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Original Scientific Paper

Polarographic Determination of Stability Constants of Glycolato and Chloroacetato Complexes of Copper, Zinc, Cadmium and Lead

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By measuring the half-wave potentials of metal ions in buffer solutions of glycolic and chloroacetic acid the limit concentrations of these acids in the buffer were determined, at which no hydrolysis of metal glycolato and chloroacetato complexes takes place. Furthermore, stability constants of glycolato and chloroacetato complexes of copper, zinc, cadmium and lead were determined under such conditions.

In our former papers¹⁻³ it was shown that the concentration of monocarboxylic acid in the monocarboxylate buffer influence the half-wave potential of the metal ion and that it is possible to determine stability constants of the corresponding complexes at the minimum limit concentration of monocarboxylic acid in the buffer, at which the hydrolysis of monocarboxylato complexes does not yet take place.^{4,5} This paper gives the results of the continuation of these investigations of monocarboxylato complexes, namely of glycolato and chloroacetato complexes of copper, zinc, cadmium and lead. The limit concentrations of glycolic and chloroacetic acid in their buffer solutions were determined, at which no hydrolysis of the corresponding glycolato and chloroacetato complexes takes place in the whole investigated concentration range of glycolate and chloroacetate. Then stability constants were derived from the shift of the half-wave potential of metal ions in such buffers by applying the graphic method of DeFord and Hume⁶.

EXPERIMENTAL

Measurements were performed with the same polarographic equipment (Manual polarograph B MK II, The Electrochemical Laboratories), with the same polarographic cell and in the same way as described in the former paper⁴. The same is valid also for the determination of the half-wave potential of the free metal ion. All half-wave potentials refer to the calomel electrode with a saturated solution of sodium chloride. Half-wave potentials were reproducible to ± 1 mv. Measurements in glycolate buffers were performed at the temperature of $25 \pm 0.1^\circ\text{C}$, while those in chloroacetate buffers were made at $18 \pm 1^\circ\text{C}$ in order to prevent the hydrolysis of chloroacetate. The mean value of the capillary constant ($m^{2/3} t^{1/6}$) was $2.36 \text{ mg}^{2/3} \text{ sec}^{-1/2}$, measured at the half-wave potential of lead in buffer solutions containing 0.01, 0.2 and 1.8 M of sodium glycolate.

Solutions were prepared from analytically pure chemicals. Sodium glycolate was prepared by means of crystallization from the solution obtained by the neutralization of the glycolic acid solution. After the recrystallization buffer solutions with the constant limit concentration of glycolic acid of 0.01 M were

prepared. Solutions of sodium chloroacetate were prepared by a very slow neutralization and intensively cooling the solution of chloroacetic acid in order to avoid the hydrolysis of the formed chloroacetate. This solution was kept in the refrigerator (at about 5–10° C) and from it the buffer solutions with the constant limit concentration of chloroacetic acid of 0.01 M were prepared, which were immediately polarographed at 18° C so that no hydrolysis of chloroacetate could take place. The concentration of metal ions in investigated solutions was 0.4 mM. The ionic strength of the solution was kept constant at the value 2 by means of sodium perchlorate.

RESULTS AND DISCUSSION

Results of measurements are shown in Tables I and II, and the values of the cumulative stability constants (β_1) of complexes determined by the graphic method of DeFord and Hume⁶ are given in Table III. The extrapolated values of the cumulative stability constants of complexes were checked by the method of successive approximations by Papoff and Caliumi⁷. With respect to the dissipation of experimental points it could be concluded that the extrapolated values of β_1 are within $\pm 10^0\%$.

Stability constants of the zinc chloroacetato complexes could not be determined because of the irreversible electrode process at concentrations of chloroacetate higher than 0.1 M (Fig. 1). At concentrations lower than 0.1 M the electrode process is quasi-reversible, as shown on Fig. 1.

