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NON-AQUEOUS SOLUTIONS[1]

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I. INTRODUCTION

I HAD hoped to discuss the chemical, as well as the physical, properties of non-aqueous solutions, but upon further consideration, it became clear that any such discussion would necessarily consume far more time than I have available on this occasion. I shall, therefore, limit my discussion to the physical properties of non-aqueous solutions and, indeed, to the physical properties of solutions of electrolytes. I shall first consider the influence of the physical properties of the solvent medium upon the properties of the solutions and, thereafter, I shall discuss the influence of constitution of the electrolytes upon the properties of their solutions.

II. PHENOMENA DEPENDENT UPON SOLVENT PROPERTIES

Solubility. The solubility of ordinary, inorganic salts is chiefly determined by the chemical nature rather than by the physical properties of the solvent medium. The dielectric constant of the solvent is of secondary importance as a determining factor of the solubility in the case of ordinary, inorganic salts. Many inorganic salts, for example, are readily soluble in ethylamine, whose dielectric constant is 6.2, while there are few, if any, that are readily soluble in nitrobenzene, whose dielectric constant is 35.

The solubility of salts is of great importance in the study of solutions of electrolytes. In order to investigate the phenomena of electrolytic solutions broadly, it is necessary to dissolve a given electrolyte

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[1] Address of the president of the American Chemical Society, Boston, September 14, 1939.

in a wide variety of solvents. This may be accomplished by using suitable substituted onium salts. By introducing long hydrocarbon chains into the positive ions of onium salts, it is possible to obtain electrolytes that are soluble in practically all liquids at ordinary temperatures, even in the saturated hydrocarbons.

Influence of Dielectric Constant. In order to get a picture of electrolytic solutions from a broad point of view, it is necessary to examine the properties of solutions of a typical strong electrolyte in a great variety of solvents. There are, perhaps, no experimental observations that serve this purpose more effectively than the conductance measurements of Dr. Fuoss with mixtures of dioxane and water. With these mixtures, it is possible to work with a solvent medium whose dielectric constant may be varied continuously between 78.6, that of water, and 2.2, that of dioxane. In Fig. 1 are plotted values of the logarithms of equivalent conductance, as ordinates, against the logarithms of concentration, as abscissas, for solutions of tetra*iso*amylammonium nitrate in dioxane-water mixtures. Logarithms are employed in order that all the data may be brought together in compact form; the equivalent conductance varies over a range of 1 to 1,000,000 and the concentration over a range of 1 to 100,000.

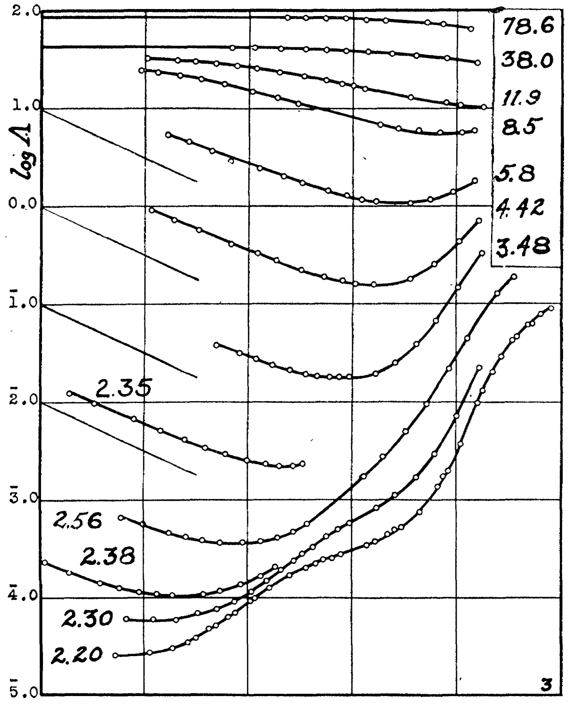

FIG. 1. Conductance of tetra*iso*amylammonium nitrate in dioxane-water mixtures.

I shall not attempt interpretation of the experimental results illustrated in the figure at this point, but the figure will serve to show the character of the phenomena with which we have to deal in solutions in non-aqueous solvents generally. Whether the two solvents be water and dioxane, or whether they be two other miscible solvents of widely differing dielectric constants, and whether the electrolyte be tetra*iso*amylammonium nitrate or some other salt, the general character of the conductance curves will closely parallel those of the figure just shown. We are clearly dealing with phenomena of perfectly general nature in which the dielectric constant of the solvent medium plays a predominant role.

Solvents of High Dielectric Constant. In solvents of high dielectric constant, such as water, typical strong electrolytes are completely dissociated into their ions and the properties of such solutions are accounted for in satisfactory manner by the ion atmosphere theory of Debye and Hückel and Onsager. According to this theory, there is a residual interaction between the ions, due to Coulomb forces, even though the solutions may be quite dilute. According to the theory, the equivalent conductance of an electrolyte should vary as a linear function of the square root of the ion concentration which, in the case of a completely dissociated electrolyte, is proportional to the total salt concentration. In Fig. 2 are plotted values of the equivalent conductance for tetra-*n*-butylammonium picrate in nitrobenzene (D.C. = 35). As may be seen from the figure, the points at lower concentration approximate a straight line whose slope is predetermined by the physical constants of nitrobenzene. Obviously, in the case of this solvent, solutions of tetrabutylammonium picrate follow the same laws as do solutions of ordinary salts in water.

