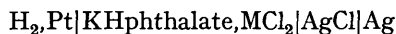


455. *Studies on Metal Complexes in Solution. Part I.
Phthalates of Some Transition Metals.*

By I. R. DESAI and V. S. K. NAIR.

Thermodynamic stability constants of the 1 : 1 complexes of manganese, cobalt, and nickel ions with the phthalate ion have been determined by a precise potentiometric method employing a Harned-type cell, at temperatures in the range 0—45°. The thermodynamic quantities, ΔG , ΔH , and ΔS for the reaction $M^{2+} + o-C_6H_4(CO_2)_2^{2-} \rightleftharpoons o-C_6H_4(CO_2)_2M$, have been derived. Also from the variation of ΔH with temperature, ΔC_p for the reaction has been estimated.

In other studies on the thermodynamics of ion association,¹ ion pairs of relatively low stability have been investigated. We have extended the studies to more stable complexes of chelate type and followed the effects of substitution and configurational factors on the thermodynamic properties of the complexes. Of the aromatic bivalent anions, phthalate was chosen because it is available in a pure form and because of the fairly high solubility of its complexes with bivalent metals. By taking a higher proportion of M^{2+} to phthalate, species such as $M[C_6H_4(CO_2)_2]_2^{2-}$ can be avoided, and the study limited to the 1 : 1 species. The Harned-type cell



has been used for studying manganese, cobalt, and nickel phthalates.

¹ Nancollas, *J.*, 1955, 1458.

EXPERIMENTAL

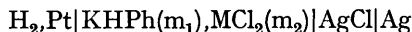
Stock solutions prepared from "AnalaR" metal chlorides were standardised by gravimetric analysis as silver chloride; agreement between duplicate estimations was better than $\pm 0.02\%$. Stock solutions of "AnalaR" potassium hydrogen phthalate were prepared by weight. Exactly 0.01M-hydrochloric acid, prepared from constant-boiling acid, was used in the standardisation of the silver-silver chloride electrodes prepared as described before.² The apparatus and procedure were similar to those described previously.² Equilibrium was attained only very slowly at the start of each run, so the cells were left overnight at 0° to come to equilibrium and the experiments completed for other temperatures the following day. Once equilibrium had been obtained at one temperature 1.5 hours were required for a constant e.m.f. to be reached at another temperature. E.m.f. readings remained constant within 30 μ V for more than 0.5 hr. Since there was no drift in the e.m.f. the chance of interaction between the phthalate and the hydrogen was discounted.

RESULTS AND DISCUSSION

Accurate values for the dissociation of phthalic acid over the range 0—60° are available from the work of Hamer *et al.*³ who used the cell *



The values of the thermodynamic dissociation constants of phthalic acid obtained by them and used in this work are given in Table 1. In the cell



the concentration of hydrogen ions is given by

$$-\log [H^+] = (E - E^0)/k + \log_{10} 2m_2 + \log_{10} \gamma_H + \gamma_{Cl^-}$$

where E is the corrected e.m.f., m represents molality, $k = 2.3026RT/F$, and γ is activity coefficient. For the concentrations of various ionic species one can write

$$m_1 = [H_2Ph] + [HPh^-] + [Ph^{2-}] + [MPh],$$

$$\text{and } m_2 = [M^{2+}] + [MPh].$$

TABLE 1.
Thermodynamic dissociation constant of phthalic acid.

	Temp.	0°	15°	25°	35°	45°
$10^8 K_1$		1.190	1.157	1.123	1.078	1.027
$10^6 K_2$		3.696	3.934	3.906	3.740	3.454

For electroneutrality,

$$[H^+] + 2[M^{2+}] + m_1 = 2m_2 + [HPh^-] + 2[Ph^{2-}] + [OH^-],$$

in which $[OH^-]$ is negligible at the pH's obtained.

