CROATICA CHEMICA ACTA CCACAA **51** (2) 151—156 (1978)

YU ISSN 0011-1643

CCA-1108

546.73:546.742:546.48:546.817:541.122

Note

Potentiometric Determination of the Stability Constants of 2-, 3- and 4-Hydroxybutyrato Complexes of Cobalt(II), Nickel(II), Cadmium(II) and Lead(II)

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Received April 3, 1978

The stability constants of the title complexes were determined potentiometrically using a quinhydrone electrode at (298.2 ± 0.1) K in buffer solutions of ionic strength 2 mol dm^{-3} adjusted by addition of $NaClO_4$. The numerical values of stability constants were evaluated from experimental data by computer program based on a weighted least squares method[1].

INTRODUCTION

The stability constants of cobalt(II) and nickel (II) complexes with 2-, 3- and 4-hydroxybutyrates have been determined by a spectrophotometric method[2] in this laboratory and polarography has been employed to determine the stability constants of cadmium(II) and lead(II) complexes with the same ligands[3]. In order to complete this study the same experimental conditions (i. e. temperature and ionic strength) have been maintained in the present potentiometric investigation of the above complexes, the results of which are presented in this communication.

EXPERIMENTAL

Potentiometric measurements with a quinhydrone electrode were carried out continuously using the same experimental set up and technique as described previously[1].

All measurements were performed at (298.2 ± 0.1) K in solutions of constant ionic strength 2 mol dm^{-3} adjusted by addition of $NaClO_4$.

Cobalt(II), nickel(II), cadmium(II) and lead(II) perchlorates were prepared from the corresponding carbonate (lead(II) perchlorate from lead(II) oxide) and perchloric acid. All metal perchlorates were three times recrystallized from aqueous solutions. The metal ion concentration in the stock solutions was determined by chelatometric potentiometric titration. The concentration of free acid in metal perchlorates was also determined and taken into account when preparing the buffer solutions.

The sodium salts of 2-, 3- and 4-hydroxybutyric acids have been purified by triple recrystallization from ethanol.

The composition of the buffer solutions was as follows:

The concentration of metal ion in cobalt(II) and nickel(II) solutions has been 50 and 100 mmol dm^{-3}, and acid-to-salt ratio with each of two metal ion concentrations has been 1:1 and 3:1 for 2- and 3-hydroxybutyrates and 1:1 only for 4-hydroxybutyrates.

The concentration of cadmium(II) ions was 10 and 20 mmol dm^{-3} in 2-hydroxybutyrate buffer, 20 and 50 mmol dm^{-3} in 3-hydroxybutyrate buffer and 50 and 80 mmol dm^{-3} in 4-hydroxybutyrate buffer. The acid-to-salt ratio in the above buffer solutions was 1:1 and 3:1 for each metal ion concentration. The total ligand concentration was up to 100, 300 and 500 mmol dm^{-3} for 2-, 3- and 4-hydroxybutyrates, respectively, due to formation of insoluble complexes at higher concentrations.

The concentration of lead(II) ion was 5 and 10 mmol dm^{-3} in 2-hydroxybutyrates and 10 and 20 mmol dm^{-3} in 3- and 4-hydroxybutyrato solutions. The acid-to-salt ratio was 3:1 and 4:1 for each metal ion concentration.

Experimental data were evaluated by a computer program on either IBM 1130 or PDP 8 computers in extended precision (10.5 significant digits) using the weighted least squares algorithm described previuosly[1].

RESULTS AND DISCUSSION

Logarithmic values of the stability constants together with 95 per cent confidence intervals are given in Table I. From transformed formation curves (Figures 1—4) it can be seen, that for all investigated systems excellent agreement is obtained using a different metal ion concentration and a different acid-to-salt ratio in buffer solutions. This agreement clearly indicates the absence of both polynuclear and/or mixed hydroxo complexes in the investigated systems under given experimental conditions.

A comparison of the results (Table II), obtained for Co(II) and Ni(II) complexes by the spectrophotometric method[2] and for Cd(II) and Pb(II) complexes by the polarographic method[3] unambiguously proves the reliability of K_1 values.

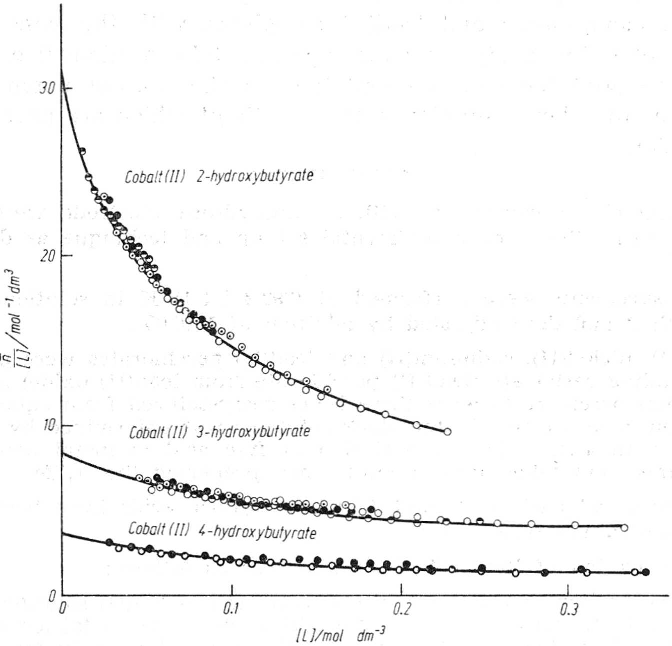

Figure 1. $\tilde{n}/[L]$ vs. $[L]$ curves for Co(II) complexes.

