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Stability Constants of Zinc Complexes with 3-Hydroxypropionate and 2-, 3-, and 4-Hydroxybutyrates

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Stability constants of zinc 3-hydroxypropionato and 2-, 3-, and 4-hydroxybutyrato complexes have been determined by potentiometric titration. The constants and their standard errors have been calculated with a digital computer. On the basis of the results obtained, the stability of these complexes is discussed with respect to the ligand basicity and the position of the hydroxyl group within the ligand molecule.

This paper describes results obtained in a study of zinc hydroxymonocarboxylato complexes, continuing a systematic investigation of metal complexes with these ligands[1,2]. The present study aims to afford an insight into the influences exerted by size and electron configuration of the central metal ions upon the stability of their hydroxymonocarboxylato complexes at constant ionic strength. Such investigations may also serve to study the relationship of complex stability and ligand basicity, as well as the relationship between stability and hydroxyl group position within the ligand molecule. The literature[3] gives only scant information on zinc complex stabilities; moreover, stability constants reported in the literature were obtained at different ionic strengths, in solutions containing »inert« salts, which can themselves enter into complexes with zinc (*e. g.* KCl).

EXPERIMENTAL

Potentiometric measurements with buffer solutions containing 2-, 3-, and 4-hydroxybutyrato, as well as *n*-butyrato zinc complexes, were carried out according to H. Thun, F. Verbeek, and W. Wanderleen[4]. The titration vessel consisted of three compartments. Compartment 1 contained the reference solution, 20.07 mM $HClO_4$, adjusted to ionic strength 2 with $NaClO_4$. Compartment 2 held 5 ml (initial volume) 50 or 100 mM zinc perchlorate, adjusted to the same ionic strength with $NaClO_4$. A buffer solution, 1 M in both NaL and HL, was simultaneously delivered in portions to the solutions in compartments 2 and 3, using a precision microburet (Metrohm E 457, reproducibility 0.001 ml). Contact between compartments was established by means of a three-branched salt bridge filled with 2 M $NaClO_4$. The bridge endings were made of special porous glass. Mixing of solution was performed by bubbling nitrogen through the liquids. During measurements mixing was interrupted, and the gas was allowed to stream over the liquids surfaces. Potential differences between compartments 1 and 2 (*E*), and compartments 1 and 3 (E_0) were measured with a Präzisions Kurbelkompensator (VEB Messtechnik), connected to a Lange Multiflex Galvanometer Model MG-3. All measurements were carried out with a quinhydrone electrode in each compartment, at 25.0 ± 0.1 °C. Good agreement between formation curves obtained at different metal ion concentrations suggested the absence of polynuclear complexes from the systems measured and the absence of interaction between the metal ion and the quinhydrone electrode; if such interaction took place, it must have been negligible.

Zinc 3-hydroxypropionato complexes were determined by continuous potentiometric titration with an E 436 Metrohm potentiograph. 10 ml of a solution (S_1) containing 20 mM NaL, 20 δ mM HL, and enough $NaClO_4$ to obtain an ionic strength of 2, was placed in to the titration vessel; another solution (S_2), containing 425 mM NaL, 425 δ mM HL, adjusted to ionic strength 2 with $NaClO_4$, was used as titrant and delivered continuously from an automatic buret. Potential differences, E_0, between the solution in the vessel and a reference solution (20 mM $HClO_4$, adjusted to ionic strength 2 with $NaClO_4$) were monitored during the titrant addition. Next, S_2 was placed into the titration vessel, and S_1 was used as the titrant. In another series, 10 ml of a solution (S_3) containing either 50 or 100 mM zinc perchlorate, in addition to 20 δ mM HL, and $NaClO_4$ to give an ionic strength of 2, was continuously titrated with a solution (S_4) composed of 425 mM NaL, 425 δ mM HL, and $NaClO_4$ up to ionic strength 2, and potential differences (E) against the above mentioned reference solution monitored during titration. Subsequently, again, the titration was repeated in reverse order of sample and titrant.

The acid-to-salt (HL to NaL) ratio in one set of buffers was 1 : 1 (*i. e.* $\delta = 1$), and in another set 3 : 1 ($\delta = 3$). Here, too, good agreement of formation curves (Fig. 1), recorded with different metal ion concentrations, and different acid-to-salt ratios, indicated the absence of polynuclear and hydroxo coplexes.

