On the Formation of Complex Ions Applied in Analytical Chemistry. IV : Studies on Complexes of Lead and Cadmium Citrates

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Studies on Complexes of Lead and Cadmium Citrates*

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Synopsis

Complexbilities of various ions applied in chemical analysis had been measured and reported in the previous papers. In the present study, the complexbilities of lead and cadmium citrates were measured by the usual potentiometric compensation method, using an ion concentration cell, a quinhydrone electrode and a hydrogen electrode. The following results were obtained at 25°C: lead citrate, $K = 7.81 \times 10^{-3}$; cadmium citrate, $K = 5.70 \times 10^{-4}$.

I. Introduction

From the standpoint of analytical chemistry, complexbilities of various ions applied in chemical analysis are desired to be measured. In the previous papers[1], complexbilities of copper, zinc, lead and cadmium tartrates and copper and zinc citrates were reported. In the present experiment, complexbilities of lead and cadmium citrates were measured by the same method as reported in the previous papers[1].

II. Lead citrate complex

1. Reagents and apparatus

(a) Reagents

Lead nitrate solution used was prepared by the same method as in the second report[2] and its concentration was determined with gravimetric method, using 8-hydroxyquinoline. Pb-Hg electrode (10 per cent of Pb) used as the electrode of ion concentration cell was prepared by the same method of electrolysis as in the second report[2]. Citric acid was the same as used in the last paper [3], and the concentration of this solution was standardized by the standard sodium hydroxide solution, using phenolphthalein as an indicator. In each case, mercury and water used were purified by redistillation.

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* The 701st report of the Research Institute for Iron, Steel and Other Metals. Published in the Journal of the Chemical Society of Japan, **73** (1952), 92.

(1) S. Suzuki, Sci. Rep. RITU, **A 3** (1951), 292, **4** (1952), 176, **4** (1952), 464.

(2) S. Suzuki, Sci. Rep. RITU, **A 4** (1952), 176.

(3) S. Suzuki, Sci. Rep. RITU, **A 4** (1952), 464.

(b) Cell

The combination of the ion concentration cell used was as follows:

$$Pb\text{-}Hg \mid Pb(NO_3)_2 \parallel KNO_3 \parallel \text{citric acid}, Pb(NO_3)_2 \mid Pb\text{-}Hg$$

and the cell, made of hard glass, was the same type as shown in the first report[4]. One side of the cell was composed of the electrode of Pb-Hg (10 per cent of Pb) and 0.05 M lead nitrate solution, and the other side was composed of the same electrode of Pb-Hg and lead citrate solution. The lead citrate complex solution was prepared by adding a certain amount of 0.01 M lead nitrate solution to 25 ml of 0.01 M citric acid solution. The saturated solution of potassium nitrate was used as the junction liquid. The concentrations of hydrogen ions were measured by using the quinhydrone electrode with the saturated caromel electrode as the reference cell. The combination of the quinhydrone electrode used was as follows:

$$Hg \mid HgCl, KCl \parallel KCl \parallel \text{citric acid}, Pb(NO_3)_2, \text{quinhydrone} \mid Pt\ ,$$

the cell being of the same type as shown in the second report[2]. The standard solution of the hydrogen ion concentration was prepared by mixing the equal volumes of 1/5 M acetic acid and 1/5M sodium acetate solution.

2. Experimental results

After the cells were kept standing in a thermostat, the temperature of which was kept at 25°C±0.007°C, the electromotive forces of the ion concentration cell and quinhydrone electrode were measured by the usual potentiometric compensation method.

In this reaction, the following equilibrium formula would be assumed:

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

and the dissociation constant in this case was given by the following equation:

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

From the observed electromotive forces, the concentrations of the dissociated lead ions and hydrogen ions were calculated, and then the dissociation constant was 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 lead nitrate solution, the value of 0.464, measured by A.P. Vanselow,[5] was used.

