CCA-526

545.33:546.48:546.815

Note

Polarographic Determination of Stability Constants of Glycerato Complexes of Cadmium and Lead

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Received June 24, 1968

Stability constants of glycerato complexes of cadmium and lead were determined by the polarographic method. Measurements were performed in buffer solutions of sodium salt of DL-glyceric acid. The concentration of the glyceric acid in the buffer solutions was constant: 0.07 *M* for cadmium, and 0.05 *M* for lead. The ionic strenght of solutions was 2 and it was kept constant by means of sodium perchlorate. The following cumulative stability constants were obtained: Cadmium: $\beta_1 = 40$, $\beta_2 = 130$, $\beta_3 = 340$, $\beta = 210$. Lead: $\beta_1 = 340$, $\beta_2 = 5.7 \times 10^3$, $\beta_3 = 2.8 \times 10^3$, $\beta_4 = 4.8 \times 10^3$.

Literature data about the investigation of metal glycerato complexes are very scarce[1]. However, the investigation of metal glycerato complexes from the point of view of the chemistry of complex compounds is interesting not only because of the fact that glyceric acid is biologically important, but also in order to obtain a closer insight into the influence of the hydroxyl group in monocarboxylic acids, or their anions, on the composition and stability of the corresponding complexes[2]. Therefore the determination of the stability constants of glycerato complexes of cadmium and lead was performed by the polarographic method. Buffer solutions with constant limiting concentration of glyceric acid were used, at which the hydrolysis of cadmium and lead glycerato complexes does not yet occur[2,3]: 0.07 *M* for cadmium, and 0.05 *M* for lead. The ionic strength of the solutions was 2 and it was kept constant by means of sodium perchlorate.

EXPERIMENTAL

Polarographic measurements were made on the polarograph Polariter PO4 Radiometer in the way described in a previous paper[4]. All half-wave potentials are given with respect to the calomel electrode with a saturated solution of sodium chloride. All measurements were carried out under constant temperature of 25 ± 0.1^0 C. The concentration of cadmium and lead in investigated solutions was 0.5 m*M*. By the addition of sodium perchlorate the ionic strength of the solutions was kept at a constant value of 2. The values $m^{2/3} t^{1/6}$ of the capillary employed at the half-wave potentials of lead and cadmium in the buffer solutions with the concentration of sodium glycerate of 0.01 *M* were: 2.420 for lead, and 2.411 for cadmium.

The buffer solutions were prepared from 65% DL-glyceric acid Fluka, *purum*. For that purpose the saponification of glyceric acid with a small excess of sodium hydroxyde was performed by heating on a water bath for 15 minutes (in order to destroy the lactons present). The excess of sodium hydroxide was then determined by potentiometric titration. From the alkaline solution of sodium glycerate thus obtained, buffer solutions were prepared by addition of the required quantity of

perchloric acid, so that the concentration of the liberated glyceric acid was constant: 0.07 *M* in cadmium solutions, and 0.05 *M* in lead solutions. At such concentrations of glyceric acid in the buffer no hydrolysis of complexes ocurred in the solutions of sodium glycerate in the concentration range from 0.01 to 1.8 *M*[2,3].

The half-wave potentials of cadmium and lead in the buffer solutions of glycerate were corrected to zero concentration of glyceric acid[2,3]. The half-wave potentials of the »free« ions of cadmium and lead were determined in slightly acidic solutions of sodium perchlorate (2*M*) by extrapolation to zero concentration of perchloric acid.

RESULTS AND DISCUSSION

Tables I and II represent the results of measurements and give cumulative (β_j) and stepwise (K_j) stability constants determined by the graphic method of DeFord and Hume[5]. The extrapolated values for the cumulative stability constants were checked to give the best fit by the method of successive approximations[6]. The confidence limits of the extrapolated constants β_j deduced from the dissipation of the experimental points depending on the precision of the half-wave potential measurements ($\pm$ 1 to 2 mV) are within $\pm$ 10%.

In Table III the obtained values for stability constants of monoligand (K_1) glycerato complexes are compared with those of glycolato[8] and lactato[2] complexes, which were also determined by the polarographic method under analogous experimental conditions. It is seen that the order of stability of monoligand complexes as measured by K_1 is: glycolate < lactate < glycerate. It is evident that the stability of glycerato complexes is not determined by

