"reaction velocity," which may be shown from Equations 3 and 4 to change more uniformly than the rate, and the conclusion is reached that the change is due to increasing activity coefficients of the hydrogen ion and of the sucrose. It has been shown above that the present more precise treatment makes these conclusions untenable. The evidence for the increase in the hydrogen-ion activity appears sound, but these results indicate that there must be some compensating tendency to diminish the rate. It is much less certain that the activity coefficient of the sucrose increases during the inversion. The point of view of Pennycuick's paper is very similar to that presented by Moran and Lewis[2] except that other factors considered in the earlier paper are not discussed in the more recent one. This point of view has been criticized in detail in earlier papers.[3]

Summary

The precise measurements by Pennycuick of the rate of inversion of sucrose have been treated by a mathematical method more accurate than any hitherto applied to reaction rates. The rates have been determined graphically and an equation has been derived relating the change of rate to the time of reaction. From the nature of the change in rate it is shown that several possible experimental errors give no disturbance, and that the change cannot be due to a change in the environment but is most probably due to slightly inefficient mixing. It is concluded that in homogeneous solutions the rates of inversion are constants within a few parts per thousand, and the most probable values of these rates are given.

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SOME THERMODYNAMIC PROPERTIES OF ELECTROLYTES IN ACETIC ACID AND IN LIQUID AMMONIA

BY T. J. WEBB[1]

The freezing-point lowerings and other colligative properties of non-aqueous solvents, interpreted on the basis of ideal-solution relationships, led to the idea that electrolytes exist in a large number of non-aqueous solvents as simple molecules in equilibrium with associated molecules and with a small number of the ions of the electrolyte. At different concentrations, variations in the value of the colligative properties from that demanded by the laws of ideal solutions, were attributed to a shift in the equilibrium between ions, simple molecules and polymerized molecules. That such equilibria exist and that variations in the number of each molecu-

[2] Moran and Lewis, J. Chem. Soc., 121, 1613 (1922).

[3] Scatchard, THIS JOURNAL, 43, 2387, 2406 (1921); 45, 1580 (1923).

[1] National Research Fellow.

lar species depend upon the concentration of the electrolyte, are postulates which seem beyond doubt. The marked non-ideality, however, of solutions of electrolytes in which any appreciable number of ions are present, particularly in solvents of low dielectric constants, renders almost valueless any deductions to be made solely on the basis of the simple relationships obtaining in solutions approaching the ideal. It is to be remembered that, in order for any colligative property to be a direct measure of the number or state of the solute particles, the free energy of the solution at a given temperature and pressure must depend solely on the mole fractions of the constituents, while for a solution of ions there is a considerable contribution from the attractions and repulsions of the ions. The purpose of the present paper is to determine how far the freezing-point lowerings of certain non-aqueous solvents containing dissolved electrolytes may be explained on the assumption of *practically complete* ionization and the Debye-Hückel[2] theory of inter-ionic attractions, and to indicate the method of calculation of the activity coefficients of the ions in the solvents considered.

In accord with the theory of Debye and Hückel, the freezing-point lowering of a solvent containing a dissolved electrolyte is related in the following way to the properties of the solvent, the properties of the electrolyte and the composition of the solution

$$1 - \frac{\Delta}{\nu \Delta_K} = w \frac{\epsilon^2}{6 \, DkT} \sqrt{\frac{4\pi\epsilon^2}{DkT} \nu n} \; \sigma \tag{1}$$

where Δ is the observed freezing-point depression, Δ_K the freezing-point depression produced by an equivalent amount of an ideal solute, ν the total number of ions to be obtained from a molecule of the electrolyte, w a valence factor (equal to unity for uni-univalent electrolytes), ϵ the elementary charge of electricity, D the dielectric constant of the pure solvent, k the Boltzmann constant, T the temperature, n the number of molecules of the electrolyte (as would be determined by chemical analysis) per cubic centimeter and σ a function defined as follows,

$$\sigma = \frac{3}{\kappa^3 a^3} \left[1 + \kappa a - \frac{1}{1 + \kappa a} - 2 \log (1 + \kappa a) \right]$$

where a is the mean effective radius of the ions in solution, and κ is defined by the following equation:

$$\kappa^2 = \frac{4\pi\epsilon^2}{DkT} \sum_i n_i z_i^2$$

The value of the mean activity coefficient of the ions, derivable from the above expression for the freezing-point lowering, is

$$\log_e f = \frac{-z_i^2 \epsilon^2 \kappa}{2 \, DkT} \frac{1}{(1 + \kappa a)} \tag{2}$$

where z_i is the valence of the ion being considered.

