CCA-510

545.33:547.29.546.4

Original Scientific Paper

On the Polarographic Determination of Stability Constants of Formato, Acetato, Propionato, Butyrato, and Lactato Complexes of Copper, Zinc, Cadmium, and Lead

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Received April 25, 1968

The half-wave potential of the metal ion is shifted to more positive values when the concentration of the monocarboxylic acid in the monocarboxylate buffer increases. At low monocarboxylic acid concentrations, in which no hydrolysis of complexes occurs, there is a linear relation between the half-wave potential and acid concentration. It makes possible the determination of the limit acid concentration in which no hydrolysis of complexes has yet occurred. At such conditions the stability constants of the formato, acetato, propionato, butyrato, and lactato complexes of copper, zinc, cadmium, and lead were determined.

Our investigations have shown[1,2] that the concentration of the monocarboxylic acid in the monocarboxylate buffer exerts an influence on the half-wave potential of the metal ion. When the monocarboxylic acid concentration increases the half-wave potential is shifted to more positive values. Investigations on the monovalent ion of thallium, which does not form notable monocarboxylate complexes, have shown that the shift of the half-wave potential is due to the change of the liquid junction potential, to the change of the activity coefficient of the metal ion and the change of the solution viscosity. As this influence is opposite to the one caused by the formation of complexes, stability constants of monocarboxylate complexes of metal ions have to be determined in buffers with a constant monocarboxylic acid concentration, and not in buffers with a constant salt-acid ratio.

However, as a consequence arises the problem of the determination of the half-wave potential of the *free* metal ion, which, in this case, can be determined only by extrapolation to the zero ligand concentration[3-7]. The extrapolation is certainly the better, the lower the monocarboxylic acid concentration in the buffer, because this means, at the same time, a lower ligand concentration with the absence of sodium monocarboxylate. Besides, when the monocarboxylic acid concentration is low its above mentioned influence on the half-wave potential is reduced to a minimum. However, when the monocarboxylic acid concentration is low there is a possibility of mixed hydroxo monocarboxylate complexes being formed. Therefore it is necessary to find the lowest limit concentration of monocarboxylic acid at which such mixed complexes do not yet appear in the whole investigated concentration range of monocarboxylates.

In this work such limit concentrations of monocarboxylic acid in monocarboxylate buffers have been determined and then the stability constants of monocarboxylate complexes have been derived from the shift of the half-wave potentials of metal ions in these buffers by means of the DeFord and Hume graphic method[8].

EXPERIMENTAL

Measurements were performed by polarographic devices described in previous papers[4–7] and by the Radiometer Polariter PO4 and by Manual polarograph B MK II (The Electrochemical Laboratories). The potential drop across the potentiometer of the polarograph amounted to 500 mV, which was attained by switching in of corresponding resistances in front of and behind the potentiometer. This potential drop was checked by a compensation potentiometer to the nearest ± 1 mV and was adjusted before each measurement with a Weston standard cell. The determination of the half-wave potential, the diffusion current and the diffusion current constant was performed in the same way as described previously[4]. As the electrode process of zinc in the investigated carboxylate buffers is quasi-reversible, the reversible half-wave potential of zinc was determined according to H. Matsuda, Y. Ayabe, and K. Adachi[9]. All half-wave potentials are given relative to the calomel electrode with a saturated solution of sodium chloride.

The polarographic cell and other equipment, as well as the preparation of solutions did not differ from that described in the previous papers[4–7]. The concentration of metal ions in the investigated solutions was 0.4 m*M*, except in lactate solutions where it was 0.48 m*M*. By addition of sodium perchlorate the ionic strength of the solutions was kept at a constant value 2. The relative coefficients of viscosity (against water) were determined by means of an Ostwald viscosimeter. All measurements were carried out under constant temperature of 25 ± 0.1 °C.

