

On the Formation of Complex Ions Applied in Analytical Chemistry. VII : Studies on Complexes of Silver Citrate and Lead Acetate

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On the Formation of Complex Ions Applied
in Analytical Chemistry. VII
Studies on Complexes of Silver Citrate and Lead Acetate*

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Synopsis

Complexibilities of various ions applied to chemical analysis have been investigated. In the present experiment, the complexibilities of silver citrate and lead acetate were measured by the usual potentiometric compensation method, using the ion concentration cell and quinhydrone electrode. The following results were obtained at 25°C: for silver citrate $K=1.14 \times 10^{-3}$ and for lead acetate $K=1.45 \times 10^{-4}$.

I. Introduction

From the standpoint of analytical chemistry, complexibilities of various ions applied to chemical analysis are desired to be measured. In the previous experiments⁽¹⁾, complexibilities of tartrates, citrates and malonates of copper, zinc, lead and cadmium were measured by the usual potentiometric compensation method, using ion concentration cell, hydrogen electrode and quinhydrone electrode. In the present case, studies on complexes of silver citrate and lead acetate were carried out by the same method as reported in the previous papers⁽¹⁾. It is well known that one molecule of lead would combine with two molecules of acetic acid, but complexibilities of silver citrate and lead acetate have not yet been reported.

II. Silver citrate complex

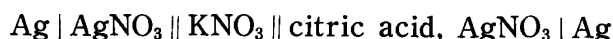
1. Reagents and apparatus

(a) Reagents

Silver nitrate used was purified by Kolthoff and Lingane's method⁽²⁾. Silver electrode used was prepared by electrolyzing the silver nitrate solution purified by the method mentioned above and then by electroplating the silver on the surface of platinum wire as anode. Citric acid used was purified by recrystallizing four times with water and, in each case, redistilled water was used.

(b) Cells

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



* The 711th report of the Research Institute for Iron, Steel and Other Metals.

(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.

(2) I. M. Kolthoff and J. J. Lingane, *J. Am. Chem. Soc.*, **57** (1935), 2126.

The cell of quinhydrone electrode type was used as shown in Fig. 1 and made of hard glass. One side of the cell was composed of the silver electrode prepared by the above mentioned method and 0.05 M silver nitrate solution, and

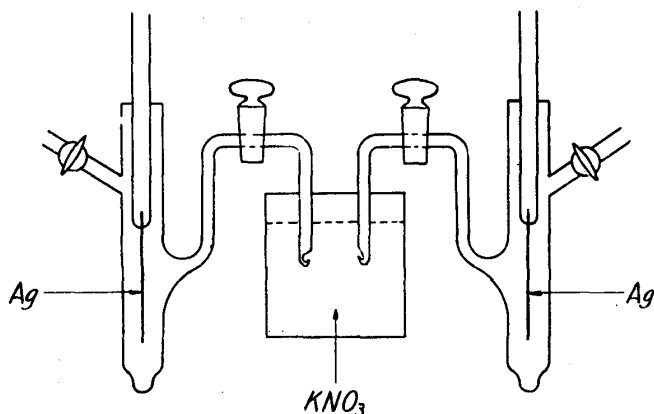
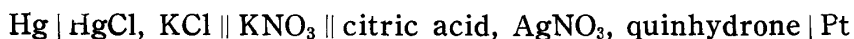


Fig. 1

the other was composed of the same silver electrode and silver citrate complex solution. The silver citrate complex solution was prepared by adding a certain amount of 0.01 M silver nitrate solution to 25 ml of 0.05 M citric acid solution. The saturated solution of potassium nitrate was used as the junction liquid. The concentration of hydrogen ions was measured

by using the quinhydrone electrode with the saturated calomel electrode as the reference cell. The cell was the same type as shown in the second report⁽³⁾. The combination of the quinhydrone electrode used was as follows:

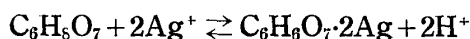


In this experiment, the standard solution of the hydrogen ion concentration was prepared by mixing the equal volumes of 1/5 M acetic acid and 1/5 M sodium acetate solution.

2. Experimental results

After the cell had stood in a thermostat, the temperature of which was kept at $25^\circ\text{C} \pm 0.007^\circ\text{C}$, the electromotive forces of the ion concentration cell and quinhydrone electrode were measured by the usual compensation method.

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



and the dissociation constant was given by the following equation:

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

From the observed electromotive forces, the concentrations of the dissociated silver ions and hydrogen ions were calculated in each case, and then dissociation constant of silver citrate complex was determined by the above equation. The results of the measurements and calculations are shown in Table 1. The value 0.783 in the Landolt's table was used as the average activity coefficient of 0.05 M silver nitrate solution.

