The Conductivity of Silver Nitrate in Non-aqueous and Mixed Solvents. Part III.[*]

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The conductivity of silver nitrate in acetone solutions containing pyridine, the three picolines, quinoline, or γ-collidine is reported and discussed.

IT is usually accepted that the dissociation of an electrolyte is dependent on two factors, namely, the dielectric constant of the medium and the ionic radii, and many attempts have been made to study the effects of these variables separately. As far as the dielectric constant is concerned, it is usual to assume that no changes in solvation occur, and that the bulk dielectric constant controls the association–dissociation process (see James, *J.*, 1950, 1094; 1951, 153). Where the ionic radii are concerned it is general to calculate the value of the radii from the use of Stokes's hydrodynamics or to cansider the " *a* " parameter of the Bjerrum–Fuoss treatment (*Kgl. Danske Vidensk. Selskab*, 1926, **7**, No. 9; *J. Amer. Chem. Soc.*, 1933, **55**, 1019) which assumes that purely electrostatic forces are involved in the formation of ion-pairs.

Hasted, Ritson, and Collie (*J. Chem. Phys.*, 1948, **16**, 1) have shown that at distances less than 4 Å from an ion, the dielectric constant is a rapidly varying quantity and it appears doubtful whether the bulk dielectric constant should be used in these calculations. In a recent series of papers Fuoss and his co-workers (*J. Amer. Chem. Soc.*, 1950, **72**, 301; 1953, **75**, 3076, 5172; 1954, **76**, 5897, 5902, 5905) have criticised the so-called " sphere-in-continuum " model used to describe electrolytic solutions, and a tentative solution has been proposed involving the breakdown of solvent structure in the case of solvents which associate in the pure form, but as yet it appears that each solvent mixture must be treated on its own merits. According to Fuoss *et al.*, the formation of an ion-pair is described by the approach of two ions through the solvent until only one molecule, the solvate molecule, separates them. This is then followed by a further separate step in which the solvate molecule is expelled. It is emphasised that in this process the dielectric constant will vary from its bulk value to that obtaining at electrical saturation, as the two ions approach.

Grunwald (*Analyt. Chem.*, 1954, **26**, 1696) discusses the fact that the removal of the single solvate molecule from the ion-pair will need very considerable energy. Further, he points out that in polar solvents the ions exist in a solvation sheath, the radius of which has been estimated to be about 5 Å. Thus, if both ions are solvated to this extent, when the interionic distance is less than 10 Å the solvation shells overlap, and this overlapping will occur at the expense of solvation energy. This energy change may well go to offset the effect of changing dielectric constant near the ions owing to electrical saturation.

It thus seems necessary to consider the conductivity of electrolytes in different solvents in terms of changing dielectric constant, and ionic size in terms of specific solvent–solute interaction, remembering that in binary mixtures of solvents the addition of the second component may modify the structure of the other component with consequent changes in solvation.

It would appear that systems containing the Ag^+ ion should give much useful information, since it has been shown that this ion interacts strongly with certain organic molecules owing to its electron-accepting properties (see Griffiths, *J.*, 1954, 686). Further, silver nitrate in acetone is a very weak electrolyte (see Griffiths and Lawrence, *J.*, 1955, 1208; Ross-Kane, *Ann. Reports*, 1930, **27**, 340) and it was thought that if small quantities of solvents possessing electron-donating properties were added to such solutions, then the latter should interact strongly with the Ag^+ ion, giving a larger ion and possible increase in the degree of dissociation, whilst the bulk dielectric constant would not be altered

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[*] Part II, *J.*, 1955, 1208.

appreciably. To this end the conductivity of silver nitrate in acetone solutions containing traces of organic bases was measured.

Results. These are shown in tabular and graphical form. In the Tables, c is the molar concentration of silver nitrate, and the weight percentages in Table 2 correspond to 0·0735 mole % of base in acetone.

TABLE 1.

