806. *The Conductivity of Silver Salts in Non-aqueous and Mixed Solvents. Part VII.*[1]

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The conductivity of silver nitrate in benzonitrile and in benzonitrile solutions containing ethanol and of silver perchlorate in pure and binary mixtures of acetone, *cyclo*hexanone, and *iso*butyl alcohol is reported and discussed.

Previous investigations [1] have all been directed at the preferential solvation of silver ions in non-aqueous solvents and solvent mixtures, the nature of the complex ions so formed, and the effects of the solvation on the dissociation of the salt and the mobility of the cation. Wherever solvation has occurred to any reasonable extent it has increased the dissociation. This has been explained as being because (*a*) increase in the size of the ion favours the dissociation process, (*b*) complex-ion formation effectively removes the ions formed by dissociation, and (*c*) preferential solvation of silver ions by one component of a binary solvent mixture may alter the dielectric constant and viscosity in the immediate vicinity of an ion from the bulk value. Effects (*a*) and (*b*) are inseparable but by choosing solvents of closely similar dielectric constants effect (*c*) can largely be eliminated and hence some idea of its importance obtained.

The conductivity of silver nitrate in benzonitrile and benzonitrile–ethanol and of silver perchlorate in pure and binary mixtures of acetone, *cyclo*hexanone, and *iso*butyl alcohol has been studied. The results for the silver nitrate solutions have been compared with those for the same electrolyte in other solvents having similar dielectric constants, due to other workers. The results are shown in the Figures and the Table.

Solvent	Solute	$10^2\eta$ (P)	10^3K	Λ_0	a (Å)	$\Lambda_0\eta$	D
Ammonia (−33°) [a]	$AgNO_3$	0·26	4·85	291	3·38	0·756	22
Ethanol [b]	$AgNO_3$	1·09	4·40	44·8	2·72	0·489	24
90% Acetone–10% water [c]	$AgNO_3$	0·44	1·18	124	2·02	0·544	24
99% Benzonitrile–1% ethanol	$AgNO_3$	1·24	0·48	53·8	1·70	0·667	25
Benzonitrile	$AgNO_3$	1·24	0·25	55·2	1·58	0·684	25
Acetone [d]	$AgClO_4$	0·31	0·54	181	2·75	0·56	21
*cyclo*Hexanone	$AgClO_4$	2·2	0·88	27·5	2·99	0·60	18
*iso*Butyl alcohol	$AgClO_4$	4·3	1·47	12·2	3·42	0·53	18
22% Acetone–78% *cyclo*hexanone	$AgClO_4$	1·09	1·46	53·2	3·19	0·58	19
40% *iso*Butyl alcohol–60% *cyclo*hexanone	$AgClO_4$	2·55	0·95	21·2	3·05	0·54	18
55% Acetone–45% *iso*butyl alcohol	$AgClO_4$	0·68	2·18	81·4	3·20	0·55	20

[a] Franklin and Kraus, *Amer. Chem. J.*, 1900, **23**, 277. [b] Copely, Murray-Rust, and Hartley, *J.*, 1930, 2492. [c] Part III. [d] Part V.

Shedlovsky's extrapolation method [2] was used to determine the dissociation constants and values of Λ_0 from the experimental results and all plots were linear.

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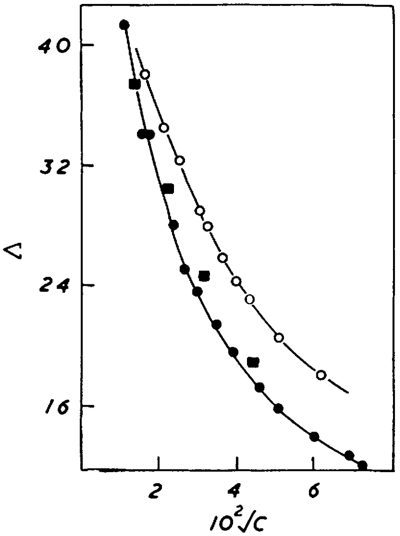
[1] Parts I—VI, *J.*, 1954, 686; 1955, 1208, 2797; 1956, 473; 1957, 3243; 1958, 309.

