

634. The Conductivity of Silver Salts in Non-aqueous and Mixed Solvents. Part V.¹

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The conductivities of silver perchlorate and silver nitrite in acetone and ethylene glycol have been measured. The effects of small additions of organic bases, benzene, and nitromethane have been observed.

MUCH information on the conductance of salts in non-aqueous solutions is available in the literature. In previous papers of this series attention was focused on silver salts. Griffiths and Lawrence² used solvent mixtures containing a small amount of organic base, and thus investigated the effects of dielectric constant and ionic radius on the dissociation of silver nitrate since it was known that the electrophilic cation interacts strongly with organic bases, thus allowing some variation in the size of the cation at will. The effect of organic bases on the conductivity of silver salts in non-aqueous solvents was either (a) an increase due to increased dissociation or (b) a decrease due to decreased ion-mobility. It was claimed that effect (b) is always present but that it is more than nullified by effect (a) in the case of a "weak" silver salt, e.g., silver nitrate in acetone.

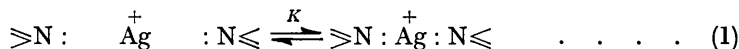
The investigations now reported were carried out in an attempt to extend this work, primarily to silver perchlorate and nitrite in acetone and ethylene glycol as main solvents. In addition to organic bases, the effects of benzene and nitromethane have been investigated. Benzene was chosen because spectrometric investigations by Taufen, Murray, and Cleveland³ support Winstein and Lucas's theory⁴ of π -complex formation, though the effect on the mobility of the silver ion appears not to have been investigated previously.

Salt	Solvent	Additive (1%)	Dissociation constant (10^3K)	Conductivity (Λ_0)	Radius of cation (r_+) (Å)	Bjerrum parameter (a) (Å)
AgClO ₄	Acetone	—	—	181.55	2.86	—
AgClO ₄	Acetone	Pyridine	2.78	167.42	3.39	3.16
AgClO ₄	Acetone	Picoline	2.84	166.33	3.34	3.16
AgClO ₄	Acetone	Collidine	7.65	161.16	3.68	4.48
AgNO ₂	(CH ₂ ·OH) ₂	—	1.43	9.038	1.00	1.05
AgNO ₂	(CH ₂ ·OH) ₂	Pyridine	92.4	6.761	2.03	4.36
AgNO ₂	(CH ₂ ·OH) ₂	Picoline	10.3	7.027	1.81	4.68
* AgClO ₄	Pyridine	—	1.91	81.9 †	3.94	—
† AgClO ₄	Benzene	—	— §	150	—	4.89

* Results of Luder and Kraus (*J. Amer. Chem. Soc.*, 1947, **69**, 2481). † Results of P. Kraus and Fuoss (*ibid.*, 1936, **58**, 255). ‡ λ_0^+ = 34.3. § K = 0.78×10^{-20} .

The results are presented in Figs. 1 and 2, and in the Table. The values of the conductivity (Λ_0) and the dissociation constant were calculated by Shedlovsky's extrapolation method.⁵ Linear variation of dielectric constant and viscosity with solvent composition was assumed for the solvents used (see Griffiths and Lawrence²).

The effect of basic additives on the conductivity of the relatively strong electrolyte silver perchlorate, in acetone, was as follows. Substantial reductions in the equivalent conductivity were observed, indicating that the mobility of the cation is severely impaired by formation of an ionic complex presumably of the type:



At first sight the magnitude of the change appears to depend solely on the size of the complex-forming molecule, but it should be noted that for the bases used the basic strength

¹ The paper by Griffiths and Lawrence, *J.*, 1956, 473, is considered to be Part IV.

² *Idem*, *J.*, 1955, 2797.

³ Taufen, Murray, and Cleveland, *J. Amer. Chem. Soc.*, 1941, **63**, 3500.

⁴ Winstein and Lucas, *ibid.*, 1938, **60**, 836.

