values so derived for hydrochloric acid in ethyl alcohol and in an equimolal mixture of alcohol and water, for lithium chloride in methyl and ethyl alcohols, and for sodium ethylate in ethyl alcohol have been used to test the inter-ionic attraction theory, assuming that the deviation resulted wholly from this source and not at all from incomplete ionization. The results are shown to be in general agreement with that theory as in the case of aqueous solutions; and especially it is proved (what it was the main object of this research to test) that the logarithm of the activation is, at least approximately, inversely proportional to the three-halves power of the dielectric constant, thus demonstrating the electrical origin of the effect. The actual numerical coefficients in the equation expressing the relation between activation and its parameters are, however, again found to be one-third to one-fourth less than the theoretical ones at $0.01 - 0.02\ N$, but they are changing with decreasing concentration in the direction of the theoretical limiting value.

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[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 66]

THE INTER-IONIC ATTRACTION THEORY OF IONIZED SOLUTES. IV. THE INFLUENCE OF VARIATION OF DIELECTRIC CONSTANT ON THE LIMITING LAW FOR SMALL CONCENTRATIONS

BY P. DEBYE AND LINUS PAULING

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Introduction

There has recently been derived[1] with the aid of Poisson's equation and the Boltzmann principle an equation representing the mutual electrical effect of ions in solution and expressing the activities of ions and various properties of ionized solutes. The effect arises from the tendency of every ion to attract towards itself ions of unlike sign and repel those of like sign; as a consequence every ion is, owing to its ion-atmosphere, at an average potential P_0, of sign opposite to that of its charge.

It has been shown that for ions of any finite size in a solution of uniform dielectric constant K, the expression for this quantity P_0 reduces for very dilute solutions to the limiting value

$$\mathrm{P}_0 = -\frac{z\,e\,B}{\mathrm{K}} \tag{1}$$

where

$$B^2 = \frac{4\pi\,e^2\,\Sigma(n_i z_i{}^2)}{\mathrm{K}\,kT} \tag{1a}$$

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[1] (a) Debye, "Hand. v. h. XIX Nederlansch Natuur en Geneeskundig Congres," April, **1923**. (b) Debye and Hückel, *Physik. Z.*, **24**, 185 (1923). (c) Debye, *ibid.*, **25**, 97 (1924). For a re-presentation of this theory in somewhat different form see also Noyes, THIS JOURNAL, **46**, 1080 (1924).

in which z represents the valence (taken algebraically) of the ion under consideration, e the electronic charge, k Boltzmann's constant, T the absolute temperature, and n_i and z_i the concentration and valence of an ion of the ith sort, the summation of $n_i z_i^2$ being taken over all ion-sorts in the solution. The expression for the activation of the ion as derived from this potential P_0 is

$$-ln\ \alpha = \frac{z^2\ e^2\ B}{2\ \kappa\ kT} \tag{2}$$

It is known that the dielectric constant of a solution containing ions is not that of the pure solvent; furthermore, the very great electrical fields produced by an ion must cause in its immediate neighborhood variations in the dielectric constant. Question might therefore be raised as to whether the influence of these variations is such as to cause P_0 and $ln\ \alpha$ to be proportional not to the square root of the concentration, as required by Equations 1 and 2, but to some other power, or to cause the coefficients to have values other than those obtained by introducing for κ the macroscopic value for the pure solvent.

It is the purpose of this paper to show that these variations of the dielectric constant do not change the limiting law that is approached as the concentration approaches zero, and that correct values of the coefficients are obtained by substituting for κ the value for the pure solvent.

Effect of Variation of the Dielectric Constant[2]

Let us consider why a variation of the dielectric constant in the immediate neighborhood of the ion is to be expected. Such variations may be produced in at least four ways. (1) In the presence of the very great electrical fields near the ion saturation of the dielectric, a phenomenon similar to magnetic saturation may occur, resulting in a decreased dielectric constant. (2) The dielectric constant would be expected to vary with the increase in density of the solvent produced by electrostriction. (3) The strong attraction by the ion of the permanent dipoles of the dielectric is not, in general, experienced by the other ions, which usually have no electric moment in the absence of a field, and become polarized only through deformation. The resultant electrostriction pressure of the medium is equivalent to superposing on the coulomb forces an effective repulsion of other ions, which can be expressed as due to a change in the dielectric constant near the ion. (4) At small distances the microscopic rather than the macroscopic point of view is required, in order to determine the influences of the sizes and shapes of the ions and of the molecules composing the dielectric medium. These influences have an effect only at small distances, and can accordingly be treated as equivalent to a change in the value of the dielectric constant near the ion.

