On the Formation of Complex Ions Applied in Analytical Chemistry. XI

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

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Synopsis

Using the radioisotope element, Sb^{125}, and the ion exchange resin of Amberlite 1R-120, the complexbilities of antimonous tartrate, citrate and malonate were measured by the same method as J. Schubert studied, and the following results were obtained at 25°C : tartrate, $K=2.3\times10^{-3}$; citrate, $K=0.5$; malonate, $K=0.5$.

I. Introduction

From the standpoint of analytical chemistry, complexbilities of various compounds between metallic ions and organic acids or other reagents applied to chemical analysis are projected to be measured systematically. In the previous papers[1], the complexbilities of tartrates, citrates and cyanides of copper, zinc, lead and cadmium were reported, using the ion concentration cell, hydrogen electrode and quinhydrone electrode; and the complexbilities of tartrates, citrates and malonates of ferric iron and cobalt were reported by using the radioisotope elements and the ion exchange resin. It is well known that the complexes would be formed between antimonous ions and these organic acids. In the present experiments, using the radioisotope element, Sb^{125}, the complexbilities of antimonous tartrate, citrate and malonate were studied with the same method as in the case of iron and cobalt.

II. Fundamental experiments

1. Reagents

Tin and other impurities were contained in the radioisotope element of metallic Sb^{125} imported from U. S. A. by the allowance of United States Atomic Energy Commission, and so after the separation of Sb^{125} from the tartaric acid-hydrochloric acid solution by the ion exchange resin of Amberlite 1R-120, Sb^{125} was precipitated with hydrogen sulfide and then antimonous chloride solution having the moderate radiation activity was prepared by dissolving the precipitates with concentrated hydrochloric acid. The cation exchange resin used was air-dried Amberlite 1R-120

(1) S. Suzuki, Sci. Rep. RITU, A3 (1951), 292 ; 4 (1952), 176 ; 464 : 5 (1953), 16 ; 47 ; 147 ; 153 ; 227 ; 311 ; 318.

and in all cases, 1.0 g ˚of this resin was used. All the other reagents used was purified by recrystallization or other methods.

2. Experimental method

The experimental procedure was as follows: take a certain amount of Sb^{125} and tartaric acid solution (or citric and malonic acid) into a dried 100 ml Erlenmeyer flask, add 20 ml of 0.5 M sodium chloride solution to keep the ionic strength of this solution constant, and then dilute the solution to 50 ml of total volume. Add 1.0 g of air-dried Amberlite 1R-120, and then corked. After the flask was fixed in a shaker and shaken for the definite time in a thermostat, the temperature of which was kept at 25°C, pipette 2 ml of the solution into the cell for measurement. Evaporate and dry up the solution and then measure the time with a stop watch until the position of compass-needle moves from 20 up to 30 divisions of the scale of the electroscope of the Lauritzen type made in Scientific Research Institute in Japan. The concentrations of the hydrogen ion of the solutions were measured by the quinhydrone electrode with the saturated caromel electrode as the reference cell. In this case, the standard solution of the concentration of the hydrogen ion was prepared by mixing the equal volumes of 1/5 M acetic acid and 1/5 M sodium acetate solution.

3. Shaken time

In the above-mentioned experiments, to determine the time till the equilibrium state was attained between antimonous ions remaining in solution and that adsorbed by the resin, various shaken times were taken under the condition in which the definite amount of Sb^{125}, 1.0 g of Amberlite 1R-120, final concentrations of 0.0708 M of tartaric acid and 0.2 M of sodium chloride were contained in 50 ml of total volume. The results are tabulated in Table 1. As shown in Table 1, it was required 60~90 minutes to attain the equilibrium state. Therefore, all the measurements of the radiation and others were made after the solution was shaken for 2 hours.

Table 1

Shaken time (min)	Time measured (sec/10 div)
10	190
20	194
30	199
45	200
60	206
90	208
120	211
150	209
180	209
240	208

4. Relation between λ_0 and pH

In the reaction between antimonous ion and tartaric acid or citric acid or malonic acid, the same combination as in the case of ferric complexes reported in the eighth report[2] might be considered, that is, two molecules of antimonous ions might combine with three molecules of tartaric acid or malonic acid; one molecule of antimonous ion might combine with one molecule of citric acid. By using the equation in the eighth report[2] derived from the ion-exchange method reported by J. Schubert[3], these complexbilities, K, were calculated by the following equation:

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

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

when tartaric acid or malonic acid was used as the complex-forming reagent,

$$K = \frac{\lambda_0^2 \, [M^{+a} - \frac{MR_a}{\lambda_0}] \, [H^+]^6}{[MR_a]^2 \, [A]^3} \tag{1}$$

and when citric acid was used as the complex-forming reagent,

$$K = \frac{\lambda_0 \, [M^{+a} - \frac{MR_a}{\lambda_0}] \, [H^+]^3}{[MR_a] \, [A]} \tag{2}$$

where MR_a = percentage of antimonous ion adsorbed by the ion exchange resin of Amberlite 1R-120 at equilibrium, M^{+a} = percentage of antimonous 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 might be assumed to be constant at the same value of pH, provided that a complex-forming organic acid was absent. Relations between λ_0 and pH were studied by varying pH of the sample solution and by keeping other conditions constant. As shown in Fig. 1, the relations between λ_0 and pH were linear in the range of pH from 0.3 to 1.1. From these results, the complexbilities of antimonous tartrate, citrate and malonate were measured and calculated.
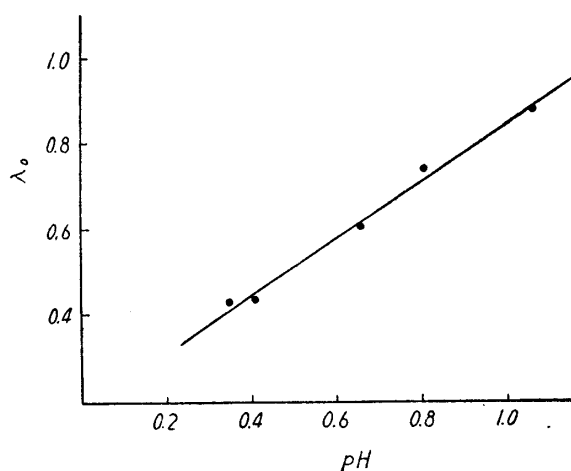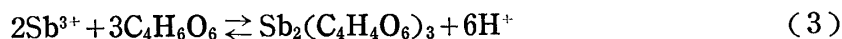

Fig. 1

III. Tartrate complex

In the reaction between antimonous ion and tartaric acid, the following equilibrium formula (3) was assumed and its complexbility was given by Eq. (4), and so from Eq. (1) the complexbility was calculated by Eq. (5).

$$2Sb^{3+} + 3C_4H_6O_6 \rightleftarrows Sb_2(C_4H_4O_6)_3 + 6H^+ \tag{3}$$

$$K = \frac{[Sb_2(C_4H_4O_6)_3] \, [H^+]^6}{[Sb^{3+}]^2 \, [C_4H_6O_6]^3} \tag{4}$$

$$= \frac{\lambda_0^2 \, [M^{+a} - \frac{MR_a}{\lambda_0}] \, [H^+]^6}{[MR_a]^2 \, [C_4H_4O_6]^3} \tag{5}$$

The results of the measurements and the calculations are shown in Table 2. From these results, the value of complexbility of antimonous tartrate was determined at 25°C as follows:

$$K = 2.3 \times 10^{-3}.$$

<div align="center">Table 2</div>

Concent-ration of tartaric acid(M)	Quinhydrone electrode				Time measured sec/10 div	Per cent of Sb^{3+} remained in solution	Per cent of Sb^{3+} adsorbed in resin	Dissoci-ation constant K 10^{-3}
	e. m. f. (V)	$-Eh$ (V)	pH	λ_0				
0.0708	0.3922	0.0612	0.89	0.89	10.80	89.81	10.19	1.0
"	0.3969	0.0565	0.96	0.83	11.67	83.12	16.88	0.8
"	0.3996	0.0538	0.91	0.80	11.90	81.51	18.49	1.1
"	0.4020	0.0514	0.89	0.77	11.27	86.07	13.93	3.5
"	0.4073	0.0461	0.78	0.71	13.00	74.62	25.38	1.7
"	0.4101	0.0433	0.73	0.68	13.13	73.88	26.12	2.7
"	0.4132	0.0402	0.68	0.65	12.79	75.83	24.17	6.5
"	0.4146	0.0399	0.67	0.64	13.47	72.01	27.99	3.7
"	0.4179	0.0355	0.60	0.60	14.03	69.14	30.86	4.7
"	0.4203	0.0331	0.56	0.56	14.91	65.04	34.96	0.8
0.0659	0.3833	0.0701	1.19	0.99	8.36	97.73	2.27	4.7
"	0.3885	0.0649	1.10	0.93	9.03	90.48	9.52	0.7
"	0.3925	0.0609	1.03	0.89	9.47	86.27	13.73	0.7
"	0.3971	0.0563	0.95	0.83	9.93	82.28	17.72	0.9
"	0.4014	0.0520	0.88	0.78	9.87	82.78	17.22	2.3
"	0.4070	0.0464	0.79	0.72	11.00	74.27	25.73	2.0
"	0.4126	0.0408	0.69	0.65	11.83	69.06	30.94	2.4
"	0.4169	0.0365	0.62	0.61	12.39	65.90	34.10	2.2

