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On the Formation of Complex Ions Applied
in Analytical Chemistry. VIII
Studies on Complexibilities of Ferric Compounds
by the Use of Radioisotope Element*

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Synopsis

Applying the ion exchange method reported by J. Schubert, the complexibilities of ferric tartrate, citrate and malonate were measured by the use of the radioisotope element of Fe^{59} and the ion exchange resin of Amberlite 1R-120. The hydrogen ion concentrations of the solution were measured by the use of the quinhydrone electrode. All the measurements were made at 25°C and the following results were obtained: ferric tartrate, $K=3.1 \times 10^{-8}$; citrate, $K=2.2 \times 10^{-5}$; malonate, $K=2.5 \times 10^{-10}$.

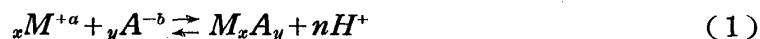
I. Introduction

Complexibilities of various compounds between various metallic ions and organic acids or other reagents applied to chemical analysis are projected to be measured, and tartrates, citrates and malonates of copper, zinc, lead and cadmium have been measured, using ion concentration cell, hydrogen electrode and quinhydrone electrode⁽¹⁾.

In the present study, complexibilities of ferric tartrate, citrate and malonate were measured by the ion exchange method reported by J. Schubert⁽²⁾, using the radioisotope of Fe^{59} and the ion exchange resin of Amberlite 1R-120. Jellinek and Gordon⁽³⁾ have studied ferric tartrate and reported that the concentration of dissociated ferric ion was of the order of 10^{-39} M/L, when the concentrations of tartaric acid, ferric tartrate complex and hydrogen ion were 1 M/L, 10^{-3} M/L and 10^{-14} M/L, respectively. However, complexibilities of ferric citrate and malonate have not yet been reported.

II. Method and reagents

When a complex ion M_xA_y is formed between a metallic ion M^{+a} and an organic acid A^{-b} , the following equilibrium formula is considered:



* The 717th report of the Research Institute for Iron, Steel and Other Metals. Read at the Annual Meeting of the Chemical Society of Japan in April, 1952.

(1) S. Suzuki, Sci. Rep. RITU, A 3 (1951), 292; 4 (1952), 176; 4 (1952), 464; 5 (1953), 16; 5 (1953), 47; 5 (1953), 148; 5 (1953), 154.

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

(3) K. Jellinek and H. Gordon, Physik. Chem., 112 (1924), 241.

and the complexibility is given by the following equation:

$$K = \frac{[M_x A_y][H^+]^n}{[M^{+a}]^x [A^{-b}]^y} \quad (2)$$

In this case, the following formula will be assumed by the application of the ion exchange method reported by J. Schubert⁽²⁾, when A^{-b} is absent:

$$\frac{MR_a}{M^{+a}} = \lambda_0, \quad (3)$$

where MR_a = percentage of metallic ion adsorbed by the ion exchange resin at equilibrium.

M^{+a} = percentage of metallic ion remaining in solution at equilibrium; actually $M^{+a} = 100 - MR_a$.

If this value of λ_0 can be assumed to be constant at the constant value of pH, Eq. (2) will be written as follows:

$$K = \frac{\lambda_0^x [M_x A_y][H^+]^n}{[MR_a]^x [A^{-b}]^y} = \frac{\lambda_0^x [M^{+a} - \frac{MR_a}{\lambda_0}][H^+]^n}{[MR_a]^x [A^{-b}]^y} \quad (4)$$

The complexibilities of ferric complexes can be calculated by this formula, because M^{+a} , MR_a and λ_0 can be measured by the use of the radioisotope element of Fe^{59} and the ion exchange resin of Amberlite 1R-120 in the case of ferric complexes, and the concentration of hydrogen ion can also be measured by means of the quinhydrone electrode. In the present studies, complexibilities of ferric tartrate, citrate and malonate were measured by the above-mentioned method.

1. Reagents and experimental procedure

(a) Reagents

In all cases, the adsorbent used was the cation exchanger Amberlite 1R-120. The resin was converted to the hydrogen form, HR, by treating with 1N solution of hydrochloric acid and then converted to the ammonium form, NH_4R , by treating the hydrogen form of this resin with the ammonium chloride solution. The resin was washed with distilled water to be free from excess salt and was air-dried. In each experiment, 0.5 g of this resin was used. All the reagents used were purified by recrystallization or by other methods. The radioisotope element of Fe^{59} used was the hydrochloric acid solution of ferric chloride which was imported by the allowance of the United States Atomic Energy Commission and was prepared by diluting to the moderate radiation activity.

