255. *Studies on Metal Complexes in Solution. Part II.*[1] *Zinc Malonate and Phthalate.*

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Thermodynamic stability constants of the 1 : 1 complex of zinc ion with the malonate and phthalate ions have been determined at temperatures in the range 0—45° in aqueous solution by means of a precise e.m.f. method. The thermodynamic quantities ΔG^0, ΔH^0, ΔS^0, and ΔC_p for the association

$$Zn^{2+}{}_{aq} + A^{2-}{}_{aq} \rightleftharpoons ZnA_{aq}$$

reaction have been obtained, and are discussed.

In Part I of this Series,[1] the phthalates of manganese, cobalt, and nickel were studied. The malonates of these metals were considered in another Series.[2] It is of interest to see how data for zinc compare with those for the transition metals.

The e.m.f. cell was the same as that used previously:

$$H_2,Pt \mid H_2Mal(m_1),NaOH(m_3),NaCl(m_4),ZnCl_2(m_2) \mid AgCl \mid Ag \qquad (1)$$

or

$$H_2,Pt \mid KHPh(m_1),ZnCl_2(m_2) \mid AgCl \mid Ag \qquad (2)$$

where H_2Mal is malonic acid, and KHPh is potassium hydrogen phthalate.

Experimental

Malonic acid was recrystallised from 1 : 1 ether–benzene containing 5% of light petroleum (b. p. 60—80°), and was dried *in vacuo* at 40—50° (Found: H, 4·0; C, 34·5. Calc. for $C_3H_3O_4$: H, 3·9; C, 34·6%). AnalaR potassium hydrogen phthalate was used without further purification. Stock solutions, prepared by weight, were checked against standard solution of sodium hydroxide. Carbon dioxide-free sodium hydroxide solution, prepared by dilution of a saturated solution with air-free conductivity water under soda lime, was standardised and used. Zinc chloride was prepared by dissolving AnalaR zinc oxide in a weighed amount of standard hydrochloric acid (obtained from the constant-boiling acid), keeping the zinc oxide in excess, and filtering the solution through a sinter. The solution was analysed gravimetrically for zinc (as zinc ammonium phosphate) and for chloride (as silver chloride).

The method of preparing the cell solutions, the experimental procedure, and the e.m.f. cell have been described previously.[3]

Results and Discussion

The two dissociation constants, K_1 and K_2, of phthalic acid, as well as K_2 for malonic acid, over the temperature range 0—60°, have been reported by Hamer *et al.*[4] Values for K_1, the primary dissociation constant of malonic acid, are available for the range 0—45°.[2] In the e.m.f. cells (1) and (2), m_{H^+}, the hydrogen ion molality, is given by

$$-\log m_{H^+} = (E - E^0)/k + \log (2m_2 + m_4) + 2 \log \gamma_1,$$

where m denotes molality, E and E^0 are the e.m.f. of the cell (corrected for hydrogen pressure and for temperature) and the standard electrode potential of the Ag|AgCl electrode, respectively, and $k = 2{\cdot}3026\boldsymbol{R}T/F$. γ_z, the mean activity coefficient of an ion of charge z, is obtained from the expression due to Davies:[5]

$$-\log \gamma_z = Az^2[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - CI].$$

[1] Part I, Desai and Nair, *J.*, 1962, 2360.
[2] Nair and Nancollas, *J.*, 1961, 4367.
[3] Nair and Nancollas, *J.*, 1958, 4144.
[4] Hamer, Pinching, and Acree, *J. Res. Nat. Bur. Stand.*, 1945, **35**, 539; Hamer and Acree, *ibid.*, p. 381; Hamer, Burton, and Acree, *ibid.*, 1940, **24**, 292.
[5] Davies, *J.*, 1938, 2093.

The concentrations of the various species are inter-related, leading to the ionic strength I:

$$I = \tfrac{1}{2}\left[m_{H^+} + 6m_2 - 4m_1 + m_3 + 2m_4 + m_{HA^-}\left(5 + \frac{4m_{H^+}\gamma_1^2}{k_1} + \frac{8k_2}{m_{H^+}\gamma_2}\right)\right],$$

and
$$m_{HA^-} = \frac{2m_1 - m_3 - m_{H^+}}{1 + \dfrac{2m_{H^+}\gamma_1^2}{k_1}}.$$

Successive approximations were made to obtain constant values for ionic strength and

TABLE 1.

