448. *Thermodynamic Dissociation Constants of Some Cobalt*(II) *Ion-pairs Determined at 25° by Cation-exchange Resin Studies*

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A verified empirical function which allows for the mass-action effect of sodium ions is used in calculating the dissociation constants of a number of cobalt ion-pairs from ion-exchange equilibria. These were obtained by means of cobalt-60, and Amberlite or Zeo-Karb resins at ionic strengths $\not> 0{\cdot}1$. If only one stage of association is involved, runs may be made at various ionic strengths. The results, which are for dissociation constants ranging from 0·00002 to 0·05, are in good agreement with those obtained by other methods.

MOST of the many reported studies of ion-association by means of ion-exchange resins [1,2] refer to media of high ionic strengths, the information being analysed by methods such as that of Fronaeus.[3,4] A few systems have been examined at low ionic strengths, particularly by Schubert and his associates,[5,6] but these are mainly restricted to bivalent cations and ligands that form a single uncharged ion-pair. It is assumed that this species does not partition between resin and solution, and the treatment for deriving the association constants is relatively simple. In the present work, Schubert's method is applied at ionic strengths that rarely exceed 0·1, so that thermodynamic dissociations can be calculated and thus compared with results obtained by other methods.

The various equilibria that are involved when, *e.g.*, the Na^+ ion form of a cation-exchange resin is equilibrated with a solution containing M^{z+} ions and L^{y-} ion-pairing ligands may be represented by

$$m\mathrm{Na^+}_{\mathrm{R}} + \mathrm{ML}_n{}^{m+} \rightleftharpoons (\mathrm{ML}^{m+})_{\mathrm{R}} + m\mathrm{Na}^+ \qquad (1)$$

where $m = z - ny \geqslant 1$, R = resin phase, n = number of ligands associating with M^+. Following the treatment of Rossotti,[2] the partition coefficient P_n for each cationic species is defined by

$$P_{\mathrm{n}} = [\mathrm{ML}_n{}^{m+}]_{\mathrm{R}}/[\mathrm{ML}_n{}^{m+}] \qquad (2)$$

while an overall partition coefficient q_{B} is defined by

$$q_{\mathrm{B}} = \sum_0^{c+} [\mathrm{ML}_n{}^{m+}]_{\mathrm{R}}/[\mathrm{ML}_n{}^{m+}] \qquad (3)$$

$$= \sum_0^{c+} P_{\mathrm{n}}\beta_{\mathrm{n}}[\mathrm{L}]^n / \sum_0^{N} \beta_{\mathrm{n}}[\mathrm{L}]^n \qquad (4)$$

where the stability constants β_{n} are (leaving out charges) expressed by

$$\beta_{\mathrm{n}} = [\mathrm{ML}_n]/[\mathrm{M}][\mathrm{L}]_n, \qquad (5)$$

c_+ is the maximum number of cationic species taken up by the resin and N is the maximum number of ML_n ion-pairs formed in solution.

When M^{2+} is introduced as tracer quantities and incorporates a radio-isotope, if R_1 is

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[1] J. Bjerrum, G. Schwarzenbach, and L. G. Sillén, " Stability Complexes of Metal–Ion Complexes," *Chem. Soc. Special Publ.* No. 6, 1957; No. 7, 1958.

[2] F. J. C. Rossotti and H. Rossotti, " The Determination of Stability Constants," McGraw-Hill, London, 1961.

[3] S. Fronaeus, *Acta Chem. Scand.*, 1951, **5**, 859.

[4] S. Fronaeus, *Acta Chem. Scand.*, 1925, **6**, 1200.

[5] N. C. Li, W. M. Westfall, A. Lindenbaum, J. M. White, and J. Schubert, *J. Amer. Chem. Soc.*, 1957, **79**, 5864.

