{\Gamma(n+1)} \right\} \\ &= \sum_{n=1}^{\infty} \frac{n^n h^n}{n! n!} \left\{ \log_e (nh) + 1 + 2\gamma - 2 \sum_{n=1}^n \frac{1}{n} \right\}, \end{aligned} \quad (29)$$

where

$$\gamma = \text{Euler's constant} = 0.5772157 \dots \quad (30)$$

We shall write

$$g_n = \log_e n + 1 + 2\gamma - 2 \sum_{n=1}^n \frac{1}{n}. \quad (31)$$

By combining formulas (22), (29) and (31), we finally have for Λ ,

$$\Lambda = \frac{c}{2\kappa} \sum_{n=1}^{\infty} \frac{n^n h^n}{n! n!} (\log_e h + g_n). \quad (32)$$

It is clear that, for binary electrolytes, Λ denotes the number of moles of solute "negatively" adsorbed per unit increase of interface area. The relation between the change of surface tension and Λ is given by the adsorption equation of Gibbs, which can be put into the form⁹

$$\Lambda = -(\partial \sigma / \partial \bar{F}_2)_s = -\partial \sigma / RT \partial \log_e a_2; \quad (33)$$

s is the area of the surface, \bar{F}_2 and a_2 , the partial molal free energy and the activity of the solute, respectively. Hence, from Eqs. (32) and (33),

$$d\sigma = -RT d \log_e a_2 \frac{c}{2\kappa} \sum_{n=1}^{\infty} \frac{n^n h^n}{n! n!} (\log_e h + g_n), \quad (34)$$

where, for the electrolytes considered, a_2 is defined by

⁹ Lewis and Randall, *Thermodynamics*, p. 250, McGraw-Hill, 1923.

$$\log_e a_2 = 2(\log_e c + \log_e f). \quad (35)$$

The Debye-Hückel expression for f , the mean activity coefficient of the solute, is

$$\log_e f = -e^2 \kappa / 2DkT(1 + \kappa a) = -q\kappa / (1 + \kappa a), \quad (36)$$

whence $d \log_e f = -[q/(1 + \kappa a)^2] d\kappa$; and, since $\kappa^2 = (8\pi N e^2 / DkT)c = 16\pi N q c$, Eq. (34) readily assumes the form

$$d\sigma = -\frac{kT}{16\pi q} \sum_{n=1}^{\infty} \frac{n^n}{n!n!} \left(2 - \frac{q\kappa}{(1 + \kappa a)^2} \right) h^n (\log_e h + g_n) d\kappa. \quad (37)$$

If we adopt the approximation $a=0$, which amounts to the well-known Debye-Hückel procedure of treating the ions as point charges, the individual terms in the series can be integrated in closed form. We shall write

$$y = \kappa q = h; \quad (38)$$

then the surface tension σ of a solution containing c moles of electrolyte per cc is given by

$$\begin{aligned} \sigma - \sigma_0 = \Delta\sigma &= -\frac{kT}{16\pi q^2} \sum_{n=1}^{\infty} \frac{n^n}{n!n!} \int_0^y (2-y)y^n (\log_e y + g_n) dy \\ &= -\frac{kT}{16\pi q^2} \sum_{n=1}^{\infty} \frac{n^n}{n!n!} \left\{ \frac{2y^{n+1}}{n+1} \left(\log_e y - \frac{1}{n+1} + g_n \right) - \frac{y^{n+2}}{n+2} \left(\log_e y - \frac{1}{n+2} + g_n \right) \right\} \\ &\equiv \frac{kT}{16\pi q^2} (Y_c + Y_f) \equiv \frac{kT}{16\pi q^2} Y. \end{aligned} \quad (39)$$

In the limit, neglecting the contribution from the activity coefficient,

$$\Delta\sigma = -(kT/16\pi q^2) y^2 (\log_e y - \frac{1}{2} + g_1) = -(Ne^2/2D)c \{ \log_e (\kappa q) - 0.34557 \}, \quad (40)$$

where N denotes Avogadro's number. For uni-univalent electrolytes the limiting law becomes

$$\sigma = \sigma_0 + (79.517/D)m \log_{10} (1.143 \times 10^{-13} (DT)^3/m); \quad (41)$$

m is the concentration of the solute in moles per liter. Thus, with water as the solvent, formula (41) gives

$$\Delta\sigma_{273} = 0.904m \log_{10} (1.585/m), \quad \Delta\sigma_{293} = 0.989m \log_{10} (1.493/m), \quad (41a)$$

