

449. *Dissociation Constants of Some Cobalt(II) Ion-pairs from pH (Glass Electrode) Measurements at 25°*

By C. B. MONK

Precision pH studies have been used to evaluate the thermodynamic dissociation constants of seven cobalt(II) dicarboxylates at 25°. The results are compared with those previously obtained by five other methods.

SEVERAL recent reports¹⁻⁷ on ion-association in dilute solutions include figures for cobalt(II) dicarboxylates which are in some disagreement. Some of the divergencies can be attributed to unsuspected features or experimental uncertainties such as are mentioned later on. Also, in a few cases a "best" answer cannot be selected on a majority basis. It is hoped that the present results will resolve these and thus indicate which systems require re-examination. Our information is founded on the cell:

Glass electrode | H₂L (*m*₁), NaOH (*m*₂), CoCl₂ (*m*₃) | Sat. KCl, Calomel

As described previously,⁸ E_0 was found by means of E (± 0.1 mv) for $m_1 + m_2$, and the known K_1 and K_2 values⁹ of the dicarboxylic acids H₂L so that the pH's (± 0.002) of $m_1 + m_2 + m_3$ were obtained from

$$E = E_0 - (2.303RT/F)\text{pH}$$

¹ R. G. Seys and C. B. Monk, preceding Paper.

² R. H. Jones and D. I. Stock, *J.*, 1962, 306.

³ P. G. Manning and C. B. Monk, *Trans. Faraday Soc.*, 1961, 57, 1996.

⁴ A. McAuley and G. H. Nancollas, *J.*, 1961, 2215.

⁵ V. S. K. Nair and G. H. Nancollas, *J.*, 1961, 4367.

⁶ A. McAuley and G. H. Nancollas, *J.*, 1961, 4458.

⁷ J. Schubert, E. L. Lind, W. M. Westfall, R. Pfeifer, and N. C. Li, *J. Amer. Chem. Soc.*, 1958, 80, 4799.

⁸ D. W. Archer and C. B. Monk, *J.*, 1965, 3117.

⁹ R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1955.

The calculated first thermodynamic dissociation constants of the ion-pair CoL are shown in Table 1. In several runs, unless CoL_2^{2-} was allowed for, $K(\text{CoL})$ increased steadily with increasing m_3 . To deal with this, values of $K(\text{CoL}_2^{2-})$ were tried until $K(\text{CoL})$ was constant. For example, the following figures summarise the effect of varying $K(\text{CoL}_2^{2-})$ for the malonate system:

$K(\text{CoMal}_2^{2-})$	0.03	0.04	0.05	0.06
$10^6 K(\text{CoMal})$	$193 \pm 6\%$	$177 \pm 1.2\%$	$168 \pm 2.1\%$	$163 \pm 6\%$

Accordingly, $K(\text{CoL}_2^{2-})$ was taken as 0.04 in deriving the $K(\text{CoMal})$ figures of Table 1, and similarly $K(\text{CoOx}_2^{2-}) = 0.0035$, $K(\text{CoPhthalate}_2^{2-}) = 0.2$. Apart from oxalate, repeat runs were made with different $m_1 : m_2$ proportions. All the runs, together with average answers from other sources,¹⁻⁸ are shown in Table 2.

