318. *The Specific Effect of the Solvent in Electrolytic Dissociation.*

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Electrolytes may be conveniently arranged in three groups, according to the adequacy with which their behaviour in dilute solution has been explained. The first group comprises completely ionised electrolytes, the behaviour of which is satisfactorily explained by the Debye–Hückel–Onsager interionic attraction theory. The second group, incompletely ionised electrolytes, may be subdivided into :

(1) Acids, for which the shape of the conductivity–concentration curve in solvents of high dielectric constant is defined by mass action and interionic attraction, and the extent of ionisation by structural considerations, the Brönsted–Lowry theory, and the variation of ionic activity with dielectric constant (Brönsted, *J. Physical Chem.*, 1926, **30**, 777; Hammett, *J. Amer. Chem. Soc.*, 1928, **50**, 2666; Halford, *ibid.*, 1931, **53**, 2939; Wynne-Jones, *Proc. Roy. Soc.*, 1933, *A*, **140**, 440).

(2) Salts, mainly of the substituted ammonium type, for which the extent of ionisation is more or less defined by the dielectric constant of the solvent (Walden, "*Elektrochemie nichtwässerige Lösungen*," 1924, p. 355; *Z. physikal. Chem.*, 1930, **147**, 1; Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 21, 1019), but which may exhibit conductivity curves of abnormal shape in solvents of low dielectric constant.

(3) Salts in which the ions depart from inert-gas structure, for which the shape of the conductivity curve in water is determined largely by incomplete dissociation and auto-complex formation (Davies, " Conductivity of Solutions," 1933, p. 190). The extent of ionisation of this class of salt must be governed mainly by specific ionic and solvent effects.

The third group consists of abnormal electrolytes, the behaviour of which has been explained only by rejecting the ordinary electrolytic dissociation theory (Kendall, *Proc. Nat. Acad. Sci.*, 1921, **7**, 56; Fredenhagen, *Z. physikal. Chem.*, 1931, **152**, 321, etc.).

It is possible that the study of salts containing ions of non-inert gas structure will throw considerable light on the whole problem of electrolytic dissociation. Riley and Fisher (J., 1929, 2006) suggested that the tendency of the cation to act as an acceptor of electrons and the co-ordinating tendency of the anion were two major factors influencing degree of ionisation. This view has been supported by subsequent work (Riley, J., 1930, 1642; Ives and Riley, J., 1931, 1998; 1932, 1766) showing the relationship of dissociation constants of salts of the type MA with the nature of the cation and with the co-ordinating tendency of the anion, as measured by the stability of the corresponding complex anion $[M(A)_x]'$. The present work is concerned, not only with these two factors, but also with the part played by the solvent.

Riley and Fisher (*loc. cit.*) observed that copper malonate was a very weak electrolyte compared with zinc malonate, whereas copper and zinc sulphates were electrolytes of equal strength. This has been attributed (Ives and Riley, J., 1931, 1998) to the powerful co-ordinating tendency of the malonate ion, which, with the help of the high localisation of charge on the copper ion, is able to break down the sheath of water molecules normally solvating the cation. The abnormality of copper malonate therefore might be expected to disappear in a solvent providing a more stable solvated sheath. The search for such a solvent is limited by solubility, but this difficulty can be overcome to some extent by adding a suitable second liquid to the aqueous solution and observing the trend of the conductivity changes which may occur. Pyridine has been selected for this purpose, since it has a high co-ordinating tendency (as shown by the stability of pyridino-complex salts) and is completely miscible with water. The effects of pyridine additions to aqueous solutions of copper malonates, oxalate and sulphate, zinc malonate and sulphate, and nickel malonate and sulphate have been studied, and the results, which lend considerable support to the above views, are discussed in a later section.

