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Polarographic Investigations of Some Metal Monocarboxylato Complexes. I. Monocarboxylato Complexes of Lead

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By the polarographic method of DeFord and Hume the stability constants of plumbous monocarboxylato complexes have been determined, in water solutions of a constant ionic strength 2 and a constant concentration of 2 *M* of monocarboxylic acid. The examinations were carried out in the monocarboxylate concentration range up to 2 *M*. The following values of stability constants were obtained: formiato complexes $\beta_1 = 13$, $\beta_2 = 50$, $\beta_3 = 30$; acetato complexes $\beta_1 = 150$, $\beta_2 = 900$, $\beta_3 = 3000$; propionato complexes $\beta_1 = 170$, $\beta_2 = 2200$, $\beta_3 = 5800$; butyrato complexes $\beta_1 = 120$, $\beta_2 = 2000$, $\beta_3 = 5800$. It is evident that with the increase of base strength and the size of the monocarboxylate ion the complex stability increases in the majority of cases.

The investigations of plumbous monocarboxylato complexes carried out heretofore[1–10] have shown that the differences in the results of investigations are caused by variations in the working conditions and that under identical working conditions the polarographic method gives results which are in accord with those of other methods.[5] It is generally known that the polarographic method offers great advantages because of its rapidity and simplicity of manipulation. Consequently, a systematic investigation of monocarboxylato complexes of such metallic ions as could be determined by the polarographic method seemed to offer considerable interest. To enable the comparison of the obtained results and to draw conclusions about the influence of the basicity and the size and ramification of the ligands on one side and the nature (charge and electronic configuration) and size of the central atom on the other, all investigations were carried out under the same working conditions and the obtained results were interpreted by the same method. In this first part the results of investigation of the plumbous monocarboxylato complexes are given.

EXPERIMENTAL

Polarographic equipment. The measurements were carried out on the polarograph »Československá Zbrojovka Brno« model V-301 for automatic recording of the polarographic curve as well as by manual registration of the current-voltage curve by means of a Kohlrausch drum, a mirror galvanometer and a shunt. The potential drop across the bridge of the polarograph or the Kohlrausch drum was as low as about 500 mV, which was attained by switching of corresponding resistances in front of and behind the bridge or Kohlrausch drum. 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 maximal accuracy of the half-wave potential determinations was obtained, which was ± 1 mV.

For dropping electrodes the Radiometer capillaries were used. Their values od $m^{2/3}$ $t^{1/6}$ for the investigated solutions (formates, acetates, propionates, butyrates) at the potential of the saturated calomel electrode were as follows: 1.91, 2.31, 1.85 and 1.89 $mg^{2/3}$ $sek^{-1/2}$.

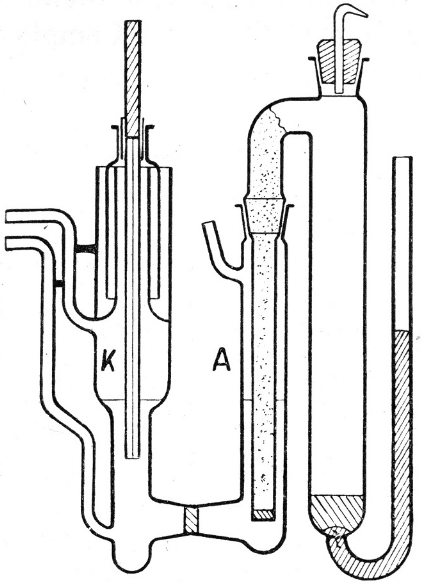

Fig. 1. Polarographic cell

In order to eliminate entirely the effect of the chloride solution of the external anode on the solution in the cathodic part, a polarographic cell shown in Fig. 1 was used. A glass filter of porosity G3 enables a slow streaming of the investigated solution from the cathodic into anodic part of the cell and prevents the electrolyte diffusion from the anodic into the cathodic compartment during the measurement. The work with the cell is carried out in the following way: into the cathodic part *K* of the cell about 12 ml. of the investigated solution is filled and a stream of hydrogen is passed through for half an hour. During this time the solution passes slowly through the filter G3 into the anodic compartment *A*, until the levels are equal, or until the contact of the solution with the calomel electrode in the anodic compartment is established. The velocity of the solution passing through the filter is regulated by means of a clip on the opening in the upper part of the anodic compartment. During the measurement the polarographic cell was kept in a water thermostat at 25,0 ± 0,2°C.

A calomel electrode with a saturated solution of sodium chloride was used as external anode.[5,10] All half-wave potentials are given with respect to this calomel electrode.

