THE BEHAVIOR OF ELECTROLYTES IN DILUTE METHYL ALCOHOL SOLUTION

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The development of the modern ideas concerning the nature of electrolytes in solution may be said to have begun with the theory of Arrhenius. But because the apparently anomalous behavior of strong electrolytes in solution could not be satisfactorily explained on the basis of the van't Hoff law of dilute solutions and the classical law of mass action it has been necessary to modify the original theory in a number of important details. More recent investigators have been able to overcome a number of these difficulties with the strong electrolytes by considering them to be completely ionized and assuming that the electrical forces between the ions account quantitatively for the observed deviations. The most successful of these interionic attraction theories we owe to Debye and Hückel who showed that it was possible to explain in a purely theoretical manner the empirical fact that the change of the activity coefficient of ions with concentration and the change of electrical conductance with concentration can be represented by a square root law, *provided* the solution is dilute enough so that the salt may be considered to be completely dissociated into ions. The explanation of these square root laws is based on the fact that the thickness of the ionic atmosphere surrounding each ion is proportional to the square root of the concentration. To obtain this result it is necessary to assume that the principal forces between the ions are given by Coulomb's law and are, therefore, inversely proportional to the square of the distances between them.

In this general discussion the properties of ions and molecules in non-aqueous solvents are considered. It is the purpose of this paper to discuss the behavior of electrolytes in dilute methyl alcohol solution with particular reference to the interionic attraction theories of activity and conductance, and the extent to which they may be considered to be verified in this solvent. It will be well to have before us, then, the manner in which these theories are developed. Both theories involve two basic assumptions: (*a*) the electrolyte is completely dissociated; (*b*) the *principal* forces between the ions are Coulomb forces.

APPLICATION OF THE ACTIVITY THEORY TO THE AVAILABLE DATA FOR METHYL ALCOHOL SOLUTIONS

If the principal forces between the ions are Coulomb forces, that is, if they are inversely proportional to the square of the distance between them, a random distribution of the ions in the solution is impossible, but, owing to the electrical attractions, an ion of a given sign will, on the average, be surrounded by more ions of unlike sign than of like sign. The whole charge of this atmosphere of ions is, of course, equal and opposite to the charge of the ion responsible for it. But, due to the existence of the oppositely charged ionic atmosphere, there will be a difference between the electrostatic potential at the surface of the ion in an infinitely dilute solution where no atmosphere can form and the potential for a finite concentration where the atmosphere does form. The difference between these potentials, ψ, depends on the distance over which the total charge is spread out. There will also exist an average electrical density, ρ, at any distance, r, from the central ion. This density represents the excess of the electricity of opposite sign to be found, on the average, in a little element of volume which is imagined at the distance r from the ion in question, and is given by the ordinary Boltzmann principle, as follows:

$$\rho = n\,\epsilon \left(e^{-\frac{\epsilon\psi}{kT}} - e^{\frac{\epsilon\psi}{kT}} \right)$$

where ϵ is the charge of a positive univalent ion,
n is the number of positive ions in 1 cc.,
ψ is the average electrical potential due to ionic atmosphere,

k is the Boltzmann constant, and
T is the absolute temperature.
A uni-univalent salt in dilute solution is being considered here.

The next step in the development is an exceedingly important one. Debye and Hückel combined the equation of Poisson, which relates the electrical potential, ψ, and the density of electricity, ρ, with the equation of Boltzmann and eliminated ρ between them. But, as Kramers (1) and Fowler (2) have pointed out, such a procedure is legitimate when, and only when, certain fluctuation terms can be neglected as small. Thus, Debye and Hückel could use this method for very dilute solutions and in a solvent of sufficiently high dielectric constant. It is in this way that a result is obtained from which ψ may be determined.