0·1% *Pyridine*

10^4c	Λ	10^4c	Λ	10^4c	Λ
0·2620	150·9	1·275	104·3	2·109	88·69
0·5477	130·7	1·461	100·0	2·388	84·98
0·7616	120·5	1·658	96·09	2·693	81·47
1·054	110·3	1·873	92·32	3·368	75·09

$\Lambda_0 = 193{\cdot}7$; $K = 0{\cdot}754 \times 10^{-4}$.

1·0% *Pyridine*

10^4c	Λ	10^4c	Λ	10^4c	Λ
0·2302	164·6	1·202	123·9	2·980	96·66
0·4268	149·9	1·642	114·6	2·922	95·31
0·5696	144·3	1·709	111·8	3·854	89·09
0·7659	136·3	2·167	106·3	4·070	85·45
0·8567	132·9	2·257	103·2		

$\Lambda_0 = 188{\cdot}9$; $K = 1{\cdot}42 \times 10^{-4}$.

TABLE 2.

0·118% *α-Picoline*

10^4c	Λ	10^4c	Λ	10^4c	Λ
0·1265	169·9	0·5765	131·6	1·060	112·5
0·2626	153·4	0·7385	123·9	1·305	105·8
0·3926	142·9	0·8336	120·1	1·514	101·1
0·4980	135·9	0·9195	117·0	1·798	95·69

0·118% *β-Picoline*

10^4c	Λ	10^4c	Λ	10^4c	Λ
0·2218	157·4	1·085	110·9	1·706	96·76
0·4174	139·7	1·230	107·0	1·881	93·76
0·6751	125·7	1·398	102·9	2·149	89·69
0·8713	117·8	1·580	99·14	2·641	83·59

0·118% *γ-Picoline*

10^4c	Λ	10^4c	Λ	10^4c	Λ
0·1665	169·1	0·8033	132·0	1·451	114·2
0·3069	156·0	0·9630	126·7	1·575	111·6
0·4850	145·7	1·148	121·4	1·746	108·4
0·6452	138·2	1·292	117·8	2·007	104·1

0·153% *γ-Collidine*

10^4c	Λ	10^4c	Λ	10^4c	Λ
0·07526	178·3	0·4038	152·9	0·7742	139·8
0·1638	170·3	0·4924	148·5	0·9303	131·8
0·2336	164·8	0·5971	143·7	1·096	126·9
0·3253	157·4	0·7027	139·5	1·311	121·7

0·163% *Quinoline*

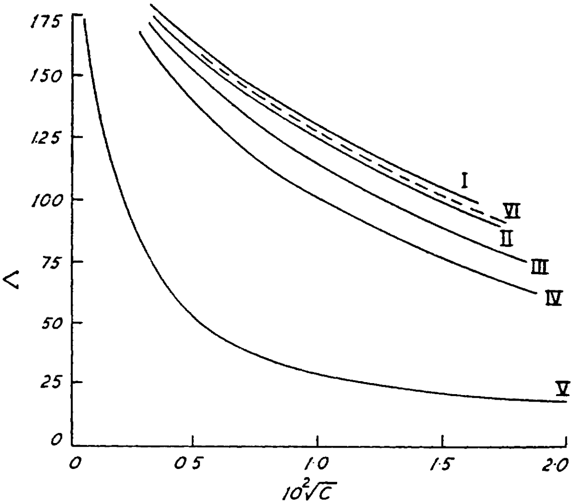
10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ
0·1821	147·9	0·5044	120·0	0·8421	104·7	1·129	95·86	1·414	89·11	1·776	82·47
0·3670	129·1	0·6948	110·5	0·9276	101·7	1·220	93·49	1·567	86·07	2·147	77·09

Discussion.—Shedlovsky's extrapolation method (*J. Franklin Inst.*, 1938, **225**, 739) was used to calculate the values of Λ_0 and K for the electrolyte solutions. The viscosities of the mixtures containing the bases were taken to be those of acetone, since additions of up to 0·5% of base did not give viscosity variations which were detectable by ordinary techniques. In the first instance, where any data were available, a linear relation was assumed to hold between dielectric constant of the solvent mixtures and their composition, but it was found that, with the concentration of base added, there was little difference from the value holding for the dielectric constant of acetone. It was thus decided to use the constants for acetone for the solvent mixtures.