RESULTS AND DISCUSSION

Figs. 1—3 represent examples of the relation between the half-wave potential of lead ion and the monocarboxylic acid concentration (of formic, acetic, and butyric acid) for different monocarboxylate concentrations in the buffer. The full line corresponds to the uncorrected values and the dashed line to the ones corrected for the change in viscosity of the buffer solution. Such investigations have shown with all investigated metal ions (*i. e.* lead, cadmium,

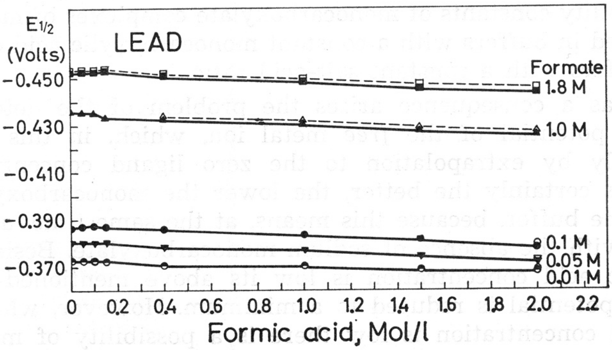

Fig. 1. Half-wave potential of lead versus formic acid concentration in buffers with constant formate concentration: 0.01, 0.05, 0.1, 1.0 and 1.8 *M*.

copper, and zinc) that up to 10 m*M* of monocarboxylic acid (formic, acetic, propionic, butyric, and lactic acid) in buffer an almost linear shift of the half-wave potential is observed regardless of the concentration of the corresponding monocarboxylate in the buffer. Only with the copper ion in lactate buffer solutions this lowest concentration of lactate acid is 30 m*M*. With even lower monocarboxylic acid concentrations, especially with lead and copper, a formation of precipitate or an abrupt shift of the half-wave potential to more negative values may occur, this being evidence of the complex hydrolysis or the formation of mixed hydroxo complexes. Accordingly, with investigated systems, 10 m*M*, or 30 m*M* of lactic acid in case of copper, may be considered the limit monocarboxylic acid concentration at which the complex hydrolysis does not yet occur.

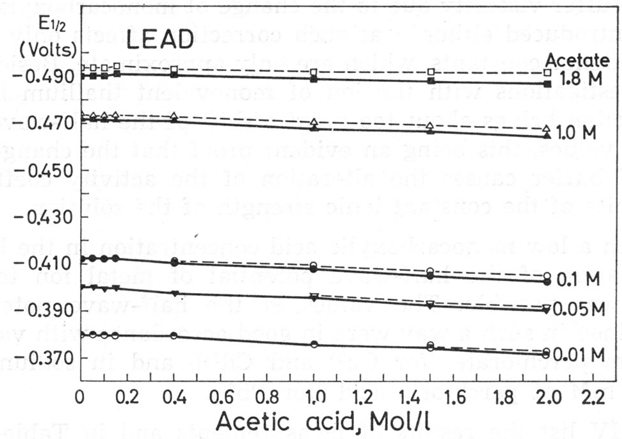

Fig. 2. Half-wave potential of lead versus acetic acid concentration in buffers with constant acetate concentration: 0.01, 0.05, 0.1, and 1.8 *M*.

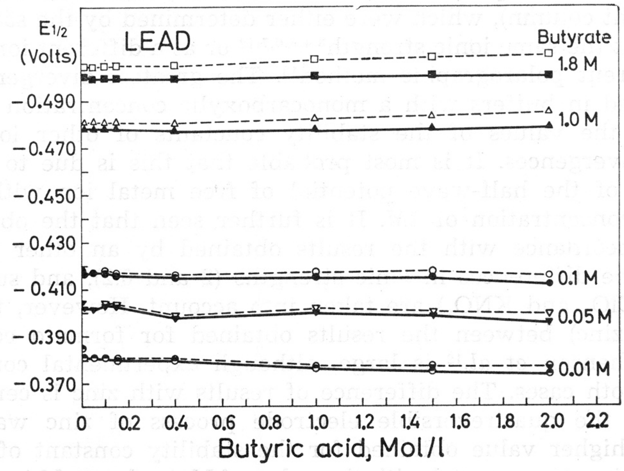

Fig. 3. Half-wave potential of lead versus butyric acid concentration in buffers with constant butyrate concentration: 0.01, 0.05, 0.1, 1.0 and 1.8 *M*.