Next, experiments were measured with the same procedure as mentioned above, using 0.05M solution of citric acid. The measured and the calculated results are shown in Table 2. The complexbility of lead citrate shown in Table 2 coincides with the result shown in Table 1.

From the above results, the value of the complexbility of lead citrate at 25°C was determined as follows:

$$K = 7.81 \times 10^{-3}\ .$$

(4) S. Suzuki, Sci. Rep. RITU, **A 3** (1951), 292.
(5) A.P. Vanselow, J. Am. Chem. Soc., **46** (1924), 241.

Table 1

0.01M Pb added (ml)	Concentration of Pb added (M)	Concentration of citric acid (M)	Ion concentration cell			Quinhydrone electrode			Dissociation * degree	K 10^{-3}
			e.m.f. (V)	Concentration of dissociated Pb (M)	Concentration of complex formed (M)	e.m.f. (V)	$-Eh$ (V)	$[H^+]$ 10^{-3}		
3.0	0.001071	0.008212	0.05367	0.000355	0.000716	0.2902	0.1632	1.74	0.50	7.43
3.2	0.001134	0.008107	0.05284	0.000378	0.000756	0.2906	0.1628	1 79	0.50	7.90
3.4	0.001197	0.008003	0.05220	0.000398	0.000799	0.2910	0.1624	1.80	0.50	8.13
3.6	0.001259	0.007903	0.05146	0.000421	0.000838	0.2914	0.1620	1.82	0.50	8.34
3.8	0.001319	0.007844	0.04972	0.000483	0.000836	0.2917	0.1617	1.84	0.58	7.47
4.0	0.001379	0.007748	0.04905	0.000508	0.000871	0.2920	0.1614	1.86	0.58	7.66
4.2	0.001438	0.007662	0.04831	0.000539	0.000899	0.2923	0.1611	1.88	0.60	7.69
4.4	0.001497	0.007576	0.04759	0.000570	0.000927	0.2925	0.1609	1.91	0.61	7.83
4.6	0.001554	0.007494	0.04685	0.000603	0.000951	0.2929	0.1605	1.93	0.63	7.84
4.8	0.001611	0.007416	0.04613	0.000638	0.000973	0.2932	0.1602	1.95	0.66	7.82
5.0	0.001667	0.007343	0.04537	0.000677	0.000990	0.2935	0.1599	1.98	0.68	7.99
5.2	0.001722	0.007265	0.04479	0.000709	0.001013	0.2937	0.1597	2.00	0.70	7.87
5.4	0.001776	0.007187	0.04423	0.000740	0.001036	0.2938	0.1596	2.01	0.71	7.87
5.6	0.001830	0.007109	0.04372	0.000770	0.001060	0.2940	0.1594	2.02	0.73	7.90
5.8	0.001883	0.007038	0.04316	0.000805	0.001078	0.2943	0.1591	2.04	0.75	7.92
6.0	0.001935	0.006971	0.04258	0.000842	0.001093	0.2944	0.1590	2.05	0.77	7.83
6.2	0.001987	0.006905	0.04201	0.000880	0.001107	0.2947	0.1587	2.06	0.80	7.73
6.4	0.002038	0.006832	0.04150	0.000909	0.001129	0.2949	0.1585	2.09	0.81	7.94
6.6	0.002089	0.006771	0.04104	0.000949	0.001140	0.2951	0.1583	2.11	0.83	7.90
6.8	0.002138	0.006709	0.04055	0.000986	0.001152	0.2953	0.1581	2.12	0.86	7.83
7.0	0.002187	0.006648	0.04008	0.001023	0.001164	0.2955	0.1579	2.14	0.88	7.84

Mean value: dissociation degree = 0.68; $K = 7.84 \times 10^{-3}$.

* Dissociation degree $= \dfrac{[\text{dissociated } Pb^{++}]}{[\text{complex formed}]}$.

