

CCA-281

545.33:547.29:546.48:546.56
Original Scientific Paper

Polarographic Investigations of Some Metal Monocarboxylato Complexes. III. Monocarboxylato Complexes of Cadmium and Copper

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Received December 3, 1962

The stability constants of cadmium and copper monocarboxylato complexes have been determined by the polarographic method in water solutions of a constant ionic strength 2 and a constant monocarboxylic acid concentration of 2 M. The examinations were carried out in the monocarboxylate concentration range up to 2 M. The following values of cumulative stability constants were obtained:

Cadmium: formato complexes $\beta_1 = 20 \pm 2$, $\beta_2 = 50 \pm 5$, $\beta_3 = 40 \pm 8$, $\beta_4 = 36 \pm 8$; acetato complexes $\beta_1 = 40 \pm 5$, $\beta_2 = 110 \pm 10$, $\beta_3 = 110 \pm 15$, $\beta_4 = 215 \pm 20$; propionato complexes $\beta_1 = 30 \pm 2$, $\beta_2 = 80 \pm 20$, $\beta_3 = 400 \pm 50$, $\beta_4 = 290 \pm 30$; butyrate complexes $\beta_1 = 17 \pm 2$, $\beta_2 = 160 \pm 20$, $\beta_3 = 400 \pm 50$, $\beta_4 = 480 \pm 60$.

Copper: formato complexes $\beta_1 = 45 \pm 5$, $\beta_2 = 200 \pm 30$, $\beta_3 = 200 \pm 40$, $\beta_4 = 270 \pm 40$; acetato complexes $\beta_1 = 100 \pm 10$, $\beta_2 = 500 \pm 50$, $\beta_3 = 1000 \pm 100$, $\beta_4 = 1250 \pm 200$; propionato complexes $\beta_1 = 110 \pm 10$, $\beta_2 = 450 \pm 50$, $\beta_3 = 1100 \pm 200$, $\beta_4 = 1100 \pm 200$, $\beta_5 = 950 \pm 200$; butyrate complexes $\beta_1 = 80 \pm 10$, $\beta_2 = 600 \pm 100$, $\beta_3 = 2000 \pm 300$, $\beta_4 = 1700 \pm 300$, $\beta_5 = 2000 \pm 300$.

Only formato and acetato complexes of cadmium and copper have been investigated somewhat more extensively¹⁻¹⁰, whereas data on propionato and butyrate complexes of copper are rather scarce⁸. No data are to be found in the literature on cadmium propionato and butyrate complexes.

Besides, the results obtained by various methods of investigation, under different experimental conditions show considerable discrepancies. It is therefore impossible to draw conclusions about factors which influence the stability of complexes from such values. For this reason the following investigation of cadmium and copper monocarboxylato complexes has been carried out under identical experimental conditions. The polarographic method of investigation was applied and the constants were evaluated by the method of DeFord and Hume¹¹ as described in a previous paper, dealing with monocarboxylato complexes of lead¹² and zinc¹³.

* Part of the thesis presented to the University of Zagreb, 1961, in partial fulfilment of the requirements for the degree of Doctor of Chemistry (Ph. D.).

EXPERIMENTAL

The measurements were performed with a »Leybold« No. 35 polarograph. The polarographic cell and other equipment did not differ from that described in the previous paper¹².

The determination of the diffusion current (i_0), the half-wave potential ($E_{1/2}$), the diffusion current constant (I) and the half-wave potential of the free ion was performed in the same way as described previously¹². The half-wave potentials were reproducible to ± 1 mv. All electrode reactions were polarographically reversible.

The solutions were prepared from reagent grade salts and acids. The concentration of cadmium as cadmium nitrate was 0.63 mM, and that of copper as copper nitrate was 0.82 mM in formate and butyrate solutions, and 0.7 mM in acetate and propionate solutions.