Therefore buffer solutions of monocarboxylate with the quoted concentrations of the corresponding monocarboxylic acid were used for the determination of stability constants of complexes of the above mentioned ions. With such a low acid concentration the correction of the half-wave potential was not necessary, it being considerably within the error limits of the half-wave potential measurement. Similarly, the correction of the half-wave potential for the change of buffer viscosity due to the change of monocarboxylate concentration was not introduced either,[1,2] as such correction affects only the values of the third and higher constants, which are only approximate. Besides, the above mentioned investigations with the ion of monovalent thallium have shown[1,2] that this correction brings about too great a shift of the half-wave potential to more negative values, this being an evident proof that the change of the ionic composition of buffer causes the alteration of the activity coefficient of the metal ion in spite of the constant ionic strength of the solution.

Due to such a low monocarboxylic acid concentration in the buffer, a very exact extrapolation of the half-wave potential of metal ion to zero ligand concentration was possible. The values of the half-wave potential of *free* metal ion obtained in such a way were in good accordance with values obtained in pure sodium perchlorate (for Cu^{2+} and Cd^{2+}), and in sodium perchlorate containing 0.1 mM of perchloric acid (for Pb^{2+}).

Tables I—IV list the results of measurements and in Table V are given cumulative (β_j) and stepwise stability constants (K_j) determined by the graphic method of DeFord and Hume[8]. Table VI gives mean values of capillary constants ($m^{2/3}t^{1/6}$) measured at the half-wave potential in buffer solutions containing 0.01, 0.2, and 1.8 M sodium monocarboxylate. The extrapolated values for the cumulative stability constants were checked by the method of successive approximations to give the best fit, as recommended by Papoff and Caliumi.[10] The confidence limits of the extrapolated constants β_1 and β_2, deduced from the dispersion of the experimental points are within ± 10%.

In Table VII the values of the stability constants of monoligand complexes (K_1) obtained in our experiments (left column) are compared with those from literature (right column), which were either determined by the same polarographic method at the same ionic strength[3,4,5,6,7,12] or at a different ionic strength[9,21] or by a different polarographic method[13]. The greatest divergences from the values obtained in buffers with a monocarboxylic concentration of 2 M occur with copper; the values of the stability conctants of other ions show also appreciable divergences. It is most probable that this is due to the incorrect extrapolation of the half-wave potential of free metal ion with a monocarboxylic acid concentration of 2M. It is further seen that the obtained results are in fair accordance with the results obtained by an other polarographic method[13], if the differences in ionic strengths (2 and 0.2), and supporting electrolytes ($NaClO_4$ and KNO_3) are taken into account. However, the difference (except with zinc) between the results obtained for formato complexes and those of Hershenson *et al.*[12] is large, although experimental conditions were the same in both cases. The difference of results with zinc is certainly due to the fact that the quasireversible electrode process of zinc was taken into account. The higher value obtained for the stability constant of monoacetato complexes of zinc as compared with the value of Matsuda *et al.*[9] is most probably