K_1 and K_2 are the thermodynamic first and second dissociation constants of phthalic acid. Brannan and Nancollas⁴ have shown that for ion association between nickel and substituted malonate ions the Davies equation⁵

$$-\log \gamma_z = Az^2[I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0.2I]$$

can be used for computing activity coefficients up to an ionic strength of 0.2m. In the present work, therefore, I being always less than 0.1m, the Davies equation has been used. Ionic strength,

$$I = \frac{1}{2}\{[H^+] + 6m_2 - 3m_1 + [HPh^-](5 + 8K_2/[H^+])\gamma_2 + 4[H^+]\gamma_1^2/K_1\}$$

* Throughout this paper, Ph denotes phthalate.

² Nair and Nancollas, *J.*, 1958, 4144.

³ Hamer, Pinching, and Acree, *J. Res. Nat. Bur. Stand.*, 1945, 35, 539; Hamer and Acree, *ibid.*, p. 381.

⁴ Brannan and Nancollas, *Trans. Faraday Soc.*, 1962, 58, 354.

⁵ Davies, *J.*, 1938, 2093.

Successive approximations of the above equations to constant ionic strength enabled the various ionic concentrations to be evaluated; the stability constant of MPh was calculated from the relation

$$K = [\text{MPh}]/[\text{M}^{2+}][\text{Ph}^{2-}] \gamma_2^2.$$

Table 2 gives the results for manganese, cobalt, and nickel phthalates for all temperatures; the last column shows the constancy of the K values. At any one temperature the deviation among the K values is always less than 1%. There are only very scanty recorded data on stability constants of bivalent metal phthalates; * as would be expected the $\log_{10} K$ values of all these three transition-metal ions are higher than the corresponding values for barium (2.33) and calcium⁷ (2.43) at 25°. The K values increase in the order $\text{Mn} < \text{Co} < \text{Ni}$, as observed by Irving and Williams⁸ for a large number of ligands.

TABLE 2.
Manganese phthalate

	1	2	3	4	5	6
$10^3 m_1$	8.9623	12.942	16.490	9.9301	13.784	17.939
$10^3 m_2$	8.8445	9.4789	11.425	8.9468	10.598	12.487
$(E - E_0)$	$10^3 I$	$10^4 [\text{H}^+]$	$10^3 [\text{HPh}^-]$	$10^4 [\text{Ph}^{2-}]$	$10^4 [\text{MPh}]$	K
At 0°						
1.	0.31163	34.85	1.410	7.545	3.882	3.909 (461)
2.	0.30947	40.49	1.472	10.908	5.602	5.306 444
3.	0.30417	49.53	1.573	13.845	7.041	6.971 434
4.	0.31163	36.14	1.401	8.387 ₅	4.387	4.026 423
5.	0.30637	44.57	1.522	11.587	5.910	5.838 ₅ 437
6.	0.30170	54.00	1.620	15.031	7.617	7.734 429
						433.4 ± 3
At 15°						
1.	0.32802	34.81	1.463	7.479	4.030	4.116 483
2.	0.32538	40.35	1.550	10.787	5.718	5.834 497
3.	0.31983	49.36	1.656	13.689	7.201	7.629 ₅ 484
4.	0.32761	36.03	1.477	8.293	4.467	4.457 477
5.	0.32209	44.41	1.604	11.454	6.028	6.423 490
6.	0.31715	53.79	1.709	14.855	7.767	8.509 483
						485.7 ± 2.6
At 25°						
1.	0.33920	34.72	1.484	7.432	3.958	4.436 544
2.	0.33646	40.21	1.571	10.718	5.622	6.283 560
3.	0.33076	49.19	1.677	13.604	7.093	8.173 542
4.	0.33869	35.90	1.503	8.236	4.371	4.851 545
5.	0.33281	44.20	1.643 ₅	11.360	5.854	7.089 574
6.	0.32798	53.60	1.733	14.758	7.644	9.128 543
						551.3 ± 5.2
At 35°						
1.	0.35076	34.59	1.481	7.393	3.810	4.776 626
2.	0.34822	40.10	1.553	10.679	5.476	6.615 ₅ 623
3.	0.34200	48.96	1.678	13.524	6.814	8.854 631
4.	0.35039	35.80	1.492	8.201	4.237	5.156 614
5.	0.34468	44.13	1.610	11.337	5.769	7.273 614
6.	0.33934	53.41	1.720 ₅	14.692	7.418	9.678 612
						620.0 ± 3.3
At 45°						
1.	0.36287	34.48	1.451	7.368	3.618 ₅	5.080 720
2.	0.36007	39.89	1.532	10.628	5.160	7.176 739
3.	0.35360	48.69	1.659	13.451	6.409	9.613 754
4.	0.36222	35.63	1.476	8.158	3.977	5.622 735
5.	0.35633	43.90	1.593 ₅	11.275	5.417	7.926 736
6.	0.35078	53.09	1.706	14.605	6.956	10.568 738
						737.0 ± 3.3

