96. *The Conductivity of Silver Nitrate in Non-aqueous and Mixed Solvents. Part IV.**

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The conductivity of silver nitrate solutions in ethylene glycol, in aqueous binary mixtures of ethylene glycol, and in mixtures of the glycol with pyridine and quinoline is reported and discussed.

HYDROXYLIC solvents have been used extensively in the study of the conductivity of electrolytes in non-aqueous and mixed solvents. Although water has received the most attention as a hydroxylic solvent the behaviour of many electrolytes in ethanol and methanol has also been investigated. Gurney [1] discusses the fact that ethylene glycol is a " suitable solvent for comparison with water, without the eccentricities of the latter," but there are relatively few data available for solutes in ethylene glycol, either alone or in binary mixtures. Muller, Raschka, and Wittman [2] studied electrolytic behaviour in this solvent and calculated values of Λ_0 for a number of salts, but it is felt that certain of their values require further investigation in the light of modern theory. Garrett and his co-workers [3, 4] reported the conductivities of thallous chloride and lead chloride over the complete range of aqueous ethylene glycol concentrations. For the former salt, they found that the dissociation constant was a minimum for solutions containing 60% of ethylene glycol and suggested that this might be due to a " solvent sorting effect " which would reduce the value of the dielectric constant in the immediate neighbourhood of the ions, facilitating the formation of triple ions. With lead chloride the discrepancies between theory and experiment were accounted for by differences between the macroscopic and so-called " microscopic " dielectric constant, the values of the latter being calculated from experimental results. However, James [5] showed that the experimental data could be satisfactorily treated without recourse to a microscopic dielectric constant, by use of the concept of ion-association and the assumption of the existence of the $PbCl^+$ ion in solutions of lead chloride, an assumption supported by spectroscopic evidence (cf. Fromherz and Kun-Hou Lih [6]). Binary mixtures of aqueous ethylene glycol were used by James [7] in an investigation of the type of forces involved in association, where it was found that in water-rich mixtures the deviations from Onsager's theory could be explained by the formation of ion-pairs being governed by purely electrostatic forces, but as the dielectric constant fell this assumption became less tenable.

In a previous paper [8a] it was shown that, for silver nitrate in acetone and binary aqueous mixtures, the dissociation constant was not entirely dependent on the dielectric constant of the solvent and it was suggested that forces other than the electrostatic attraction between the ions were involved in the association. It was thought that if the behaviour of silver nitrate in the ethylene glycol–water system was studied in a similar manner to the acetone–water system further information regarding the association–dissociation process would be obtained. Further the effect of change in the effective size of the cation would be obtained if certain organic bases, *e.g.*, pyridine and quinoline, which interact strongly with the argentous ion were added to the ethylene glycol solutions.

RESULTS AND DISCUSSION

The conductivity of silver nitrate in ethylene glycol, and in solutions containing water, pyridine, and quinoline are given in Tables 1 and 2, all solvent compositions being given as weight percentages. The derived constants are given in Table 3.

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* Part III, *J.*, 1955, 2797.

[1] Gurney, " Ionic Process in Solution," McGraw-Hill, New York, 1953, p. 187.

[2] Muller, Raschka, and Wittman, *Monatsh.*, 1927, **48**, 659.

[3] Garrett and Vellenga, *J. Amer. Chem. Soc.*, 1945, **67**, 225.

[4] Garrett and Norman, *ibid.*, 1947, **69**, 110.

[5] James, *ibid.*, 1949, **71**, 3243.

[6] Fromherz and Kun-Hou Lih, *Z. phys. Chem.*, 1931, *A*, **153**, 321.

[7] James, *J.*, 1950, 1094; 1951, 153.

[8] Griffiths and Lawrence (*a*) *J.*, 1955, 2797; (*b*) 1952, 1326.

The Λ–$\sqrt{c}$ plots for the mixtures over the concentration range studied were linear and showed only small deviations from the theoretical Onsager slope, indicating that the salt was dissociated to a very large extent. Shedlovsky's extrapolation method[9] with the tabulated extrapolation functions given by Daggett[10] was used to determine Λ_0 and K, but since the elctrolyte is almost completely dissociated the value of the latter will not be very accurate. The parameter "a" was calculated by Bjerrum's theory[11] (1926, 7, No. 9). The values for the Stokes radius "r" were obtained by assuming the mobility of the anion and cation to be equal and using Walden's rule in the form

TABLE 1. *Conductivity of silver nitrate in ethylene glycol and in aqueous binary mixtures.*

