

### 875. *The Electrolyte Type of Ionized Complexes.*

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A method is described for the determination of electrolyte type in aqueous and non-aqueous solvents.

THE behaviour of simple electrolytes in dilute solutions can be easily understood in terms of the Debye-Hückel or Onsager equation. These have been shown to agree well with the experimental results obtained for strong electrolytes in aqueous media, as well as in some non-aqueous solvents.<sup>1</sup> Conductances of solutions are widely used, particularly in co-ordination chemistry, for the determination of electrolyte type (uni-uni-valent, uni-bivalent, etc.). In most cases, measurements are made at one concentration (*ca.*  $10^{-4}$  M), and by using an assumed molecular weight, the molar conductance ( $\Lambda_M$ ) is calculated; this value is then compared to  $\Lambda_M$  of known types of electrolytes. It is then concluded that the ion type of the complex is the same as that of the known type that most closely corresponds in its value of  $\Lambda_M$ . However, the problem that arises with ionized complexes with the general formula  $[ML_n]_z[X]_{yz}$  is that of determining the molecular complexity  $z$  in solution. Unfortunately, neither the molar conductivity  $\Lambda_m$  nor the equivalent conductivity  $\Lambda_e$  independently determines  $z$ . On the other hand, the *change* in  $\Lambda_e$  with concentration is a direct function of the charge on the ions involved and therefore of  $z$ . This property has been used previously to establish the charges of various

<sup>1</sup> Prutton and Maron, "Fundamental Principles of Physical Chemistry," The Macmillan Co., New York, 1951, p. 460.

polyanions in aqueous solutions. This method has not, however, been generally applied to metal complexes in aqueous, and particularly non-aqueous, solvents. The use of this property in establishing the charge of ionized complexes in solution is the subject of this Paper.

In order to calculate the equivalent concentration  $c$  and the equivalent conductivity  $\Lambda_e$  the equivalent weight of the complex must be known. For this reason, it is usually convenient to choose complexes containing univalent cations or anions, such as  $\text{Na}^+$ , or  $\text{ClO}_4^-$ , that do not form complexes. For those complexes where the cation or anion does not enter into the co-ordination sphere of the complex, the equivalent weight is independent of the molecular complexity  $z$ . For example, the equivalent weight of  $[\text{ML}_n]^{2+}[\text{ClO}_4]_2^-$  is 1/2 the formula weight, while the equivalent weight of  $[\text{M}_2\text{L}_{2n}]^{4+}[\text{ClO}_4]_4^-$  is  $2 \times$  the formula weight/4 or 1/2 the formula weight. Examples of complexes in which the anion or cation enters into the co-ordination sphere of the complex will be discussed below.

In some cases, the value of  $\Lambda_0$  can be used to establish the equivalent weight. For example, the complex  $\text{ML}_n\text{Cl}_2$  could be ionized as either  $[\text{ML}_n\text{Cl}]^+\text{Cl}^-$  or  $[\text{ML}_n]^{2+}\text{Cl}_2^-$ . If the value of  $\Lambda_0$  as calculated for  $[\text{ML}_n\text{Cl}]^+\text{Cl}^-$  was  $120 \text{ ohm}^{-1}$  (in water), the value of  $\Lambda_0$  as calculated for  $[\text{ML}_n]^{2+}\text{Cl}_2^-$  would be  $240 \text{ ohm}^{-1}$ . This would be much too high a value for  $\Lambda_0$  in water, and thus one would conclude that the complex was in fact  $[\text{ML}_n\text{Cl}]^+\text{Cl}^-$ . On the other hand, if the values of  $\Lambda_0$  had been 75 and  $150 \text{ ohm}^{-1}$ , respectively, either value would be acceptable, and some other means would be necessary for distinguishing between these possibilities (see below).

The equation representing the conductivity as a function of the equivalent concentration is commonly written in the form  $\Lambda_e = \Lambda_0 - B\sqrt{c}$ . In order to present the values for different electrolyte types on a single graph,  $\Lambda_0$  was determined for each compound. This then allowed the use of the above equation in the form:  $\Lambda_0 - \Lambda_e = B\sqrt{c}$ . Fig. 1 shows the results of such a plot for different known types of electrolytes in water.<sup>2</sup> It is clear from this Figure that, although there is some variation between the slopes of different electrolytes of the same ion type, the ions of one type can easily be distinguished from those of another. This variation in slope within a group of similar electrolytes is expected since  $B$  is a function of  $\Lambda_0$ .<sup>1</sup>

Electrolytes in dilute solutions also behave similarly in suitable non-aqueous solvents such as methanol and nitromethane. The conductivity of selected 1 : 1, 2 : 1, and 3 : 1 electrolytes in nitromethane is shown in Fig. 2. These materials were selected as model compounds by using the following criteria: (1) the ions formed should be inert to chemical reactions that would lead to ions with other charges; (2) the ions should be large and spherical in order to decrease ion-pair formation. The concentration at which ion pair formation becomes important is that concentration where the plot of  $\Lambda_e$  against  $\sqrt{c}$  deviates markedly from linearity; (3) the compounds should be reasonably soluble in the solvent being used. This is one of the greatest difficulties in non-aqueous solvents, since compounds containing the more highly charged ions are usually insoluble, or only slightly soluble, in these solvents.

