On the Stability of Formato, Acetato, Propionato, Butyrato, Glycolato and Chloroacetato Complexes of Cobalt, Nickel, Copper, Zinc, Cadmium and Lead

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Stability constants of formato, acetato, propionato, butyrato, glycolato and chloroacetato complexes of cobalt, nickel, copper, zinc, cadmium and lead have been determined by the potentiometric method. The change of concentration of hydrogen ions in the monocarboxylate buffer has been measured. Stability constants have been obtained by means of a digital computer applying the Gauss Z programme devised by R. S. Tobias. On the basis of these results as well as the results obtained in the former investigations by the polarographic and spectrophotometric method, the stability of the investigated monocarboxylato complexes has been discussed and the corresponding orders of stability were established.

The former papers[1-3] give the results of the determination of stability constants of formato, acetato, propionato, butyrato, glycolato and chloroacetato complexes by the polarographic[1,2] and spectrophotometric[3] methods. The present paper reports the results of the determination of stability constants of the above mentioned monocarboxylato complexes by the potentiometric method, obtained by measuring the hydrogen ion concentration in the monocarboxylate buffer. In this way each of the investigated monocarboxylato complexes was investigated with two essentially different methods of determining stability constants, and the relation of the stability of the complex could be better estimated both with regard to the central ion and to the ligand. This is especially important because the values of stability constants, which can be found in literature[5] for some systems, differ considerably for one and the same system.

EXPERIMENTAL

A »Universal Precision Potentiometer« No. 7565, (W. G. Pye Co. Ltd.), and a »Präzisions-Kurbelkompensator« (V. E. B. Messtechnik) were used for potential measurements. A »Multiflex Galvanometer« MG-3 (B. Lange) was used as zero indicator. The H-type cell used and the rest of the equipment were described earlier[6] as well as the procedure of measuring the electromotive force of the cell[4,6]. All measurements were performed at the temperature of $25 \pm 0.1^\circ$ C except those in chloroacetate buffers where it was $18 \pm 0.1^\circ$ C in order to avoid the hydrolysis of the chloroacetate[2].

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Solutions were prepared from analytically pure chemicals or they were purified by recrystallization (sodium glycolate)[2]. Metal perchlorates were prepared as described before[1-3]. The ionic strength of investigated solutions was kept constant at $2M$.

The possibility of applying the quinhydrone electrode for the measurement of the hydrogen ion concentration in the presence of metal ions (Co^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+} and Pb^{2+}) was investigated. The differences of potential with the same hydrogen ion concentration were within 0.2 mV for Zn^{2+} and Cd^{2+}, 0.25 mV for Pb^{2+}, 0.8 mV for Co^{2+} and 1 mV for Ni^{2+}. Accordingly, the quinhydrone electrode is satisfactory for the measurements with Zn^{2+}, Cd^{2+} and Pb^{2+} completely. Probably a weak inter-action with quinhydrone takes place with Co^{2+} and Ni^{2+}. However, the quinhydrone electrode was used in these systems as well.

The absence of polynuclear complex species was established by measurements with different concentrations (up to 100 mM) of the metal ion.

The proportion of monocarboxylic acid and its salt in the buffer was chosen so as not to allow the hydrolysis of monocarboxylato complexes. It was experimentally established by changing the above mentioned proportion.

Results of measurements could be best reproduced in acetate, propionate, butyrate and glycolate buffers within ±0.3 mV. A somewhat less good reproducibility of results was obtained in chloroacetate buffers. In formate buffers the results of measurements could be reproduced within ±1 mV. The reproducibily of the measurement of emf. was better in the solution with a lower concentration of formate in the buffer. Besides, in formate buffers the establishment of a constant emf. of the cell was very slow and it was the slower, the higher the ratio of the concentration of formic acid and the concentration of sodium formate in the buffer. Therefore the emf. was read always at the same time after adding quinhydrone into the cell (5 min.).