the subscripts in $\Delta\sigma$ indicating the absolute temperature.¹⁰

We shall confine our numerical computations to uni-univalent electrolytes in water. Inasmuch as the surface tension increment is extremely small for very low salt concentrations, the limiting law (41) cannot be tested directly. We may, however, employ formula (39), which can be easily modified to allow for the size of the ions. Numerical calculations show that the values for $\Delta\sigma$ are practically independent of the exact value chosen for a , the Debye-Hückel mean distance of approach for the ions, and hence, if we take for convenience

$$a = q = e^2 / (2DkT) \quad (42)$$

($q_{273} = 3.457\text{\AA}$; $q_{293} = 3.527\text{\AA}$), we have

$$h = \kappa q (e^{\kappa a} / (1 + \kappa q)) = y (e^y / (1 + y)).$$

We then obtain from Eq. (37)

$$\Delta\sigma = (kT/16\pi q^2) (Y_c' + Y_f') = (kT/16\pi q^2) Y', \quad (43)$$

¹⁰ The dielectric constants of water have been calculated from Wyman's equation (Phys. Rev. **35**, 623 (1930)),

$D = 78.54 [1 - 0.00460(t - 25) + 0.0000088(t - 25)^2]$, where t is the temperature in degrees centigrade.

where

$$Y_c' = - \sum_{n=1}^{\infty} \frac{2n^n}{n!n!} \int_0^y y^n \left(\frac{e^y}{1+y} \right)^n \left\{ \log_e \frac{y}{1+y} + y + g_n \right\} dy,$$

$$Y_f' = \sum_{n=1}^{\infty} \frac{n^n}{n!n!} \int_0^y \frac{y^{n+1}}{(1+y)^2} \left(\frac{e^y}{1+y} \right)^n \left\{ \log_e \frac{y}{1+y} + y + g_n \right\} dy. \quad (43a)$$

The integrations can be performed by multiplying the absolutely convergent series e^{ny} and $(1+y)^{-m}$, $y^2 < 1$. Then all the integrals are reduced to an easily integrable single type, and the series involved converge very rapidly for the concentrations in which we are interested.

Expression (39) (or (43)) can be put into the useful form

$$\frac{Y}{y^2} = \frac{Y_c + Y_f}{y^2} = \frac{2 \times 10^3 \sigma_0 D}{N \epsilon^2} \left(\frac{\Delta \sigma}{m \sigma_0} \right) \equiv A \Delta \alpha. \quad (44)$$

$\Delta \alpha$ is the increase in surface tension per mole divided by the surface tension of the solvent, and

$$y^2 = \kappa^2 q^2 = (1.746 \times 10^{13} / (DT)^3) m \equiv Bm. \quad (44a)$$

The magnitudes of $A \Delta \alpha$ for concentrations up to about 0.18 mol./l., computed without and with allowance for the ionic diameter a , are given in parts I and II of Table I. The contributions to $A \Delta \alpha$

TABLE I. Theoretical values of $A \Delta \alpha$ for uni-univalent electrolytes in water.

I				II			
y^2	Y_c/y^2	Y_f/y^2	$A \Delta \alpha$	y^2	Y_c'/y^2	Y_f'/y^2	$A \Delta \alpha$
0.			∞	0.			∞
0.0063	3.048	-0.076	2.972				
0.0126	2.747	-0.097	2.650				
0.0189	2.576	-0.111	2.465				
0.0315	2.367	-0.134	2.233				
0.0378	2.295	-0.141	2.154	0.0378	2.308	-0.107	2.201
0.0630	2.095	-0.163	1.932	0.0850	2.003	-0.125	1.878
0.0944	1.944	-0.184	1.760				
0.1259	1.840	-0.203	1.637	0.1259	1.867	-0.132	1.735
0.1574	1.760	-0.217	1.543				
0.1889	1.697	-0.228	1.469	0.1963	1.718	-0.139	1.579
0.2014	1.675	-0.232	1.443				
0.2266	1.634	-0.241	1.394				

from the concentration factor and from the activity coefficient factor in the activity of the solute are shown separately.

The contribution to the surface tension increment from the linear term βc of the activity-coefficient expression

$$\log_e f = -q\kappa/(1+\kappa a) + \beta c,$$

where β is a constant characteristic of the individual electrolyte, is given by

$$\Delta \sigma_\beta = - \frac{2RT\beta}{(16\pi N)^2 q^2} \sum_{n=1}^{\infty} \frac{n^n q^n}{n!n!a^{n+3}} \int_0^{\kappa a} (\kappa a)^{n+2} \left(\frac{e^{\kappa a}}{1+\kappa a} \right)^n \left\{ \log_e \frac{\kappa a}{1+\kappa a} + \kappa a + \log_e \frac{q}{a} + g_n \right\} d(\kappa a).$$

For the highest concentrations considered this total effect is found to be small, and hence individual differences between electrolytes have been neglected in the numerical computations. It has already been mentioned that differences in the value for a , the ionic diameter, hardly affect the numerical result. For example, at $m = 0.1$, assuming $a = q = 3.46\text{\AA}$, $A \Delta \alpha$ has the value 1.735; if we take $a = 2.81\text{\AA}$, $A \Delta \alpha$, computed from formulas (37) and (44), is 1.715. At low concentrations, individual differences due to these two characteristics are still smaller.

