

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

著者	SUZUKI Shin
journal or publication title	Science reports of the Research Institutes, Tohoku University. Ser. A, Physics, chemistry and metallurgy
volume	3
page range	292-296
year	1951
URL	http://hdl.handle.net/10097/26438

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

Shin SUZUKI

The Research Institute for Iron, Steel and Other Metals.

(Received March 29, 1951)

Synopsis

In this report, the measurements of the complexibilities of copper and zinc tartarates were made by the usual potentiometric compensation method, using the ion concentration cell and hydrogen electrode. The following results were obtained: copper tartarate: $K=9.32 \times 10^{-4}$, zinc tartarate: $K=4.44 \times 10^{-4}$

I. Introduction

There are many cases in which the formations of complexes between various metallic ions and organic acids or other reagents are applied in the chemical analysis. There have been, however, few studies on the complexibilities of these compounds. From the standpoint of the analytical chemistry, the author studied complexibilities of various ions applied for analytical purpose, using ion concentration cell, hydrogen electrode and others.

In this paper, studies on copper and zinc tartarates are reported. Some investigators⁽¹⁾⁽²⁾ have studied copper and zinc tartarates with the absorption spectrum and conductometric methods, and reported that one molecule of copper or zinc would combine with one molecule of tartaric acid and that the complexibility of copper tartarate was of the order of 10^{-3} .

II. Copper tartarate complex

1. Reagents and apparatus

a) Reagents

Copper sulfate was purified by the usual method and recrystallized three times with water, and the concentration of the solution of this salt was determined with gravimetric method using 8-hydroxyquinoline. Cu-Hg electrode (3.5% Cu) was prepared by electrolyzing the purified copper sulfate solution mentioned above, applying purified mercury as anode and platinum as cathode. Tartaric acid was purified by recrystallizing three times with water, and the concentration of this solution was standardized by the standard sodium hydroxide solution, using phenolphthalein as an indicator. Mercury was purified by the usual method and then distilled three

* The 632nd report of the Research Institute for Iron, Steel and Other Metals. Published in the Journal of the Chemical Society of Japan, 72 (1951), 524.

(1) S. Hakomori, J. Chem. Soc. of Japan, 52 (1933), 738.

(2) W. M. Latimer, Oxidation Potentials, 1st Ed., New York (1936), 175.

times. In each case, redistilled water was used.

b) Cells

The combination of the ion concentration cell was as follows:



The cell made of hard glass is shown in Fig. 1. It was composed of the electrode of Cu-Hg (3.5% Cu), 0.1 M copper sulfate solution and copper tartarate complex solution. Copper tartarate complex solution was prepared by adding the known volume of 0.01 M copper sulfate solution to 25 ml of 0.1 M tartaric acid solution. The saturated solution of potassium chloride was used as the junction liquid.

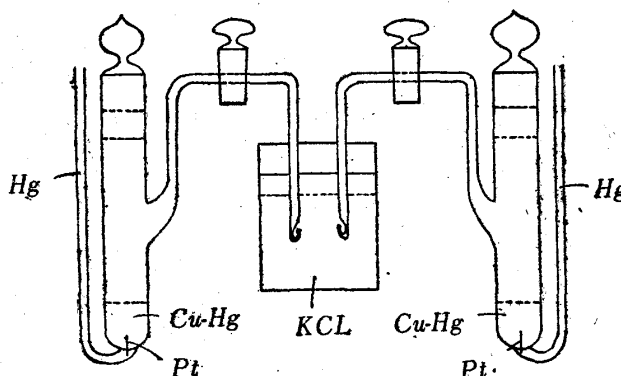


Fig. 1. Ion concentration cell.

The concentration of hydrogen ions was measured by the use of the hydrogen electrode with the saturated carmel electrode as the reference cell. The cell is shown in Fig. 2.