[6] J. Schubert, E. L. Lind, W. M. Westfall, R. Pfleger, and N. C. Li, *J. Amer. Chem. Soc.*, 1958, **80**, 4799.

the count-rate of unit volume of solution before equilibration with the resin, R_2 is the corresponding count-rate at equilibrium, V is the volume of solution, and m is the mass of resin, then, if m is very small,

$$q_{\mathrm{B}} = V(R_1 - R_2)/mR_2 \tag{6}$$

Also, if K_{n} is the equilibrium constant for reaction (1), then

$$K_{\mathrm{n}} = ([\mathrm{ML}_n{}^{m+}]_{\mathrm{R}}[\mathrm{Na}^+]^m\gamma_{\mathrm{ML}n(\mathrm{R})}\gamma^m{}_{\mathrm{Na}})/([\mathrm{Na}^+]^m{}_{\mathrm{R}}[\mathrm{ML}_n{}^{m+}]\gamma_{\mathrm{Na(R)}}{}^m\gamma_{\mathrm{ML}n}) \tag{7}$$

By using high concentrations of sodium perchlorate so that $[\mathrm{Na}^+]$ and the ionic strength are essentially constant as [L] is varied over a small range, and by keeping the load $[\mathrm{ML}_n]_{\mathrm{R}}$ small so that $[\mathrm{Na}^+]_{\mathrm{R}}$ also keeps virtually constant, from eqns. (2) and (7), if δ represents the $[\mathrm{Na}^+]^m{}_R$ and γ terms,

$$K_{\mathrm{n}} = P_n[\mathrm{Na}^+]^m\delta \tag{8}$$

Letting
$$P_0 = q_{\mathrm{B}} \text{ at } [\mathrm{L}] = 0 \tag{9}$$

P_0 was determined over a range of sodium perchlorate concentrations. Some figures are given in Table 1. These show that P_0 depends on $[\mathrm{Na}^+]^2$, *i.e.*,

$$\mathrm{P}_0[\mathrm{Na}^+]^2 = K_0/\delta = P'_0 \quad (I \not> 0{\cdot}1) \tag{10}$$

It is likewise assumed that

$$q_B' = q_B[\mathrm{Na}^+]^2 = K_n/\delta \quad (I \not> 0{\cdot}1) \tag{11}$$

for the present system in which tracer amounts of Co^{2+} were used. Similar results were obtained with Zeo-Karb-225, and in 20% aqueous ethanol. It is possible that equation (11) may not hold at lower or higher ionic strengths or for other resins. In such cases a plot of the left hand side of eqn. (12) against $[\mathrm{Na}^+]$ could be used for interpolation purposes.

TABLE 1

Distribution of Co(II) between Amberlite CG-120 and sodium perchlorate solutions at 25° (V = 100 or *90 ml.; 300 sec. counts)

m	0	0·0300	0·0404	0·0572	0·0977	0·1183	0 *	0·1490 *	0·1819 *	0·2158 *
$R \times 10$	4130	2589	5098	8592	10,648	16,136	12,887	4506	4097	3547
NaClO_4	—	0·0150	0·0250	0·0400	0·0600	0·0900	—	0·10	0·10	0·10
$P_0[\mathrm{Na}^+]^2$	—	11·05	11·0	10·65	10·6	10·7	—	11·27	10·6	11·0

When ML_n has a zero or negative charge, *i.e.*, $m = z - ny \leqslant 0$, such species are assumed to remain entirely in the aqueous phase, and, from equations (4), (10), and (11),

$$q_{\mathrm{B}}' = P_0'/\sum_0^N \beta_n[\mathrm{L}]^n \tag{12}$$

Also, if $N \leqslant 2$, Schubert's method [5,6] may be used; from eqn. (12),

$$\{(P_0'/q_{\mathrm{B}}') - 1\}/[\mathrm{L}] = \beta_1 + \beta_2[\mathrm{L}] \tag{13}$$

whence β_1 and β_2 are obtainable by plotting procedures.

