604. *The Influence of Mixed Solvents on the Dissociation Constant of Silver Acetate.*

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By means of the solubility of silver bromate in various organic solvent–water mixtures containing sodium acetate, the variations in the dissociation constant of silver acetate with changing dielectric constant have been followed. These variations are influenced by the nature of the organic solvent. The results have been used to interpret the solubility of silver acetate in various solvents.

While the influence of solvents of varying dielectric constants on the extent of ionisation of electrolytes has a qualitative explanation, there is still no adequate theoretical treatment which can rigidly account for the observed variations. Consequently it would be useful to compare experimental results with the theoretical interpretations. So far as salt solutions are concerned, however, there is very little available material. Hogge and Garrett (*J. Amer. Chem. Soc.*, 1941, **63**, 1089) developed a solubility method to find the dissociation constant of thallous chloride in ethanol–water solutions; Black and Garrett (*ibid.*, 1943, **65**, 862) studied the same salt in glycol–water; and James (*ibid.*, 1949, **69**, 110) used available data to calculate the extent of dissociation of lead chloride in glycol–water, and later (*J.*, 1950, 1094; 1951, 153) reported conductivity results from which the dissociation constants of lanthanum ferricyanide, of copper sulphate, and of zinc sulphate and malonate in four different types of solvents were found. In the present paper we report results for the ionisation of silver acetate in six different types of organic solvent–water mixtures, obtained by measuring the solubility of silver bromate in these solvents in the presence of sodium acetate, an excess of acetic acid being used to suppress hydrolysis.

EXPERIMENTAL.

Silver bromate was prepared, and the solubilities (at 25° ± 0·03°) were obtained, as described elsewhere (Monk, *Trans. Faraday Soc.*, 1951, **47**, 292). The organic solvents used were of laboratory grade except in the case of dioxan (AnalaR). Sufficient excess of AnalaR acetic acid was added to the solvent mixtures after the addition of sodium hydroxide to keep the pH at 5—6. The solubilities are reported in Table II. In most cases the exact composition of the solvents, *i.e.*, the proportion of organic solvent, was found by determination of the solubility in the solvent mixture alone and interpolation from available data (Owen, *J. Amer. Chem. Soc.*, 1933, **55**, 1922; Neuman, *ibid.*, 1934, **56**, 28), but in a few cases these were supplemented by density measurements. Dielectric constants were obtained from Akerlof's data (*ibid.*, 1932, **54**, 4125).

DISCUSSION.

For purposes of calculation, a general form of activity-coefficient expression was derived from that given by Davies (*J.*, 1938, 2093) for aqueous solutions at 25°, *i.e.*,

$$-\log f_{\pm} = 0{\cdot}5\,[I/(1 + I^{\frac{1}{2}}) - 0{\cdot}2\,I]$$

by modifying it to the form

$$-\log f_{\pm}^{2} = (78{\cdot}54/D)^{3/2}[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0{\cdot}2I] = F'(I)$$

where 78·54 is the dielectric constant of water (Harned and Owen, " The Physical Chemistry of Electrolytic Solutions," New York, 1943, p. 118), D is the dielectric constant of the solvent, and I is the ionic strength. The following expressions were also used :

$$\begin{aligned}
\log\,[\mathrm{Ag}^{\cdot}][\mathrm{BrO_3}'] - F'(I) &= \log S_0 \\
\log\,[\mathrm{AgBrO_3}] &= \log\,[\mathrm{Ag}^{\cdot}][\mathrm{BrO_3}'] - \log K_1 - F'(I) \\
\log\,[\mathrm{NaBrO_3}] &= \log\,[\mathrm{Na}^{\cdot}][\mathrm{BrO_3}'] - \log K_2 - F'(I) \\
[\mathrm{OAc}'] &= [\mathrm{Ag}^{\cdot}] + [\mathrm{Na}^{\cdot}] - [\mathrm{BrO_3}'] \\
\log K &= \log\,[\mathrm{Ag}^{\cdot}][\mathrm{OAc}'] - \log\,[\mathrm{AgOAc}] - F'(I)
\end{aligned}$$

where S_0 is the solubility product of silver bromate, and K, K_1, and K_2 are dissociation constants. In water, K_1 may be taken as 0·5 by analogy with silver perchlorate (K_1 = 0·6) (Monk, *J. Amer. Chem. Soc.*, 1948, **70**, 3281) and K_2 is 3·8 (Banks, Righellato, and Davies, *Trans. Faraday Soc.*, 1931, **27**, 621), but these will be different in the mixed solvents. As an approximation it has been assumed that they vary at the same rate that the dissociation constant of silver acetate varies, *i.e.*, after preliminary values of K were obtained, K_1 and K_2 were modified by the ratio $K(\text{solvent})/K(\text{water})$.

