

Tartrate Complex of Cadmium(II)

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Tartrate complex of cadmium(II) has been studied by pH titration and conductometric measurement methods. At comparatively lower pH the reaction between cadmium ion and tartaric acid results in the formation of a neutral complex C with the liberation of two protons. With increasing pH the neutral complex C undergoes stepwise dissociation resulting in the formation of anionic complexes C_1^- and C_2^{2-} . The equilibrium constant values of the reactions $Cd^{2+} + H_2T \rightleftharpoons C + 2H^+$, $C \rightleftharpoons C_1^- + H^+$, $C_1^- \rightleftharpoons C_2^{2-} + H^+$, $Cd^{2+} + HT^- \rightleftharpoons C + H^+$, and $Cd^{2+} + T^{2-} \rightleftharpoons C$ are calculated and found to be 6.46×10^{-6} , 2.59×10^{-9} , 5.23×10^{-11} , 3.80×10^{-2} and 73.2 respectively.

Shin Suzuki¹ from e.m.f. measurements reported the value for the equilibrium constant as $K = [\text{Complex}][H^+]^2/[Tartaric\ acid][Cd^{2+}] = 1.2 \times 10^{-3}$.

V. K. Zolotukhin and co-workers² from polarographic measurements reported that cadmium ion co-ordinates with one tartrate ion in the pH range 5.3 to 10.0, the instability constant in the pH range 5.3 to 8.0 and at pH 10.0 being 1.5×10^{-3} and 4.07×10^{-4} respectively.

I. A. Korshunov and co-workers³ employing ion exchange method reported the formation of $[Cd(C_4H_4O_6)_2]^{2-}$, the instability constant value being 3.25×10^{-5} .

P. Kovalenko⁴ used potentiometric and polarographic methods and reported that cadmium co-ordinates with two tartrate ions in the pH range 4.0 to 8.0 with K value changing in the indicated interval from 4.20×10^{-4} to 5.01×10^{-4} .

Other works reported on cadmium tartrate complex^{5,6,7,8} indicate the formation of both 1 : 1 and 1 : 2 complexes.

EXPERIMENTAL

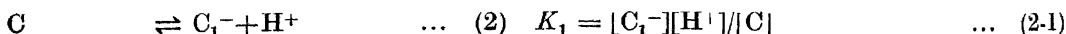
Five pH and two conductometric titrations were performed at $33 \pm 1^\circ$ the details of which are recorded in Table 1.

All chemicals used were of B.D.H. (Analar) grade and double distilled water was used to prepare the solutions.

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RESULTS AND DISCUSSION

The reactions taking place in experiments 1 and 2 in the pH ranges 3.6 to 5.8, 6.0 to 8.5 and 9.0 to 9.5 may be represented respectively in the following manner



In experiment 1 where the metal ligand ratio is 1 : 1.5 a precipitate was formed beyond pH 7.5 during the pH titration. The precipitate was insoluble in excess sodium hydroxide and the analysis indicated it to be cadmium hydroxide which is in agreement with the observations made by O. I. Komolev and Z. G. Galanets⁹. The precipitation however could be avoided upto pH 9.5 in experiment 2 by maintaining a higher metal ligand ratio (1 : 5). All calculations pertaining to the determination of K , K_1 and K_2 were made as discussed in case of tartrate complexes of manganese(II)¹⁰ and cobalt(II)¹¹. The values of K and K_1 were calculated from experiment 1 and that of K_2 was obtained from experiment 2 since it is not possible to calculate the value of K_2 from experiment 1 due to the precipitation of cadmium hydroxide. The value of K and K_1 were also calculated from experiment 2 which is found to be in agreement with those obtained from experiment 1 thus indicating the formation of 1 : 1 complex only. The mean value of K , K_1 and K_2 thus obtained are 6.46×10^{-6} , 2.59×10^{-9} and 5.23×10^{-11} respectively and are recorded in tables 2 and 3.

