On the Formation of Complex Ions Applied in Analytical Chemistry. III : Studies on Complexes of Copper and Zinc Citrates

On the Formation of Complex Ions Applied in Analytical Chemistry. III
Studies on Complexes of Copper and Zinc Citrates*

Shin SUZUKI

The Research Institute for Iron, Steel and Other Metals

(Received July 15, 1952)

Synopsis

From the standpoint of analytical chemistry, complexbilities of various ions applied to chemical analysis have been measured. In the present study, the complexbilities of copper and zinc citrates were measured by usual potentiometric compensation method, using the ion concentration cell and hydrogen electrode. The following results were obtained at 25°C : copper citrate : $K=3.37\times10^{-4}$; zinc citrate : $K=2.19\times10^{-4}$.

I. Introduction

Complexbilities of various complexes applied to chemical analysis are desirable to be measured. In the previous papers,(1) the studies on the complexbilities of copper, zinc, lead and cadmium tartrates were reported. In the present case, complexbilities of copper and zinc citrates were measured by using ion concentration cell and hydrogen electrode. Copper citrate has been studied by absorption spectrum,(2) and it was reported that one molecule of copper would combine with one molecule of citric acid. Studies on zinc citrate, however, has not yet been reported.

II. Copper citrate complex

1. Reagents and apparatus

a) Reagents

Copper sulfate and Cu-Hg electode (5.0% Cu) were prepared by the method mentioned in the first report.(1) Citric acid was purified by recrystallizing it four times with water, and the concentration of this solution was standardized by the standard sodium hydroxide solution, using phenolphthalein as an indicator. Mercury and water were purified by the same method as in the previous case.(1)

b) Cells

The cell used was of the same type as in the previous experiments, being made of hard glass, and the following combination of the ion concentration cell was used :

$$\text{Cu-Hg}|\text{CuSO}_4||\text{KCl}||\text{ citric acid, }\text{CuSO}_4|\text{Cu-Hg}$$

* The 689th report of the Research Institute for Iron, Steel and Other Metals. Published in the Journal of the Chemical Society of Japan, **72** (1951), 974.

(1) S. Suzuki, Sci. Rep. RITU, A **3** (1951), 292 ; **4** (1952), 176.

(2) S. Hakomori, J. Chem. Soc. of Japan, **47** (1926), 92.

It was composed of the electrode of Cu-Hg (5% Cu), 0.05M copper sulfate solution and copper citrate solution. The copper citrate complex solution was prepared by adding a certain specified volume of 0.01M copper sulfate solution to 25 ml of 0.05M citric acid solution. The saturated solution of potassium chloride was used as the junction liquid. The combination of the hydrogen electrode was as follows:

$$Hg|HgCl, KCl||KCl||\text{ citric acid, } CuSO_4|H_2$$

The cells were measured with the saturated caromel electrode as the reference cell.

The standard solution of hydrogen ion concentration was prepared by mixing the equal volumes of 1/5M acetic acid and 1/5M sodium acetate solution.

2. Experimental results

The electromotive forces of the ion concentration cell and hydrogen electrode were measured by usual compensation method. The temperature of the thermostat was kept at 25℃±0.007℃. According to S. Hakomori,[2] one molecule of copper would combine with one molecule of citric acid as mentioned above and, accordingly, the following equilibrium formula might be assumed:

$$C_6H_8O_7 + Cu^{2+} \rightleftarrows C_6H_6O_7{\cdot}Cu + 2H^+$$

and the dissociation constant would be given by the following equation:

$$K = \frac{[\text{complex}]\,[H^+]^2}{[\text{citric acid}]\,[Cu^{2+}]}$$

From the observed electromotive forces, the concentrations of the dissociated

Table. 1

0.01M Cu added (ml)	Concentration of Cu added (M)	Concentration of citric acid (M)	Ion concentration cell			Hydrogen electrode			Dissociation degree	K 10^{-4}
			e. m. f. (v)	Concentration of dissociated Cu^{++} (M)	Concentration of complex formed (M)	e. m. f. (v)	−Eh (v)	$[H^+]$ 10^{-3}		
2.0	0.000741	0.03976	0.03424	0.000088	0.000653	0.3854	0.1936	4.36	0.13	3.54
2.2	0.000809	0.03883	0.03295	0.000097	0.000712	0.3855	0.1397	4.33	0.14	3.54
2.4	0.000876	0.03793	0.03171	0.000107	0.000769	0.3857	0.1399	4.31	0.14	3.51
2.6	0.000942	0.03702	0.03069	0.000116	0.000826	0.3858	0.1400	4.28	0.14	3.52
2.8	0.001007	0.03615	0.02962	0.000126	0.000881	0.3860	0.1402	4.26	0.14	3.51
3.0	0.001071	0.03530	0.02860	0.000137	0.000934	0.3861	0.1403	4.24	0.15	3.47
3.2	0.001135	0.03444	0.02763	0.000147	0.000988	0.3863	0.1405	4.21	0.15	3.45
3.4	0.001197	0.03362	0.02672	0.000158	0.001039	0.3864	0.1406	4.18	0.15	3.41
3.6	0.001259	0.03282	0.02574	0.000171	0.001088	0.3866	0.1408	4.16	0.16	3.35
3.8	0.001319	0.03204	0.02486	0.000183	0.001136	0.3867	0.1409	4.13	0.16	3.30
4.0	0.001379	0.03126	0.02403	0.000195	0.001184	0.3869	0.1411	4.11	0.16	3.28
4.2	0.001438	0.03051	0.02321	0.000208	0.001230	0.3870	0.1412	4.08	0.17	3.23
4.4	0.001497	0.02974	0.02247	0.000220	0.001277	0.3872	0.1414	4.06	0.17	3.22
4.6	0.001554	0.02901	0.02180	0.000232	0.001322	0.3873	0.1415	4.04	0.18	3.20
4.8	0.001611	0.02826	0.02122	0.000243	0.001368	0.3874	0.1416	4.02	0.18	3.22
5.0	0.001667	0.02751	0.02073	0.000252	0.001415	0.3876	0.1418	4.00	0.18	3.27
5.2	0.001722	0.02678	0.02026	0.000261	0.001461	0.3878	0.1420	3.97	0.18	3.29
5.4	0.001776	0.02606	0.01981	0.000271	0.001505	0.3879	0.1421	3.95	0.18	3.32
5.6	0.001830	0.02535	0.01939	0.000280	0.001550	0.3881	0.1423	3.92	0.18	3.35
5.8	0.001883	0.02462	0.01905	0.000287	0.001596	0.3882	0.1424	3.90	0.18	3.15
6.0	0.001935	0.02392	0.01872	0.000295	0.001640	0.3884	0.1426	3.88	0.18	2.87

Mean value: dissociation degree = 0.16, $K = 3.41 \times 10^{-4}$

copper ions and hydrogen ions were calculated and then dissociation constant were determined by the above equation. The results of the measurements and the calculations are shown in Table 1. As the average activity coefficient of 0.05M copper sulfate solution, the value, 0.230, in the Landolt's table was used.

Next experiments were made with the same procedure as before, using 0.01M solution of citric acid. The calculated results are shown in Table 2. The complexbility of copper citrate shown in Table 2 coincides with the result shown in Table 1. From the these results, the complexbility of copper citrate at 25°C was determined by the above equation as follows:

$$K = 3.37 \times 10^{-4}$$

Dissociation degrees were also calculated in this case, and the result obtained at pH 2.4~2.7 was as follows:

$$\text{dissociation degree} = \frac{[\text{dissociated } Cu^{2+}]}{[\text{complex}]} = 0.16 \ .$$

