620. *Dissociation Constants of Some Barium, Europium, and Hexa-amminecobalt Ion-pairs by Use of Sparingly Soluble Iodates containing Radiotracers.*

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The solubilities of barium iodate containing iodine-131, europium iodate containing europium-(152 + 154), and hexa-amminecobalt iodate containing cobalt-60 in salt solutions of ion-pairing ligands have been measured by relating the count-rates to the solubilities in water at 25° as found by volumetric estimation of the iodate concentrations. The results, combined with Davies's general activity-coefficient expression, have been used to calculate the corresponding dissociation constants.

It is also demonstrated that such calculations may be made with only rough estimates of the solubilities in water combined with the relative count-rates of the aqueous salt solutions.

One of the best-established ways of obtaining quantitative information about ion-pair formation is to follow the solubilities of sparingly soluble salts in salt solutions. Most of the information thus obtained is reviewed in monographs [1-3] while the essential features of the method of calculation adopted here are those devised by Davies [1,4] who has shown that it is essential to make very accurate determinations of the solubilities, particularly when the extent of ion-pairing with the ligand of the solvent salt is small. This has meant choosing sparingly soluble salts, which are suitable for exact methods of analyses (in addition to the fact that their dissociation constants must be found by other methods or estimated by analogy with similar soluble types); and when the solubilities are very low this involves handling very large volumes. Radiotracers offer a way of avoiding this problem particularly if active gamma-emitters can be incorporated. Further, one is not then restricted by considerations of accurate analytical methods since, as shown below, if the approximate solubility in water is known, relative count-rates may be used to estimate dissociation constants.

The use of radioisotopes for the present purpose has previously been examined by others. These include Martin and his associates [5] who have thereby measured the solubilities of lanthanide oxalates M_2Ox_3 in sodium oxalate and of silver iodate in salt solutions. From the first of these two studies they have estimated the dissociation constants K_1, K_2 of some MOx^+ and MOx_2^- ion-pairs while from the latter those of $AgIO_3$ and $Ag(IO_3)_2^-$ were derived. Feibush, Rowley, and Gordon [6] have also applied Martin's method to yttrium oxalate; they concluded that MOx_3^{3-} is also formed and have derived K_1, K_2, and K_3; Matorma and Moskvin [7] have likewise studied plutonium(III) oxalate. The disadvantage of using such salts as oxalates is that, since these are weak electrolytes, the first calculated concentrations of M are apparent so that several series of calculations are needed to derive reliable data by using successive values of K_1 and K_2 to obtain K_s (defined below).

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[1] Davies, " Ion Association," Butterworths Scientific Publns., London, 1962.

[2] Monk, " Electrolytic Dissociation," Academic Press, New York, 1961.

[3] Robinson and Stokes, " Electrolytic Solutions," Butterworths Scientific Publns., London, 1959.

[4] Davies, *J.*, 1930, 2421.

[5] Crouthamel and Martin, *J. Amer. Chem. Soc.*, 1950, **72**, 1382; Jonte and Martin, *ibid.*, 1952, **74**, 2052; Renier and Martin, *ibid.*, 1956, **78**, 1833.

[6] Feibush, Rowley, and Gordon, *Analyt. Chem.*, 1958, **30**, 1610.

[7] Matorma and Moskvin, *Soviet J. At. Energy*, 1957, **3**, 1115.

In the present work sodium salts of ion-pairing ligands were used and the appropriate expressions are:[1,4]

$$\log K_s = \log\,[\mathrm{M}][\mathrm{IO_3}]^y - y(y+1)\mathrm{f}(I) \qquad (1)$$

$$2\mathrm{f}(I) = \sqrt{1}/(1+\sqrt{I}) - QI \qquad (2)$$

$$\log\,[\mathrm{NaIO_3}] = \log\,[\mathrm{Na^+}][\mathrm{IO_3^-}] - 0{\cdot}5 - 2\mathrm{f}(I) \qquad (3)$$

$$\log\,[\mathrm{HL}] = -\mathrm{pH} + \log\,[\mathrm{L}] - \log K_2 - 3\mathrm{f}(I) \qquad (4)$$

$$[\mathrm{ML}] = s - [\mathrm{M}] \qquad (5)$$

$$\log K = \log\,[\mathrm{M}][\mathrm{L}]/[\mathrm{ML}] - 2xy\mathrm{f}(I) \qquad (6)$$

where K_s is the activity solubility product, K_2 is the dissociation constant of $\mathrm{HL^-}$, the function f(I) is defined by equation (2), s is the solubility in molarities, x and y are the valencies of the ligand L and of the cation, respectively, K is the dissociation constant of the ion-pair ML, and Q is a parameter.

