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Polarographic Investigations of Some Metal Monocarboxylato Complexes. II. Monocarboxylato Complexes of Zinc

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The stability constants of zinc monocarboxylato complexes have been determined by the polarographic method of DeFord and Hume in water solutions of a constant ionic strength 2 and a constant monocarboxylic acid concentration of 2 M. The examinations were carried out in the monocarboxylate concentration range up to 2 M. The following values for cumulative stability constants were obtained: formato complexes $\beta_1 = 4$, $\beta_2 = 3$, $\beta_3 = 4$, $\beta_4 = 6$; acetato complexes $\beta_1 = 4$, $\beta_2 = 9$, $\beta_3 = 12$, $\beta_4 = 31$; propionato complexes $\beta_1 = 8$, $\beta_2 = 2$, $\beta_3 = 15$, $\beta_4 = 43$; butyrato complexes $\beta_1 = 7$, $\beta_2 = 3$, $\beta_3 = 26$, $\beta_4 = 103$.

Until recently the zinc monocarboxylato complexes have been sparingly investigated.¹⁻⁴ Various investigation methods under different experimental conditions have given different results. For this reason the monocarboxylato complexes of zinc as well as those of lead⁵ were investigated by the polarographic method under constant experimental conditions, *i. e.* a constant ionic strength 2 of the solution and a constant concentration of 2 M monocarboxylic acid (formic, acetic, propionic and butyric). For the calculation of the stability constants from the experimental data the same method of DeFord and Hume⁶ was employed.

EXPERIMENTAL

The polarographic equipment and the polarographic cell were the same as described in the previous paper.⁵ In the investigated solutions, at a potential of 1 volt *versus* the saturated calomel electrode, the values $m^{2/3} t^{1/6}$ of the capillaries employed were: 2.45 (for formates), 2.48 (for acetates), 2.57 (for propionates) and 2.28 $\text{mg}^{2/3}\text{sec}^{-1/2}$ (for butyrates).

The measurements of the diffusion current (i_d) by usual methods, were rendered difficult by the steep slope of the limiting current, *i. e.* the plateau of the polarographic wave, owing to the hydrogen discharge in acid solutions. Consequently the value for the diffusion current was obtained by tracing a tangent to the curve at an angle of 45° and measuring (at the half-wave potential) the vertical distance between the point of contact of this tangent and the residual current.⁷ The diffusion current constant (I) of the *free* ion, the half-wave potential ($E_{1,2}$) of the complex and the *free* ion were determined in the same way as described in the previous paper.⁵ The half-wave potentials were reproducible in duplicate experiments to ± 2 mV. In the propionate and butyrate solutions of the concentration range from 0 to 0.1 M the half-wave potential is shifted to more positive values with the increase in the concentration of the complex forming substance. Only with propionate and butyrate concentrations higher than 0.1 M, a shift of the half-wave potential to more negative values was

observed with the increase of the salt concentration. This fact made the determination of the half-wave potential of the *free* ion in the propionate and butyrate solutions somewhat difficult. All electrode processes were polarographically reversible.

All chemicals used for the preparation of solutions were chemically pure. The concentration of zinc as the corresponding monocarboxylic acid salt was 0.4 mM. The concentration of the monocarboxylates (sodium formate, acetate, propionate and *n*-butyrate, respectively) was varied from 0 to 2 M. The concentration of monocarboxylic acid was held constant at 2 M, to prevent a possible hydrolysis of the complexes. It has been found that with the increase in the concentration of the monocarboxylic acid the half-wave potential of zinc is shifted to more positive values and the more so the lower the monocarboxylate concentration. The ionic strength of the solutions was kept at a constant value 2 by addition of the corresponding amount of sodium perchlorate. Gelatin was not present in the examined solutions.

RESULTS AND DISCUSSION

The constitution of the complexes, the cumulative stability constants (β_j) and the consecutive constants (K_j) were determined by the graphic method of DeFord and Hume⁶, as described in the previous paper.⁵ On the basis of the dissipation of the experimental points and the measurement precision of the half-wave potential (which was ± 2 mV), it can be concluded that the obtained values for stability constants have an accuracy within $\pm 20\%$.

TABLE I
Formate Solutions

[L] M	$E_{1/2}$ V	<i>I</i>	F_0 ([L])	F_1 ([L])	F_2 ([L])	F_3 ([L])	F_4 ([L])
0.000	-0.968	2.70	—	—	—	—	—
0.011	-0.969	2.85	1.01	—	—	—	—
0.061	-0.972	2.80	1.32	5.25	—	—	—
0.08	-0.971	2.72	1.25	3.13	—	—	—
0.10	-0.974	2.82	1.57	5.70	—	—	—
0.20	-0.977	2.80	1.96	4.80	4.00	—	—
0.40	-0.984	2.85	3.32	5.80	4.50	—	—
0.60	-0.991	2.76	5.91	8.18	6.97	6.62	4.37
0.80	-0.999	2.73	11.0	12.8	10.9	9.93	7.41
1.00	-1.005	2.82	17.2	16.2	12.2	9.21	5.21
1.20	-1.012	2.76	30.4	24.5	17.0	11.7	6.42
1.40	-1.018	2.63	50.5	35.4	22.4	13.9	7.06
1.60	-1.024	2.66	80.9	50.0	28.3	16.1	7.50
1.80	-1.025	2.60	84.1	46.3	23.5	11.4	4.15
2.00	-1.028	2.60	113	55.9	25.9	11.5	3.74
			$\beta_0 = 1$	$\beta_1 = 4$ $K_1 = 4$	$\beta_2 = 3$ $K_2 = 0.75$	$\beta_3 = 4$ $K_3 = 1.3$	$\beta_4 = 6$ $K_4 = 1.5$