$$\nabla^2 \psi = -\frac{4\pi\epsilon n}{D}\left(e^{-\frac{\epsilon\psi}{kT}} - e^{\frac{\epsilon\psi}{kT}}\right)$$

$$= \frac{8\pi\epsilon n}{D} \sinh \frac{\epsilon\psi}{kT}$$

For small potentials the quantity $\sinh \frac{\epsilon\psi}{kT}$ may be replaced by $\frac{\epsilon\psi}{kT}$, the first term of the expansion of the exponential terms of the above equation, with the result,

$$\nabla^2 \psi = \frac{8\pi n\epsilon\psi}{DkT} = k^2 \psi,$$

where

$$k^2 = \frac{8\pi n\epsilon^2}{DkT}.$$

Before proceeding with the solution of this equation, it may be pointed out that the mathematical simplicity of the original Debye and Hückel activity theory was based upon an approximation which made possible the combination of the Boltzmann and Poisson equations. Since this combination of equations involves a certain degree of approximation which is completely justified only in very dilute solutions and in solvents of a sufficiently high dielectric constant it does not seem proper, as has been done in several cases (3), to attempt to extend the theory to the other solvents, to the more concentrated solutions, and to the water solutions containing ions of the higher valence types by considering not only the $\frac{\epsilon\psi}{kT}$ term but also the next members in the expansion of the hyperbolic sine function without considering the limitations which will have been imposed by the mathematical approximations made prior to the expansion.

It must be admitted that the magnitude of these fluctuation terms is at present unknown, nevertheless they may be proven to be small enough to be neglected only under the conditions mentioned above. There is undoubtedly a certain utility in making use of higher members of the expansion, but the treatment cannot be made exact in this manner alone.[1]

Furthermore, as will be pointed out later, the effect of a close approach of ions and the effect of ions, particularly those of the higher valence types, in orienting the solvent dipoles in their immediate neighborhood has not been sufficiently considered in the attempted extensions of the theory to more concentrated solutions, to solvents of appreciably lower dielectric constant, and to cases where ions of the higher valence types are involved. These effects are capable of seriously limiting the correctness of the two basic assumptions which have been mentioned; in other words, the fundamental ideas of the Debye and Hückel theory itself do not lend themselves to an exact treatment in these cases.

To proceed briefly with the derivation, the average potential in the space around the selected ion depends only upon the distance, r, from it, therefore

$$\frac{d^2\psi}{dr^2} + \frac{2}{r}\cdot\frac{d\psi}{dr} = k^2\,\psi.$$

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[1] This point is treated more exactly in forthcoming monographs by Falkenhagen (Hirzel, Leipzig) and by Williams and Falkenhagen (Chemical Catalog Co., New York).

The general solution of this differential equation is,

$$\psi = \frac{c}{r} e^{-kr} + \frac{c'}{r} e^{kr},$$

where c and c' are constants. The particular solution demanded by the boundary conditions is

$$\psi = \frac{c}{r} e^{-kr}$$

In words, the significant factor which represents the decrease in the density of electricity with the distance is the exponential e^{-kr} where κ has the dimension of a reciprocal length and is given by the formula

$$\kappa = \sqrt{\frac{4\,\pi}{DkT} \cdot \Sigma\, n_i z_i^2}$$

In this equation there has been introduced the necessary valence factor to make the expression conform to a salt of any valence type. The ionic strength is defined by the equation

$$\mu = \tfrac{1}{2}\, \Sigma\, n_i z_i^2$$

where n_i is the concentration of ion of i^{th} kind per 1000 grams of water, and z_i is the valence of ion of i^{th} kind in the solution.

The expression for the potential of an ion of the i^{th} sort is, by making a further approximation,

$$\psi = -\frac{\epsilon\, z_i\, \kappa}{D}.$$

From this potential ψ it is possible to determine the thermodynamic functions of the solution by methods which are beyond the scope of this article. Since we are concerned here with the expression for the activity coefficient of a salt in solution the end result will be written at once.

$$-\log f_s = \frac{\Sigma\, v_i z_i^2}{\Sigma\, v_i} \cdot \frac{\epsilon^2}{2\,DkT} \sqrt{\frac{4\,\pi}{DkT} \cdot \Sigma\, n_i z_i^2}$$

where v_i is the number of ions formed by each molecule of the i^{th} kind.