The solvent should be unreactive, have a high dielectric constant, and especially have a low viscosity. Nitromethane was chosen in preference to nitrobenzene because of its lower viscosity. The slope in nitrobenzene is about 65 for a 1 : 1 electrolyte,<sup>3</sup> while in nitromethane the value is about 200 (Fig. 2). A larger slope gives greater sensitivity in these dilute solutions. Some solvents that the authors and others have found to be useful, along with the values found for the slopes for various suitable standard electrolytes, are listed in Table 1; this is not intended to be an exhaustive list, but merely to indicate that this behaviour is general for strong electrolytes in ionizing solvents.

<sup>2</sup> These data are taken from (a) "The International Critical Tables," Vol. VI, The McGraw-Hill Book Co., Inc., New York, N.Y., 1929; and (b) "Handbuch der Anorganische Chemie," Kobalt B, Vol. 58, Verlag Chemie, Berlin, Germany, 1930.

<sup>3</sup> Taylor and Kraus, *J. Amer. Chem. Soc.*, 1947, **69**, 1731.

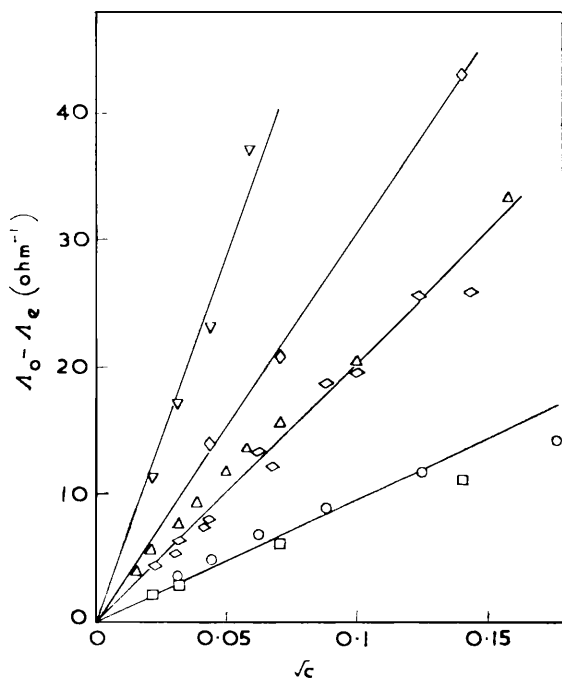
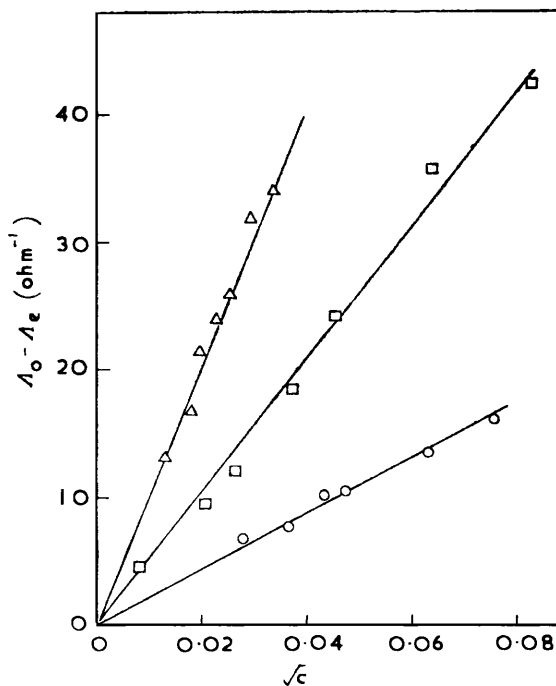


FIG. 1. The behaviour of  $\Lambda_0 - \Lambda_e$  for various types of electrolytes in water.

- $\text{Co}(\text{NH}_3)_4(\text{NO}_2)_2\text{Cl}$ ,
- $\text{NaCl}$ ,
- ◇  $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{Cl}_2$ ,
- △  $\text{CaCl}_2$ ,
- ◇  $[\text{Co}(\text{NH}_3)_4]\text{Cl}_3$ ,
- ▽  $\text{K}_4[\text{Fe}(\text{CN})_6]$ .