Some results for cobalt oxalate at $I = 0{\cdot}10$ are shown in Table 2. As the last line indicates, both CoOx and $\mathrm{Co(Ox)_2}^{2-}$ form, and for these a plot of the left-hand side of eqn. (13) against [L] has an intercept $\beta_1 = 7500$ and a slope $\beta_2 = 1{\cdot}5 \times 10^6$. Since $\beta_1 = k_1$ and $\beta_2 = k_1k_2$, where k represents association constants, $k_2 = 200$. Also, by means of Davies's equation,[7]

$$-\log f_{\mathrm{i}} = 0{\cdot}5z_{\mathrm{i}}{}^2\{I^{\frac{1}{2}}/(1 + I^{\frac{1}{2}}) - 0{\cdot}3I\} \tag{14}$$

(I = ionic strength, z_{i} = ion charge, f = activity coefficient) the thermodynamic dissociation constants K_1 and K_2 at $I = 0$ were calculated to be $1{\cdot}9 \times 10^{-5}$ and 0·005, respectively. Runs at $I = 0{\cdot}05$ and 0·03 were also made; these are summarised in Table 5 together with results for other ligands. Allowance was made for $NaSO_4^-$ ion-pairs[7] ($K = 0{\cdot}2$); without this, $K_1(CoSO_4)$ is about 20% higher.

A similar study of cobalt malonate led to a smooth but slightly downward curving plot as $[L] \longrightarrow 0$. This suggested that the experimental value of $P_0' = 12{\cdot}18$ was slightly wrong. Tests showed that $P_0' = 12{\cdot}25$ gave a linear plot while with $P_0' = 12{\cdot}30$ the plot curved slightly upwards as $[L] \longrightarrow 0$. This process can therefore be applied if P_0' is not obtained directly or if the experimental value is suspect, but the experimental values of q_B' must themselves be reliable at low values of [L].

TABLE 2

Cobalt oxalate ($I = 0{\cdot}10$; Amberlite; 300 sec. counts)

m (g.)	0	0·1183	0·7002	0·8004	0·9107	1·0803	1·4158
$[L] = Na_2L$	0	0	0·0015	0·0020	0·0025	0·0030	0·0040
$NaClO_4$	—	0·100	0·0955	0·0940	0·0925	0·0960	0·0880
$10R$	45,469	19,368	29,932	31,631	33,507	33,473	34,571
q_B'	—	11·39	0·719	0·525	0·373	0·312	0·205
$\{(P_0'/q_B') - 1\}/[L]$	—	—	9890	10,350	11,820	11,830	13,630

Since P_0' does not vary in the range $I = 0{\cdot}02$—$0{\cdot}1$ (Table 1), runs should be possible at various ionic strengths, K_1 and K_2 being derived from a modified form of eqn. (13), namely,

$$\{(P_0'/q_B') - 1\}/[L]f_M f_L = (1/K_1) + [L]/K_1K_2 \qquad (14)$$

This is illustrated for cobalt succinate in Table 3; only K_1 is involved. The average agrees well with a separate run at $I = 0{\cdot}10$ (cf. Table 5); it is $10^4K_1 = 40 \pm 10\%$, or $39 \pm 4\%$ if the two largest deviations are ignored.

TABLE 3

Cobalt succinate ($I = 0{\cdot}034$—$0{\cdot}112$; Amberlite; 300 sec. counts; $[L]/C_L = 0{\cdot}899$, $[Na^+] = NaClO_4 + [L] + C_L$)

m (g.)	...0	0·0424	0·0336	0·0364	0·0376	0·0317	0·0377	0·0364	0·0413
C_L	0	0	0·0050	0·0100	0·0100	0·020	0·025	0·030	0·040
$NaClO_4$	—	0·050	0·020	0·010	0·020	0	0	0	0
$10R$	48,399	16,495	10,897	122,130	165,410	21,078	24,889	30,356	35,766
q_B'	—	11·40	8·91	6·85	7·79	5·90	5·65	5·31	4·94
I	—	—	0·034	0·043	0·032	0·056	0·070	0·086	0·112
10^4K_1	—	—	42	31	52	39	39	37	37

Except for oxalate, sulphate, and acetate (+trace of acetic acid), where sodium salts were used, stock solutions of ligands were made from known amounts of acid and of slight deficiencies of standard sodium hydroxide. For these stock solutions, $[L] = NaOH - C_1$, where C_L = total acid molarity.

