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Original Scientific Paper

Polarographic Determination of Stability Constants of Cadmium and Lead Complexes in Buffer Solution of 3-Hydroxypropionic Acid and 2-, 3-, and 4-Hydroxybutyric Acids

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Stability constants of 3-hydroxypropionate and 2-, 3-, and 4-hydroxybutyrate complexes of cadmium and lead have been determined by the improved three-electrode polarographic technique. The ligand solution was delivered discontinuously, directly into the electrolytic cell. Refined half-wave potentials and diffusion currents were obtained by simultaneous computer treatment of graphically determined rough data, utilizing a least-squares program. The same program was subsequently used to calculate values of the $F_0([L])$-function, according to the method by De Ford and Hume. These values were weighted following a suggestion by Momoki, Sato and Ogawa. By least-squares fitting of the weighted polynomials, stability constants and corresponding standard errors were obtained.

In pursuing our systematic investigation of the stability of complexes containing cobalt, nickel, copper, zinc, cadmium, and lead, and substituted monocarboxylic acid anions, by means of polarographic[1,2], potentiometric[3], and spectrophotometric[4,5] methods, further results were obtained with an improved technique of the three-electrode polarographic method[6] and are reported in this paper. The stability constants of 3-hydroxypropionate and 2-, 3-, and 4-hydroxybutyrate complexes of cadmium and lead have been determined. These investigations are aimed at gaining some insight into the relationships of the stability of the complexes mentioned *vs.* the donor properties of ligands, *i. e.* their basicity, as well as the position of OH groups in ligands.

EXPERIMENTAL

Measurements were carried out with the three-electrode polarographic equipment, as described in a previous paper[6]. Preparation of solutions directly in the electrolytic cell by discontinuous addition of ligand solutions was also described previously[6]. Ligand concentrations varied from 0 to 1.99 M. Ionic strength of solutions was kept at the value of 2 by adding necessary amounts of sodium perchlorate. Concentration of free monocarboxylic acids in polarographed buffer solutions were adjusted to 0.01 M by adding an adequate amount of perchloric acid to the hydroxymonocarboxylate solution. A previous study[1,7] demonstrated that the presence of monocarboxylic acid in buffered solutions opposed the influence of complex formation upon half-wave potential. The shift of the half-wave potential with the increase of the monocarboxylic acid concentration to more positive values is due to the change of the

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liquid junction potential, the change of the activity coefficient of the metal ion and the change of the solution viscosity. Therefore the 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 acid-to-salt ratio (in buffers of constant pH). The concentration of 0.01 M hydroxymonocarboxylic acid in polarographed buffer solutions was selected as the minimum concentration to suppress hydroxo complex formation[1]. Each system was prepared and recorded in triplicate. In measuring potentials the reproducibility was 0.2 mV. Individual half-wave potential values of independently prepared identical solutions agreed within 1 mV. The electrode processes of the investigated complexes were reversible, *i. e.* the ratio $\Delta E_{\mathrm{d.e.}}/\Delta \log [(i_{\mathrm{d}} - i)/i]$ was within 29.5 ± 0.8 mV. The capillary constant ($m^{2/3}\, t^{1/6}$) was 1.87 mg$^{2/3}$ s$^{-1/2}$, as measured in open circuit. The drop time was maintained at 3.74 s by an electromagnetic detacher. Tridistilled mercury was used throughout. All measurements were carried out at a temperature of 25.0 ± 0.1 °C.

For the preparation of solutions analytical grade chemicals were used exclusively. Sodium salts of 3-hydroxypropionic, and 2-, 3-, and 4-hydroxybutyric acids (purchased from FLUKA A. G., Buchs, Switzerland) were purified by recrystallizing three times from absolute ethanol. Cadmium and lead perchlorates were prepared from cadmium carbonate and lead(II) oxide, respectively, and the crystals obtained were recrystallized three times. Metal contents of these perchlorates in solution were determined by potentiometric chelometric titration[8]. Free perchloric acid in metal perchlorate solutions was also titrated potentiometrically.

RESULTS

Refined half-wave potentials and diffusion currents were obtained by simultaneous treatment of graphically determined rough data with an IBM 1130 computer[6], utilizing a least-squares program. The same program was subsequently used for calculation of values of function $F_0([\mathrm{L}])$, according to the method by DeFord and Hume. These values were weighted following a suggestion by Momoki, Sato, and Ogawa[9]. By the least-squares fitting of these weighted polynomials, stability constants and correspoding standard errors were obtained. The least-squares fitting was made with either an *a priori* assumed number of complex species, which can be derived graphically from experimental data, or else, separate calculations are made for each, two, three, *etc.* up to six assumed complex species in the system.