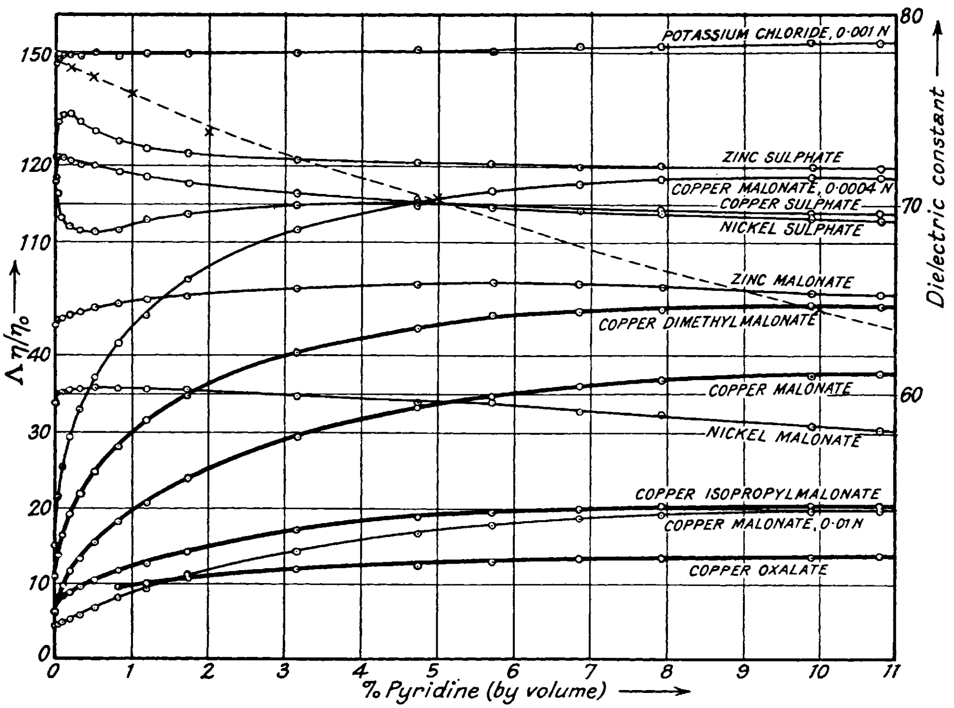
EXPERIMENTAL.

A solution of the salt under investigation was titrated with a second solution, of the same molarity with respect to the salt, containing a known concentration of pyridine. The aqueous salt solutions were made up by weight in a 1 l. wide-mouthed Pyrex flask and, by means of previously determined density data, adjusted to have an exact concentration at 25°. The flask was fitted with a stopper carrying a dipping conductivity cell, a thermometer, and a burette, and was immersed in a thermostat at 25° ± 0·01°. For each titration, two aqueous pyridine solutions were made up by volume at room temperature, one containing 5% of pyridine (at 25°) for the detailed study of the early stages of the titration, and the second containing 40% of pyridine (at 25°).

The bridge and the method of purification of the salts have already been described (Ives and Riley, *loc. cit.*). The pyridine was purified by a preliminary distillation from potassium hydroxide and finally by two distillations from calcium oxide, head and tail fractions being rejected.

After each addition of the aqueous pyridine solution from the burette, the conductivity flask was shaken and a conductivity reading taken when sensible constancy had been obtained. Accuracy of measurement was not favoured by the conditions of the experiments, but was sufficient for the present purposes. A solvent correction was applied by subtracting the specific conductivities observed during a similar titration using water and pyridine alone, the maximum correction being of the order of $8{\cdot}0 \times 10^{-6}$ reciprocal ohm. Whilst this cannot be considered strictly accurate, such a correction is probably of the right order, since most of the solutions examined contained a very large excess of pyridine over salt. Equivalent conductivities were calculated and corrected for the relative viscosity of the solvent, and are shown graphically in the figure, where the concentration of salt is $0{\cdot}002N$ unless otherwise stated. Titrations at normalities of 0·01 and 0·0004 were also carried out with similar results to those at 0·002 : some of these curves also are shown in the figure.