To illustrate that the activity-coefficient expression and the assumptions concerning the variations of K_1 and K_2 with D are reasonably correct, some data of Davis, Ricci, and Sauter (*J. Amer. Chem. Soc.*, 1939, **61**, 3274) for the solubility of silver acetate in 10% dioxan–water containing sodium nitrate have been used to calculate S_0 values by using the value of K obtained by interpolation from the results given in Table II. K was then found to alter from 0·23 in water to 0·14 in this solvent, so that the dissociation constants of sodium nitrate and silver nitrate have been altered from 3·8 in water (Davies, *Trans. Faraday Soc.*, 1927, **23**, 351) to 2·2, and from 1·5 in water (Davies, *Endeavour*, 1945, **4**, No. 15) to 0·88, respectively. These calculations are shown in Table I, where the concentrations are expressed in millimols. and mg.-ions per l. S represents the solubility of silver acetate. The constancy of S_0 over an ionic strength of 0·1 (the limit of the original activity expression) supports the assumptions made.

TABLE I.

Solubility of silver acetate in 10% dioxan-water.

$\mathrm{NaNO_3}$	S	$[\mathrm{Ag}^{\cdot}]$	$[\mathrm{OAc}']$	[AgOAc]	$[\mathrm{NaNO_3}]$	$[\mathrm{AgNO_3}]$	$10^3 I$	$-\log S_0$
—	50·32	41·97	41·97	8·37	—	—	41·97	2·947
5·08	50·81	42·32	42·47	8·34	0·01	0·15	47·47	2·949
9·92	51·16	42·56	42·84	8·32	0·03	0·28	52·30	2·950
49·79	54·13	44·47	45·81	8·32	0·58	1·34	93·63	2·949

In Table II, the dissociation constant of silver acetate obtained in a number of mixed solvents is recorded. The values were obtained by an approximation method by using the expressions quoted above. The average results are plotted as log K against D in Fig. 1, from which it is

TABLE II.

Silver bromate solubilities.

(All figures, × 10^{-3}; S_A = solubility in the mixed solvent; S_B = solubility in the same solvent containing sodium acetate.)