COMPARISON WITH EXPERIMENT

That, for low concentrations, neither of the factors characterizing individual electrolytes (a and β) enters prominently in the theoretical expressions is in accord with the conclusion drawn by Heydweiller,¹ and more recently by Schwenker,¹¹ that for a given concentration the increase in surface tension is the same for all uni-univalent electrolytes examined, within the limits of the experimental error.

In Fig. 3, we have plotted the values of $A\Delta\alpha$

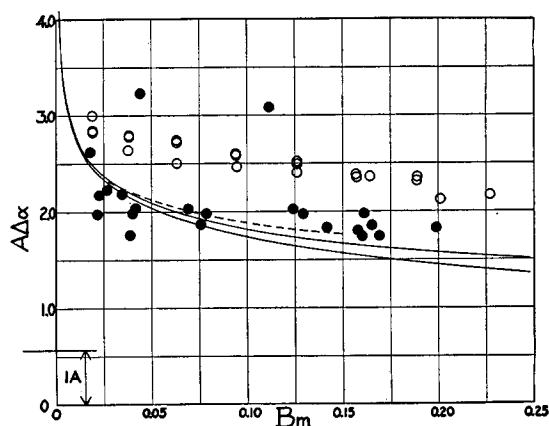


FIG. 3. Theoretical variation of $A\Delta\alpha$ for uni-univalent electrolytes (solid and dotted curves), and $A\Delta\alpha$ values from the available experimental data.

given in Table I against $y^2 = Bm$; the upper curve shows the effect of introducing the size of the ions. The dotted curve has been drawn through the four points calculated by Wagner for $T=291$. The full dots correspond to the values experimentally determined by Heydweiller and his co-workers for LiCl, NaCl, KCl, NH_4Cl , NaNO_3 and KNO_3 . The data of Schwenker (for LiCl, KCl and NaCl) are represented by the circles; his measurements were carried out at $T=273$. The values of the constants A and B (see Eqs. (44) and (44a)) for the two temperatures are (at $T=273$, $D=88.00$, $\sigma_0=75.597$ dynes/cm; at $T=291$, $D=81.103$, $\sigma_0=72.8$ dynes/cm)

$$\begin{aligned} A_{273} &= 96.32; & B_{273} &= 1.259 \\ A_{291} &= 85.49; & B_{291} &= 1.328. \end{aligned} \quad (45)$$

As a crude scale for comparing the magnitude of the total effect we have given the value for $A\Delta\alpha$ obtained on the assumption that $c(x)=c$ for

$x > 1A$, and $c(x)=0$ for $x < 1A$ (this value is 0.579 at $T=273$ and 0.568 at $T=291$).

The agreement between the data of Heydweiller and those of Schwenker leaves a great deal to be desired; probably, Schwenker's measurements represent an advanced technique. We must bear in mind, however, that the effect to be measured is quite small. Schwenker estimates that the relative error of his measurements is 0.011 percent, which, on the large scale of Fig. 3, corresponds to changes in $A\Delta\alpha$ of $0.0133/(Bm)$ units.

Examination of the data for the individual salts indicates that, for low concentrations, $\Delta\alpha$ increases rapidly with decreasing concentration, an observation which did not escape Heydweiller. Yet, the comparison between Schwenker's data and the theoretical curve is not entirely conclusive, partly due to the approximations made in the theory, and partly because of the experimental uncertainty. It is evident from the analysis given in a preceding section that an exact computation would raise the theoretical curve; also, it is possible that a revision of Schwenker's measurements might lower the experimental curve. If, however, the difference is real, it would mean that there are additional repulsive forces at play between the ion and the surface, besides the Coulomb image force. In the present stage of theory and experiment, all that can be done is to estimate limits for the possible magnitude and range of these additional forces.

The Coulomb image force, whose potential is inversely proportional to the first power of the distance, represents an ion-dipole attraction. The possible corrections would involve quadrupole and second order dipole effects, etc., so that their potential ought to decrease at least as the third power of the distance. Repulsive forces of this type would practically exclude all ions within their effective range, which is then the only important measure of the forces. A comparison between Figs. 2 and 3 shows immediately the effect to be expected from forces at a given range.

Thus interpreted, the available data on the surface tensions of uni-univalent electrolytes indicate that Coulomb's law is valid for distances greater than a molecular diameter (3×10^{-8} cm) from the surface.

¹¹ Schwenker, Ann. d. Physik **11**, 525 (1931).