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

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The variation of the conductivity of silver nitrate in 1 : 4-dioxan–water solutions, in acetone, and in acetone–water mixtures is reported and discussed.

THE effect of solvent composition on the conductivity of electrolytes has been studied frequently, the greatest attention having been paid to water-rich binary aqueous organic solvent solutions. James (*J.*, 1950, 1094; 1951, 153) showed that for certain electrolytes (*e.g.*, lanthanum ferricyanide and zinc and copper sulphates) in water-rich acetone, glycol, ethanol, and dioxan solutions the deviations from Onsager's theory (*Physikal. Z.*, 1927, **28**, 277) could reasonably be accounted for in terms of ion-association based upon Bjerrum's theory (*Kgl. Danske Videnskab. Selsk.*, 1926, **7**, No. 9) which supposes purely coulombic forces to exist between the constituent ions. However the data for zinc malonate could not be treated as satisfactorily on this basis and it was suggested that the association in this salt is not governed solely by coulombic forces. Support for this idea can be found in the behaviour of organic acids in mixed solvents, *e.g.*, the data of Harned and Done for formic acid in 20%-dioxan–water solutions (*J. Amer. Chem. Soc.*, 1941, **63**, 2579) give a dissociation constant 100 times as great as that calculated on the basis of simple electrostatic forces by use of a Bjerrum " *a* " parameter obtained for aqueous solutions.

Although many data are available for the variation of conductivity in organic solvents

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* Part I, *J.*, 1954, 686.

which can be used to test Bjerrum's ion-association theory, organic-solvent rich water mixtures have not been as fully studied. Consequently it was decided to study the behaviour of silver nitrate in mixed solvents of the latter type and to apply to the results Bjerrum's theory in an attempt to determine whether or not forces other than simple electrostatic forces obtain in the ion-association process. The results are presented in the Table.

Conductivities of silver nitrate in the acetone–water system at 25°.

10^4C	Λ	10^4C	Λ
	Dry acetone.		
0·21997	56·38	8·8483	14·12
0·39361	44·45	9·3171	13·74
0·65037	35·94	11·147	13·29
1·1157	28·63	12·755	12·92
1·4260	25·92	13·981	12·70
1·9440	22·89	14·949	12·48
2·6740	20·42	16·153	12·34
4·1271	17·40	17·257	12·22
5·3988	15·98	18·870	12·09
6·1277	15·56	20·335	11·98
7·6585	14·37	22·428	11·82
7·7054	14·61		
	1%-Water.		
0·01418	155·4	0·9188	53·16
0·02106	151·6	1·222	47·14
0·03577	143·4	1·402	43·74
0·05588	132·4	1·713	40·80
0·08413	120·3	2·131	36·88
0·09233	116·6	2·547	34·50
0·1377	104·7	2·825	32·81
0·3001	81·87	3·495	29·80
0·3699	73·98	4·359	27·64
0·4150	72·92	5·453	25·31
0·7017	59·39		
	2%-Water.		
0·03842	157·5	1·503	61·37
0·06290	149·4	2·159	51·43
0·08769	146·7	3·078	44·70
0·1409	128·8	4·642	37·87
0·2485	112·4	6·306	33·51
0·3548	101·8	7·913	30·63
0·5417	88·97	9·528	28·50
0·7688	78·80	11·79	26·29
1·166	67·64		
	5%-Water.		
0·07440	142·8	2·105	91·00
0·1464	138·9	2·494	86·27
0·2387	133·9	3·356	79·32
0·3286	129·4	4·307	72·71
0·4646	123·9	7·920	58·85