We have made measurements of the activity coefficients of salts of valence types 1-1, 2-1, and 3-1 in very dilute methyl alcohol solution at 20°C. in order to test the validity of this equation in this solvent which has a dielectric constant of 30 at this temperature. The data for the salts of valence type 1-1 and 2-1 have been reported (4), but the data for the salt of valence type 3-1 are now to be reported for the first time. Substituting the values of the universal and variable constants, the equation for the logarithm of the activity coefficient of a salt in methyl alcohol solution becomes

$$-\log f_s = 2.0\, z_1 z_2 \sqrt{\mu}$$

where z_1, z_2 are the valences of the ions in question, and μ is the ionic strength of the solution.

The activity coefficients were determined by means of the effect of solvent salts of different valence types on the solubility of highly insoluble saturating salts of the valence types mentioned. The apparatus for the saturation of the solutions was of the usual construction. The solvent and saturating salts were all subjected to a careful purification. The methyl alcohol was purified according to a recognized method.

The data for the solubility of the tri-univalent salt, luteo bromide, in methyl alcohol solutions of potassium sulfocyanate are given in table 1.

If one plots these, and the similar data of the previous article (4), by taking the logarithms of the solubility ratio, $\log \frac{s}{s_0}$, as abscissae against the square roots of the ionic strengths as ordinates, lines having but a slight curvature will be obtained. The limiting slopes of the resulting curves should be expressible by the factor 2.0 $z_1 z_2$ of the above equation, if the Debye and Hückel activity theory in its simplest form is to be verified. The comparison of the limiting slopes obtained for the different systems with those predicted on the basis of this theory in its simplest form is made possible by table 2. An inspection of this table shows that for salts of the valence type 1-1 the limiting law is obeyed with the same degree of exactness that one finds for similar systems in water solution. When the theory is tested in the case of saturating salts of valence type 2-1 it is found that the agreement with theory, though approximate, is less satisfactory, and in the case of the 3-1 valence type salt the conclusion is that there is no agreement. The data in this last case are admittedly meagre, but it may be pointed out that KSCN is undoubtedly the best solvent salt possible, and it was used in this particular case.

TABLE 1

Solubility relations of tri-univalent salt luteo bromide in methyl alcohol at 20°C.

Solvent salt—KSCN

CONCENTRATION OF SOLVENT SALT	NUMBER OF DETERMINATIONS	SOLUBILITY $\times 10^5$	μ	$\sqrt{\mu}$	$\log \frac{s}{s_0}$
mols per liter					
0.000000	2	2.962	0.000178	0.01335	0.0000
0.000313	4	3.897	0.000546	0.02334	0.1193
0.000625	2	4.540	0.000898	0.02997	0.1855
0.001250	2	6.129	0.001618	0.04030	0.3158
0.002500	2	7.718	0.002963	0.05443	0.4159
0.005000	2	9.988	0.005599	0.07483	0.5279

TABLE 2

Comparison of experimental and theoretical slopes

SATURATING SALT	VALENCE TYPE	SOLVENT SALT	OBSERVED LIMITING SLOPE	THEORETICAL SLOPE
Croceo chloride	1-1	$C_6H_5SO_3Na$	1.7	2.0
Croceo chloride	1-1	KSCN	1.7	2.0
Croceo chloride	1-1	$Ba(ClO_3)_2$	2.5	2.0
Croceo chloride	1-1	$(C_6H_5COO)_2Sr$	1.7	2.0
Chloropentammine cobalt nitrate	2-1	KSCN	4.0	4.0
Chloropentammine cobalt nitrate	2-1	$Ba(ClO_3)_2$	8	4.0
Xantho chloride	2-1	KSCN	4.0	4.0
Xantho chloride	2-1	$Ba(ClO_3)_2$	6	4.0
Xantho chloride	2-1	$(C_6H_5COO)_2Sr$	6	4.0
Luteo bromide	3-1	KSCN	11.5	6.0

In order to make sure that these conclusions from the experimental work were proper, Hansen and Williams (5) have studied the activity coefficients of ions of these three valence types in ethyl alcohol-water mixtures, in which it was possible to vary the dielectric constant of the solvent at will by changing the molecular ratio of ethyl alcohol to water. In all these experiments sodium chloride was used as solvent salt. The comparison of the observed and calculated limiting slopes of the curves which represent the experimental data are given in table 3.

TABLE 3

Experimental and theoretical slopes in ethyl alcohol-water mixtures at 25°C.