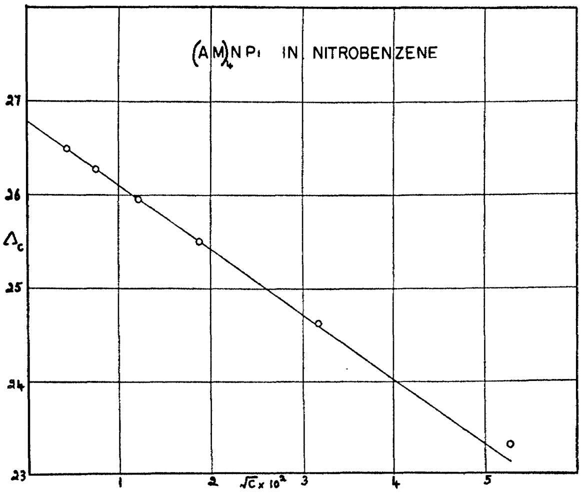

FIG. 2. Showing approximation to theoretical slope for tetra*iso*amylammonium picrate in nitrobenzene.

Ion Association. While the assumption of complete dissociation of electrolytes in conjunction with the ion atmosphere theory of Debye and Hückel and Onsager gives an excellent account of the properties of electrolytic solutions at lower concentrations in solvents of high dielectric constant, it fails to account for the properties of electrolytic solutions in solvents of lower dielectric constant. This is well illustrated in Fig. 3, where values of Λ are plotted against values of the square root of total salt concentration for solutions of tetra*iso*amylammonium nitrate in dioxane-water mixtures whose dielectric constants range from 78.6 to 5.8. The values of the dielectric constant are shown on the figure. As may be seen from the figure, in the two uppermost curves for solvents having dielectric constants of 78.6 and 37.0, respectively, the conductance curves approach the theoretical slope tangentially in accord with the theory. For the solvent mixture having a dielectric constant of 17, the conductance curve fails to approach a limiting tangent. In solvents of still lower dielectric constant, the aberration from the simple ion-atmosphere theory is even more marked.

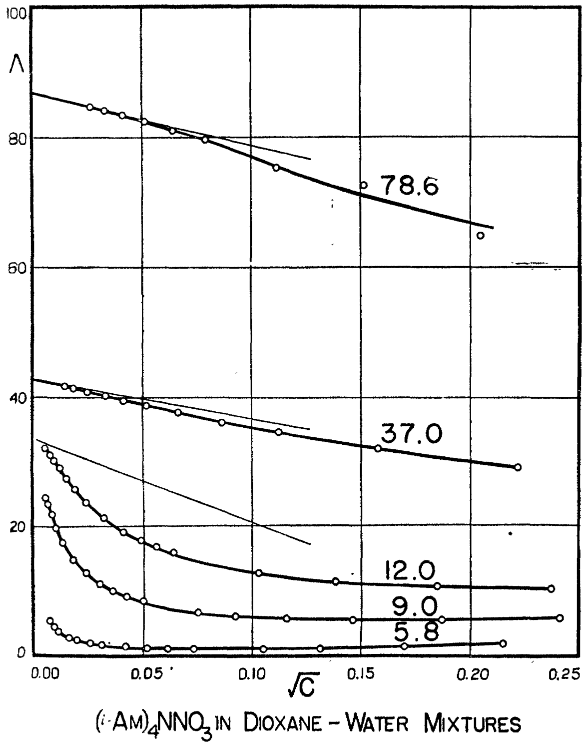

FIG. 3. Illustrating deviations from theoretical slope in solvents of lower dielectric constant.

It is evident that in solvents of lower dielectric constant, a new phenomenon intervenes as a result of which the conductance diminishes much more rapidly with concentration than is called for by the ion atmosphere theory. What happens is that, in solvents of low dielectric constants, the energy of a pair of ions in contact becomes sufficiently great to render such a pair of ions measurably stable; in other words, complete dissociation of the electrolyte no longer occurs at measurable concentrations. It is, therefore, necessary to take into account an equilibrium between associated ions (ion pairs) and free ions in accordance with the equation:

$$M^+X^- \rightleftharpoons M^+ + X^-. \qquad (A)$$

This equilibrium is subject to the law of mass action, but, since the ions exist in the presence of other ions, their long-range interactions must be taken into account in accordance with the theory of Debye and Hückel and Onsager.

Assuming the associated ions, or ion pairs, to be normal in their thermodynamic behavior, while the free ions conform to the ion atmosphere theory, relations are readily obtained by means of which conductance data may be conveniently treated. In general, suitable functions are plotted such that if the assumed relations are correct, they lead to a linear plot. From the plots may be derived the value of the limiting conductance, Λ_0, and the dissociation constant, K, of the mass action equilibrium (A).

In Fig. 4 are shown such plots for solutions of tetramethyl- and tetra-*n*-butylammonium picrates in ethylene chloride (D.C. 10.3). As may be seen from the figure, the points, for both electrolytes, lie upon a straight line well within the limit of experimental error, which is less than 0.1 per cent. In the case of tetrabutylammonium picrate, concentrations have been carried as low as 1×10^{-5} N.