10^4C	Λ	10^4C	Λ
	5%-Water.		
0·6316	119·4	12·22	50·15
0·6824	116·6	16·50	44·75
1·082	107·5	22·02	40·07
1·508	99·37	26·99	37·05
	10%-Water.		
0·1042	120·9	1·251	110·8
0·2205	120·2	1·455	110·0
0·2429	119·0	1·821	107·6
0·4859	117·9	2·059	105·7
0·6941	116·2	3·045	101·0
0·8214	114·5	4·591	94·40
0·9321	114·0	7·491	85·91
1·214	111·8	10·92	78·83
	20%-Water.		
0·6365	93·52	2·330	90·55
0·6938	93·26	3·017	89·61
0·8140	93·06	3·521	89·06
0·9789	92·75	3·565	89·16
1·229	92·37	5·010	87·49
1·255	91·95	6·637	86·06
1·601	91·52	9·640	83·49
2·008	91·12	11·37	82·31
	40%-Water.		
0·3015	78·51	2·594	76·83
0·6882	78·15	2·968	76·73
0·7686	77·95	3·499	76·45
1·174	77·64	3·608	76·33
1·327	77·53	4·210	76·16
1·713	77·34	4·856	76·03
1·970	77·16	5·380	75·61
2·356	76·96	6·176	75·48
	50%-Water.		
0·6062	76·99	1·919	76·37
0·8477	76·82	2·088	76·21
1·058	76·67	2·347	76·21
1·112	76·67	2·632	76·07
1·326	76·55	2·933	75·91
1·596	76·45	3·611	75·75

Conductivities of silver nitrate in the dioxan–water system.

10^4C	Λ	10^4C	Λ
	10%-Water.		
1·804	1·46	5·882	0·92
2·280	1·35	7·853	0·82
2·886	1·27	7·960	0·80
2·889	1·23	9·610	0·75
3·349	1·15	12·96	0·66
4·256	1·05	14·44	0·64
4·908	0·99	16·00	0·61
5·408	0·96	19·65	0·55
		25·05	0·50

10^4C	Λ	10^4C	Λ
	20%-Water.		
0·611	32·36	3·235	23·55
0·774	31·00	3·572	22·93
1·055	29·84	4·339	22·12
1·464	28·06	5·984	20·13
1·971	26·79	8·222	18·64
2·482	25·28	11·22	17·05
	30%-Water.		
2·264	42·71	12·82	36·33
4·402	40·80	13·95	35·71
6·661	39·41	16·04	35·01
8·409	38·40	17·32	34·63
8·935	38·12	20·55	33·75
11·35	36·98		

Percentage of organic solvent	Λ_0	K	D	$\Lambda_0 . \eta$ *	a, Å
		Acetone–water system.			
100	206	3×10^{-6}	19·1	0·63	1·5
99	185·18	$9{\cdot}90 \times 10^{-6}$	19·6	0·60	1·62
98	185·77	$2{\cdot}23 \times 10^{-5}$	20·1	0·62	1·68
95	154·49	$1{\cdot}62 \times 10^{-4}$	21·6	0·57	1·85
90	124·45	$1{\cdot}18 \times 10^{-3}$	24·0	0·54	2·02
80	95·83	$9{\cdot}86 \times 10^{-3}$	29·6	0·59	2·36
60	79·05	$4{\cdot}51 \times 10^{-2}$	41·8	0·83	2·06
50	77·72	$9{\cdot}07 \times 10^{-2}$	48·2	0·96	1·91
		Dioxan–water system.			
90	25	5×10^{-7}	5·6	0·35	4·7
80	41·32	$1{\cdot}54 \times 10^{-4}$	10·71	0·72	5·05
70	47·62	$2{\cdot}96 \times 10^{-3}$	17·69	0·91	5·98
0 †	133·36	1·47	78·5	1·19	2·65

* η is the viscosity of the solvent. † From Davies and Robinson (*J.*, 1951, 574).

DISCUSSION

From the experimental results shown values of Λ_0 and of K, the dissociation constant, were calculated by Shedlovsky's extrapolation method (*J. Franklin Inst.*, 1938, **225**, 739), by use of values of the extrapolation function tabulated by Daggett (*J. Amer. Chem. Soc.*, 1951, **73**, 4977). Many of the results were also treated by the extrapolation methods of Fuoss and Kraus (*ibid.*, 1933, **55**, 476) as modified by Fuoss (*ibid.*, 1935, **57**, 488) and Davies (*J.*, 1933, 645), giving values of Λ_0 and K very close to those obtained by the Shedlovsky extrapolation (see Harned and Owen " The Physical Chemistry of Electrolytic Solutions," 2nd Edn., 1949, Reinhold, New York, p. 190, 591; James, *J.*, 1951, 153). A representative set of results, those for silver nitrate in an aqueous dioxan solution containing 80% by weight of dioxan, is shown.