Table. 2

0.01M Cu added (ml)	Concentration of Cu added (M)	Concentration of citric acid (M)	Ion concentration cell			Hydrogen electrode			Dissociation degree	K 10^{-4}
			e. m. f. (v)	Concentration of dissociated Cu^{++} (M)	Concentration of complex formed (M)	e. m. f. (v)	−Eh (v)	$[H^+]$ 10^{-3}		
2.0	0.000741	0.008616	0.03279	0.000099	0.000643	0.40405	0.15825	2.11	0.15	3.36
2.2	0.000809	0.008491	0.03150	0.000109	0.000700	0.40424	0.15844	2.09	0.16	3.30
2.4	0.000876	0.008366	0.03047	0.000118	0.000758	0.40447	0.15867	2.07	0.16	3.29
2.6	0.000942	0.008242	0.02953	0.000126	0.000816	0.40463	0.15883	2.06	0.15	3.33
2.8	0.001007	0.008121	0.02870	0.000135	0.000872	0.40486	0.15906	2.04	0.15	3.31
3.0	0.001071	0.008001	0.02792	0.000144	0.000927	0.40509	0.15929	2.02	0.16	3.28
3.2	0.001135	0.007882	0.02719	0.000152	0.000983	0.40532	0.15952	2.00	0.15	3.28
3.4	0.001197	0.007767	0.02651	0.000161	0.001036	0.40550	0.15970	1.99	0.16	3.28
3.6	0.001259	0.007651	0.02588	0.000169	0.001090	0.40573	0.15993	1.97	0.16	3.27
3.8	0.001319	0.007538	0.02530	0.000177	0.001142	0.40596	0.16061	1.95	0.15	3.25
4.0	0.001379	0.007425	0.02485	0.000183	0.001196	0.40620	0.16040	1.94	0.15	3.31
4.2	0.001438	0.007314	0.02432	0.000191	0.001247	0.40642	0.16062	1.92	0.15	3.29
4.4	0.001497	0.007204	0.02380	0.000198	0.001299	0.40668	0.16088	1.90	0.15	3.29
4.6	0.001554	0.007098	0.02331	0.000206	0.001348	0.40689	0.16109	1.89	0.15	3.29
4.8	0.001611	0.006992	0.02283	0.000214	0.001397	0.40710	0.16130	1.87	0.15	3.21
5.0	0.001667	0.006887	0.02241	0.000221	0.001446	0.40725	0.16145	1.86	0.15	3.29
5.2	0.001722	0.006784	0.02200	0.000228	0.001494	0.40744	0.16164	1.84	0.15	3.27
5.4	0.001776	0.006683	0.02161	0.000235	0.001541	0.40765	0.16185	1.83	0.15	3.28
5.6	0.001830	0.006582	0.02124	0.000242	0.001588	0.40788	0.16208	1.81	0.15	3.26
5.8	0.001883	0.006484	0.02086	0.000250	0.001633	0.40807	0.16227	1.80	0.15	3.26

Mean value: dissociation degree = 0.15, $K = 3.33 \times 10^{-4}$

III. Zinc citrate complex

1. Reagents and apparatus

a) Reagents

Zinc sulfate used was purified by the same method as in the previous case.[1] Zn-Hg electrode was also prepared by heterogeneous amalgam of 7 per cent Zn, and citric acid was the same as in the case of copper citrate.

b) Cells

The combination of the ion concentration cell was as follows:

$$Zn\text{-}Hg|ZnSO_4||KCl||\text{ citric acid, } ZnSO_4|Zn\text{-}Hg.$$

The same cell was used as before, and experiments were carried out in the same way. The concentrations of hydrogen ions were measured by the hydrogen electrode, using the saturated caromel electrode as the reference cell, and the same electrode and the same method were utilized as before. The combination of the hydrogen electrode was as follows:

$$Hg|HgCl, KCl||KCl||\text{ citric acid, } ZnSO_4|H_2$$

2. Experimental results

After the cells had stood in a thermostat, the temperature of which was kept at 25°C±0.007°C, all the electromotive forces of the cells were measured by usual compensation method. In this reaction, the same equilibrium formula as that between copper ion and citric acid was assumed, namely,

$$C_6H_8O_7 + Zn^{2+} \rightleftarrows C_6H_6O_7 \cdot Zn + 2H^+$$

and the complexbility of zinc citrate was calculated as follows:

$$K = \frac{[\text{complex}]\,[H^+]^2}{[\text{citric acid}]\,[Zn^{2+}]}$$

From the observed electromotive forces of the cells, the concentration of every term in this equation was calculated, which is shown in Table 3. As the average activity coefficient of 0.05M zinc sulfate solution, the value, 0.220, in the Landolt's table was used.