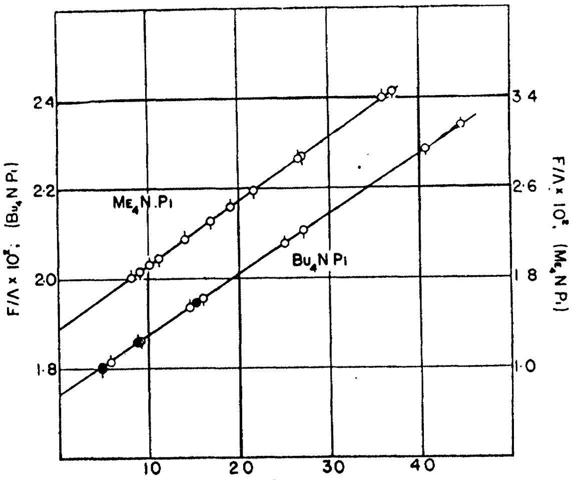

FIG. 4. Illustrating agreement of experimental and theoretical values for solutions in ethylene chloride.

Bjerrum's Theory of Ion Association. Some years ago, Bjerrum developed a theory of ion association.

Without going into details, it may be stated that he derived a relation connecting the association constant (reciprocal of dissociation constant) with the temperature, the dielectric constant of the medium and the sum of the ionic radii. The association constant stands in reciprocal relation to the product of these parameters, so that the dissociation constant is the greater, the larger the dielectric constant of the solution and the larger the radii of the ions. From the conductance data for solutions of tetra*iso*amylammonium nitrate in mixtures of dioxane and water, values of dissociation constants have been obtained by the method indicated above. Knowing the dissociation constants of the electrolyte for the different mixtures and the value of the dielectric constant for these mixtures, it becomes possible to make a test of Bjerrum's theory. While the ion diameters of the electrolytes of these solutions are not known, ion diameters may be assumed of such value as to pass the theoretical curve through one of the experimentally determined K-values. If the theory is correct, the curve should then pass through the remainder of the experimental K-values within the limit of experimental error. In Fig. 5 is shown a plot of the negative logarithm of the dissociation constant (-log K) against the logarithm of the dielectric constant of the solvent medium (log D). The continuous curve is based on a value of 6.4 Å for the sum of the ionic radii. Inspection of the plot will show that the theoretical curve passes through all experimental values well within the limit of experimental error. The plot also shows that at a certain value of the dielectric constant, the curve turns sharply downward and crosses the axis of log D. For mixtures having dielectric constants in this region, the dissociation constant of the electrolyte is very large, which means that for these mixtures and other mixtures of higher dielectric constant, the electrolyte is completely dissociated into its ions.

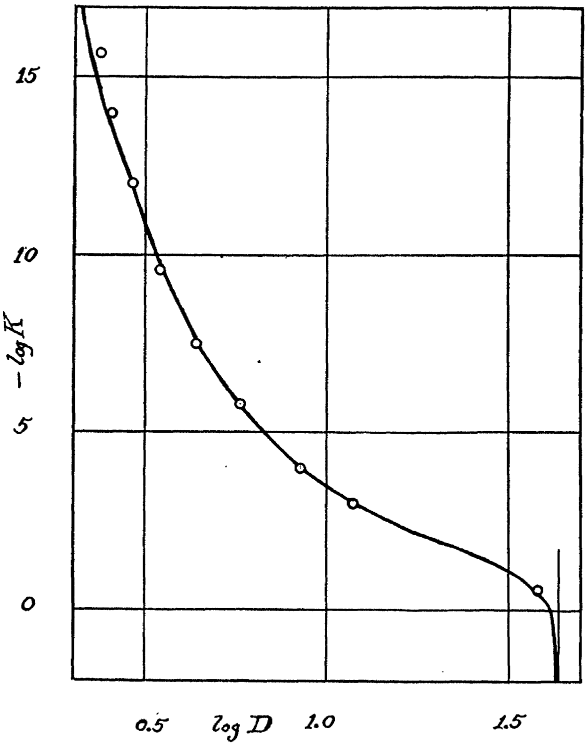

FIG. 5. Experimental and theoretical values of dissociation constants compared.

Mixtures of Electrolytes with a Common Ion. If, in a solvent of lower dielectric constant, we have two salts with a common ion, each of which conforms to the requirements of theory, then it should be possible to compute the conductance of a mixture of these two electrolytes if the conductance curves of the pure compounds are known. In Fig. 4 were shown plots for two such electrolytes, namely, tetramethyl- and tetra-*n*-butylammonium picrates, in ethylene chloride. Values of Λ_0 and K were determined from these plots and therefrom were computed conductance values for mixtures of these two components in the same solvent. In Fig. 6 are shown the experimentally determined values (open circles) for the pure components. The continuous curves passing through these points are the theoretical curves. Between these curves is shown the computed curve for a 50-50 mixture of the two electrolytes; the experimental values are indicated by black circles. The experimental and computed values are in agreement within the error limit of 0.1 per cent.

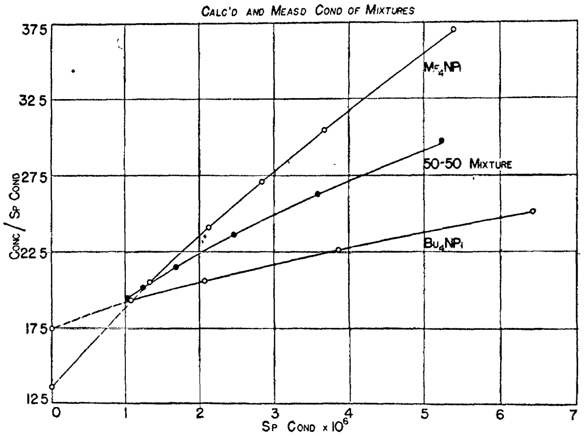

FIG. 6. Showing agreement of experimental and computed conductances for mixtures of electrolytes.