⁵ Shedlovsky, *J. Franklin Inst.*, 1938, **225**, 739.

increases with the size of the molecule. Breuhlman and Verhuek⁶ calculated the value of K for eqn. (1) for pyridine, α -picoline, and γ -picoline, and found that it increases linearly with basic strength. Fyfe⁷ also showed that the stability of the silver-ammine complexes could be related to the mobility of the π -electrons on the nitrogen atoms. Since K of eqn. (1) depends on the basic strength of the electron-donor, and hence the stronger the base the greater is the number of silver ions involved in complex-formation, the basic strength of the additive will also affect the equivalent conductivity. On the other hand, if the salt is not completely dissociated in the pure solvent, the base will tend to increase the dissociation since the formation of a complex effectively removes one of the ionic species, and the increased ionic size will tend to inhibit ion-pair formation. Experimental support for this is supplied by Griffiths and Lawrence,² this being the effect they referred

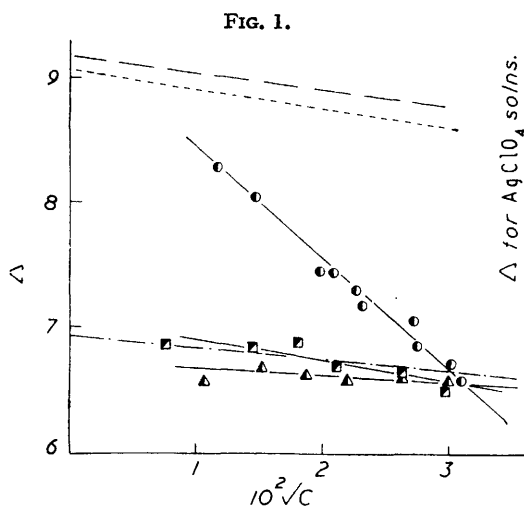
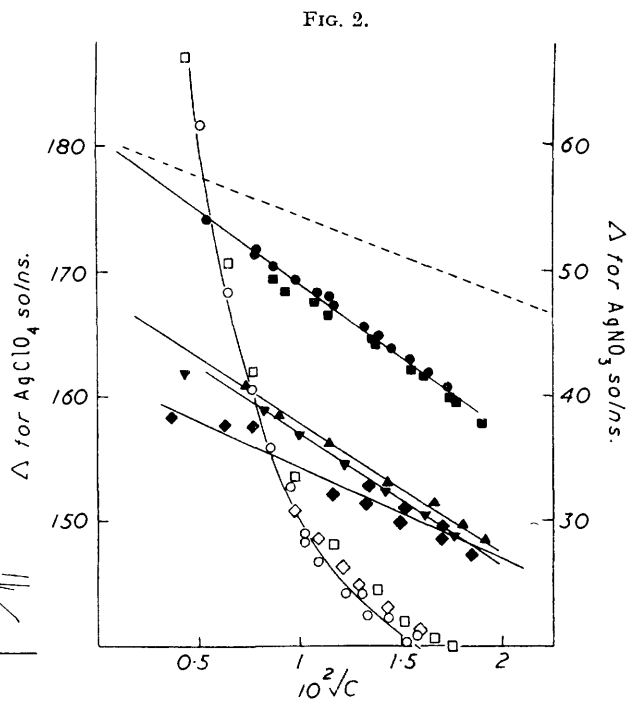


Fig. 1. Λ for AgClO_4 solns. Λ for AgNO_3 solns.

AgNO₃ in (○) pure acetone; in acetone containing 1% of (□) benzene or (◇) nitromethane.
 AgClO₄ in (●) pure acetone; in acetone containing 1% of (■) benzene, (▲) pyridine, (▼) β -picoline, or (◆) collidine.
 AgNO₃ in (○) pure ethylene glycol; in glycol containing 1% of (◻) γ -picoline or (▲) pyridine.
 - - - - Theoretical Onsager slope.
 - - - - Results of Griffiths and Lawrence¹ for AgNO₃ in pure ethylene glycol.
 - - - - Results of Griffiths and Lawrence¹ for AgNO₃ in ethylene glycol containing 1% of pyridine.



to as more than nullifying the decrease in conductivity caused by complex-ion formation. Hence the slope of the plot of Λ against \sqrt{c} for the binary solvent will conform more closely to the theoretical Onsager slope than will the slope for the pure non-basic solvent. The combined influence of both effects, namely, the decrease in conductivity due to decreased cation-mobility, and the increase in conductivity at real concentrations due to increased dissociation, will be to decrease the intercept and slope of the Λ - \sqrt{c} plot.

