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Potentiometric Determination of Stability Constants of Cobalt(II), Nickel(II), Copper(II), Zinc(II), Cadmium(II) and Lead(II) Complexes in Buffer Solutions of 2- and 3-Hydroxypropanoic Acids

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Stability constants of 2- and 3-hidroxypropanoate complexes of Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Pb(II) have been determined by potentiometric titration in buffer solutions at constant ionic strength of 2 mol dm^{-3}. The stability constants and their 95 per cent confidence intervals were calculated with a digital computer using weighted least squares procedure.

This paper describes results obtained in a study of complexes specified in the title, continuing a systematic investigation of metal complexes with hydroxymonocarboxylate ligands by different methods at constant ionic strength[1–8]. Such investigations aim to afford an insight into the influences exerted by size and electron configuration of the central metal ions, and hydroxyl group position within the ligand molecule upon the stability of hydroxymonocarboxylate complexes.

EXPERIMENTAL

Chemicals

Sodium 2-hydroxypropanoate was prepared by neutralization of commercially available 2-hydroxypropanoic acid (»Kemika«, p. a.) with sodium hydroxide, while sodium 3-hydroxypropanoate was prepared as described earlier[9]. Buffer solutions were prepared by adding perchloric acid to the above sodium salt solutions, and the concentration of salt in buffer solution was determined potentiometrically in glacial acetic acid medium[8].

The preparation of all investigated metal perchlorates did not differ from that described in the previous papers[1,3,10], and the metal ion concentrations were determined by chelatometric potentiometric titration.

Procedure

The continous potentiometric measurements were carried out with type E 436 potentiograph (Metrohm) in the same manner as described in one of earlier papers[7]. All measurements were performed at constant ionic strength of 2 mol dm^{-3} (by addition of $NaClO_4$) and at constant temperature of (298.2 ± 0.1) K.

Each investigated system was recorded at two metal ion concentrations, each at two acid-to-salt ratios 3 : 1 and 1 : 1. Concentrations of Pb(II) were 10 and 20 mmol dm^{-3}, while those of Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) were 20 and 50 mmol

