167. *The Conductivity of Silver Nitrate in Non-aqueous and Mixed Solvents. Part VII.**

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Measurements of the conductivity of silver nitrate in methanol and in binary mixtures of methanol containing 0·1 mole % of pyridine, α-picoline, acetonitrile, benzonitrile, nitromethane, nitroethane, water, or benzene at 25° are reported and discussed. The molecular volume of the additive appears to influence the mobility and extent of association of silver nitrate though other factors are clearly involved.

The variation of equivalent conductivity at infinite dilution and of degree of dissociation for a given salt in a binary solvent mixture, comprising a main solvent and a small amount of an organic substance likely to interact exclusively with cations, has been investigated by several workers. Griffiths, Lawrence, and Pearce [1] observed the effects of the addition of a small amount of organic base on the ionic mobility and degree of dissociation of silver salts in non-hydroxylic media. They observed that a decrease in ionic mobility at infinite dilution, which corresponds to an increase in Stokes's cationic radii, is accompanied by a decrease in dissociation. Such a trend was attributed to an increase in either the basicity or the molecular volume of the additive, although it was suggested that these factors might act in concert. The variation in Stokes's cationic radii was ascribed to variation in solvent–cation interaction. It was decided to extend the knowledge of solvent-ion effects by a similar study of the effects of the presence of an electron-donating additive present in sufficient amount (0·1 mole %) to interact appreciably with the cation but not to alter the viscosity and dielectric constant of the main solvent effectively. Silver nitrate was chosen as the electrolyte since the small electrophilic silver ion would be likely to take part in solvent-ion interaction.

From the experimental results shown (Tables 1 and 2), values of Λ_0 and K_A, the association constant, were calculated by Shedlovsky's extrapolation method.[2] Some of the results were submitted to Fuoss's extrapolation method [3] based on the Fuoss–Onsager

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* Part VI, Griffiths and Pearce, *J.*, 1958, 1557.

[1] Griffiths and Lawrence, *J.*, 1955, 2797; Griffiths and Pearce, *J.*, 1957, 3243.

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

[3] Fuoss, *J. Amer. Chem. Soc.*, 1958, **80**, 3163.

theory [4] of electrolytic conductance and these are shown for comparison. The Λ_0 values calculated by the Fuoss method are a little greater than the Shedlovsky values although agreement is quite close.

In Fig. 1 values of Λ_0 are plotted against the molecular volume of the additive. The trends A and C probably indicate an increasing tendency of the additive to build up structure round the silver ion. Trend B, on the other hand, may indicate an increasing tendency of the additive to break down structure round the silver ion. If it is assumed that molecules of the main solvent and/or additive molecules attach themselves to the silver ion, it is possible that such molecules still play some part in the pseudo-crystalline structure of the solvent, either by changing places or interacting with molecules comprising the pseudo-crystalline structure of the solvent. This is more likely to be the case in pure methanol than in the solvent mixtures since, in the latter case, the structure of the cationic species probably ceases more abruptly at the periphery. Thus, the point for pure methanol may represent a special case. If the theory of Frank, Evans, and Wen-Yang Wen [5] of water–ion interaction is applied to methanol solutions, then competition between (*a*) solvent-molecule immobilisation in the region adjacent to an ion on the one hand, and (*b*) structure breakage beyond the periphery of the ionic species, on the other, determines the extent of the net structure-breaking or -making effect. In methanol–acetonitrile, –pyridine, and –α-picoline, effect (*a*) must offset (*b*) to a greater extent than in methanol or methanol–water, –benzonitrile and –benzene. Nitromethane and nitroethane stand out from the other additives as they produce much more pronounced effects: the ionic mobility at infinite dilution is increased by as much as 9% and association is considerably enhanced. The situation in methanol and methanol–water, –benzonitrile and –benzene may, therefore, be represented as competition between (*a*) and (*b*) which is more equal than in methanol–nitromethane and –nitroethane. In the last two cases effect (*b*) appears to be more important than (*a*). Thus, the presence of nitroparaffins incurs an increase in (*b*) and/or a decrease in (*a*). It is doubtful if the extent of effect (*b*) is very much different from that in the other solvent

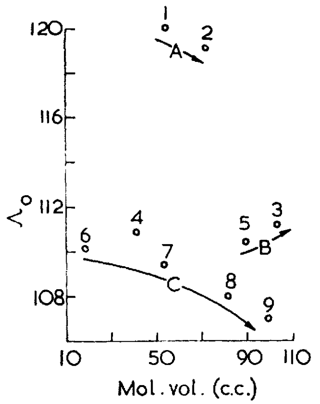

FIG. 1. Plot of Λ_0 against molecular volume for silver nitrate in pure methanol and mixed solvents.

