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Polarographic Investigations of Lactato Complexes of Copper, Lead, Cadmium, and Indium

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The stability constants of copper, lead, and cadmium lactate complexes have been determined by the polarographic method in water solutions of a constant ionic strength 2. The examinations were carried out in the lactate concentration range up to 2 *M*. The following values of cumulative costants were obtained:

Copper: $\beta_1 = 330$, $\beta_2 = 1.1 \times 10^4$, $\beta_3 = 2.9 \times 10^4$, $\beta_4 = 5 \times 10^3$, $\beta_5 = 1.5 \times 10^4$.

Lead: $\beta_1 = 75$, $\beta_2 = 660$, $\beta_3 = 1350$, $\beta_4 = 1450$.

Cadmium: $\beta_1 = 30$, $\beta_2 = 35$, $\beta_3 = 540$, $\beta_4 = 80$, $\beta_5 = 300$.

Thus far, only few investigations of lactato complexes of metal ions have been carried out. In the literature[1,2] there can be found only data about copper[1] and zinc[2,3] lactato complexes, which were investigated by the spectrophotometric or potentiometric method. For this reason the following investigation of copper, lead, cadmium and indium lactato complexes has been carried out. The polarographic method of investigation was applied and the stability constants of copper, lead and cadmium were evaluated by the method of DeFord and Hume[4], as described in a previous paper.[5] The calculation of the stability constants of indium lactato complexes was not possible, since the half-wave potential of the free indium ion could not be obtained experimentally[6] because of irreversibility of the electrode process in the absence of the lactate. The thallium (I), zinc and bismuth lactato complexes were also investigated, but their stability constants could not be determined, because of polarographic irreversibility of the electrode process with zinc and bismuth and because of the rather small shift of the half-wave potential (about 5 *mV*) with thallium (I).

EXPERIMENTAL

The measurements were performed with a Radiometer PO3 polarograph. The potential drop across the potentiometer of the polarograph was as low as 500 *mV*, which was attained by switching of corresponding resistances in front of and behind the potentiometer. This potential drop was determined by a compensation potentiometer to the nearest ± 1 *mV* and was adjusted before each measurement with a Weston standard cell. In this way a maximum accuracy of the

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half-wave potential determinations of ±1 *mV* (±2 *mV* for indium) was achieved. The polarographic cell and other equipment did not differ from that described in the previous paper[5]. The determination of the diffusion current, the half-wave potential and the diffusion current constant was performed in the same way as described previously[5]. All half-wave potentials are given with respect to the calomel electrode with a saturated solution of sodium chloride.

The solutions were prepared from chemically pure reagents. Lactic acid »Analar« of The British Drug Houses Ltd. was used. The concentration of copper, lead and cadmium (as nitrate) was 0.6 *mM*, whereas that of indium (as perchlorate) was 0.4 *mM*. The concentration of the lactate was varied from 0 to 2 *M*. The lactate was obtained by addition of a known excess of sodium hydroxide to the solution of lactic acid. In this way even condensation products of the lactic acid were converted to the lactate. From such an alkaline solution of a lactate, the solution of the lactate buffer of a constant ionic strength 2 was prepared by addition of a corresponding amount of perchloric acid and sodium perchlorate. In order to obtain the lowest possible concentration of lactate ion, in solutions containing only lactic acid the dissociation of the acid was suppressed by addition of a known amount of perchloric acid. In such solutions and in buffer solutions with a low concentration of sodium lactate, the concentration of the lactate ion was calculated from the dissociation constant of the lactic acid. The concentration of the lactic acid in buffer solutions was constant[7], *i.e.* in solutions of lead and cadmium complexes it was 2 *M*, whereas with copper and indium it was 0.1 *M*. Under such experimental conditions, the electrode processes of these ions were polarographically reversible in the entire investigated concentration range of the lactate ion. In buffer solutions with a higher concentration of lactic acid (2 *M*) and a low content of lactate ion, the half-wave potentials of copper became more negative with decreasing lactate ion concentration, instead of more positive as usual.

The described experimental conditions made possible the determination of the half-wave potential of the »free« metal ions, by extrapolation to zero lactate concentration[5], but only for copper, lead and cadmium. For ndium this was not possible, since the curve representing the relation of the half-wave potential against lactate concentration was too steep. Besides, the electrode process of indium in solutions without the complex forming substance is irreversible[6].

It is interesting to note that the electrode reaction of indium was polarographically reversible only in buffer solutions which did not contain more than 0.1 moles/l of the free lactic acid. The *p*H value of such solutions was between 1 and 5. In buffers with a higher lactic acid concentration, the electrode processes were irreversible. An analogous behaviour, *i.e.* irreversible reduction of indium, was found by D. Cozzi and S. Vivarelli[8] in solutions with *p*H less than 1.