Zinc malonate

	1	2	3	4	5	6
10^3m_1	3·7550	5·6439	8·3908	10·9208	8·770	9·3537
10^3m_2	3·6624	6·6647	4·3030	8·9309	6·5063	6·3323
10^3m_3	3·3373	4·7238	$7·8998_5$	9·9133	8·0210	8·6507
10^3m_4	0·4237	0·7711	$0·4978_5$	1·0333	0·7528	0·7326

	$(E - E^0)$	10^3I	$10^4[H^+]$	$10^3[HA^-]$	$10^4[A^{2-}]$	$10^4[MA]$	$10^{-3}K$
				At 0°			
1.	0·31533	14·31	2·461	3·0155	0·418	2·421	4·31
2.	0·29195	24·77	3·883	4·2635	0·423	3·820	4·66
3.	0·31335	19·87	2·377	6·7449	1·040	5·923	4·50
4.	0·28771	35·46	3·631	8·2565	0·960	9·139	4·62
5.	0·29759	26·58	3·156	6·7601	0·840	7·042	4·85
6.	0·29951	26·54	2·989	7·2697	0·954	7·445	4·69
						Mean	4·61 ± 0·3
				At 15°			
1.	0·33087	14·25	2·675	2·9943	0·383	2·669	5·33
2.	0·30606	24·68	4·249	4·2220	0·385	4·248	5·88
3.	0·32815	19·73	2·633	6·4018	0·934	6·448	5·66
4.	0·30202	35·41	3·910	8·2484	0·899	9·381	5·25
5.	0·31222	26·50	3·426	6·7329	0·776	7·378	5·69
6.	0·31407	26·43	3·267	7·2281	0·873	7·873	5·61
						Mean	5·57 ± 0·3
				At 25°			
1.	0·34134	14·21	2·793	2·9799	0·349	2·835	6·34
2.	0·31581	24·63	4·419	4·2073	0·354	4·438	6·85
3.	0·33871	19·66	2·732	6·6777	0·860	6·617	6·45
4.	0·31107	35·24	4·157	8·1744	0·803	9·970	6·43
5.	0·32194	26·41	3·596	6·6995	0·704	7·701	6·71
6.	0·32402	26·37	3·407	7·2081	0·799	8·117	6·47
						Mean	6·54 ± 0·3
				At 35°			
1.	0·35243	14·18	2·842	2·9683	0·319	2·947	7·37
2.	0·32601	24·58	4·507	4·1852	0·322	4·644	(8·08)
3.	0·34953	19·63	2·800	6·6578	0·781	6·753	7·41
4.	0·32078	35·10	4·295	8·1053	0·721	10·467	7·74
5.	0·33236	26·34	3·666	6·6730	0·643	7·930	7·76
6.	0·33416	26·24	3·519	7·1530	0·718	8·530	7·79
						Mean	7·61 ± 0·3
				At 45°			
1.	0·36354	14·13	2·889	2·9448	0·281	3·126	9·05
2.	0·33645	24·52	4·548	4·1558	0·287	4·827	9·65
3.	0·36077	19·51	2·823	6·6135	0·696	7·148	9·05
4.	0·33056	34·90	4·421	8·0017	0·627	11·142	9·78
5.	0·34260	26·20	3·759	6·6001	0·562	8·422	9·71
6.	0·34438	26·08	3·618	7·0715	0·625	9·081	9·82
						Mean	9·51 ± 0·4

TABLE 1. (*Continued.*)