The concentration range of the monocarboxylate (i.e. sodium formate, acetate, propionate and butyrate) was varied from 0 to 2 M. In addition all solutions contained a constant amount (2 M) of the free monocarboxylic acid to suppress hydrolysis. Accordingly, in solutions with a low monocarboxylate concentration it was necessary to calculate the monocarboxylate ion concentration, taking into

TABLE I
Cadmium formate solutions

| [L] M | $E_{1/2}$ v | I | $F_0([L])$ | $F_1([L])$ | $F_2([L])$ | $F_3([L])$ | $F_4([L])$ |
|----------|----------------|------|---------------|------------------------------|-------------------------------|-------------------------------|-------------------------------|
| 0.000 | -0.543 | 2.68 | | | | | |
| 0.039 | -0.551 | 2.67 | 1.85 | 21.6 | — | — | — |
| 0.045 | -0.552 | 2.67 | 1.97 | 21.5 | — | — | — |
| 0.092 | -0.558 | 2.65 | 3.13 | 23.1 | — | — | — |
| 0.110 | -0.560 | 2.63 | 3.90 | 26.4 | 58.2 | — | — |
| 0.205 | -0.569 | 2.69 | 7.61 | 32.2 | 59.5 | 46.3 | — |
| 0.30 | -0.576 | 2.61 | 13.6 | 42.0 | 73.3 | — | — |
| 0.40 | -0.582 | 2.59 | 21.2 | 50.5 | 76.2 | 65.5 | — |
| 0.50 | -0.586 | 2.56 | 30.9 | 59.8 | 79.6 | 59.2 | 38.4 |
| 0.60 | -0.588 | 2.61 | 44.1 | 72.0 | 86.6 | 61.0 | 35.0 |
| 0.70 | -0.595 | 2.61 | 62.3 | 87.6 | 96.5 | 66.5 | 37.8 |
| 0.80 | -0.599 | 2.52 | 83.5 | 103 | 103 | 66.2 | 32.7 |
| 0.90 | -0.602 | 2.61 | 113 | 124 | 115 | 72.2 | 35.8 |
| 1.00 | -0.606 | 2.48 | 149 | 148 | 128 | 78.0 | 38.0 |
| 1.10 | -0.609 | 2.45 | 193 | 175 | 141 | 82.7 | 38.8 |
| 1.20 | -0.612 | 2.50 | 245 | 203 | 153 | 85.8 | 38.2 |
| 1.30 | -0.615 | 2.50 | 299 | 230 | 161 | 85.4 | 34.9 |
| 1.40 | -0.617 | 2.48 | 367 | 261 | 172 | 87.1 | 33.6 |
| 1.50 | -0.620 | 2.43 | 454 | 302 | 188 | 92.0 | 34.6 |
| 1.60 | -0.622 | 2.43 | 555 | 346 | 204 | 96.2 | 35.1 |
| 1.70 | -0.625 | 2.41 | 675 | 396 | 221 | 101 | 36.0 |
| 1.80 | -0.627 | 2.39 | 816 | 453 | 245 | 108 | 37.7 |
| 1.90 | -0.629 | 2.37 | 923 | 485 | 245 | 102 | 32.6 |
| 2.00 | -0.632 | 2.32 | 1187 | 593 | 286 | 118 | 39.0 |
| | | | $\beta_0 = 1$ | $\beta_1 = 20$ $K_1 = 20$ | $\beta_2 = 50$ $K_2 = 2.5$ | $\beta_3 = 40$ $K_3 = 0.8$ | $\beta_4 = 35$ $K_4 = 0.9$ |