In experiment 3 since the pH decreases with increasing addition of sodium bitartrate, the reaction taking place can be represented as



the formation of neutral complex being assumed as the pH of the system always remains below 5.8 (the value below which the neutral complex is formed in experiments 1 and 2). The value of K_3 was calculated as discussed in case of cobalt tartrate complex¹¹ and is recorded in table 4, the mean value thus obtained being 3.80×10^{-2} .

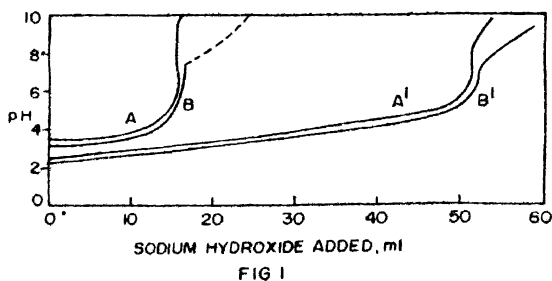


TABLE 1,
(*pH titrations*)).

	Experiment	Contents in g.mole	Total volume	Titrated against	Results
1. a)	Sodium Perchlorate Tartaric Acid	1.0×10^{-2} 7.5×10^{-4}	200 ml.	0.9615 <i>M</i> /10 Sodium Hydroxide	Fig. 1, Curve A
b)	Sodium Perchlorate Tartaric Acid Cadmium Sulphate	1.0×10^{-2} 7.5×10^{-4} 5.0×10^{-4}	-do-	-do-	Fig. 1, Curve B
2. a)	Sodium Perchlorate Tartaric Acid	1.0×10^{-2} 2.5×10^{-3}	-do-	-do-	Fig. 1, Curve A ¹
b)	Sodium Perchlorate Tartaric Acid Cadmium Sulphate	1.0×10^{-2} 2.5×10^{-3} 5.0×10^{-4}	-do-	-do-	Fig. 1, Curve B ¹
3. a)	Sodium Perchlorate	1.0×10^{-2}	100 ml.	<i>M</i> /20 Sodium Bitartrate.	Fig. 2, Curve A
b)	Sodium Perchlorate Cadmium Sulphate	1.0×10^{-2} 5.0×10^{-4}	-do-	-do-	Fig. 2, Curve B
4. a)	Sodium Perchlorate	1.0×10^{-2}	-do-	<i>M</i> /20 Sodium Tartrate.	Fig. 3, Curve A
b)	Sodium Perchlorate Cadmium Sulphate	1.0×10^{-2} 5.0×10^{-4}	-do-	-do-	Fig. 3, Curve B
5. a)	Sodium Perchlorate Sodium Tartrate	1.0×10^{-2} 2.5×10^{-3}	-do-	0.9615 <i>M</i> /10 Sodium Hydroxide	Fig. 4, Curve A
b)	Sodium Perchlorate Sodium Tartrate Cadmium Sulphate	1.0×10^{-2} 2.5×10^{-3} 5.0×10^{-4}	-do-	-do-	Fig. 4, Curve B

(Conductometric titrations)

6.	Sodium Tartrate	5.0×10^{-4}	-do-	<i>M</i> /20 Sodium Hydroxide.	Fig. 5.
	Cadmium Sulphate	5.0×10^{-5}			
7.	Concentration of Sodium Tartrate	0.01 <i>M</i>			
	Concentration of Cadmium Sulphate	0.01 <i>M</i>	-do-		Fig. 6.
	Total concentration	0.03 <i>M</i> (Curve A) 0.02 <i>M</i> (Curve B) 0.01 <i>M</i> (Curve C)			