S_A	S_B	NaOH	HOAc	[Ag$^{\cdot}$]	[AgBrO$_3$]	[NaBrO$_3$]	[OAc′]	[AgOAc]	10^3I	K
Water, D = 78·54.										
8·11	9·28	31·80	54·18	8·41	0·11	0·05	31·04	0·76	40·15	0·238
	9·54	39·75	45·01	8·41	0·11	0·07	38·73	1·02	48·09	0·216
	10·24	71·52	77·60	8·51	0·11	0·12	69·90	1·62	79·91	0·230
43·5% Methanol, D = 59·3.										
1·58	2·13	19·53	22·72	1·57	0·03	0·04	19·00	0·53	21·06	0·037
	2·35	31·25	37·86	1·57	0·03	0·07	30·50	0·75	32·75	0·038
	2·47	39·06	56·79	1·56	0·03	0·08	38·18	0·88	40·54	0·039
53·8% Methanol, D = 54·6.										
1·09	1·58	19·53	22·72	1·08	0·02	0·04	19·05	0·48	20·57	0·026
	1·78	31·25	35·63	1·07	0·02	0·07	30·56	0·69	32·25	0·027
	1·84	35·15	41·65	1·07	0·02	0·08	34·40	0·75	36·14	0·027
29·5% Ethanol, D = 61·8.										
2·69	3·86	39·06	45·44	2·68	0·05	0·10	37·93	1·13	41·64	0·053
	4·28	66·36	67·00	2·69	0·05	0·15	57·02	1·54	61·10	0·054
40·6% Ethanol, D = 54·7.										
1·86	3·05	39·06	45·44	1·84	0·04	0·11	37·89	1·17	40·79	0·032
	3·20	46·87	53·01	1·84	0·04	0·13	45·56	1·32	48·59	0·032
52·2% Ethanol, D = 47·7.										
1·14	1·88	19·53	22·72	1·07	0·03	0·08	18·75	0·78	20·52	0·014
	2·25	35·15	41·66	1·07	0·03	0·15	33·99	1·15	36·06	0·015
21·1% Acetone, D = 65·7.										
3·98	4·94	25·26	38·37	4·07	0·09	0·06	24·46	0·78	29·29	0·084
	5·37	42·10	51·80	4·11	0·09	0·13	40·93	1·17	46·07	0·087
26·1% Acetone, D = 60·5.										
3·18	4·32	29·72	57·90	3·21	0·07	0·09	28·68	1·04	32·83	0·054
	4·67	41·28	80·88	3·17	0·07	0·12	39·85	1·43	44·33	0·050
	5·19	63·91	123·6	3·16	0·07	0·19	61·95	1·96	66·88	0·052
38·4% Acetone, D = 55·6.										
2·16	3·18	25·26	34·53	2·09	0·05	0·08	24·24	1·04	27·29	0·029
	3·70	42·10	50·84	2·03	0·05	0·15	40·48	1·62	43·98	0·027
39·5% Acetone, D = 54·9.										
2·07	3·51	37·05	72·37	1·93	0·06	0·16	35·53	1·52	38·82	0·024
	3·62	41·28	80·88	1·93	0·06	0·17	39·65	1·63	43·04	0·024
	3·83	49·54	106·5	1·91	0·06	0·21	47·68	1·86	51·24	0·025
39·3% Glycol, D = 66·8.										
5·27	6·98	56·76	117·8	5·65	0·08	0·10	55·51	1·23	62·31	0·145
51·2% Glycol, D = 62·8.										
4·61	5·52	24·40	28·40	4·92	0·06	0·04	23·87	0·54	29·28	0·139
	6·06	43·92	52·06	4·96	0·06	0·07	42·88	1·04	48·81	0·118
63·1% Glycol, D = 59·0.										
3·98	4·91	24·40	28·40	4·27	0·05	0·04	23·81	0·59	28·63	0·105
15·0% Dioxan, D = 63·3.										
5·16	6·52	30·96	35·22	5·34	0·10	0·08	29·89	1·07	36·21	0·092
	7·07	51·60	57·76	5·43	0·11	0·14	50·07	1·53	56·89	0·100
22·5% Dioxan, D = 55·5.										
4·03	6·05	50·41	56·49	4·25	0·10	0·17	48·71	1·70	54·49	0·061
31·7% Glycerol, D = 69·5.										
7·09	8·33	30·96	34·37	7·46	0·10	0·05	30·18	0·77	38·37	0·194
	8·90	51·60	57·76	7·57	0·10	0·09	50·37	1·23	59·08	0·187
42·3% Glycerol, D = 66·4.										
6·75	8·01	29·27	33·81	7·10	0·10	0·05	28·46	0·81	36·32	0·159
	8·60	51·60	57·76	7·27	0·10	0·09	50·39	1·23	58·80	0·173

seen that the different solvents give characteristic slopes, although there is little to choose between methanol, ethanol, and acetone. The average value of K in water (0·23) is comparable with that (0·19) obtained by an e.m.f. method (MacDougall and Peterson, *J. Physical Chem.*, 1947, **51**, 1346).

The variation of log K with D predicted by Bjerrum's equation (*Kgl. Danske Vidensk. Selskab.*, 1926, **7**, No. 9) is the broken line in Fig. 1. Its failure to coincide with any of the experimental lines may not be due to any error in the equation, which is based essentially on the forces of association being electrostatic in nature. Use of the value of K obtained with aqueous solutions leads to 0·91 Å as the mean distance of approach of the two ions as calculated from Bjerrum's equation, whereas the radius of the unhydrated silver ion is itself 1·26 Å (Harned and Owen, *loc. cit.*), which suggests that the association may well be founded on chelation forces.