The half-wave potential $(E_{1/2})_c$ read from the polarogram was corrected for the voltage drop of $(i_d/2)R$ volt, and the half-wave potential of the free ion $(E_{1/2})_s$ was determined by extrapolation to zero monocarboxylate concentration.[10] The half-wave potentials could be reproduced to ±1 — 1.5 mV. The diffusion current i_d was measured at the half-wave potential and was corrected for the residual current. The diffusion current constant ($I = i_d/Cm^{2/3}\,t^{1/3}$) of the free ion I_s was also determined by extrapolation to zero monocarboxylate concentration. All electrode processes were polarographically reversible, i.e. the relation $\triangle E/\triangle \log[(i_d-i)/i]$ amounted to about 30 mV.

The solutions were prepared from chemically pure reagents. The concentration of lead, added as plumbous nitrate was 0,4 mM. The concentration of the monocarboxylate was varied from 0 do 2 *M*. In order to prevent the hydrolysis of the monocarboxylato complexes, a constant amount of free monocarboxylic acid, to the concentration of 2 *M* was present.[5] The ionic strength of the solution was maintained at the constant value 2 by adding the corresponding quantity of sodium perchlorate. No gelatin was added to the solutions.

RESULTS AND DISCUSSION

The composition and the cumulative stability constants of the complexes

$$\beta_j = \frac{[PbL_j^{+2-j}]}{[Pb^{+2}][L^-]^j}$$

were determined by the graphic method of DeFord and Hume.[10,11] By extrapolation of the function

$$F_0([L]) = \text{antilog}\left\{16{,}95n\,[(E_{1/2})_s - (E_{1/2})_c] + \log \frac{I_s}{I_c}\right\}$$

to $[L] = 0$ the value for the constant of the free ion β_0 was obtained. The succeeding functions F_j ([L]) are given by the expression

$$F_1\,([L)] = \frac{F_0\,([L]) - \beta_0}{[L]}$$

and the stability constants of the complexes β_1 were determined by extrapolation of these functions to $[L] = 0$, i. e.

$$\beta_1 = \lim F_1([L])$$

etc. until the last function $F_j([L])$ is obtained, which is a straight line parallel with the axis [L]. In these expressions: [L] is the concentration of the ligand, i.e. monocarboxylate, $(E_{1/2})_s$ the half-wave potential of the free ion, $(E_{1/2})_c$ the half-wave potential of the complex ion, I_s the diffusion constant of the free ion, I_c the diffusion current constant of the complex ion and n the number of electrons in the electrode reaction. In view of the dissipation of the experimental points and the accuracy of ±1 — 1.5 mV with which the half-wave potential was measured, it can be concluded that the values of the stability constants of the complexes are exact to ± 10 — 15%. From cumulative stability constants the consecutive stability constants of each complex (K_j) were computed by means of the relation

$$\beta_j = K_1 \times K_2 \times \ldots . \times K_j$$

In tables 1 to 4 the measurement results for solutions of the formates, acetates, propionates and *n*-butyrates are summarized. The obtained cumulative stability constants differ from those published previously, evidently because of differing experimental conditions and especially because of the presence of gelatin in the investigated solutions.[9,10] The stability constants of the plumbous acetato complexes are in accordance with those which were obtained under the same experimental conditions by E. A. Burns and D. N. Hume.[5] However, the values for the stability constants of the plumbous formiato complexes are different from those found by H. M. Hershenson, R. Thompson-Brooks and M. E.

TABLE I

Formate medium

[L] M	$E_{1/2}$ V	I	$F_0([L])$	$F_1([L])$	$F_2([L])$	$F_3([L])$
0.000	—0.368	3.25	—	—	—	—
0,01	—0.369	3.17	1.07	—	—	—
0,02	—0.371	3.14	1.3	—	—	—
0,03	—0.372	3.12	1.4	14.8	—	—
0.04	—0.373	3.10	1.6	13.4	—	—
0.06	—0.376	3.08	2.0	17.3	—	—
0.08	—0.378	3.04	2.4	17.6	—	—
0.10	—0.381	3.00	2.9	18.9	—	—
0.20	—0.390	2.98	5.9	24.4	57.0	—
0.40	—0.403	2.94	16.7	39.3	65.7	—
0.60	—0.411	2.90	31.2	50.3	62.1	—
0.80	—0.419	2.89	58.4	71.7	73.3	29.1
1.00	—0.425	2.87	95.4	94.4	81.4	31.4
1.20	—0.429	2.84	135	112	82.0	26.6
1.40	—0.435	2.82	210	149	96.8	33.4
1.60	—0.439	2.79	290	181	104	33.8
1.80	—0.440	2.72	327	181	93.2	24.0
2.00	—0.444	2.71	452	223	106	28.1
			$\beta_0 = 1$	$\beta_1 = 13$ $K_1 = 13$	$\beta_2 = 50$ $K_2 = 3.9$	$\beta_3 = 30$ $K_3 = 0.60$