TABLE 1

First thermodynamic dissociation constants of Co(II) ion-pairs at 25°

	Oxalate. $E_0 = 375.6$ mv, $K(\text{CoL}_2^{2-}) = 0.0035$								Malonate. $E_0 = 379.2$ mv, $K(\text{CoL}_2^{2-}) = 0.04$								
$10^5 m_1$	72.2	66.3	64.5	62.8	61.2	59.7	58.3	1504	1432	1419	1406	1393	1367	1355			
$10^5 m_2$	120.3	110.3	107.4	104.6	101.9	99.4	97.0	2313	2203	2182	2162	2142	2103	2084			
$10^5 m_3$	0	24.9	32.3	39.4	46.0	52.4	58.4	0	479	569	658	745	915	997			
E (mv)	104.6	117.9	122.5	127.1	131.2	134.6	136.9	50.3	71.7	77.0	82.3	87.5	96.5	100.2			
$10^4 K(\text{CoL})$	—	0.203	0.212	0.208	0.201	0.197	0.203	—	1.84	1.73	1.77	1.77	1.75	1.76			
		Succinate. $E_0 = 377.7$ mv								Succinate. $E_0 = 375.9$ mv							
$10^5 m_1$	2046	1986	1930	1877	1827	1779	1734	1034	975	949	923	899	876	855			
$10^5 m_2$	3354	3256	3164	3077	2995	2917	2852	1677	1582	1539	1497	1458	1421	1386			
$10^5 m_3$	0	293	569	831	1078	1312	1535	0	569	831	1078	1312	1535	1746			
E (mv)	42.2	44.6	46.8	48.7	50.5	52.1	53.5	50.5	56.2	58.3	59.9	61.3	62.5	63.6			
$10^4 K(\text{CoL})$	—	47	44	46	44	44	44	—	63	63	64	65	63	63			
		Adipate. $E_0 = 376.5$ mv															
$10^5 m_1$	3248	3153	3064	2980	2900	2824	2753										
$10^5 m_2$	5551	5389	5237	5093	4956	4827	4707										
$10^5 m_3$	0	293	569	831	1078	1312	1535										
E (mv)	47.3	48.5	49.6	50.6	51.5	52.4	53.3										
$10^4 K(\text{CoL})$	—	72	72	71	72	72	70										
		Tartrate. $E_0 = 377.9$ mv, $K(\text{CoL}_2^{2-}) = 0.2$								Phthalate. $E_0 = 378.2$ mv							
$10^5 m_1$	637	625	618	613	607	601	595	1378	1312	1288	1264	1241	1219	1198			
$10^5 m_2$	1011	991	982	972	963	954	945	2255	2148	2107	2069	2032	1996	1961			
$10^5 m_3$	0	197	293	387	479	569	658	0	220	404	582	752	917	1076			
E (mv)	116.6	124.4	128.0	131.4	134.4	137.1	139.4	56.3	60.6	64.5	68.1	71.4	74.4	76.8			
$10^4 K(\text{CoL})$	—	8.4	8.2	8.7	8.4	8.2	8.1	—	13.7	14.6	14.3	14.2	14.3	14.7			

Considering first the oxalate data, they are all in fair agreement but the e.m.f. result seems low, while that by solvent extraction is high. In the former, if CoL_2^{2-} was allowed for, the answer would be slightly higher. The solvent-extraction study is uncorrected for HL^- ions, CoAc^+ ion-pairs formed by the acetate buffer used,³ and for the presence of cobalt oxinate in the aqueous phase.¹⁰ Correction for the first of these raises $K(\text{CoL})$ by only 1%, and the second by³ about 3%, but at present the last correction is unknown. Three further uncertainties are that $K(\text{CoL}_2^{2-})$ is not at present known to better than $0.006 \pm 40\%$, while $\text{Co}(\text{HL})^+$ and NaL^+ ion-pairs may form. The formation of $\text{Co}(\text{HL})^+$ would only be significant in the glass electrode and e.m.f. studies. Schubert⁷ obtained estimates of $K\{\text{Co}(\text{HL})^+\}$ and of $K\{\text{Co}(\text{HL})_2^+\}$ by ion-exchange, namely 0.022 and 0.06 at $I = 0.16$ (0.16M-perchloric acid, 0.001–0.006 HL). However, with 1M-perchloric acid and up to 0.8M-oxalic acid no evidence of ion-pairing was found, and since some HL^- was present his values may be too small. The only related survey seems to be that of McAuley and Nancollas⁶ who deduced that $K\{\text{Ni}(\text{HL})\} = 0.05$ and $K\{\text{Mn}(\text{HL})\} = 0.07$ for the succinate system, but concluded that $\text{Co}(\text{HL})$ does not appear to be formed. If $\text{Co}(\text{HOx})^+$ is formed, it could account for $K\{\text{CoOx}_2^{2-}\}$ from the glass-electrode study being lower than

¹⁰ J. E. Prue, personal communication.