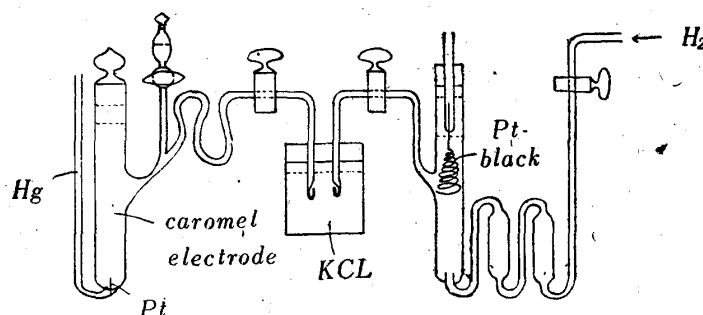
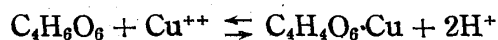


Fig. 2. Hydrogen electrode.

The standard solution of the concentration of hydrogen ions used 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 cells had stood in a thermostat, the temperature of which was kept at $25^\circ\text{C} \pm 0.007^\circ\text{C}$, all the electromotive forces of the cells were measured by the usual compensation method. In this reaction, the following equilibrium formula was assumed:



and the dissociation constant was given by the following equation:

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

From the observed electromotive forces of the cells, the concentrations of the dissociated copper ions and hydrogen ions were calculated, and then dissociation constants were determined by the above equation. The results of the measurements and the calculation are shown in Table 1. As the average activity coefficient of 0.1 M copper sulfate solution, the value 0.164 in the Landolt's table was used.

Table I.

0.01 M Cu added (ml)	Concen- tration of Cu added (M)	Concen- tration of tartaric acid(M)	Ion concentration cell			Hydrogen electrode			Dis- socia- tion de- gree *	K 10 ⁻⁴
			e. m. f. (V)	Concen- tration, of dissociat- ed Cu ⁺⁺ (M)	Concen- tration of complex formed(M)	e. m. f. (V)	-Eh (V)	[H ⁺] 10 ⁻³		
0.6	0.000234	0.09766	0.0670	0.000088	0.000145	0.37140	0.12560	7.51	0.61	9.49
0.8	0.000310	0.09690	0.0635	0.000117	0.000193	0.37162	0.12582	7.44	0.61	9.42
1.0	0.000385	0.09615	0.0605	0.000147	0.000238	0.37175	0.12595	7.41	0.62	9.25
1.2	0.000485	0.09542	0.0583	0.000174	0.000284	0.37182	0.12602	7.39	0.61	9.34
1.4	0.000530	0.09470	0.0564	0.000203	0.000327	0.37178	0.12598	7.40	0.62	9.31
1.6	0.000602	0.09399	0.0546	0.000233	0.000369	0.37187	0.12607	7.37	0.63	9.15
1.8	0.000672	0.09328	0.0534	0.000256	0.000416	0.37209	0.12629	7.31	0.62	9.31
2.0	0.000741	0.09259	0.0522	0.000281	0.000460	0.37226	0.12646	7.26	0.61	9.32
2.2	0.000809	0.09191	0.0511	0.000305	0.000504	0.37245	0.12665	7.19	0.61	9.35
2.4	0.000876	0.09124	0.0501	0.000331	0.000545	0.37263	0.12683	7.14	0.61	9.15
2.6	0.000942	0.09058	0.0492	0.000356	0.000586	0.37284	0.12704	7.08	0.61	9.17
2.8	0.001007	0.08993	0.0484	0.000378	0.000630	0.37290	0.12710	7.07	0.60	9.33
3.0	0.001071	0.08929	0.0476	0.000402	0.000668	0.37296	0.12716	7.05	0.60	9.32
3.2	0.001134	0.08865	0.0468	0.000427	0.000703	0.32303	0.12723	7.03	0.61	9.25
3.4	0.001197	0.08803	0.0459	0.000457	0.000743	0.37311	0.12731	7.01	0.62	9.15
3.6	0.001259	0.08741	0.0453	0.000480	0.000780	0.37317	0.12737	6.99	0.62	9.17
3.8	0.001319	0.08681	0.0447	0.000503	0.000817	0.37325	0.12745	6.97	0.62	9.17
4.0	0.001379	0.08620	0.0440	0.000532	0.000848	0.37334	0.12754	6.95	0.63	9.03

Mean value dissociation degree = 0.61, $K = 9.26 \times 10^{-4}$

$$* \text{ Dissociation degree} = \frac{[\text{dissociated Cu}^{++}]}{[\text{complex formed}]}$$

Next, measurements were done with the same procedure as above, using 0.05 M solution of tartaric acid. Calculated results are shown in Table 2.