TABLE II

Acetate medium

[L] M	$E_{1/2}$ V	I	$F_0([L])$	$F_1([L])$	$F_2([L])$	$F_3([L])$
0,000	—0.368	3.33	—	—	—	—
0,01	—0.379	3.24	2.58	158	—	—
0,02	—0.387	3.20	5.16	208	—	—
0.03	—0.391	3.17	6.44	181	—	—
0,05	—0.397	3.11	10.5	189	—	—
0,07	—0.403	3.07	16.0	215	—	—
0.10	—0.408	3.02	25.2	242	920	—
0,20	—0.423	2.94	83.6	413	1315	—
0.40	—0.443	2.83	414	1032	2205	—
0.60	—0.456	2.79	1151	1917	2945	—
0,80	—0.464	2.68	2305	2880	3413	3141
1,00	—0.471	2.58	4006	4005	3855	2955
1,20	—0.478	2.55	7115	5929	4816	3263
1.40	—0.482	2.41	10453	7466	5226	3090
1.60	—0.486	2,38	14192	8869	5449	2844
1.80	—0.491	2.32	21055	11697	6415	3064
2,00	—0,494	2.23	27005	13502	6678	2889
			$\beta_0 = 1$	$\beta_1 = 150$ $K_1 = 150$	$\beta_2 = 900$ $K_2 = 6$	$\beta_3 = 3000$ $K_3 = 3.3$

TABLE III

Propionate medium

[L] M	$E_{1/2}$ V	I	$F_0([L])$	$F_1([L])$	$F_2([L])$	$F_3([L])$
0,000	—0.367	3.42	—	—	—	—
0.02	—0.386	3.13	4.97	—	—	—
0.04	—0.397	3.07	11.6	267	2449	—
0.07	—0.406	3.03	23.9	332	2348	—
0.09	—0.413	3.01	41.2	447	3078	—
0.19	—0.430	2.94	154	805	3342	6010
0.30	—0.440	2.85	369	1227	3523	—
0.39	—0.449	2.78	735	1882	4389	5613
0.49	—0.475	2.70	1380	2814	5396	6522
0.60	—0.462	2.67	2120	3532	5603	5672
0.69	—0.467	2.60	3105	4498	6273	5903
0.79	—0.470	2.55	4193	5306	6501	5444
0.90	—0.475	2.51	6053	6732	7299	5672
1.00	—0.478	2.50	7622	7621	7452	5252
1.30	—0.487	2.38	16420	12639	9599	5696
1.60	—0.494	2.32	29770	18629	11551	5852
2.00	—0.502	2.14	61700	30850	15340	6570
			$\beta_0 = 1$	$\beta_1 = 170$ $K_1 = 170$	$\beta_2 = 2200$ $K_2 = 13$	$\beta_3 = 5800$ $K_3 = 2,6$

TABLE IV

Butyrate medium

[L] M	$E_{1/2}$ V	I	$F_0([L])$	$F_1([L])$	$F_2([L])$	$F_3([L])$
0.000	—0.368	2.59	—	—	—	—
0.01	—0.376	2.33	2.10	—	—	—
0.02	—0.384	2.28	3.81	140	—	—
0.03	—0.389	2.24	5.96	165	—	—
0.04	—0.393	2.20	8.29	182	—	—
0.06	—0,400	2,14	14.2	222	—	—
0,08	—0,407	2.08	25.5	307	2331	—
0,10	—0,412	2,02	38.1	371	2507	—
0,20	—0,425	1,97	148	733	3068	—
0,40	—0,448	1,83	742	1851	4328	5820
0.60	—0.461	1.77	2132	3551	5719	6198
0.80	—0,470	1.71	4213	5265	6431	5539
1.00	—0,477	1.64	7933	7932	7812	5812
1.20	—0.483	1.58	12791	10659	8782	5651
1.40	—0.489	1.53	19549	13963	9887	5634
1.60	—0,494	1.47	32104	20065	12465	6541
1.80	—0,498	1.42	46623	25901	14323	6846
2.00	—0,503	1.35	72264	36131	18006	8002
			$\beta_0 = 1$	$\beta_1 = 120$ $K_1 = 120$	$\beta_2 = 2000$ $K_2 = 16$	$\beta_3 = 5800$ $K_3 = 2,9$

Murphy.[7] Moreover, also the composition of the complexes is different, because the authors cited have found the complex $Pb(HCOO)_4^{-2}$ to exist also. This fact is certainly in connection with the low concentration of the free acid in the investigated solutions.