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[2] For approximate calculations of the effect of variation of the dielectric constant on the properties of concentrated solutions of strong electrolytes, see Hückel, *Physik. Z.*, **26**, 93 (1925).

Now let us consider the influence of the possible variations on the potential of the ion. In Fig. 1 is represented a particular ion whose valence is z and whose distance of closest approach to the centers of other ions is a. Each ion in the solution is considered as having some spherically symmetrical distribution of its total charge within a radius compatible with this distance of closest approach such, for example, as the location of the total charge at the center, or its uniform distribution throughout the volume or over the surface of a sphere. From the radius a to a certain greater radius r_1 the dielectric constant K is to be regarded as a function of r, and beyond r_1 it is to be considered constant and equal to K_1, that of the solution in mass.

The potential $d\mathrm{P}_0$ produced at the ion by a given charge $d\mathrm{Q}$ distributed uniformly over a spherical shell of thickness dr and radius r greater than r_1 depends only on $d\mathrm{Q}$, K and K_1, and not at all on the dielectric constant at points within the shell. This is evident when it is recalled that the energy change $-ze\, d\mathrm{P}_0$ of removing the ion from the shell must equal that $-ze\, d\mathrm{Q}/\mathrm{K}_1 r$ of removing the shell to infinity, and this latter cannot involve the dielectric constant within the shell. Another evidence is given by the fact that in the interior of such a shell of constant surface-density no electric forces exist, and therefore the potential is constant throughout the whole volume. The contribution of the shell to the potential of the ion is, therefore, equal to the potential at the surface of the shell, and this can depend only on the dielectric properties of the medium beyond the radius of the shell.

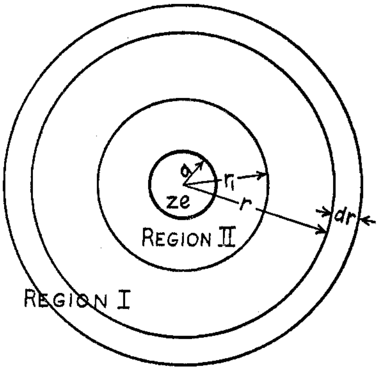

Fig. 1.

The charge $d\mathrm{Q}$, however, is not arbitrary, but is induced by the charge of the ion and therefore depends on the values of the dielectric constant within the shell. The charge in a shell of radius r depends on the total potential at that radius produced by the central ion and its ion atmosphere, and the distribution and hence the potential of the ion atmosphere are influenced by variations in the dielectric constant. But as the solution is made more and more dilute the mutual electrical effect of ions becomes smaller and smaller; the charge of the ionic layer compensating the charge of the central ion will, therefore, be spread over a volume which increases beyond any limit as the concentration of the electrolyte tends to zero. For the case of a constant dielectric constant throughout the whole medium this corresponds to the fact that according to (2) the value $1/B$, which may be called the thickness of the corresponding ionic layer, is proportional to the reciprocal of the square root of the concentration. Now, the whole compensating charge of the layer is always equal (but opposite in sign) to the charge of the central ion. In the limit for low concentrations all but a negligible part of the charge will, therefore, be distributed in shells within the region of invariable dielectric constant K_1. Therefore, the potential P_0 and the activity coefficient will be given by Equations 1 and 2 with K replaced by K_1; that is,

$$\mathrm{P}_0 = -\frac{z\,e\,B_1}{\mathrm{K}_1} \tag{3}$$

and

$$-ln\ \alpha = \frac{z^2\,e^2\,B_1}{2\mathrm{K}_1\,kT} \tag{4}$$

where

$$B_1{}^2 = \frac{4\pi\,e^2\,\Sigma(n_iz_i{}^2)}{\mathrm{K}_1\,kT} \tag{4a}$$

These arguments could easily be put into mathematical form, and constitute therefore a mathematical proof of the theorem that variations of the dielectric constant in the neighborhood of the ions do not affect the limiting law. Still it seems worth while to verify the arguments by a consideration of a simplified model for which explicit formulas can be derived. Suppose the dielectric constant is given the constant value K_1 in the region I in which r is greater than r_1, and the constant value K_2 in the region II where r lies between r_1 and a. Poisson's equation and the Boltzmann principle can then be applied here as in the case of a uniform dielectric constant. Upon expanding the exponential expressions and neglecting terms after the second in each expansion in the usual way, there are obtained the equations