(b) Experimental procedure

The experimental procedure was as follows: take a certain amount of Fe^{59} and tartaric acid solution (or citric and malonic acid) into two dried 300 ml Erlenmeyer flasks, add 10 ml of 1M ammonium hydrochloride solution in order to kept 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 NH_4R into only one of the flask and not into the other flask, and then corked. After these flasks were fixed in a shaker and shaken for the definite time at 25°C in a thermostat, pipette out

2 ml of these solution into cells for measuring. Evaporate and dry up the solution and then measure the time with a stop watch until the position of compass-needle move from 20 up to 30 on the scale, using the Lauritzen type electroscope made in Scientific Research Institute. The hydrogen ion concentrations of the solutions were measured by the use of the quinhydrone electrode.

2. Shaken time

In order to determine the time until the sample solution became the equilibrium state in the case of the above-mentioned procedure, the time measurements were made by varying the shaken time under the condition under which the definite volume of Fe^{59} solution, 0.5 g of NH_4R , final concentrations of 0.03694 M of tartaric acid and 0.2 M of ammonium chloride were contained in 50 ml of the total solution. Results obtained are tabulated in Table 1. As shown in Table 1, it was required over 1.5 hours to attain the equilibrium state. Hence, all the measurements were made, after the solution was shaken for 2.5 hours.

Table 1

Shaken time (min)	Time measured (min/10div.)
15	9.17
30	9.62
60	11.65
90	12.50
120	12.87
180	12.95
300	12.87

3. Relation between λ_0 and pH

In Eq. (3) λ_0 was assumed to be constant at the constant value of pH. Relations between this value of λ_0 and pH were studied by the following experiments: The experiments were made by varying pH of the sample solution without any addition of organic acid such as tartaric acid. As shown in Fig. 1, the relations between the value of λ_0 and pH were linear in the range of pH from 1.3 up to 2.7.

Applying the results obtained in the above fundamental experiments, the complexibilities of ferric tartrate, citrate and malonate were measured and calculated. They will individually be mentioned below.

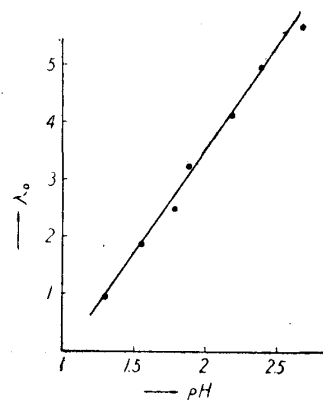
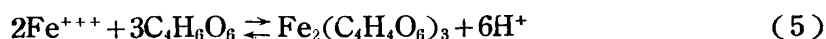


Fig. 1

III. Tartrate complex

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



and the dissociation constant was given by the following equation:

$$K = \frac{[\text{Fe}_2(\text{C}_4\text{H}_4\text{O}_6)_3][\text{H}^+]^6}{[\text{Fe}^{+++}]^2 [\text{C}_4\text{H}_6\text{O}_6]^3} \quad (6)$$

The results of the measurements and the calculations are shown in Table 2.

From the above results, the value of the complexibility of ferric tartrate was given as follows:

$$K=3.1 \times 10^{-8}$$

When the values reported by Jellinek and Gordon⁽³⁾ is introduced to Eq. (6), the value K becomes to be of the order of 10^{-9} , which is nearly in agreement with the experimentally observed value given in Table 2.

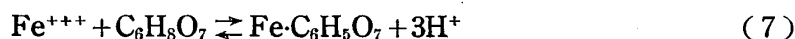
Table 2

Concentration of tartaric acid (M)	Quinhydrone electrode				Time measured when resin is present (min/10 div.)	Time measured when resin is absent (min/10 div.)	Per cent of Fe ⁵⁹ adsorbed	Per cent of Fe ⁵⁹ in solution	Dissociation constant $K \times 10^{-8}$
	e. m. f. (V)	-Eh (V)	pH	λ_0					
0.03694	0.3494	0.1040	1.76	2.65	20.42	8.02	60.42	39.58	1.2
"	0.3490	0.1044	1.83	2.85	12.23	7.78	38.46	61.54	5.3
0.01847	0.3365	0.1169	2.01	3.47	14.33	7.17	49.00	51.00	2.7
"	0.3383	0.1151	1.95	3.25	13.40	6.50	52.40	47.60	4.4
"	0.3305	0.1229	2.08	3.67	9.07	6.05	33.27	66.73	3.7
"	0.3327	0.1207	2.04	3.55	14.48	6.18	55.88	44.12	1.1

Mean value: $K=3.1 \times 10^{-8}$

IV. Citrate complex

In the reaction between ferric ion and citric acid, the following equilibrium formula was assumed:



and the dissociation constant was given by the following equation:

$$K = \frac{[\text{Fe} \cdot \text{C}_6\text{H}_5\text{O}_7][\text{H}^+]^3}{[\text{Fe}^{+++}][\text{C}_6\text{H}_5\text{O}_7]} \quad (8)$$