Reproducibility of added volumes in these titrations was 0.01 ml, and that of potential measurements 0.2 mV. The solutions were mixed either magnetically, or by bubbling nitrogen.

All chemicals were analytical grade, except the sodium salts of 2-, 3-, and 4-hydroxybutyric and of 3-hydroxypropionic acids. These salts were purified before use; sodium hydroxybutyrates were recrystallized twice from ethanol, and sodium 3-hydroxypropionate from a mixture of ethanol and methanol. Zinc perchlorate was prepared from zinc oxide and perchloric acid, and purified by three recrystallizations. Sodium perchlorate was also purified by three recrystaliizations.

RESULTS AND DISCUSSION

Table I shows a typical set of results for different buffer compositions. Zinc concentration in these buffers was 100 mM, and the acid-to-salt ratio was 1 : 1.

Experimental data were treated with an IBM 1130 computer programmed to calculate average numbers, $\bar{n}$, of ligands bound to the central atom, as well as values of free-ligand concentrations, [L], according to well-known relationships[4]. In addition, a numerical treatment was applied to Fronaeus' graphical method[5], to give values for the function $F_0\,([L]) = 1 + \sum_{i=1}^{N} \beta_i\,[L]^i$. By solving these polynominals, using a weighted least-squares procedure, the stability constants and their standard errors were obtained. The weighted least-squares routine was the same as in a previous work[6]. Other details of the numerical treatment and the computer program will be discussed elsewhere.

Table II shows the stability constants obtained and their standard errors. Taken together with reported data[7,8], the results from Table II and Fig. 1 demonstrate that the central atom binds a maximum of three ligands in the hydroxypropionato, and a maximum of four in the hydroxybutyrato complex series, provided the same zinc concentration and approximately the same ligand concentrations are used. This difference is obviously unrelated to the order of stabilities, since the 2-hydroxybutyrato complexes are considerably more stable than the 3- and 4-hydroxybutyrato complexes. However, the latter complexes containing three ligands, ML_3^-, are very unstable (K_3 values