RESULTS

Barium Ion-pairs.—The solubility in water was taken as[8] $8{\cdot}10 \times 10^{-4}$ mole l.$^{-1}$, whence, with $Q = 0{\cdot}3$ $-\log K_s = 8{\cdot}8115$. Results for tartrate and malonate are summarised in Table 1 where R is the count-rate per min. Allowance for $\mathrm{HL^-}$ was made by using known[3] K_2 values.

TABLE 1.

Data for barium tartrate and malonate.

Tartrate (pH = 7·2)

$10^5[\mathrm{Na_2L}]$	0	1000	2000	3000	4000	5000
R	5295	8440	9845	11,020	11,880	125,900
$10^6 s$	810	1291	1506	1686	1817	1926
$10^5 K$ ...	—	235	240	225	220	225

Av. = 230 ± 3%

Malonate (pH = 7·2)

$10^5[\mathrm{Na_2L}]$	0	250	1000	4000	5000
$10R$	1004	1136	1359	1783	1841
$10^6 s$	810	916	1096	1438	1485
$10^3 K$ ...	—	12	10	8	9

Av. = 10 ± 20%

Cobalthexammine Ion-pairs.—In water, s was found to be $5{\cdot}37 \times 10^{-3}$ mole l.$^{-1}$ as compared with $5{\cdot}27 \times 10^{-3}$ obtained by Hansen and Williams[9] by ammonia determination. Some measurements were made with sodium perchlorate solutions to find the most suitable value of Q for equation (2). The figures, as Table 2 shows, indicate that $Q = 0{\cdot}02$, and that $-\log K_s = 8{\cdot}559$. [Allowance was made for $\mathrm{NaIO_3}$ ion-pairs by use of equation (3).]

TABLE 2.

Solubility of cobalthexammine iodate in sodium perchlorate.

$10^4[\mathrm{NaL}]$	0	244	488	610
$10^5 s$	537	634	710	743
$-\log K_s$	8·558	8·559	8·556	8·565

Our results for associating ligands are summarised in Table 3. Allowance was made for $\mathrm{NaSO_4^-}$, by taking $K(\mathrm{NaSO_4^-})$ as[1] 0·2 and for $\mathrm{HMal^-}$ by taking pK_2 as[3] 5·70.

Europium Ion-pairs.—It was found that $s = 8{\cdot}18 \times 10^{-4}$ mole l.$^{-1}$ in water. This is a little lower than figures reported for lanthanum iodate[10,11] ($9{\cdot}48$—$8{\cdot}90 \times 10^{-4}$ mole l.$^{-1}$, depending on the crystal size). Table 4 refers to solubilities in potassium chloride solutions, which were designed to find Q of equation (2). They lead to $Q = 0{\cdot}2$ and $-\log K_s = 11{\cdot}285 \pm 6\%$. Allowance was made for $\mathrm{KIO_3}$ ion-pairs, by taking $K(\mathrm{KIO_3})$ as[1] 2·0.

Table 5 outlines the results obtained with three associating ligands. Allowance was made for $\mathrm{HSO_4^-}$, $\mathrm{NaSO_4^-}$, and $\mathrm{KIO_3}$ ion-pairs as mentioned above, for $\mathrm{HL^-}$ glycollate ions with[3] pK(acid) = 3·88, and for $\mathrm{KFe(CN)_6^{2-}}$ for which[1] pK = 1·3.

[8] Macdougall and Davies, *J.*, 1935, 1416.
[9] Hansen and Williams, *J. Amer. Chem. Soc.*, 1930, **52**, 2759.
[10] La Mer and Goldman, *J. Amer. Chem. Soc.*, 1929, **51**, 2632.
[11] Monk, *Trans. Faraday Soc.*, 1951, **47**, 1233.

TABLE 3.

Data for cobalthexammine sulphate, tartrate, malonate, lactate, and thiocyanate.