The results for silver perchlorate in acetone bear out this concept. The slopes of the Λ - \sqrt{c} plots do decrease with increasing basicity of the solvent, and the intercepts decrease

⁶ Breuhlman and Verhuek, *J. Amer. Chem. Soc.*, 1948, **70**, 1401.

⁷ Fyfe, *Nature*, 1952, **169**, 69.

with increasing molecular volume of the additive. On the other hand, the pyridine and γ -picoline plots for silver nitrite in ethylene glycol (Fig. 2) do not show this trend. A possible explanation appears in that the quantitative values of the basic strengths considered are in all cases the basic strengths in water. The strength of a base in two different solvents will not be the same and it is even possible that the order of strengths in water of the bases used, *viz.*, pyridine < α -picoline < γ -picoline < collidine, may not be the same in another solvent. The fact that the pyridine solution has a lower Λ_0 than the picoline solution may be due to the hydroxylic nature of the solvent, *i.e.*, a levelling solvent. Hence undoubtedly some solvation of the cation by glycol molecules occurs and this, combined with our comparative ignorance of the nature of the ionic complex formed, leads to the possibility that the pyridine complex is relatively more solvated by glycol molecules than is the picoline complex.

Griffiths and Lawrence's results for silver nitrate in glycol are included in Fig. 2 for comparison. From a theoretical standpoint it seems probable that the dissociation of the nitrate and nitrite should be similar in glycol solutions containing 1% of pyridine and hence their slopes in Fig. 2 should be approximately parallel. This is indeed the case. It is a reasonable assumption that the effects, if any, of basic additives on the anion will be negligible compared with the effect on the cation. Hence in applying Walden's rule in the form:

$$\lambda_0^\pm \eta = \frac{eF}{3\pi} \left\{ \frac{1}{r_+} + \frac{1}{r_-} \right\}$$

where λ_0^\pm = ionic mobility, η = viscosity, r_- = radius of anion, and r_+ = radius of cation, it may be safely assumed that for binary mixtures only r_+ has changed. This, together with the necessary assumption that r_+ and r_- are equal for the pure solvent, allows the calculation of the Stokes radii for all the solvent mixtures used. The Table lists the Stokes radii for the various solutions investigated together with the corresponding Bjerrum parameters. Both factors increase with the molecular volume of the base added, thus lending considerable support to the theory of the formation of an ionic complex of the type shown in eqn. (1). Since the validity of the Bjerrum parameter depends on the assumption that only electrostatic forces are involved, the values derived may be accepted only as guides to the magnitude of the distance between the centres of charge. The Stokes radii give a far more realistic picture of the sizes of the ions involved.

It appears that the association-dissociation process depends to quite a large extent on the size of the ions involved. However, if, as seems probable, a reversible process, such as that indicated in eqn. (1) is involved, the dissociation will also depend directly on the basic strength of the complex-forming component of the solvent. In other words, the extent to which preferential solvation takes place, apart from the actual size of the ion so produced, will also affect the degree of dissociation.

Addition of benzene to silver nitrate (see Fig. 1) and silver perchlorate in acetone (see Fig. 1) caused slight changes in the conductivity of each solution. Moreover, in both cases the change was as would be expected from the change produced by organic bases, *i.e.*, an increase for the nitrate and a decrease for the perchlorate. The results are of interest since they are compatible with π -complex formation. These actual differences are small and quantitative interpretation would be unjustifiable until a more refined experimental technique is developed, but any significance which can be associated with the results tends to support π -complex formation. Nitromethane had no effect on the conductivity of the silver nitrate solution, indicating that it is the availability of the electrons on the nitrogen atoms that determines the effect of nitrogenous additives on the conductivity of the electrolyte solution.

Experimental.—This was as described earlier.^{1,2}

Acetone, ethylene glycol, and organic bases were purified as described by Griffiths and

Lawrence,^{1,2} Benzene was purified by the method of Rybicka and Wynne-Jones,⁸ and nitromethane was purified by distillation in a stream of nitrogen at reduced pressure.

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⁸ Rybicka and Wynne-Jones, *J.*, 1950, 3671.