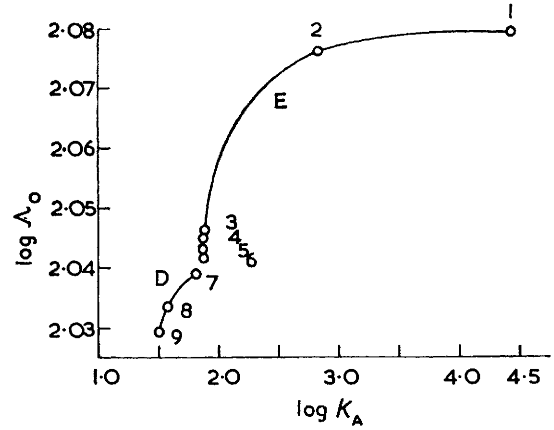

FIG. 2. Plot of $\log \Lambda_0$ against $\log K_A$ for silver nitrate in pure methanol and mixed solvents.

Key to both Figs.: (4) Pure methanol. Other points are for 99·9 mole % of methanol with 0·1 mole % of (1) nitromethane, (2) nitroethane, (3) benzonitrile, (5) benzene, (6) water, (7) acetonitrile, (8) pyridine, and (9) α-picoline.

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[4] Fuoss and Onsager, *J. Phys. Chem.*, 1957, **61**, 668.

[5] Frank and Evans, *J. Chem. Phys.*, 1945, **13**, 507; Frank and Wen-Yang Wen, *Discuss. Faraday Soc.*, 1957, **24**, 133.

TABLE 1.

Conductivities of silver nitrate at 25°.

Pure methanol

10^4c	Λ
0·3659	103·05
0·4397	103·60
0·4915	106·41
0·4939	103·98
0·7242	107·86
0·7733	108·16
0·8846	107·92
1·1484	107·32
1·1650	107·46
1·1697	107·25
1·2365	107·10
1·3714	107·28
1·4039	107·01
1·6958	106·44
2·2160	105·75
2·3181	105·57
2·4594	105·57
2·5116	105·48
2·6372	105·10
2·7845	104·91
2·8119	105·06
2·8595	104·92
3·4831	104·06
3·6764	104·02
3·8879	103·77
4·0009	103·62
4·1215	103·46
4·1774	103·29
4·4857	103·10
4·9121	102·54
5·3200	102·25
6·0710	101·39
6·1200	101·41
6·7376	100·99
7·1349	100·54
7·6343	100·09
7·8746	99·97
8·3205	99·45
9·0377	99·16
9·4331	98·66
9·6461	98·43
12·8259	96·47
16·8137	94·20

Methanol 99·9 moles %–pyridine 0·1 mole %

10^4c	Λ
0·7730	105·21
1·6022	104·27
1·9077	103·79
2·8006	102·98
3·4853	102·38
3·7794	102·15
5·4114	100·81
5·9600	100·43
7·0414	99·75
7·8653	99·20

Methanol 99·9 moles %–α-picoline 0·1 mole %

10^4c	Λ
0·4010	99·71
0·9464	103·53
1·6624	103·27
3·0385	101·87
4·7190	100·58
6·9343	99·10
8·8668	97·94
11·0081	96·82
13·3527	95·77

Methanol 99·9 moles %–acetonitrile 0·1 mole %

10^4c	Λ
0·5533	107·28
1·5607	105·30
1·7246	105·15
2·2866	104·28
2·7016	103·88
3·8640	102·59
4·7640	101·69
5·3819	101·13
6·7770	99·94
7·3625	99·50
8·3901	98·68

Methanol 99·9 moles %–benzonitrile 0·1 mole %

10^4c	Λ
0·3681	103·08
0·5396	106·72
1·2209	107·35
1·2960	106·95
2·5501	105·57
3·7379	104·11
5·8010	101·98
7·6021	100·43
9·3777	98·98

Methanol 99·9 moles %–nitromethane 0·1 mole %

10^4c	Λ
0·5558	112·79
0·8448	111·07
1·2452	109·61
1·6065	108·65
1·8058	108·12
1·9993	107·87
2·4986	107·02
2·9818	106·25
3·2496	105·99
3·9031	105·16
4·7042	104·17
4·7141	104·11
5·9918	102·91
6·5447	102·34
7·6343	101·36
8·8539	100·30
11·0325	98·61

Methanol 99·9 moles %–nitroethane 0·1 mole %

10^4c	Λ
0·3601	108·40
0·7216	108·60
0·9525	108·16
1·3652	107·98
1·5620	107·40
1·8477	107·10
2·4093	106·41
3·4012	105·37
4·5733	104·06
6·1003	102·71
7·1519	101·94

Methanol 99·9 moles %–water 0·1 mole %

10^4c	Λ
0·8822	106·65
1·7715	105·44
2·1694	105·09
2·7625	104·19
3·6273	103·38
3·7454	103·16
5·1698	101·66
5·2042	101·71
6·1673	100·75
6·5514	100·49
7·4084	99·71
7·6301	99·58

Methanol 99·9 moles %–benzene 0·1 mole %

10^4c	Λ
1·1860	106·78
1·2355	106·64
2·9118	104·58
3·3712	103·83
3·8951	103·24
4·2693	103·08
4·8925	102·20
5·4853	101·85
5·9281	101·21
6·6626	100·76
7·0259	100·20
8·2801	99·39

TABLE 2.