No polarographic maxima were observed, probably because of the capillary activity of the lactic acid. Accordingly, no gelatine was added to the solutions.

All measurements were carried out under constant temperature of 25 ± 0.1°C.

RESULTS AND DISCUSSION

The composition of the complexes and their cumulative stability constants have been determined by the graphic method od DeFord and Hume[4,5]. The extrapolated values for the cumulative stability constants were checked to give the best fit, by the method of successive approximations, as recommended by P. Papoff and M. Caliumi[10]. The confidence limits of the extrapolated constants, deduced from the dissipation of he experimental points depending on the precision of the half-wave potential measurements[11], are within ± 10% for lead lactato complexes, and ± 15% for cadmium and copper lactato complexes. The results are shown in Tables I—IV.

It is interesting to mention that the amount of lactic acid in the buffer has a distinct influence on the diffusion currents of all investigated cations and particularly on the indium ion. The polarographic wave of indium even disappears completely at greater concentrations of lactic acid. The concentration of lactic acid at which the wave disappears depends on the con-

TABLE I

Copper Lactate Solutions

[L] M	$E_{1/2}$ V	I	F_0[L]	F_1([L])	F_2([L])	F_3([L])	F_4([L])	F_5([L])
0.000	+0.043	3.20	—	—	—	—	—	—
0.011	+0.021	3.06	6.06	459	11727	—	—	—
0.016	+0.015	3.04	9.37	523	12062	—	—	—
0.021	+0.011	3.02	12.7	557	10809	—	—	—
0.03	+0.005	2.98	20.7	658	10933	—	—	—
0.04	—0.001	2.97	32.7	792	11550	—	—	—
0.06	—0.010	2.94	68.9	1131	13350	—	—	—
0.08	—0.017	2.89	116	1438	13850	—	—	—
0.10	—0.021	2.87	165	1637	13070	—	—	—
0.15	—0.032	2.86	391	2597	15113	—	—	—
0.20	—0.041	2.82	787	3932	18010	—	—	—
0.25	—0.047	2.79	1253	5009	18716	30864	—	—
0.30	—0.053	2.75	2031	6768	21460	34867	—	—
0.40	—0.061	2.69	4129	10319	24972	34930	—	—
0.50	—0.069	2.65	7334	14666	28672	35344	—	—
0.60	—0.076	2.56	12997	21660	35550	40917	—	—
0.70	—0.080	2.52	19357	27651	39030	40043	15775	15393
0.80	—0.086	2.50	29133	36415	45106	42632	17040	15050
0.90	—0.090	2.43	41555	46171	50964	44404	17115	13461
1.00	—0.094	2.38	60213	60212	59882	48882	19882	14882
1.10	—0.098	2.35	84528	76842	69556	52233	21121	14655
1.20	—0.102	2.32	11.3×10^4	93907	77981	55817	22347	14456
1.30	—0.106	2.28	15.4×10^4	11.9×10^4	91042	61571	25055	15427
1.40	—0.109	2.23	19.9×10^4	14.2×10^4	10.1×10^4	64536	25383	14559
1.50	—0.112	2.22	25.9×10^4	17.3×10^4	11.5×10^4	69314	26876	14584
1.60	—0.115	2.16	33.7×10^4	21.0×10^4	13.1×10^4	75207	28879	14924
1.70	—0.119	2.11	46.3×10^4	27.2×10^4	16.0×10^4	87681	34518	17363
1.80	—0.121	2.08	56.8×10^4	31.5×10^4	17.5×10^4	91110	34505	16391
1.90	—0.124	2.01	71.8×10^4	37.8×10^4	19.9×10^4	98879	36778	16725
2.00	—0.127	1.98	94.2×10^4	47.1×10^4	23.5×10^4	11.2×10^4	41601	18300
				$\beta_1 = 330$	$\beta_2 = 1.1 \times 10^4$	$\beta_3 = 2.9 \times 10^4$	$\beta_4 = 5 \times 10^3$	$\beta_5 = 1.5 \times 10^4$