FIG. 2. The behaviour of  $\Lambda_0 - \Lambda_e$  for various types of electrolytes in nitromethane

- $\text{Na}[\text{BPh}_4]$ ,
- $[\text{Ni}(o\text{-phenan})_3][\text{ClO}_4]_2$ ,
- △  $[\text{Co}(\text{bipy})_3][\text{ClO}_4]_3$ .



In order to establish the ion type of a compound of unknown complexity, it is only necessary to measure the equivalent conductivity as a function of the equivalent concentration in a suitable solvent and compare this to similar values for complexes of known ion type. In order to minimize the variation in the slope  $B$ , the standard compound should

TABLE 1.

 $\Lambda_0 - \Lambda_e/\sqrt{c}$  for standard iron types in various solvents.

Ion type	Compound	Solvent			Ref.
		Water	Methanol	Nitromethane	
1 : 1	[Bu <sup>n</sup> <sub>4</sub> N]Br	—	256	183	
	Na[BPh <sub>4</sub> ]	—	—	216	
	KCl	92	261	—	2
2 : 1	[Ni( <i>o</i> -phenan) <sub>3</sub> ]Cl <sub>2</sub> <sup>a</sup>	—	514	420	
	[Ni( <i>o</i> -phenan) <sub>3</sub> ][ClO <sub>4</sub> ] <sub>2</sub>	—	513	465	
	[Co(NO <sub>2</sub> )(NH <sub>3</sub> ) <sub>5</sub> ]Cl <sub>2</sub>	185	—	—	2
3 : 1	[Pd(Ph <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> PPh <sub>2</sub> ) <sub>2</sub> ][ClO <sub>4</sub> ] <sub>2</sub>	—	—	510	
	[Co(bipy) <sub>3</sub> ][ClO <sub>4</sub> ] <sub>3</sub>	—	—	1020	
4 : 1	K <sub>3</sub> [Fe(CN) <sub>6</sub> ]	285	—	—	2
	K <sub>4</sub> [Fe(CN) <sub>6</sub> ]	526	—	—	2

<sup>a</sup> As the tetrahydrate.

TABLE 2.

Ion type as determined by conductivity measurements.

Compound	Solvent	$\Lambda_0$ (ohm <sup>-1</sup> )	Slope	Ion type	Ref.
[Pd <sub>2</sub> {PEt <sub>2</sub> Ph <sub>2</sub> (Ph <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> PPh <sub>2</sub> ) <sub>2</sub> ][BPh <sub>4</sub> ] <sub>2</sub>	Me·NO <sub>2</sub>	76·0	410	2 : 1	4
[Pd <sub>2</sub> {PEt <sub>2</sub> Ph <sub>2</sub> ( <i>o</i> -phenan) <sub>2</sub> ][BPh <sub>4</sub> ] <sub>2</sub> .....	Me·NO <sub>2</sub>	88·0	392	2 : 1	4
[Pd <sub>2</sub> {PPh <sub>2</sub> en <sub>2</sub> ][BPh <sub>4</sub> ] <sub>2</sub> .....	Me·NO <sub>2</sub>	86·4	430	2 : 1	4
[Pd <sub>2</sub> {PPh <sub>2</sub> Ph <sub>2</sub> (Ph <sub>2</sub> PC <sub>2</sub> H <sub>4</sub> PPh <sub>2</sub> ) <sub>2</sub> ][ClO <sub>4</sub> ] <sub>2</sub>	Me·OH	120·9	552	2 : 1	4
[Co <sub>2</sub> N <sub>2</sub> O <sub>2</sub> (NH <sub>3</sub> ) <sub>10</sub> ][NO <sub>3</sub> ] <sub>4</sub> .....	H <sub>2</sub> O	168·0	538	4 : 1	5
[Ru <sub>2</sub> Cl <sub>3</sub> {PEt <sub>2</sub> Ph <sub>2</sub> }]Cl .....	Me·NO <sub>2</sub>	85·5	151	1 : 1	
[Ru <sub>2</sub> Cl <sub>3</sub> {PEt <sub>2</sub> Ph <sub>2</sub> }[ClO <sub>4</sub> ]] .....	Me·OH	104·0	288	1 : 1	

have a value of  $\Lambda_0$  similar to that of the unknown. For example, it is preferable to compare a complex perchlorate with another perchlorate, rather than with a chloride, tetraphenylborate, etc. This method has been used previously to establish most of the compounds listed in Table 2.<sup>4,5</sup> Ionic complexes of the type [Ru<sub>2</sub>Cl<sub>3</sub>(PEt<sub>2</sub>Ph)<sub>6</sub>]X (X = 3I, ClO<sub>4</sub>, etc.) are known, and the ion type was determined by measurements carried out at a single concentration.<sup>6</sup> The conductivities have now been obtained over a range of concentration and have confirmed the previous conclusion that these complexes are 1 : 1 electrolytes (see Table 2).