Table 2

0.01M Pb added (ml)	Concentration of Pb added (M)	Concentration of citric acid (M)	Ion concentration cell			Quinhydrone electrode			Dissociation * degree	K 10^{-3}
			e.m.f. (V)	Concentration of dissociated Pb (M)	Concentration of complex formed (M)	e.m.f. (V)	$-Eh$ (V)	$[H^+]$ 10^{-3}		
3.0	0.001071	0.043991	0.05149	0.000420	0.000651	0.3149	0.1385	4.57	0.65	7.36
3.2	0.001134	0.043645	0.05053	0.000453	0.000681	0.3153	0.1381	4.62	0.67	7.35
3.4	0.001197	0.043300	0.04972	0.000483	0.000714	0.3156	0.1378	4.68	0.68	7.46
3.6	0.001259	0.042956	0.04903	0.000509	0.000750	0.3159	0.1375	4.73	0.68	7.67
3.8	0.001319	0.042622	0.04829	0.000539	0.000780	0.3161	0.1373	4.77	0.69	7.73
4.0	0.001379	0.042296	0.04755	0.000572	0.000807	0.3163	0.1371	4.79	0.71	7.65
4.2	0.001438	0.041975	0.04682	0.000605	0.000833	0.3165	0.1369	4.85	0.73	7.72
4.4	0.001497	0.041660	0.04610	0.000640	0.000857	0.3168	0.1366	4.90	0.75	7.72
4.6	0.001554	0.041349	0.04543	0.000674	0.000880	0.3170	0.1364	4.97	0.77	7.80
4.8	0.001611	0.041038	0.04489	0.000703	0.000908	0.3173	0.1361	4.99	0.77	7.84
5.0	0.001667	0.040645	0.04435	0.000733	0.000934	0.3175	0.1359	5.00	0.78	7.86
5.2	0.001722	0.040434	0.04380	0.000765	0.000957	0.3176	0.1358	5.08	0.80	7.98
5.4	0.001776	0.040139	0.04328	0.000797	0.000979	0.3178	0.1356	5.16	0.81	8.14
5.6	0.001830	0.039845	0.04282	0.000826	0.001004	0.3179	0.1355	5.13	0.82	8.03
5.8	0.001883	0.039557	0.04236	0.000856	0.001027	0.3182	0.1352	5.18	0.83	8.14
6.0	0.001935	0.039282	0.04179	0.000895	0.001040	0.3183	0.1351	5.20	0.86	8.00
6.2	0.001987	0.039006	0.04131	0.000929	0.001058	0.3185	0.1349	5.23	0.88	7.99
6.4	0.002038	0.038734	0.04084	0.000964	0.001074	0.3186	0.1348	5.25	0.90	7.93
6.6	0.002089	0.038467	0.04037	0.001000	0.001089	0.3189	0.1345	5.31	0.92	7.98

Mean value: dissociation degree = 0.74; $K = 7.78 \times 10^{-3}$.

* Dissociation degree $= \dfrac{[\text{dissociated } Pb^{++}]}{[\text{complex formed}]}$.

Further, dissociation degree were calculated in this case, the result obtained at pH 2.3~2.7 being as follows:

$$\text{dissociation degree} = \frac{[\text{dissociated } Pb^{2+}]}{[\text{complex}]} \approx 0.7 .$$

III. Cadmium citrate complex

1. Reagents and apparatus

(a) Reagents

Cadmium chloride and Cd-Hg electrode (12.5 per cent of Cd) used were prepared by the same method as in the second report(2), and others used were the same reagents as those used in the study of lead citrate complex.

(b) Cells

The combination of the ion concentration cell was as follows:

$$Cd\text{-}Hg \mid CdCl_2 \parallel KCl \parallel \text{citric acid}, CdCl_2 \mid Cd\text{-}Hg .$$

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

$$Hg \mid HgCl, KCl \parallel KCl \parallel \text{citric acid}, CdCl_2 \mid H_2 .$$

2. Experimental results

The temperature of the thermostat was kept at 25°C±0.007°C and the electromotive forces of the ion concentration cell and hydrogen electrode were measured by the usual potentiometric compensation method.