SOLVENT	DIELECTRIC CONSTANT	OBSERVED SLOPE	CALCULATED SLOPE
1. 1-1 Type salt. Croceo tetranitrodiamminocobaltiate			
1.00 mole fraction H_2O	78.8	0.50	0.50
0.80 mole fraction H_2O, 0.20 mole fraction EtOH	54.0	0.89	0.89
0.60 mole fraction H_2O, 0.40 mole fraction EtOH	41.4	1.31	1.32
0.40 mole fraction H_2O, 0.60 mole fraction EtOH	33.8	1.90	1.80
2. 1-2 Type salt. Croceo sulfate			
1.00 mole fraction H_2O	78.8	1.10	1.08
0.80 mole fraction H_2O, 0.20 mole fraction EtOH	54.0	1.74	1.76
0.60 mole fraction H_2O, 0.40 mole fraction EtOH	41.4	2.74	2.65
3. 3-1 Type salt. Luteo iodate			
1.00 mole fraction H_2O	78.8	1.52	1.51
0.80 mole fraction H_2O, 0.20 mole fraction EtOH	54.0	4.0	2.65
0.60 mole fraction H_2O, 0.40 mole fraction EtOH	41.4	6.1	3.98

This table definitely substantiates the statements made with regard to the behavior of these salts in methyl alcohol solution. One sees from it that in the case of the salt of simplest valence type, even when the dielectric constant of the medium has been reduced to 30, any deviation from the limiting slope is a second order effect; in the case of the 2-1 valence type salt the deviations are beginning to appear in the solvent of dielectric constant 40; and in the case of the 3-1 valence type salt the deviations are already large when the dielectric constant has been reduced to two-thirds of the ordinary water value. Thus the figures found for the slopes in methyl alcohol of dielectric constant 30 could have been fitted into table 3 without difficulty.

There have been stated in the derivation of the activity equation the reasons why the writer does not believe that these discrepancies between theory and experiment can be explained by the expedient of including the higher terms in the expansion of the hyperbolic sine function. The step in the development of the theory leading to this hyperbolic sine function is not exact.

It has also been suggested that the fundamental assumptions upon which the theory is based will have to be modified if the theory is to account for the behavior of ions of higher valence types in solvents like methyl alcohol. Bjerrum (6) has indeed recognized the fact that the assumption which assigns to each and every ion an electrical effect must be modified. Bjerrum, in studying not only the stronger salt solutions in water but also the behavior of salts in methyl and ethyl alcohol solutions considers two ions within a certain critical distance from one another as "associated" and therefore without electrical effect. The number of these ion pairs has been calculated by the Boltzmann principle and the law of mass action. The activity theory is then applied to the remainder of the ions. This method, one which modifies the first basic assumption, actually gives a result for salt solutions of the higher valence types in water and for salt solutions of 1-1 valence type in methyl alcohol which more nearly approximates the result of experiment.

More recently there has been considerable discussion concerning the assumption of 100 per cent dissociation, and the consensus of opinion seems to be that the assumption is not justified, even in water solution. One certainly may expect even greater difficulties with it in methyl alcohol solution for the tendency of ions to associate, which is also increasing with increasing charge, will be more pronounced in this solvent. But quite apart from this difficulty the simple Debye-Hückel theory does not account for the influence of changes in the dielectric properties in the neighborhood of ions, particularly those of the higher valence types, for it is a well-known fact that the latter may exert a segregating and orienting effect on dipole molecules, producing what is termed solvation. This effect will probably be of even greater significance in methyl alcohol than in water. The increased electric forces in the alcohol will cause larger deviations from the ideal laws of solutions, and the interionic attraction term which corrects for these deviations will become not only larger but much less amenable to reasonably exact calculation. It appears that the dielectric constant of the medium has been introduced into the equations in an inexact way, for from the statements made above it will be evident that the main part of D arises from the orientation of the solvent dipoles by the field of the ions and would therefore be different from the dielectric constant of an infinitely dilute solution, that is, the bulk constant for the pure solvent, which is actually used. A rigorous and quantitative examination of this particular point will no doubt involve considerable mathematical difficulty. It is an effect which would be expected to be of considerable importance in the case of ions of the higher valence types in methyl alcohol, and will make the application of Coulomb's law an approximation at best.