TABLE II
Cadmium acetate solutions

| [L] M | $E_{1/2}$ V | I | $F_0([L])$ | $F_1([L])$ | $F_2([L])$ | $F_3([L])$ | $F_4([L])$ |
|----------|----------------|------|---------------|------------------------------|--------------------------------|--------------------------------|--------------------------------|
| 0.000 | — 0.543 | 2.48 | | | | | |
| 0.006 | — 0.549 | 2.48 | — | — | — | — | — |
| 0.012 | — 0.549 | 2.48 | 1.60 | — | — | — | — |
| 0.021 | — 0.553 | 2.48 | 2.01 | 48.1 | — | — | — |
| 0.04 | — 0.556 | 2.48 | 2.89 | 47.4 | — | — | — |
| 0.06 | — 0.560 | 2.46 | 3.81 | 46.8 | — | — | — |
| 0.08 | — 0.563 | 2.46 | 5.05 | 50.6 | — | — | — |
| 0.10 | — 0.566 | 2.44 | 6.13 | 51.4 | 114 | — | — |
| 0.20 | — 0.577 | 2.38 | 14.7 | 68.0 | 140 | 150 | 200 |
| 0.40 | — 0.591 | 2.31 | 45.9 | 112 | 180 | 175 | 162 |
| 0.60 | — 0.603 | 2.23 | 120 | 198 | 263 | 255 | 242 |
| 0.80 | — 0.612 | 2.15 | 252 | 314 | 343 | 291 | 226 |
| 1.00 | — 0.620 | 2.08 | 483 | 482 | 442 | 332 | 222 |
| 1.20 | — 0.626 | 2.01 | 793 | 660 | 516 | 338 | 190 |
| 1.40 | — 0.632 | 1.96 | 1273 | 909 | 621 | 365 | 182 |
| 1.60 | — 0.638 | 1.87 | 2277 | 1423 | 864 | 471 | 226 |
| 1.80 | — 0.643 | 1.81 | 3401 | 1889 | 1027 | 509 | 222 |
| 2.00 | — 0.649 | 1.73 | 5909 | 2954 | 1455 | 672 | 286 |
| | | | $\beta_1 = 1$ | $\beta_1 = 40$ $K_1 = 40$ | $\beta_2 = 110$ $K_2 = 2.7$ | $\beta_3 = 110$ $K_3 = 1.0$ | $\beta_4 = 215$ $K_4 = 2.0$ |

account the dissociation constant of the monocarboxylic acid. The constant used was an apparent dissociation constant¹⁴, valid for an ionic strength 2, as all solutions were maintained at that ionic strength by addition of sodium perchlorate.

None of the investigated solutions of cadmium contained gelatine, and the same was true for copper formate and propionate solutions. It was necessary, however, to add 0.005% of gelatine to copper acetate solutions and 0.01% of gelatine to the copper butyrate solutions in order to suppress polarographic maxima.

RESULTS

The composition of the complexes, their cumulative stability constants, as well as the consecutive constants have been determined by the graphic method of DeFord and Hume. The extrapolated values for the cumulative stability constant were checked to give the best fit by the method of successive approximations, as recommended by P. Papoff and M. Calumi¹⁵. The confidence limits of the extrapolated constant are given with respect to the dissipation of the experimental points, depending on the precision of the half-wave potential measurements^{15,16}.

In Tables I—VIII the results for copper and cadmium formates, acetates, propionates and butyrates are shown. The half-wave potentials are given with respect to the calomel electrode prepared with a saturated solution of sodium chloride instead of potassium chloride, in order to prevent precipitation with sodium perchlorate.

From the results it can be seen that in all examined monocarboxylate solutions the maximum number of monocarboxylate ligands for cadmium is 4. For copper formates and acetates the maximum ligand number is 4, whereas for propionates and butyrates it is 5. For complexes which have been investigated by other authors too, i.e. for formates and acetates, the authors have found the same number of ligands^{6,7,9} except P. K. Karmalkar and L. N. Dhoot¹⁰ who found complexes of copper acetates with 5 ligands. The numerical values of the constants for copper formates on comparison with those obtained by H. M. Hershenson *et al.*⁹ show an agreement within the experimental error limits, as well as the values for copper acetates on comparison with those found by S. Fronaeus⁷. Somewhat greater are the differences for cadmium formates⁹ and acetates⁶, but the values are still of the same order of magnitude.

