164. *The Limiting Conductivities of Salts in Non-aqueous Solvents.*

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WHEN Onsager's equation is compared with the results of conductivity measurements in dilute non-aqueous solutions, it is usually found that the slope of the experimental conductivity curve is greater than that predicted, although the agreement sometimes improves at the lowest concentrations. This behaviour can be explained by supposing that ion-pairs are present at finite concentrations, the relative number of these being governed by a mass-action equilibrium. To study the consequences of this hypothesis, the appropriate value for the conductivity of the electrolyte at infinite dilution must be known, and the object of the present note is to describe a way of determining this constant, since Kohlrausch's square-root method, which is usually employed for extrapolating the data, is obviously incompatible with the postulation of partial association.

The dissociation of a binary electrolyte is governed by the expression $f^2\alpha^2C/(1-\alpha)=K$, where f is the mean ion activity coefficient, α the degree of dissociation at concentration C (g.-mols./l.), and K the dissociation constant. If Λ_a is a "corrected" conductivity, defined by the equation $\alpha=\Lambda_a/\Lambda_0$, the mass-action expression becomes $f^2\Lambda^2{}_aC/\Lambda_0(\Lambda_0-\Lambda_a)=K$, or $f^2\Lambda_aC=K{\Lambda_0}^2/\Lambda_a-K\Lambda_0$. This is equivalent to the Kraus transposition of Ostwald's dilution law except that it contains the two corrections required by the interionic attraction theory. In sufficiently dilute solutions, the Onsager and the Debye–Hückel equation can be used to calculate respectively the mobility change and the activity coefficient; and as an approximation, when the degree of association is not high, the two correction terms can be calculated as if the ionic concentration were equal to the total concentration. The activity coefficient is therefore calculated from the equation $-\log f=AC^{\frac{1}{2}}$, where A is the limiting Debye–Hückel slope. Similarly, from the equations $\Lambda/(\Lambda_0-bC^{\frac{1}{2}})=\alpha=\Lambda_a/\Lambda_0$, where b is the Onsager slope, it follows that $\Lambda_a=\Lambda+\Lambda bC^{\frac{1}{2}}/(\Lambda_0-bC^{\frac{1}{2}})$; if the degree of association is not high, $\Lambda_a=\Lambda+bC^{\frac{1}{2}}$; b can be determined with sufficient accuracy from an approximate Λ_0 value. These calculated values being used, $f^2\Lambda_aC$ is plotted against $1/\Lambda_a$, and the resultant straight line when extrapolated to zero concentration gives $1/\Lambda_0$.

Obviously the approximation made in this derivation, that the ionic is equal to the total concentration, will lead to errors that are greater the weaker the electrolyte, but these do not seriously affect the Λ_0 value derived owing to a compensation of errors. In calculating $f^2\Lambda_aC$, the value taken for f^2 is too low and that for Λ_a is too high by almost as great a proportion. The term $1/\Lambda_a$ is also slightly too low, since Λ is over-corrected, but the error is practically proportional to the value of $f^2\Lambda_aC$ so long as the degree of association is not very high. The correct limiting value is obtained by extrapolation so long as the method is limited to data for which the degree of dissociation is greater than 70% (in solvents of very low dielectric constant the permissible range will be more restricted); for weaker electrolytes, the true Λ_0 value may be obtained by carrying out a second approximation in which the approximate value of αC is substituted for C in the equations. The graph obtained should not be used to estimate K, since its slope will not be exactly that required by the theoretical equation.

The methods of extrapolation that have been used in recent work are those of Kohlrausch and of Ferguson and Vogel, and an approximate method of plotting the conductivity against the two-thirds power of the concentration. There is no object in comparing these methods with the new, since all rest on different assumptions and naturally lead to different values. It is often claimed that a purely empirical method of extrapolation is superior to one based on preconceptions as to the behaviour of the system investigated, but this is illogical; in both cases the value derived may be right or wrong, and the only respect in which the empirical method gains in expediency is that it is the less easily discredited, if wrong. Onsager, however, has suggested (*Physikal. Z.*, 1927, **28**, 277) a method resting on similar grounds to the one now proposed, and a comparison of the two is of value. Onsager's method is the easier to apply, but, as will be shown, it involves such extensive approximations as to be applicable only to very highly dissociated electrolytes.

There are two ways in which the new method can be tested. First, a correct extrapolation method must satisfy the law of the independent migration of ions; if, therefore, the method gives additive Λ_0 values where the older methods failed, this supports the underlying assumption of an equilibrium between molecules that do not conduct and ions for which the limiting Debye–Onsager equations are valid. Secondly, the Λ_0 value obtained can be used to calculate from each measured conductivity the corresponding value of K, and the degree of constancy of these will show to what extent the graphical method fulfils its function, *i.e.*, what errors are introduced by the approximations. First, we shall apply the method to aqueous solutions for which the true Λ_0 values are already known.