Next experiments were carried out with the same method and the same cells as above, using 0.01 M solution of citric acid. The results are shown in Table 2. The complexibility of silver citrate shown in Table 2 coincides with the result shown in Table 1. From the above results, the value of complexibility of silver

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

citrate was determined as follows:

$$K = 1.14 \times 10^{-3}$$

Then dissociation degrees were also calculated in this case, and the results

Table 1

0.01M Ag added (ml)	Concentration of Ag added (M)	Concentration of citric acid (M)	Ion concentration cell			Quinhydrone electrode			Dis- soci- ation con- stant degree	Dis- soci- ation con- stant $K 10^{-3}$
			e.m.f. (V)	Concen- tration of dissociat- ed Ag (M)	Concen- tration of complex formed (M)	e.m.f. (V)	-Eh (V)	[H ⁺] 10^{-3}		
1.0	0.000385	0.047853	0.1204	0.000162	0.000223	0.3227	0.1307	6.17	0.73	1.10
1.2	0.000458	0.047444	0.1159	0.000193	0.000265	0.3230	0.1304	6.24	0.73	1.13
1.4	0.000530	0.047040	0.1123	0.000222	0.000308	0.3232	0.1302	6.28	0.72	1.16
1.6	0.000602	0.046643	0.1090	0.000253	0.000349	0.3235	0.1299	6.36	0.72	1.20
1.8	0.000672	0.046252	0.1061	0.000283	0.000389	0.3237	0.1297	6.41	0.73	1.22
2.0	0.000741	0.045868	0.1035	0.000313	0.000428	0.3239	0.1295	6.46	0.73	1.24
2.2	0.000809	0.045486	0.1014	0.000340	0.000469	0.3242	0.1292	6.54	0.72	1.30
2.4	0.000876	0.045116	0.0991	0.000372	0.000504	0.3244	0.1290	6.58	0.74	1.30
2.6	0.000942	0.044752	0.0969	0.000405	0.000537	0.3247	0.1287	6.65	0.75	1.31
2.8	0.001007	0.044402	0.0945	0.000445	0.500562	0.3249	0.1285	6.71	0.79	1.28
3.0	0.001071	0.044059	0.0921	0.000488	0.000583	0.3252	0.1282	6.73	0.84	1.23
3.2	0.001134	0.043728	0.0898	0.000536	0.000598	0.3255	0.1279	6.87	0.90	1.20
3.4	0.001197	0.043401	0.0875	0.000584	0.000613	0.3258	0.1276	6.95	0.95	1.14
3.6	0.001259	0.043081	0.0854	0.000634	0.000625	0.3261	0.1273	7.03	1.01	1.13
3.8	0.001319	0.042765	0.0835	0.000682	0.000637	0.3264	0.1270	7.11	1.07	1.10
4.0	0.001379	0.042453	0.0818	0.000729	0.000650	0.3266	0.1268	7.18	1.12	1.08
4.2	0.001438	0.042177	0.0792	0.000807	0.000631	0.3269	0.1265	7.26	1.27	0.98
4.4	0.001497	0.041888	0.0773	0.000869	0.000629	0.3271	0.1263	7.32	1.38	0.93

Mean value: dissociation degree = 0.88, $K = 1.12 \times 10^{-3}$.

Table 2

0.01M Ag added (ml)	Concentration of Ag added (M)	Concentration of citric acid (M)	Ion concentration cell			Quinhydrone electrode			Dis- soci- ation con- stant degree	Dis- soci- ation con- stant $K 10^{-3}$
			e.m.f. (V)	Concen- tration of dissociat- ed Ag (M)	Concen- tration of complex formed (M)	e.m.f. (V)	-Eh (V)	[H ⁺] 10^{-4}		
1.0	0.000385	0.009323	0.1347	0.000093	0.000292	0.2967	0.1567	2.24	0.32	1.69
1.2	0.000458	0.009203	0.1283	0.000119	0.000339	0.2970	0.1564	2.27	0.35	1.60
1.4	0.000530	0.009087	0.1230	0.000147	0.000383	0.2972	0.1562	2.28	0.38	1.49
1.6	0.000602	0.009015	0.1180	0.000178	0.000424	0.2975	0.1559	2.31	0.42	1.41
1.8	0.000672	0.008866	0.1138	0.000210	0.000462	0.2977	0.1557	2.33	0.45	1.35
2.0	0.000741	0.008765	0.1096	0.000247	0.000494	0.2979	0.1555	2.34	0.55	1.25
2.2	0.000809	0.008364	0.1062	0.000282	0.000527	0.2982	0.1552	2.37	0.54	1.21
2.4	0.000876	0.008569	0.1029	0.000321	0.000555	0.2984	0.1550	2.39	0.58	1.15
2.6	0.000942	0.008474	0.1001	0.000358	0.000584	0.2986	0.1548	2.41	0.61	1.12
2.8	0.001007	0.008377	0.0978	0.000391	0.000616	0.2989	0.1545	2.43	0.63	1.11
3.0	0.001071	0.008269	0.0955	0.000428	0.000643	0.2991	0.1543	2.45	0.67	1.09
3.2	0.001134	0.008197	0.0933	0.000466	0.000668	0.2994	0.1540	2.48	0.70	1.08
3.4	0.001197	0.008109	0.0913	0.000504	0.000693	0.2997	0.1537	2.51	0.73	1.07
3.6	0.001259	0.003024	0.0894	0.000542	0.000717	0.3001	0.1533	2.55	0.76	1.07
3.8	0.001319	0.007954	0.0871	0.000593	0.000726	0.3004	0.1530	2.59	0.82	1.03
4.0	0.001379	0.007882	0.0851	0.000641	0.000738	0.3006	0.1528	2.61	0.87	1.00
4.2	0.001438	0.007819	0.0830	0.000696	0.000742	0.3008	0.1526	2.62	0.94	0.94
4.4	0.001497	0.007752	0.0812	0.000746	0.000751	0.3010	0.1524	2.65	0.99	0.91