It was found that, whilst the addition of a small percentage of pyridine considerably increased the equivalent conductivity, the effect of greatly increasing this concentration had little further effect (see curves III and VI). Since it is reasonable to expect that the cation will be solvated by the base whilst the anion will be little solvated (see Ulich, *Trans. Faraday Soc.*, 1927, **23**, 388) it would be expected that the mobility of the cation would be decreased as compared with the mobility in acetone, leading to a decrease in conductivity on addition of a little pyridine. It thus appears that the expected fall in conductivity due to the formation of the complex cation must be more than nullified by some larger effect acting in the opposite sense, and it is suggested that this is an increase in the degree of dissociation of the electrolyte. In acetone the dissociation constant of $AgNO_3$ is approx. 4×10^{-6}, whilst in solutions containing 0·1% of pyridine the dissociation of the complex is $0{\cdot}75 \times 10^{-4}$ (Table 3). It is noteworthy that in the case of the latter solutions the extrapolation plots are linear as compared with those obtained for pure acetone which show marked deviations from linearity much below Fuoss's critical concentration (*J. Amer. Chem. Soc.*, 1935, **57**, 2604; see also Griffiths and Lawrence, *Research*, 1953, **6**, No. 11).

The value of Λ_0 remains substantially of the same order as in pure acetone even though the value of K is greatly increased, suggesting that the latter is responsible for the increase in conductivity.

The other bases used showed characteristics similar to those of pyridine, the actual magnitude of the effects produced being illustrated in the figure, where all the base concentrations are of the same molar %, and are equivalent to a 0·1% w/w solution of pyridine in acetone. The mixtures containing quinoline showed a smaller conductivity than those containing pyridine, possibly owing to the lower cationic mobility of the quinoline–silver complex. On the grounds of size alone, equal numbers of molecules of base being assumed to be attached to the silver ion, it might be expected that γ-collidine would have the lowest conductivity. It is found that this is not the case (see Figure), and the reason is probably to be found in the fact that this system gives the largest K value of the group studied. It is possible in this instance that the ion–solvent interaction is very strong owing to the stronger basic nature of γ-collidine. The α- and β-picolines showed results very similar to those obtained with pyridine, but with γ-picoline a larger dissociation constant was obtained than with either of the other picolines or pyridine, and this might be accounted for by an effectively larger ion in the case of the γ-picoline–silver complex. It is of interest to compare the sequence of the strengths of the bases involved with the sequence of the dissociation constants for silver nitrate in the acetone solutions containing the bases.* A review of the data for the base strengths in water shows the following sequence: Quinoline = pyridine < β-picoline = γ-picoline < α-picoline < γ-collidine (Remick, "Electronic Interpretations of Organic Chemistry," 2nd Edn., Chapman and Hall, 1949, p. 301; Conway, "Electrochemical Data," Elsevier Publ. Co., 1952, p. 186; Heilbron, "Dictionary of Organic Compounds," Eyre and Spottiswoode, London, 1934), whilst the order of the dissociation constants for silver nitrate in acetone containing these bases is: Quinoline < pyridine < α-picoline = β-picoline < γ-picoline < γ-collidine. It can be seen that there is some similarity between these two series but since different solvents are involved, namely, water and acetone, it is perhaps inadvisable to draw too many conclusions from these comparisons.



Conductivity of silver nitrate in mixed solvents.
(I) γ-Collidine and acetone.
(II) γ-Picoline and acetone.
(III) Pyridine and acetone (and α- and β-picoline and acetone).
(IV) Quinoline and acetone.
(All 0·0735 mole % of first-named solvent.)
(V) Pure acetone.
(VI) 1% (w/w) Pyridine in acetone.