TABLE II

Lead Lactate Solutions

[L] M	$E_{1/2}$ V	I	$F_0([L])$	$F_1([L])$	$F_2([L])$	$F_3([L])$	$F_4([L])$
0.0000	—0.363	2.71	—	—	—	—	—
0.010	—0.370	2.61	1.83	83.4	—	—	—
0.017	—0.373	2.59	2.32	77.5	—	—	—
0.019	—0.374	2.58	2.56	82.0	—	—	—
0.022	—0.376	2.56	3.01	91.3	—	—	—
0.026	—0.378	2.54	3.43	93.6	—	—	—
0.029	—0.379	2.52	3.89	99.7	—	—	—
0.037	—0.382	2.49	4.90	105	—	—	—
0.046	—0.385	2.47	6.05	110	—	—	—
0.064	—0.389	2.44	8.78	122	727	—	—
0.083	—0.394	2.42	12.5	139	772	—	—
0.103	—0.397	2.40	16.7	153	757	—	—
0.152	—0.405	2.36	31.9	203	844	—	—
0.201	—0.412	2.32	56.1	274	990	1650	—
0.251	—0.418	2.29	85.1	335	1037	1506	—
0.30	—0.423	2.25	131	434	1195	1783	1443
0.40	— 0.431	2.19	262	651	1441	1952	1505
0.50	—0.438	2.14	451	900	1650	1980	1260
0.60	—0.445	2.09	766	1275	2000	2233	1472
0.70	—0.450	2.05	1176	1679	2291	2330	1400
0.80	—0.455	1.99	1771	2212	2672	2515	1456
0.90	—0.459	1.95	2568	2853	3086	2695	1494
1.00	—0.464	1.93	3701	3700	3625	2965	1615
1.10	—0.467	1.89	4778	4342	3879	2926	1433
1.20	—0.470	1.85	6443	5368	4411	3126	1480
1.30	—0.473	1.82	8295	6380	4850	3223	1441
1.40	—0.476	1.78	10766	7689	5439	3413	1473
1.50	—0.479	1.74	13390	8926	5900	3493	1428
1.60	—0.481	1.70	16793	10495	6512	3657	1442
1.70	—0.484	1.68	20420	12011	7021	3742	1407
1.80	—0.487	1.63	26038	14465	7994	4074	1513
1.90	—0.488	1.61	29996	15787	8308	4025	1408
2.00	—0.491	1.57	37536	18767	9383	4361	1505
				$\beta_1 = 75$	$\beta_2 = 660$	$\beta_3 = 1350$	$\beta_4 = 1450$

centration of the lactate in the buffer. The greater the amount of lactate, the greater the decrease of the height of the polarographic wave of indium with increasing lactic acid concentration. This effect is certainly caused by the change of viscosity[12] of the buffer resulting from the increasing concentration of lactic acid. However, the observed disappearance of the polarographic wave of indium ion, when greater amounts of the lactic acid are present in the buffer, is presumably due to its capillary activity, *i.e.* to the change of the double layer structure on the surface of the dropping mercury electrode[8].

The lactato complexes of cadmium, lead, and copper are weak complexes, as are complexes of these ions with other monocarboxylate ligands[5,13,14]. In the table given below, the stability constants (β_1) of lactato complexes of cadmium, lead, and copper are presented along with characteristics which influence the stability of complexes such as: the ionic potential (z/r or z^2/r,

TABLE III

Cadmium Lactate Solutions

[L] M	$E_{1/2}$ V	I	$F_0([L])$	$F_1([L])$	$F_2([L])$	$F_3([L])$	$F_4([L])$	$F_5([L])$
0.0000	−0.538	2.50	—	—	—	—	—	—
0.010	−0.542	2.46	1.33	33.6	—	—	—	—
0.017	−0.544	2.45	1.59	35.0	—	—	—	—
0.019	−0.544	2.45	1.67	35.3	—	—	—	—
0.022	−0.545	2.44	1.74	33.7	—	—	—	—
0.026	−0.546	2.43	1.89	34.4	—	—	—	—
0.029	−0.546	2.42	1.94	32.6	—	—	—	—
0.037	−0.548	2.40	2.19	32.1	56.7	—	—	—
0.046	−0.549	2.38	2.52	33.0	65.2	—	—	—
0.064	−0.552	2.36	3.19	34.1	64.1	—	—	—
0.083	−0.555	2.33	4.04	36.7	80.2	545	—	—
0.103	−0.558	2.31	4.99	38.8	85.3	488	—	—
0.152	−0.564	2.26	8.43	48.9	124	587	—	—
0.201	−0.570	2.22	13.3	61.1	155	596	—	—
0.251	−0.575	2.18	20.6	78.0	191	622	—	—
0.30	−0.580	2.14	29.9	96.3	221	620	—	—
0.40	−0.588	2.08	59.5	146	291	639	247	—
0.50	−0.595	2.02	106	210	359	649	218	276
0.60	−0.602	1.98	180	297	446	684	240	267
0.70	−0.607	1.94	289	412	545	729	270	271
0.80	−0.614	1.90	478	596	707	840	375	368
0.90	−0.618	1.86	683	757	808	859	354	304
1.00	−0.622	1.82	999	998	968	933	393	313
1.10	−0.627	1.78	1418	1288	1144	1008	425	314
1.20	−0.631	1.75	1968	1639	1341	1088	457	314
1.30	−0.634	1.70	2658	2044	1549	1165	481	308
1.40	−0.638	1.68	3605	2575	1817	1273	523	316
1.50	−0.640	1.65	4472	2980	1967	1288	499	279
1.60	−0.644	1.61	6001	3750	2325	1431	557	298
1.70	−0.647	1.58	7627	4486	2621	1521	577	292
1.80	−0.649	1.55	9360	5199	2872	1576	575	275
1.90	−0.652	1.52	12325	6486	3398	1770	647	298
2.00	−0.655	1.48	15391	7695	3832	1898	679	299
				$\beta_1 = 30$	$\beta_2 = 35$	$\beta_3 = 540$	$\beta_4 = 80$	$\beta_5 = 300$