Table. 3

0.01M Zn added (ml)	Concentration of Zn added (M)	Concentration of citric acid (M)	Ion concentration cell			Hydrogen electrode			Dissociation degree	K 10^{-4}
			e. m. f. (v)	Concentration of dissociated Zn^{++} (M)	Concentration of complex formed (M)	e. m. f. (v)	−Eh (v)	$[H^+]$ 10^{-3}		
1.6	0.000602	0.04690	0.03142	0.000095	0.000507	0.38393	0.13813	4.61	0.19	2.41
1.8	0.000672	0.04607	0.02997	0.000107	0.000565	0.38427	0.13847	4.55	0.19	2.37
2.0	0.000741	0.04567	0.02850	0.000120	0.000621	0.38464	0.13884	4.48	0.19	2.27
2.2	0.000809	0.04527	0.02728	0.000131	0.000678	0.38486	0.13906	4.45	0.19	2.26
2.4	0.000876	0.04489	0.02601	0.000145	0.000731	0.38509	0.13929	4.41	0.20	2.18
2.6	0.000942	0.04450	0.02493	0.000158	0.000784	0.38531	0.13959	4.37	0.20	2.13
2.8	0.001007	0.04412	0.02400	0.000170	0.000837	0.38550	0.13970	4.34	0.20	2.10
3.0	0.001071	0.04375	0.02324	0.000180	0.000891	0.38568	0.13988	4.31	0.20	2.10
3.2	0.001135	0.04337	0.02263	0.000189	0.000946	0.38587	0.14007	4.27	0.20	2.10
3.4	0.001197	0.04301	0.02216	0.000196	0.001001	0.38611	0.14031	4.23	0.20	2.12
3.6	0.001259	0.04264	0.02169	0.000203	0.001056	0.38629	0.14049	4.21	0.19	2.16
3.8	0.001319	0.04229	0.02113	0.000212	0.001107	0.38653	0.14073	4.17	0.19	2.15
4.0	0.001379	0.04194	0.02062	0.000221	0.001158	0.38670	0.14090	4.14	0.19	2.14
4.2	0.001438	0.04159	0.02018	0.000229	0.001209	0.38698	0.14118	4.09	0.19	2.12
4.4	0.001497	0.04125	0.01963	0.000238	0.001259	0.38731	0.14158	4.03	0.19	2.08
4.6	0.001554	0.04091	0.01917	0.000247	0.001307	0.38753	0.14173	4.01	0.19	2.08
4.8	0.001611	0.04058	0.01872	0.000256	0.001355	0.38779	0.14199	3.97	0.19	2.06
5.0	0.001667	0.04026	0.01833	0.000264	0.001403	0.38806	0.14226	3.93	0.19	2.04

Mean value: dissociation degree = 0.19, $K = 2.16 \times 10^{-4}$

Next experiments were made with the same method and the same cells as the above, using 0.01M solution of citric acid. The calculated results are shown in Table 4. The complexbility of zinc citrate shown in Table 4 coincides with the result shown in Table 3. From the above results, the complexbility of zinc

citrate was determined by the above equation as follows:

$$K = 2.19\times10^{-4}\,.$$

Then, dissociation degrees were calculated, and the following results were obtained at pH 2.4 and 2.7, respectively:

$$\text{dissociation degree} = \frac{[\text{dissociated } Zn^{2+}]}{[\text{complex}]} = 0.19 \text{ and } 0.23$$