Results for pure methanol as solvent and for 99·9 moles % of methanol plus 0·1 mole % minor solvent additive.

Solvent additive (0·1 mole %)	Λ_0 (Shedlovsky)	Λ_0 (Fuoss)	K_A (Shedlovsky)	K_A (Fuoss)	a_K	$a_K\Lambda_0$
(Pure methanol)	110·88	111·00	73·8	67·8	2·28	5·2
Pyridine	108·01	108·10	37·2	30·1	2·68	5·0
α-Picoline	107·01	—	32·2	—	2·78	—
Nitromethane...........	120	—	30,700	—	1·11	—
Nitroethane	119·09	—	691	—	1·60	—
Benzonitrile	111·21	—	75·3	—	2·27	—
Acetonitrile	109·41	—	63·9	—	2·34	—
Water	110·17	—	72·5	—	2·28	—
Benzene	110·47	110·66	71·8	78·5	2·29	8·3

mixtures since the structure of the cationic species should be discontinued at its periphery quite abruptly in all such cases. It is convenient to suggest that the nitroparaffins probably take part in permanent solvation, whereby a conducting ionic species is formed that is significantly smaller than that existing in pure methanol. In the latter solvent the solvation sheath is probably composed of methanol molecules which may either bond to, or interchange with, adjacent methanol molecules in the bulk of the solvent, giving rise to a larger conducting ionic species. The bases pyridine and α-picoline are also likely permanently to solvate the silver ion since the π-electron density in the region of the nitrogen atom is considerable [6] and there is evidence for the existence of cationic complexes of the type $Ag(pyr)_2^+$.[7] In all other solvents under consideration the solvent sheath is either modified little from that in methanol, and/or solvent molecules, particularly those of the additive, move into and out of the solvent sheath, thereby inhibiting approach of an oppositely charged ion less than if solvation had been of a more permanent type.

Successive differentiation with respect to $1/a$ of the equation

$$\ln K_{\mathrm{A}} = \ln \frac{4\pi Na^3}{3000} + \frac{\boldsymbol{e}^2}{Da\boldsymbol{k}T}, \tag{1}$$

derived by Fuoss,[8] reveals that a plot of log K_{A} against $1/a$ should pass through a minimum at which

$$a_{\mathrm{min.}} = \boldsymbol{e}^2/3D\boldsymbol{k}T. \tag{2}$$

The value of $a_{\mathrm{min.}}$ for methanol is 5·9 Å. If the value of $a_{\mathrm{min.}}$ is exceeded the geometric probability of finding an anion, say, within a distance a of a cation becomes more important than the electrostatic weighting factor $\boldsymbol{e}^2/Da\boldsymbol{k}T$ in determining ln K_{A}. It is difficult to test equation (2) as the only independent values of the parameter a available in the present cases are those obtained from the Fuoss–Onsager theory. Since these are sensitive to small variations in the value of the dielectric constant they may not be reliable, particularly in cases where an additive is present. However, Λ_0 should reflect (if not in the precise manner predicted by Stokes's law) variation in ion size for the same ion from solvent to solvent. A plot of log K_{A} against log Λ_0 (Fig. 2), in fact, reveals two curves D and E, the latter appearing to approach the condition cited by equation (2) more quickly than the former. This curve passes through a minimum value of log K_{A} at which the value of Λ_0 is 110·5, whereas curve D approaches a minimum value of log K_{A} at a much lower value of Λ_0. Pyridine, α-picoline, and acetonitrile are known to form complexes with the silver ion,[7,9] and the first two of these are likely to form complexes of the type $Ag(pyr)_2^+$ and $Ag(\alpha\text{-picoline})_2^+$ which, like the $Ag(NH_3)_2^+$ ion, are probably linear. If ionic species of such a 1 : 2 type (or of a 1 : 1 type if only one molecule of base is involved in permanent solvation) are present, the geometric probability of finding an anion within a certain distance of the cation would be different from that suggested for a spherical cation. Approach of oppositely charged ions would then have to be directionally specific if association is to occur, *i.e.*, there would be an effective decrease in the geometric probability of finding an anion within certain close distances of the cation. Thus, the smaller values of K_{A} in the presence of acetonitrile, pyridine, and α-picoline may result from the deviation of the ionic species from the spherical model. The decreasing trend in K_{A} with increasing molecular volume in these three cases would support such an idea.