i.e. the ion charge divided by ion radius), the ionization potential I_n ($Me^{(n-1)+} \rightarrow Me^{n+} + e^-$, *i.e.* the electron affinity) and the polarizability (α):

	z/r[15] ($z/Å$)	I_n[16] (*eV*)	$\alpha \times 10^{24}$[17] (cm^3)	β_1
Cd^{2+}	2.06	16.9	1.03	30
Pb^{2+}	1.67	15.0	4.32	75
Cu^{2+}	2.78	20.2	0.70	280

It is obvious that in the case of cadmium and copper the ionic potential and the ionization potential are the principal factors controlling the stability of complexes (Cd $<$ Cu). With a large ion such as the lead ion, its polarizability is decisive, and accordingly the stability of the lead lactato complexes is intermediate between the stabilities of cadmium and copper: Cd $<$ Pb $<$ Cu.

TABLE IV

Indium Lactate Solutions

[L] M	$E_{1/2}$ V	I
0.011	—0.546	4.03
0.016	—0.553	4.02
0.021	—0.560	3.99
0.03	—0.569	3.98
0.04	—0.576	3.96
0.06	—0.587	3.94
0.08	—0.595	3.91
0.10	—0.602	3.89
0.15	—0.614	3.83
0.20	—0.624	3.79
0.25	—0.632	3.74
0.30	—0.638	3.70
0.40	—0.648	3.63
0.50	—0.656	3.55
0.60	—0.663	3.47
0.70	—0.668	3.43
0.80	—0.673	3.33
0.90	—0.678	3.27
1.00	—0.682	3.23
1.10	—0.685	3.14
1.20	—0.690	3.09
1.30	—0.693	3.03
1.40	—0.697	2.97
1.50	—0.699	2.91
1.60	—0.702	2.84
1.70	—0.705	2.80
1.80	—0.708	2.76
1.90	—0.710	2.70
2.00	—0.713	2.65

This series is completely in accordance with the series for other complexes, given by Irving and Williams[18], Mellor and Maley[19], Prue[20] and Federsen[21]. Therefore, these investigation results confirm the conclusion that the ionization potential and the polarizability of the central ion ought to be considered as principally responsible for a greater or smaller stability of the complexes with monocarboxylate ions.

With respect to ligands, the stability of complexes depends on their basicity (*i.e.* on the electron donor character). As the basicity of the monocarboxylate ligands is increasing in the series: formate < lactate < acetate < propionate, the stability of the corresponding lead complexes is increasing accordingly[5] : $\beta_1 = 13, 75, 150, 170$. Cadmium complexes[13] are showing the same sequence for the first three ligands. Copper lactato complexes are more stable, probably due to the presence of the hydroxyl group in the lactate ion. However, it is rather difficult to judge if lactate ion acts as chelate group in investigated systems. The fact that the maximum of stability is achieved in the third complex may perhaps be taken as evidence of a tendency for chelate formation.

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IZVOD

Polarografska istraživanja laktato-kompleksa bakra, olova, kadmija i indija

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Polarografskom metodom DeForda i Humea određeni su sastav i konstante stabilnosti bakarnih, olovnih i kadmijevih laktato-kompleksa. Otopine su bile ionske jakosti 2, a koncentracija laktata varirana je do 2 M uz konstantnu koncentraciju mliječne kiseline u tamponskoj otopini (0,1 M kod bakra i indija i 2 M kod olova i kadmija). Dobivene su ove kumulativne konstante stabilnosti:

bakar: $\beta_1 = 330$, $\beta_2 = 1.1 \times 10^4$, $\beta_3 = 2.9 \times 10^4$, $\beta_4 = 5 \times 10^3$, $\beta_5 = 1.5 \times 10^4$

olovo: $\beta_1 = 75$, $\beta_2 = 660$, $\beta_3 = 1350$, $\beta_4 = 1450$;

kadmij: $\beta_1 = 30$, $\beta_2 = 35$, $\beta_3 = 540$, $\beta_4 = 80$, $\beta_5 = 300$.

Konstante stabilnosti indijevih laktato kompleksa nisu se mogle odrediti zbog ireverzibilnosti elektrodne reakcije u otopinama indija koje ne sadrže stvaraoca kompleksa.

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