TABLE 4

Cobalt glycollate ($I = 0{\cdot}10$; Amberlite; 300 sec. counts; $[L] = C_L$; $V = 90$ ml.)

m (g.)	0	0·1484	0·1489	0·1489	0·1486	0·1487	0·1487	0·1490	0·1490
C_L	0	0	0·020	0·030	0·040	0·050	0·060	0·070	0·080
$NaClO_4$	—	0·10	0·080	0·070	0·060	0·050	0·040	0·030	0·020
$10R$	43,535	14,511	20,122	22,786	24,873	26,762	28,606	29,706	30,961
q_B	—	121·3	70·3	55·0	45·4	37·9	31·6	28·1	24·5
$\{(P_0/q_B) - 1\}/[L]$	—	—	36·3	40·2	41·8	44·0	47·3	47·3	49·3
f	—	—	1030	1090	1160	1230	1320	1360	1420
$(f - f_0)/[L]$	—	—	6500	6300	6500	6600	7000	6600	6500
$(P_0 - q_B)/[L]$	—	—	2550	2200	1900	1670	1500	1330	1210

With cobalt acetate and glycollate, if I is kept constant during a run, $[Na^+]$ is also constant, but since ML^+ can also partition, equation (4) applies. Some figures relating to the glycollate are given in Table 4. Schubert's method, in which only P_0 is considered, leads

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

to $\beta_1 = 33 \pm 2$, $\beta_2 = 7$. The method of Fronaeus[3,4] takes P_1 into account, and, as pointed out by Rossotti,[2] equation (4) gives

$$\beta_1 q_B - \beta_1 P_1 = (P_0 - q_B)/[\mathrm{L}] \qquad (15)$$

so β_1 and $-\beta_1 P_1$ are the slope and intercept of a plot of the right-hand side against q_B. Such a plot gives a slope $\beta_1 = 32$, while the intercept is 45, so $P_1 = -1{\cdot}4$, *i.e.*, it is negligible.

An alternative procedure is[2] to extrapolate a plot of $\phi = \{(P_0/q_B) - 1\}/[\mathrm{L}]$ against [L] to [L] = 0. This gives $\phi_0 = 33$. Then values of f are calculated, where

$$f = \{(P_0/q_B)(\phi_0[\mathrm{L}] - 1) + 1\}/[\mathrm{L}]^2 \qquad (16)$$

and $(f - f_0)/[\mathrm{L}]$ is plotted against $(\phi - \phi_0)/[\mathrm{L}]$, when the slope should give β_1(f_0 is the limiting value of f at [L] = 0; it is 900). However, as Table 4 shows, values of $(f - f_0)/[\mathrm{L}]$ scarcely differ, so this procedure fails here.

TABLE 5

Summary of results for cobalt(II) ion-pairs

Run	Ligand	I	C_2	K_1	K_2
1	Oxalate	0·10	0·001—0·004	0·000019 ± 7%	0·005 ± 10%
2	Oxalate	0·10	0·0002—0·0008	0·000017 ± 10%	0·007 ± 10%
3	Oxalate	0·10	0·0004—0·0024	0·000019 ± 7%	0·007 ± 10%
4	Oxalate	0·05	0·0004—0·0020	0·000019 ± 10%	0·007 ± 10%
5	Oxalate	0·03	0·0004—0·0020	0·000020 ± 10%	0·005 ± 5%
6	Malonate	0·10	0·0005—0·004	0·000185 ± 5%	0·05 ± 10%
7	Malonate	0·05	0·005—0·017	0·00017 ± 5%	0·04 ± 20%
8	Malonate	0·035	0·0004—0·0025	0·000155 ± 5%	—
9	Malonate	0·03—0·04	0·001—0·0113	0·00018 ± 3%	—
10	Succinate	0·10	0·002—0·037	0·0038 ± 13%	—
11	Succinate	0·034—0·112	0·005—0·037	0·0039 ± 4%	—
12	Glutarate	0·10	0·010—0·025	0·0045 ± 3%	—
13	Glutarate	0·05—0·10	0·010—0·035	0·0050 ± 10%	—
14	Adipate	0·10	0·010—0·025	0·0055 ± 6%	—
15	Adipate	0·05—0·14	0·010—0·035	0·0062 ± 6%	—
16	Phthalate	0·10	0·005—0·030	0·0018 ± 5%	0·11 ± 20%
17	Phthalate	0·05	0·003—0·14	0·0017 ± 5%	0·17 ± 20%
18	Tartrate	0·10	0·005—0·030	0·001 ± 5%	0·055 ± 10%
19	Tartrate	0·05	0·005—0·017	0·00090 ± 5%	0·075 ± 10%
20	Sulphate (water)	0·10	0·007—0·030	0·0039 ± 3%	—
21	Sulphate (water)	0·07	0·007—0·022	0·0039 ± 5%	—
22	Sulphate (water)	0·03—0·09	0·010—0·030	0·0037 ± 5%	—
23	Sulphate (10% vol. EtOH)	0·10	0·005—0·030	0·0028 ± 5%	—
24	Sulphate (10% vol. EtOH)	0·05	0·003—0·012	0·0030 ± 5%	—
25	Sulphate (20% vol. EtOH)	0·08	0·0017—0·0052	0·0022 ± 6%	—
26	Sulphate (20% vol. EtOH)	0·06	0·0017—0·0034	0·0025 ± 3%	—
27	Acetate	0·10	0·01—0·06	0·051 ± 5%	—
28	Glycollate	0·10		0·011 ± 5%	0·09 ± 5%