$$\left.\begin{aligned} &\nabla^2\mathrm{P}_1 \equiv \frac{d^2\mathrm{P}_1}{dr^2} + \frac{2}{r}\frac{d\mathrm{P}_1}{dr} = B_1{}^2\,\mathrm{P}_1, \text{ in region I}\\ \text{and}\quad &\nabla^2\mathrm{P}_2 \equiv \frac{d^2\mathrm{P}_2}{dr^2} + \frac{2}{r}\frac{d\mathrm{P}_2}{dr} = B_2{}^2\,\mathrm{P}_2, \text{ in region II}\\ \text{with}\quad &B_1{}^2 = \frac{4\pi\,e^2\,\Sigma(n_iz_i{}^2)}{\mathrm{K}_1\,kT} \text{ and } B_2{}^2 = \frac{4\pi\,e^2\,\Sigma(n_iz_i{}^2)}{\mathrm{K}_2\,kT} \end{aligned}\right\} \tag{5}$$

The solutions of these equations are

$$\left.\begin{aligned} &\mathrm{P}_1 = I_1\,\frac{e^{-B_1r}}{r} + I_1{}'\,\frac{e^{B_1r}}{r}, \text{ in region I}\\ \text{and}\quad &\mathrm{P}_2 = I_2\,\frac{e^{-B_2r}}{r} + I_2{}'\,\frac{e^{B_2r}}{r}, \text{ in region II} \end{aligned}\right\} \tag{6}$$

Since the potential must tend to zero as r becomes infinite, $I_1{}'$ is zero. Furthermore, at $r = r_1$ and at $r = a$ the potential and the induction must be continuous; that is,

$$\mathrm{P}_1 = \mathrm{P}_2, \text{ and } \mathrm{K}_1\,\frac{d\mathrm{P}_1}{dr} = \mathrm{K}_2\,\frac{d\mathrm{P}_2}{dr} \text{ at } r = r_1, \tag{7}$$

$$\mathrm{P}_2 = \frac{ze}{\mathrm{K}_2r} - \frac{ze}{\mathrm{K}_2r_1} + \frac{ze}{\mathrm{K}_1r_1} + \mathrm{P}_0, \text{ and } \mathrm{K}_2\,\frac{d\mathrm{P}_2}{dr} = -\frac{ze}{r^2} \text{ at } r = a \tag{8}$$

With these equations the three remaining constants of integration and the potential P_0 of the central ion due to its ion atmosphere may be evaluated.

The expression obtained for P_0 is

$$\mathrm{P}_0 = \frac{ze}{\mathrm{K}_2 r_1} - \frac{ze}{\mathrm{K}_1 r_1} - \frac{ze}{\mathrm{K}_2 a}$$

$$+ \frac{ze}{\mathrm{K}_2 a} \cdot \frac{\mathrm{K}_1(1 + B_1 r_1)\{e^{B_2(r_1 - a)} - e^{-B_2(r_1 - a)}\}}{\mathrm{K}_1(1 + B_1 r_1)\{(1 + B_2 a)\ e^{B_2(r_1 - a)} - (1 - B_2 a)\ e^{-B_2(r_1 - a)}\}}$$

$$\frac{-\mathrm{K}_2\{(1 - B_2 r_1)\ {}^{B_2(r_1 - a)} - (1 + B_2 r_1)e^{-B_2(r_1 - a)}\}}{-\mathrm{K}_2\{(1 - B_2 r_1)(1 + B_2 a)e^{B_2(r_1 - a)} - (1 + B_2 r_1)(1 - B_2 a)e^{-B_2(r_1 - a)}\}} \qquad (9)$$

On expanding this it is found that the first term in the expansion is that given in Equation 3; the remaining terms involve the first power and higher powers of the concentration, and so are negligible in very dilute solutions.

