# *The Conductivity of Electrolytes in Non-aqueous and Mixed Solvents. Part I.*

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Measurements of the conductivity of silver nitrate in binary mixtures of acetone–water, 1 : 4-dioxan–water, pyridine–water, and ethanol–pyridine over the complete solvent mixture concentration range are reported and discussed.

The variation of the conductivity of electrolytes with solvent composition has been extensively investigated by a variety of methods and techniques. Ives (*J.*, 1933, 1360) has shown that much information can be obtained about the behaviour of electrolytes in water-rich aqueous pyridine mixtures, and his simple titration technique was essentially the method used in this work. The electrolyte most used was silver nitrate, because it is reasonably soluble in a variety of non-aqueous solvents, and it is known that $Ag^+$ interacts strongly with certain organic molecules owing to its electron-accepting properties. Indeed, Kraus and Burgess (*J. Amer. Chem. Soc.*, 1948, **70**, 706) conclude from their work in a variety of solvents that the silver ion is exceptional in this respect. Thus by choosing a solvent with electron-donating powers it is possible to obtain a system wherein the cation is likely to be preferentially and very strongly solvated. For instance, if the solvent is pyridine, then the existence of complex ions of the type $Ag(py)_2^+$ (Woodman and Corbett, *J.*, 1925, **127**, 2461; Schmidt and Keller, *Z. physikal. Chem.*, 1929, **141**, *A*, 331; Britton and Williams, *J.*, 1935, 798) and $Ag(py)^+$ (Vosburgh and Cogswell, *J. Amer. Chem. Soc.*, 1943, **65**, 2412) demonstrates extremely strong cation–solvent interaction. The formation of large singly-charged ions is likely to discourage further solvation. Further, Ulich (*Trans. Faraday Soc.*, 1927, **23**, 388) has shown that the anion is little solvated with pyridine, so that, for the purpose of this work, this system may be regarded as a limiting case of " cationic solvation." It was thought that if the conductivities of silver nitrate in pyridine–water mixtures were compared with the conductivities in aqueous solutions of other solvents possessing electron-donating properties, some indication of the relative cation–solvent interaction would be obtained. The solvents used were 1 : 4-dioxan and acetone, and, for further comparison, ethanol, the last being assumed to solvate both anion and cation. Consequently, the effect of adding pyridine, 1 : 4-dioxan, acetone, and ethanol to aqueous solutions, and pyridine to ethanolic solutions, of silver nitrate, the concentration of electrolyte being kept constant, has been studied and the results for 0·0005M-solutions are shown graphically. Other concentrations of electrolyte (0·0003 and 0·0008M) were also used but the essential character of the curves was the same.

## RESULTS

Generally, the results are shown in graphical form, but two sets of typical results are shown in the Table. From large-scale plots, equivalent conductivities, fluidities, and dielectric constants were interpolated at any required solvent composition, and thus any derived quantity was calculated.

*Equivalent conductivities of* 0·0005M-$AgNO_3$ *in mixed solvents.*

(*a*) $C_5H_5N$–$H_2O$

| $C_5H_5N$, mol. % | Λ | $C_5H_5N$, mol. % | Λ | $C_5H_5N$, mol. % | Λ |
|---|---|---|---|---|---|
| 0·000 | 131·36 | 0·139 | 98·81 | 0·387 | 95·31 |
| 0·003 | 130·50 | 0·163 | 97·93 | 0·524 | 93·56 |
| 0·036 | 104·71 | 0·196 | 97·50 | 0·584 | 93·34 |
| 0·094 | 99·46 | 0·257 | 96·84 | 1·007 | 88·31 |

(*b*) $C_2H_5{\cdot}OH$–$H_2O$

| $C_2H_5{\cdot}OH$, mol. % | Λ | $C_2H_5{\cdot}OH$, mol. % | Λ | $C_2H_5{\cdot}OH$, mol. % | Λ |
|---|---|---|---|---|---|
| 0·000 | 131·36 | 2·035 | 112·49 | 12·58 | 68·95 |
| 0·318 | 130·80 | 4·435 | 97·32 | 20·25 | 56·89 |
| 1·328 | 120·30 | 10·46 | 71·89 | | |

## DISCUSSION

Fig. 1 shows the equivalent conductivity of 0·0005M-silver nitrate corrected for viscosity changes ($\Lambda\eta/\eta_0$) plotted against mol. % of one component of the solvent mixtures, and the curves fall into two groups, one of which is made up of the mixtures containing pyridine as a component.