The initial stages of the curve for copper oxalate are missing owing to the practically complete insolubility of this salt in water. It is, however, soluble in water containing a small amount of pyridine, so the curve could be obtained without difficulty. The initial stages of the curves for the copper malonates were almost linear, and an extrapolation of the oxalate curve to zero pyridine concentration was made in order to estimate the dissociation of this salt in water. To obtain as accurate a result as possible, some measurements were made in a cell of more satisfactory type (Cell II; Ives and Riley, *loc. cit.*), all solutions being made up by weight and containing as low a pyridine concentration as 0·1%. Owing to the exceedingly small conductivities involved and the uncertainty of the solvent correction, little more could be done than fix an upper limit of the dissociation constant, which was obtained as $0{\cdot}14 \times 10^{-5}$. This value, considerably less than that of the malonate ($0{\cdot}51 \times 10^{-5}$), is in conformity with Riley and Fisher's views, since oxalato-complex salts are more stable than the corresponding malonato-salts (Riley, J., 1929, 1307), indicating a higher co-ordinating tendency, as might be expected from the greater localisation of charge on the carboxyl groups caused by the absence of the buffering action of the median methylene group.



Discussion.

The most striking feature of the results is the increase in the conductivity of the copper malonate solutions with increasing concentration of pyridine. Although the results have been corrected for the viscosity of the solvent and hence for the changes of mobility of inert ions (as shown by the constancy of $\Lambda\eta/\eta_0$ for potassium chloride), the correction will only be partial for those cases where the solvent has a definite co-ordinating action on the cation. The increase in conductivity of the copper salts, therefore, almost certainly represents a still greater increase in ionisation. Such mobility changes have been neglected in working out approximate degrees of dissociation in the following text, but this omission does not affect the arguments concerning the copper salts alone.

It was thought that the decrease observed in the conductivity of the nickel malonate solutions was probably due to such mobility changes; the highly dissociated sulphates of the three metals were therefore examined. The sharp decrease shown by copper sulphate indicates an initial fall in the mobility of the copper ion, followed by a slight increase due to increasing ionisation, small in extent owing to the already extensive dissociation of the salt. The steady decrease shown by nickel sulphate may be interpreted as due to a decrease in mobility, any increase in ionisation being so small as to be completely masked. Zinc sulphate was found to be slightly hydrolysed in the presence of pyridine, but after the resulting initial rise, a sensibly constant value of $\Lambda\eta/\eta_0$ was obtained.

These results indicate that, if a complete correction for changes of ionic mobility were possible, it is likely that copper malonate would show a still larger increase in ionisation, nickel malonate an appreciable increase, and zinc malonate a small increase.

It may be suggested that, since the addition of pyridine to a solution of copper malonate causes the formation of a complex salt (compare Koch, J., **1931**, 1418; Auméras and Tamisier, *Bull. Soc. chim.*, 1933, **53**, 97), and since all complex salts that have been studied by the conductivity method are highly ionised, an increase in ionisation is only to be expected. This may be so, but it is nevertheless a striking fact that the conductivities of copper, nickel, and zinc malonates in 10% aqueous pyridine bear a relationship to each other similar to that between the conductivities of the corresponding sulphates in water. This is shown in Table I, giving approximate degrees of dissociation in 0·01*N*-solution. The values for the sulphates have been taken from Landolt–Börnstein's "Tabellen," and, since they are derived from conductivity ratios, are only approximately correct, but are probably reliable relatively (thus, according to Cowperthwaite, *Trans. Faraday Soc.*, 1933, **29**, 593, zinc sulphate is completely dissociated in 0·01*M*-solution).

TABLE I.

Salt.	Solvent.	% Dissociation.	Salt.	Solvent.	% Dissociation.
Copper malonate ...	Water	3·7	Zinc malonate	10% Aq. pyridine	20
Nickel malonate ...	,,	14·3	Copper sulphate ...	Water	62
Zinc malonate	,,	20·2	Nickel sulphate ...	,,	60
Copper malonate ...	10% Aq. pyridine	17	Zinc sulphate	,,	64
Nickel malonate ...	,,	13			

It may be suggested, by analogy, that the high conductivity of copper sulphate in water is due to the formation of a complex salt, and that the solvation of ions may, in general, vary between the limits of definite complex formation and the mere orientation of solvent dipoles round the charged ion (compare Hughes and Hartley, *Phil. Mag.*, 1933, **15**, 610).

The suggestion regarding the breaking down of the solvated sheath of the copper ion in aqueous solutions of copper malonate (Ives and Riley, *loc. cit.*) is supported in the manner expected, and an attempt is now made to express this phenomenon in a manner capable of more general application.

