32. *The Electrolytic Dissociation of Zinc Sulphate, Copper Sulphate, and Zinc Malonate in Mixed Solvents.*

By J. C. James.

Conductivity measurements are reported for dilute solutions of zinc sulphate, copper sulphate, and zinc malonate in binary mixtures of water with dioxan, acetone, ethylene glycol, and ethanol at 25°. Dissociation constants have been derived, and the variation of dissociation constant with dielectric constant is discussed. It is suggested that dissociation constants become less dependent on dielectric constant when association is not completely determined by Coulomb forces. Conductivity measurements are also reported for aqueous zinc malonate solutions at 25° and 30°; dissociation constants have been calculated and thence ΔH, ΔG, and ΔS for dissociation.

Recently (James, *J.*, 1950, 1094), conductivity measurements on a 3–3 valency type electrolyte, lanthanum ferricyanide, were reported for a series of mixed solvents, and it was shown that, for the water-rich mixtures studied, the variation in dissociation constant with dielectric constant could be accounted for satisfactorily by the Bjerrum ion-pair treatment. This work has now been extended to salts of the 2–2 valency type, and measurements are reported for solutions of zinc sulphate, copper sulphate, and zinc malonate in binary mixtures of water with dioxan, acetone, ethylene glycol, and ethanol at 25°. With zinc sulphate and copper sulphate, the stable electronic structures of the ions indicate that association is purely electrostatic, to give ion pairs. Zinc malonate, however, behaves as a comparatively weak electrolyte in aqueous solution, and it has been suggested (Ives and Riley, *J.*, 1931, 1998; Bjerrum, *Chem. Reviews*, 1950, **46**, 381) that a chelate ring structure is involved. The purpose of the present investigation was to compare dissociation-constant data for these salts in mixed solvents, and thereby to obtain information as to the nature of the association involved. Also, as the dissociation constant of zinc malonate can be determined with considerable accuracy by the conductivity method, it is possible to obtain values of ΔH and ΔS for the dissociation process from measurements at different temperatures. Conductivity measurements have therefore been made on dilute aqueous zinc malonate solutions at 25° and 30°.

Experimental.

The experimental procedure and methods used for solvent purification have been described previously (James, *loc. cit.*). Zinc malonate was prepared by the method of Ives and Riley (*loc. cit.*) (Found: Zn, 32·1. Calc. for $C_3H_2O_4Zn,2H_2O$: Zn, 32·1%). Pure zinc sulphate and copper sulphate were prepared by recrystallising AnalaR-quality specimens twice from conductivity water, and drying them over the partly dehydrated salts.

Discussion.

Aqueous Zinc Malonate Solutions.—The results for aqueous zinc malonate solutions at 25° and 30° are given in Table I. At 25°, combination of the value $\Lambda_0(\text{Zn}) = 53{\cdot}0$ given by Owen and Gurry (*J. Amer. Chem. Soc.*, 1938, **60**, 3074) for the zinc ion with Jeffery and Vogel's (*J.*, 1935, 21) value of 64·7 for the malonate ion leads to $\Lambda_0 = 117{\cdot}7$ for the conductivity at infinite dilution. Application of the method given by Davies (*J.*, 1933, 645) for the extrapolation of experimental results for incompletely dissociated electrolytes gives $\Lambda_0 = 117{\cdot}6$, in good agreement. At 30°, application of this method gives $\Lambda_0 = 130{\cdot}7$ and, although no independent value can be obtained for comparison, the excellent agreement at 25° suggests that the use of this method at 30° is permissible. For the purpose of comparison of dissociation constants the values $\Lambda_0^{25} = 117{\cdot}6$ and $\Lambda_0^{30} = 130{\cdot}7$ were adopted, the limiting Onsager and Debye–Hückel equations then becoming

$$\Lambda = \alpha[117{\cdot}6 - 228{\cdot}0I^{\frac{1}{2}}],\ -\log f_{\pm}^{2} = 4{\cdot}074I^{\frac{1}{2}} \text{ at } 25^\circ$$
$$\Lambda = \alpha[130{\cdot}7 - 255{\cdot}7I^{\frac{1}{2}}],\ -\log f_{\pm}^{2} = 4{\cdot}113I^{\frac{1}{2}} \text{ at } 30^\circ$$