Table. 4

0.01M Zn added (ml)	Concentration of Zn added (M)	Concentration of citric acid (M)	Ion concentration cell			Hydrogen electrode			Dissociation degree	K 10^{-4}
			e. m. f. (v)	Concentration of dissociated Zn^{++} (M)	Concentration of complex formed (M)	e. m. f. (v)	$-Eh$ (v)	$[H^+]$ 10^{-3}		
1.2	0.000458	0.009168	0.03295	0.000085	0.000373	0.40394	0.15814	2.11	0.23	2.15
1.4	0.000530	0.009036	0.03126	0.000096	0.000434	0.40416	0.15836	2.10	0.22	2.20
1.6	0.000602	0.008904	0.02983	0.000108	0.000494	0.40435	0.15855	2.08	0.22	2.22
1.8	0.000672	0.008775	0.02850	0.000119	0.000553	0.40457	0.15877	2.06	0.22	2.25
2.0	0.000741	0.008650	0.02720	0.000132	0.000609	0.40464	0.15884	2.06	0.22	2.26
2.2	0.000809	0.008527	0.02598	0.000145	0.000664	0.40480	0.15900	2.04	0.22	2.23
2.4	0.000876	0.008409	0.02469	0.000161	0.000715	0.40497	0.15917	2.03	0.22	2.18
2.6	0.000942	0.008292	0.02350	0.000176	0.000766	0.40513	0.15933	2.02	0.23	2.14
2.8	0.001007	0.008175	0.02241	0.000192	0.000815	0.40535	0.15955	2.00	0.24	2.08
3.0	0.001071	0.008062	0.02168	0.000204	0.000867	0.40552	0.15972	1.99	0.24	2.09
3.2	0.001135	0.007948	0.02081	0.000218	0.000917	0.40566	0.15986	1.98	0.24	2.07
3.4	0.001197	0.007834	0.02020	0.000228	0.000969	0.40581	0.16001	1.97	0.24	2.11
3.6	0.001259	0.007718	0.01976	0.000236	0.001023	0.40593	0.16013	1.96	0.23	2.16
3.8	0.001319	0.007607	0.01927	0.000245	0.001074	0.40609	0.16029	1.94	0.23	2.17
4.0	0.001379	0.007496	0.01884	0.000254	0.001125	0.40625	0.16045	1.93	0.23	2.20
4.2	0.001438	0.007385	0.01845	0.000261	0.001177	0.40642	0.16062	1.92	0.22	2.25
4.4	0.001497	0.007274	0.01811	0.000268	0.001229	0.40659	0.16079	1.91	0.22	2.30
4.6	0.001554	0.007168	0.01776	0.000276	0.001278	0.40674	0.16094	1.90	0.22	2.33
4.8	0.001611	0.007061	0.01742	0.000283	0.001328	0.40690	0.16110	1.88	0.21	2.35
5.0	0.001667	0.006957	0.01709	0.000291	0.001376	0.40715	0.16135	1.87	0.21	2.38

Mean value : dissociation degree = 0.23, $K = 2.21\times10^{-4}$

Summary

(1) In the studies of copper and zinc citrates, the following combinations of the ion concentration cell were used:

Cu-Hg|$CuSO_4$||KCl|| citric acid, $CuSO_4$|Cu-Hg

Zn-Hg|$ZnSO_4$||KCl|| citric acid, $ZnSO_4$|Zn-Hg

and following combinations of the hydrogen electrode were used:

Hg|HgCl, KCl|KCl|| citric acid, $CuSO_4|H_2$

Hg|HgCl, KCl||KCl|| citric acid, $ZnSO_4|H_2$.

All the electromotive forces of the cells were measured by usual potentiometric compensation method at 25°C.

(2) The complexbilities of copper and zinc citrates calculated from the observed results were 3.37×10^{-4} and 2.19×10^{-4}, respectively.

Acknowledgement

The author wishes to express his hearty thanks to Prof. H. Gotô for his helpful suggestions in the course of this work.