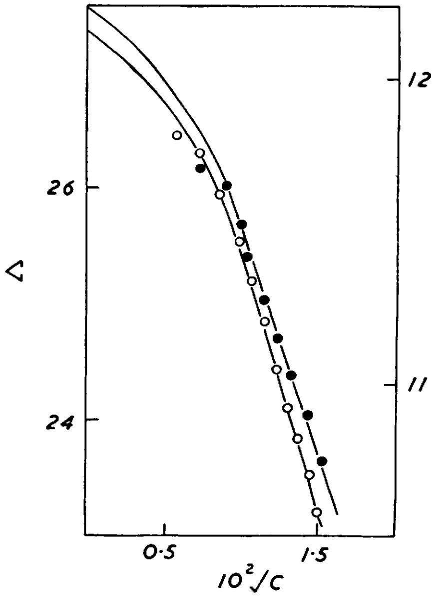
[2] Shedlovsky, *J. Franklin Inst.*, 1938, **225**, 739.

FIG. 1. *Equivalent conductances of silver nitrate solutions.*



● Benzonitrile. ○ 99% Benzonitrile–1% ethanol. ■ Martin's results for benzonitrile (ref. 3).

FIG. 2. *Equivalent conductances of silver perchlorate solutions.*



○ *cyclo*Hexanone (left-hand scale). ● *iso*-Butyl alcohol (right-hand scale).

FIG. 3. *Equivalent conductances of silver perchlorate in* 22% *acetone*–78% cyclo-*hexanone.*

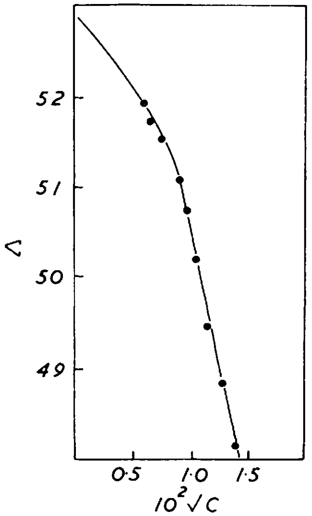
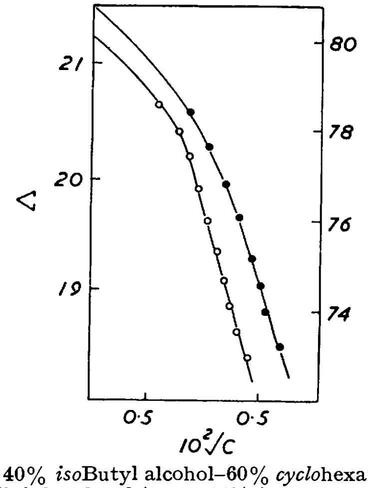


FIG. 4. *Equivalent conductances of silver perchlorate.*



○ 40% *iso*Butyl alcohol–60% *cyclo*hexane (left-hand scale). ● 55% Acetone–45% *iso*butyl alcohol (right-hand scale).

The behaviour of silver nitrate in benzonitrile has previously been studied by Martin[3] who obtained $\Lambda_0 = 52{\cdot}18$ by extrapolation. He also obtained a value for the dissociation constant of 4×10^{-4}, though more recently Davies[4] recalculated the value of Λ_0 as 50·20, thus altering the dissociation constant to $4{\cdot}72 \times 10^{-4}$. Fair agreement exists between the present results and Martin's, as shown by Fig. 1.

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[3] Martin, *J.*, 1928, 3270.

[4] Davies, "Conductivity of Solutions," Chapman and Hall, London, 1933, p. 118.

Fuoss and Kraus [5] pointed out that ammonia forms a stable complex with the silver ion and hence in this solvent the cation is relatively large and solvation, in the sense of solvent dipoles oriented by the ionic field, further increases the effective radius. They concluded that " silver nitrate was a much stronger electrolyte in ammonia of dielectric constant 22 than in benzonitrile of dielectric constant 25."