TABLE I

Copper Solutions

[L] *M*	Formate		Acetate		Propionate		Butyrate		Lactate	
	$E_{1/2}$ V	i_d μA	$E_{1/2}$ V	i_d μA	$E_{1/2}$ V	i_d μA	$E_{1/2}$ V	i_d μA	$E_{1/2}$ V	i_d μA
0	+ 0.0417	2.56	+ 0.0417	2.56	+ 0.0418	2.70	+ 0.0413	2.83	+ 0.0430	4.10
0.01	+ 0.0371	2.76	+ 0.0375	2.60	+ 0.0371	2.70	+ 0.0378	2.97	+ 0.0208	4.04
0.02	+ 0.0354	2.72	+ 0.0321	2.64	+ 0.0340	2.69	+ 0.0356	2.79	+ 0.0105	4.01
0.03	+ 0.0332	2.99	+ 0.0284	2.65	+ 0.0301	2.69	+ 0.0329	2.74	+ 0.0037	3.90
0.04	+ 0.0309	2.76	+ 0.0254	2.62	+ 0.0279	2.55	+ 0.0279	2.69	— 0.0026	3.94
0.05	+ 0.0285	2.86	+ 0.0225	2.62	+ 0.0247	2.56	+ 0.0258	2.75	—	—
0.06	+ 0.0266	2.77	+ 0.0199	2.59	+ 0.0226	2.55	+ 0.0237	2.67	— 0.0116	3.84
0.08	+ 0.0235	2.74	+ 0.0151	2.60	+ 0.0175	2.52	+ 0.0198	2.62	— 0.0185	3.79
0.10	+ 0.0198	2.70	+ 0.0109	2.50	+ 0.0139	2.53	+ 0.0153	2.60	— 0.0242	3.80
0.15	+ 0.0123	2.72	+ 0.0027	2.56	+ 0.0063	2.49	+ 0.0094	2.52	— 0.0347	3.73
0.20	+ 0.0065	2.70	— 0.0021	2.55	— 0.0002	2.45	— 0.0030	2.46	— 0.0430	3.70
0.30	— 0.0047	2.92	— 0.0108	2.46	— 0.0095	2.43	— 0.0068	2.36	— 0.0542	3.61
0.40	— 0.0097	2.42	— 0.0196	2.38	— 0.0158	2.31	— 0.0155	2.32	— 0.0632	3.54
0.50	— 0.0153	2.72	— 0.0252	2.40	— 0.0224	2.23	— 0.0227	2.31	— 0.0706	3.55
0.60	— 0.0212	2.64	— 0.0310	2.28	— 0.0287	2.22	— 0.0283	2.17	— 0.0772	3.37
0.80	— 0.0298	2.66	— 0.0405	2.26	— 0.0379	2.07	— 0.0370	2.15	— 0.0879	3.28
1.00	— 0.0367	2.76	— 0.0472	2.19	— 0.0449	2.04	— 0.0450	1.97	— 0.0969	3.17
1.20	— 0.0440	2.60	— 0.0547	2.13	— 0.0521	1.89	— 0.0514	1.96	— 0.1042	3.05
1.40	— 0.0482	2.68	— 0.0594	2.11	— 0.0574	1.89	— 0.0666	1.79	— 0.1116	2.94
1.60	— 0.0535	2.60	— 0.0643	2.04	— 0.0634	1.87	— 0.0678	1.71	— 0.1169	2.91
1.80	— 0.0598	2.46	— 0.0696	1.96	— 0.0688	1.74	— 0.0720	1.57	— 0.1231	2.75