RESULTS

In Table I one typical set of results of measurements and the composition of the buffer solution is reproduced, i. e. the concentration of sodium monocarboxylate (C_L), the ratio of the concentration of monocarboxylic acid to the concentration of sodium monocarboxylate ($C_{HL} : C_L$), and the metal ion concentration (C_M). The concentration of the free ligand ([L]) and the average ligand number ($\bar{n}$) were calculated from the electromotive force in the absence (E_0) and in the presence (E) of the metal ion. The $\bar{n}/[L]$ vs. [L] curve was obtained

TABLE I

Cobalt Solutions

Formate			Acetate			
$C_{HL}:C_L=1:1$		$C_M=50$ mM	$C_{HL}:C_L=4:1$		$C_M=50$ mM	$C_M=100$ mM
C_L mM	E_0 mV	E mV	C_L mM	E_0 mV	E mV	E mV
50	121.1	115.7	30	146.1	140.9	136.5
60	121.9	116.0	40	146.0	140.9	136.5
70	122.3	116.1	60	145.8	140.9	136.6
80	122.4	116.3	80	145.7	140.8	136.6
90	122.6	116.7	100	145.7	140.9	136.7
100	122.7	117.0	130	145.7	141.7	136.9
120	123.2	117.4	160	145.8	141.1	137.2
140	123.3	117.9	200	146.0	141.6	137.6
170	123.9	118.4	250	146.0	141.6	137.8
200	125.7	120.2	300	146.0	141.8	138.0
230	125.6	120.7	350	146.0	142.1	138.3
			400	146.1	142.3	138.9

TABLE I

(continued)

Acetate				Propionate			
C_{HL}:C_L=2:1	C_M=50 mM		C_M=100 mM	C_{HL}:C_L=4:1	C_M=50 mM		C_M=100 mM
C_L mM	E_0 mV	E mV	E mV	C_L mM	E_0 mV	E mV	E mV
20	165.1	160.1	—	10	155.0	149.7	—
30	164.7	160.0	155.1	20	154.6	149.6	144.7
40	164.5	159.9	155.1	30	154.4	149.4	144.6
60	164.3	159.8	155.2	40	154.3	149.3	144.5
80	164.4	160.0	155.4	60	154.1	149.1	144.3
100	164.4	160.0	155.5	80	154.1	149.2	144.4
130	164.3	160.0	155.6	100	154.2	149.5	144.8
160	164.3	160.0	155.7	130	154.4	149.9	145.4
200	164.3	160.1	156.0	160	154.8	150.5	146.1
200	164.3	160.2	156.2	200	154.4	151.2	146.9
300	164.4	160.4	156.6	250	156.3	152.1	148.0
300	164.4	160.5	156.9	300	157.0	152.9	148.9
400	164.4	160.7	157.2	350	157.7	153.6	149.8
				400	158.4	154.4	150.7

Butyrate				Glycolate			
C_{HL}:C_L=4:1	C_M=50 mM		C_M=100 mM	C_{HL}:C_L=1:1	C_M=50 mM		C_M=100 mM
C_L mM	E_0 mV	E mV	E mV	C_L mM	E_0 mV	E mV	E mV
5	154.4	149.4	144.6	20	120.7	99.1	—
10	153.0	148.0	144.2	30	120.5	99.9	—
20	152.4	147.5	143.7	40	120.3	100.6	87.3
30	152.2	147.3	142.6	60	120.1	101.8	88.8
40	152.2	147.4	142.8	80	119.7	103.0	90.3
60	152.3	147.6	143.0	100	119.7	104.2	91.9
80	152.8	148.2	143.6	130	119.7	105.3	92.4
100	153.6	149.1	144.6	160	119.4	106.5	95.0
130	154.8	150.4	145.9	200	119.5	107.7	97.0
160	156.1	151.8	147.5	250	119.1	109.0	98.8
200	157.8	153.7	149.4	300	117.7	109.7	100.6
250	159.9	156.0	151.8	400	117.7	110.7	103.0
300	161.1	157.4	153.4				
350	163.9	160.4	156.6				
400	165.9	162.7	159.0				

from these values. After the extrapolation of the curve on [L] = 0 a graphic integration was performed, and then the function F_o ([L]) was calculated from the value of the integral. From this function the other functions F_j ([L]) and finally the cumulative stability constants β_j were obtained. Their values are given in Table II (denoted as »graph«).