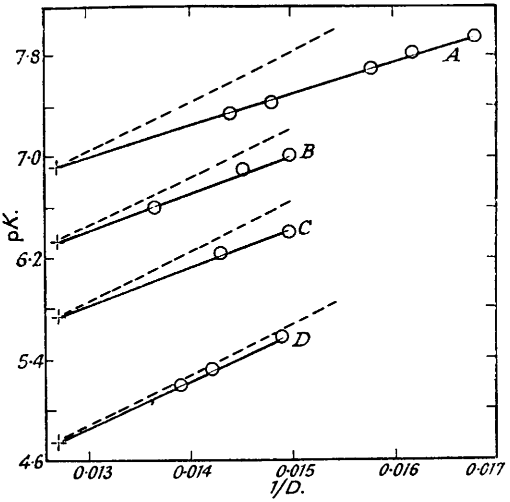
where α is the degree of dissociation. The ionic strength, I, is given by $I = 2\alpha c$, where c is the concentration in g.-equivs./l. Values of α and dissociation constants have been derived for each point from the equations

$$\log K = \log\,[\alpha^2 c/2(1 - \alpha)] - 4{\cdot}074I^{\frac{1}{2}} \text{ at } 25^\circ$$
and
$$\log K = \log\,[\alpha^2 c/2(1 - \alpha)] - 4{\cdot}113I^{\frac{1}{2}} \text{ at } 30^\circ$$

The mean values are : at 25°, $K = 1{\cdot}793 \times 10^{-4}$, and at 30°, $K = 1{\cdot}644 \times 10^{-4}$, the average deviation at each temperature being $0{\cdot}004 \times 10^{-4}$. From these dissociation constants it is found that $\Delta H = -3{\cdot}06$ kcals. between 25° and 30°, $\Delta G_{298{\cdot}1} = 5110$ cals. and $\Delta S_{298{\cdot}1} = -27{\cdot}5$ cals./°c. for the dissociation process. These values for ΔH and ΔS are of the same order but slightly greater numerically than the corresponding values obtained by Davies and James (*Proc. Roy. Soc.*, 1948, *A*, **195**, 116) for lanthanum ferricyanide ion pairs ($\Delta H = -2{\cdot}0_0$ kcals.,

FIG. 1.

Variation of dissociation constant with dielectric constant for zinc malonate in mixed solvents.



A, *Dioxan–water.* *B*, *Glycol–water.*
C, *Ethanol–water.* *D*, *Acetone–water.*

Results for ethanol–, glycol–, and dioxan–water mixtures have been displaced vertically by 1·0, 1·6, *and* 2·2 p*K units respectively, for clarity.*

TABLE I.

Conductivity of aqueous zinc malonate solutions.

Run.	$10^6\kappa_{H_2O}$.	10^4c.	$10^2c^{\frac{1}{2}}$.	Λ.	10^4K.	Run.	$10^6\kappa_{H_2O}$.	10^4c.	$10^2c^{\frac{1}{2}}$.	Λ.	10^4K.
		At 25°.						*At* 30°.			
1	0·446	1·9934	1·412	84·23	1·798	1	0·277	2·6881	1·640	85·76	1·636
		3·8952	1·974	72·07	1·803			6·5578	2·561	67·26	1·644
		7·0068	2·647	60·99	1·796			9·6489	3·106	59·52	1·644
		9·9980	3·159	54·56	1·793			13·632	3·692	52·94	1·640
		13·785	3·713	48·97	1·789			19·735	4·442	46·43	1·640
2	0·351	3·4262	1·851	74·34	1·790	2	0·246	2·1674	1·472	90·31	1·635
		6·2112	2·492	63·21	1·794			4·9798	2·231	73·08	1·652
		10·767	3·281	53·21	1·792			9·0854	3·014	60·74	1·647
		15·684	3·960	46·83	1·788			13·254	3·641	53·47	1·642
		22·222	4·714	41·38	1·788			18·473	4·299	47·57	1·641

$\Delta S_{298\cdot1} = -23\cdot9$ cals./°c.), although the experimental uncertainty is possibly too great for any significance to be attached to such differences.

Mixed Solvents.—The results for zinc malonate, zinc sulphate, and copper sulphate in mixed solvents are given in Table II. Values for Λ_0 have been derived by Davies's method (*loc. cit.*),

TABLE II.

(A) *Conductivity of zinc malonate in mixed solvents.*

Dioxan–water.