Ethylene glycol		10% Water		20% Water		40% Water		60% Water		80% Water	
10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ
0·5445	9·05	2·0491	13·11	1·7058	18·84	1·0885	34·37	0·5056	57·47	1·1165	90·59
1·5441	8·99	2·7808	13·07	2·5004	18·71	1·6397	34·30	1·1789	57·38	2·0465	90·27
2·8938	8·93	3·6454	13·01	3·3260	18·67	2·4198	34·17	2·0158	57·15	3·2762	89·83
4·3172	8·89	4·8613	12·95	4·3788	18·59	3·2370	34·11	3·2161	57·10	4·5931	89·59
6·5899	8·84	6·3110	12·92	6·1499	18·50	4·5088	34·04	4·2185	56·95	6·2041	89·39
9·5209	8·76	7·5620	12·87	8·0632	18·47	6·6016	33·90	5·3618	56·80	7·5808	89·25
11·648	8·73	9·2355	12·83	9·4954	18·40	8·3693	33·79	7·4443	56·52	9·0771	89·06
13·941	8·67	11·146	12·79	11·618	18·32	10·774	33·64	10·178	56·34	10·770	88·82
16·416	8·63	12·572	12·77	13·432	18·30	13·632	33·55	12·548	56·25	12·147	88·62
18·932	8·59	15·560	12·72	18·526	18·16	16·236	33·44	15·084	56·12	13·303	88·52
21·919	8·55	18·680	12·67	—	—	20·191	33·31	19·312	55·86	14·886	88·37
24·427	8·51	—	—	—	—	—	—	25·813	55·62	17·381	88·17

TABLE 2. *Conductivity of silver nitrate in ethylene glycol solutions containing small additions of pyridine and quinoline.*

1% Pyridine						1·62% Quinoline					
10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ	10^4c	Λ
0·4483	6·89	2·6788	6·77	7·6113	6·62	0·8564	6·30	4·2211	6·21	8·8638	6·13
0·8781	6·86	3·4844	6·73	9·2300	6·59	1·4123	6·27	5·3657	6·19	11·168	6·09
1·3082	6·82	4·3143	6·71	12·370	6·55	1·9586	6·25	6·1780	6·17	—	—
1·7802	6·78	6·1463	6·69	18·251	6·48	3·3541	6·23	7·4195	6·14	—	—

TABLE 3. *Ethylene glycol–water mixtures.*

Organic solvent (%)	D	Λ_0	K	$\Lambda_0\eta$	r (Å) *	a (Å)
100	37·7	9·14	0·11	1·653	2·0	4·6
90	43·7	13·27	0·18	1·838	1·8	4·0
80	49·3	19·00	0·12	1·929	1·7	2·3
60	59·4	34·62	0·24	1·627	2·0	2·1
40	66·6	57·76	0·72	1·386	2·4	2·8
20	72·8	91·17	0·28	1·258	2·6	1·3
	Ethylene glycol–pyridine base mixtures.					
1% Pyridine	37·7	6·93	0·08	1·254	2·6	3·9
1·62% Quinoline ...	37·7	6·38	0·71	1·154	2·8	6·9

* r = Stokes's radius.

TABLE 4. *Walden's rule for silver nitrate in various hydroxylic solvents.*

Solvent	Ethylene glycol	Water	Methanol	Ethanol
$\Lambda_0\eta$	1·65	1·19	0·605	0·483

$$\Lambda_0\eta = \frac{eF}{6\pi}\left(\frac{1}{r_+} + \frac{1}{r_-}\right)$$

where η is the viscosity, and r_+ and r_- the apparent ionic radii ($r_+ + r_- = r$). Application of this assumption to the data for silver nitrate in water gives "r" a value of 2·7 Å, which

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

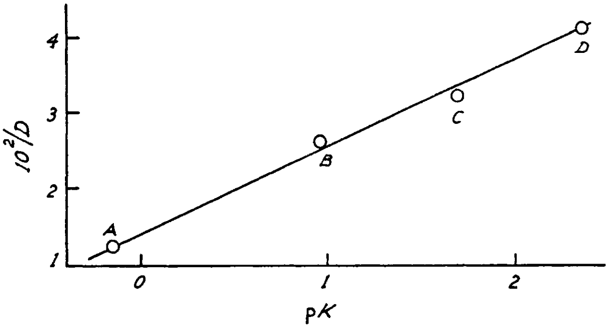
[10] Daggett, *J. Amer. Chem. Soc.*, 1951, **73**, 4977.

[11] Bjerrum, *Kgl. Danske Videnskab.*, 1926, **7**, No. 9.

compares favourably with the sum of the radii determined from ionic mobilities (2·68 Å) (cf. Moelwyn-Hughes [12]).