It is believed that the behaviour of at least this class of electrolyte can be expressed in terms of the electron-accepting tendency of the cation and the co-ordinating tendencies of the anion and of the solvent. These three factors must be considered together, and their mode of operation is suggested under the following headings.

(1) If the co-ordinating tendency of the anion is greater than that of the solvent, dissociation will tend to be small; if the co-ordinating tendency of the solvent is the greater, it will tend to be large. The extent to which this competition between the anion and the solvent is effective will depend upon the electron-accepting tendencies of the cation.

(2) If the anion has the greater co-ordinating tendency, the differences in the degrees of ionisation of a series of salts with a common ion due to the specific properties of the other ion will be apparent.

(3) If the solvent has the greater co-ordinating tendency, the differences in the degrees of ionisation of a series of salts (*a*) with a common anion may more or less completely disappear owing to the stable solvation of the various cations, (*b*) with a common cation (which will be stably solvated) may still be apparent but to a small or vanishing extent on account of the recessive part played by the anions in controlling the ionisation.

The similarity of this scheme to that suggested by Hunt and Briscoe (*J. Chem. Education*, 1929, **6**, 1716) for acids, and, in particular, to the Brönsted–Lowry theory of acids (Brönsted, *Rec. trav. chim.*, 1923, **42**, 718; Lowry, *Chem. and Ind.*, 1923, **42**, 43), will be at once apparent, and it is, indeed, likely that a theory which has been applied so successfully to one class of weak electrolytes should have some bearing on another class of weak electrolytes. The analogy will also be seen with the so-called "levelling effect" of water on the strengths of acids (Hantzsch, *Ber.*, 1925, **58**, 612; Conant and Hall, *J. Amer. Chem. Soc.*, 1927, **49**, 3062;

Hammett, *loc. cit.*; Hantzsch and Voigt, *Ber.*, 1929, **62**, 975) and with the differentiating solvents of Walden and Birr (*Z. physikal. Chem.*, 1933, **163**, 263).

In Table II approximate degrees of dissociation for some malonates and sulphates in 0·01*N*-aqueous solution are shown. The co-ordinating tendency of the malonate ion is much greater than that of water, and the individual differences due to the different cations are thus very marked; the co-ordinating tendency of the sulphate ion is less than that of water and the individual differences are lost.

TABLE II.

Cation	Mg	Cd	Zn	Ni	Cu
% Dissociation: malonate	46·7	34	20·2	14·3	3·7
sulphate	67	61	64	60	62

It is apparent from the figure that the copper salts show markedly different behaviour on titration with pyridine, and in Table III approximate degrees of dissociation in 0·002*N*-aqueous and 10% aqueous pyridine solution are shown.

TABLE III.

	% Dissociation.	
Copper salt.	In water.	In 10% aqueous pyridine.
Dimethylmalonate	8·1	44
Malonate	4·9	33
*iso*Propylmalonate	4·1	20
Oxalate	2·6	11

(shown by heavy lines in the figure)

It will be seen that the ratio of the dissociation of the oxalate to that of the *iso*propylmalonate in water is almost unaltered in the pyridine solution, that between the *iso*propylmalonate and the malonate greatly increased, and between the malonate and the dimethylmalonate reduced. The suggested interpretation of these results is as follows. The co-ordinating tendency of 10% aqueous pyridine lies somewhere in the region between those of the *iso*propylmalonate and the malonate ions, being slightly greater than those of the malonate and the dimethylmalonate and slightly less than those of the *iso*propylmalonate and the oxalate. The latter two salts therefore retain their difference, whereas the former are beginning to lose their specific characteristics. In other words, the same relationship exists, to a lesser extent, between copper malonate and copper *iso*propylmalonate in aqueous pyridine as that between copper sulphate and malonate in water.

It has been pointed out (Riley, private communication) that the assignment of a definite co-ordinating tendency to a solvent (particularly a mixed one) is hardly permissible, except possibly under rigidly defined conditions. Many factors must come into play, the chief of which is statistical, involving the relative probabilities of the occurrence of suitable conjunctions of ions and molecules for the formation of undissociated molecules and stable ion–solvent complexes, in relation to the prevailing conditions of concentration of the respective species. A further factor may be the *type* of stability of the solvated ion. It may be that the removal of one solvent molecule from the co-ordinated sheath is followed by an immediate loss of stability of the whole sheath.