TABLE I
Glycolate Solutions

[L] M	Cu ²⁺		Zn ²⁺		Cd ²⁺		Pb ²⁺	
	E _{1/2} mV	i _d μA	E _{1/2} mV	i _d μA	E _{1/2} mV	i _d μA	E _{1/2} mV	i _d μA
0	+ 0.042 ₀	2.90	— 0.974 ₀	2.85	— 0.555 ₀	3.12	— 0.370 ₀	3.50
0.01	+ 0.026 ₈	2.85	— 0.983 ₁	2.79	— 0.557 ₉	3.07	— 0.378 ₁	3.34
0.02	+ 0.016 ₈	2.83	— 0.988 ₀	2.76	— 0.560 ₆	3.04	— 0.383 ₇	3.26
0.03	+ 0.008 ₉	2.82	— 0.992 ₅	2.74	— 0.562 ₇	3.01	— 0.389 ₀	3.21
0.04	+ 0.004 ₈	2.81	— 0.996 ₅	2.68	— 0.565 ₁	2.98	— 0.393 ₅	3.16
0.05	— 0.000 ₃	2.79	— 0.999 ₈	2.67	— 0.566 ₉	2.96	— 0.395 ₄	3.14
0.06	— 0.002 ₄	2.78	— 1.002 ₈	2.66	— 0.568 ₉	2.93	—	—
0.07	—	—	— 1.006 ₁	2.65	—	—	— 0.399 ₂	3.10
0.08	— 0.010 ₉	2.74	— 1.008 ₀	2.59	— 0.572 ₂	2.90	— 0.402 ₇	3.07
0.09	—	—	— 1.010 ₁	2.57	—	—	— 0.403 ₂	3.06
0.10	— 0.013 ₅	2.73	— 1.012 ₀	2.55	— 0.575 ₁	2.88	— 0.407 ₇	2.99
0.15	— 0.021 ₈	2.71	— 1.020 ₁	2.49	— 0.582 ₁	2.83	— 0.410 ₅	2.95
0.20	— 0.030 ₄	2.69	— 1.026 ₈	2.48	— 0.587 ₄	2.78	— 0.418 ₃	2.90
0.30	— 0.042 ₇	2.63	— 1.037 ₀	2.42	— 0.597 ₈	2.68	— 0.434 ₅	2.79
0.40	— 0.053 ₇	2.60	— 1.046 ₀	2.37	— 0.605 ₉	2.63	— 0.442 ₀	2.74
0.50	— 0.059 ₀	2.44	— 1.053 ₀	2.31	— 0.612 ₇	2.56	— 0.446 ₈	2.68
0.60	— 0.066 ₃	2.39	— 1.060 ₀	2.27	— 0.618 ₀	2.52	— 0.453 ₀	2.63
0.70	— 0.070 ₉	2.33	— 1.066 ₀	2.22	— 0.623 ₀	2.46	— 0.458 ₅	2.57
0.80	— 0.075 ₇	2.28	— 1.070 ₀	2.19	— 0.627 ₉	2.42	— 0.462 ₁	2.52
0.90	— 0.081 ₄	2.22	— 1.075 ₀	2.13	— 0.632 ₁	2.39	— 0.466 ₉	2.45
1.00	— 0.084 ₄	2.19	— 1.079 ₀	2.06	— 0.636 ₀	2.36	— 0.470 ₆	2.43
1.20	— 0.092 ₉	2.16	— 1.086 ₀	2.02	— 0.642 ₆	2.30	— 0.476 ₅	2.41
1.40	— 0.098 ₃	2.15	— 1.091 ₃	1.94	— 0.648 ₃	2.27	— 0.482 ₁	2.38
1.60	— 0.105 ₉	2.14	— 1.096 ₀	1.85	— 0.653 ₄	2.25	— 0.486 ₀	2.35
1.80	— 0.113 ₁	2.13	— 1.101 ₀	1.80	— 0.658 ₃	2.20	— 0.491 ₁	2.32