10^4c.	Λ.	10^4c.	Λ.	10^4c.	Λ.	10^4c.	Λ.	10^4c.	Λ.
10·30% Dioxan (1).		12·37% Dioxan (2).		17·11% Dioxan (3).		18·98% Dioxan (4).		21·30% Dioxan (5).	
2·7327	48·69	2·3835	44·15	4·1747	28·75	1·7430	35·16	4·5181	20·947
6·6686	36·75	5·2049	35·02	9·8272	20·515	3·2999	27·93	7·3221	17·138
10·813	30·80	8·1200	29·96	15·176	17·144	5·2249	23·26	12·385	13·697
16·034	26·44	11·728	26·09	21·076	14·955	8·0178	19·524	17·977	11·688
22·146	23·27	15·889	23·16	31·152	12·710	10·804	17·217	23·961	10·356

Acetone–water.

11·83% Acetone (6).		14·41% Acetone (7).		19·78% Acetone (8).	
2·9613	43·26	2·5418	39·81	4·6885	24·00
6·2507	33·58	5·5384	30·34	8·9471	18·404
10·726	27·35	8·9340	25·24	12·460	16·040
15·041	23·94	16·022	19·926	15·697	14·553
20·192	21·28	23·135	17·134	19·861	13·184

Ethanol–water.

13·71% Ethanol (13).		20·50% Ethanol (14).	
5·1030	27·55	9·2507	13·408
9·5415	21·74	11·834	12·151
12·161	19·789	14·568	11·155
15·546	17·936	17·585	10·321
19·407	16·395	21·357	9·533

Glycol–*water.*

10^4c.	Λ.	10^4c.	Λ.	10^4c.	Λ.	10^4c.	Λ.
18·65% Glycol (9).		26·41% Glycol (10).		33·17% Glycol (11).		39·57% Glycol (12).	
2·8790	42·34	4·5674	26·68	6·7743	17·060	8·6244	11·391
5·3867	34·82	9·5145	20·38	8·9948	15·301	10·857	10·380
9·8274	28·20	11·844	18·736	11·411	13·938	14·154	9·297
12·255	25·92	16·366	16·508	14·461	12·675	16·649	8·724
15·336	23·78	19·801	15·307	17·051	11·856	21·855	7·806

(B) *Conductivity of zinc sulphate in mixed solvents.*

Dioxan–water.

10^4c.	Λ.	10^4c.	Λ.	10^4c.	Λ.
17·26% Dioxan (15).		25·52% Dioxan (16).		30·83% Dioxan (17).	
2·4537	88·01	1·9084	72·60	2·2514	58·41
5·5810	81·08	3·6704	66·59	3·9133	52·81
8·7159	76·41	5·9643	61·36	6·0127	48·11
12·772	71·95	9·3663	56·14	8·1264	44·72
17·985	67·67	11·8599	53·31	12·059	40·32

Acetone–water.

10^4c.	Λ.	10^4c.	Λ.	10^4c.	Λ.
10·95% Acetone (18).		13·67% Acetone (19).		26·33% Acetone (20).	
1·7956	100·93	1·8519	89·27	2·5469	72·34
4·4583	95·26	4·1558	83·90	4·6201	66·77
7·1500	91·25	6·6064	79·82	6·9280	62·39
10·087	87·72	9·745	79·85	9·590	58·64
14·183	83·47	12·517	73·09	12·642	55·29

Glycol–water.

10^4c.	Λ.	10^4c.	Λ.	10^4c.	Λ.
27·11% Glycol (21).		39·14% Glycol (22).		52·20% Glycol (23).	
4·2167	64·21	3·3558	46·91	3·6641	31·23
6·8957	61·67	5·5285	44·95	9·0800	27·84
10·616	58·92	9·0525	42·55	11·783	26·68
14·244	56·84	12·711	40·63	15·411	25·45
17·630	55·23	15·913	39·27	19·453	24·34

Ethanol–water.

10^4c.	Λ.	10^4c.	Λ.
18·01% Ethanol (24).		24·99% Ethanol (25).	
1·4817	71·60	2·7452	57·47
2·5575	69·23	4·0232	54·91
3·7938	67·01	5·8235	52·14
5·5262	64·48	8·2938	49·18
6·4600	63·32	10·3623	47·21

(C) *Conductivity of copper sulphate in mixed solvents.*

10^4c.	Λ.	10^4c.	Λ.	10^4c.	Λ.	10^4c.	Λ.
23·43% Dioxan (26).		20·19% Acetone (27).		35·03% Glycol (28).		21·17% Ethanol (29).	
2·3673	78·28	2·1380	81·99	4·3105	50·84	2·0445	62·86
4·2966	71·93	3·5929	77·88	5·8384	49·58	3·9848	58·85
6·3692	67·12	5·5829	73·55	7·9846	48·00	6·3738	55·17
8·5847	63·25	9·2403	67·82	10·954	46·16	9·9302	51·25
11·720	59·09	12·191	64·40	15·956	43·17	12·323	49·21

and thermodynamic dissociation constants have been calculated as described above. In water, the values $K = 0{\cdot}0049$ for zinc sulphate and $K = 0{\cdot}0043$ for copper sulphate given by Owen and Gurry (*loc. cit.*) have been adopted. Values of pK (= $-\log K$) (cf. Table III) have been plotted against $1/D$ in Figs. 1, 2, and 3; in each case the variation is linear, within the limits of experimental error, over the range studied.