The results of the measurements and the calculations are shown in Table 3. From the above results, the value of the dissociation constant of ferric citrate was given as follows:

$$K=2.2 \times 10^{-5}$$

Table 3

Concentration of citric acid (M)	Quinhydrone electrode				Time measured when resin is present (min/10 div.)	Time measured when resin is absent (min/10 div.)	Per cent of Fe ⁵⁹ adsorbed	Per cent of Fe ⁵⁹ in solution	Dissociation constant K
	e. m. f. (V)	-Eh (V)	pH	λ_0					
0.14244	0.3219	0.1315	2.22	4.11	6.62	4.48	32.30	67.70	1.2×10^{-5}
"	0.3379	0.1155	1.95	3.35	8.00	4.23	47.12	52.88	2.7×10^{-5}
"	0.3654	0.0880	1.49	1.67	7.77	3.95	49.17	50.83	8.2×10^{-6}
"	0.3773	0.0761	1.29	1.04	8.87	4.37	50.74	49.26	9.1×10^{-6}
0.28488	0.3742	0.0792	1.34	1.20	8.48	4.08	51.90	48.10	3.8×10^{-5}
"	0.3557	0.0977	1.65	2.25	8.30	4.45	46.37	53.63	6.3×10^{-5}
"	0.3478	0.1056	1.79	2.72	8.53	4.58	46.31	53.69	3.2×10^{-5}
"	0.3375	0.1159	1.96	3.28	8.17	4.40	46.15	53.85	1.3×10^{-5}
"	0.3333	0.1201	2.03	3.50	7.45	4.40	40.96	59.04	1.2×10^{-5}
"	0.3268	0.1266	2.14	3.82	7.05	4.65	34.08	65.92	8.6×10^{-6}

Mean value: $K=3.2 \times 10^{-5}$

V. Malonate complex

In the case of malonate complex, the following equilibrium formula was assumed:



and the dissociation constant was given by the following equation:

$$K = \frac{[\text{Fe}_2(\text{C}_3\text{H}_2\text{O}_4)_3][\text{H}^+]^6}{[\text{Fe}^{+++}]^2[\text{C}_3\text{H}_4\text{O}_3]^3}$$

The results of the measurements and the calculations are shown in Table 4. From the above results, the value of the dissociation constant of ferric malonate was given as follows:

$$K = 2.5 \times 10^{-10}$$

Table 4

Concentration of malonic acid (M)	Quinhydrone electrode				Time measured when resin is present (min/10 div.)	Time measured when resin is absent (min/10 div.)	Per cent of Fe ⁵⁹ adsorbed	Per cent of Fe ⁵⁹ in solution	Dissociation constant K 10 ⁻¹⁰
	e. m. f. (V)	-Eh (V)	pH	λ ₀					
0.18367	0.3334	0.1200	2.03	3.51	8.48	6.82	19.58	80.42	2.6
"	0.3379	0.1155	1.95	3.22	9.18	6.65	27.59	72.41	2.8
"	0.3481	0.1053	1.78	2.67	9.48	6.73	29.00	71.00	1.7
"	0.3306	0.1228	2.08	3.67	8.18	6.82	16.64	83.36	3.1
"	0.3204	0.1330	2.25	4.20	7.48	6.92	7.47	92.53	1.5
0.12526	0.3365	0.1169	1.98	3.35	8.85	6.85	22.60	77.40	3.5
"	0.3446	0.1088	1.84	2.87	9.12	6.98	23.48	76.52	4.6
"	0.3286	0.1248	2.11	3.75	8.35	6.67	20.08	79.92	2.9
"	0.3241	0.1293	2.19	4.00	8.12	6.68	17.70	82.30	1.5
"	0.3190	0.1344	2.27	4.27	7.68	6.90	10.14	89.86	1.9
"	0.3149	0.1385	2.34	4.50	7.42	6.88	7.23	92.77	1.6

Mean value: $K = 2.5 \times 10^{-10}$

Summary

1) Using the radioisotope element of Ee⁵⁹ and the ion exchange resin of Amberlite 1R-120, the complexibilities of ferric tartrate, citrate and malonate were obtained at 25°C.

2) The values of the complexibilities of ferric tartrate, citrate and malonate were 3.1×10^{-8} , 2.2×10^{-5} and 2.5×10^{-10} , respectively.

3) Considering the dissociation degrees of these complexes, it was found that the strength of the complex formation of malonate should be larger than that of tartrate or of citrate, and that the strength of the complex formation of tartrate was nearly the same as that of citrate.

Acknowledgement

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