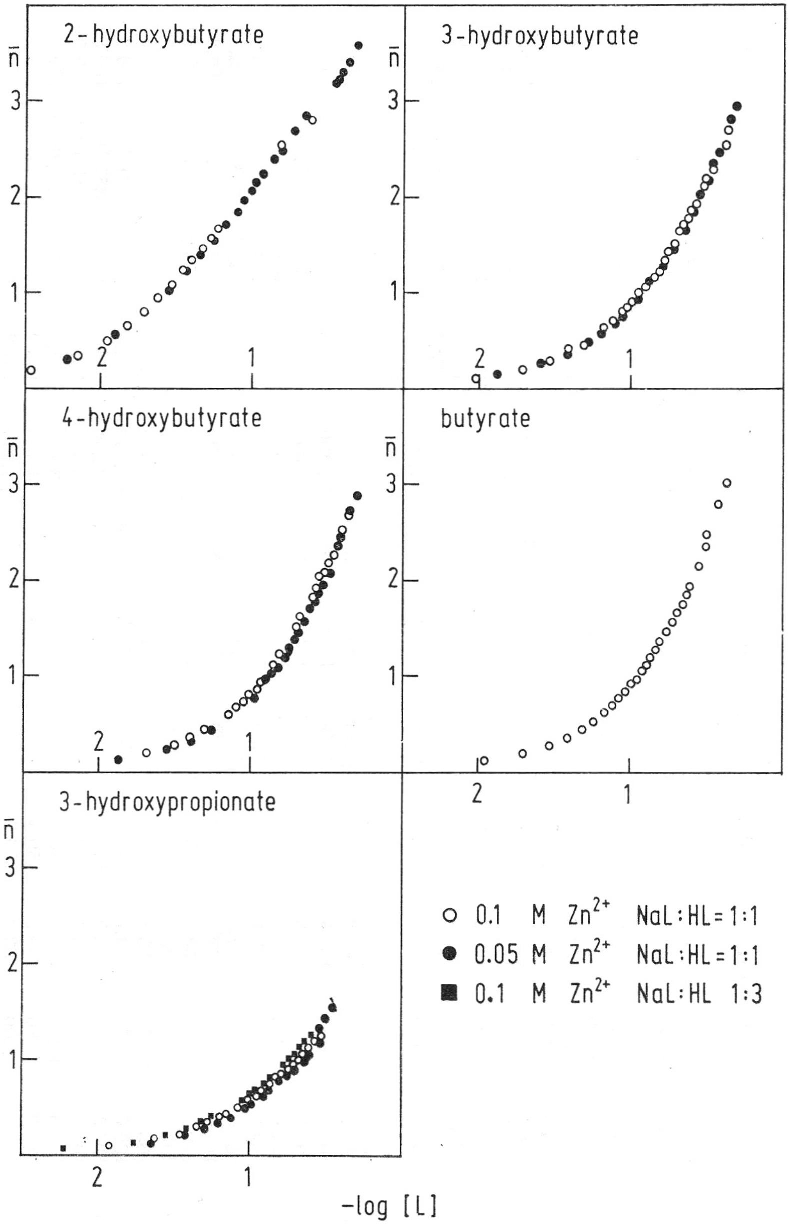

Fig. 1. Formation curves of zinc 3-hydroxypropionate, n-butyrate, 2-hydroxybutyrate, 3-hydroxybutyrate and 4-hydroxybutyrate complex systems

TABLE I

Zinc Solutions

2-Hydroxybutyrate			3-Hydroxybutyrate			4-Hydroxybutyrate			Butyrate			3-Hydroxypropionate		
Soln. S_1 ml	E_0/mV	E/mV	Soln. S_1 ml	E_0/mV	E/mV	Soln. S_1 ml	E_0/mV	E/mV	Soln. S_1 ml	E_0/mV	E/mV	C_L/mM	E_0/mV	E/mV
0.100	117.7	73.7	0.100	158.7	140.8	0.200	171.2	155.3	0.110	179.7	162.9	20.00	169.8	156.5
0.200	116.5	73.1	0.200	158.0	140.8	0.300	171.0	155.3	0.200	179.2	162.8	39.29	169.8	156.8
0.300	116.2	73.9	0.300	157.8	141.0	0.400	170.8	155.4	0.300	179.1	163.1	56.82	169.8	156.9
0.400	116.2	75.0	0.400	157.7	141.4	0.500	170.8	155.9	0.400	179.2	163.5	72.83	169.8	157.0
0.500	116.1	76.5	0.500	157.7	141.7	0.700	170.7	156.6	0.500	179.3	163.9	87.50	169.8	157.2
0.600	116.1	77.9	0.700	157.7	142.5	0.800	170.7	156.9	0.600	179.5	164.4	101.00	169.8	157.4
0.700	116.1	79.3	0.800	157.7	142.9	0.900	170.7	157.3	0.700	179.7	164.8	113.46	169.8	157.5
0.800	116.1	80.8	0.905	157.7	143.3	1.000	170.6	157.6	0.800	179.8	165.2	125.00	169.8	157.7
0.900	116.2	82.0	1.000	157.7	143.4	1.100	170.6	157.7	0.901	179.9	165.7	135.71	169.8	157.9
1.000	116.2	83.6	1.100	157.7	143.9	1.200	170.6	157.8	1.001	180.0	166.0	146.55	169.8	158.0
1.100	116.3	84.9	1.200	157.7	144.1	1.500	170.8	158.9	1.100	180.1	166.2	155.00	169.8	158.1
1.200	116.3	85.8	1.350	157.7	144.6	1.650	170.8	159.0	1.200	180.2	166.7	171.88	169.8	158.3
1.800	116.6	90.3	1.500	157.8	145.2	2.200	170.9	160.1	1.300	180.4	167.1	186.76	169.8	158.5
2.000	116.6	93.1	1.650	157.8	145.5	2.400	170.9	160.4	1.400	180.6	167.5	200.00	169.8	158.6
2.200	116.7	95.0	1.802	157.8	146.0	3.000	171.0	161.7	1.500	180.7	167.8	211.84	169.8	158.8
2.400	116.8	97.6	2.000	157.8	146.3	3.250	171.1	162.1	1.650	181.0	168.4	222.50	169.8	158.9
2.600	116.8	99.3	2.200	157.9	146.9	3.500	171.1	162.2	1.801	181.2	168.9	233.16	169.8	158.9
2.800	116.9	100.8	2.400	157.9	147.1	3.750	171.2	162.8	2.000	181.5	169.6	245.00	169.8	159.0
3.000	117.0	101.7	2.600	158.0	147.8	4.099	171.2	163.2	2.200	181.6	170.3	258.24	169.8	159.2
3.250	117.1	102.9	2.800	158.0	148.2	4.252	171.3	163.5	2.400	181.9	170.9	273.13	169.8	159.4
3.500	117.2	104.1	3.001	158.0	148.5	4.500	171.3	163.8	2.600	182.1	171.5	290.00	168.8	159.5
3.750	117.3	105.1	3.206	158.1	148.9	5.500	171.4	164.7	2.800	182.5	172.1	309.29	169.8	159.7
4.000	117.4	106.0	3.400	158.1	149.1	6.500	171.4	165.5	3.000	182.6	172.6	331.54	169.8	159.9
4.250	117.4	106.8	3.620	158.2	149.4				3.250	183.0	173.0	357.50	169.8	160.1
4.500	117.5	107.4	3.800	158.2	149.8				3.502	183.3	173.9	388.18	169.8	160.4
5.500	117.7	109.5	4.000	158.2	150.0				3.750	183.7	174.3	425.00	169.8	160.9
6.500	117.9	111.0	4.250	158.2	150.3				4.000	183.9	174.9			
			4.500	158.2	150.6				4.250	184.2	175.4			
			5.500	158.4	151.6				4.501	184.4	176.0			
			6.500	158.4	152.4				5.500	185.2	177.7			
									6.500	186.1	179.3			