Mean value: dissociation degree = 0.63, $K = 1.16 \times 10^{-3}$.

obtained at pH 2.2 and 2.6 were as follows:

$$\text{dissociation degree} = \frac{[\text{dissociated Ag}^+]}{[\text{complex}]} = 0.9 \text{ and } 0.6,$$

respectively.

III. Lead acetate complex

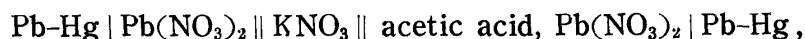
1. Reagents and apparatus

(a) Reagents

Lead nitrate used was purified by the same method as in the second⁽³⁾ and the fourth reports⁽⁴⁾. Pb-Hg electrode (10% Pb) used as the electrode of the ion concentration cell was prepared by the same method of electrolysis as in the last report⁽⁵⁾. Acetic acid, mercury and water used were purified by redistillation.

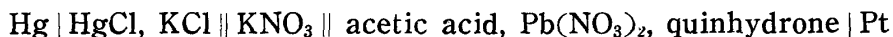
(b) Cells

The following combination of the ion concentration cell was used:



which was the same type as shown in the first report⁽⁶⁾. One side of the cell was composed of the electrode of Pb-Hg (10% Pb) and 0.05 M lead nitrate solution, and the other was composed of the same electrode of Pb-Hg and lead acetate solution which was prepared by adding a certain amount of 0.01 M lead nitrate solution to 25 ml of 0.02 M acetic acid solution.

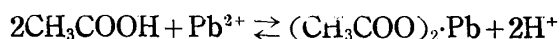
The following concentrations of hydrogen ions were measured by the use of the quinhydrone electrode and the cell was the same type as in the study of silver citrate.



2. Experimental results

All the electromotive forces of the cells in the thermostat, keeping the temperature at $25^\circ \pm 0.007^\circ \text{C}$, were measured by the usual potentiometric compensation method. From the observed electromotive forces of the cells, the concentrations of dissociated lead ions and hydrogen ions were calculated.

In this reaction, the following equilibrium formula was assumed:



Therefore, the dissociation constant was given by the following equation:

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

The results of the measurements and calculations are shown in Table 3. The value 0.464 measured by A. P. Vanselow⁽⁷⁾ was used as the average activity coefficient of 0.05 M lead nitrate solution.

(4) S. Suzuki, Sci. Rep. RITU, A 5 (1953), 16.

(5) S. Suzuki, Sci. Rep. RITU, A 5 (1953), 147.

(6) S. Suzuki, Sci. Rep. RITU, A-3 (1951), 292.

(7) A. P. Vanselow, J. Am. Chem. Soc., 46 (1924), 241.

Next experiments were made with the same method and the same cells as above, using 0.05 M solution of acetic acid. The results of the measurements and the calculations are shown in Table 4. The complexibility of lead acetate shown in Table 4 coincides with the results shown in Table 3. From the above results, the value of complexibility of lead acetate was determined at 25°C as follows:

$$K = 1.45 \times 10^{-4}$$

Dissociation degrees were also calculated and the result obtained at pH 3.0~3.4 was as follows:

$$\text{Dissociation degree} = \frac{[\text{dissociated Pb}^{2+}]}{[\text{complex}]} = \text{about } 3.3$$