² Debye and Hückel, *Physik. Z.*, **24**, 185 (1923); **25**, 97 (1924); **26**, 93 (1925).

Application to Very Dilute Solutions of Electrolytes in Acetic Acid

The typical strong electrolytes sufficiently soluble in acetic acid for the purpose of experimentation are lithium halides, sodium bromide and the acetates. Substitution of numerical values in Equation 1 yields $1 - (\Delta/2\Delta_K) = j = 6.77\sqrt{2c}\,\sigma$, where c is the concentration of the electrolyte in moles per liter.

A series of freezing-point experiments with acetic acid containing several salts at low concentrations has been made. The apparatus consisted of a Dewar vessel of capacity approximately 1 liter, which fitted into a metal container provided with closely fitting cover. This arrangement permitted keeping the air in the apparatus practically free from water vapor, since the apparatus could be filled with air dried over phosphorus pentoxide. The temperature was measured by means of a large Beckmann thermometer, calibrated to 0.002°, and with the use of a telescope freezing temperatures could be determined to within 0.001°. Various amounts of a saturated stock solution of the salt in acetic acid were added to the solvent in equilibrium with its solid phase, and the freezing-point depressions thus measured. The contents of the Dewar vessel were stirred by a motor-driven paddle, the shaft of which was securely packed so as to give a connection practically gas-tight.

After the attainment of equilibrium the stirring was suspended and portions of the solution were withdrawn through an especially arranged pipet so constructed as to cause minimum contamination of the solution with water vapor. The solutions were analyzed for halide ion by titration with silver nitrate and potassium thiocyanate, ferric alum being used as an indicator. In the case of the solution containing acetate as solute, the acetate was converted to chloride, and the same procedure followed.

The acetic acid was prepared from the ordinary commercial 99% acetic acid. This was frozen and allowed to melt partially and the liquid poured off. This process was repeated until the acid froze at a constant tempera-

TABLE I

Lithium bromide		Sodium bromide		Sodium acetate	
m	j	m	j	m	j
0.00422	0.35	0.00489	0.47	0.00728	0.47
.00561	.34	.00613	.45	.0148	.54
.00714	.34	.00892	.40	.0215	.57
.00912	.37	.0126	.51	.0335	.568
.0118	.48	.0151	.48	.0502	.562
.0194	.481	.0184	.50	.0169	.563
.0272	.485	.0208	.50	.0770	.559
.0334	.479	.0242	.50	.0984	.555
.0409	.497			.1242	.552
.0468	.498				
.0540	.514				
.0651	.525				

ture of approximately 16.6°. The salts were thoroughly dried by passing air (which had previously been passed over phosphorus pentoxide) over them. Subsequent analysis showed their purity to be entirely sufficient for these experiments. The experimental results for lithium bromide, sodium bromide and sodium acetate are given in Table I. Under the columns headed m the concentrations of the salts are given in moles per 1000 g. of acetic acid, and in the columns following are the corresponding values of j.

The comparison of the experimental results with those calculated is given graphically in Figs. 1, 2 and 3. The solid curves in the figures represent the graph of the equation

$$j = 6.77 \sqrt{2c} \cdot \sigma \tag{3}$$

where

$$\sigma = \frac{3}{x^3}\left[1 + x - \frac{1}{1 + x} - 2 \log (1 + x)\right]$$

and

$$x = 0.677 \sqrt{2c} \times 10^8 \times a$$

The mean effective radius of the ions of an electrolyte is represented by a, and is the only specific property for the various electrolytes in a given solvent. The value of a for lithium bromide (Fig. 1) is 7.1×10^{-8}, that
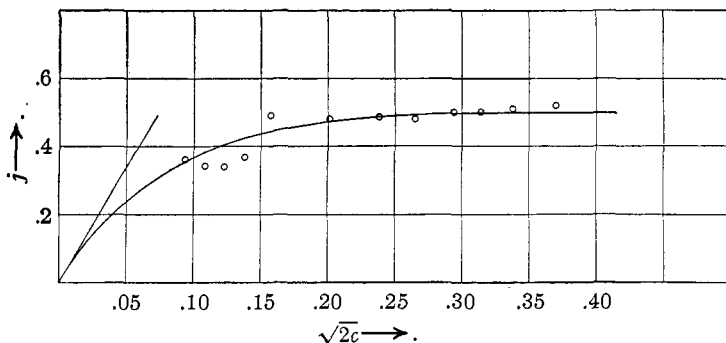