The problem now remains to determine the effect resulting from the fact that K_1, the dielectric constant of the solution in mass, is not in general equal to K, that of the pure solvent. Theoretical considerations as well as experimental evidence, show that for sufficiently dilute solutions the variation of the dielectric constant from that of the pure solvent is proportional to the concentration of the solute; that is, we can write $\mathrm{K}_1 = \mathrm{K}(1 + \beta n)$. Upon substituting this in Equations 3 and 4, and expanding, they reduce to Equations 1 and 2 multiplied by the factor $1 + 3\ \beta n/2 + \ldots$; the correction terms introduced, involving as they do higher powers of the concentration, drop out in dilute solutions.

In obtaining an expression such as (2) for the activation of an ion it is necessary to take into consideration not only the energy change accompanying the transfer of the ion from the potential P_0 due to its ion atmosphere in the solution considered to that in an infinitely dilute one, but also that accompanying the removal of the ion from one dielectric medium to the other. The change in potential involved in the latter operation is $\frac{ze}{r_1}\left(\frac{1}{\mathrm{K}} - \frac{1}{\mathrm{K}_1}\right)$; replacing K_1 by $\mathrm{K}(1 + \beta n + \ldots)$ this becomes $\frac{ze}{\mathrm{K}r_1}\beta n + \ldots$, which evidently is negligible in comparison with P_0 in sufficiently dilute solutions.[3]

Conclusions and Summary

The considerations that have been presented in this article lead to the conclusion that neither the variation of the dielectric constant in the immediate neighborhood of the ions nor the deviation of the dielectric constant of the solution in mass from that of the pure solvent has any effect on the limiting law for very dilute solutions of strong electrolytes (as expressed by Equations 1 and 2 above). It is further proved that for such solutions the value of the ordinary dielectric constant for the pure solvent in mass is to be substituted. The experiments of Brönsted and La Mer[4] at *very* low concentrations have completely confirmed this theoretical limiting law.

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[3] This conclusion has been previously stated by Debye, Ref. 1 c, p. 99.

[4] Brönsted and La Mer, THIS JOURNAL, **46**, 555 (1924).

The fact that some other experimental results at fairly low concentrations have led to smaller values of the numerical coefficient than those given by these equations can be attributed to variations of the dielectric constant only if it be assumed that the solutions investigated were still too concentrated to make the limiting law strictly applicable.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF COLORADO]

NITROGEN TETRASULFIDE AND NITROGEN TETRASELENIDE[1]

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Nitrogen Tetrasulfide

Preparation.—Various investigators have stated that sulfur monochloride is inferior to sulfur dichloride for the preparation of nitrogen tetrasulfide, but we found that the monochloride serves very well. Ruff and Geisel[2] were able to obtain only 57% of the calculated yield from sulfur dichloride and ammonia, while the monochloride gives a yield of about 65%. We used the following method in the preparation: 5 cc. of sulfur monochloride was diluted to about 150 cc. with ether and a stream of dry ammonia was passed through. The reaction is $16\ NH_3 + 6\ S_2Cl_2 = 12\ NH_4Cl + N_4S_4 + 8\ S$. The yield is greatest when the gas is passed through at the rate of 900–1000 cc. per minute. The mixture turns brown at first, but after about half an hour becomes orange. On standing, an orange precipitate separates out, leaving a bright red solution. The precipitate is extracted with ether and the solution is allowed to evaporate in the air, leaving orange-yellow crystals having a very strong, characteristic odor. When the solution is evaporated by heating, most of the crystals decompose into sulfur, nitrogen and perhaps some other sulfide of nitrogen. In order to avoid the loss of ether while the reaction between the sulfur monochloride and ammonia is taking place, the flask should be immersed in an ice-bath and fitted with a reflux condenser. Even with these precautions, a large part of the ether is lost and the supply may have to be replenished before the completion of the experiment. It is interesting to note that, while the solution formed in this manner is bright red, we did not find it possible to prepare a red solution by dissolving crystals of nitrogen tetrasulfide in ether.

We tried benzene and carbon disulfide as solvents in place of ether, but the yield was not nearly so good in either case as when ether was used. Benzene, however, gave better results than carbon disulfide.

[1] Adapted from a thesis submitted by John C. Bailar, Jr., in partial fulfilment of the requirements for the degree of Master of Arts in Chemistry at the University of Colorado.

[2] Ruff and Geisel, *Ber.*, **38**, 2659 (1905).