TABLE I

(continued)

Glycolate				Chloroacetate			
$C_{HL}:C_L=2:1$		$C_M=50$ mM	$C_M=100$ mM	$C_{HL}:C_L=1:1$		$C_M=50$ mM	
C_L mM	E_0 mV	E mV	E mV	C_L mM	E_0 mV	E mV	
15	103.2	82.7	—	15	68.6	61.8	
20	103.1	86.6	70.1	20	68.0	62.2	
30	102.6	83.3	70.3	25	67.4	62.0	
40	102.5	83.9	71.1	30	67.1	62.0	
60	102.4	85.2	72.3	40	66.5	62.1	
80	101.9	85.8	73.2	50	66.5	62.0	
100	101.7	86.7	74.4	60	66.5	62.6	
130	101.6	88.0	76.0	70	65.8	62.5	
160	101.3	88.6	77.3	80	65.8	62.5	
200	100.9	89.8	78.7	90	65.7	62.4	
250	100.7	90.2	80.3	100	65.0	62.5	
300	100.0	91.1	87.7	120	65.0	62.4	
400	99.4	91.9	84.2	140	64.9	62.7	
				170	64.2	62.8	
				200	64.0	63.0	
				230	64.2	63.2	
				260	64.6	63.1	
				300	64.9	63.4	
				350	65.3	63.5	
				400	66.2	63.8	

The values of β_j, obtained by means of the above mentioned graphic treatment, served as initial estimates and were refined by means of the Gauss Z programme written by R. S. Tobias. The obtained values of the cumulative stability constants and their standard errors are given in Table II (denoted as »comp.«).

DISCUSSION

The values of stability constants of monoligand monocarboxylato complexes, determined by the potentiometric, polarographic[1,2] and spectrophotometric[3] methods are given in Table III. It can be seen that remarkable disagreement exists between the values obtained by two essentially different methods for the copper monocarboxylato complexes (except chloroacetate). A further study of this discrepancy is in course. In the systems of lead monocarboxylato complexes differences are greater in acetato, propionato and butyrato complexes. However, most of the investigated systems give a good or satisfactory agreement, especially for Co^{2+}, Ni^{2+} and Cd^{2+}.

With regard to the values of stability constants in Table III and taking into consideration lower accuracy of the potentiometric measurements in formate buffers as compared with spectrophotometric measurements, the following orders can be established according to the increasing stability of monoligand complexes:

Formato complexes   : Co < Ni < Zn < Cd < Pb < Cu
Acetato complexes   : Co < Ni < Zn < Cd < Pb,   Cu
Propionato complexes   : Co < Ni < Zn < Cd < Pb,   Cu
Butyrato complexes   : Co < Ni < Zn < Cd < Pb,   Cu
Glycolato complexes   : Co < Ni < Cd < Zn,   Pb < Cu

Chloroacetato complexes : Co,   Ni < Zn < Cd < Cu < Pb

or:

Co : ClAc < Form < Ac,   But < Prop < Glycol
Ni : ClAc < Form < Ac,   But < Prop < Glycol
Cu : ClAc < Form < But < Ac < Prop < Glycol
Zn : ClAc < Form < Ac < Prop,   But < Glycol
Cd : ClAc < Form < Ac < Prop,   But < Glycol
Pb : Form < ClAc < Glycol < But < Ac < Prop