Fig. 1.—The relationship between j and the concentration of the solution for lithium bromide in acetic acid.

for sodium bromide (Fig. 2) is 6.8×10^{-8}, that for sodium acetate (Fig. 3) is 6.2×10^{-8}. The values of a were found by taking one point from the experimental curves in the range of high concentrations, where the error in determining j is presumably least, and calculating the corresponding a by means of the equations above. The points in the figures, deviating most widely from the theoretical curves, represent a discrepancy between calculated and observed freezing-point lowerings of less than 0.004°. For example, in Fig. 3, the deviation of the point at the lowest concentration represents a deviation in the freezing-point depression of 0.0018°.

In so far as Equation 3 represents the experimental behavior of the freezing-point lowering by the presence of the electrolytes, the following equa-

tion may be used for the calculation of the mean activity coefficient of the ions.

$$\log_{10} f = \frac{-8.86\ \sqrt{2c}}{1 + 0.677\ \sqrt{2c} \times 10^8 \times a}$$

By means of this equation the activity coefficient of the ions of lithium bromide at a concentration of 0.00005 mole per liter is calculated to be 0.823, and at a concentration of 0.005 mole per liter to be 0.252.
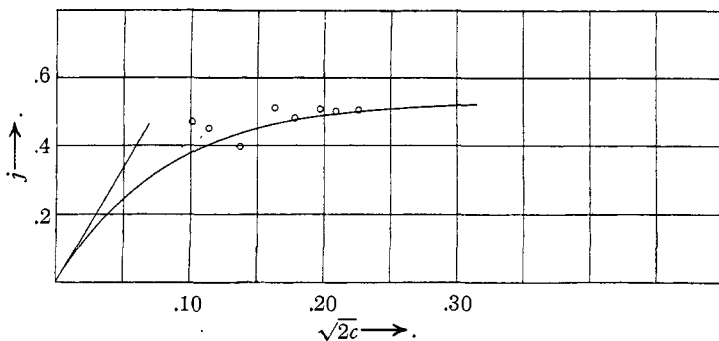

Fig. 2.—The relationship between j and the concentration of the solution for sodium bromide in acetic acid.

The Behavior of Electrolytes at Higher Concentrations in Acetic Acid

The general equation for j given above shows a slight maximum for j at values of the concentration depending upon the values of the constants
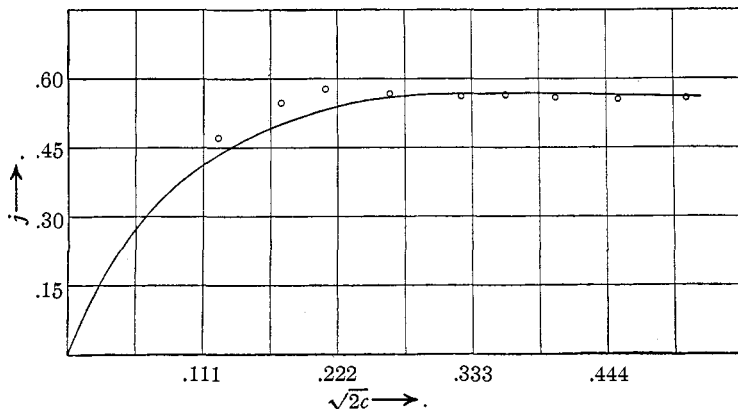

Fig. 3.—The relationship between j and the concentration of the solution for sodium acetate in acetic acid.

entering the equation. For aqueous solutions and solutions of a similar type a maximum for j is the rule, beyond which maximum the values of j fall very rapidly with increasing concentration, much more rapidly than corresponds with the theoretical equation. In solutions of other types

(acetic acid as solvent, for example) it is observed that j reaches a practically constant value, or continues to increase in value beyond the point corresponding with the maximum of the theoretical equation. Hückel[3] has considered the effects calculable for water solutions on the assumption that the dielectric constant of the solution is different from that of the pure solvent. On account of the electric fields arising from the ions, the solvent molecules in virtue of their electric moments will be oriented in the vicinity of the ion and will give rise to a sphere of solvent surrounding each ion not contributing its normal share to the polarization of the medium. This effect for aqueous solutions has been found experimentally by Walden, Ulich and Werner,[4] and calculated by Sack.[5]

In addition to the effect due to the orientation of the solvent molecules, the effect of adding to the solvent ions which are less polarizable than the solvent molecules tends to lower the dielectric constant. The phenomenon of electrostriction, however, increases the density of the solvent molecules in the vicinity of the ion and this effect, considered apart from saturation effects, would seem to result in an increase of the dielectric constant, but it is to be remembered that very near the ion where the increase of the density of the solvent is appreciable the polarization of the medium has already fallen almost to the value which corresponds with the optical polarizability of the medium.