Triple Ion Equilibrium. As shown in the first figure, for solutions of tetra*iso*amylammonium nitrate in mixtures of dioxane and water, all conductance curves in mixtures of lower dielectric constant exhibit a minimum. This phenomenon is a very general one and can only mean that in the region where the conductance increases with increasing concentration, the relative number of ions which carry the current is likewise increasing. This may be accounted for by assuming a further interaction due to Coulomb forces, namely, an interaction between the ion pairs and simple ions. The ion pairs are electrical dipoles and have a measurable electric moment. If, therefore, an ion comes into the neighborhood of an ion pair, a force acts between them which varies inversely as the cube of the distance. In solvents of lower dielectric constant, the energy due to this interaction becomes sufficiently great to render systems of this type stable. We thus have equilibria in accordance with the equations:

$$\begin{array}{l} M^+X^- + M^+ = M^+X^-M^+ \\ M^+X^- + X^- = X^-M^+X^- \end{array} \qquad (B)$$

The complex ions, called triple ions, $M^+X^-M^+$ and $X^-M^+X^-$, carry, each, one unit of charge. As a result of the existence of these equilibria (B), the number of ions in solution at a given concentration will be greater than it would be if only the simple equilibrium (A) were involved. In solutions of a weakly dissociated electrolyte, the fraction of electrolyte present as triple ions increases with increasing concentration and a point is ultimately reached where the increase in the number of triple ions exceeds the decrease in the number of simple ions. It is evident, therefore, that, as a result of these equilibria, the conductance curve will exhibit a minimum.

In Fig. 7 are shown conductance curves for tetrabutylammonium thiocyanate and tetrabutylammonium nitrate in anisole (D.C. 4.29). The form of these curves is characteristic of solutions of binary electrolytes in solvents of lower dielectric constant. The slope of the curves at lower concentrations is characteristic of the equilibrium between simple ions and ion pairs for a weakly dissociated electrolyte.

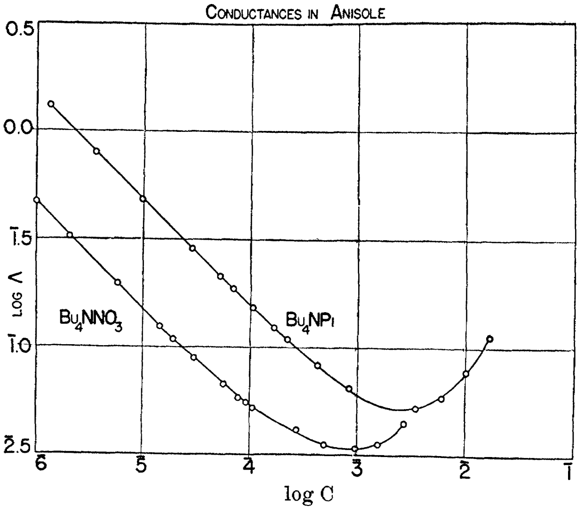

FIG. 7. Typical conductance curves in solvents of lower dielectric constant.

Taking into account the equilibria (A) and (B), together with the ion atmosphere effect for the free ions, simple as well as triple, functions may be plotted, such that if the theory is applicable, the experimental points will lie upon a straight line. Such a plot is shown in Fig. 8 for solutions of tetrabutylammonium picrate in anisole. As may be seen from the plot, the points approximate a straight line within the limits of experimental error. There seems little doubt that in solvents of lower dielectric constant, interaction between the ion pairs and free ions comes into play.

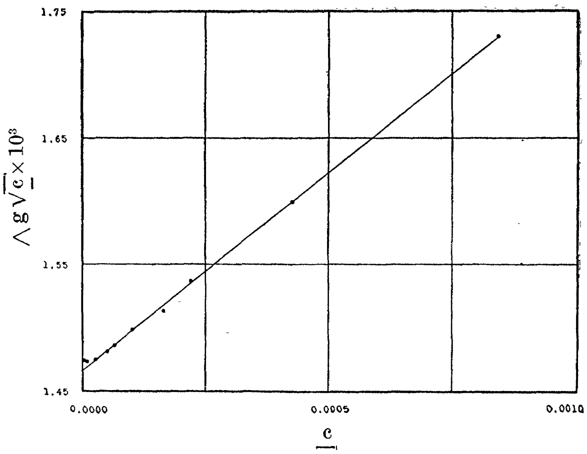

FIG. 8. Test of the Triple Ion Equilibrium.