James (*loc. cit.*, 1950) has shown that Bjerrum's equation accounts reasonably well for the variations in the dissociation constant of lanthanum ferricyanide when the organic solvent mixed with water is dioxan, glycol, acetone, or ethanol, but that this is not so with copper sulphate, zinc sulphate, or zinc malonate (although with the last salt it is again probable that the associating forces are of a chelating character so that Bjerrum's treatment is scarcely valid). With zinc and copper sulphates it is possible that ion solvation is an important factor in influencing the rate of change of K with D, and that this varies with the nature of the solvent. It is worth notice in this respect that the rate of change with different solvents is in the same order with these sulphates as in the case of silver acetate, *i.e.*, ethanol $>$ acetone $>$ dioxan $>$ glycol (over the same range of D). Unfortunately it is difficult to reconcile this view of varying ion solvation with the behaviour of lanthanum ferricyanide where no really large differences appear on change of the solvent. In addition, both with this salt and with the zinc and copper salts, all of which were studied by the conductivity method, the Walden–Stokes product, $\Lambda^{\circ}\eta$, remains approximately constant when the proportion of organic solvent is increased, indicating that the effective ionic radii are not changing markedly. This suggests that water molecules are being replaced in the sphere of ion solvation by organic solvent molecules. This, of course, is the basic idea of Debye's "salting effect" (Debye and McAulay, *Physikal. Z.*, 1925, **26**, 22), namely, that in a solution of mixed polar molecules the ions tend to sort out the dipoles, the more polar molecules tending to concentrate round the ions. There is, however, lack of agreement between this theory and experimental evidence, as pointed out by Scatchard (*J. Chem. Physics*, 1941, **9**, 34) and others, probably owing to neglect of the discrete structure of the solvent.

FIG. 1.

Dissociation constants of silver acetate.

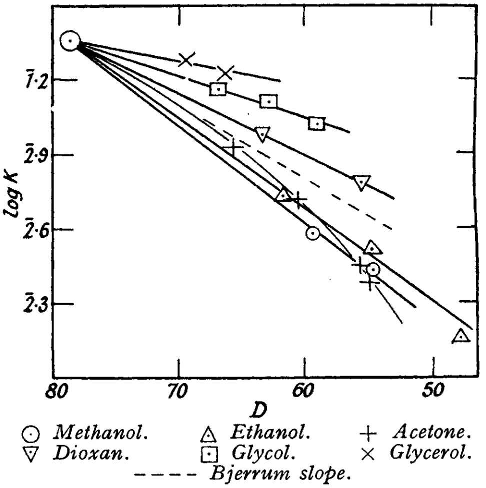
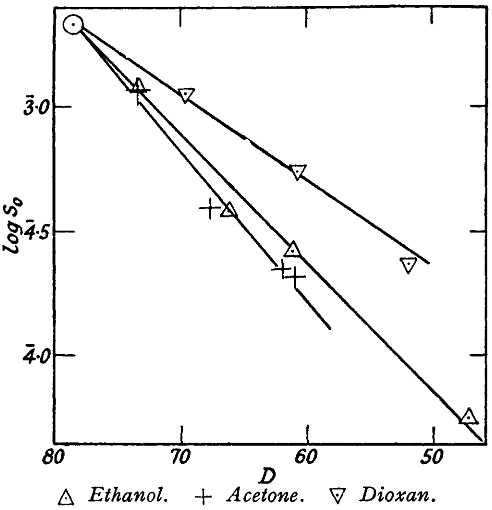


FIG. 2.

Silver acetate solubilities.