* For nickel a value of 2.14 for $\log_{10} K$ at $I = 0.1\text{M}$ has been reported⁶ (which corresponds to the value for $\log_{10} K$ of 3.02) at 25° from a pH-titration method.

⁶ Yasuda, Suzuki, and Yamasaki, *J. Phys. Chem.*, 1956, **60**, 1649.

⁷ Topp and Davies, *J.*, 1940, 87.

⁸ Irving and Williams, *J.*, 1953, 3192.

TABLE 2. (Continued).

At 15°							
1.	0.33488	25.53	1.474	5.882	2.902	4.086	798
2.	0.33088	28.51	1.559	6.454	3.095	4.776	824
3.	0.31979	41.71	1.815	10.545	4.818	8.394	823
4.	0.31416	50.01	1.942	12.573	5.660	10.444	808
5.	0.33279	27.13	1.521	6.295	3.055	4.512	815
6.	0.32415	34.60	1.596	7.432	3.450	5.949	825
7.	0.31504	47.44	1.925	11.334	5.069	9.608	828
8.	0.31180	53.41	1.994	12.981	5.807	11.050	799
							815 ± 5.0
At 25°							
1.	0.34637	25.46	1.489	5.846	2.858	4.314	876
2.	0.34222	28.43	1.576	6.413	3.047	5.035	903
3.	0.33075	41.57	1.835	10.475	4.749 ₅	8.824	903
4.	0.32509	49.89	1.953	12.501	5.621	10.846	870
5.	0.34422	27.06	1.537	6.257	3.009	4.758	894
6.	0.33523	34.50	1.717	7.381	3.391 ₅	6.273	908
7.	0.32581	47.29	1.949	11.253	4.990	10.104	911
8.	0.32262	53.28	2.007	12.904	5.761	11.488	(863)
							895 ± 6.4
At 35°							
1.	0.35821	25.37	1.483	5.816	2.752	4.570	987
2.	0.35392	28.33	1.563	6.379	2.919	5.327 ₅	1002
3.	0.34235	41.47	1.812	10.434	4.631 ₅	9.133	986
4.	0.33623	49.69	1.948	12.426	5.419	11.419	980
5.	0.35606	26.97	1.527	6.227	2.908	5.002	996
6.	0.34670	34.39	1.711	7.340	3.268	6.601 ₅	(1019)
7.	0.33723	47.17	1.926	11.208	4.865	10.444	995
8.	0.33363	53.07	2.006	12.820	5.540	12.126	981
							990 ± 3.5
At 45°							
1.	0.37038	25.27	1.462	5.788	2.591	4.859	1144
2.	0.36600	28.22	1.546	6.349	2.768	5.620	1169
3.	0.35400	41.27	1.788	10.377	4.360 ₅	9.679	1145
4.	0.34767	49.46	1.924	12.354	5.101	12.086	1139
5.	0.36817	26.86	1.505	6.197	2.739	5.309	1153
6.	0.35850	34.26	1.688	7.301 ₅	3.078	6.971	1175
7.	0.34870	46.96	1.902	11.143	4.579	11.043	1155
8.	0.34496	52.82	1.984	12.742	5.210	12.835	1139
							1152.4 ± 5.3

The $\log_{10} K$ values of the oxalates,⁹ malonates,¹⁰ and succinates¹¹ of manganese, cobalt, and nickel at 25°, along with those for the phthalates, are given in Table 3. The stabilities decrease along the series oxalate, malonate, and succinate, and the ring size increases from 5-membered to 7-membered. However, in the case of phthalate, steric effects favour the orientation of the two carboxyl groups nearer to each other in a planar structure, and the stability of the phthalate of each metal is greater than that of the corresponding succinate. Also, the increase in stability found for the oxalates and the

TABLE 3.

