On the Formation of Complex Ions Applied in Analytical Chemistry. X: Studies on Complexbilities of Cobalt Compounds by the Use of Radioisotope Element

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Studies on Complexbilities of Cobalt Compounds by the Use of Radioisotope Element*

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Synopsis

Using the radioisotope element of Co^{60} and the cation exchange resin Amberlite 1R-120, the complexbilities of cobalt tartrate, citrate and malonate were measured, and the following results were obtained : tartrate, $K=2.5 \times 10^{-9}$; citrate, $K=1.4 \times 10^{-8}$; malonate, $K=3.5 \times 10^{-8}$.

I. Introduction

Complexbilities of various compounds between metallic ions and organic acids or other complexes forming reagents applicable to chemical analysis are desirable to be measured systematically. So, in the previous reports[1], the complexbilities of tartrates, citrates, malonates and cyanides of copper, zinc, lead and cadmium were measured by the usual potentiometric compensation method, using the ion concentration cell, hydrogen electrode and quinhydrone electrode, and the complexbilities of ferric tartrate, citrate and malonate were measured by the use of the radioisotope element of Fe^{59} and the cation exchange resin. In the present experiments, using the radioisotope of Co^{60} and the ion exchange resin of Amberlite 1R-120, studies on the complexbilities of cobalt tartrate, citrate and malonate were made with the same method as in the eighth report,[1] in which the studies on the complexbilities of ferric compounds by the use of Fe^{59} with the ion exchange method reported by J. Schubert[2] were stated.

II. Fundamental experiments

1. Reagents and experimental method

  (a) Reagents

The radioisotope element of Co^{60} used was the cobaltous chloride solution imported from U. S. A. by the allowance of United States Atomic Energy Commission and was prepared by diluting to the moderate radiation activity. The cation exchange resin used was air dried Amberlite 1R-120 and in all cases, 0.5g of this

(1) S. Suzuki, Sci. Rep. RITU. A 3 (1951), 292 ; 4 (1952), 176 ; 464 ; 5 (1953), 16 ; 47 ; 147 ; 153 ; 227 ; 311.

(2) J. Schubert, J. Phys. Colloid Chem., 52 (1948), 340.

resin was used. All the other reagents used were purified by recrystallizing and other method.

 (b) Experimental method

 The experimental procedure was as follows: Take the known volumes of Co^{60} and tartaric acid solution (or citric acid and malonic acid solution) into a dried 100 ml Erlenmeyer flask, add 20 ml of 0.5 M sodium chloride solution in order to keep the ionic strength of this solution constant, and then dilute the solution to 50 ml of total volume. Add 0.5 g of air dried cation exchanger Amberlite 1R-120. After the flask was fixed in a shaker and shaken for the desired time in a thermostat, the temperature of which was kept at 25°C, pipette out 2 ml of the solution into the cell for measuring. Evaporate and dry up the solution and then measure the time required with a stop watch until the positions of compass-needle move from 20 up to 30 on the scale, using the Lauritzen type electroscope made in Scientific Research Institute. The concentrations of hydrogen ions were measured in the same thermostat as mentioned above by using the quinhydrone electrode with the saturated caromel electrode as the reference cell. In this experiments, the standard solution of the hydrogen ion concentration was prepared by mixing the equal volumes of 1/5 M acetic acid and 1/5 M sodium acetate solution.

2. Shaken time

 In order to determine the time required for attainment of the equilibrium state in the case of the above mentioned experimental method, the experiments were made by varying the shaken time under the condition in which the definite volume of Co^{60} solution, 0.5 g of the ion exchanger, final concentrations of 0.06563 M of tartaric acid and 0.5 M of sodium chloride were contained in 50 ml of the total volume. As shown in Table 1, it was required 60~90 minutes for attainment of the equilibrium state. Accordingly, all the measurements were made, after the solution was shaken for two hours.

Table 1

Shaken time (min)	Time measured (sec/10 div)
10	83
20	100
30	110
45	118
60	127
90	130
120	130
150	129
180	130
240	130

3. Relation between λ_0 and pH

 It was reported[4] that one molecule of cobalt ion would combine with one molecule of tartaric acid and citric acid, and the same combination as above was also assumed in the case of malonic acid. Hence, these complexbilities, K, was calculated by the following equation[5]:

$$K = \frac{\lambda_0 \left[M^{+a} - \dfrac{MR_a}{\lambda_0} \right] [H^+]^2}{[MR_a][A]} , \tag{1}$$

where MR_a = percentage of cobalt ion adsorbed by the ion exchanger Amberlite 1R-120 at equilibrium,

 (4) S. Hakomori, J. Chem. Soc. of Japan, **44** (1922), 738, **47** (1925), 92.