DISCUSSION

The results of these investigations show the monocarboxylato complexes of cadmium and copper to be of a low stability, similar to the correspondent complexes of lead¹² and zinc¹³. The stability of these complexes, with respect to the first stability constant is increasing in the order: Zn < Cd < Cu < Pb, and with respect to the ligands β_1 it is increasing in the order: formate < acetate < propionate > butyrate.

TABLE III
Cadmium propionate solutions

| [L] M | E _{1/2} v | I | F ₀ ([L]) | F ₁ ([L]) | F ₂ ([L]) | F ₃ ([L]) | F ₄ ([L]) |
|----------|-----------------------|------|----------------------|------------------------------|-------------------------------|--------------------------------|--------------------------------|
| 0.000 | — 0.543 | 2.15 | | | | | |
| 0.005 | — 0.546 | 2.15 | 1.23 | — | — | — | — |
| 0.012 | — 0.547 | 2.15 | 1.47 | — | — | — | — |
| 0.021 | — 0.550 | 2.15 | 1.68 | 32.4 | — | — | — |
| 0.04 | — 0.554 | 2.15 | 2.31 | 32.7 | — | — | — |
| 0.06 | — 0.558 | 2.15 | 3.21 | 37.0 | 116 | — | — |
| 0.08 | — 0.561 | 2.15 | 4.18 | 39.7 | 121 | — | — |
| 0.10 | — 0.564 | 2.15 | 5.21 | 42.1 | 121 | — | — |
| 0.20 | — 0.577 | 2.08 | 15.9 | 74.5 | 222 | — | — |
| 0.40 | — 0.594 | 2.01 | 63.5 | 156 | 315 | 584 | — |
| 0.60 | — 0.607 | 1.93 | 172 | 285 | 425 | 575 | 291 |
| 0.80 | — 0.616 | 1.87 | 359 | 447 | 521 | 551 | 188 |
| 1.00 | — 0.625 | 1.81 | 763 | 762 | 732 | 652 | 252 |
| 1.20 | — 0.632 | 1.76 | 1338 | 1114 | 903 | 686 | 238 |
| 1.40 | — 0.639 | 1.69 | 2518 | 1798 | 1263 | 845 | 318 |
| 1.60 | — 0.645 | 1.65 | 3960 | 2474 | 1527 | 904 | 315 |
| 1.80 | — 0.650 | 1.59 | 5988 | 3326 | 1831 | 973 | 318 |
| 2.00 | — 0.653 | 1.45 | 8217 | 4108 | 2039 | 979 | 289 |
| | | | $\beta_0 = 1$ | $\beta_1 = 30$ $K_1 = 30$ | $\beta_2 = 80$ $K_2 = 2.6$ | $\beta_3 = 400$ $K_3 = 5.0$ | $\beta_4 = 290$ $K_4 = 0.7$ |