Method	Λ_0	10^4K	Method	Λ_0	10^4K
Fuoss and Kraus	41·30	1·79	Davies	41·61	1·73
Shedlovsky	41·32	1·54			

The extrapolation plots for aqueous dioxan and aqueous acetone solutions were linear up to Fuoss's critical concentration (*J. Amer. Chem. Soc.*, 1935, **57**, 2604) but those obtained for the acetone solutions were somewhat puzzling. Whichever method of extrapolation was used, very marked deviations from linearity occurred at concentrations very much smaller than the critical concentration, and indeed Λ_0 and K were obtained by the extrapolation of the linear portion of the curve to give a value of $\Lambda_0 = 206$, which compares favourably with the sum of the mobilities (208) given by Davies (" Conductivity of Solutions," 2nd Edn., Chapman and Hall, London, 1933, p. 207). It has been suggested tentatively that in such solutions triple-ion formation occurs [see Griffiths and Lawrence (*Research*, 1953, **6**, No. 11); cf. French and Roe (*Trans. Faraday Soc.*, 1953, **49**, 627)] and Kraus (*J. Phys. Chem.*, 1954, **58**, 673) has pointed out that as the dielectric constant decreases to a value in the neighbourhood of $D = 20$ triple-ions are formed, but as yet no satisfactory quantitative conclusion has been reached. It must be emphasised that the accuracy of the results obtained for both Λ_0 and K in acetone and in aqueous dioxan solutions containing 90% of dioxan is not of the highest order in view of the weakness of the electrolyte in these solvents (Kilpatrick, *J. Chem. Phys.*, 1940, **8**, 306).

Bjerrum's " *a* " parameter (*loc. cit.*) was calculated for all solutions, the value in aqueous dioxan varying between 4·7 and 6·0 Å suggesting that solvation molecules may be retained in the ion-association process (cf. Burgess and Kraus, *J. Amer. Chem. Soc.*, 1948, **70**, 706). In acetone and aqueous acetone solutions however the order of the " *a* " parameter was 2 Å, a value smaller than the sum of the ionic radii, which may be taken to indicate that there is greater interaction between the ions than would be expected if only electrostatic forces obtained. It must be remembered, however, that the macroscopic dielectric constant has been used in these calculations, whereas Hasted, Ritson, and

Collie (*J. Chem. Phys.*, 1948, **16**, 1) have shown that in aqueous solutions at distances of less than 4 Å from an ion the dielectric constant is a rapidly varying quantity, and not too great a reliance should be placed upon these values (cf. Bell and George, *Trans. Faraday Soc.*, 1953, **49**, 619; Kraus *loc. cit.*). The $\Lambda_0\eta$ values in both systems show a considerable variation beyond a concentration of 10% of water, a fact that is often taken to indicate that solvation changes are occurring (James, *loc. cit.*), an idea which is not easy to reconcile with other features of this work. For instance, with these mixed solvents, in solutions containing even small quantities of water, the water molecules greatly outnumber the ions [Hughes and Hartley (*Phil. Mag.*, 1933, **15**, 610) show that in a 0·0001N-salt solution containing 0·25% of water the ratio of salt ions : water molecules : methanol molecules is 1 : 500 : 125,000] and since, on general grounds, solvation by water molecules would be a predominating process, it is to be expected that the first additions of water will have the major effect as far as solvation is concerned.

It is seen that as the water content of the solution increases, the value of K increases, *i.e.*, it appears that dissociation is increasing with increasing dielectric constant.

Moelwyn-Hughes ("The Kinetics of Reactions in Solution," 2nd Edn., 1947, p. 198) discusses the variation of K with dielectric constant in terms of the Wynne-Jones equation

$$\frac{d(\ln K)}{d(1/D)_{T,P}} = \frac{Z_A Z_B e^2}{rkT}$$

where r is the sum of the ionic radii, D the dielectric constant of the solvent, and $Z_A Z_B$ are the valencies of the ionic species.