Calculated values of the cumulative stability constants, and their standard errors are given in Table I. Values for constant β_3, with 3-hydroxypropionate and 3- and 4-hydroxybutyrate cadmium complexes, obtained by numerical treatment, are negative, and hence physically meaningless. Therefore these values have been omitted from Table I. Momoki, Ogawa, and Sato[10] give an explanation of similar cases. This problem will receive further consideration.

TABLE I

Cumulative Stability Constants

Metal Ion	Ligand	β_1	β_2	β_3	β_4
Cd^{2+}	3-OH-Propionate	14 ± 2	159 ± 19		180 ± 22
	2-OH-Butyrate	17 ± 3	136 ± 30	176 ± 74	279 ± 46
	3-OH-Butyrate	13 ± 2	160 ± 23		226 ± 26
	4-OH-Butyrate	28 ± 2	158 ± 21		267 ± 26
Pb^{2+}	3-OH-Propionate	135 ± 13	1263 ± 121	3643 ± 144	
	2-OH-Butyrate	126 ± 19	596 ± 192	3712 ± 280	
	3-OH-Butyrate	149 ± 19	996 ± 206	5045 ± 273	
	4-OH-Butyrate	189 ± 23	1412 ± 265	4380 ± 301	

DISCUSSION

Previous investigations[1-4] of metal complexes with unsubstituted and substituted monocarboxylic acid anions have shown the central ion's tendency towards polarization to play the principal role in determining the stability of its complexes. Present results (Table I) are in accordance with this constatation, since cadmium complexes were found to be considerably less stable than lead complexes.

In order to obtain better knowledge of the ligand's influence upon complex stability, values of stability constants for monoligand complexes of unsubstituted and substituted monocarboxylates are collected in Table II. This table also gives pK_A values of corresponding acids, characterizing the ligand basicities.

TABLE II

Stability Constants (β_1) *of Monoligand Complexes*

Ligand	pK_A^*	β_1	
		Cd^{2+}	Pb^{2+}
2-OH-Propionate[1]	3.82	21	140
3-OH-Propionate	4.56	14 ± 2	135 ± 13
2-OH-Butyrate	3.80	17 ± 3	126 ± 19
3-OH-Butyrate	4.53	13 ± 2	149 ± 19
4-OH-Butyrate	4.85	28 ± 2	189 ± 19
OH-Acetate[2]	3.77	26	80
Acetate[1]	4.74	20	140
Propionate[1]	4.89	20	220
Butyrate[1]	4.86	20	120

* Our results. E. m. f. method with quinhydrone electrode, ionic strength 2 ($NaClO_4$).

As can be seen from Table II, the presence of a hydroxyl group in a monocarboxylate ligand obviously causes no major change in stability for cadmium and lead complexes. This suggests that the hydroxymonocarboxylate ions behave as monodentate ligands to cadmium and lead ions, and bind the metal ion only via the carboxylic group. With lead the stability differences between the 2- and 3-hydroxypropionate complexes are insignificant, while the stabilities of 2-, 3-, and 4-hydroxybutyrate complexes increase with ligand basicity. These complexes are still a little more stable than the complex with the more strongly basic, unsubstituted butyrate ion.

Therefore, we may draw the conclusion that hydroxyl groups in hydroxymonocarboxylates bind only very weakly to the cadmium and lead ions, or do not bind at all, and the hydroxymonocarboxylate ions thus acting as monodentate ligands with donor properties governed solely by their basicity. Cobalt(II), nickel(II) and copper(II) ions[5,11], as well as zinc ion[12], behave, however, in a different way, *i. e.* their 2-hydroxymonocarboxylate complexes are more stable than the corresponding unsubstituted complexes.

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IZVOD

Polarografsko određivanje konstanata stabilnosti kompleksa kadmija i olova u tamponskim otopinama 3-hidroksipropionske kiseline i 2-, 3- i 4-hidroksimaslačne kiseline

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Određene su konstante stabilnosti kadmijevih i olovnih 3-hidroksipropionato-kompleksa i 2-, 3- i 4-hidroksibutirato-kompleksa primjenom poboljšane tehnike rada trielektrodne polarografije. Polarografirana otopina pripremana je izravno u elektrolitskoj ćeliji. Vrijednosti poluvalnih potencijala ($E_{1/2}$) i difuzijskih struja (i_d) rafinirane su na elektroničkom računalu. Primjenom metode najmanjih kvadrata izračunate su zatim na elektroničkom računalu funkcije $F_0([L])$ te konstante stabilnosti s odgovarajućim standardnim pogreškama.

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