TABLE I

Cumulative Stability Constants and their ± 95 per cent Confidence Intervals

Metal ion	Ligand	log K_1	log β_2	log β_3
Co(II)	2-hydroxybutyrate	1.49 ± 0.03	2.38 ± 0.01	3.04 ± 0.01
	3-hydroxybutyrate	0.91 ± 0.02	1.08 ± 0.07	1.26 ± 0.04
	4-hydroxybutyrate	0.45 ± 0.01		
Ni(II)	2-hydroxybutyrate	1.72 ± 0.03	2.89 ± 0.01	3.63 ± 0.01
	3-hydroxybutyrate	1.00 ± 0.01	1.34 ± 0.04	1.71 ± 0.03
	4-hydroxybutyrate	0.63 ± 0.01	0.18 ± 0.10	
Cd(II)	2-hydroxybutyrate	1.29 ± 0.01	2.07 ± 0.01	3.00 ± 0.01
	3-hydroxybutyrate	1.28 ± 0.01	2.10 ± 0.01	2.49 ± 0.01
	4-hydroxybutyrate	1.33 ± 0.01	2.00 ± 0.01	2.68 ± 0.01
Pb(II)	2-hydroxybutyrate	2.16 ± 0.05	3.32 ± 0.02	4.03 ± 0.03
	3-hydroxybutyrate	2.09 ± 0.01	3.39 ± 0.01	3.81 ± 0.02
	4-hydroxybutyrate	2.08 ± 0.02	3.54 ± 0.01	3.81 ± 0.04

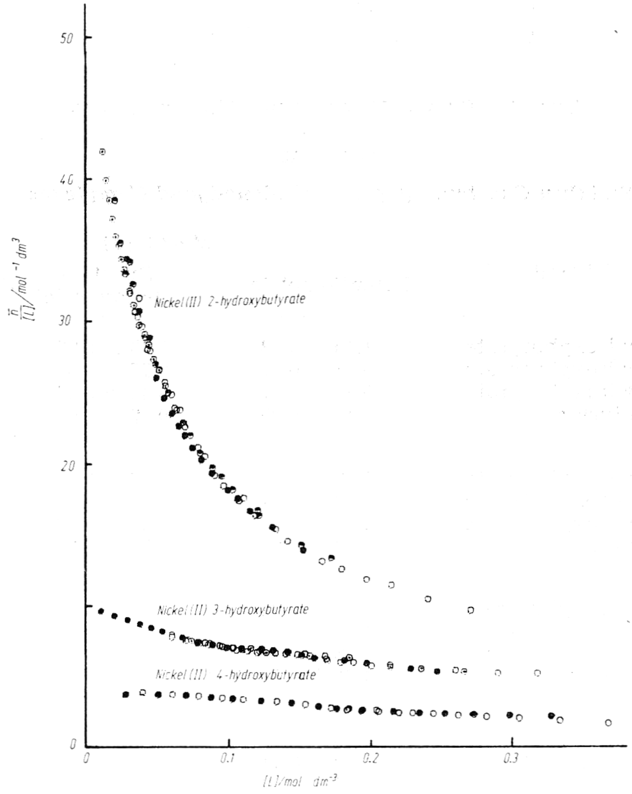

Figure 2. $\bar{n}/[L]$ vs. $[L]$ curves for Ni(II) complexes.

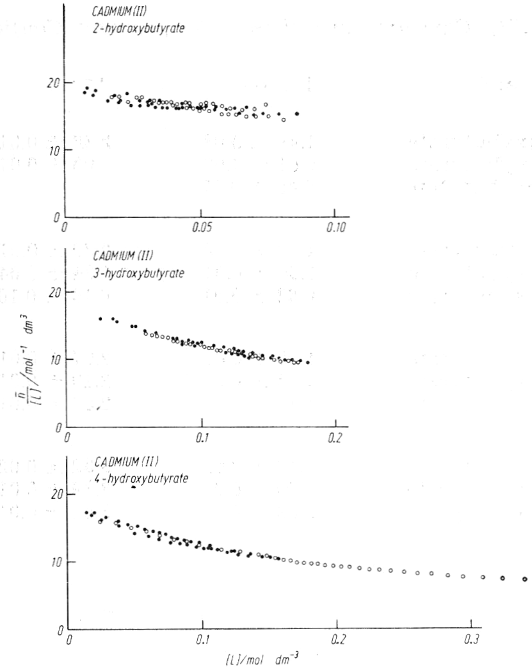

Figure 3. $\tilde{n}/[L]$ vs. [L] curves for Cd(II) complexes.