Zinc phthalate

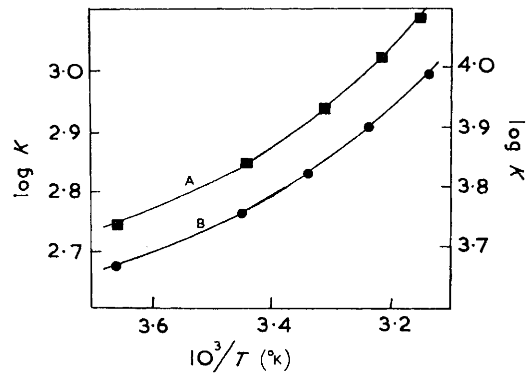
	10^3m_1	10^3m_2		10^3m_1	10^3m_2		10^3m_1	10^3m_2
1.	7·1145	6·1410	6.	11·711	9·5784	11.	18·433	13·981
2.	9·8923	7·8618	7.	20·708	13·085	12.	22·448	13·905
3.	13·700	10·663	8.	10·407	7·0522	13.	14·524	9·4632
4.	17·637	11·591	9.	3·1571	2·2830	14.	17·279	11·205
5.	9·9334	7·4392	10.	12·618	11·644	15.	10·553	6·2043

	$(E - E^0)$	10^3I	$10^4[H^+]$	$10^3[HA^-]$	$10^4[A^{2-}]$	$10^4[MA]$	$10^{-1}K$
				At 0°			
1.	0·32127	25·1	1·292	6·0136	3·107	3·043	5·48
2.	0·31357	$32{\cdot}6_5$	1·447	8·2954	4·090	4·618	5·69
3.	0·30456	44·3	1·632	11·382	5·413	6·990	5·71
4.	0·30235	50·7	1·681	14·665	7·036	8·668	5·47
5.	0·31499	31·4	1·433	8·3378	4·118	4·582	5·84
6.	0·30798	39·3	1·546	9·7751	4·752	5·710	5·52
7.	0·29857	57·7	1·782	17·123	8·052	10·763	5·72
8.	0·31636	30·8	1·413	8·7579	4·358	4·595	5·79
9.	0·35073	9·98	0·9032	2·7277	1·664	0·9348	5·70
						Mean	5·66 ± 0·2
				At 15°			
1.	0·33726	24·9	1·390	5·9234	3·068	3·583	6·76
2.	0·32937	32·5	1·544	8·1788	4·083	5·256	6·73
3.	0·31991	$44{\cdot}0_5$	1·738	11·217	5·416	$7{\cdot}861_5$	6·69
4.	0·31752	50·3	1·797	14·446	7·022	9·832	6·51
5.	0·33117	31·3	1·510	8·2386	4·165	5·064	6·60
6.	0·32322	39·1	1·662	9·6207	4·699	6·583	6·69
7.	0·31356	57·3	1·903	16·866	8·047	12·115	6·75
8.	0·33259	30·6	1·501	8·6430	4·372	5·198	6·78
						Mean	6·69 ± 0·2
				At 25°			
1.	0·34842	24·8	1·426	5·8738	2·965	3·952	7·91
2.	0·34028	32·3	1·583	8·1085	3·952	5·759	7·83
3.	0·33054	43·8	1·781	11·120	5·254	$8{\cdot}532_5$	7·71
4.	0·32778	50·0	1·861	14·290	6·724	10·94	7·81
5.	0·34209	31·1	1·552	8·1659	4·021	5·592	7·76
6.	0·33386	38·9	1·712	9·5271	4·522	7·253	7·87
7.	0·32393	57·0	1·953	16·710	7·794	$13{\cdot}17_5$	7·84
8.	0·34364	30·4	1·537	8·5726	4·238	$5{\cdot}703_5$	7·88
9.	0·38128	9·91	0·967	2·6847	1·639	$1{\cdot}206_5$	7·80
						Mean	7·82 ± 0·1
				At 35°			
2.	0·35091	32·0	1·639	8·0068	3·651	6·596	10·03
4.	0·33826	49·6	1·908	14·129	6·192	12·21	9·65
6.	0·34459	38·6	1·753	9·4251	4·241	8·065	9·65
7.	0·33395	56·4	2·028	16·474	7·182	15·00	10·07
8.	0·35450	30·2	1·583	8·4744	3·937	6·518	10·00
9.	0·39389	9·85	0·976	2·6680	1·557	1·377	9·56
10.	0·33808	45·4	1·886	10·061	4·409	9·318	9·64
11.	0·33178	57·0	2·063	14·599	6·279	13·915	9·91
12.	0·33228	60·3	2·054	17·862	7·854	16·10	9·72
13.	0·34486	40·7	1·769	$11{\cdot}719_5$	5·307	9·601	9·76
14.	0·33938	48·2	1·883	13·963	6·196	11·83	9·65
15.	0·35885	27·9	1·511	8·6541	4·125	6·127	9·85
						Mean	9·79 ± 0·3
				At 45°			
1.	0·37146	24·5	1·457	5·7741	2·575	4·856	11·81
2.	0·36262	31·9	1·629	7·9547	3·409	7·094	11·88
3.	0·35166	43·1	1·872	10·850	4·419	10·76	12·37
4.	0·34914	49·1	1·926	$13{\cdot}98_5$	5·764	13·46	12·05
5.	0·36446	30·7	1·601	8·0077	3·455	6·974	11·97
6.	0·35578	38·4	1·762	9·3397	3·903	8·834	11·83
9.	0·40677	9·77	0·976	2·6524	1·439	1·572	12·07
						Mean	12·0 ± 0·3