Table 3

0.01M Pb added (ml)	Concentration of Pb added (M)	Concentration of acetic acid (M)	Ion concentration cell			Quinhydrone electrode			Dis- soci- ation degree	Dis- soci- ation con- stant $K 10^{-4}$
			e.m.f. (V)	Concen- tration of dissociat- ed Pb (M)	Concen- tration of complex formed (M)	e.m.f. (V)	-Eh (V)	$[H^+]$ 10^{-4}		
1.0	0.000385	0.018951	0.0567	0.000280	0.000105	0.2463	0.2071	3.14	2.67	1.03
1.5	0.000566	0.018722	0.0515	0.000420	0.000146	0.2471	0.2063	3.24	2.88	1.04
2.0	0.000741	0.018317	0.0483	0.000539	0.000202	0.2478	0.2056	3.33	2.67	1.24
2.5	0.000909	0.017954	0.0453	0.000681	0.000228	0.2485	0.2049	3.42	2.99	1.21
3.0	0.001071	0.017584	0.0431	0.000808	0.000273	0.2491	0.2043	3.51	2.96	1.35
3.5	0.001228	0.017239	0.0414	0.000923	0.000305	0.2500	0.2034	3.63	3.03	1.47
4.0	0.001379	0.016915	0.0397	0.001053	0.000326	0.2505	0.2029	3.70	3.23	1.48
4.5	0.001525	0.016685	0.0380	0.001203	0.000322	0.2512	0.2022	3.80	3.74	1.39
5.0	0.001667	0.016330	0.0367	0.001330	0.000337	0.2518	0.2016	3.89	3.95	1.44
5.5	0.001803	0.016040	0.0356	0.001450	0.000353	0.2524	0.2010	3.98	4.11	1.50
6.0	0.001935	0.015749	0.0347	0.001555	0.000380	0.2530	0.2004	4.07	4.09	1.63
6.5	0.002063	0.015440	0.0341	0.001630	0.000433	0.2538	0.1996	4.21	3.76	1.98

Mean value: dissociation degree=3.34, $K=1.40 \times 10^{-4}$.

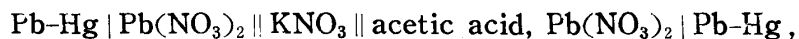
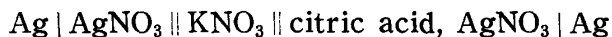
Table 4

0.01M Pb added (ml)	Concentration of Pb added (M)	Concentration of acetic acid (M)	Ion concentration cell			Quinhydrone electrode			Dis- soci- ation degree	Dis- soci- ation con- stant $K 10^{-4}$
			e.m.f. (V)	Concen- tration of dissociat- ed Pb (M)	Concen- tration of complex formed (M)	e.m.f. (V)	-Eh (V)	$[H^+]$ 10^{-4}		
2.0	0.000741	0.051568	0.0485	0.000531	0.000210	0.2708	0.1826	8.16	2.52	0.99
2.5	0.000909	0.050597	0.0455	0.000670	0.000239	0.2716	0.1818	8.42	2.80	0.99
3.0	0.001071	0.049660	0.0432	0.000802	0.000269	0.2725	0.1809	8.71	2.98	1.03
3.5	0.001228	0.048769	0.0411	0.000944	0.000284	0.2731	0.1803	8.91	3.32	1.00
4.0	0.001379	0.047873	0.0398	0.001045	0.000334	0.2738	0.1796	9.17	3.12	1.17
4.5	0.001525	0.047040	0.0383	0.001175	0.000350	0.2745	0.1789	9.42	3.35	1.19
5.0	0.001667	0.046223	0.0371	0.001290	0.000377	0.2752	0.1782	9.68	3.42	1.28
5.5	0.001803	0.045427	0.0361	0.001394	0.000409	0.2759	0.1775	9.95	3.40	1.36
6.0	0.001935	0.044657	0.0352	0.001495	0.000440	0.2767	0.1767	10.5	3.39	1.63
6.5	0.002063	0.043885	0.0346	0.001567	0.000496	0.2774	0.1760	10.6	3.15	1.85

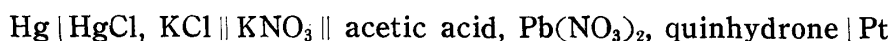
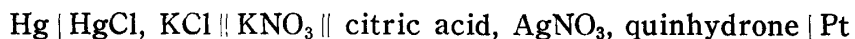
Mean value: dissociation degree=3.15, $K=1.50 \times 10^{-4}$.

Summary

(1) In the studies of silver citrate and lead acetate, the following combinations of the ion concentration cell were used:



and the following combinations of the quinhydrone electrode were used:



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

(2) From the observed results, the complexibilities of silver citrate and lead acetate were calculated, resulting in 1.14×10^{-3} and 1.45×10^{-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.