TABLE II
 Chloroacetate Solutions

[L] M	Cu ²⁺		Zn ²⁺		Cd ²⁺		Pb ²⁺	
	E _{1/2} mV	i _d μA	E _{1/2} mV	i _d μA	E _{1/2} mV	i _d μA	E _{1/2} mV	i _d μA
0	+ 0.042 ₀	2.50	— 0.974 ₀	2.11	— 0.555 ₀	2.70	— 0.370 ₀	3.00
0.01	+ 0.040 ₀	2.49	— 0.978 ₂	2.07	— 0.556 ₁	2.68	— 0.375 ₅	2.90
0.02	+ 0.037 ₉	2.47	— 0.979 ₃	2.11	— 0.557 ₁	2.68	— 0.378 ₂	2.89
0.03	+ 0.035 ₅	2.44	— 0.980 ₅	2.18	— 0.558 ₈	2.66	— 0.379 ₄	2.85
0.04	+ 0.033 ₃	2.43	— 0.981 ₆	2.12	— 0.559 ₆	2.65	— 0.380 ₅	2.82
0.05	+ 0.032 ₅	2.42	— 0.981 ₉	2.08	— 0.560 ₂	2.63	— 0.381 ₄	2.79
0.06	+ 0.032 ₁	2.39	— 0.982 ₄	2.08	— 0.561 ₀	2.63	— 0.382 ₅	2.76
0.07	+ 0.030 ₀	2.37	— 0.982 ₈	2.08	— 0.561 ₈	2.62	—	—
0.08	+ 0.029 ₉	2.36	— 0.983 ₂	2.11	— 0.562 ₃	2.62	— 0.384 ₆	2.74
0.09	+ 0.029 ₅	2.35	— 0.983 ₅	2.15	— 0.563 ₀	2.60	—	—
0.10	+ 0.028 ₉	2.33	— 0.983 ₈	2.13	— 0.563 ₃	2.57	— 0.387 ₅	2.68
0.15	+ 0.023 ₇	2.32	— 0.984 ₉	2.13	— 0.565 ₇	2.54	— 0.392 ₀	2.60
0.20	+ 0.021 ₉	2.31	— 0.985 ₆	2.15	— 0.568 ₃	2.50	— 0.395 ₆	2.57
0.30	+ 0.015 ₇	2.29	— 0.987 ₀	2.23	— 0.572 ₉	2.47	— 0.402 ₃	2.52
0.40	+ 0.011 ₂	2.28	— 0.988 ₀	2.23	— 0.576 ₃	2.41	— 0.410 ₆	2.49
0.50	+ 0.005 ₈	2.25	— 0.990 ₀	2.30	— 0.580 ₀	2.34	— 0.415 ₇	2.44
0.60	+ 0.002 ₂	2.14	— 0.991 ₀	2.30	— 0.583 ₁	2.32	— 0.418 ₇	2.41
0.70	+ 0.000 ₂	2.12	— 0.992 ₈	2.30	— 0.585 ₉	2.28	— 0.423 ₂	2.38
0.80	— 0.004 ₀	2.11	— 0.994 ₅	2.32	— 0.588 ₉	2.22	— 0.424 ₂	2.33
0.90	— 0.006 ₆	2.09	— 0.996 ₀	2.35	— 0.591 ₈	2.18	— 0.429 ₇	2.30
1.00	— 0.008 ₃	2.04	— 0.997 ₀	2.37	— 0.594 ₂	2.15	— 0.432 ₅	2.25
1.20	— 0.013 ₃	2.01	— 1.000 ₀	2.37	— 0.599 ₈	2.08	— 0.437 ₈	2.15
1.40	— 0.018 ₇	1.94	— 1.002 ₄	2.38	— 0.603 ₈	1.98	— 0.442 ₀	2.08
1.60	— 0.021 ₇	1.88	— 1.004 ₈	2.38	— 0.609 ₈	1.90	— 0.444 ₈	2.01
1.80	— 0.026 ₃	1.80	— 1.007 ₀	2.42	— 0.613 ₅	1.88	— 0.450 ₂	1.94