TABLE II

Zinc Solutions

[L] M	Formate $E_{1/2}$ V	Formate i_d μA	Acetate $E_{1/2}$ V	Acetate i_d μA	Propionate $E_{1/2}$ V	Propionate i_d μA	Butyrate $E_{1/2}$ V	Butyrate μA i_d
0.	—0.974	3.10	— 0.973	2.80	— 0.972	3.06	— 0.972	3.09
0.01	—	—	— 0.977	2.80	— 0.974	2.94	— 0.973	3.05
0.02	— 0.975	3.05	— 0.976	2.86	— 0.971	3.07	— 0.974	2.98
0.03	— 0.976	2.98	— 0.977	2.70	— 0.975	3.00	— 0.974	3.04
0.04	— 0.977	3.07	— 0.978	2.72	— 0.973	3.01	— 0.976	3.00
0.05	— 0.978	3.09	— 0.979	2.77	— 0.980	3.03	— 0.977	3.06
0.06	— 0.978	2.91	— 0.980	2.74	— 0.980	2.95	— 0.977	3.04
0.08	— 0.979	3.06	— 0.981	2.78	— 0.981	2.94	— 0.978	2.95
0.10	— 0.980	2.95	— 0.985	2.77	— 0.983	3.03	— 0.981	2.98
0.15	— 0.983	2.93	— 0.988	2.67	— 0.987	2.93	— 0.984	2.88
0.20	— 0.085	2.96	— 0.990	2.70	— 0.989	2.82	— 0.987	2.84
0.30	— 0.990	3.06	— 0.995	2.72	— 0.995	2.79	— 0.993	2.68
0.40	— 0.995	3.00	— 1.001	2.62	— 1.001	2.70	— 0.997	2.61
0.50	— 1.000	3.00	— 1.007	2.64	— 1.007	2.62	— 1.002	2.42
0.60	— 1.004	2.98	— 1.011	2.62	— 1.011	2.58	— 1.007	2.34
0.80	— 1.010	2.91	— 1.020	2.44	— 1.013	2.46	— 1.012	2.29
1.00	— 1.016	2.87	— 1.027	2.30	— 1.025	2.32	— 1.021	2.11
1.20	— 1.022	2.85	— 1.034	2.29	— 1.032	2.23	— 1.027	1.97
1.40	— 1.026	2.97	— 1.041	2.20	— 1.037	2.17	— 1.033	1.88
1.60	— 1.030	2.90	— 1.044	2.06	— 1.044	2.13	— 1.039	1.80
1.80	— 1.034	3.03	— 1.048	2.04	— 1.048	2.03	— 1.045	1.67

TABLE III

Cadmium Solutions

[L] *M*	Formate		Acetate		Propionate		Butyrate		Lactate	
	$E_{1/2}$ V	i_d μA	$E_{1/2}$ V	i_d μA	$E_{1/2}$ V	i_d μA	$E_{1/2}$ V	i_d μA	$E_{1/2}$ V	i_d μA
0	— 0.5525	3.04	— 0.5525	3.11	— 0.5525	3.04	— 0.5525	3.03	— 0.5560	4.18
0.01	— 0.5543	3.08	— 0.5546	3.09	— 0.5540	3.04	— 0.5548	3.01	— 0.5583	4.11
0.02	— 0.5553	3.04	— 0.5581	2.93	— 0.5562	2.99	— 0.5567	2.97	— 0.5608	4.06
0.03	— 0.5593	3.06	— 0.5588	3.04	— 0.5597	2.84	— 0.5587	2.92	— 0.5622	4.00
0.04	— 0.5588	3.06	— 0.5608	2.96	— 0.5605	2.89	— 0.5604	2.89	— 0.5639	3.95
0.05	— 0.5581	3.04	— 0.5624	2.97	— 0.5628	2.95	—0.5613	2.86	—	—
0.06	— 0.5582	3.10	— 0.5638	3.02	— 0.5632	2.95	— 0.5630	2.86	— 0.5675	3.89
0.08	— 0.5610	3.11	— 0.5668	2.97	— 0.5670	2.92	— 0.5661	2.77	— 0.5710	3.81
0.10	— 0.5633	2.94	— 0.5712	2.95	— 0.5704	2.90	— 0.5694	2.74	— 0.5739	3.80
0.15	— 0.5671	3.04	— 0.5757	2.89	— 0.5763	2.77	— 0.5754	2.65	— 0.5808	3.71
0.20	— 0.5733	3.04	— 0.5808	2.88	— 0.5825	2.77	— 0.5803	2.65	— 0.5862	3.62
0.30	— 0.5780	2.99	— 0.5890	2.78	— 0.5909	2.67	— 0.5893	2.54	— 0.5953	3.51
0.40	— 0.5839	2.95	— 0.5967	2.85	— 0.5977	2.60	— 0.5975	2.43	— 0.6032	3.43
0.50	— 0.5895	2.98	— 0.6019	2.69	— 0.6043	2.53	— 0.6017	2.35	— 0.6094	3.32
0.60	— 0.5935	2.91	— 0.6067	2.61	— 0.6094	2.51	— 0.6082	2.26	— 0.6147	3.23
0.80	— 0.6030	2.89	— 0.6141	2.53	— 0.6178	2.37	— 0.6174	2.15	— 0.6246	3.09
1.00	— 0.6083	2.84	— 0.6223	2.53	— 0.6250	2.33	— 0.6245	2.09	— 0.6327	3.00
1.20	— 0.6150	2.84	— 0.6294	2.47	— 0.6308	2.21	— 0.6307	1.98	— 0.6399	2.89
1.40	— 0.6191	2.81	— 0.6346	2.39	— 0.6373	2.12	— 0.6364	1.86	— 0.6462	2.74
1.60	— 0.6235	2.75	— 0.6382	2.25	— 0.6426	1.97	— 0.6416	1.80	— 0.6524	2.66
1.80	— 0.6282	2.65	— 0.6439	2.26	— 0.6468	1.98	— 0.6468	1.71	— 0.6577	2.57