Sulphate

$10^5[Na_2L]$	0	800	1001	1201	1601	2001
$10R$	4272	5700	5966	6281	6861	7342
10^5s	537	716	750	791	862	923
10^6K ...	—	230	265	255	250	240

Av. = 250 ± 4%

Tartrate (pH = 6·8)

$10^5[Na_2L]$	0	800	1000	1204	1606
$10R$ ...	7438	9038	9366	9737	10,340
10^5s ...	537	672	699	731	791
10^5K ...	—	68	74	70	60

Av. = 68 ± 6%

Malonate (pH = 6·5)

$10^5[Na_2L]$	0	801	1001	1201	1602	2002
$10R$	4217	5330	5620	5901	6279	6616
10^5s	537	679	716	752	800	843
10^5K	—	50	45	43	48	48

Av. = 47 ± 3%

Lactate (pH = 6·0)

$10^5[NaL]$	0	1004	1607	2009
$10R$	4279	4638	4826	4954
10^5s	537	583	606	622
10^2K	—	20	24	20

Av. = 21 ± 5%

Thiocyanate (pH = 4·0)

$10^5[NaL]$	0	4090	5110	8180
$10R$	3672	4754	4980	5527
10^5s	537	696	729	809
10^2K	—	12	13	14

Av. = 13 ± 8%

TABLE 4.

Solubility of europium iodate in potassium chloride.

$10^5[KCl]$	0	2046	3580	5115
10^6s	817	1076	1180	1252
$-\log K_s$	11·305	11·265	11·270	11·295

TABLE 5.

Data for europium sulphate, ferricyanide, and glycollate.

Sulphate (pH = 4·10)

$10^6[Na_2L]$	0	3029	4722	6869	9462	12,040
$100R$ ...	1252	1932	2183	2481	2793	2877
10^6s	818	1262	1426	1621	1760	1880
10^6K ...	—	215	205	175	180	175

Av. = 190 ± 10%

Ferricyanide (pH = 4·1)

$10^6[KL]$	0	1193	2999	5404	9907
$100R$ ...	1421	1847	2170	2490	2763
10^6s ...	818	1061	1246	1429	1585
10^6K ...	—	100	125	105	110

Av. = 110 ± 10%

Glycollate (pH = 4·03,* 4·25)

$10^6[NaL]$	0	1076*	1669	2450	3019
$10R$	4609	5433	5931	6465	6803
10^6s	818	964	1053	1147	1207
10^5K ...	—	35	33	37	32

Av. = 32 ± 7%

DISCUSSION

There are several previous figures to compare with the present answers. Thus for barium tartrate, $10^5K = 290$, 110, and 210 follow from conductance,[12] e.m.f.,[13] and ion-exchange [14] studies (the second and third have been converted to the basis of $I = 0$). The first and last of these are in fair accord with the present result of 230. This comment also applies to barium malonate, for which $10^3K = 14$ and 7·5 have been obtained by colorimetric pH[15] and conductances [16] (present result = 10).

For the cobalthexammine systems, $10^6K =$ (*a*) 277, (*b*) 300, (*c*) 480, and (*d*) 1120 have been obtained for the sulphate by others from (*a*) conductances,[17] (*b*) solubilities,[4] and

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[12] Topp and Davies, *J.*, 1940, 87.

[13] Joseph, *J. Biol. Chem.*, 1946, **164**, 529.

[14] Schubert, *J. Amer. Chem. Soc.*, 1954, **76**, 3442.

[15] Jones and Stock, *J.*, 1962, 306.

[16] Peacock and James, *J.*, 1951, 2233.

[17] Jenkins and Monk, *J.*, 1951, 68.

(*c, d*) spectrophotometry,[18,19] as compared with the present answer of 250. This confirms what had been found in certain other cases,[2] namely, that the spectrophotometric method can often lead to answers which are distinctly higher than those obtained in other ways. The only other comparative figure for this cation is $10^5K = 29$ for the malonate (present value = 47) obtained from potentiometric–pH data; [16] such figures are very dependent on the taken pK_2 of the acid and this was not given, so no comment can be made as to the difference between these two figures.

Regarding the europium series, our answer of $10^5K = 19$ for the sulphate is a little lower than that of (*a*) 22 which is given for the closely related lanthanides samarium and gadolinium from conductances; [20] this applies to (*b*) 24·5 for lanthanum,[2] (*c*) 24 for lanthanum from solubilities,[4] and (*d*) 27·5 for europium by solvent extraction.[21] For the ferricyanide, $10^6K = 180$ has been obtained from conductances,[22] as compared with the present value of 110. Clearly more work is needed to explain this difference. Lastly, $10^5K = 25$ has been obtained by solvent extraction for the glycollate [21] and 30 on correction to $I = 0$ of the data of Sonesson [23] based on ion-exchange studies at $I = 0{\cdot}21$ and 20°; these two answers agree well with the present estimate of 32.

It was mentioned earlier that, even if the reference solubility in water is not known accurately, the relative count-rates can still be used to estimate K values. In order to see how dependent the answers are on the reference values two examples are given.