FIG. 2.

Variation of dissociation constant with dielectric constant for zinc sulphate in mixed solvents.

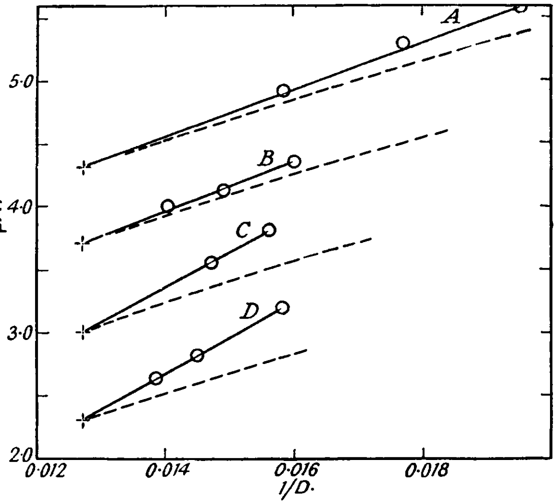
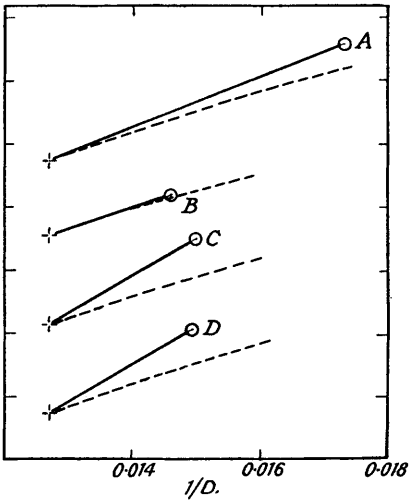


FIG. 3.

Variation of dissociation constant with dielectric constant for copper sulphate in mixed solvents.



A, *Dioxan–water.* *B*, *Glycol–water.* *C*, *Ethanol–water.* *D*, *Acetone–water.*

Results for ethanol–, glycol–, and dioxan–water mixtures have been displaced vertically by 0·7, 1·4 *and* 2 pK *units respectively, for clarity.*

TABLE III.

Dissociation constants in mixed solvents.

Solvent.	Run.	D.	Λ_0.	$10^3\eta$.	$\Lambda_0\eta$.	10^5K.	Solvent.	Run.	D.	Λ_0.	$10^3\eta$.	$\Lambda_0\eta$.	10^5K.
		Zinc malonate.							*Zinc sulphate.*				
Dioxan–	1	69·40	95·0	10·42	0·990	7·19	Dioxan–	15	63·20	99·1	12·40	1·229	120·6
water	2	67·60	88·0	11·40	1·003	5·61	water	16	56·00	88·2	14·10	1·244	48·5
	3	63·40	86·0	12·35	1·062	3·13		17	51·20	77·2	15·25	1·177	25·8
	4	61·60	84·5	12·75	1·077	2·39	Acetone–	18	72·40	108·0	11·17	1·206	222·0
	5	59·60	83·0	13·43	1·015	1·70	water	19	68·90	97·2	12·17	1·183	152·0
Acetone–	6	71·90	89·0	11·33	1·008	6·36		20	61·60	86·3	12·75	1·100	63·4
water	7	70·40	86·0	11·80	1·015	4·77	Glycol–	21	70·65	72·0	17·50	1·260	251·0
	8	67·10	80·0	12·60	1·008	2·70	water	22	66·90	52·7	24·00	1·265	184·0
Glycol–	9	73·20	79·0	14·00	1·106	8·44		23	62·20	36·7	35·00	1·284	110·0
water	10	70·85	63·0	17·20	1·084	6·40	Ethanol–	24	68·20	77·3	17·05	1·318	138·4
	11	68·75	51·5	20·50	1·056	4·91	water	25	64·10	67·6	19·75	1·335	76·6
	12	66·72	42·0	24·50	1·029	3·78							
Ethanol–	13	70·70	70·0	15·10	1·057	5·81							
water	14	66·80	50·0	18·10	0·905	3·97							
							Copper sulphate.						
Dioxan–water	26	57·80	95·0	13·67	1·299	49·4	Glycol–water	28	68·20	57·8	21·50	1·243	208·0
Acetone–water	27	66·90	93·0	12·65	1·176	90·5	Ethanol–water	29	66·40	71·0	18·10	1·285	89·7