TABLE 2

pH	$\Delta[\text{NaOH}] \times 10^5$	$-\Delta[\text{T}] \times 10^5$	$[\text{CdSO}_4] \times 10^3$	a/b	n	$[\text{C}] \times 10^5$	$[\text{Cd}^{2+}] \times 10^3$	$[\text{H}_2\text{T}] \times 10^5$	$K \times 10^6$	$K_1 \times 10^9$
3.6	13.50	0.50	2.405	1.03	1.08825	14.44	2.2606	52.64	7.660	—
4.0	13.10	0.50	2.373	1.337	1.39501	20.76	2.1654	17.11	5.604	—
4.4	12.80	0.40	2.351	1.613	1.67020	34.73	2.0037	4.155	6.616	—
5.0	4.20	0.20	2.330	1.872	1.89163	35.74	1.9726	0.3607	5.023	—
5.8	1.00	0.10	2.322	1.977	1.982157	52.07	1.8010	0.009585	7.560	—
7.0	6.10	0.30	2.319	1.998	2.02689	—	—	—	—	2.764
7.2	8.40	0.30	2.318	1.999	2.03783	—	—	—	—	2.480
7.5	15.80	0.70	2.316	2.000	2.07427	—	—	—	—	2.537

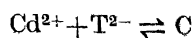
TABLE 3

pH	$\Delta[\text{NaOH}] \times 10^5$	$-\Delta[\text{T}] \times 10^5$	$[\text{CdSO}_4] \times 10^3$	a/b	n	$[\text{C}] \times 10^5$	$[\text{Cd}^{2+}] \times 10^3$	$[\text{H}_2\text{T}] \times 10^5$	$K \times 10^6$	$K_1 \times 10^9$	$K_2 \times 10^{11}$
3.6	35.00	4.00	2.211	1.030	1.2070	40.33	1.8077	161.70	8.702	—	—
4.0	31.00	4.00	2.127	1.337	1.5078	54.83	1.5787	51.51	6.742	—	—
5.0	10.00	1.00	2.012	1.872	1.9310	92.74	1.0846	1.05	8.147	—	—
6.0	3.00	5.00	1.991	1.986	2.00605	—	—	—	—	6.088	—
7.0	7.00	6.00	1.987	1.998	2.03926	—	—	—	—	4.087	—
8.0	59.00	7.50	1.972	2.000	2.3753	—	—	—	—	6.006	—
8.5	109.00	14.30	1.957	2.000	2.7031	—	—	—	—	7.491	—
9.0	161.00	20.80	1.942	2.000	3.0430	—	—	—	—	—	4.493
9.2	166.00	21.60	1.938	2.000	3.0790	—	—	—	—	—	5.412
9.5	177.00	23.00	1.932	2.000	3.1550	—	—	—	—	—	5.799

TABLE 4

pH	$[\text{T}] \times 10^3$	$[\text{CdSO}_4] \times 10^3$	$[\text{HT}^-] \times 10^3$	$[\text{C}] \times 10^3$	$[\text{Cd}^{2+}] \times 10^3$	$K_3 \times 10^2$
3.50	1.456	4.855	0.7238	0.366	4.489	3.562
3.45	2.381	4.762	1.231	0.513	4.249	3.534
3.40	3.271	4.673	1.666	0.712	3.961	4.293

In experiment 4 since the pH of the system increases continuously with increasing addition of sodium tartrate, the reaction taking place below the 1 : 1 equivalence point may be represented as



$$\dots (5) \quad K_4 = [\text{C}] / ([\text{Cd}^{2+}][\text{T}^{2-}])$$

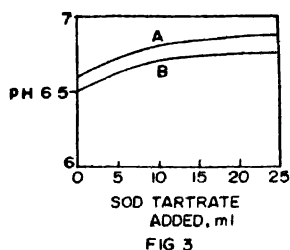
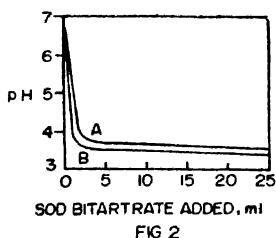
... (5-1)

However as the pH of the system is above 5.8, there is every probability of the neutral complex C dissociating to form complex C_1^- according to equation 2 and this has been taken into account during the determination of the value of K_4 . The value of K_4 was calculated as discussed in case of manganese tartrate complex¹⁰ and is recorded in table 5, the mean value being 73.2.