individual ionic concentrations, and finally the thermodynamic stability constant of the 1 : 1 complex ZnA;

$$K = \frac{m_{ZnA}}{m_{Zn^{2+}} \cdot m_{A^{2-}} \cdot \gamma_2^{\,2}},$$

by programming an " Elliott 803 " computer. The results are given in Table 1. It was necessary to assume only formation of the 1 : 1 complex, as is revealed by the constancy of the K values in the ionic-strength range used. In the original Davies equation, the coefficient C was 0·2, but it has been recently suggested [6] that, in some cases, $C = 0{\cdot}3$ might



Plot of log K against T^{-1}. A, Zinc phthalate (left-hand ordinates). B, Zinc malonate (right-hand ordinates).

give a better agreement among the K values. However, Nancollas and his co-workers [7] have found that the choice is arbitrary, either value giving consistent K values in the case of many 2 : 2 electrolytes. In the present work, we use $C = 0{\cdot}2$.

The stability constant for zinc malonate at 25° is to be compared with $K = 4{\cdot}76 \times 10^3$, obtained by means of the conductivity method.[8] There are no comparable results for zinc phthalate.

As with the dicarboxylates of the transition metals, the zinc salts also give plots of log K against T^{-1} (shown in the Figure) which are non-linear. A quadratic equation,

$$\log K = a + bT + cT^2,$$

fits the results, the best values for a, b, and c being obtained by the method of least-squares. These values are given in Table 2. Values of log K calculated from this equation, for any

TABLE 2.

Parameters for temperature-dependence of log K.

	a	-10^2b	10^5c
ZnMal	8·8941	4·1469	8·1835
ZnPh	7·6348	3·9555	7·9371

temperature, agree with the experimental mean value to better than 0·5%.

ΔG^0, ΔH^0, ΔS^0, and ΔC_p for the formation reaction

$$Zn^{2+} + A^{2-} \longrightarrow ZnA$$

in aqueous solution, are obtained from $\Delta G^0 = -2{\cdot}3026\ \boldsymbol{R}T \log K$, $\Delta H^0 = 2{\cdot}3026\ \boldsymbol{R}T^2(b + 2cT)$, $\Delta C_p = 4{\cdot}6052\ \boldsymbol{R}T(b + 3cT)$, and $\Delta S^0 = (\Delta H^0 - \Delta G^0)/298{\cdot}1$, and are given in Table 3.

[6] C. W. Davies, " Ion Association," Butterworths, London, 1962.

[7] Brannan, Dunsmore, and Nancollas, *J.*, 1964, 304; Brannan and Nancollas, *Trans. Faraday Soc.*, 1962, **58**, 354.

[8] Money and Davies, *Trans. Faraday Soc.*, 1932, **28**, 609.

TABLE 3.

Thermodynamic functions for complex-formation.