TABLE IV
Lead Solutions

[L] *M*	Formate		Acetate		Propionate		Butyrate		Lactate	
	$E_{1/2}$ V	μA i_d	$E_{1/2}$ V	μA i_d	$E_{1/2}$ V	μA i_d	$E_{1/2}$ V	μA i_d	$E_{1/2}$ V	μA i_d
0	— 0.3704	3.38	— 0.3706	3.38	— 0.3709	2.93	— 0.3696	2.91	— 0.3700	4.63
0.01	— 0.3731	3.36	— 0.3801	3.34	— 0.3908	2.72	— 0.3727	2.83	— 0.3807	4.30
0.02	— 0.3740	3.36	— 0.3869	3.32	— 0.3932	2.78	— 0.3928	2.60	— 0.3869	4.16
0.03	— 0.3765	3.36	— 0.3933	3.30	— 0.3970	2.81	— 0.3958	2.68	— 0.3922	4.02
0.04	— 0.3790	3.34	— 0.3970	3.26	— 0.4014	2.77	— 0.3996	2.65	— 0.3963	3.93
0.05	— 0.3795	3.34	— 0.4002	3.24	— 0.4057	2.79	—0.4053	2.54	—	—
0.06	— 0.3826	3.32	— 0.4028	3.22	— 0.4083	2.69	— 0.4071	2.51	— 0.4020	3.89
0.08	— 0.3852	3.32	— 0.4077	3.16	— 0.4133	2.67	— 0.4133	2.42	— 0.4064	3.85
0.10	— 0.3883	3.32	— 0.4123	3.14	— 0.4182	2.69	— 0.4189	2.44	— 0.4105	3.81
0.15	— 0.3945	3.32	— 0.4209	3.14	— 0.4270	2.58	— 0.4269	2.27	— 0.4199	3.78
0.20	— 0.3994	3.26	— 0.4282	3.06	— 0.4332	2.50	— 0.4332	2.83	— 0.4261	3.73
0.30	— 0.4069	3.28	— 0.4378	2.98	— 0.4432	2.54	— 0.4440	2.16	— 0.4363	3.64
0.40	— 0.4125	3.20	— 0.4459	2.92	— 0.4513	2.44	— 0.4520	2.12	— 0.4441	3.54
0.50	— 0.4173	3.18	— 0.4519	2.88	— 0.4576	2.37	— 0.4570	2.05	— 0.4506	3.48
0.60	— 0.4219	3.16	— 0.4570	3.04	— 0.4676	2.34	— 0.4645	2.07	— 0.4561	3.47
0.80	— 0.4289	3.12	— 0.4651	2.71	— 0.4713	2.26	— 0.4702	1.95	— 0.4649	3.31
1.00	— 0.4356	3.12	— 0.4719	2.64	— 0.4794	2.15	— 0.4789	1.86	— 0.4720	3.17
1.20	— 0.4411	3.06	— 0.4784	2.54	— 0.4853	2.13	— 0.4821	1.79	— 0.4790	3.08
1.40	— 0.4444	3.04	— 0.4826	2.50	— 0.4906	2.01	— 0.4921	1.49	— 0.4837	2.95
1.60	— 0.4485	3.04	— 0.4866	2.44	— 0.4944	1.90	— 0.4968	1.72	— 0.4883	2.86
1.80	— 0.4526	3.02	— 0.4907	2.42	— 0.4995	1.88	— 0.5015	1.61	— 0.4931	2.76