Table II.

0.01 M Cu added (ml)	Concen- tration of Cu added (M)	Concen- tration of tartaric acid (M)	Ion concentration cell			Hydrogen electrode			Dis- socia- tion de- gree	K 10 ⁻⁴
			e. m. f. (V)	Concen- tration of dissociat- ed Cu ⁺⁺ (M)	Concen- tration of complex formed (M)	e. m. f. (V)	-Eh (V)	[H ⁺] 10 ⁻³		
0.6	0.000234	0.04883	0.0673	0.000088	0.000147	0.38068	0.13488	5.23	0.59	9.55
0.8	0.000310	0.04850	0.0634	0.000117	0.000193	0.38053	0.13473	5.26	0.61	9.41
1.0	0.000385	0.04808	0.0608	0.000144	0.000241	0.38072	0.13492	5.22	0.60	9.48
1.2	0.000458	0.04771	0.0583	0.000175	0.000283	0.38063	0.13483	5.24	0.62	9.31
1.4	0.000530	0.04735	0.0564	0.000203	0.000327	0.38054	0.13474	5.26	0.62	9.41
1.6	0.000602	0.04699	0.0545	0.000234	0.000368	0.38047	0.13467	5.27	0.64	9.29
1.8	0.000672	0.04664	0.0532	0.000260	0.000412	0.38059	0.13479	5.25	0.63	9.36
2.0	0.000741	0.04630	0.0518	0.000290	0.000451	0.38053	0.13473	5.26	0.64	9.29
2.2	0.000809	0.04596	0.0509	0.000312	0.000497	0.38071	0.13491	5.22	0.63	9.44
2.4	0.000876	0.04562	0.0498	0.000340	0.000536	0.38077	0.13497	5.21	0.63	9.49
2.6	0.000942	0.04529	0.0487	0.000369	0.000573	0.38081	0.13501	5.20	0.64	9.39
2.8	0.001007	0.04496	0.0476	0.000401	0.000609	0.38087	0.13507	5.19	0.66	9.22
3.0	0.001071	0.04464	0.0468	0.000429	0.000641	0.38090	0.13510	5.19	0.67	9.15
3.2	0.001134	0.04433	0.0461	0.000453	0.000677	0.38095	0.13515	5.18	0.67	9.17
3.4	0.001197	0.04401	0.0455	0.000473	0.000727	0.38099	0.13519	5.17	0.65	9.49
3.6	0.001259	0.04371	0.0451	0.000490	0.000770	0.38103	0.13523	5.16	0.64	9.72
3.8	0.001319	0.04340	0.0444	0.000516	0.000804	0.38111	0.13531	5.14	0.64	9.66
4.0	0.001379	0.04310	0.0440	0.000533	0.000847	0.38116	0.13536	5.13	0.63	9.89

Mean value dissociation degree = 0.63, $K = 9.37 \times 10^{-4}$

The dissociation constant shown in Table 1 coincides with the results shown in Table 2. From the above results, the value of the complexibility of copper tartarate is given as follows:

$$K = \frac{[\text{complex}][\text{H}^+]^2}{[\text{tartaric acid}][\text{Cu}^{++}]} = 9.32 \times 10^{-4},$$

which fairly coincides with that mentioned already,⁽²⁾ namely, the order of 10^{-3} .

III. Zinc tartarate complex

1. Reagents and apparatus

a) Reagents

Zinc sulfate was purified by the usual method and recrystallized three times with water. Zn-Hg electrode (7% Zn) was prepared by the same method as Cu-Hg electrode. The same reagents were used as in the case of copper tartarate.

b) Cells

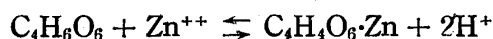
The combination of the ion concentration cell was as follows:



The same cell was used as before, and experiments were carried out in the same way.