In particular, solutions of silver nitrate in water, methanol, and ethanol were considered and it is shown that a plot of ΔG against $1/D$ gives a straight line from the slope of which an r value of 2·681 Å is calculated, compared with the sum of the ionic radii determined from ionic mobilities, 2·675 Å. This value would thus appear to be independent of solvent. If the matter be pursued further, it can be shown that the data for other solvents, *e.g.*, pyridine, ethylenediamine, acetonitrile, etc., plotted in this manner give points which are widely dispersed about the line joining the points for water, methanol, and ethanol. It is perhaps significant that the latter hydroxylic solvents are considered to be the levelling solvents whilst the former are the differentiating solvents (Davies, "Conductivity of Solutions," 2nd Edn., 1933, Chapman and Hall, p. 229, 231; Glasstone, "Electrochemistry of Solutions," 2nd Edn., 1937, Methuen, London, p. 176) where it would be unwise to suppose that the sum of the ionic radii is independent of solvent.

However, in the work described here it was felt that if the preferential solvation of the ions with water molecules occurs, then at least within any one system the plot of pK against $1/D$ should be linear. This was found to be so in the case of aqueous dioxan solutions, but the acetone–water system gave points which fitted a steep curve.

It thus appears that whilst dioxan–water systems give satisfactory results when treated with theories based on electrostatic forces between ions, the acetone–water systems present many problems. It is clear that silver nitrate in acetone is a much weaker electrolyte ($K = 4 \times 10^{-6}$) than would be expected in a solvent with a dielectric constant of about 20 [*e.g.*, ethanol, $D = 24$, $K = 4{\cdot}4 \times 10^{-3}$ (Copley, Murray-Rust, and Hartley, *J.*, 1930, 2492)]. The very marked curvature of the extrapolation plots (Griffiths and Lawrence, *Research*, 1953, **6**, No. 11) is of interest, since Reynolds and Kraus (*J. Amer. Chem. Soc.*, 1948, **70**, 1709) applied Fuoss and Kraus's method (*loc. cit.*) to the conductivity data for a variety of salts in acetone and obtained only very slight deviations from linearity, whilst several workers, *e.g.*, Corignan and Kraus (*J. Amer. Chem. Soc.*, 1949, **71**, 2983), Luder and Kraus (*ibid.*, 1947, **69**, 2481), Bromley and Luder (*ibid.*, 1944, **66**, 107), who used silver nitrate in basic solvents also obtained almost linear plots. It thus appears that the combination of silver nitrate and acetone leads to "abnormal" results, and an attempt has been made to explain them in terms of acid–base forces (Griffiths and Lawrence, *loc. cit.*). As the water content of the system increases the dissociation constant rises, and it is interesting to note that in 90%-acetone solutions where $D = 24{\cdot}0$, K is of the same order, *i.e.*, $1{\cdot}18 \times 10^{-3}$, as that holding in ethanol solutions, namely $4{\cdot}4 \times 10^{-3}$.

EXPERIMENTAL

Procedure.—Conductivity measurements were made at 25° ± 0·01° with the apparatus described by Davies (*J.*, **1937**, 432). A Sullivan amplifier detector was added to the apparatus for certain measurements. The cells were of the Hartley–Barrett type (*J.*, 1913, **103**, 786), made of borosilicate glass and fitted with greyed platinum electrodes. The solvents were freshly distilled and all solutions were made up by weight. " Dilution run " techniques were used, five or six experimental points were obtained per run and the runs were so arranged that considerable overlap of experimental points was obtained. In order to prevent access of air and impurities the apparatus was all-glass and solvents and solutions were manipulated by the " blowing-over " technique with dry nitrogen. Solvent corrections were usually negligible, the mixed solvents having conductivities of the same order as the pure organic liquids.

Measurements were made at approx. 1, 1·5, and 3 kc./sec. but no polarisation effects were detected.

Materials.—Water of specific conductivity better than 0·6 gemmho was used. The electrolytes were recrystallised several times from such conductivity water.

The solvents were purified as described by Griffiths (*J.*, 1952, 1326) and the physical constants of the mixtures were taken from sources given by him (*J.*, 1954, 686). Particular care was paid to the drying of the acetone (Dippy and Hughes, *J.*, 1954, 953) and Karl Fischer determinations of moisture were made by the method described by Mitchell and Smith (" Aquametry," Interscience Publ., New York, 1948), and purification was continued until the acetone was dry. It was found that as the solvent became progressively drier, the salt became more and more difficult to dissolve in it, and high concentrations of electrolyte could not be obtained (see Griffiths and Lawrence, *loc. cit.*).

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