TABLE II

Cumulative Stability Constants

Ligand	β_1	β_2	β_3	β_4
3-Hydroxypropionate	7.2 ± 0.1	13 ± 1	27 ± 1	
2-Hydroxybutyrate	52 ± 1	1 059 ± 16	6 974 ± 173	17 415 ± 262
3-Hydroxybutyrate	9.8 ± 0.1	51 ± 1	31 ± 5	313 ± 6
4-Hydroxybutyrate	9.2 ± 0.1	36 ± 1	34 ± 3	239 ± 4
n-Butyrate	9.4 ± 0.1	45 ± 2	54 ± 9	373 ± 14

are 0.6 and 0.9, respectively), while type ML_4^{2-} complexes have much greater stabilities (K_4 values: 10 and 7, respectively). The relative stability of ML_4^{2-} type complexes is in accordance with the zinc coordination number of 4.

The effects of presence and position of a hydroxy group in the monocarboxylate anion, and the effect of the latter's basicity, upon zinc complex stabilities can be seen from data presented in Table III. This Table shows

TABLE III

Stability Constants of Monoligand Complexes at Ionic Strength 2 ($NaClO_4$)

Ligand	β_1	pK_A^*
Acetate[7]	7.0 ± 0.6	4.74
2-Hydroxyacetate[7]	52 ± 7	3.77
Propionate[7]	9.9 ± 0.7	4.89
2-Hydroxypropionate[6]	40.7	3.82
3-Hydroxypropionate	7.2 ± 0.1	4.56
n-Butyrate	9.4 ± 0.1	4.86
2-Hydroxybutyrate	52 ± 1	3.80
3-Hydroxybutyrate	9.8 ± 0.1	4.53
4-Hydroxybutyrate	9.2 ± 0.1	4.85

* Our measurements.

values of stability constants for monoligand complexes (β_1), along with pK_A values for the corresponding monocarboxylic acids, characterizing ligand basicity. It is clear that a 2-hydroxy group stabilizes the corresponding zinc monoligand complex quite considerably, despite a low ligand basicity. When, however, the hydroxyl group occupies positions 3 or 4, it does not influence complex stability, the hydroxymonocarboxylate ions thus acting as monodentate ligands, and bind the metal ion only *via* the carboxylic group. Such circumstances are in good accordance with the well-known property of ring formation to contribute to complex stability, since a stable ring can be formed only with the hydroxy group in position 2[9]. Ring stabilization depends, however, on the size of the central metal atom[2], *e. g.* there is no difference in stability between cadmium complexes with unsubstituted and substituted monocarboxylate anions.

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IZVOD

Konstante stabilnosti cinkovih kompleksa s 3-hidroksipropionatom i 2-, 3- i 4-hidroksibutiratom

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Određene su konstante stabilnosti 3-hidroksipropionato i 2-, 3- i 4-hidroksibutirato-kompleksa cinka potenciometrijskom titracijom. Konstante stabilnosti i njihove standardne pogreške dobivene su pomoću elektroničkog računala. Na osnovu rezultata diskutirana je stabilnost kompleksa s obzirom na bazičnost liganda i položaj hidroksilne skupine u ligandu.

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