The validity of the use of Coulomb's law to express the principal forces between ions is directly involved in the close approach of two ions, particularly those of higher charge. In this event the force between them will be modified so as to involve some other power of the distance, and therefore the limiting or square root law, based upon the assumption of ordinary Coulomb forces always acting between ions, will be only approximate. Since the greatest discrepancies between experiment and theory are always noted in the cases of ions of the higher valence types it appears reasonable that this difficulty exists.

The corrections to be applied to Coulomb's law for the effect due to the close approach of ions and for the effect of segregation and orientation of solvent dipoles is an extremely difficult problem, yet it may eventually be solved.

Conclusion

From the standpoint of the interionic attraction theory of activity methyl alcohol may be considered to be a "water-like" solvent. Differences in the behavior of electrolytes dissolved in it rather than in water are shown to be differences of degree only. The activity data in this solvent are valuable in that they demonstrate the inadequacy in non-aqueous solutions of the two basic assumptions of Debye and Hückel. They also indicate the nature of the additional assumptions which will have to be made if experiment and theory are to agree.

APPLICATION OF THE CONDUCTANCE THEORY TO THE AVAILABLE DATA FOR METHYL ALCOHOL SOLUTIONS

The interionic attraction theory of conductance has been developed by the use of methods which are similar to those used in dealing with the activity problem. The original theory of Debye and Hückel (7) was modified by Onsager (8), and it is in this latter form that it has been most successful. It cannot be said to have achieved the success that the activity theory has, yet it has stimulated a widespread interest in the accumulation of precision data for the conductances of salts in very dilute solution and in a number of solvents, and it has revolutionized the mode of treatment of these data. The reason that the conductance theory is less exact than the activity theory is not difficult to explain; in the conductance theory an irreversible process is being considered, while in the activity theory there is investigated an equilibrium condition to which the exact laws of thermodynamics may be applied. It means that a greater number of assumptions will be required in the former case, and an increase in the number of assumptions is always accompanied by a decrease in the accuracy with which a given phenomenon may be described.

In the classical theory of Arrhenius the decrease in equivalent conductance or molar conductance with increasing concentration was explained by assuming that the number of ions, that is, the number of carriers of the current, was continually decreasing. But in the interionic attraction theories the number of ions present is assumed to be always exactly proportional to the total concentration, so that the classical explanation for the decrease in molar conductance with increase in concentration must be discarded. In its place Debye and Hückel assumed that the conductance changed with concentration because the mobilities of the ions changed, and it could be shown that the ionic atmosphere surrounding each ion provided the necessary explanation, because in addition to having a definite thickness, the atmosphere is characterized by a definite time of relaxation. As the ion moves through the liquid the atmosphere of opposite sign is continually forming about it and relaxing behind it. Since this process requires a definite period of time the ion will be moving away from an atmosphere of opposite sign, and will consequently be subjected to a force which decreases its mobility. This force is called the electrical force of relaxation. In addition there is a retarding force due to the fact that since the ions of opposite charge are moving in opposite directions through the solvent, and in moving tend to carry with them a certain amount of the solvent, each ion may be considered to be moving not in a stationary medium, but in one that is moving in a direction opposite to its motion. This is the so-called electrophoretic effect.

In the quantitative theory the magnitude of these forces has been calculated, both by Debye and Hückel and by Onsager. These calculations will not be given in this article; rather their result will be given in the simplified form adopted by Williams and Falkenhagen (9) in a recent review article devoted to the problem of conductance. The molar conductance at any concentration, Λ, is given by the expression

$$\Lambda = \Lambda_\infty - \Lambda_{\mathrm{I}} - \Lambda_{\mathrm{II}}$$

where Λ_∞ is the ordinary molar conductance at infinite dilution,
Λ_{I} is the electrical force of relaxation expressed as conductance,
Λ_{II} is the electrophoretic force expressed as conductance.