Iodic acid in water at 25°. Kraus and Parker's figures (*J. Amer. Chem. Soc.*, 1922, **44**, 2429) show that there is little association ($<0.03\%$) in the range of concentration ($<0.002N$) for which Onsager's equation is valid. Both the new method and Onsager's method give $\Lambda_0=391.1_5$, in agreement with the value calculated from the mobilities (390.9 ± 0.3).

o-*Nitrobenzoic acid in water at* 25°. This is a much weaker electrolyte. Kendall's data (J., 1912, **101**, 1275) from 0·001N to 0·016N were used, and for these the degree of dissociation varies from 88% to 47%. The line obtained showed curvature at degrees of dissociation less than 60% but at lower concentrations the straight line led to $\Lambda_0 = 384·5$. The value calculated from the mobilities is 383·5. For this electrolyte Onsager's method fails to yield a straight line, the square-root method leads to a value well over 400, and Kraus's method for weak electrolytes (*J. Amer. Chem. Soc.*, 1913, **35**, 1315) gives $\Lambda_0 = 379·1$. For an electrolyte of this strength, the new method is the most satisfactory, though for accurate work it would be better to carry out the second approximation.

Silver nitrate in methyl alcohol at 25°. Methyl alcohol is the only solvent apart from water in which Λ_0 values can be checked by independently determined mobilities. Application of the method to Frazer and Hartley's figures for silver nitrate (*Proc. Roy. Soc.*, 1925, *A*, **109**, 351) yields the value $\Lambda_0 = 111·0$, whereas the value obtained by the square-root method was 112·95. That the first of these is correct is shown by the further measurements of Copley and Hartley (J., 1930, 2488) on silver perchlorate. This salt is completely dissociated, and the square-root method is therefore applicable; it yields 50·3 for the mobility of the silver ion, and combination of this with Frazer and Hartley's value 60·8 for the nitrate ion gives 111·1 for the theoretical limiting conductivity of silver nitrate. Onsager's method for this salt gives $\Lambda_0 = 110·5$, which is certainly too low.

Benzonitrile solutions. In his work on salts in benzonitrile (J., 1928, 3270), Martin used two methods of extrapolation, the square-root method and that of Ferguson and Vogel, and with the aid of the Λ_0 values so obtained he determined the dissociation constants of his salts on the basis of the Debye–Onsager equations. His results for two salts are as follows:

$K \times 10^3$ at dilution (litres):

Salt.	20,000.	10,000.	5,000.	2,000.	1,000.
KI	16	13	11	9	9
$AgNO_3$	0·31	0·36	0·40	0·40	0·40

There is a pronounced drift in the values at the lowest concentrations, as would be expected if erroneous Λ_0 values had been used. Moreover, the variation in each case is in the expected direction, since the square-root method used for silver nitrate gives, for incompletely dissociated electrolytes, Λ_0 values that are too high and consequently K values that fall off with decreasing concentration, whilst the Ferguson and Vogel method, used for potassium iodide, will normally have the reverse effect.

The new method applied to potassium iodide gives $\Lambda_0 = 51·31$, as compared with 52·12 from the square-root rule and 51·11 by Ferguson and Vogel's method. The subsequent calculation of the dissociation constant is shown in the following table, in which Λ represents the measured conductivity at dilution v litres, α is the calculated degree of dissociation, and K the true dissociation constant. The constancy is extremely good in view of the high dilutions.

Potassium iodide in benzonitrile; $\Lambda_0 = 51·31$.

v	39,186	14,774	8,806	4,543	3,256	1,185
Λ	50·45	49·70	49·29	48·30	47·60	44·40
α	0·996	0·991	0·989	0·980	0·973	0·936
$K \times 10^3$	6	6·5	8·8	8·9	8·6	8·2

For silver nitrate, the Ferguson–Vogel method is inapplicable, the square-root extrapolation gives $\Lambda_0 = 52·18$, and the new value is 50·20. The dissociation constant is recalculated below:

Silver nitrate in benzonitrile; $\Lambda_0 = 50·20$.

v	41,278	21,972	11,680	7,559	3,276
Λ	47·28	45·79	42·88	40·17	34·72
α	0·954	0·929	0·8750	0·8240	0·7213
$K \times 10^3$	0·45	0·51	0·472	0·449	0·475

The agreement again is very good for this much weaker electrolyte, showing that the extrapolation method satisfactorily fulfils its purpose. Onsager's graphical method for this salt gives $\Lambda_0 = 49{\cdot}52$, $K \times 10^3 = 0{\cdot}79$; this K value is far too high, since the drastic approximations of Onsager's method make it unsuitable for so weak a salt.

The method described in this paper has been applied during the last two years to numerous conductivity measurements, and it is hoped shortly to present the results.

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