 (5) S. Suzuki, Sci. Rep. RITU. A **5** (1953), 227.

M^{+a} = percentage of cobalt ion remaining in the solution at equilibrium, actually $M^{+a} = 100 - MR_a$,

A = concentration of complex forming organic acid,

$\lambda_0 = MR_a/M^{+a}$.

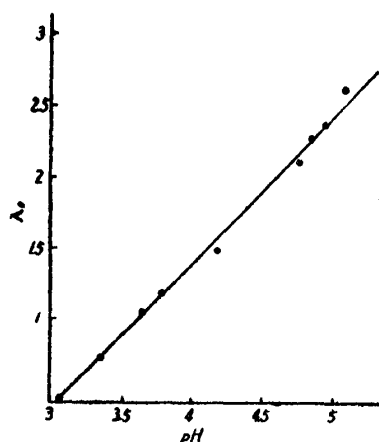λ_0 would be assumed to be constant at the same value of pH, when a complex forming organic acid was absent. Relations between λ_0 and pH were studied by varying pH of the sample solution without addition of such an organic acid as tartaric acid. As shown in Fig. 1, the relations between λ_0 and pH were linear in the range of pH from 3.3 up to 5.0. From these results complexbilities of cobalt tartrate, citrate and malonate were measured.

Fig. 1

III. Tartrate complex

In the reaction between cobalt ion and tartaric acid, the following equilibrium formula was assumed:

$$Co^{++} + C_4H_6O_6 \rightleftarrows C_4H_4O_6\cdot Co + 2H^+, \qquad (2)$$
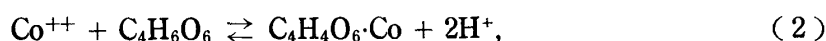
and the dissociation constant of this complex was obtained by

$$K = \frac{[C_4H_4O_6\cdot Co][H^+]^2}{[Co^{++}][C_4H_6O_6]} \qquad (3)$$

$$= \frac{\lambda_0\left[M^{+a} - \dfrac{MR_a}{\lambda_0}\right][H^+]^2}{[MR_a][C_4H_6O_6]} \qquad (4)$$

The results of the measurements and the calculations are shown in Table 2. From the above results, the value of the complexbility of cobalt tartrate was given as follows:
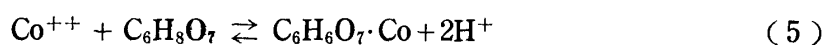
$$K = 2.5 \times 10^{-9} .$$

Table 2

Concentration of tartaric acid (M)	Quinhydron electrode				Time measured sec/10 div	Per cent of Co^{2+} remained in solution	Per cent of Co^{2+} adsorbed in resin	Dissociation constant K 10^{-9}
	e. m. f. (V)	$-Eh$ (V)	pH	λ_0				
0.06563	0.1945	0.2589	4.37_9	1.78	74	40.53	59.47	5.7
,,	0.1814	0.2720	4.60_1	2.00	84	35.70	64.30	1.1
,,	0.1499	0.3035	5.13_3	2.53	94	31.92	68.08	0.2
,,	0.1559	0.2975	5.03_2	2.46	91	32.97	67.03	0.3
,,	0.1872	0.2662	4.50_2	1.90	80	37.54	62.46	2.1
,,	0.1987	0.2547	4.30_8	1.70	76	39.52	60.48	4.1
0.01807	0.1524	0.3010	5.09_1	2.50	65	46.19	53.81	4.2
,,	0.1423	0.3111	5.26_3	2.68	60	50.02	49.98	2.8
,,	0.1538	0.2996	5.06_7	2.47	70	42.87	57.13	3.5
,,	0.1888	0.2646	4.47_5	1.87	79	37.98	62.02	2.4
,,	0.1827	0.2707	4.57_8	1.98	87	34.47	65.53	1.6

Time measured, when resin is absent = 30 sec/10 div. Mean value, $K = 2.5 \times 10^{-9}$

IV. Citrate complex

In the reaction between cobalt ion and citric acid, the following equilibrium formula (5) was assumed:

$$Co^{++} + C_6H_8O_7 \rightleftarrows C_6H_6O_7 \cdot Co + 2H^+ \tag{5}$$

The dissociation constant was obtained by

$$K = \frac{[C_6H_6O_7 \cdot Co][H^+]^2}{[Co^{++}][C_6H_8O_7]} , \tag{6}$$

$$= \frac{\lambda_0 \left[M^{+a} - \dfrac{MR_a}{\lambda_0} \right][H^+]^2}{[MR_a][C_6H_8O_7]} \tag{7}$$

The results of the measurements and the calculations are shown in Table 3, and the value of the complexbility of cabalt citrate was given as follows:
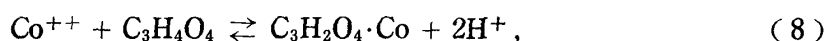
$$K = 1.4 \times 10^{-8} .$$