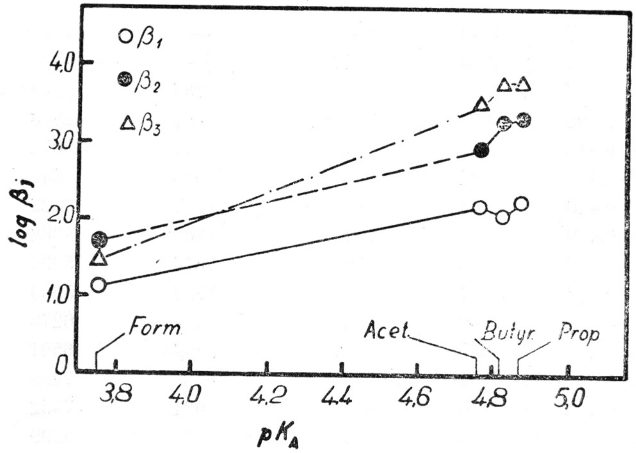

Fig. 2. Relationship between the logarithm of cumulative stability constants (β_j) of monocarboxylatato complexes of lead and the negative logarithm of ionisation constants (pK_A) of corresponding monocarboxylic acids.

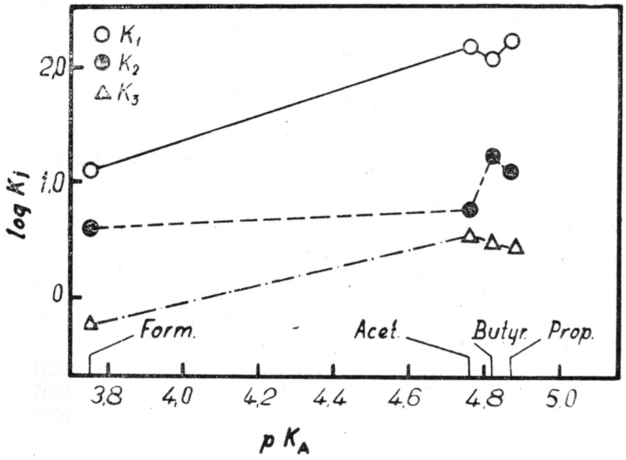

Fig. 3 Relationship between the logarithm of consecutive stability constants (K_j) of monocarboxylato complexes of lead and the negative logarithm of ionisation constants (pK_A) of corresponding monocarboxylic acids.

In all examined monocarboxylate solutions it was found that only three kinds of complexes of the type PbL^+, PbL_2 and PbL_3^- exist. Only in the butyrate solutions at concentrations higher than 7.5 M it could be concluded from the discontinuity of the curve $F_3([L])$ — $[L]$, that a complex of the type PbL_4^{-2} may exist. It is interesting that the ion Pb^{+2} preferably coordinates three ligands (the fourth being probably a water molecule in water solutions) not only in these weak monocarboxylato complexes but also in the much stronger hydroxo complexes.[12] This could be in connection with the three free 6p orbitals of the Pb^{+2} ion. However, a complex of the type PbL_4^{-2} was recently found also by P. Kivalo and A. Ekman in plumbous iodo complexes.[13] A coordination of three monocarboxylate ions could indicate a certain ionic character of the bond between the plumbous ion and the monocarboxylate ion, because the binding of the fourth ligand to the already negative charged complex ion $Pb(H_2O)L^-_3$ requires a considerable bond energy to overcome the electrostatic repulsion.

However, in spite of the weak complexes, a considerable coordinative character of the bond between the plumbous and the monocarboxylic ion is evidenced by the fact that the stability of the monocarboxylato complexes is increasing with the mobility of the ligand-electrons, i. e. with basicity of ligand and its tendency to polarization, in that case the possibility of the formation of donor bonds between the central ion and the ligands being greater. The diagram in the Fig. 2 shows the interdependence of the complex stability, i. e. the logarithm of the stability constant ($\log \beta_j$) and the ligand basicity, i.e. the negative logarithm of the ionisation constant (pK_A) of the corresponding monocarboxylic acid. The complex stability increases with increasing ligand basicity, showing a smaller discontinuity of the butyrates for the first complex.