From the observed electromotive forces, the concentrations of the dissociated cadmium ions and hydrogen ions were calculated.

In this reaction, the following equilibrium formula would be assumed:

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

and the dissociation constant was given by the following equation:

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

The results of the measurements and the calculations are shown in Table 3. The value 0.277, measured by Scatchard and Tefft(6), was used as the average activity coefficient of 0.05M cadmium chloride solution. Dissociation degrees were also calculated in this case, the result obtained at pH 2.4~2.8 being as follows:

$$\text{dissociation degree} = \frac{[\text{dissociated } Cd^{2+}]}{[\text{complex}]} \approx 0.6 .$$

Next, experiments were made with the same procedure as above, using 0.05M solution of citric acid. The results of the measurements and the calculations are shown in Table 4. The complexbility of cadmium citrate shown in Table 4 coincides with the results shown in Table 3. The value of the complexbility

(6) Scatchard, Tefft, J. Am. Chem. Soc., **56** (1934), 2274.

of cadmium citrate at 25°C was determined from the above results as follows:

$$K = 5.70 \times 10^{-4},$$

and the value of the dissociation degree was given at pH 2.3~2.7 as follows:

dissociation degree $\simeq$ 0.7 .

Table 3

0.01M Cd added (ml)	Concentration of Cd added (M)	Concentration of citric acid (M)	Ion concentration cell: e.m.f. (V)	Ion concentration cell: Concentration of dissociated Cd (M)	Ion concentration cell: Concentration of complex formed (M)	Hydrogen electrode: e.m.f. (V)	Hydrogen electrode: −Eh (V)	Hydrogen electrode: $[H^+]$ 10^{-3}	Dissociation * degree	K 10^{-3}
2.4	0.000876	0.0008593	0.01785	0.000345	0.000531	0.4081	0.1623	1.80	0.65	5.80
2.6	0.000942	0.0008487	0.01690	0.000371	0.000571	0.4084	0.1626	1.78	0.65	5.74
2.8	0.001007	0.0008380	0.01615	0.000394	0.000613	0.4086	0.1628	1.76	0.64	5.75
3.0	0.001071	0.0008273	0.01544	0.000416	0.000655	0.4089	0.1631	1.74	0.64	5.76
3.2	0.001135	0.0008168	0.01479	0.000438	0.000697	0.4092	0.1634	1.72	0.63	5.76
3.4	0.001197	0.0008065	0.01418	0.000459	0.000738	0.4094	0.1636	1.71	0.62	5.82
3.6	0.001259	0.0007962	0.01360	0.000480	0.000779	0.4098	0.1640	1.68	0.62	5.75
3.8	0.001319	0.0007864	0.01301	0.000503	0.000816	0.4101	0.1643	1.66	0.62	5.68
4.0	0.001379	0.0007769	0.01242	0.000527	0.000852	0.4103	0.1645	1.65	0.62	5.66
4.2	0.001438	0.0007674	0.01183	0.000551	0.000887	0.4105	0.1647	1.64	0.62	5.64
4.4	0.001497	0.0007581	0.01129	0.000575	0.000922	0.4108	0.1650	1.62	0.62	5.55
4.6	0.001554	0.0007487	0.01084	0.000595	0.000959	0.4111	0.1653	1.60	0.62	5.51
4.8	0.001611	0.0007391	0.01047	0.000613	0.000998	0.4113	0.1655	1.59	0.61	5.56
5.0	0.001667	0.0007294	0.01016	0.000628	0.001039	0.4116	0.1658	1.57	0.60	5.59

Mean value: dissociation degree = 0.63 ; $K = 5.68 \times 10^{-4}$.

* dissociation degree $= \dfrac{[\text{dissociated } Cd^{++}]}{[\text{complex formed}]}$.