Further,

$$\Lambda_{\mathrm{I}} = \frac{|\epsilon_1 \epsilon_2|}{3\,DkT}\,\kappa\,\Lambda_\infty \frac{q}{1+\sqrt{q}}$$

and

$$\Lambda_{\mathrm{II}} = \frac{n_1 \epsilon_1^2 + n_2 \epsilon_2^2}{6\,\pi\,\eta} \cdot \frac{1000}{\gamma} \cdot \frac{1}{9 \times 10^{11}} \cdot \kappa$$

In these equations

$$\kappa^2 = \frac{4\,\pi}{DkT} \cdot \frac{\epsilon^2\,N}{1000}\,\gamma\,\Sigma\,v_i z_i^2$$

$$q = \frac{L_1\,z_2 + L_2\,z_1}{(z_1 + z_2)\,(L_1\,z_2^2 + L_2\,z_1^2)} \cdot z_1 z_2$$

γ = the concentration of salt expressed in moles per liter.
N = the Avogadro number.
η = the coefficient of viscosity of the medium.
L_1, L_2 = the mobilities of individual ions, and the other symbols have the significance assigned to them in the discussion of the activity theory.

Introducing the universal constants, the expression for the molecular conductance of a simple electrolyte takes the form

$$\Lambda = \Lambda_\infty - \left(\frac{0.985 \times 10^6}{(DT)^{\frac{3}{2}}}\,w\,\Lambda_\infty \sqrt{\Sigma\,v_i z_i^2} + \frac{29.0}{(DT)^{\frac{1}{2}}\,\eta}\,(\sqrt{\Sigma\,v_i z_i^2})^3\right)\sqrt{\gamma}$$

$$= \Lambda_\infty - \alpha\,\sqrt{\gamma}$$

where

$$w = \frac{2\,q}{1 + \sqrt{q}}.$$

The molar conductance, Λ, is therefore given by an equation which is identical in form with the equation found empirically by Kohlrausch. It may then be said to be proven that the interionic attraction theory is adequate to explain Kohlrausch's law.

Since the conductance data now existent for dilute solutions in methyl alcohol are expressed in equivalent conductance rather than in molar conductance the above expression may be written for our discussion in terms of equivalent conductances, as follows:

$$\Lambda^* = \Lambda^*_\infty - \left(\frac{0.985 \times 10^6}{(DT)^{\frac{3}{2}}}\,w\,\Lambda^*_\infty + \frac{29.0\,(z_1 + z_2)}{(DT)^{\frac{1}{2}}\,\eta}\right)\sqrt{(z_1 + z_2)\,\gamma^*}$$

$$= \Lambda^*_\infty - \alpha^*\,\sqrt{(z_1 + z_2)\,\gamma^*}$$

where γ^* is the equivalent concentration,
Λ^* and Λ^*_∞ are equivalent conductances, and

$$\alpha^* = \frac{0.985 \times 10^6}{(DT)^{\frac{3}{2}}} w \Lambda^*_\infty + \frac{29.0 (z_1 + z_2)}{(DT)^{\frac{1}{2}} \eta}.$$

If the dielectric constant of methyl alcohol at 25°C. is assumed to be 30 and the values of the other constants are introduced, the limiting slope of the curve obtained when the equivalent conductance Λ^* is plotted against $\sqrt{\gamma^*}$ is given by the equation

$$\alpha^* = 109 + 1.15 w \Lambda^*_\infty$$

provided the discussion is limited to uni-univalent electrolytes. Fraser and Hartley (10) have determined the equivalent conductances of a number of salts of this valence type in methyl alcohol over the range of concentration, $\gamma^* = 0.0001$ to $\gamma^* = 0.002$ and have shown that the square root law is the correct one to explain the change of conductance with concentration. In order to test the interionic attraction theory further it is necessary to compare the limiting slopes calculated by it, using the relation given above, with the results of the experimental work. This comparison is given in table 4. In a number of cases the differences between the theoretical and actual slopes must be considered to be real deviations from the limiting law. It is true, however, that we cannot be absolutely sure with the data now available that the experiments have been made in sufficiently dilute solution.