TABLE II

Stability Constants (log K_1) of Monoligand Complexes

Metal ion	Ligand	Method		
		Potentiometric	Spectro-photometric[2]	Polarographic[3]
Co(II)	2-hydroxybutyrate	1.49 ± 0.03	1.43 ± 0.03	
	3-hydroxybutyrate	0.91 ± 0.02	0.75 ± 0.06	
	4-hydroxybutyrate	0.45 ± 0.01	0.48 ± 0.03	
	n-butyrate	0.66 ± 0.05	0.59 ± 0.02	
Ni(II)	2-hydroxybutyrate	1.72 ± 0.03	1.72 ± 0.03	
	3-hydroxybutyrate	1.00 ± 0.01	1.00 ± 0.08	
	4-hydroxybutyrate	0.63 ± 0.01	0.52 ± 0.08	
	n-butyrate	0.73 ± 0.03	0.71 ± 0.05	
Cd(II)	2-hydroxybutyrate	1.29 ± 0.01		1.23 ± 0.07
	3-hydroxybutyrate	1.28 ± 0.01		1.11 ± 0.07
	4-hydroxybutyrate	1.33 ± 0.01		1.45 ± 0.03
	n-butyrate	1.20 ± 0.03 (ref 4)		1.30 (ref 5)
Pb(II)	2-hydroxybutyrate	2.16 ± 0.05		2.10 ± 0.06
	3-hydroxybutyrate	2.09 ± 0.01		2.12 ± 0.05
	4-hydroxybutyrate	2.08 ± 0.02		2.27 ± 0.05
	n-butyrate	2.17 ± 0.05 (ref 4)		2.08 (ref 5)

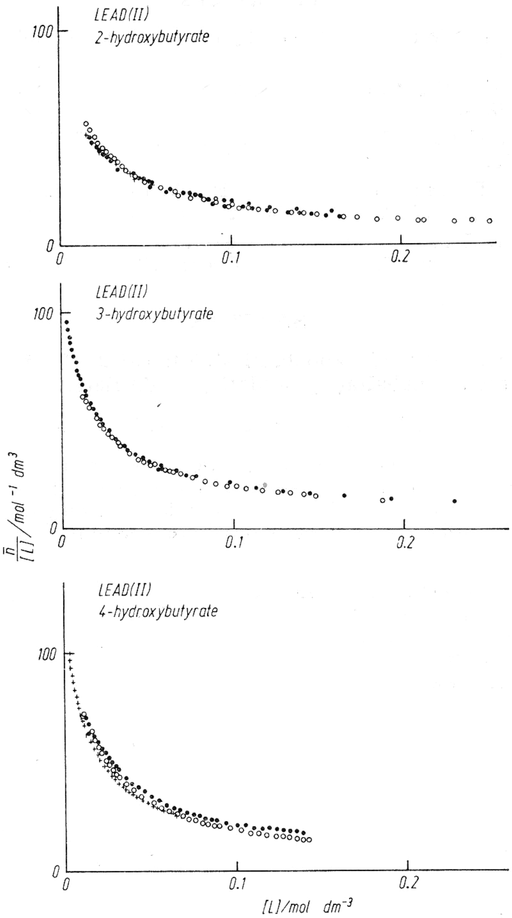

Figure 4. $\tilde{n}/[L]$ vs. $[L]$ curves for Pb(II) complexes.

Taking the pK_A values of monocarboxylic acids as a measure for the basicity of corresponding ligands (anions), it would be expected that the *n*-butyrato and 4-hydroxybutyrato complexes are more stable than 3-hydroxybutyrato complexes since the basicity is decreasing in the same order ($pK_A = 4.86$, 4.85, 4.53 and 3.80, respectively). The obtained results indicate that apart from basicity the OH-group also contributes to the stability of the complexes by direct or indirect (via H_2O) coordination to the metal ion. The magnitude of this additional chelate stabilization is influenced by the position of the OH-group in the ligand. Position *2* of the OH-group is the most favourable for chelate coordination and therefore the contribution of chelate stabilization is greatest in 2-hydroxybutyrato complexes. The positions *3* and *4* of OH-group are farther away from the carboxylic group and therefore they are less favourable for chelate coordination wich is in accordance with the obtained results.

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SAŽETAK

Potenciometrijsko određivanje konstanti stabilnosti 2-, 3-, i 4-hidroksibutirato-kompleksa kobalta(II), nikla(II), kadmija(II) i olova(II)

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Ispitivana je stabilnost kompleksa navedenih u naslovu. Konstante stabilnosti kompleksa određene su potenciometrijskom metodom uz primjenu kinhidronske elektrode pri temperaturi (298.2 ± 0.1) K i ionskoj jakosti 2 mol dm^{-3} ($NaClO_4$). Eksperimentalni rezultati obrađeni su na elektroničkom računalu vaganom metodom najmanjih kvadrata[1].

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