This method will also yield information on the more complex problem of partial dissociation,<sup>7</sup> which can be treated in a way analogous to that of the dissociation of weak acids in water. Another somewhat more difficult problem is that of complexes of the type ML<sub>n</sub>Cl<sub>2</sub> described above. Even this problem can be at least partially solved by the measurement of the conductivity over a range of concentration. In the example cited above, if the complex in solution actually was [ML<sub>n</sub>Cl]<sup>+</sup>Cl<sup>-</sup>, while the complex was assumed to be [ML<sub>n</sub>]<sup>2+</sup>Cl<sub>2</sub><sup>-</sup>, the slope would be too small by a factor of 1/√8, and thus would appear to be less than a 1 : 1 electrolyte. In general, this type of problem can better be solved in conjunction with chemical methods, such as making other derivatives or analogues.

## EXPERIMENTAL

**Materials.**—The compounds [Bu<sup>n</sup><sub>4</sub>N]Br, Na[BPh<sub>4</sub>], and KCl were obtained from the Fisher Scientific Company and were used without further purification.

The tris(*o*-phenanthroline)nickel salts were prepared by adding excess of *o*-phenanthroline to a concentrated aqueous solution of the nickel salt. The perchlorate was precipitated as white crystals, which were filtered off and dried (Found: C, 53·7, 53·8; H, 3·2, 3·1; Cl, 8·8, 8·9; N, 10·1, 10·2; Ni, 6·9, 6·55; O, 17·7, 17·3. C<sub>36</sub>H<sub>24</sub>Cl<sub>2</sub>N<sub>6</sub>NiO<sub>8</sub> requires C, 54·2; H, 3·0; Cl, 8·9;

<sup>4</sup> Hayter, *J. Amer. Chem. Soc.*, 1962, **84**, 3046; Hayter and Humiec, *Inorg. Chem.*, 1963, **2**, 306.<sup>5</sup> Feltham, *Inorg. Chem.*, 1964, **3**, 1038.<sup>6</sup> Chatt and Hayter, *J.*, 1961, 896.<sup>7</sup> Harris, Nyholm, and Phillips, *J.*, 1960, 4379.

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N, 10.5; Ni, 7.35; O, 16.0%). The chloride crystallized on evaporation of the solution and was recrystallized from ethanol-acetone, being obtained as pink crystals of the tetrahydrate (Found: C, 57.9; H, 4.9; Cl, 9.5; N, 11.4. Calc. for  $C_{30}H_{32}Cl_2N_6Ni_4O_4$ : C, 58.25; H, 4.35; Cl, 9.55; N, 11.3%).

$[Pd(Ph_2PC_2H_4PPh_2)_2][ClO_4]_2$  was prepared by the method of Chatt, Hart, and Watson,<sup>8</sup> the cation being precipitated by the addition of an excess of aqueous sodium perchlorate. Crystallization from nitromethane-methanol gave prisms (Found: Cl, 6.2; P, 10.9; Pd, 8.9.  $C_{52}H_{48}Cl_2O_8P_4Pd$  requires: Cl, 6.4; P, 11.25; Pd, 9.6%).

The ruthenium complexes were prepared and purified as previously described.<sup>6</sup>

Distilled de-ionized water, spectral-grade nitromethane (Fisher Scientific Co.), and absolute methanol (J. T. Baker Chemical Co.) were used as solvents.

*Apparatus.*—The conductivities were measured with an Industrial Instruments Inc. conductivity bridge, model RC-16B2. The cell constant was determined by use of a standard aqueous solution of potassium chloride.

*Treatment of Results.*—At least five separate measurements of the conductivity of each compound were made in the concentration range  $10^{-2}$ – $10^{-5}$ M. The equivalent conductivity  $\Lambda_e$  was first plotted graphically as a function of  $\sqrt{c}$ , where  $c$  is the equivalent concentration. Then the conductivity  $\Lambda_e$  was extrapolated to infinite dilution to determine  $\Lambda_0$ . Next,  $\Lambda_0 - \Lambda_e$  was plotted as a function of  $\sqrt{c}$ . From this plot, the slopes of various electrolyte types can be easily compared.

#### CONCLUSIONS

Although the measurement of the molar conductivity at one or two concentrations has been of demonstrated value, there are inherent limitations to such measurements. The most severe restriction is the need for an independent determination of the molecular weight or equivalent weight. This difficulty can be overcome by using the method described here. For all but certain special cases indicated above, the measurement of  $\Lambda_0 - \Lambda_e$  as a function of concentration will unequivocally determine the ion type as well as the equivalent weight and molecular complexity.

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<sup>8</sup> Chatt, Hart, and Watson, *J.*, 1962, 2537.