Stabilities of transition-metal dicarboxylates at 25°.

	$\log_{10} K$	Oxalate	Malonate	Succinate	Phthalate
Mn ²⁺		3.967	3.193	2.265	2.741
Co ²⁺		4.791	3.758	2.217	2.831
Ni ²⁺		5.158	4.100	2.344	2.952

malonates in the series Mn, Co, and Ni is observed for the phthalates but not for the succinates.

Plots of $\log_{10} K$ against T^{-1} shown in the Figure are not linear, indicating that ΔC_p for complex formation is appreciable. This is similar to the well-known observations on

⁹ McAuley and Nancollas, *J.*, 1961, 2215.

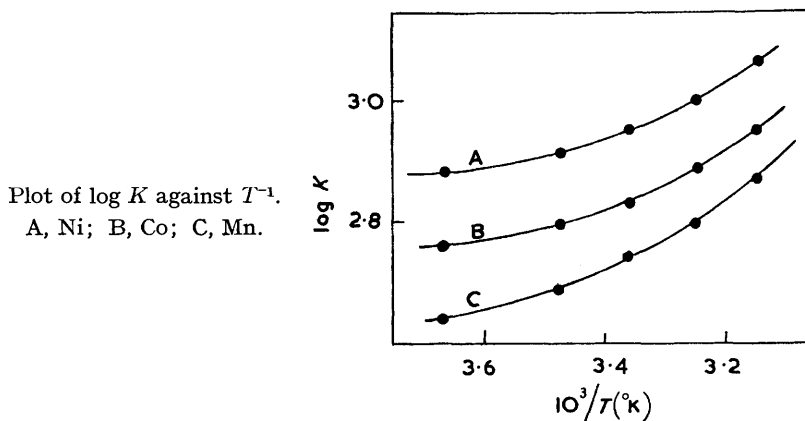
¹⁰ Nair and Nancollas, *J.*, 1961, 4367.

¹¹ McAuley and Nancollas, *J.*, 1961, 4458.

dissociation of weak acids. For complex-forming reactions of metals values of ΔC_p have been reported for transition-metal oxalates,⁸ malonates,¹⁰ and succinates.¹¹ Since ΔH varies appreciably with temperature, the variation of $\log_{10} K$ can be represented as a quadratic in T ,

$$\log_{10} K = a + bT + cT^2.$$

The values of a , b , and c obtained by the method of least squares from the K values at all



the five temperatures are given in Table 4. The values of K calculated from them are not more than 1.5% different from the observed values.

TABLE 4.
Parameters for temperature-dependence of $\log_{10} K$.

	a	-10^2b	10^5c
MnPh	6.365	2.975	5.897
CoPh	5.690	2.374	4.752
NiPh	7.795	3.867	6.912

The thermodynamic functions ΔG , ΔH , ΔC_p , and ΔS for the complex formation were calculated from the relations, $\Delta G = -2.3026RT \log_{10} K$, $\Delta H = 2.3026RT^2(b + 2cT)$, $\Delta C_p = 4.6052RT(b + 3cT)$, and $\Delta S = (\Delta H - \Delta G)/T$, and are given in Table 5. Un-

TABLE 5.
Thermodynamic functions.

Reaction	ΔH (kcal. mole ⁻¹)	$-\Delta G$ (kcal. mole ⁻¹)	ΔS (cal. deg. ⁻¹ mole ⁻¹)	ΔC (cal. deg. ⁻¹)
$Mn^{2+} + Ph^{2-} \rightarrow MnPh$...	2.20 ± 0.05	3.739 ± 0.006	19.9 ± 0.3	63 ± 20
$Co^{2+} + Ph^{2-} \rightarrow CoPh$	1.87 ± 0.05	3.860 ± 0.004	19.2 ± 0.2	51 ± 15
$Ni^{2+} + Ph^{2-} \rightarrow NiPh$	$1.76_s \pm 0.05$	4.026 ± 0.005	19.4 ± 0.3	68 ± 20

certainties in the last three quantities were estimated by using different combinations of experimental K values at three temperatures in the experimental range for the calculation of the parameters a , b , and c . ΔC_p is subject to great uncertainties.