With regard to other results, the present ones are compared with them in the following Paper. There are only two previous ion-exchange figures to match against ours. These were obtained by Schubert at $I = 0{\cdot}16$, and converting them to $I = 0$ gives K_1(oxalate) = $2{\cdot}1 \times 10^{-5}$, K_2(oxalate) = 0·005, K_1(glycollate) = 0·0087 ± 7%.

Another comparison made here concerns K_1(sulphate). In water, from conductance, this was calculated to be[8] 0·0034, while from e.m.f. measurements[9] $K_1 = 0{\cdot}0043$. The present average is 0·0038 ± 8%. With this, Bjerrum's equations give a mean ion-pair diameter of 3·91 Å. In 10% ethanol (by vol.), the dielectric constant D is[10] (by interpolation) 74·0, whence K_1 (calc.) = 0·0030 compared with 0·0029 (found). Likewise, in 20% ethanol (by vol.; $D = 69{\cdot}0$), K_1 (calc.) = 0·0020, K_1 (found) = 0·0022. Davies and

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

[9] V. S. K. Nair and G. H. Nancollas, *J.*, 1959, 3934.

[10] G. C. Akerlof, *J. Amer. Chem. Soc.*, 1932, **54**, 4125.

Thomas[11] obtained $K_1 = 0{\cdot}0026$ in 10% ethanol (by wt.; $D = 72{\cdot}8$) by conductance compared with K_1 (calc.) $= 0{\cdot}0022$, but in 30% ethanol (by wt.; $D = 72{\cdot}8$) $K_1 = 0{\cdot}0056$ by conductance compared with K_1 (calc.) $= 0{\cdot}0087$. These figures suggest that the predicted trend in K_1 with D holds up to about 20% of ethanol. Trends for similar sulphates in ethanol–water follow the same general pattern[7,11] but are somewhat dependent on the associating cations.

EXPERIMENTAL

The resins were air-dried Amberlite CG-120 (100—200 mesh) and Zeo-Karb-225 in their Na^+ forms, and cobalt-60 was obtained as the aqueous chloride (Radiochemical Centre, Amersham). AnalaR grade reagents were used in making the stock solutions, except malonate, glutarate, adipate, and glycollate. The equilibrations were effected in Pyrex tubes (about 120 ml. capacity) with narrow necks fitted with rubber bungs. These were rocked for 24 hr. in baths at 25° ± 0·1°. The rockers consisted of clips mounted on a brass frame which was connected by an arm to a motor geared to 2 revs./min. After equilibration, the tubes were shaken to make the resin settle, let stand vertically for 15 min., and gently shaken again to wash down traces of resin from the necks and bungs. Samples (5 ml.) were counted in a sodium iodide well-type crystal fitted to a scintillation counter (Ekco Ltd.). Corrections were made for backgrounds, lost counts, and relative efficiencies of the four counting tubes used (these varied from one another by up to 1%).

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[11] C. W. Davies and G. O. Thomas, *J.*, 1958, 3660.