2. Experimental results

After the cells had stood in a thermostat, the temperature of which was kept at $25^\circ\text{C} \pm 0.007^\circ\text{C}$, all the electromotive forces of the cells were measured by the usual compensation method. In this reaction, the same equilibrium formula as that between copper and tartaric acid was assumed, namely,



and the complexibility of zinc tartarate was calculated.

Table III.

0.01 M Zn added (ml)	Concentration of Zn added (M)	Concentration of tartaric acid (M)	Ion concentration cell			Hydrogen electrode			Dis-sociation degree	K 10^{-4}
			e. m. f. (V)	Concentration of dissociated Zn^{++} (M)	Concentration of complex formed (M)	e. m. f. (V)	-Eh (V)	$[\text{H}^+] 10^{-3}$		
1.1	0.000422	0.04789	0.0372	0.000231	0.000181	0.38142	0.13562	5.08	1.28	4.22
1.2	0.000458	0.04771	0.0359	0.000256	0.000202	0.38160	0.13580	5.05	1.27	4.22
1.3	0.000494	0.04753	0.0354	0.000267	0.000227	0.38171	0.13591	5.03	1.18	4.52
1.4	0.000530	0.04735	0.0344	0.000288	0.000242	0.38176	0.13596	5.02	1.19	4.47
1.5	0.000566	0.04717	0.0337	0.000301	0.000265	0.38180	0.13600	5.01	1.14	4.68
1.6	0.000602	0.04699	0.0330	0.000322	0.000280	0.38185	0.13605	5.00	1.15	4.63
1.7	0.000636	0.04682	0.0324	0.000338	0.000298	0.38192	0.13612	4.98	1.14	4.67
1.8	0.000672	0.04664	0.0316	0.000359	0.000313	0.38191	0.13611	4.99	1.15	4.66
1.9	0.000706	0.04647	0.0309	0.000379	0.000327	0.38203	0.13623	4.96	1.16	4.57
2.0	0.000741	0.04630	0.0301	0.000403	0.000338	0.38209	0.13629	4.95	1.19	4.43
2.1	0.000775	0.04612	0.0293	0.000430	0.000345	0.38212	0.13632	4.94	1.25	4.24
2.2	0.000809	0.04595	0.0286	0.000454	0.000355	0.38221	0.13641	4.93	1.28	4.14
2.3	0.000842	0.04579	0.0279	0.000479	0.000363	0.38222	0.13642	4.93	1.32	4.02
2.4	0.000876	0.04562	0.0274	0.000498	0.000378	0.38234	0.13654	4.92	1.32	4.03
2.5	0.000909	0.04545	0.0269	0.000518	0.000391	0.38233	0.13653	4.92	1.32	4.02
2.6	0.000942	0.04529	0.0265	0.000535	0.000407	0.38230	0.13650	4.92	1.31	4.07
2.7	0.000975	0.04512	0.0261	0.000551	0.000424	0.38240	0.13660	4.90	1.30	4.09
2.8	0.001007	0.04496	0.0257	0.000569	0.000438	0.38240	0.13660	4.90	1.30	4.11
2.9	0.001039	0.04480	0.0253	0.000587	0.000452	0.38251	0.13671	4.88	1.30	4.09
3.0	0.001071	0.04464	0.0250	0.000601	0.000470	0.38254	0.13674	4.88	1.28	4.17
3.1	0.001103	0.04448	0.0245	0.000625	0.000478	0.38252	0.13672	4.88	1.31	4.09
3.2	0.001135	0.04432	0.0243	0.000634	0.000501	0.38251	0.13671	4.88	1.27	4.24
3.3	0.001166	0.04417	0.0240	0.000649	0.000517	0.38264	0.13684	4.86	1.26	4.26

Mean value dissociation degree = 1.25, $K = 4.29 \times 10^{-4}$

From the observed electromotive forces of the cells, the concentration of every term was calculated which is shown in Table 3. As the average activity coefficient

Table IV.