TABLE 2

First thermodynamic dissociation constants of cobalt(II) ion-pairs determined by various methods at 25°

Method	Oxalate	Malonate	Succinate	Glutarate
pH (Glass electrode)	0.000020 ₅ ± 2% (a, b)	0.000177 ± 2% (a, b)	0.0045 ± 2% (a)	0.0063 ₅ ± 1% (a)
pH (Glass electrode)	—	0.000190 ± 1% (a, c)	0.0041 ± 3% (a)	0.0060 ± 3% (a)
Ion-exchange resins	0.000018 ± 15% (d, e, f)	0.00017 ± 10% (d, e)	0.0039 ± 15% (d)	0.0045 ± 20% (d)
E.m.f. (H ₂ , AgCl cell)	0.0000162 (g)	0.000175 (h)	0.0060 (i)	—
Solvent extraction...	0.000023 (j)	0.00025 (j)	0.0016 (j)	—
pH (Colorimetry) ...	—	0.00019 (k)	0.0037 (k)	—
Conductance	0.000020 (l)	—	—	—
	Adipate	Tartrate	Phthalate	
pH (Glass electrode)	0.0071 ± 2% (a)	0.00083 ₅ ± 2% (a)	0.00143 ± 2% (a)	
pH (Glass electrode)	0.0068 ± 2% (a)	0.00083 ± 5% (a)	0.00134 ± 1% (a)	
Ion-exchange resins	0.006 ± 15% (d)	0.00095 ± 5% (d, e)	0.0017 ₅ ± 15% (d, e)	
E.m.f. (H ₂ , AgCl cell)	—	—	—	
Solvent extraction...	0.0040 (j)	0.00083 (j)	—	
pH (Colorimetry) ...	0.016 (k)	—	—	
Conductance	—	—	—	

(a) Present work. (b) Allowing for $K(\text{CoL}_2^{2-})$: (CoL₂²⁻) oxalate = 0.0035, malonate = 0.04, tartrate = 0.2. (c) Solns. about 0.1 as dilute, $m_2 \sim 2m_1$, CoL₂²⁻ negligible. (d) Ref. 1. (e) Allowing for $K(\text{CoL}_2^{2-})$: oxalate = 0.007 ± 10%, malonate = 0.045 ± 10%, tartrate = 0.065 ± 20%, phthalate = 0.14 ± 30%. (f) Ref. 7; corrected to $I = 0$; also gives $K(\text{CoL}_2^{2-}) = 0.005$. (g) Ref. 4; (h) Ref. 5. (i) Ref. 6. (j) Ref. 3. (k) Ref. 2. (l) R. W. Money and C. W. Davies, *Trans. Faraday Soc.*, 1932, 28, 609.

that obtained from ion-exchange. Since $K\{\text{CoOx}_2^{2-}\}$ was adjusted until $K\{\text{CoOx}\}$ became constant, the latter is probably corrected for $\text{Co}(\text{HOx})^+$ formation. On the other hand if NaOx^- ion-pairs are formed, all the answers are a little high. There is some evidence that NaL^- occurs,¹¹ e.g., for malonate, succinate, and phthalate, $K(\text{NaL})$ appearing to be around 0.2—0.4, but these require confirmation before applying them. For instance, it would be instructive to use $m_2 =$ potassium hydroxide since, by analogy with the acetates,⁸ potassium appears to have less tendency than sodium to associate with organic ligands.

Many of the above observations apply to all the systems considered here, so the remaining comments are more concerned with divergent answers. Thus, among the answers for cobalt malonate that from solvent extraction appears to be too high, the rest being in very good agreement. In contrast, the corresponding answer for the succinate seems very low while the e.m.f. result seems high. The ion-exchange method appears to give low answers for glutarate and adipate. This may be a consequence of the empirical function upon which the answers are based,¹ i.e., in its present form it begins to break down if $K > 0.004$. Finally, $K(\text{CoL})$ for adipate from solvent extraction is low, while colorimetry² has produced a distinctly high value. The authors² have indicated that when $K(\text{ML})$ is high their method requires comparable estimates of $K(\text{HL})$ and $K(\text{HL}_2)$, otherwise $[\text{ML}]$ is too small, whence K is too high.

EXPERIMENTAL

Experimental.—pH's were measured with a Radiometer pH-meter (type PHM 4c) and a polythene cell⁸ placed in an oil thermostat both at 25° ± 0.1°. AnalaR chemicals were used when available. The molarity of the stock solution of cobalt(II) chloride was found by means of H⁺-ion resins and sodium hydroxide titrations.

THE EDWARD DAVIES CHEMICAL LABORATORY,
UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH.

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¹¹ D. W. Archer, D. A. East, and C. B. Monk, *J.*, 1965, 720.