Accordingly, the stabilities of the investigated monocarboxylato complexes are in a complete agreement with the »natural order« given by Irving and Williams[8]:

$$Co < Ni < Cu > Zn$$

The stability of monocarboxylato complexes of zinc, cadmium and lead, increasing in the order: $Zn < Cd < Pb$ (with exception of glycolato complexes), is in agreement with their tendency to polarization (i. e. with the mobility of electrons), because it increases in the same order ($\alpha \times 10^{24}$: 0.11, 0.96 and 4.34 cm³)[9]. The especially strong tendency of the lead ion towards polarization certainly causes the relatively high stability of its monocarboxylato complexes.

The position of the copper monocarboxylato complexes in the above given orders of the stability complexes was discussed earlier[1,3] on the ground of its d^9 electronic configuration, which enables the ligand field stabilization effect as well as the additional Jahn-Teller stabilization effect[10,11] to take place.

With regard to the ligand component, for all investigated metal ions, except lead ion, the observed orders of complex stability are in agreement with the order of ligand basicity[5,11], with the exception of glycolato complexes. The highest stability of glycolato complexes, except those of lead, is due to the presence of the OH group in the glycolate ion which is bonded to the metal ion as well[12]. In the lead glycolato complexes such a bond does not probably exist because the position of glycolato complexes in the above stability order corresponds to the basicity of the glycolate ion[5] with regard to the other monocarboxylate ions. A markedly higher stability of the lead chloroacetato complexes is in contradiction with the basic properties of this ligand and the explanation of this phenomenon cannot be given as yet.

TABLE II

Stability Constants of Monocarboxylato Complexes at I = 2 M (NaClO₄)

Ligand	Metal Ion	β_1 graph.	β_1 comp.	β_2 graph.	β_2 comp.	β_3 graph.	β_3 comp.	β_4 graph.	β_4 comp.
Formate	Co^{2+}	5.0	5.4 ± 0.2	11	15 ± 1				
	Ni^{2+}	3.0	2.9 ± 0.1	1.9	2.6 ± 0.2				
	Zn^{2+}	5.1	5.0 ± 0.3	10	12 ± 3	20	16 ± 4		
	Cd^{2+}	6.7	7.0 ± 0.2	7.0	6.9 ± 1.6				
	Pb^{2+}	16	13 ± 1	31	50 ± 7	194	155 ± 19		
Acetate	Co^{2+}	4.5	4.6 ± 0.4	6	6.2 ± 3.4	7	7.4 ± 6.4		
	Ni^{2+}	5.5	5.3 ± 0.2	11	14 ± 2	5	2.5 ± 1.3		
	Zn^{2+}	7.0	7.0 ± 0.6	20	23 ± 2				
	Cd^{2+}	12	12 ± 1	47	49 ± 5	120	124 ± 18		
	Pb^{2+}	56	82 ± 6	480	263 ± 111	3650	6111 ± 399		
Propionate	Co^{2+}	4.4	5.0 ± 0.3	7	4.2 ± 0.9	8	15 ± 3		
	Ni^{2+}	5.2	5.4 ± 0.3	8	7.1 ± 2.2	9	9.3 ± 1.9		
	Zn^{2+}	9.6	9.9 ± 0.7	12	9.2 ± 5.4	124	135 ± 2		
	Cd^{2+}	16	17 ± 1	80	63 ± 7	196	292 ± 39		
	Pb^{2+}	120	118 ± 18	2187	2240 ± 160				

TABLE II
(continued)