Although, on the basis of a simple electrostatic treatment ion association should increase regularly with decreasing dielectric constant, in a number of systems it appears that marked specific interaction effects occur. Thus Burgess and Kraus (*J. Amer. Chem. Soc.*, 1948, **70**, 706) have shown that the addition of relatively small amounts of water to solutions of metal picrates in pyridine causes abrupt increases in K. Effects of this nature have been attributed to specific interaction between solute ions and added solvent molecules leading to changes in a, the apparent distance of closest approach for an ion pair. From the present results it appears, however, that no marked specific interaction effects occur in the water-rich binary mixtures studied. The approximate constancy of the Walden–Stokes product $\Lambda_0\eta$ indicates that the effective radii of the free ions undergo no great change, and the similarity and regularity of the pK–$1/D$ curves indicate that decrease in dielectric constant is the main factor responsible for decrease in K.

If association is purely electrostatic to give ion pairs, then it is possible to predict the variation of K with D. On substituting the appropriate values for dissociation constants in water into the Bjerrum equation (*Kgl. Danske Vidensk. Selskab.*, 1926, **7**, No. 9), the values 2·14, 4·52, and 4·23 A. are obtained for the " a " parameters of zinc malonate, zinc sulphate, and copper sulphate respectively. Assuming these values to remain unchanged, the pK–$1/D$ curves shown as broken lines in Figs. 1, 2, and 3 have been calculated. In order to examine the extent to which the results were dependent on the nature of the extrapolation function used, values for Λ_0 and pK have also been derived using the extrapolation methods given by Fuoss and Kraus (*J. Amer. Chem. Soc.*, 1933, **55**, 476) and by Shedlovsky (*J. Franklin Inst.*, 1938, **225**, 739). The values obtained for a typical series of results are compared in Table IV. It appears that, whilst the values found for K depend to some extent on the manner in which $\alpha\Lambda$ is assumed to approach the limiting law, the magnitude of such dependence is small.

TABLE IV.

Zinc sulphate in 18·01% *w/w ethanol solutions* (*run* 24).

Extrapolation method.	Λ_0.	pK.
Davies	77·3	2·859
Shedlovsky	77·5	2·921
Fuoss and Kraus	77·5	2·887

The pK–$1/D$ curves for zinc sulphate and copper sulphate are almost coincident and are slightly less steep than the corresponding curves for zinc malonate. With both zinc sulphate and copper sulphate the increase in pK with decrease in D is somewhat greater than predicted; the reason for this is not clear, although it is of interest that measurements on lanthanum ferricyanide solutions in mixed solvents (James, *loc. cit.*) show similar but smaller deviations. It may be that errors are introduced by the use of the solvent dielectric constant in the Bjerrum equation when the value for " a " is small, as it appears that at distances of less than about 4 A. from an ion the dielectric constant is a rapidly varying quantity (Collie, Hasted, and Ritson, *J. Chem. Physics*, 1948, **16**, 1).

With zinc malonate, deviations from the theoretical Bjerrum curve are in the opposite sense, the observed decrease in K with decrease in D being less than calculated. Few measurements for other salts are available for comparison, although similar behaviour has been observed with the abnormally weak salt, lead chloride, and with organic acids in mixed solvents (James, *loc. cit.*). It is possible that such behaviour is characteristic and that dissociation constants are less dependent on dielectric constant when association is not determined purely by Coulomb forces. Ives (*J.*, 1933, 1360) and Jones, Monk, and Davies (*J.*, 1949, 2693) have pointed out that, in a given solvent, dissociation constants depend mainly on two factors, the solvation energies and the energy of interaction of the ions. With weak salts such as zinc malonate, the energy of interaction prevails, and no solvent molecules can intervene between anion and cation. With salts such as zinc sulphate, copper sulphate, and lanthanum ferricyanide, the interaction energy is much less, and ion pairs are formed between solvated ions.

The author thanks Dr. J. C. Speakman for many valuable discussions.

CHEMISTRY DEPARTMENT, GLASGOW UNIVERSITY. [*Received, September* 11*th*, 1950.]