Hückel, by considering that the dielectric constant decreases linearly with the increase of concentration of the ions, obtains the following equation for the activity coefficient of an ion in aqueous solution,

$$\log f = \frac{-z_i^2 \epsilon^2 \kappa}{2\, DkT} \frac{1}{(1 + \kappa a)} + 2cK \tag{4}$$

where K is a positive constant accounting for the changed dielectric properties of the solvent. The corresponding equation for j is

$$j = \frac{w\epsilon^2}{6\, DkT} \sqrt{\frac{4\pi\epsilon^2}{DkT}\, vn} \cdot \sigma - cK \tag{5}$$

The measurements made with lithium bromide, sodium bromide and sodium acetate were at concentrations too low to test Equation 5. A few measurements[6] have been made with lithium iodide and lithium nitrate, however, at high concentrations, which are of some importance for such a test. The data are given in Table II.

In the case of lithium iodide, if the values for j at the lower concentrations are used for the calculations of the constants a and K, they are found to be 6.75×10^{-8} and -1.38, respectively. The value for j at the highest concentration, as calculated from the resulting equation, is 0.725, as com-

[3] Hückel, *Physik. Z.*, **26**, 93 (1925).

[4] Walden, Ulich and Werner, *Z. physik. Chem.*, **116**, 261 (1925).

[5] Sack, *Physik. Z.*, **27**, 7 (1926).

[6] Turner and Bissett, *J. Chem. Soc.*, **105**, [2] 1782 (1914).

pared with 0.710 found by experiment. In like manner for lithium nitrate, the constant a is found to be 7.17×10^{-8} and K to be -0.88. The value of j calculated for the highest concentration from the resulting equation is 0.650 as compared with 0.663 found by experiment.

TABLE II

THE FUNCTION j FOR ELECTROLYTES AT RELATIVELY HIGH CONCENTRATIONS IN ACETIC ACID

Lithium iodide		Lithium nitrate	
$\sqrt{2c}$	j	$\sqrt{2c}$	j
0.431	0.652	0.376	0.558
.496	.683	.540	.586
.579	.710	.689	.663

The agreement for these few values is considered fair, but the significance of the negative value of the constant K is not readily explained. If the electrolytes are practically completely ionized, almost every prediction to be made on a theoretical basis is that the dielectric constant is lowered
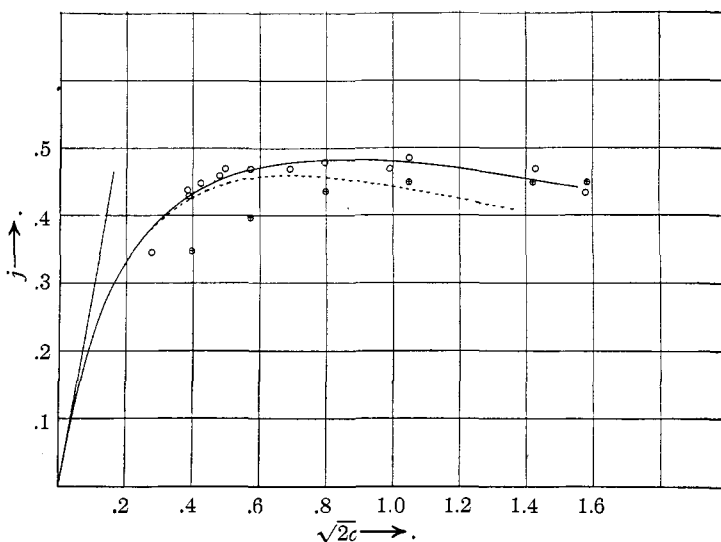

Fig. 4.—The relationship between j and the concentration of the solution for sodium nitrate in liquid ammonia.

by the presence of the ions, which fact in turn means that K is a positive quantity. The indication is that the electrolyte is not completely ionized in acetic acid. This viewpoint is to some extent confirmed by the experimental measurements of Walden and Ulich[7] of the dielectric constants of organic solvents containing dissolved electrolytes. In these measurements the dielectric constants of the solutions were found to be greater than those of the pure solvents. Whatever the real significance of the constants a

[7] Walden and Ulich, Z. physik. Chem., 110, 43 (1924).

and K, the effects of the dielectric constant and the concentration seem properly accounted for by the theory of Debye and Hückel; furthermore, the two-constant equation is obviously an extremely useful means of interpolation.