0.01 M Zn added (ml)	Concentration of Zn added (M)	Concentration of tartaric acid (M)	Ion concentration cell			Hydrogen electrode			Dis- socia- tion de- gre	K 10 ⁻⁴
			e. m. f. (V)	Concen- tration of dissociat- ed Zn ⁺⁺ (M)	Concen- tration of complex formed (M)	e. m. f. (V)	-Eh (V)	(H ⁺) 10 ⁻³		
1.1	0.000422	0.009579	0.0374	0.000229	0.000193	0.40210	0.15630	2.27	1.19	4.53
1.2	0.000458	0.009542	0.0364	0.000246	0.000212	0.40216	0.15636	2.27	1.16	4.65
1.3	0.000494	0.009506	0.0353	0.000270	0.000224	0.40229	0.15649	2.26	1.21	4.46
1.4	0.000530	0.009470	0.0344	0.000289	0.000241	0.40234	0.15654	2.25	1.20	4.46
1.5	0.000566	0.009434	0.0337	0.000305	0.000261	0.40235	0.15655	2.25	1.17	4.59
1.6	0.000602	0.009399	0.0329	0.000326	0.000276	0.40239	0.15659	2.25	1.18	4.52
1.7	0.000636	0.009363	0.0323	0.000341	0.000295	0.40241	0.15661	2.24	1.16	4.64
1.8	0.000672	0.009328	0.0315	0.000362	0.000310	0.40249	0.15669	2.24	1.17	4.61
1.9	0.000706	0.009294	0.0308	0.000381	0.000325	0.40259	0.15679	2.23	1.17	4.56
2.0	0.000741	0.009250	0.0304	0.000395	0.000346	0.40263	0.15683	2.22	1.14	4.71
2.1	0.000775	0.009225	0.0298	0.000414	0.000361	0.40277	0.15697	2.21	1.15	4.62
2.2	0.000809	0.009191	0.0291	0.000436	0.000363	0.40280	0.15700	2.21	1.20	4.42
2.3	0.000842	0.009157	0.0285	0.000457	0.000385	0.40294	0.15714	2.20	1.19	4.45
2.4	0.000876	0.009124	0.0280	0.000475	0.000401	0.40293	0.15713	2.20	1.18	4.48
2.5	0.000909	0.009091	0.0276	0.000491	0.000418	0.40301	0.15721	2.20	1.17	4.53
2.6	0.000942	0.009058	0.0272	0.000506	0.000436	0.40314	0.15724	2.19	1.16	4.56
2.7	0.000975	0.009025	0.0268	0.000522	0.000453	0.40315	0.15735	2.19	1.15	4.61
2.8	0.001007	0.008993	0.0265	0.000534	0.000473	0.40326	0.15746	2.18	1.13	4.68
2.9	0.001039	0.008960	0.0262	0.000547	0.000492	0.40342	0.15762	2.16	1.11	4.68
3.0	0.001071	0.008928	0.0258	0.000564	0.000507	0.40340	0.15760	2.16	1.11	4.69
3.1	0.001103	0.008897	0.0255	0.000578	0.000525	0.40352	0.15772	2.17	1.10	4.80

Mean value dissociation degree = 1.16, $K = 4.58 \times 10^{-4}$

of 0.01 M zinc sulfate solution, the value 0.421 in the Landolt's table was used.

Next, measurements were done with the same procedure as above, using 0.01 M solution of tartaric acid. The calculated results are shown in Table 4. The complexibility of zinc tartarate shown in Table 3 coincides with the result shown in Table 4. From the above results, the value of the complexibility of zinc tartarate was determined as follows:

$$K = \frac{[\text{complex}][\text{H}^+]^2}{[\text{tartaric acid}][\text{Zn}^{++}]} = 4.44 \times 10^{-4}$$

Summary

(1) From the standpoint of the analytical chemistry, the author studies complexibilities of various ions applied for analytical purpose, using ion concentration cell, hydrogen electrode and others. In this report, the results obtained for copper and zinc tartarates are given.

(2) Combinations of the ion concentration cells used were as follows.



The concentrations of hydrogen ions were measured, using the hydrogen electrode.

(3) The complexibilities of copper and zinc tartarates were calculated to be 9.32×10^{-4} and 4.44×10^{-4} , respectively.

Acknowledgement

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