In these arguments it has also been tacitly assumed that the ions associate to form simple molecules. Actually this process must be followed by the formation of auto-complexes, but since the same factors determine the stability of the latter, this probably does not invalidate the arguments. In spite of these complications, it is believed that the relationships suggested are true.

On the basis of this theory, a high degree of dissociation may be due to two causes:

(*a*) Inertness of the cation, the anion having a greater co-ordinating tendency than the solvent. Here the specific characteristics of the ions will have full play, and the individual differences due to the different anions will be apparent. Thus, although the zinc malonates as a class are much stronger electrolytes than the copper malonates, individual differences due to different substituents are just as marked (Ives and Riley, J., 1931, 1998).

(*b*) The greater co-ordinating tendency of the solvent as compared with that of the anion, when specific effects are not apparent.

It is thus clear that the behaviour of an electrolyte cannot be taken as direct evidence of the properties of the ions unless it can be proved that the ions are taking a greater control of the dissociation than the solvent, and it is also clear that a solvent which may be a " differentiating solvent " for one series of electrolytes may be a " levelling solvent " for another series.

Recent work has shown how difficult the interpretation of conductivity results may be, many cases of the reversal of the relative strengths of acids on changing from one solvent to another having been reported (Rabinovitch, *Z. physikal. Chem.*, 1928, **132**, 83; Hunt and Briscoe, *loc. cit.*; Halford, *J. Amer. Chem. Soc.*, 1931, **53**, 2944; Wynne-Jones, *loc. cit.*). Walden (*Z. physikal. Chem.*, 1930, **148**, 45) has reported changes in the relative strengths of electrolytes between solvents of about the same dielectric constant. The reversal of the order of magnitude of the conductivities of copper and nickel malonates on changing from water to aqueous pyridine is another interesting case, although it is possible that this anomaly would disappear if a complete correction for mobility changes were made.

The question arises as to why the titration curves of the copper salts show signs of having reached a maximum at about 10% of pyridine; if pyridine has a higher co-ordinating tendency than water, why does the increase in conductivity not persist until the solvent is 100% pyridine? The answer to this question is probably found in the increase of the *absolute* activities of the ions due to the decreasing dielectric constant of the solvent (shown in the figure by a broken line), whereas the activities of the undissociated molecules are little changed (compare Bjerrum and Larsson, *Z. physikal. Chem.*, 1927, **127**, 358; Brönsted, *Chem. Rev.*, 1928, **5**, 231; Hammett, *loc. cit.*). Hartley, Thomas, and Applebey (J., 1908, **93**, 538) have also observed that a mixture of pyridine and water appears to be a more strongly dissociating solvent than either component alone, and Walden, Audrieth, and Birr (*Z. physikal. Chem.*, 1932, **160**, 337) have found that silver and alkali-metal salts in pure pyridine, far from being completely dissociated, exhibit marked differences in dissociation, the silver salts being the most highly conducting. These differences, apart from the fact that the silver ion probably has a greater electron-accepting tendency than the other ions (compare Koch, J., 1931, 1138), must be mainly due to variations of ionic activity in a solvent of low dielectric constant as a function of ionic size. In other words, in a solvent of low dielectric constant electrostatic forces governed by Coulomb's law become of major importance compared with " co-ordinative " forces, which are chemical in nature and are probably not governed by Coulomb's law.

Another factor tending to make pure pyridine a solvent of comparatively small ionising power is the small tendency which it must possess to solvate anions, since it has " donor " properties only (compare Ulich, *Trans. Faraday Soc.*, 1927, **23**, 388, who found that anions were little solvated in pyridine).

Another process which may operate in determining the ionisation of an electrolyte is the converse of that so far considered, namely, the competition between the cation and the solvent for the anion, but this will probably seldom play a great part, since the electron-donating tendencies of most solvents outweigh their electron-accepting tendencies.

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