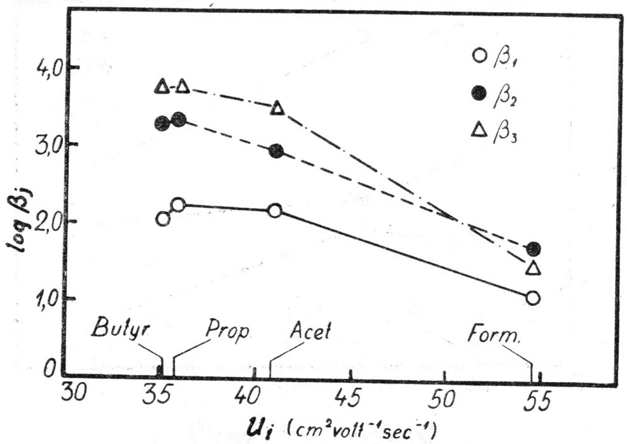

Fig. 4. Relationship between the logarithm of cumulative stability constants (β_j) of monocarboxylato complexes of lead and the limiting ion mobilities (u_i) of corresponding monocarxylate ions.

A complete analogy exists between the binding strength of each ligand to the plumbous ion and the binding of the protons in polyprotonic acids, i.e., the strongest bond exists with the first and the weakest with the third ligand ($K_1 > K_2 > K_3$). However, the stability of the bond with the second and the third ligand (i. e. the values of the consecutive constants K_2 and K_3) does not always increase with a greater ligand basicity as shown in diagram Fig. 3. Only in the formate-acetate series the stability of the bond increases for all three ligands with the increase of their base strength.

The influence of the monocarboxylate ion size on the stability of the complex is shown on the diagram in Fig. 4 and 5, where the relation between cumulative and consecutive stability constants and ionic mobility of the monocarboxylate ions is given, which according to Stokes's law is directly proportional to the average ion radius. Here two opposed effects can be expected, i.e. increase of the complex stability with the increase of the ligand size (or u_i). In this case the tendency of the ligand to polarization is greater and with it also the strength of the coordinative bond with the central ion. On the other hand, the complex stability decreases with the ligand size because the density of ion-ligand charge decreases and with it the electrostatic attraction between the ligand and the central ion. Accordingly the increase of the coordinative and decrease of the ionic character of the bond with the size of the monocarboxylate ion can influence in different ways the stability of the monocarboxylato complex as shown on diagram in Fig. 5. However, here the general tendency of the stability increase of monocarboxylato complexes with the monocarboxylate ion size is met again, in contrast with some published data[14].

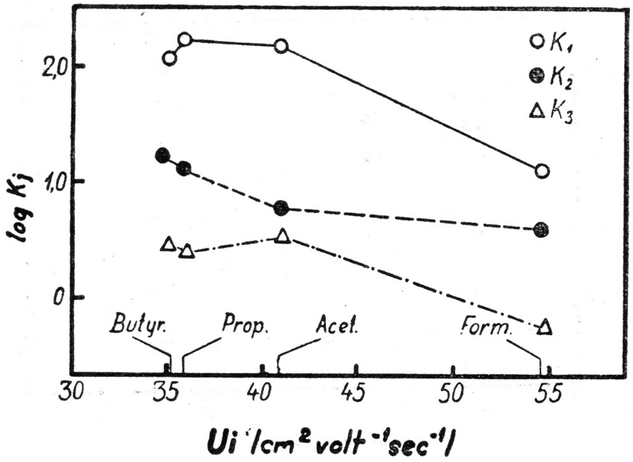

Fig. 5. Relationship between the logarithm of consecutive stability constants (K_j) of monocarboxylato complexes of lead and the limiting ion mobilities (ui) of corresponding monocarboxylate ions.

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IZVOD

Polarografska istraživanja monokarboksilato-kompleksa nekih metala. I. Olovni monokarboksilato-kompleksi

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Polarografskom metodom DeForda i Humea određene su konstante stabilnosti olovnih monokarboksilato-kompleksa u vodenim otopinama konstantne ionske jakosti 2 i konstantne koncentracije monkarbonske kiseline 2 *M*. Ispitano je područje koncentracije monokarboksilata do 2 *M*. Dobivene su slijedeće vrijednosti konstanata stabilnosti: formijato-kompleksi $\beta_1 = 13$, $\beta_2 = 50$, $\beta_3 = 30$; acetato-kompleksi $\beta_1 = 150$, $\beta_2 = 900$, $\beta_3 = 3000$; propionato-kompleksi $\beta_1 = 170$, $\beta_2 = 2200$, $\beta_3 = 5800$; butirato-kompleksi $\beta_1 = 120$, $\beta_2 = 2000$, $\beta_3 = 5800$. Očito je, da usporedno s porastom bazičnosti i veličine monokarboksilat-iona u većini slučajeva raste i stabilnost kompleksa.

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