Time measured, when resin is absent,   Mean value, $K=2.3\times10^{-3}$

9.70 min/10 div at 0.0708 M of tartaric acid

8.17 min/10 div at 0.0659 M of tartaric acid

<div align="center">IV. Citrate complex</div>

As mentioned above, one molecule of antimonous ion might combine with one molecule of citric acid and, accordingly, the following equilibrium formula (6) would be assumed. The complexbility K of antimonous citrate was given by Eq. (7). Therefore, from Eq. (2), the complexbility was calculated by Eq. (8).

$$Sb^{3+}+C_6H_8O_7 \rightleftarrows C_6H_5O_7 \cdot Sb+3H^+ \qquad (6)$$
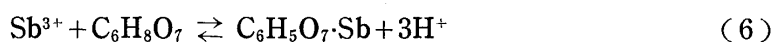
$$K = \frac{[C_6H_5O_7 \cdot Sb][H^+]^3}{[Sb^{3+}][C_6H_8O_7]} \qquad (7)$$

$$= \frac{\lambda_0[M^{+a}-\frac{MR_a}{\lambda_0}][H^+]^3}{[MR_a][C_6H_8O_7]} \qquad (8)$$

The results of the measurements and calculations are tabulated in Table 3. From these results, the value of the complexbility of antimonous citrate was given at 25°C as follows :

$$K = 0.5 .$$

<div align="center">V. Malonate complex</div>

In the case of malonate complex, the same reaction as in the case of tartrate might be assumed, that is, two molecules of antimonous ions might combine with thre molecules of malonic acid. The following equilibrium formula (9) would be considered and the complexbility K was given by Eq. (10). Hence, from Eq. (1), the complexbility was calculated by Eq. (11).
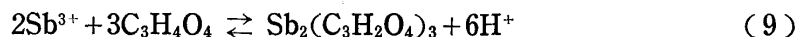
$$2Sb^{3+}+3C_3H_4O_4 \rightleftarrows Sb_2(C_3H_2O_4)_3+6H^+ \qquad (9)$$

Table 3

Concent-ration of citric acid (M)	Quinhydrone electrode				Time measured sec/10 div	Per cent of Sb^{3+} remained in solution	Per cent of Sb^{3+} adsorbed in resin	Dissoci-ation constant K
	e. m. f. (V)	−Eh (V)	pH	λ_0				
0.0712	0.4234	0.0300	0.51	0.53	15.37	87.83	12.17	1.2
,,	0.4296	0.0238	0.40	0.45	16.27	82.97	17.03	1.0
,,	0.4303	0.0231	0.39	0.45	16.87	80.02	19.98	0.8
,,	0.4315	0.0219	0.37	0.43	18.67	72.31	27.69	0.1
,,	0.4330	0.0204	0.35	0.42	18.40	73.39	26.61	0.2
,,	0.4341	0.0193	0.33	0.40	17.30	78.03	21.97	0.7
,,	0.4363	0.0171	0.29	0.38	18.16	74.30	25.70	0.3
,,	0.4376	0.0158	0.27	0.36	17.73	76.14	23.86	0.3
0.0487	0.4284	0.0250	0.42	0.47	19.97	69.45	30.55	0.1
,,	0.4296	0.0238	0.40	0.45	18.83	73.66	26.34	0.3
,,	0.4307	0.0227	0.38	0.44	19.13	72.50	27.50	0.3
,,	0.4324	0.0210	0.36	0.42	19.43	79.58	20.42	1.1
,,	0.4335	0.0199	0.34	0.41	18.00	77.06	22.94	0.4
,,	0.4353	0.0181	0.31	0.39	17.90	77.49	22.51	0.8

Time measured, when resin is absent, Mean value, $K = 0.5$
  13.50 min/10 div at 0.0712 M of citric acid
  13.87 min/10 div at 0.0487 M of citric acid

$$K = \frac{[Sb_2(C_3H_2O_4)_3][H^+]^6}{[Sb^{3+}]^2[C_3H_4O_4]^3} \tag{10}$$

$$= \frac{\lambda_0^2[M^{+a} - \frac{MR_a}{\lambda_0}][H^+]^6}{[MR_a]^2[C_3H_4O_4]^3} \tag{11}$$

The results measured and calculated are shown in Table 4. From these results, the value of the complexbility of antimonous malonate at 25°C was obtained as follows: $K = 0.5$.