In the tables I-IV the measurement results for the formate, acetate, propionate and *n*-butyrate solutions are shown. All half-wave potentials are given *versus* calomel electrode with a saturated solution of sodium chloride. Cumulative stability constants of formate complexes are of the same order of magnitude

TABLE II
Acetate Solutions

$\frac{[L]}{M}$	$\frac{E_{1/2}}{V}$	I	$F_0([L])$	$F_1([L])$	$F_2([L])$	$F_3([L])$	$F_4([L])$
0.000	-0.966	2.34	—	—	—	—	—
0.01	-0.967	2.35	—	—	—	—	—
0.03	-0.969	2.56	—	—	—	—	—
0.05	-0.971	2.54	1.06	—	—	—	—
0.10	-0.973	2.50	1.53	5.84	—	—	—
0.20	-0.979	2.52	2.30	6.50	12.5	—	—
0.30	-0.984	2.51	3.77	9.26	17.8	—	—
0.40	-0.990	2.51	6.40	13.5	23.8	—	—
0.50	-0.996	2.50	9.40	16.4	24.8	31.6	—
0.60	-1.001	2.22	15.2	23.7	32.8	39.7	—
0.70	-1.005	2.33	20.6	28.0	34.7	36.7	—
0.80	-1.009	2.22	29.4	35.5	39.4	38.0	32.5
0.90	-1.014	2.22	41.2	44.6	45.1	40.1	31.2
1.00	-1.018	2.18	57.3	65.3	61.3	—	—
1.10	-1.021	2.02	83.0	74.5	64.1	—	—
1.20	-1.024	2.22	93.4	77.0	60.8	—	26.0
1.30	-1.027	2.04	131	99.9	73.8	49.9	29.2
1.40	-1.030	2.04	166	118	81.4	51.7	28.4
1.50	-1.034	2.00	226	150	97.3	58.9	31.3
1.60	-1.037	2.00	275	171	104	59.4	29.7
1.70	-1.039	1.96	347	204	118	64.1	30.7
1.80	-1.042	1.90	450	247	135	70.0	32.2
1.90	-1.044	1.93	516	271	141	69.5	30.3
2.00	-1.047	1.82	680	339	168	79.5	33.8
			$\beta_0 = 1$	$\beta_1 = 4$ $K_1 = 4$	$\beta_2 = 9$ $K_2 = 2.3$	$\beta_3 = 12$ $K_3 = 1.3$	$\beta_4 = 31$ $K_4 = 2.6$

as those found by H. M. Hershenson, R. Thompson Brooks, and M. E. Murphy⁴, only the first and fourth constant (β_1 and β_4) being in good numerical agreement. In accordance with the above mentioned authors it has been found that the investigated solutions contain complexes with a maximum number of 4 monocarboxylate ligands. In the acetate, propionate and butyrate solutions as well, only complexes with a maximum of 4 monocarboxylate ligands have been found in contradiction to the investigation results of H. Brintzinger *et al.*² The values for the first cumulative stability constants (β_1) for acetate, propionate and butyrate complexes are somewhat lower than those found by R. K. Cannan and A. Kibrick.³ Besides, in contradiction with our results, according to these authors the acetate complex ($\beta_1 = 10.7$) is the strongest, the propionate ($\beta_1 = 10.2$) and butyrate ($\beta_1 = 10.0$) complexes being weaker, although the difference in the numerical value of the stability constants is very small.

The zinc monocarboxylate complexes are very weak in general, presumably on account of the saturated electronic configuration of the zinc ion or its low polarisability ($\alpha = 0.5 \times 10^{-24} \text{ cm}^3$).⁸ Regarding the bond strength of the first