Ethanol is a " levelling " solvent (Part IV [1]), *i.e.*, one which solvates both the anion and cation. Hence, allowing for the retention of solvent molecules in the ion-pair and overlap of the solvent shells,[6] we are not surprised that the dissociation constant in this solvent is of the same order as in ammonia where only the cation is strongly solvated. Like ammonia, and in contrast to ethanol, benzonitrile is a " differentiating " solvent, and for silver nitrate it will solvate the cation preferentially, but its tendency to do so, compared with that of ammonia, is not likely to be so great, as the forces between solvent molecules and cations will be weaker than they are in ammonia, so that in benzonitrile association and electrolytic weakness will be favoured; the dissociation constant in benzonitrile, being the lowest in the Table, demonstrates this. However, benzonitrile and ethanol have very similar dielectric constants (25 and 24 respectively). Thus if preferential solvation by one component of a mixture of them should occur it is reasonable to assume that this would have less effect on the microscopic dielectric constant than if the two solvents had vastly different dielectric constants, as in the case of water and acetone. It has already been clearly demonstrated [1] that the value of the bulk dielectric constant is not the main factor in determining electrolyte strength—silver nitrate is a very weak electrolyte in acetone (Part II [1]), indicating little or no solvation of the ions in a solvent of dielectric constant of approximately 20—but the addition of a small quantity of organic base greatly increases the strength of the electrolyte whilst altering the dielectric constant of the solvent but little. This is not to say, however, that the increase in ionic size is the only factor influencing the dissociation constant, since the preferential absorption of the base will affect both the microscopic dielectric constant and viscosity, *i.e.*, the properties in the immediate vicinity of the ions. If any of the latter factors could be affected in any way the results would be of interest; although the use of ethanol and benzonitrile cannot eliminate the effects, it is possible that at least one of them could be reduced. The addition of 1% of ethanol to benzonitrile solutions of silver nitrate does increase the dissociation constant to some extent, probably mainly owing to solvation of the anion which increases the distance of closest approach of the ions.

With regard to silver perchlorate solutions the results indicate that a considerable degree of solvation, probably of both ionic species, exists in solutions containing *iso*butyl alcohol and also, to a small extent, those containing *cyclo*hexanone. It is difficult to see, however, why the dissociation is greater in acetone–alcohol than in the pure alcohol, though it is noteworthy that the values of the Bjerrum parameter for these two solutions are very similar. A possible explanation may be that the values of the dielectric constant for the solvent mixtures investigated, which were found by assuming a linear relationship with composition, are wrong. Indeed Osipov, Panina, and Lempert [7] showed that the dielectric isotherms for *iso*butyl alcohol–acetone mixtures were markedly curved. These values were obtained over a wide concentration range and no datum is available for small concentrations of either component, but on general grounds a sudden variation from linearity over the concentration range studied in the present paper is unlikely. Earlier papers [1] have described the technique of introducing deliberate errors into the computations in order to estimate their effect, and the variation in the dissociation constant seems unlikely to be explained on the assumption that the dielectric constant varies greatly.

The effects of solvation on the dissociation constant and distance of closest approach of the ions are qualitatively (Part VI [1]) and quantitatively similar to the effects of organic

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[5] Fuoss and Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 1019.

[6] Grunwald, *Analyt. Chem.*, 1954, **26**, 1696.

[7] Osipov, Panina, and Lempert, *Zhur. obshchei Khim.*, 1953, **25**, 662.

bases on the conductivity of the same salt in pure acetone, and since for the present investigations there are likely to be smaller variations of the dielectric constant in the vicinity of the ion than in the previous systems studied, it appears that variations in the dielectric constant play a relatively minor part in determining the dissociation constant. Hence the increase in the dissociation observed on the addition of a complex-forming solvent to a solution is due primarily to the inhibiting effect of the increase in ion size on the association process and/or possibly the formation of a new ionic species, rather than any variation in the dielectric constant near the ion.

On calculating the functions $\Lambda_0\eta$ and $V_0\eta/D$ for the solutions studied, we found that the latter is more constant as has also been observed by Ulich and Birr [8] for a variety of ions in solvents which do not extensively solvate them and by Rysselberghe and Frinstrom [9] for solutions of magnesium perchlorate in water, nitromethane, methyl alcohol and *iso*propyl alcohol; as yet no theoretical explanation has been found for this.

Experimental.—Procedure was as described in Part II.[1] " AnalaR " benzonitrile was distilled under reduced pressure, the middle fraction being dried ($CaCl_2$) and then repeatedly fractionated under reduced pressure in a stream of dry nitrogen until the specific conductivity was below $0{\cdot}04 \times 10^{-6}$ ohm^{-1} cm.$^{-1}$. *cyclo*Hexanone and *iso*butyl alcohol was fractionated twice under reduced pressure in a stream of nitrogen. The purification of ethanol, acetone, and electrolytes was as described in Part I.[1]

The variation of viscosity with composition for binary mixtures of acetone, *cyclo*hexanone, and *iso*butyl alcohol was examined with an Ostwald viscometer.

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[8] Ulich and Birr, *Z. angew. Chem.*, 1928, **41**, 443.

[9] Rysselberghe and Frinstrom, *J. Amer. Chem. Soc.*, 1945, **67**, 680.