TABLE 5

pH	$[T]$ $\times 10^3$	$[CdSO_4]$ $\times 10^3$	$[HT^-]$ $\times 10^5$	$[C_1^-]$ $\times 10^5$	$[C]$ $\times 10^5$	$[Cd^{2+}]$ $\times 10^3$	$[T^{2-}]$ $\times 10^3$	K_4 $\times 10^{-1}$
6.64	2.830	4.718	0.7194	0.7423	65.66	4.054	2.167	7.474
6.65	3.271	4.673	0.8221	0.8445	73.00	3.935	2.533	7.323
6.66	3.704	4.630	0.9194	0.9413	79.50	3.826	2.899	7.166

In experiment 5 the metal ligand ratio is 1 : 5 and the formation of the complex can be assumed to be complete. The reactions represented by equations 2 and 3 can therefore be assumed to be taking place here also. The determination of K_1 and K_2 which represent the equilibrium constants of the above reactions were carried out as was done in case of



manganese tartrate complex¹⁰ and the values are recorded in tables 6 and 7 respectively. The mean values of K_1 and K_2 thus obtained are 6.96×10^{-9} and 3.15×10^{-11} respectively which is in agreement with those obtained in experiments 1 and 2.

TABLE 6

pH	$[NaOH]$ $\times 10^3$	$[CdSO_4]$ $\times 10^3$	$[T]$ $\times 10^3$	$[C_1^-]$ $\times 10^3$	$[C]$ $\times 10^3$	K_1 $\times 10^9$
7.5	0.8576	4.957	24.78	0.8667	4.090	6.701
8.0	2.0230	4.895	24.46	2.0260	2.869	7.062
8.5	3.3400	4.826	24.13	3.3410	1.485	7.114

TABLE 7

pH	$[NaOH]$ $\times 10^3$	$[CdSO_4]$ $\times 10^3$	$[C_2^{2-}]$ $\times 10^3$	$[C_1^-]$ $\times 10^3$	K_2 $\times 10^{11}$
9.0	4.883	4.746	0.137	4.609	2.973
9.2	5.013	4.741	0.272	4.469	3.841
9.5	5.099	4.736	0.363	4.373	2.625

It can be shown that $K_4 \times k_1 \times k_2 = K$, where k_1 and k_2 represent the first and second dissociation constants for tartaric acid. Substitution of the respective values gives the value of K to be 5.56×10^{-6} which is in agreement with that obtained in experiment 1. It can also be shown that $K_3 \times k_1 = K$ and substitution of the respective values gives the value of K to be 41.8×10^{-6} as compared with the value of $K = 6.46 \times 10^{-6}$ in experimental.

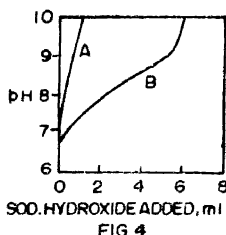


FIG 4

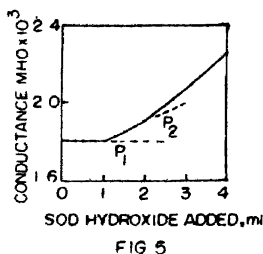


FIG 5

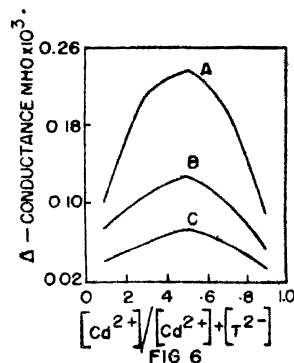


FIG 6

Conductometric Titrations : In experiment 6 the breaks at P_1 and P_2 correspond to the addition of one and two equivalents of sodium hydroxide per g. atom of cadmium respectively thus indicating the neutralisation of the first and second proton liberated by the dissociation of the neutral complex C. The existence of complexes C, C_1^- and C_2^{2-} is thus confirmed.

In experiment 7 the peak corresponding to the values of 0.5 for the ratio $[Cd^{2+}]/[Cd^{2+}] + [T^{2-}]$ obtained by Job's method further confirms the formation of 1 : 1 complex only.

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