Concentrated Solutions. In solvents of very low dielectric constant, interactions of still higher type occur. This is illustrated, for example, by the complexity of the conductance curves at higher concentrations. Depending upon the nature of the electrolyte, the conductance curves may or may not exhibit several inflection points in the concentrated region. In Fig. 9 are shown plots of the logarithms of equivalent conductance and of concentration for solutions of tetra*iso*amylammonium picrate and thiocyanate in ben-

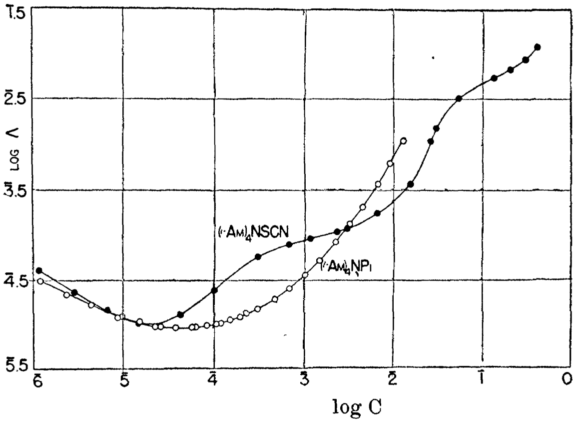

FIG. 9. Typical conductance curves in benzene.

zene solution. As may be seen from the figure, the curve for the picrate is everywhere concave upward, while that for the thiocyanate exhibits several inflection points. The latter type of curve is the more common.

A study of the molecular weight of electrolytes in benzene solution gives further evidence indicating the complexity of the interactions in concentrated solutions of electrolytes in benzene. In Fig. 10 are shown values of the apparent molecular weight as a function of concentration for solutions of tetra*iso*amylammonium thiocyanate in benzene. The formula weight of this electrolyte is 356.4; at approximately 1×10^{-3} N, the molecular weight is 1,500, and thereafter it increases with increasing concentration until it reaches a maximum of 9,200 at a concentration of 0.12 N. Thereafter, the molecular weight diminishes with increasing concentration, reaching a value of 4,100 at a concentration of 0.425 N.

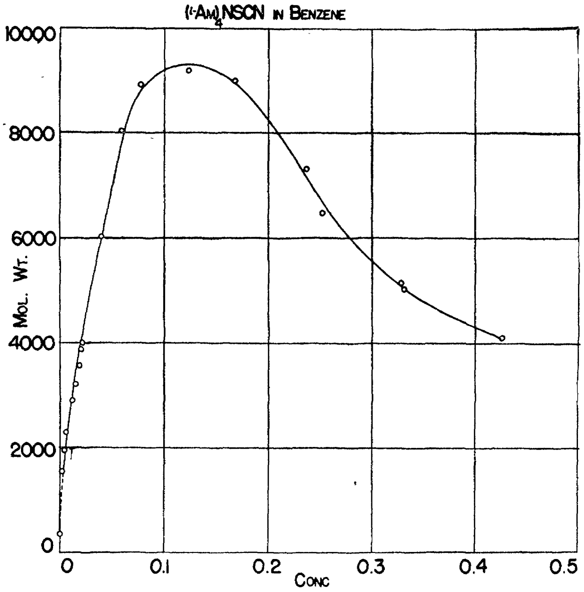

FIG. 10. Molecular weight of tetra*iso*amylammonium thiocyanate in benzene.

Ion Dipoles. From conductance measurements, there is obtained evidence of the existence of ions, but information relating to uncharged molecular species depends upon inference. If ions associate to form ion pairs, such ion pairs must have relatively high polar moments. If, therefore, an electrolyte is dissolved in a non-polar medium, the dielectric constant of the solution should be markedly greater than that of the pure solvent. Experiment has shown that this is actually the case. From dielectric constant measurements with solutions of electrolytes in benzene, molecular polarization values have been computed; these values are shown in Fig. 11. As may be seen, these polarization values are high, ranging all the way from 1,500 to 8,000 cubic centimeters. The polar moments range from 8 to 20 Debye units. Ordinary, highly polar molecules, such as nitrobenzene, have molecular polarization values in the neighborhood of 500 cubic centimeters. The properties of dilute solutions of electrolytes in benzene, therefore, give direct evidence of the existence of ion pairs.

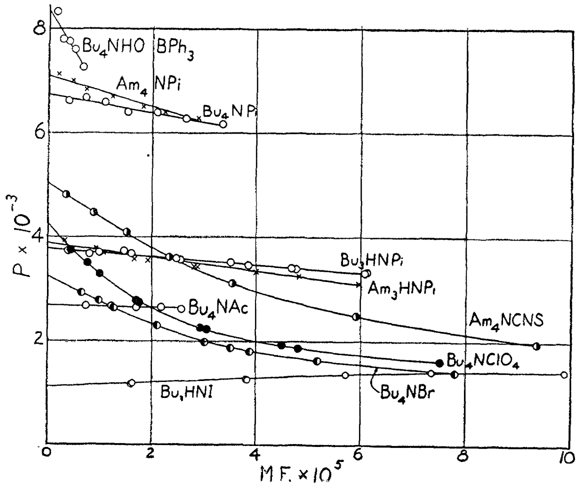

FIG. 11. Polarization curves of electrolytes in benzene solution.

III. INFLUENCE OF CONSTITUTIONAL FACTORS

Size and Configuration. Having discussed the behavior of solutions of electrolytes in various solvents without regard to the constitution of the ions themselves, we may now briefly consider the influence of such constitutional factors upon the properties of electrolytes. According to theory, an electrolyte should be the stronger in a given medium, the larger its ions. Since the conductance of an electrolyte is the lower, the larger its ions, we should expect that as the conductance of an electrolyte is lower, in a given medium, its dissociation constant will be greater.