Table 3

Concentration of citric acid (M)	Quinhydrone electrode				Time measured sec/10 div	Per cent of Co^{2+} remained in solution	Per cent of Co^{2+} adsorbed in resin	Dissociation constant K 10^{-8}
	e. m. f. (V)	$-Eh$ (V)	pH	λ_0				
0.09845	0.1883	0.2651	4.48_4	1.88	57	50.87	49.13	1.0
,,	0.1842	0.2692	4.55_4	2.16	53	54.73	45.27	1.2
,,	0.1944	0.2590	4.38_1	1.78	65	44.61	55.39	0.8
,,	0.2009	0.2525	4.27_1	1.67	71	40.84	59.16	0.5
,,	0.1590	0.2944	4.98_0	1.58	69	42.02	57.98	0.6
,,	0.1493	0.3041	5.14_3	1.25	55	52.73	47.27	0.7
0.04938	0.1774	0.2756	4.66_2	2.06	48	60.41	39.59	1.1
,,	0.1981	0.2553	4.31_9	1.72	50	58.00	42.00	6.4
,,	0.2115	0.2419	4.09_2	1.48	69	42.02	57.98	1.2
,,	0.1920	0.2614	4.42_1	1.82	72	40.28	59.72	0.7
,,	0.1837	0.2697	4.56_2	1.96	61	47.53	52.47	1.2

Time measured, when resin is absent = 29 sec/10 div.   Mean value, $K = 1.4 \times 10^{-8}$

V. Malonate complex

Though there is no report on the malonate complex, the same combination as in the cases of tartrate and citrate complexes may be assumed and one molecule of cobalt ion will combine with one molecule of malonic acid. Therefore, the following equilibrium formula was assumed:

$$Co^{++} + C_3H_4O_4 \rightleftarrows C_3H_2O_4 \cdot Co + 2H^+ , \tag{8}$$

The dissociation constant was obtained by

$$K = \frac{[C_3H_2O_4 \cdot Co][H^+]^2}{[Co^{++}][C_3H_4O_4]} \tag{9}$$

$$= \frac{\lambda_0 \left[M^{+a} - \dfrac{MR_a}{\lambda_0} \right][H^+]^2}{[MR_a][C_3H_4O_4]} \tag{10}$$

The results of the measurements and the calculations are shown in Table 4, and the value of the complexbility of cobalt malonate was given as follows:

$$K = 3.5 \times 10^{-8} .$$

Table 4

Concentration of malonic acid (M)	Quinhydrone electrode				Time measured sec/10 div	Per cent of Co^{2+} remained in solution	Per cent of Co^{2+} adsorbed in resin	Dissociation constant K 10^{-8}
	e. m. f. (V)	$-Eh$ (V)	pH	λ_0				
0.06168	0.1893	0.2641	4.46_8	1.87	67	40.29	59.71	0.5
,,	0.1778	0.2756	4.66_2	2.07	60	45.00	55.00	0.5
,,	0.1904	0.2630	4.44_9	1.85	73	41.10	58.90	0.6
,,	0.2439	0.2095	3.54_3	0.92	56	53.59	46.41	8.2
,,	0.2619	0.1915	3.23_9	0.61	48	62.50	37.50	10.0
0.1162	0.1921	0.2631	4.42_0	1.82	77	38.97	61.03	0.2
,,	0.2075	0.2459	4.15_9	1.56	72	41.67	58.33	0.5
,,	0.2156	0.2378	4.02_2	1.40	67	44.79	55.21	1.1
,,	0.2250	0.2284	3.87_3	1.27	63	47.61	52.39	2.4
,,	0.2391	0.2143	3.62_5	1.01	56	53.59	46.41	8.0
,,	0.2501	0.2033	3.43_9	0.82	53	56.62	43.38	6.7
,,	0.2605	0.1929	3.26_3	0.64	49	61.24	38.76	2.8

Time measured, when resin is absent $= 27$ sec/10 div.　　Mean value, $K = 3.5 \times 10^{-8}$

Summary

1) Using the radioisotope element of Co^{60} and the ion exchange resin of Amberlite 1R-120, the complexbilities of cobalt tartrate, citrate and malonate were measured.

2) The value of the complexbilities of cobalt tartrate, citrate and malonate at 25°C were 2.5×10^{-9}, 1.4×10^{-8} and 3.5×10^{-8}, respectively.

3) From the dissociation degrees of these cobalt complexes, it was found that the strength of the complex formation increased in the order of tartrate, malonate and citrate, but, there were not so large differences among them, and especially, the strength of the complex formation of malonate was nearly the same as that of citrate.

Acknowledgement