Reaction	ΔH^0 (kcal. mole^{-1})	$-\Delta G^0$ (kcal. mole^{-1})	ΔS^0 (cal. deg.$^{-1}$ mole^{-1})	ΔC_p (cal. deg.$^{-1}$)
$Zn^{2+} + Mal^{2-} \longrightarrow ZnMal$ ...	2.98 ± 0.1	5.20 ± 0.02	27.4 ± 0.4	86.5 ± 20
$Zn^{2+} + Ph^{2-} \longrightarrow ZnPh$	3.16 ± 0.1	3.95 ± 0.02	23.8 ± 0.4	85.7 ± 20

As with the transition-metal dicarboxylates, the enthalpy terms oppose the formation of zinc dicarboxylates from hydrated zinc ions. However, the reaction is brought about by the positive entropy-change associated with the charge neutralisation.

$\Delta S_{hyd}(ZnA)$ has been calculated from the relationship:

$$\Delta S_{hyd}(ZnA) = \Delta S^0 + S^0(Zn^{2+}) + S^0(A^{2-}) - S_g(ZnA),$$

where the subscripts indicate hydration and gas entropies. Calculation of $S_g(MA)$ has been described elsewhere.[9] $S^0(A^{2-})$ was obtained from $S_g(A^{2-})$ and $\Delta S_{hyd}(A^{2-})$, the latter having been estimated from a plot of ΔS_{hyd} of bivalent anions against r^{-1}. $S^0(Zn^{2+})$ is reported by Staveley and Randall [10a] and by Latimer.[10b] The results are given in Table 4.

TABLE 4.

Entropy values (cal. deg.$^{-1}$ mole^{-1}).

Species	ΔS^0	S^0 (Zn^{2+})	S^0 (A^{2-})	S_g (ZnA)	$-\Delta S_{hyd}$ (ZnA)
ZnMal	27·4	−25·45	5·5	70·4	62·95
ZnPh	23·8	−25·45	4·6	73·7	70·75

It is of interest to consider whether the thermodynamic functions for bivalent-metal ion-pairs reveal any information about the type of bonding. The relevant functions are given in Table 5, in which the data for the sulphates are taken from ref. 11.

TABLE 5.

Thermodynamic data for metal ion-pairs.

(1. Sulphate. 2. Malonate. 3. Phthalate.)

	Mn	Co	Ni	Zn
	ΔH^0 (kcal. mole^{-1})			
1.	3·37	1·74	3·31	4·01
2.	3·53	2·57	1·77	2·98
3.	2·20	1·87	1·76	3·16
	ΔS^0 (cal. deg.$^{-1}$ mole^{-1})			
1.	22·6	16·6	21·7	24·4
2.	26·8	25·8	24·8	27·4
3.	19·9	19·2	19·4	23·8
	$-\Delta S_{hyd}$ (MA) (cal. deg.$^{-1}$ mole^{-1})			
1.	63·4	(71·0)	67·0	67·3
2.	55·9	61·0	63·0	62·95
3.	67·0	71·8	72·6	70·75

In all of these cases of ion-association, in which ionic ligands take part, the enthalpy term is opposing the reaction, which is brought about by the very favourable gain in entropy. It is significant, however, that the heat-change is less unfavourable for cobalt and nickel than for manganese and zinc. It has been found [12] for transition-metal ions that, if the calculated crystal-field stabilisation energies, obtained from spectroscopic Δ values, are subtracted from their heats of hydration, the resultant hydration energies

[9] Nair and Nancollas, *J.*, 1958, 3706.

[10] (*a*) Staveley and Randall, *Discuss. Faraday Soc.*, 1958, **26**, 157; (*b*) Latimer, " Oxidation Potentials," Prentice-Hall Inc., New York, 1953.

[11] Nair and Nancollas, *J.*, 1958, 3706; 1959, 3934.

[12] L. E. Orgel, " An Introduction to Transition-Metal Chemistry. Ligand-field Theory," Methuen, London, 1960, p. 73.

show a linear variation from V^{2+} to Zn^{2+}. Similarly, it may be seen that the ligand-field effects will contribute to the increased stability of Co^{2+} and Ni^{2+} complexes, thereby lowering the unfavourable ΔH term, whereas no such ligand-field contribution will take place in the cases of Mn^{2+} and Zn^{2+}, which have d^5 and d^{10} structures. The interaction between the metal ion and the ligand in all these cases is mainly electrostatic, and $-\Delta S_{\mathrm{hyd}}(\mathrm{MA})$ varies linearly with r_c^{-1}, where r_c is the cationic radius.

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