TABLE I

ION CONDUCTANCES AND K-VALUES OF PICRATES IN ETHYLENE CHLORIDE

Ion	Λ_o^+	$K \times 10^4$
Me_4N^+	42.6	0.326
Et_4N^+	38.2	1.59
n-Pr_4N^+	31.5	1.90
n-Bu_4N^+	26.2	2.18
n-Am_4N^+	23.3	2.38

In the second column of Table I are given conductance values of tetramethyl-, tetraethyl-, tetra-*n*-propyl-, tetra-*n*-butyl- and tetra-*n*-amylammonium ions, in ethylene chloride at 25°. In the third column are given values of the dissociation constant of picrates of the same ions.

In Fig. 12, these values of the ion conductances and

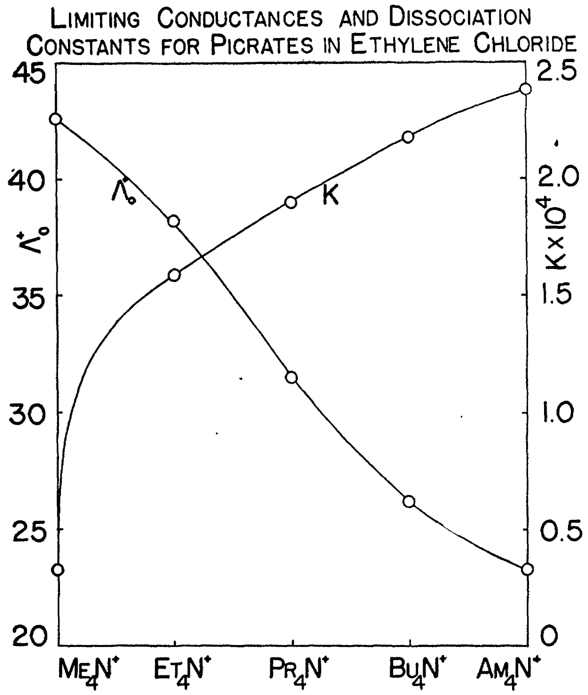

FIG. 12. Illustrating dependence of dissociation constant on ion size.

dissociation constants are shown graphically as functions of the number of carbon atoms in the substituent alkyl groups. It may be seen from the figure, as from the table, that as an ion is more complex and its conductance is lower, the dissociation constant of its salt is greater. The greatest increase of dissociation constant per carbon atom takes place between the tetramethyl- and the tetraethylammonium salts. This regularity, which has been found to hold in ethylene chloride solutions, likewise holds in all other solvents that have thus far been investigated.

If we consider a series of salts of various negative ions, we again find similar relationships, namely, that the larger the ion, the greater the dissociation of the electrolyte. In the case of unsymmetrical ions, that is, ions where the central negative charge is asymmetrically located with respect to the structure of the ion as a whole, we must take into account, not merely the size of the ion, but also its configuration. In Table II are given values of Λ_0 and K for sodium salts of a number of negative ions in liquid ammonia at its boiling point.

TABLE II

CONSTANTS OF SODIUM SALTS IN LIQUID AMMONIA

Salt	Λ_0	$K \times 10^4$
$NaOC_6H_5$	279.4	3.82
$Na\beta\text{-}OC_{10}H_7$	268.1	6.50
$Na\alpha\text{-}OC_{10}H_7$	265.3	8.08
$NaSC_2H_5$	281.4	22.5
$NaSC_6H_5$	275.1	36.0
$NaSn(C_6H_5)_3$	220.	150.

It will be noted that sodium β-naphtholate is a markedly stronger electrolyte than sodium phenolate. The larger dissociation constant of the naphtholate is due to the greater size of the naphthyl group. With the phenolic oxygen atom in the α in place of the β position, the strength of the electrolyte is further increased by about 30 per cent. It is not alone the size of the group attached to the oxygen atom that must be considered but also the relation of the oxygen atom to other atoms in the ion.

It is interesting to compare the dissociation constant of sodium phenolate with that of sodium thiophenolate. In the case of the thiophenolate ion, the charge is localized on the sulfur atom, which is markedly larger than the oxygen atom. As a result, the dissociation constant of the thiophenolate is nearly ten times that of the phenolate. Even sodium ethylsulfide is a markedly stronger electrolyte than sodium phenolate. In this connection, it may be stated that the dissociation constant of potassium chloride is 8.73×10^{-4}. By localizing the charge of the negative ion on still larger atoms and by associating large groups with such atoms, it is possible to build up electrolytes that are even stronger than those already considered. Sodium triphenylstannide $NaSn(C_6H_5)_3$ has a dissociation constant of approximately 150×10^{-4} in liquid ammonia; in other words, it is nearly twenty times as strong an electrolyte as potassium chloride.

Choline Salts. It is of interest to determine what influence elements other than carbon and hydrogen may have on the strength of electrolytes when introduced into the positive ion. For example, a hydroxyethyl group may be introduced into a quaternary ammonium ion in place of an ethyl group. The hydroxy group of a compound of this type may be replaced by halogens and other suitable groups and, in place of an ethyl group, methyl or other organic groups may be employed. In Table III are given values of the dissociation constant for a series of electrolytes of this type, dissolved in ethylene chloride.

TABLE III

CHOLINE SALTS IN ETHYLENE CHLORIDE AND NITROBENZENE

Salt	$K \times 10^4$	
	$C_2H_4Cl_2$	$C_6H_5NO_2$
$Et \cdot Me_3NPi$	0.460	575.0
$HOC_2H_4 \cdot Me_3NPi$	0.0659	67.0
$CH_3OCH_2 \cdot Me_3NPi$	0.254	262.0
$BrC_2H_4 \cdot Me_3NPi$	0.132	....
$BrCH_2 \cdot Me_3NPi$	0.078	....