Table 4

Concent-ration of malonic acid (M)	Quinhydrone electrode				Time measured sec/10 div	Per cent of Sb^{3+} remained in solution	Per cent of Sb^{3+} adsorbed in resis	Dissoci-ation constant K
	e. m. f. (V)	−Eh (V)	pH	λ_0				
0.0851	0.4260	0.0274	0.46	0.49	16.23	89.16	10.84	0.4
,,	0.4293	0.0241	0.41	0.46	16.17	89.48	10.52	0.1
,,	0.4342	0.0192	0.32	0.40	17.03	84.97	15.03	0.6
,,	0.4348	0.0186	0.31	0.39	16.63	87.01	12.99	1.0
,,	0.4358	0.0176	0.30	0.38	16.39	86.13	13.87	1.0
0.0634	0.4214	0.0320	0.54	0.55	21.97	87.71	12.27	0.3
,,	0.4247	0.0287	0.49	0.51	23.67	81.41	18.59	0.2
,,	0.4270	0.0264	0.45	0.48	23.93	80.53	19.47	0.2
,,	0.4291	0.0243	0.41	0.46	21.55	89.42	10.58	0.3
,,	0.4307	0.0227	0.38	0.44	26.02	74.06	25.94	0.1
,,	0.4330	0.0204	0.35	0.41	25.59	76.05	23.95	0.2
,,	0.4369	0.0165	0.28	0.37	23.67	81.41	18.59	1.0

Time measured, when resin is absent, Mean value, $K = 0.5$
  14.47 min/10 div at 0.0851 M of malonic acid
  19.27 min/10 div at 0.0634 M of malonic acid

VI. Consideration

All the results obtained in this series of studies were as follows: the complex-bilities of copper, zinc, lead, cadmium, ferric, cobalt and antimonous tartrates were

respectively 9.32×10^{-4}, 4.44×10^{-4}, 1.24×10^{-3}, 1.20×10^{-4}, 3.1×10^{-8}, 2.5×10^{-9} and 2.3×10^{-3}; the complexbilities of these citrates were 3.37×10^{-4}, 2.19×10^{-4}, 7.81×10^{-3}, 5.70×10^{-4}, 2.2×10^{-5}, 1.4×10^{-8} and 0.5; the complexbilities of these malonates were 5.22×10^{-4}, 1.21×10^{-4}, 4.49×10^{-5}, 7.14×10^{-5}, 2.5×10^{-10}, 3.5×10^{-8} and 0.5; the complexbilities of copper, zinc and cadmium cyanides were 2.77×10^{-28}, 1.75×10^{-17} and
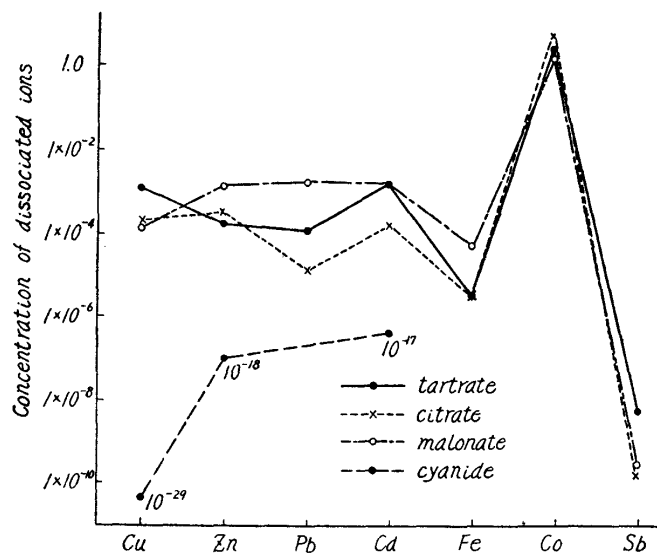

Fig. 2

9.09×10^{-17}. For the purpose of the concrete comparison of the strengths of these complex formations with one another, the concentrations of these dissociated metal ions were calculated under the conditions in which the pH was 3.00, the concentration of the complex-forming organic acid was 1M and the concentration of complex formed was 0.1M. Results are shown in Fig. 2. As shown in Fig. 2, the strength of the complex formation of citrate with metal ions was larger than that of tartrate or of malonate, especially, in lead and cadmium complexes. Further, the strength of the complex formation of tartrate was large and in malonates copper complex was slightly larger than that of the complex formation between copper ions and other complex-forming organic acid. Considering these metal ions, it was clearly seen that the strength of the complex formation of antimonous complexes was larger than that of other ions and that the strength of the formation of cobalt complexes was smaller than that of other ions.

Summary

（1） Using the radioisotope element Sb^{125} and the ion exchange resin of Amberlite 1R-120, the complexbilities of antimonous tartrate, citrate and malonate were determined by the ion-exchange method of J. Schubert.

（2） The value of the complexdilities of antimonous tartrate, citrate and malonate at 25°C were 2.3×10^{-3}, 0.5 and 0.5, respectively.

（3） From the dissociation degrees of these complexes at the same pH it was found that the strength of the complex formation of citrate was larger than that of tartrate or malonate, and that the strength of the complex formation of tartrate was nearly the same as that of malonate.