The initial effect of adding pyridine to an aqueous solution of silver nitrate is a sharp decrease of $\Lambda\eta/\eta_0$, which can be attributed to the formation of a complex cation of reduced mobility as compared with the silver ion. Once this change is complete, then $\Lambda\eta/\eta_0$ shows relatively little change over the rest of the composition range. This implies that the dissociation remains complete and that the conductivity remains essentially a function of the fluidity of the medium, in spite of the decreasing dielectric constant. The behaviour of potassium chloride and nitrate in similar solvent mixtures is quite different from that of silver nitrate in so far as $\Lambda\eta/\eta_0$ shows a reasonable constancy up to a considerable pyridine concentration (see Fig. 2) and lends strong support to the formation of the complex ion in the case of silver nitrate. The general conclusions are summarised in Fig. 5, which shows the relative conductivities, fluidities, and dielectric constants (*i.e.*, the ratio of the physical quantity concerned in mixed and pure solvents) plotted against solvent composition.

The initial addition of pyridine to ethanolic solutions causes an abrupt, but not large, increase in $\Lambda\eta/\eta_0$ which cannot reasonably be attributed to an increase in ionic mobility. It seems probable that the effect is a result of more than one process. It is to be expected that a complex cation will be formed, as in water, of reduced mobility. The resulting fall in conductivity is more than nullified by some larger effect operating in the opposite sense. It is suggested that this is an increase in dissociation of the electrolyte, since silver nitrate is only about 92% dissociated in ethanol at the concentration concerned (see Davies, " Conductivity of Solutions," 2nd Edn., Chapman and Hall, 1933, p. 118), and, when the larger complex cation is formed, the dissociation proceeds to completion. Again, in this system, after the establishment of the fully dissociated complex as the real solute, the conductivity remains essentially a function of the fluidity of the medium over a very considerable solvent composition range, as is shown by Fig. 8.

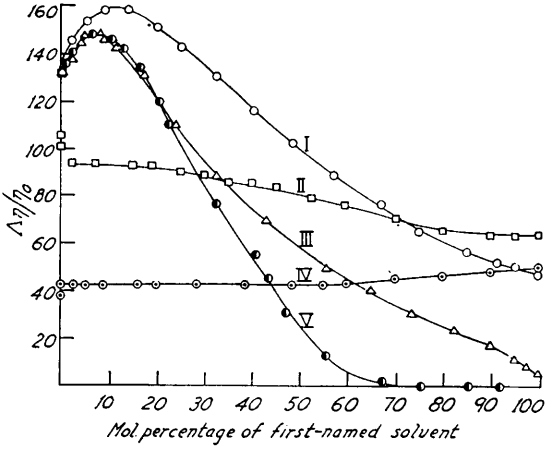


FIG. 1. *Conductivity of silver nitrate (0·0005M) in mixed solvents.*

I, Ethanol-water.
II, Pyridine–water.
III, Acetone–water.
IV, Pyridine–ethanol.
V, Dioxan–water.

*Viscosity-corrected equivalent conductivities of various salts* (0·0005M).