Ligand	Metal Ion	β_1		β_2		β_3		β_4	
		graph.	comp.	graph.	comp.	graph.	comp.	graph.	comp.
Butyrate	Co^{2+}	4.5	4.6 ± 0.1	7	7.6 ± 0.3	20	22 ± 2		
	Ni^{2+}	5.1	5.4 ± 0.0	8	6.3 ± 1.2	117	146 ± 19		
	Zn^{2+}	8.4	9.6 ± 1	12	5.0 ± 3.7				
	Cd^{2+}	16	16 ± 1	96	108 ± 5				
	Pb^{2+}	144	148 ± 20	4600	4891 ± 653	26 300	35215 ± 4845		
Glycolate	Co^{2+}	27	30 ± 2	237	194 ± 15	90	333 ± 48		
	Ni^{2+}	50	49 ± 2	430	500 ± 21	1 500	1120 ± 60		
	Zn^{2+}	60	52 ± 7	640	754 ± 120	1 130	1000 ± 290		
	Cd^{2+}	30	32 ± 1	60	69 ± 3				
	Pb^{2+}	68	68 ± 7	590	730 ± 100	2 900	1400 ± 1000	1.1×10^4	$1.9 \pm 0.3 \times 10^4$
Chloro-acetate	Co^{2+}	1.4	2.4 ± 0.2						
	Ni^{2+}	1.4	1.6 ± 0.1						
	Zn^{2+}	2.5	2.5 ± 0.1	5.2	3.7 ± 0.6	31	35 ± 2		
	Cd^{2+}	6.7	6.9 ± 0.1	70	113 ± 25				
	Pb^{2+}	30	32 ± 6						

TABLE III

Stability Constants of Monoligand Complexes (β_1)

Ligand	Co²⁺		Ni²⁺		Cu²⁺		Zn²⁺		Cd²⁺		Pb²⁺	
	pot.	sp.	pot.	sp.	sp.	pol.	pot.	pol.	pot.	pol.	pot.	pol.
Formate	5.4 ± 0.2	2.5 ± 0.3	2.9 ± 0.1	3.5 ± 0.4	45 ± 6	25	5.0 ± 0.3	5	7.0 ± 0.2	11	13 ± 1	17
Acetate	4.6 ± 0.4	4.1 ± 0.1	5.3 ± 0.2	6.6 ± 0.3	129 ± 3	70[1]	7.0 ± 0.6	11	12 ± 1	20	82 ± 6	140
Propionate	5.0 ± 0.3	6.0 ± 0.2	5.4 ± 0.3	7.2 ± 0.6	145 ± 3	70[1]	9.9 ± 0.7	12	17 ± 1	20	118 ± 17	220
Butyrate	4.6 ± 0.1	4.1 ± 0.1	5.4 ± 0.2	6.5 ± 0.7	121 ± 5	35	9.6 ± 1.0	10	16 ± 1	20	148 ± 20	120
Glycolate	30 ± 2	20 ± 1	49 ± 2	42 ± 6	171 ± 10	250	52 ± 7	84	32 ± 1	26	68 ± 7	80
Chloro-acetate	2.4 ± 0.2	1.0 ± 0.1	1.6 ± 0.1	—	18 ± 8	16	2.5 ± 0.1	—	6.9 ± 0.1	9	32 ± 6	30

[1] Unpublished results

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IZVOD

O stabilnosti formiato-, acetato-, propionato-, butirato-, glikolato- i kloroacetato-kompleksa kobalta, nikla, bakra, cinka, kadmiuma i olova

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Određene su konstante stabilnosti formiato-, acetato-, propionato-, butirato-, glikolato- i kloroacetato-kompleksa kobalta, nikla, cinka, kadmiuma i olova potenciometrijskom metodom. Mjerena je promjena koncentracije vodikovih iona u monokarboksilatnom puferu. Konstante stabilnosti dobivene su računskim putem na elektronskom računskom stroju primjenom programa Gauss Z od R. S. Tobiasa. Na temelju ovih rezultata, kao i rezultata dobivenih prijašnjim istraživanjima polarografskom i spektrofotometrijskom metodom, provedena je diskusija o stabilnosti istraživanih monokarboksilato-kompleksa i dani su odgovarajući nizovi stabilnosti.

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