It might be expected that solutions of silver nitrate in ethylene glycol would show certain similarities to solutions in water (cf. ref. 1) if allowances could be made (*a*) for reduced mobilities of the ions owing to the high viscosity of the solvent, (*b*) for any solvation differences, and (*c*) for the greater possibility of ion association due to the lower dielectric constant of the glycol ($D = 37{\cdot}7$). In the systems studied this latter is not of cardinal importance since it has been seen that the salt is very largely dissociated even in pure ethylene glycol. As far as changes in solvation are concerned it is usually accepted that the value of the Walden product $\Lambda_0\eta$ gives an indication of such changes. Table 4 gives the value of this product for a number of hydroxylic solvents and it can be seen that the value is largest in ethylene glycol. This leads to the conclusion that the ions are less solvated in this solvent than in any of the others (see Davies [13]) and indeed it may well be that the ions possess no primary solvation in glycol.

Moelwyn-Hughes [12] showed that when ΔG^0 was plotted as a function of $1/D$ for an electrolyte in hydroxylic solvents a linear relationship existed. The figure shows a similar plot (pK–$1/D$) for silver nitrate in some hydroxylic solvents including the value for this electrolyte in ethylene glycol, and it can be seen that the collinearity is maintained.



Plot of $1/D$ *against* pK *for silver nitrate in hydroxylic solvents at* 25°.

A, Water.
B, Ethylene glycol.
C, Methanol.
D, Ethanol.

However, when such a plot was made for the ethylene glycol–water system no such simple relation held, as was also noted with the acetone–water system (Griffiths and Lawrence [8a, 8b]), the value of K being smaller than would be expected in a pure hydroxylic solvent of the same bulk dielectric constant. The reason is not clear but there are several factors which may contribute, namely, (i) a partial breakdown of the hydrogen-bonded structure of the ethylene glycol (cf. Sadek and Fuoss [14]); (ii) a change from the bulk dielectric constant of the solvent due to electrical saturation near the ion;[15] or (iii) preferential solvation leading to the formation of a region near the ion which is predominantly of one component of the binary mixture with resulting changes in dielectric constant. Yet another factor is that preferential solvation could lead to the microscopic viscosity's differing from the bulk value of the solution (see Griffiths [16]). Further, in aqueous solutions the silver ion, because of its charge and size, is an order-producing ion whilst the nitrate ion is of the disorder-producing type (Gurney, ref. 1, p. 250), but in glycol solutions both ions may be of the order-producing type. The addition of water to such electrolyte solutions will thus affect the order-producing properties of the ions which will modify such solvent interaction as may occur when the second component is added.

On considering the solutions to which small additions of pyridine and quinoline were added, it can be seen that r increases somewhat over the value holding in glycol. Although the solutions have essentially the same bulk dielectric constant, the K values are markedly

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[12] Moelwyn-Hughes, " The Kinetics of Reactions in Solution," Oxford Univ. Press, 1947, 2nd Edn., p. 198.

[13] Davies, " Conductivity of Solutions," Chapman and Hall, London, 1933, 2nd Edn., pp. 117, 118.

[14] Sadek and Fuoss, *J. Amer. Chem. Soc.*, 1954, **76**, 5897.

[15] Robinson and Stokes, " Electrolytic Solutions," Butterworths, London, 1955, p. 30.

[16] Griffiths, *J.*, 1954, 686.

different, being 0·08 for solutions containing pyridine and 0·71 for those containing quinoline, and this fact is reflected in the "*a*" parameters of 3·9 Å and 6·9 Å respectively.

It is thus evident that pure ethylene glycol solutions of silver nitrate show characteristics common to the other hydroxylic solvents mentioned, in as far as the dissociation appears to be controlled by variation of the bulk dielectric constant. When binary mixtures are considered, however, no such simple relationship holds, a fact which is particularly emphasised in solutions containing organic bases, where the bulk dielectric constant remains sensibly the same but the dissociation constant alters appreciably.

EXPERIMENTAL

Procedure.—This is as described in Part II.[18]

Materials.—Ethylene glycol was purified by Smyth and Walls's method.[17] It was distilled under reduced pressure, and the middle fraction was then shaken with anhydrous sodium sulphate and twice redistilled, the middle fraction being retained each time. All distillations were carried out in dry nitrogen. The ethylene glycol had b. p. 197°/760 mm. and its specific conductivity was 0·03—0·06 $\times 10^{-6}$ mho. It was stored under nitrogen. Other solvents and the electrolyte were purified as described previously.[18]

The authors thank The Morgan Crucible Co., Ltd., for a scholarship (to K. S. L.), the Central Research Fund of the University of London for a grant (to V. S. G.) and Imperial Chemical Industries Limited for a grant for the provision of glassware and cells.

BATTERSEA POLYTECHNIC, LONDON, S.W.11. [*Received, June 9th*, 1955.]

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[17] Smyth and Walls, *J. Amer. Chem. Soc.*, 1931, **53**, 2115.
[18] Griffiths and Lawrence, *J.*, 1955, 1208.