TABLE V

Stability Constants

Ligand	Metal ion	β_1 K_1	β_2 K_2	β_3 K_3	β_4 K_4	β_5 K_5	β_6 K_6
Formate	Cu^{2+}	25	200	150	80		
		25	8	0.8	0.5		
	Zn^{2+}	5	15	5			
		5	3	0.3			
	Cd^{2+}	11	17	56			
		11	1.5	3.3			
	Pb^{2+}	17	103	57			
		17	6.1	0.6			
Acetate	Cu^{2+}	50	450	400	350		
		50	9	0.9	0.8		
	Zn^{2+}	11	6	40	23		
		11	0.5	6.7	0.6		
	Cd^{2+}	20	90	140	55		
		20	4.5	1.5	0.4		
	Pb^{2+}	140	1.5×10^3	2.1×10^3			
		140	10	1.5			
Propionate	Cu^{2+}	40	450	200	500		
		40	11	0.4	2.5		
	Zn^{2+}	12	15	32	28		
		12	1.2	2.1	0.9		
	Cd^{2+}	20	110	167	96		
		20	5.5	1.5	0.6		
	Pb^{2+}	220	5.8×10^3	8.0×10^3	1.5×10^4		
		220	26	1.4	1.9		
Butyrate	Cu^{2+}	35	300	200	900		
		35	8.6	0.7	4.5		
	Zn^{2+}	10	13	15	34		
		10	1.3	1.2	2.3		
	Cd^{2+}	20	85	217	95		
		20	4.2	2.6	0.4		
	Pb^{2+}	120	6.0×10^3	5.0×10^3	2.7×10^4		
		120	50	0.8	5.4		
Lactate	Cu^{2+}	350	1.3×10^4	3.0×10^4	1.3×10^4	1.5×10^4	
		350	37	2.3	0.4	1.2	
	Cd^{2+}	21	110	280	70	40	33
		21	5.2	2.5	0.3	0.6	0.8
	Pb^{2+}	140	1.4×10^3	1.8×10^4	900		
		140	10	1.3	0.5		

TABLE VI

Capillary Constants $m^{2/3}t^{1/6}$ ($mg^{2/3}\ sec^{-1/2}$)

	Formate	Acetate	Propionate	Butyrate	Lactate
Copper	2.25	2.24	2.05	2.29	2.65
Zinc	2.50	1.94	2.45	2.42	
Cadmium	2.40	2.40	2.40	2.40	2.64
Lead	2.36	2.36	1.97	1.97	2.58

TABLE VII

Stability Constants of Monoligand Complexes (K_1)

Ligand / Metal ion	Cu^{2+}		Zn^{2+}		Cd^{2+}		Pb^{2+}		H^+ Log K_1[11]
Formate	25	45[6] 37[12]	5	4[5] 4[12]	11	20[6] 3[12]	17	13[4] 6[12] 7[21]	3.752
Acetate	50	100[6] 53[13]	11	4[5] 5[13] 9[9]	20	40[6] 16[13]	140	150[4] 150[3] 130[13]	4.756
Propionate	40	110[6]	12	8[5]	20	30[6]	220	170[4]	4.874
Butyrate	35	80[6]	10	7[5]	20	17[6]	120	120[4]	4.820
Lactate	350	330[7]	—	—	21	30[7]	140	75[7]	3.858

due to the fact that the quoted authors worked in buffers of constant *p*H (constant salt-acid ratio), but there is also the difference in ionic strength of solutions (2 and 4) and the difference in the supporting electrolyte ($NaClO_4$ and $NaNO_3$) to be considered.