More recently there has appeared an article by Unmack, Murray-Rust and Hartley (11) in which the conductances of a number of thiocyanates in very dilute methyl alcohol solution have been measured. The results for the thiocyanates of Li, Na, K, Rb, Cs and NH_4, that is, uni-univalent salts, are shown to be in excellent agreement with the Onsager modification of the Debye-Hückel limiting law. In the case of the thiocyanates of Ca, Sr, Ba, and Mg, that is, bi-univalent salts, the limiting slope determined by experiment is always much greater than that calculated using the theory. Indeed, this result might have been predicted from experience with conductance data for water solutions, for in the case of the latter, the uni-univalent and bi-univalent salts obey the limiting law quite well, but when the data for bi-bivalent salts are considered the experimentally determined slopes are always much too high. It can be said with confidence that the chief difficulty rests not with the experimental determination of the mobilities which are required for the calculation of α^*, but with the fact that most electrolytes are "associated" in methyl alcohol solution, even at great dilution.

TABLE 4

Conductance data for electrolytes of type 1-1 in methyl alcohol

$$\alpha_{\text{theor.}}^* = 1.15\, w\, \Lambda_\infty^* + 109$$

$$\alpha_{\text{theor.}} = (1.15\, w\, \Lambda_\infty^* + 109)\, \sqrt{2}, \text{ where } w = 0.5858$$

ELECTROLYTE	Λ_∞^*	$\alpha_{\text{exp.}}$	$\alpha_{\text{theor.}}$	$\alpha_{\text{exp.}} - \alpha_{\text{theor.}}$
LiCl	90.9	223.5	240.8	−17.3
NaCl	97.0	230.5	246.6	−16.1
KCl	105.1	261.6	254.3	7.3
RbCl	108.7	281.5	257.7	23.8
CsCl	113.6	282.8	262.4	20.4
KF	94.0	236.1	243.7	−7.6
KBr	109.4	261.6	258.4	3.2
KI	114.9	260.2	263.6	−3.4
NH_4Cl	111.0	263.8	259.9	3.9
HCl	193.5	367.7	338.5	29.2
$LiNO_3$	100.3	250.3	249.7	0.6
$NaNO_3$	106.5	288.5	255.6	32.9
KNO_3	114.6	345.0	263.3	81.7
$RbNO_3$	118.2	355.0	266.8	88.2
$CsNO_3$	123.0	378.9	271.3	107.6
$AgNO_3$	113.0	451.1	261.8	189.3
NaBr	101.5	240.4	250.9	−10.5
$NaOCH_3$	98.4	222.0	247.9	−25.9
$NaClO_4$	115.1	280.0	263.8	16.2

If associated ions are present the basic assumptions of the interionic attraction theories, mentioned in the introduction, must be modified in any exact treatment. Deviations from Coulomb's law will undoubtedly occur when the distance between two ions becomes small, and they will be especially great in the case of polyvalent ions. It is only assumed that the *principal* forces between the ions are given by Coulomb's law, and the theory does account for the influence of Coulomb's forces upon the mobilities of the ions. But to make the theory exact it is clear that the deviations must also be accounted for, and it will be necessary to determine the manner in which the forces vary as the distances of approach of the ions become smaller. This is definitely a problem of the newer physics.

One may also object to explaining the change of conductance with concentration as due solely to a change in the mobilities of the ions. With "ion pairs" present the conductance should decrease because the number of carriers is decreased as well, and a quantitative theory of conductance will therefore require that a method to measure the "degree of association" be made available. For this purpose the method used by Bjerrum, already referred to, has much to recommend it.

In this discussion no cognizance has yet been taken of the fact that a portion of the discrepancy between theory and experiment may be accounted for by the consideration of second and higher order terms, involving the dimensions of the ions. If the effect of these terms is included an improvement should result, yet it is our belief that this correction will not account for the major part of the deviations.

Conclusion

Methyl alcohol may also be considered to be a "water-like" solvent from the standpoint of the interionic attraction theory of conductance. Deviations between theory and experiment are sometimes marked even in the case of the simplest type of electrolyte in dilute solution, but these may be expected when the discrepancies which are found in water solution are considered. They demonstrate the same inadequacies in the basic assumptions underlying the conductance theory which were found in the case of the activity theory, and which are to be accounted for chiefly by *association* and *solvation* of the ions. The effect of both is to limit the applicability of Coulomb's law to express the interionic forces. The association of ions, prevalent in methyl alcohol solution, also makes it impossible to completely account for the change in conductance with concentration by assuming that only changes in the ionic mobilities need be considered.

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