TABLE III
 Propionate Solutions

[L] M	$E_{1,2}$ V	I	$F_0([L])$	$F_1([L])$	$F_2([L])$	$F_3([L])$	$F_4([L])$
0.000	-0.976	2.44	—	—	—	—	—
0.01	-0.998	2.44	—	—	—	—	—
0.03	-0.989	2.42	—	—	—	—	—
0.06	-0.984	2.35	1.87	—	—	—	—
0.10	-0.985	2.34	2.04	—	—	—	—
0.20	-0.988	2.14	2.84	9.22	6.10	20.5	—
0.40	-0.999	2.18	6.59	14.0	15.0	32.5	43.7
0.60	-1.008	1.88	15.3	23.9	26.5	40.8	43.0
0.80	-1.016	1.71	32.6	39.6	39.5	46.9	40.0
1.00	-1.026	1.66	70.4	69.4	61.4	59.4	44.4
1.20	-1.032	1.51	129	106	81.7	66.4	42.8
1.40	-1.040	1.38	270	193	131	92.4	54.5
1.60	-1.048	1.34	317	198	118	72.5	42.2
1.80	-1.052	1.22	724	402	219	120	58.3
2.00	-1.057	1.18	1177	588	290	143	64.0
			$\beta_0 = 1$	$\beta_1 = 8$ $K_1 = 8$	$\beta_2 = 2$ $K_2 = 0.25$	$\beta_3 = 15$ $K_3 = 7.5$	$\beta_4 = 43$ $K_4 = 2.8$

ligand the formate and acetate complexes are of the same stability and so are the propionate and butyrate complexes. However, the complexes of this last group are evidently more stable than those of the first. This is indeed the difference between the formate complexes of lead⁵ and zinc and their other corresponding monocarboxylate complexes. The reason is probably the higher ionic potential ($z/r = 2.9$)⁸, or the greater polarization power of the smaller zinc ion, so that the formate ion is stronger polarized by zinc than by lead. The high ionic potential and the free 4s and 4p orbitals of the zinc ion allow the coordination of 4 monocarboxylate ions in contrast to the lead ion which coordinates only with three of these ions.⁵ The increase of the third and fourth consecutive stability constant (K_3 and K_4) for formates and of the fourth constant for acetates, or the third constant for propionates and butyrates can be probably attributed to the possibility of coordination with four ligands. The reason for the decrease of the fourth consecutive stability constant of propionates and butyrates may be the increase of the ligand size, although it is obvious (from the values K_3 and K_4) that the third and fourth ligand of propionate and butyrate complexes are bound stronger than those of formates and acetates. This occurs because of a greater polarisability of the larger ligand (the values of K_3 and K_4 are therefore the highest in the butyrates).

TABLE IV
 Butyrate Solutions

[L] M	$E_{1,2}$ V	I	F_0 ([L])	F_1 ([L])	F_2 ([L])	F_3 ([L])	F_4 ([L])
0.009	-0.980	2.13	—	—	—	—	—
0.01	-1.013	2.17	—	—	—	—	—
0.03	-0.993	2.01	—	—	—	—	—
0.06	-0.993	2.07	—	—	—	—	—
0.10	-0.937	2.03	1.77	7.70	7.00	—	—
0.20	-0.992	1.96	2.78	8.90	9.05	33	—
0.30	-0.998	1.75	5.05	13.5	21.7	63	—
0.40	-1.005	1.63	8.34	18.4	28.5	65	97
0.50	-1.001	1.56	15.5	27.9	41.8	78	104
0.60	-1.017	1.52	25.3	40.5	55.8	88	104
0.70	-1.023	1.58	45.1	52.2	76.8	106	114
0.80	-1.030	1.59	59.3	72.8	94.8	115	111
0.90	-1.035	1.53	102	113	117	127	112
1.00	-1.033	1.53	129	128	121	118	92
1.10	-1.042	1.42	192	173	151	135	99
1.20	-1.045	1.41	243	208	167	137	93
1.30	-1.050	1.34	377	289	217	165	107
1.40	-1.053	1.32	484	345	241	170	103
1.60	-1.059	1.48	690	431	265	160	84
1.80	-1.064	1.23	1228	682	375	209	102
2.00	-1.070	1.18	2033	1016	514	257	116
			$\beta_0 = 1$	$\beta_1 = 7$ $K_1 = 7$	$\beta_2 = 3$ $K_2 = 0.45$	$\beta_3 = 26$ $K_3 = 8.7$	$\beta_4 = 103$ $K_4 = 4$

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IZVOD

**Polarografska istraživanja monokarboksilato-kompleksa nekih metala. II.
Cinkovi monokarboksilato-kompleksi**

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Nadovezujući na ispitivanje olovnih monokarboksilato-kompleksa određene su polarografskom metodom konstante stabilnosti cinkovih monokarboksilato-kompleksa. Ispitivane su vodene otopine konstantne ionske jakosti 2 i konstantne koncentracije monokarbonske kiseline 2 *M*. Koncentracija monokarboksilata varirana je do 2 *M*. Dobivene su slijedeće kumulativne konstante stabilnosti: formijato-kompleksi $\beta_1 = 4$, $\beta_2 = 3$, $\beta_3 = 4$, $\beta_4 = 6$; acetato-kompleksi $\beta_1 = 4$, $\beta_2 = 9$, $\beta_3 = 12$, $\beta_4 = 31$; propionato-kompleksi $\beta_1 = 8$, $\beta_2 = 2$, $\beta_3 = 15$, $\beta_4 = 43$; butirato-kompleksi $\beta_1 = 7$, $\beta_2 = 3$, $\beta_3 = 26$, $\beta_4 = 103$.

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