TABLE I

Cadmium Glycerate Solutions

[L] M	$E_{1/2}$ V	i_d μA	F_0 ([L])	F_1 ([L])	F_2 ([L])	F_3 ([L])	F_4 ([L])
0	— 0.5540	4.00	—	—	—	—	—
0.01	— 0.5592	3.92	1.42	42.2	—	—	—
0.02	— 0.5617	3.77	1.84	42.0	—	—	—
0.03	— 0.5645	3.77	2.29	42.8	—	—	—
0.04	— 0.5664	3.68	2.72	43.0	—	—	—
0.06	— 0.5699	3.59	3.66	44.4	—	—	—
0.08	— 0.5732	3.56	4.78	47.2	—	—	—
0.10	— 0.5771	3.64	6.34	53.4	134	—	—
0.20	— 0.5893	3.47	17.6	81.3	206	383	208
0.30	— 0.5980	3.28	36	116	255	416	254
0.40	— 0.6046	3.00	66	162	305	437	243
0.50	— 0.6122	3.15	113	225	369	473	267
0.60	— 0.6172	3.04	173	288	413	471	219
0.70	— 0.6222	3.00	260	370	471	487	210
0.80	— 0.6263	2.86	376	468	535	507	208
0.90	— 0.6303	2.80	524	580	601	523	212
1.00	— 0.6346	2.83	724	723	683	553	215
1.10	— 0.6366	2.46	978	879	763	575	214
1.20	— 0.6405	2.59	1260	1049	841	593	210
1.30	— 0.6435	2.54	1621	1246	928	614	211
1.40	— 0.6464	2.52	2045	1460	1015	632	208
1.60	— 0.6510	2.33	3170	1981	1213	677	211
1.80	— 0.6552	2.13	4814	2674	1464	741	223
				$\beta_1 = 40$	$\beta_2 = 130$	$\beta_3 = 340$	$\beta_4 = 210$
				$K_1 = 40$	$K_2 = 3.3$	$K_3 = 2.6$	$K_4 = 0.6$

the degree of basic character of the ligand (increasing in the order: glycerate < < glycolate < lactate), but by the presence of another hydroxyl group. The higher complex stability with the dihydroxymonocarboxylate ions is probably due to a certain, though very small, chelate effect.

TABLE II

Lead Glycerate Solutions

[L] M	$E_{1/2}$ V	i_d μA	F_0 ([L])	F_1 ([L])	F_2 ([L])	F_3 ([L])	F_4 ([L])
0	— 0,3670	4.15	—	—	—	—	—
0.01	— 0.3868	3.94	4.73	373	—	—	—
0.02	— 0.3953	3.77	9.38	419	—	—	—
0.03	— 0.4017	3.89	15.1	469	—	—	—
0.04	— 0.4063	3.83	21.8	519	—	—	—
0.06	— 0.4136	3.67	40.2	653	—	—	—
0.08	— 0.4196	3.67	64.1	789	5614	—	—
0.10	— 0.4236	3.44	93.5	925	5854	—	—
0.20	— 0.4400	3.47	333	1662	6610	4550	—
0.30	— 0.4491	3.15	749	2494	7179	4930	—
0.40	— 0.4573	3.23	1389	3470	7825	5312	—
0.50	— 0.4638	3.22	2303	4604	8530	5660	—
0.60	— 0.4685	3.06	3504	5838	9156	5760	4933
0.70	— 0.4733	3.03	5164	7375	10051	6216	4880
0.80	— 0.4772	2.97	7115	8892	10690	6240	4300
0.90	— 0.4813	2.88	10098	11219	12088	7099	4777
1.00	— 0.4845	2.75	13605	13604	13264	7564	4764
1.10	— 0.4878	2.67	17969	16334	14541	8037	4761
1.20	— 0.4908	2.62	23300	19416	15897	8497	4748
1.30	— 0.4936	2.55	27997	21535	16320	8170	4131
1.40	— 0.4964	2.53	37327	26662	18810	9364	4689
1.60	— 0.5013	2.38	58213	36383	22527	10517	4823
1.80	— 0.5055	2.22	86778	48209	26594	11608	4893
				$\beta_1 = 340$	$\beta_2 = 5700$	$\beta_3 = 2800$	$\beta_4 = 4800$
				$K_1 = 340$	$K_2 = 17$	$K_3 = 0.5$	$K_4 = 1.7$

TABLE III

Stability Constants of Monoligand Complexes (K_1)

Ligand \ Metal ion	Cd^{2+}	Pb^{2+}	H^+ Log K_1[7,1]
Glycerate	40	340	3.517
Glycolate	26[8]	80[8]	3.712
Lactate	21[3]	140[3]	3.739

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IZVOD

Polarografsko određivanje konstanata stabilnosti glicerato-kompleksa kadmiuma i plumbuma

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Određene su konstante stabilnosti glicerato-kompleksa kadmiuma i plumbuma polarograskom metodom. Mjerenja su izvršena u puferskim otopinama natrijumove soli DL-glicerinske kiseline. Koncentracija glicerinske kiseline u puferu bila je konstantna i to 0,07 *M* kod kadmiuma i 0,05 *M* kod plumbuma. Ionska jakost otopina bila je 2 i održavana je konstantnom pomoću natrium-perklorata. Dobivene su ove vrijednosti kumulativnih konstanata stabilnosti:

Kadmium: $\beta_1 = 40$, $\beta_2 = 130$, $\beta_3 = 340$, $\beta_4 = 210$.

Plumbum: $\beta_1 = 340$, $\beta_2 = 5.7 \times 10^3$, $\beta_3 = 2.8 \times 10^3$, $\beta_4 = 4.8 \times 10^3$.

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Primljeno 24. lipnja 1968.