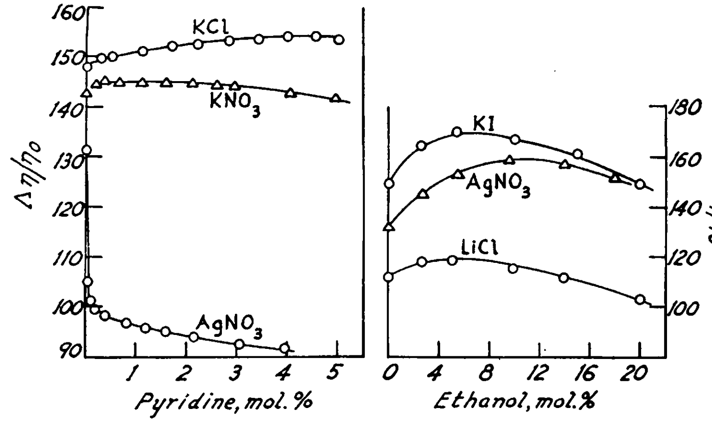
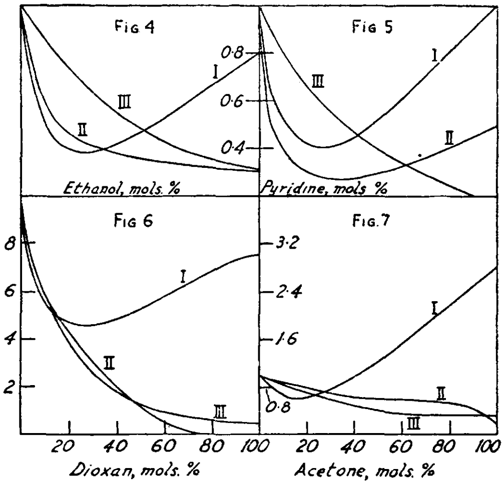


FIG. 2. *In pyridine–water mixtures.* FIG. 3. *In ethanol–water mixtures.*

The other systems, *viz.*, aqueous ethanol, dioxan, and acetone, show an interesting common feature. This is a maximum in $\Lambda\eta/\eta_0$ at approximately 10 mol. % of organic solvent, followed by a smooth fall over the remainder of the concentration range. In aqueous dioxan, the conductivity becomes almost negligible above 70 mol. % of dioxan. The reason for this behaviour is not clear but the following explanation is suggested.

The initial rise to the maximum value of $\Lambda\eta/\eta_0$, which has also been observed for potassium iodide and lithium chloride (see Connell, Hamilton, and Butler, *Proc. Roy. Soc.*, 1934, **147**, *A*, 418, and Fig. 3), cannot be due to an increase of dissociation because, for these solutes, dissociation is complete in water. It would seem reasonable to exclude complex formation, which would tend to affect the results in the opposite direction, and the increase in $\Lambda\eta/\eta_0$ must, therefore, be due to an increase in ionic mobility of a kind which is not a function of the fluidity of the bulk medium. The effect can be explained in terms of solvation of the ions, which, in a mixed solvent, may occur differentially. On general grounds it appears probable that, of the solvents concerned, water will have the greatest tendency to solvate the cations, so that the cation will be preferentially hydrated (*e.g.*, see, Shaw and Butler, *ibid.*, 1930, **129**, *A*, 519). Now the solvation, at least in the outer reaches, may be regarded as purely electrostatic in origin, in the sense that the intensely inhomogeneous field of the ion will cause the greater attraction for the more polar component of the mixture. Thus, proceeding outwards from the ion it is to be expected that there will be a change in the composition of the medium, which is predominantly aqueous at first, followed by regions where the concentration of organic solvent increases, until the bulk composition is reached. Now if, when the ion moves under the influence of the applied field, the " surface of shear " is closer to the ion than the region at which the bulk composition is attained, the shearing process, on which the ionic mobility partly depends, will be marked by a fluidity characteristic of a more aqueous medium than that of the bulk mixture. For all the mixed solvents concerned, there is an initial decrease of relative fluidity as the concentration of the organic component increases (see Figs. 4—7), and it is noteworthy that ethanol shows the lowest value of relative fluidity and the highest maximum in $\Lambda\eta/\eta_0$. It is possible that the same effect may operate in the reverse direction when the fluidity minimum has been passed.