It will be noted that hydroxyethyltrimethylammonium picrate (choline picrate) has a dissociation constant about one seventh that of ethyltrimethylammonium picrate. Throughout the series of salts appearing in the table, the dissociation constants are markedly lower than those of corresponding salts in which only hydrocarbon groups are present in the positive ions.

Partially Substituted Ammonium Salts. If, in place of the quaternary ammonium salts, partially substituted ammonium salts are employed in ethylene chloride or nitrobenzene, it is found that these substances uniformly behave as weak electrolytes. In general, their dissociation constants are approximately 1,000 times smaller than those of the corresponding completely substituted salts. In Table IV are given values of the limiting conductances and the dissociation constants of a series of butylammonium picrates dissolved in nitrobenzene at 25°.

TABLE IV

CONSTANTS OF PARTIALLY SUBSTITUTED AMMONIUM SALTS IN $C_6H_5NO_2$

Salt	Λ_0	$K \times 10^4$
NH_4Pi	34.3	1.46
$BuNH_3Pi$	32.79	1.50
Bu_2NH_2Pi	30.36	1.51
Bu_3NHPi	28.86	1.90
$BuNH_3ClO_4$	37.75	25.2
Bu_3NHI	33.48	0.943
$C_5H_{10}NH_2Pi$	33.27	1.55

On examining the table, it will be noted that ammonium picrate and monobutyl- and dibutylammonium picrates have dissociation constants of approximately 1.5×10^{-4}; tributylammonium picrate has a slightly higher constant, 1.9×10^{-4}. Tetrabutylammonium picrate is a very strong electrolyte with a constant greater than 2000×10^{-4}. The strength of a partially substituted ammonium salt depends but little upon the nature of the positive ion. Thus, the constant for pyridonium picrate is 0.53×10^{-4}, that of piperidonium picrate is 1.55×10^{-4} and that of ammonium picrate is 1.46×10^{-4}. The negative ion, however, has a marked influence on the dissociation constant. For butylammonium picrate, the constant is 1.50×10^{-4}, while for butylammonium perchlorate it is 25.2×10^{-4}.

The presence of hydrogen attached to nitrogen in the positive ion appears to introduce an energy term as a result of which the dissociation constant of the electrolyte is smaller than that of an electrolyte in which Coulomb forces alone are involved. Seemingly, there is an interaction between the proton attached to nitrogen and the negative ion. This view is supported by the fact that the partially substituted ammonium salts, including ammonium salts, are normally strong electrolytes in pyridine. Interaction between the proton and the negative ion is also indicated by the dependence of the dissociation constant upon the nature of the negative ion as exemplified by the picrate and the perchlorate in Table IV.

Acid-Base Dissociation. In the case of salts of weak bases, dissolved in non-basic solvents like nitrobenzene and ethylene chloride, an acid-base dissociation occurs. For example, in solutions of pyridonium picrate, we have to consider the two equilibria:

$$C_5H_5NH^+Pi^- \rightleftharpoons C_5H_5NH^+ + Pi^- \qquad (C_1)$$

$$C_5H_5NH^+Pi^- \rightleftharpoons C_5H_5N + HPi \qquad (C_2)$$

The fraction of electrolyte existing as free acid and base is in constant proportion to that existing as free ions. If the conductance data for solutions of pyridonium picrate are plotted in the usual way, the curve extrapolates to a value of Λ_0 much below the true one. The acid-base equilibrium may readily be repressed by adding an excess of either picric acid or pyridine. Carrying out a series of conductance measurements in the presence of an excess of acid or base, the true value of Λ_0 may be obtained. Knowing this, the value of the dissociation constant for the equilibria C_1 and C_2 may be obtained from the conductance data of the pure salt.

In Fig. 13 are shown plots of the conductance data for solutions of pyridonium picrate in pure nitrobenzene and in nitrobenzene containing 0.00203 N picric acid. The ordinates are proportional to $1/\Lambda$ and the intercepts on the axis of ordinates are the values of $1/\Lambda_0$. As may be seen from the figure, the value of Λ_0 obtained for pyridonium picrate in pure nitrobenzene (upper curve) is 22.52, while that in the presence of picric acid is 35.1. A series of measurements carried out with the addition of picric acid and of pyridine to solutions of pyridonium picrate yields 35.0 as the most probable value of Λ_0 and 0.551×10^{-4} as the most probable value of the dissociation constant for the pure electrolyte. These yield a value of 1.74×10^{-5} for the dissociation constant of the acid-base equilibrium C_2. In Table V are given values of Λ_0 and of the dissociation constant for pyridonium picrate in the presence of varying amounts of picric acid and of pyridine.

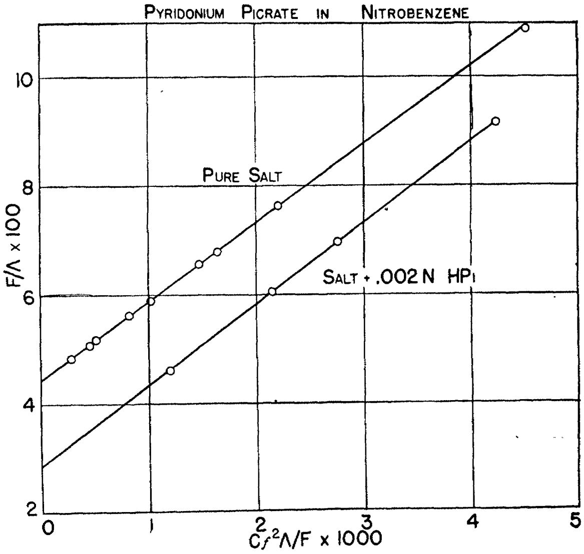

FIG. 13. Illustrating repression of ion-base dissociation in nitrobenzene.