 TABLE III
 Stability Constants

Ligand	Metal Ion	β ₁	β ₂	β ₃	β ₄
Glycolate	Cu ²⁺	250	4.5 × 10 ³	8.0 × 10 ³	1.5 × 10 ⁴
	Zn ²⁺	84	880	3.0 × 10 ³	1.0 × 10 ³
	Cd ²⁺	26	130	420	152
	Pb ²⁺	80	1.1 × 10 ³	2.4 × 10 ³	—
Chloroacetate	Cu ²⁺	16	20	30	—
	Cd ²⁺	9	4	6	7
	Pb ²⁺	30	45	93	—

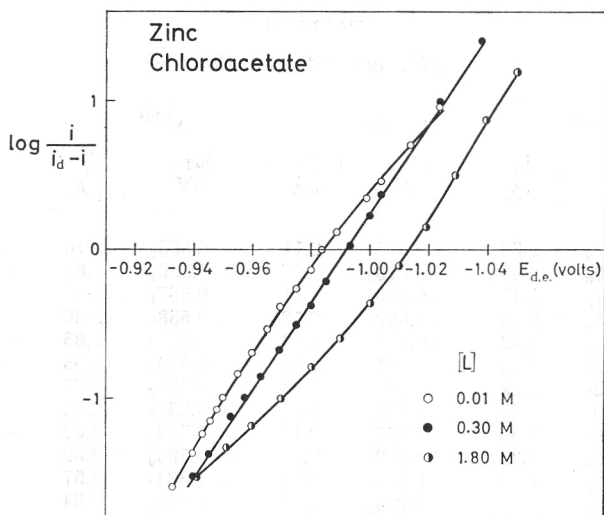


Fig. 1. Log. $i/(i_d - i)$ -E plots of the polarographic waves of zinc in presence of chloroacetate.

From the values of the cumulative stability constants (Table III) it can be seen that chloroacetato complexes of investigated metal ions are markedly weaker than glycolato complexes. If the stability of chloroacetato and glycolato complexes is compared with the stability of acetato complexes⁴, which was determined by the same polarographic method, it can be seen that the stability (β_1) of the monoligand complex increases in the order: chloroacetate < acetate < glycolate. The only exception is lead with the order: chloroacetate < glycolate < acetate. As the basic character of the ligand (pK_A : 2.855, 3.818, 4.756, respectively)⁸ increases in the same order, it could be concluded that the main factor governing the stability of the investigated lead complexes is the basicity of the ligand. At the other investigated metal ions the increased stability of glycolato complexes is certainly due to the presence of the OH group, as was also found at the other hydroxymonocarboxylate ions^{4,5,9}. The stabilization effect of the OH group is especially well-expressed for the investigated ions of the first transition series (Cu^{2+} and especially Zn^{2+}).

Though the lowest stability of chloroacetato complexes is to be expected because of the great electronegativity of the substituted chlorine atom, it is interesting that the lead chloroacetato complex is more stable than the formato complex⁴ (β_1 : 30, resp. 17), in spite of the fact that the formate ion is more basic ($pK_A = 3.752$)⁸. In order to establish whether this phenomenon is connected with the lead ion and with introducing the chlorine atom in the monocarboxylate ion, or in general with the enlargement of the chain in the monocarboxylate ion, other analogous ligands should also be investigated.

The values obtained for the first and the second stability constant (β_1 and β_2) of cadmium and lead glycolato complexes are in good agreement with those obtained recently by Jain and Gaur¹⁰ by means of the polarographic method, although under different experimental conditions.

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IZVOD

Polarografsko određivanje konstanta stabilnosti glikolato- i kloroacetato-kompleksa bakra, cinka, kadmija i olova

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Mjerenjem poluvalnih potencijala metalnih iona u tamponskim otopinama glikolne i monokloroctene kiseline određene su granične koncentracije tih kiselina u tamponu, kod kojih ne dolazi do hidrolize metalnih glikolato- i kloroacetato-kompleksa. Uz ovakve uslove određene su zatim konstante stabilnosti glikolato- i kloroacetato-kompleksa bakra, cinka, kadmija i olova.

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