*Relative fluidity* (I), *conductivity* (II), *and dielectric constant* (III) *curves for* 0·0005M-AgNO$_3$ *solutions in mixed solvents.*

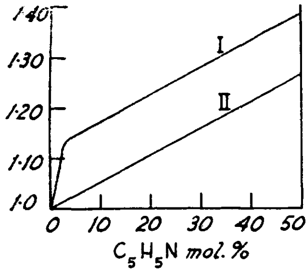


FIG. 8. *Relative conductivity* (I) *and fluidity* (II) *curves of* 0·0005M-AgNO$_3$ *solutions in ethanol–pyridine mixtures.*

As the concentration of the non-aqueous component increases, the decrease in the bulk dielectric constant will begin to play a major part, and the gradual decrease in $\Lambda\eta/\eta_0$ can be explained by assuming that increasing association of the electrolyte is occurring.

## EXPERIMENTAL

*Procedure.*—Conductivity measurements were made at 25° with the apparatus described by Davies (*J.*, 1937, 432). " Air-tight " all-glass borosilicate glass cells were used. The titration technique described by Ives (*loc. cit.*) was used for the most part. 0·0005M-Solutions in mixed solvents of known composition were made up in all-glass apparatus and a known weight of solution was blown over into the cell by means of dry nitrogen. Weighed quantities of 0·0005M-electrolyte solutions in one component of the binary mixture were added, and the cell resistance was measured after each addition. Volume changes were corrected for by adding calculated amounts of the mixed solvents, although if the change was not large it was found that the results could be corrected by multiplying the cell resistance by the ratio of real volume to total volume of cell contents plus the volume added. The results were checked by making single observations on 0·0005M-solutions in solvents of known composition.

Solvent resistances for solvent correction were obtained from runs on mixed solvents in the absence of electrolytes, and the corrections obtained were usually small. However, in solutions containing pyridine the maximum correction was approximately $7 \times 10^{-6}$ ohm$^{-1}$ at 2 mol. % of pyridine, which represents about 10% of the conductivity of 0·0005M-silver nitrate in that solvent. Ives (*loc. cit.*) obtained similar results and stated that, although the correction applied is not strictly accurate, yet it is probably of the right order, since most of the solutions contained a very large excess of pyridine over salt. This, of course, implies that the addition of the electrolyte has no effect on the ionisation equilibrium of the aqueous pyridine solution, a situation which might not hold owing to the salting-out effect of the added ions. However, from a consideration of the magnitude of the conductivity changes on the addition of silver nitrate, and the relative quantities of electrolyte and solvent present, it would seem that although the accuracy might be questioned, and no claim is made for great accuracy, yet the application of such a correction is right in principle.

*Materials.*—Good-quality conductivity water was used of specific conductivity better than 0·8 gemmho. All electrolytes were recrystallised several times from conductivity water.

All organic solvents were purified by methods described by Griffiths (*J.*, 1952, 1326), and the densities of all mixtures were those given by him. Other physical constants of the mixtures were obtained from sources shown. (*a*) Pyridine–water mixtures : fluidities, Dunstan, Thole, and Hunt (*J.*, 1907, **91**, 1728; 1908, **93**, 561) and Hartley, Thomas, and Applebey (*J.*, 1908, **93**, 538); dielectric constants, Ives (personal communication). (*b*) Pyridine–ethanol mixtures : Dunstan, Thole, and Hunt (*loc. cit.*, 1907). (*c*) Ethanol–water mixtures : fluidities, Connell, Hamilton, and Butler (*loc. cit.*) and Bingham and Jackson (*Bull. Bur. Stand.*, 1918, **14**, 59); dielectric constants, Harned and Owen (" The Physical Chemistry of Electrolytic Solutions," 2nd Edn., 1950, Reinhold Publ. Corp., p. 118). (*d*) Dioxan–water mixtures : fluidities, Geddes (*J. Amer. Chem. Soc.*, 1933, **55**, 1019) and Owen and Waters (*ibid.*, 1938, **60**, 2371); dielectric constants, *idem* (*ibid.*) and Akerlof and Short (*ibid.*, 1936, **58**, 1241). (*e*) Acetone–water mixtures : fluidities, " International Critical Tables," McGraw-Hill, 1929; dielectric constants, Akerlof (*J. Amer. Chem. Soc.*, 1932, **54**, 4125) and Harned and Owen (*op. cit.*).

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