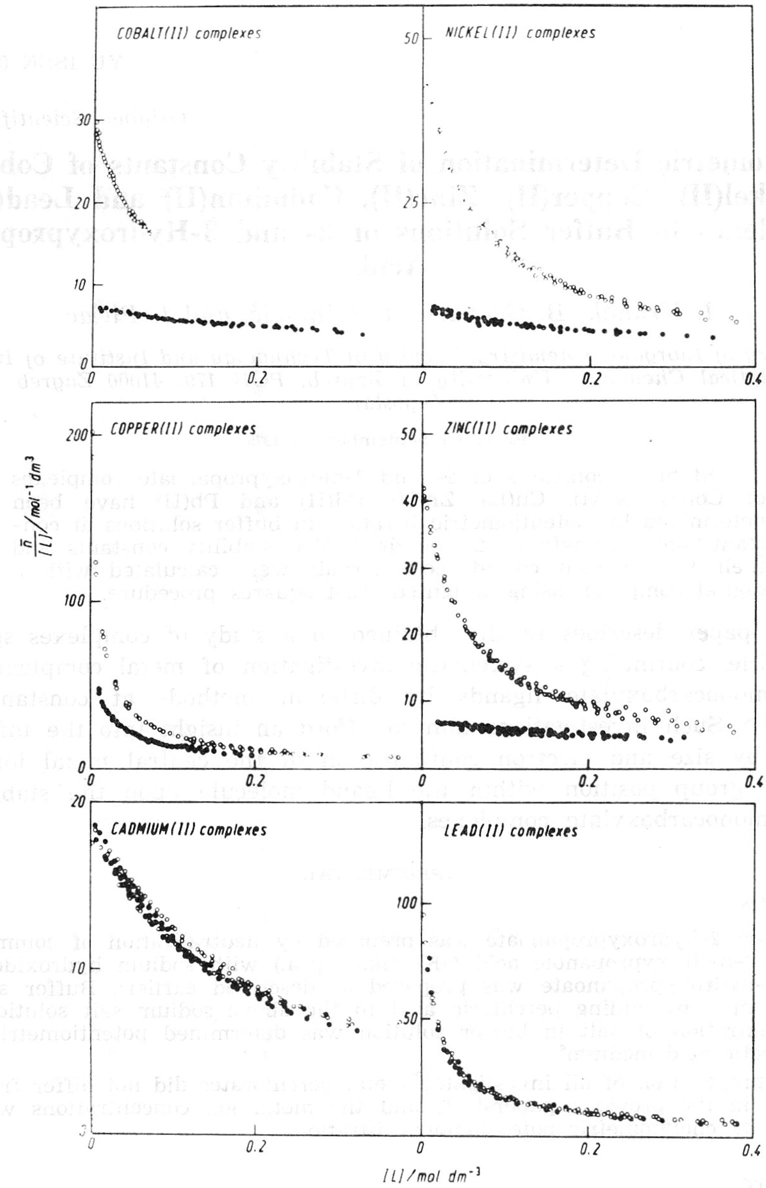

Figure 1. $\bar{n}/[L]$ vs. [L] curves for 2- and 3-hydroxypropanoate complexes.

○ 2-hydroxypropanoate complexes

● 3-hydroxypropanoate complexes

TABLE I

Stability constants of 2-hydroxypropanoate complexes

Metal ion	Method	log K_1	log β_2	log β_3
Co^{2+}	pot.	1.48 ± 0.02	2.42 ± 0.02	2.71 ± 0.02
	spe.[9]	1.28 ± 0.04	2.53 ± 0.02	
	pot.[12]	1.37	2.32	~2.52
Ni^{2+}	pot.	1.71 ± 0.02	2.84 ± 0.02	3.50 ± 0.02
	spe.[9]	1.57 ± 0.04	2.94 ± 0.02	
	pot.[12]	1.59	2.67	~2.97
Cu^{2+}	pot.	2.66 ± 0.02	4.28 ± 0.02	4.89 ± 0.02
	spe.[9]	2.63 ± 0.06	4.10 ± 0.08	5.27 ± 0.06
	pot.[12]	2.49	3.98	~4.28
Zn^{2+}	pot.	1.67 ± 0.01	2.65 ± 0.01	2.94 ± 0.01
	pot.[12]	1.61	2.85	~3.15
Cd^{2+}	pot.	1.29 ± 0.02	2.00 ± 0.02	2.64 ± 0.02
	pot.[12]	1.21	2.08	~2.28
Pb^{2+}	pot.	2.16 ± 0.02	2.23 ± 0.02	3.67 ± 0.02
	pot.[12]	1.98	2.98	
	pot.[13]	2.26	3.30	3.33

$pK_A = 3.79$

TABLE II

Stability constants of 3-hydroxypropanoate complexes

Metal ion	Method	log K_1	log β_2	log β_3	log β_4
Co^{2+}	pot.	0.86 ± 0.02	1.18 ± 0.04	1.23 ± 0.06	
	spe.[9]	0.49 ± 0.04			
Ni^{2+}	pot.	0.96 ± 0.02	1.30 ± 0.04	1.56 ± 0.02	
	spe.[9]	0.78 ± 0.06	1.32 ± 0.04		
Cu^{2+}	pot.	1.83 ± 0.02	2.79 ± 0.02	2.74 ± 0.02	
	spe.[9]	1.76 ± 0.06	3.21 ± 0.02		
Zn^{2+}	pot.[1]	0.86 ± 0.02	1.11 ± 0.08	1.43 ± 0.04	
Cd^{2+}	pot.	1.28 ± 0.04	2.12 ± 0.02	2.40 ± 0.02	
	pol.[3]	1.15 ± 0.10	2.20 ± 0.10	—	2.26 ± 0.10
Pb^{2+}	pot.	2.10 ± 0.02	3.17 ± 0.02	3.51 ± 0.02	
	pol.[3]	2.13 ± 0.08	3.10 ± 0.06	3.56 ± 0.04	