Taking barium malonate (high K) and assuming that $s(H_2O)$ is 5% lower than the found value [*i.e.*, $s(H_2O)$ is taken as $7{\cdot}7 \times 10^{-4}$ mole l.$^{-1}$], taking the most dilute solution of Na_2L (Table 1), $s = 8{\cdot}71 \times 10^{-4}$ mole l.$^{-1}$, and proceeding as before give $K = 0{\cdot}013$, which is about 10% higher than the original estimate. Similarly with europium ferricyanide (low K), assuming that $s(H_2O)$ is 5% higher than was obtained (*i.e.*, is $8{\cdot}6 \times 10^{-4}$ mole l.$^{-1}$) leads to (Table 4) $-\log K_s = 11{\cdot}197$, and taking the most dilute solution of ferricyanide (Table 5) gives $s = 11{\cdot}15 \times 10^{-4}$ mole l.$^{-1}$ and $10^6K = 100$. This is the same value as listed in Table 5 and the general conclusion is that $s(H_2O)$ need not be known to better than 95% of its true value for reliable K values to be obtained from relative count-rates.

EXPERIMENTAL

Barium iodate crystals were made by the method of Macdougall and Davies.[8] The potassium iodate contained iodine-131 (Radiochemical Centre, Amersham) that had been converted into iodate by the method of Musakin and Pushkov [24] and added to a solution of the inactive form.

For cobalthexammine iodate crystals, cobalthexammine iodate was similarly made [8] from cobaltous chloride [25] containing cobalt-60. A flocculent precipitate was formed. This was filtered off and washed, and a saturated solution of it was made at 70—80°. As this cooled overnight good crystals were formed. The mother-liquor was resaturated at 70—80° and the process continued. The crystals appeared to harden somewhat when kept for a few days before use.

Europium iodate crystals were made from the oxide (Johnson, Matthey and Co.) dissolved in a slight excess of warm perchloric acid, europium-(152 + 154) being then added as chloride followed by hot saturated potassium iodate. Part of the resulting flocculent precipitate was dissolved in water in a large dish and was evaporated on a water-bath till crystals were formed. Further portions of hot saturated solution were added and in this way good crystals were obtained.

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[18] Posey and Taube, *J. Amer. Chem. Soc.*, 1956, **78**, 15.

[19] Bale, Davies, and Monk, *Trans. Faraday Soc.*, 1956, **52**, 816; Davies and Monk, *J. Amer. Chem. Soc.*, 1958, **80**, 5032.

[20] Spedding and Jaffe, *J. Amer. Chem. Soc.*, 1954, **76**, 882.

[21] Manning and Monk, *Trans. Faraday Soc.*, 1962, **58**, 938.

[22] James and Davies, *Proc. Roy. Soc.*, 1948, *A*, **195**, 116.

[23] Sonesson, *Acta Chem. Scand.*, 1961, **15**, 1.

[24] Musakin and Pushkov, *Russ. J. Inorg. Chem.*, 1959, **4**, 217.

[25] Fernelius, " Inorganic Syntheses," Vol. II, McGraw-Hill, London, 1946.

For the solubility studies a set of glass tubes of about 50 ml. capacity, and having narrow necks fitted with rubber bungs, were used. A few grams of crystals were put into each tube, washed a few times with saturating solution, then rocked overnight in a shaker [26] built into a water-bath kept at 25° ± 0·1°. Samples were drawn off with a warm pipette fitted with 1″ length of plastic tube containing a small plug of cotton wool. For the radioactivity assays, 5 ml. samples were used, after addition of a little sodium ethylenediaminetetra-acetate. The counting equipment was an Ekco scintillation counter fitted with a well-type crystal. Sufficient counts were taken for a statistical accuracy of ±0·2%. The reference solubilities in water were found by thiosulphate titration.

For the solvent salt solutions, laboratory-grade malonic acid was recrystallised from benzene–ether–light petroleum,[27] and a solution of it was neutralised with carbonate-free standard sodium hydroxide. "AnalaR" tartaric and lactic acid were treated similarly, and so was glycollic acid made by alkaline hydrolysis of "AnalaR" chloroacetic acid.[28] For the other ligands, "AnalaR" sodium or potassium salts were used.

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[26] Manning and Monk, *Trans. Faraday Soc.*, 1961, **57**, 1996.
[27] Nair and Nancollas, *J.*, 1957, 318.
[28] Evans and Monk, *J.*, 1954, 550.