TABLE V

CONSTANTS OF PYRIDONIUM PICRATE IN THE PRESENCE OF VARYING AMOUNTS OF PICRIC ACID AND PYRIDINE

Conc. HPi	Λ_o	$K \times 10^4$	Conc. Pyridine	Λ_o	$K \times 10^4$
0.0	35.0	0.551	0.00095	34.76	0.580
.00077	35.6	.524	.0101	34.19	0.876
.00203	35.1	.545	.0272	34.00	1.34
.00420	35.8	.524	.0528	33.80	2.21

The Λ_0 values obtained on addition of the acid are subject to experimental errors of the order of one-half unit, due, in part, to the conductance of picric acid itself. It is safe to conclude, however, that both Λ_0 and K are independent of the amount of picric acid added in the concentration range of the table. In the presence of pyridine, the values of both Λ_0 and K are functions of the concentration of excess pyridine. There is a rather marked decrease in the value of Λ_0 with increasing concentration of pyridine, which seems to be a real effect and is not due to change in the viscosity of the solutions. The dissociation constant, upon addition of pyridine, increases markedly. This constant is very nearly a linear function of concentration of pyridine and extrapolates to a value of 0.551×10^{-4} for the dissociation constant of pyridonium picrate in pure nitrobenzene. This value of the constant harmonizes with the value of 35.0 for Λ_0.

Proton Interaction. The influence of bases upon the dissociation constant of electrolytes that have an active proton in the positive ion is quite a general phenomenon. In the case of the partially substituted ammonium salts, the investigation of the phenomenon is limited to a base identical with that of the salt. It is possible to investigate the phenomenon more advantageously, however, with salts of the quaternary type in which an OH group is attached to the nitrogen of the ammonium ion. In solvents such as ethylene chloride and nitrobenzene, these hydroxyammonium salts are even weaker electrolytes than are the partially substituted ammonium salts. In Table VI are given values of the dissociation constant of hydroxytrimethylammonium picrate in pure nitrobenzene and in nitrobenzene to which have been added varying amounts of different bases.

TABLE VI

INFLUENCE OF BASES ON THE CONSTANT OF HYDROXYTRIMETHYLAMMONIUM PICRATE IN NITROBENZENE

Base	$K \times 10^4$	Base (C_5H_5N)	$K \times 10^4$
0	0.169	0.00104	0.353
$C_5H_{11}N$ 0.010	11.0	.0101	1.19
$(C_2H_5)_3N$ 0.038	10.0	.037	3.33

As may be seen from the table, the salt has a dissociation constant of 0.169×10^{-4}. With addition of pyridine, the dissociation constant increases, reaching a value of 3.33×10^{-4} for a pyridine concentration of 0.037 N. The stronger the base, the greater is the increase of the dissociation constant at a given concentration of base. Thus, in a 0.01 N solution of pyridine, the dissociation constant is 1.19×10^{-4}, while in a 0.01 N solution of piperidine, the dissociation constant is 11×10^{-4}. In other words, while a 0.01 N solution of pyridine increases the dissociation constant of the electrolyte approximately seven times, a 0.01 N solution of piperidine increases it nearly seventy times. Triethylamine is intermediate in its effect on the dissociation constant; at a concentration of 0.038 N, the constant is approximately three times that of a pyridine solution of the same concentration.

The influence of bases upon the dissociation constant of salts of the type here under discussion is largely, if not wholly, due to interaction of the base with the proton of the hydroxy group of the positive ion. When these electrolytes are dissolved in basic solvents they are normally strong electrolytes. For example, the dissociation constant of phenylhydroxydimethylammonium picrate in nitrobenzene (D.C. = 35) is 0.18×10^{-4}, while dissolved in pyridine (D.C. = 12.03), its dissociation constant is 12.5×10^{-4}.

IV. CONCLUSION

The properties of solutions of typical strong electrolytes are little influenced by the chemical nature of the medium in which they are dissolved; they are chiefly, and very generally, determined by the dielectric constant of the solvent. In a solvent of high dielectric constant, electrolytes are completely dissociated into their ions. In solvents of somewhat lower dielectric constant, short-range ion interaction occurs and an equilibrium exists between simple ions and ion pairs; in solvents of still lower dielectric constant, ions and ion pairs associate to form triple ions. In solvents of very low dielectric constant, association becomes extremely complex at higher concentrations, leading to very complex relations between the concentration and the various physical properties of the solutions.

The association of ions to ion pairs depends, in the first place, upon the size of the ions. It also depends upon the geometrical structure of the ions and the distribution of charge among the various atoms of this structure.

Where interactions other than Coulombic occur between the ions or where special interactions occur between the ions and the solvent molecules, the properties of solutions depend upon the nature of the solvent medium. Certain acids, for example, are strong electrolytes in water but are very weak or non-electrolytes in nitrobenzene. In the case of nearly all the weak electrolytes, interactions other than Coulombic are present and the properties of their solutions are dependent upon the nature of the solvent medium as well as upon its dielectric constant.