Application of the Theory to Solutions in Liquid Ammonia

The equation for j for uni-univalent electrolytes in liquid ammonia, in accord with the theory of Debye and Hückel, is

$$j = 2.862 \sqrt{2c}\, \sigma - cK \tag{6}$$

where the constant 2.862 depends upon the dielectric constant of liquid ammonia at its freezing point (25.1), the freezing temperature and certain universal constants, c is the concentration of the electrolyte in moles per liter, and σ is the function as defined above. In Fig. 4 are plotted the graph of Equation 6 (solid curve) and the experimental results found by
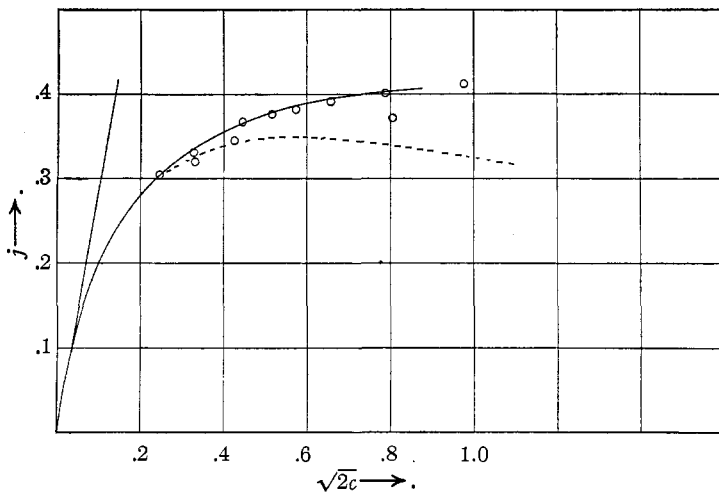

Fig. 5.—The relationship between j and the concentration of the solution for potassium iodide in liquid ammonia.

Elliott[8] for sodium nitrate, as well as the graph of the equation $j = 2.862 \sqrt{2c}\, \sigma$ (dotted curve). For the evaluation of the constant a (mean effective radius of the ions), a curve was drawn through the experimental points and the origin, and from one value of j in the region of low concentrations (where the effect of the term cK is negligible) the values of σ and of the a corresponding were calculated. The constant a was found to have the value 4.41×10^{-8} cm. and K to have the value -0.0750. The points indicated by the circles containing crosses were obtained in a single series of experiments by Elliott, and were not consistent with the results of the other two series, the points for which are represented by

[8] Elliott, *J. Phys. Chem.*, **28**, 611 (1924).

circles without crosses. The straight line intersecting the origin is the limiting tangent to the theoretical curve for the equation $j = 2.862 \sqrt{2c}\, \sigma$.

The results for potassium iodide in liquid ammonia are shown graphically in Fig. 5. The solid curve represents the graph of the two-constant equation, with the constant $a = 5.76 \times 10^{-8}$ and $K = -0.1936$. In so far as these equations represent the values of j for sodium nitrate and potassium iodide in liquid ammonia, the mean activity coefficient of their ions may be calculated from the equation

$$\log_{10} f = \frac{-3.728 \sqrt{2c}}{1 + 0.507 \times a \sqrt{2c} \times 10^8} + 2cK$$

Summary

Freezing-point depressions of acetic acid containing dissolved lithium bromide, sodium bromide and sodium acetate have been measured and the results compared with the equation of Debye and Hückel. The experimental error in very dilute solutions is too great to permit the testing of the limiting law, but at greater concentrations the physical properties of the solvent and the effective radius of the ions are found to account satisfactorily for the results. The corresponding equation for the calculation of the activity coefficients is given.

The freezing-point depressions of acetic acid, containing electrolytes at concentrations sufficiently great that altered dielectric properties of the solvent are to be expected, have been compared with the equations of Debye and Hückel. An increase of the dielectric constant of the solvent is indicated. This result does not seem to be in agreement with the hypothesis of complete ionization, but is borne out by experimental measurements of the dielectric constants of non-aqueous solutions of electrolytes.

Freezing-point depressions of liquid ammonia containing dissolved electrolytes have also been compared with the theoretical equation. The theory is in agreement with the experiments in so far as the latter are consistent, but here also an increase of the dielectric constant of the solvent is indicated.

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