$\Delta S_{hyd}(MPh)$ may be obtained from the relation

$$\Delta S_{hyd}(MPh) = \Delta S - \Delta S_g(MPh) + \Delta S_{hyd}(M^{2+}) + \Delta S_{hyd}(Ph^{2-}),$$

where ΔS_g and ΔS_{hyd} are the gas and the hydration entropies of the species indicated. ΔS_g was calculated by assuming a planar model for the metal phthalate, and the method

of calculation has been described elsewhere.¹² S° for manganese ion is that obtained by Walkley;¹³ S° for cobalt and nickel ions are those evaluated by Staveley and Randall¹⁴ (S° values are -18 , -22 , and -23 cal. deg.⁻¹ mole⁻¹ for Mn^{2+} , Co^{2+} , and Ni^{2+} , respectively). $\Delta S_{hyd}(Ph^{2-})$ was obtained by interpolation on a plot of ΔS_{hyd} of similar bivalent anions against r^{-1} , the latter being calculated from the ionic mobilities of the respective ions by applying Stokes's law. $S^\circ(Ph^{2-})$ was obtained as 4.6 cal. deg.⁻¹ mole⁻¹. Table 6 gives the entropy values.

TABLE 6.
Entropy values (cal. deg.⁻¹ mole⁻¹).

Species	ΔS	$S_g(MPh)$	$S^\circ(MPh)$	$-\Delta S_{hyd}(MPh)$	r_+ (Å) ¹⁴
MnPh	19.9	73.5	6.5	67.0	0.80
CoPh	19.2	73.6	1.8	71.8	0.72
NiPh	19.4	73.6	1.0	72.6	0.69

ΔS for the formation of the phthalate complex is essentially the same for all the three cations and is found to be of the same order as for their succinates¹¹ (18—20 cal. deg.⁻¹ mole⁻¹). The enthalpy change ΔH opposes the formation reaction, as was reported for other dicarboxylates. However, this opposition is less for phthalates than for the succinates, thereby leading to a larger $-\Delta G$ value for the phthalate formation. The reaction occurs because of the high entropy gain of the water molecules in the field of the charged ions, resulting from charge neutralisation when the complex is formed. Williams¹⁵ has suggested that for bivalent cations the heats of hydration, as well as the heats of formation of their complexes, could be represented by an empirical equation combining electrostatic and covalent interaction, together with additional stabilisation due to the different available bonding orbitals of the cations. Thus

$$-\Delta H = A(z/r_+) + BI_{02} - C(1/r_+^3)$$

where z is the cationic charge, I_{02} the ionisation potential, and A , B , and C are arbitrary constants. When the entropy of formation of a complex is small and the enthalpy term dominant, *e.g.*, with neutral ligands, the stability follows the same order as the enthalpy change for a series of cations forming complexes with the same ligand. With the dicarboxylates, however, the formation reaction is endothermic and the interaction may be mainly electrostatic rather than covalent; ΔH is less unfavourable the smaller the value of r_+ . $-\Delta S_{hyd}(MPh)$ follows the same trend as r_+^{-1} , and is slightly greater than the corresponding term for the succinates¹¹ (64.4—69.5); this probably indicates less charge neutralisation in the case of the phthalates.

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COLLEGE OF ADVANCED TECHNOLOGY,
GOSTA GREEN, BIRMINGHAM, 4.

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¹² Nair and Nancollas, *J.*, 1958, 3706.

¹³ Walkley, *J. Electrochem. Soc.*, 1948, **93**, 316; 1948, **94**, 41.

¹⁴ Staveley and Randall, *Discuss. Faraday Soc.*, 1958, **26**, 157.

¹⁵ Williams, *J. Phys. Chem.*, 1954, **58**, 121.