Table 4

0.01M Cd added (ml)	Concentration of Cd added (M)	Concentration cf citric acid (M)	Ion concentration cell: e.m.f. (V)	Ion concentration cell: Concentration of dissociated Cd (M)	Ion concentration cell: Concentration of complex formed (M)	Hydrogen electrode: e.m.f. (V)	Hydrogen electrode: −Eh (V)	Hydrogen electrode: $[H^+]$ 10^{-3}	Dissociation * degree	K 10^{-4}
2.0	0.000741	0.04175	0.02021	0.000287	0.000454	0.3884	0.1426	3.87	0.63	5.67
2.2	0.000809	0.04098	0.01914	0.000312	0.000497	0.3889	0.1431	3.80	0.63	5.61
2.4	0.000876	0.04022	0.01819	0.000336	0.000540	0.3893	0.1435	3.74	0.62	5.58
2.6	0.000942	0.03946	0.01730	0.000360	0.000582	0.3897	0.1439	3.68	0.62	5.42
2.8	0.001007	0.03869	0.01661	0.000380	0.000627	0.3901	0.1443	3.62	0.61	5.58
3.0	0.001071	0.03791	0.01598	0.000398	0.000673	0.3905	0.1447	3.57	0.59	5.68
3.2	0.001135	0.03715	0.01539	0.000418	0.000717	0.3908	0.1450	3.53	0.58	5.75
3.4	0.001197	0.03641	0.01482	0.000437	0.000760	0.3911	0.1453	3.48	0.58	5.78
3.6	0.001259	0.03567	0.01426	0.000456	0.000803	0.3915	0.1457	3.43	0.57	5.80
3.8	0.001319	0.03497	0.01372	0.000476	0.000843	0.3920	0.1462	3.36	0.56	5.71
4.0	0.001379	0.03427	0.01319	0.000496	0.000883	0.3924	0.1466	3.31	0.56	5.69
4.2	0.001438	0.03359	0.01267	0.000516	0.000922	0.3928	0.1470	3.26	0.56	5.65
4.4	0.001497	0.03290	0.01218	0.000536	0.000961	0.3931	0.1473	3.22	0.56	5.65
4.6	0.001554	0.03224	0.01174	0.000555	0.000999	0.3933	0.1475	3.20	0.56	5.71
4.8	0.001611	0.03153	0.01141	0.000570	0.001041	0.3937	0.1479	3.15	0.55	5.74
5.0	0.001667	0.03080	0.01115	0.000581	0.001086	0.3941	0.1483	3.10	0.53	5.83
5.2	0.001722	0.03010	0.01089	0.000593	0.001129	0.3944	0.1486	3.06	0.53	5.92
5.4	0.001776	0.02939	0.01065	0.000604	0.001172	0.3949	0.1491	3.01	0.52	5.98

Mean value: dissociation value = 0.58 ; $K = 5.71 \times 10^{-4}$.

* Dissociation degree $= \dfrac{[\text{dissociated } Cd^{++}]}{[\text{complex formed}]}$.

Summary

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

$Pb\text{-}Hg \mid Pb(NO_3)_2 \parallel KNO_3 \parallel$ citric acid, $Pb(NO_3)_2 \mid Pb\text{-}Hg$

$Cd\text{-}Hg \mid CdCl_2 \parallel KCl \parallel$ citric acid, $CdCl_2 \mid Cd\text{-}Hg$,

and the following combinations of the quinhydrone electrode and hydrogen electrode were used:

$Hg \mid HgCl$, $KCl \parallel KCl \parallel$ citric acid, $Pb(NO_3)_2$, quinhydrone $\mid Pt$

$Hg \mid HgCl$, $KCl \parallel KCl \parallel$ citric acid, $CdCl_2 \mid H_2$.

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

(2) From the observed results, the complexbilities of lead and cadmium citrates were calculated to be 7.81×10^{-3} and 5.70×10^{-4}, respectively.

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