From a consideration of Walden's rule (*Z. phys. Chem.*, 1906, **55**, 207; 1912, **78**, 257) taken in the form

$$\lambda_0^{\pm}\eta = \frac{eF}{6\pi}\left(\frac{1}{r^{\pm}}\right)$$

where λ_0 is the ionic mobility, η the viscosity, and $r^{\pm}$ the radius of the positive or negative ion, it might be expected that any large change in the value of the apparent ion-radius r

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* We thank a referee for this suggestion.

would show a corresponding change in $\lambda_0\eta$. The nitrate ion has been shown to be little solvated by pyridine (Ulich, *loc. cit.*), and thus the value for its mobility in acetone was taken to hold for the solvent mixtures considered. Davies (" Conductivity of Solutions," 2nd Edn., Chapman and Hall, London, 1933, p. 207) gives a value of 120, and Λ_0 for silver nitrate in acetone being taken as 206, $\lambda_0^+\eta =$ 0·268. Turning to the solutions containing the bases, the $\lambda_0^+\eta$ product decreased, indicating an increase in r, the greatest value of r being obtained for quinoline, as might be expected if there has been interaction between the cation and the relatively large base molecule.

Table 3 also shows the values of Bjerrum and Fuoss's " a " parameter (*loc. cit.*), and although these show some increase over the value holding in pure acetone (1·5 Å, Griffiths and Lawrence, *loc. cit.*), the increase was not as great as was expected in view of the large value of **6·6 Å** obtained by Burgess and Kraus (*J. Amer. Chem. Soc.*, 1948, **70**, 706) for silver nitrate in pure pyridine, and 5·78 Å for the same salt in ammonia at —33° (Fuoss and Kraus, *ibid.*, 1933, **55**, 1019). It was assumed by these authors that a relatively large cation was formed, whose effective size was then increased by further solvation. On the other hand, the data of Martin (*J.*, 1928, 3270) and of Walden and Birr (*Z. phys. Chem.*, 1929, **144**, 269) for silver nitrate in benzonitrile and acetonitrile give " a " values of 1·6 and 1·9 Å, respectively.

TABLE 3.

Solvent mixture : acetone plus	Λ_0	10^4K	$\lambda_0^+\eta$ *	a, Å	10^8r^+ (cm.)
γ-Collidine	188·3	1·49	0·218	2·15	3·94
γ-Picoline	189·7	1·26	0·213	2·17	3·89
Pyridine	193·7	0·75	0·225	2·00	3·62
α-Picoline	194·1	0·81	0·226	2·01	3·62
β-Picoline	192·9	0·80	0·223	2·01	3·67
Quinoline	184·7	0·60	0·197	1·94	4·12

* η is the viscosity of the solvent.

In these circumstances it is doubtful if any quantitative significance can be attached to these " a " values, further than that they indicate the distance between the centres of ionic charge if purely electrostatic forces prevail. It is felt that since sufficient base was added to the solution to solvate all the silver ions, then the use of Stokes's hydrodynamics gives a better estimate of the ion-size as far as this work is concerned. From Table 3 it can be seen that the larger the r value the larger the dissociation constant K, except in the case of solutions containing quinoline. Here a large ion is indicated, though the value of K is the smallest recorded, and it is suggested that this may be the result of the Ag^+ ion's interacting with one quinoline molecule, while in the other mixtures it is probable that complex ions of the type $Ag(py)_2^+$ exist (see Woodman and Corbet, *J.*, 1925, **127**, **2461**; Schmidt and Keller, *Z. phys. Chem.*, 1929, **141**, *A*, 331; Britton and Williams, *J.*, 1935, 798). It thus appears that in the mixtures investigated the dissociation of the electrolyte is largely governed by the ionic size, although it is considered that in general each case must be considered on its own merits.

Experimental.—Procedure. This was as previously described (Griffiths and Lawrence, *loc. cit.*). Conductivities of the solvent mixtures were not materially different from that of pure acetone and solvent corrections were applied in the normal way.

Materials. The acetone and pyridine were purified by the method described by Griffiths (*J.*, 1952, 1326) and the physical constants used were those given by him (*J.*, 1954, 686). The other bases were treated by repeated fractional distillation and had the following b. p.s at normal atmospheric pressure : α-picoline, 130°; β-picoline, 144°; γ-picoline, 143°; γ-collidine, 172°; quinoline, 237°. They were sealed under nitrogen in glass ampoules until required.

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