The lower solubility shown by salts as the dielectric constant is lowered is analogous to the fall in the dissociation constant. This has been investigated by numerous workers, many of whom have compared their results with the relation

$$\ln (S_1/S_2) = (z_1z_2e^2/2r\boldsymbol{k}T)(1/D_2 - 1/D_1)$$

where S_1 and S_2 are the solubilities at dielectric constants D_1 and D_2, and r is the mean radius of the electrolyte ions of valencies z_1 and z_2. This expression was obtained by both Born (*Z. Physik*, 1920, **1**, 45) and Scatchard (*Chem. Reviews*, 1927, **3**, 383). In general, it gives values of r which are too small. Since results have been published for the solubility of silver acetate in several of the mixed solvents discussed in this paper, it is worth seeing if corrections for both ion association and interionic effects can reconcile the theory with the results. When allowance is made for undissociated silver acetate and for the ionic strengths of the solutions, the above expression becomes

$$\ln (S_1^\circ/S_2^\circ) = (e^2/r\boldsymbol{k}T)(1/D_2 - 1/D_1)$$

where S_1° and S_2° are the activity solubility product calculated by an expression similar to that used for silver bromate. The calculations are summarised in Table III [the data of MacDougall and Batsch (*J. Physical Chem.*, 1936, **40**, 649), MacDougall and Larson (*ibid.*, 1937, **41**, 417), and Davis, Ricci, and Sauter (*loc. cit.*) for ethanol–water, acetone–water, and dioxan–water respectively, were used].

TABLE III.

Silver acetate solubilities (all concns., $\times 10^{-3}$).

S	K	Organic solvent, %	D	[AgOAc]	10^3I	$-\log S_0$
			Ethanol–water.			
66·3	0·23	—	78·5	9·4	56·9	2·671
50·6	0·155	9·00	73·4	7·7	42·9	2·915
29·4	0·068	25·06	64·1	5·5	23·9	3·418
24·9	0·053	30·05	61·1	5·0	19·9	3·577
12·4	0·019	50·14	48·6	3·1	9·3	4·245
			Acetone–water.			
49·90	0·15	9·27	73·4	7·86	42·04	2·932
32·37	0·097	18·83	67·7	5·15	27·22	3·400
21·40	0·060	28·25	62·0	3·74	17·66	3·648
21·31	0·056	30·02	61·0	3·74	17·57	3·676
			Dioxan–water.			
50·32	0·135	10·0	69·7	8·37	41·97	2·947
36·38	0·083	20·0	60·8	6·65	29·73	3·261
24·52	0·051	30·0	51·9	4·63	19·89	3·626

As Fig. 2 shows, each solvent again gives characteristic slopes, but these are not in the same order as those of the dissociation constants.

Wynne-Jones (*Proc. Roy. Soc.*, 1933, *A*, **140**, 440) has expressed the relations between K and D in a form similar to the above solubility expression for the dissociation of acids, which for the present purpose may be written :

$$\ln (K_1/K_2) = (z_1z_2e^2)/(r\boldsymbol{k}T)(1/D_2 - 1/D_1)$$

Although there is no specific value of r which will satisfy this equation for all three cases discussed with regard to solubilities, we might expect to find that the values of r obtained by the above two expressions are approximately equal. Calculation gives the following figures :

	Acetone–water	Ethanol–water	Dioxan–water
Dissociation constants : r(Å)	1·42	1·43	3·10
Solubilities : r(Å)	0·85	1·01	1·63
Ratios	1·17	1·4	1·9

The fluctuating ratios and their departure from unity can only suggest that there are deficiencies in both of the equations used or that, as discussed earlier, ion–solvent (or perhaps ion pair–solvent) interactions are of major importance. It is thus worth comparing an independent calculation of r with the above figures. By using Stokes' law, the limiting mobility of the acetate ion, which is 40·9 (Harned and Owen, *loc. cit.*, p. 172) gives the acetate radius as 2·2 Å, and the limiting mobility of the silver ion (61·92) gives that of silver as 1·5 Å. The average, 1·8 Å, is half to twice the tabulated figures, a range which is not supported by the conductivity evidence discussed earlier on.

Broadly speaking, the solvents may be classified into (*a*) ethanol and acetone, which markedly reduce the solubilities and the dissociation constants, and (*b*) dioxan and glycol which have less effect; these generalisations apply to the zinc, copper, and silver salts. The wider range of solvents used in the study of silver acetate further indicates that longer molecules and those with more hydroxyl groups have the smaller influence. It is of significance in this respect to find that sucrose actually increases the (aqueous) dissociation constants of several organic acids (Davey and Dippy, *J.*, 1944, 411; Kolthoff, *Rec. Trav. chim.*, 1929, **48**, 220) although sucrose solutions have lower dielectric constants than that of water.

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