In Table VII it is seen that the order of stability of monocarboxylato complexes as measured by K_1 is:

Formato: Zn $<$ Cd $<$ Pb $<$ Cu
Acetato: Zn $<$ Cd $<$ Cu $<$ Pb
Propionato: Zn $<$ Cd $<$ Cu $<$ Pb
Butyrato: Zn $<$ Cd $<$ Cu $<$ Pb
Lactato: Cd $<$ Pb $<$ Cu

and

Zn: Form $<$ But $<$ Ac $<$ Prop
Cd: Form $<$ Ac, Prop, But, Lac
Pb: Form $<$ But $<$ Ac, Lac $<$ Prop
Cu: Form $<$ But $<$ Prop $<$ Ac $<$ Lac
H: Form $<$ Lac $<$ Ac $<$ But $<$ Prop

From these orders it may be seen that zinc and cadmium form the weakest monocarboxylato complexes, which is in accordance with their stable d^{10} electronic configuration.[14] The higher stability of cadmium complexes in relation to those of zinc complexes is certainly due to the higher polarizability of the cadmium ion.[15] The relatively high stability of lead monocarboxylato complexes, especially acetato, propionato, and butyrato complexes, in spite of the stable $5d^{10}6s^2$ electronic configuration of the lead ion, is also due to the particularly high polarizability of lead ion.[15] With the divalent copper ion having a d^9 electronic configuration, a certain ligand field stabilization effect may be expected in the weak ligand field as well as the additional Jahn-Teller stabilization effect,[14,16] which is expressed by a higher stability of copper monocarboxylato complexes. The markedly increased stability of copper lactato complexes with respect to other investigated monocarboxylato complexes is certainly connected with the presence of the OH group in the lactate ion. In view of the lactate ion having a very small basicity (see Tab. VII) such a stability could not be expected otherwise. It is probably a question of a stronger Jahn-Teller stabilization effect. However, lactato complexes of cadmium and lead are also more stable than would correspond to the small basicity of the lactate ion. Accordingly, with lactato complexes of these ions, too, the stabilization effect of the OH group present in the lactate ion is seen.

With formato, acetato, propionato, and butyrato complexes of the investigated metal ions a parallelism exists between ligand basicity and complex stability,[14] especially in the sequence Form < Ac < Prop. The divergence in the case of butyrato complexes is probably connected with a more expressed inductivity effect in the presence of the metal ion. The divergence from the sequence is especially large with copper.[17]

Values of stability constants of investigated metal lactato complexes obtained by the polarographic method are in good agreement with those recently obtained by the potentiometric method.[18,19] The difference in the number of coordinated ligands is due to the high ligand concentration in the polarographic measurements, although here, too, it is evident that the strength of the bond between the metal ion and the ligand decreases abruptly when more than three ligands are bonded. On the other hand recent potentiometric investigations of lead acetato complexes[20] point to the fact that the number of coordinated acetate ions is four and not three. But again the fourth ligand is very weakly bonded ($K_4 = 0.19$). According to the cited potentiometric investigation[20] the first stability constant is somewhat higher ($K_1 = 214$) than it was found by the polarographic method.

Acknowledgment. The authors wish to express their gratitude to the Federal Fund for Scientific Work and to the Republic Fund for Scientific Work of the SR of Bosnia and Herzegovina for the financial help for these investigations.

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IZVOD

O polarografskom određivanju konstanata stabilnosti formijato, acetato, propionato, butirato i laktato kompleksa kupruma, cinka, kadmiuma i plumbuma

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Poluvalni potencijal metalnog iona pomiče se prema pozitivnijim vrijednostima potencijala s porastom koncentracije monokarboksilne kiseline u monokarboksilatnom puferu. Kod niskih koncentracija monokarboksilne kiseline, kod kojih još ne dolazi do hidrolize kompleksa, postoji linearan odnos između poluvalnog potencijala i koncentracije kiseline. To je omogućilo određivanje granične koncentracije monokarboksilne kiseline i uz taj uvjet određene su konstante stabilnosti formijato, acetato, propionato, butirato i laktato kompleksa kupruma, cinka, kadmija i plumbuma.

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Primljeno 25. travnja 1968.