$pK_A = 4.57$

dm^{-3} in 2-hydroxypropanoate buffer solutions. Concentrations of Co(II), Ni(II), Zn(II) and Cd(II) in 3-hydroxypropanoate buffer solutions were 50 and 100 mmol dm^{-3} and these of Cu(II) and Pb(II) were 10 and 20 mmol dm^{-3}. 2-hydroxypropanoate complexes of Co(II) were investigated up to only 100 mmol dm^{-3} of ligand concentration due to the low soluble complex precipitation at higher ligand concentration.

RESULTS AND DISCUSSION

Experimental data were treated with precision of 10.5 significant digits on IBM 1130 and/or PDP-8 computers programmed to calculate average numbers ($\bar{n}$) of ligands bound to the central metal ion, the values of free-ligand concentration ([L]), as well as the values for the function $F_o([L]) = 1 + \sum_{i=1}^{N} \beta_i [L]^i$ according to well-known Fronaeus' method.[11] By solving these polynomials, using a weighted least-squares procedure[2,7], the stability constants and their 95 per cent confidence intervals were obtained.

The results are given in Table I and II. The same Tables shown the pK_A values of the corresponding hydroxymonocarboxylic acids, characterizing the basicities of the hydroxymonocarboxylate ligands. The corresponding transformed formation curves, $\bar{n}/[L]$ vs. [L], are shown in Figure 1. Curves $\bar{n}/[L]$ vs. [L] show good agreement within each system for different metal ion concentrations and for different acid-to-salt ratios. Such agreement eliminates the existence of polynuclear complexes, as well as rules out the existence of hydroxy complexes.

The stability constants for 2- and 3-hydroxypropanoate complexes reported in this paper are in good accordance with values obtained by spectrophotometric[9] and polarographic[3] methods at the same ionic strength 2 mol dm^{-3}, as well as with values obtained by different potentiometric methods at the ionic strengths 1[12] and 3[13] mol dm^{-3} ($NaClO_4$).

The effect of position of hydroxy-group in ligand, and the effect of ligand basicity (expressed in pK_A values), as well as the effect of the size of the central metal atom, upon stability of investigated complexes can be seen from the values of stability constants for monoligand complexes (log K_1) presented in Tables I and II. It is clear that only the 2-hydroxy group stabilizes monoligand complexes quite considerably, but this effect occurs only in complexes of small size central metal ions, i. e Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+}. On the other hand there is almost no difference in stability between cadmium(II) complexes with propanoate[14,15] (pK_A = 4.89[3]) and 2- and 3-hydroxypropanoate anions (pK_A = 3.79 and 4.57, respectively). The same is true for analogous lead(II) complexes. This suggests, due to the less basic character of 2-hydroxypropanoate ion (pK_A = 3.79), that 2-hydroxy group is still bound but only very weakly to the cadmium and lead ions.

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SAŽETAK

Potenciometrijsko određivanje konstanti stabilnosti kobaltovih(II), niklovih(II), bakrovih(II), cinkovih(II), kadmijevih(II) i olovnih (II) kompleksa u puferskim otopinama 2- i 3-hidroksipropionske kiseline

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Konstante stabilnosti 2- i 3-hidroksipropionato-kompleksa od Co(II), Ni(II), Cu(II), Zn(II), Cd(II) i Pb(II) određene su potenciometrijskom titracijom u puferskim otopinama konstantne ionske jakosti 2 mol dm^{-3}. Konstante stabilnosti i njihovi 95 postotni intervali pouzdanosti izračunani su pomoću elektroničkog računala primjenom vagane metode najmanjih kvadrata.

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