Values of the parameter a have been calculated by the methods of (i) Fuoss [8] (a_K)

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[6] Fyfe, *Nature*, 1952, **169**, 69.

[7] Ahrland, Chatt, Davies, and Williams, *Chem. and Ind.*, 1955, 96; Woodman and Corbet, *J.*, 1925, **127**, 2461; Schmidt and Keller, *Z. phys. Chem.*, 1929, *A*, **141**, 331; Britton and Williams, *J.*, 1935, 798.

[8] Fuoss, *J. Amer. Chem. Soc.*, 1958, **80**, 5059.

[9] Sidgwick, " Chemical Elements and Their Compounds," Oxford Univ. Press, London, 1st edn., p. 136.

(which represents an improvement on the Bjerrum treatment[10] as regards both the consideration that ions have finite size and the definition of an ion pair as a pair of ions in physical contact) and (ii) from the corresponding J values ($a_{K\Lambda_0}$) obtained by Fuoss's extrapolation method[3] based on the Fuoss–Onsager theory[4] of electrolytic conductance. The values calculated by the latter method appear to approximate to the sum of the Stokes's cationic and anionic radii in some cases. However, the dielectric constant of the solvent medium between two closely approaching oppositely charged ions may be a variable and elusive value,[11] especially in mixtures of the type considered here and the parameters a calculated by both methods in such cases may have little significance. Nevertheless, it is interesting that the value of Λ_0 at which log K_A is a minimum corresponds to a sum of the Stokes's cationic and anionic radii of 5·48 Å and the most meaningful value of the parameter a ($a_{K\Lambda_0}$) is probably that of 5·24 Å in pure methanol since the dielectric constant of the medium immediately surrounding ions is more accurately known than in the solvent mixtures. Thus, the real value of $a_{\text{min.}}$ is unlikely to differ so much from either of these two values as to approach the much larger value of approximately 9 Å predicted by the Bjerrum theory[10] of ion-pair formation. In other words, the Fuoss theory,[8] which predicts a value of 5·9 Å for $a_{\text{min.}}$, appears to be more applicable here.

EXPERIMENTAL

Procedure.—Conductivities were measured at 25° ± 0·05° with apparatus similar to that described by Davies,[12] except that the oscillator and detector were incorporated in one instrument supplied by Airmec Laboratories Ltd. Most measurements were made at a frequency of 1 kc./sec., but this was varied from time to time to ensure that polarisation effects were absent. The cells were of the Hartley–Barrett type,[13] made of borosilicate glass and fitted with " greyed " platinum electrodes.

The " dilution run " technique was used. Weighed amounts of electrolyte solution were added to the solvent in the cell by a weight pipette, and solutions were made up by weight. Air and impurities were excluded by using all-glass apparatus, and solvent and solutions were " blown over " into the cell or weighing vessel with dry nitrogen freed from possible traces of carbon dioxide. Λ values were reproducible to within ±0·04% in those cases where the Fuoss extrapolation technique was used.

Materials.—Water of specific conductivity better than 0·2 gemmho was used. Potassium chloride and silver nitrate were recrystallised several times from such conductivity water.

Methanol was purified by Gillo's method.[14] In the final stages of purification the methanol was distilled at least twice from sodium. The specific conductivity was better than 0·02 gemmho.

Pyridine was purified by the method described by Griffiths[15] and benzene by the method of Rybicka and Wynne-Jones.[16] Nitromethane and nitroethane were each treated with calcium chloride and distilled once only. Other solvents were purified by repeated fractionation. The additives had the following b. p.s at atmospheric pressure: pyridine, 115·2°; α-picoline 129°; acetonitrile, 81°; benzonitrile, 189°; nitromethane, 101°; nitroethane, 114·9°; benzene, 80°. They were each stored under nitrogen in sealed ampoules until required.

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[10] Bjerrum, *Kgl. danske Videnskab. Selskab, Mat.-fys. Medd.*, 1926, **7**, No. 9; " Selected Papers," p. 108, Einar Munksgaard, Copenhagen, 1949.
[11] Hasted, Ritson, and Collie, *J. Chem. Phys.*, 1948, **16**, 1.
[12] Davies, " The Conductivity of Solutions," Wiley and Chapman, 1933, 2nd edn., p. 50.
[13] Hartley and Barrett, *J.*, 1913, **103**, 786.
[14] Gillo, *Ann. Chim. (France)*, 1939, **12**, 281.
[15] Griffiths, *J.*, 1952, 1326.
[16] Rybicka and Wynne-Jones, *J.*, 1950, 3671.