TABLE IV
Cadmium butyrate solutions

| [L] M | $E_{1/2}$ V | I | $F_0([L])$ | $F_1([L])$ | $F_2([L])$ | $F_3([L])$ | $F_4([L])$ |
|----------|----------------|------|---------------|------------------------------|--------------------------------|--------------------------------|--------------------------------|
| 0.000 | — 0.543 | 2.20 | | | | | |
| 0.012 | — 0.545 | 2.18 | 1.22 | 18.6 | — | — | — |
| 0.021 | — 0.547 | 2.11 | 1.46 | 21.9 | 233 | — | — |
| 0.06 | — 0.555 | 2.11 | 2.72 | 28.6 | 193 | — | — |
| 0.08 | — 0.559 | 1.94 | 4.07 | 38.4 | — | — | — |
| 0.10 | — 0.562 | 1.96 | 4.85 | 38.5 | 215 | 550 | — |
| 0.20 | — 0.575 | 1.75 | 15.3 | 71.3 | 271 | 555 | — |
| 0.30 | — 0.585 | 1.69 | 34.0 | 110 | 310 | 500 | — |
| 0.40 | — 0.595 | 1.64 | 74.4 | 184 | 417 | 642 | — |
| 0.50 | — 0.602 | 1.56 | 139 | 276 | 518 | 716 | — |
| 0.60 | — 0.608 | 1.56 | 218 | 362 | 575 | 691 | 485 |
| 0.70 | — 0.613 | 1.52 | 332 | 472 | 650 | 700 | 429 |
| 0.80 | — 0.618 | 1.45 | 540 | 674 | 821 | 826 | 533 |
| 0.90 | — 0.623 | 1.45 | 768 | 852 | 928 | 853 | 503 |
| 1.00 | — 0.626 | 1.43 | 1016 | 1015 | 998 | 838 | 438 |
| 1.10 | — 0.630 | 1.43 | 1378 | 1252 | 1123 | 875 | 432 |
| 1.20 | — 0.633 | 1.37 | 1844 | 1536 | 1266 | 922 | 435 |
| 1.30 | — 0.638 | 1.34 | 2672 | 2055 | 1568 | 1173 | 594 |
| 1.50 | — 0.643 | 1.26 | 4215 | 2809 | 1861 | 1134 | 489 |
| 1.70 | — 0.649 | 1.22 | 6808 | 4004 | 2349 | 1285 | 521 |
| 1.90 | — 0.654 | 1.17 | 10930 | 5752 | 3018 | 1504 | 581 |
| 2.00 | — 0.657 | 1.11 | 14270 | 7135 | 3559 | 1699 | 649 |
| | | | $\beta_0 = 1$ | $\beta_1 = 17$ $K_1 = 17$ | $\beta_2 = 160$ $K_2 = 9.4$ | $\beta_3 = 400$ $K_3 = 2.5$ | $\beta_4 = 480$ $K_4 = 1.2$ |

According to the coordination theory of bonding, the stability of metal complexes depends on different factors, such as: the electronic configuration, the ionic potential (z/r , i.e. the ion charge vs. ion radius ratio), the polarizability, the ionization potential of the central ion ($M^+ \rightarrow M^{2+} + e$, i.e. the electron affinity), the basicity of the ligand (i.e. its affinity for the proton, or by analogy, for the central metal ion) and its deformability caused by polarization. The ions of zinc, cadmium, copper and lead have the following values of the ionic potential (z/r), the polarizability coefficient (α) and the second ionization potential (I_2):

| | $z/r^{(17)}$ ($z/\text{\AA}$) | $\alpha \cdot 10^{24} {}^{(17)}$ (cm^3) | $I_2^{(18)}$ (v) |
|------------------|------------------------------------|---|---------------------|
| Zn ²⁺ | 2.9 | 0.5 | 17.89 |
| Cd ²⁺ | 2.2 | 1.15 | 16.84 |
| Cu ²⁺ | 2.9 | — | 20.34 |
| Pb ²⁺ | 1.7 | 3.6 | 14.96 |

Obviously, the stability of the investigated monocarboxylato complexes increases with increasing polarizability of the central ion $Zn < Cd < Pb$. It

seems that the polarizability has a greater effect than the ionic and the ionization potential, because the stability would be otherwise decreasing from Zn to Pb. However, with copper it seems that the influence of the ionization potential is prevailing. Therefore, the polarizability and the ionization potential of the central ion ought to be considered as principally responsible for a greater or smaller stability of the monocarboxylato complexes. As for the influence of the monocarboxylate ligands on the stability of these complexes, it is evident that with a basicity increase of the ligand the stability is generally increased too.^{12,13}

Acknowledgement. The authors wish to express their gratitude to the Federal Council for Scientific Work in Belgrade and to the Rectorate of the University of Zagreb, for the financial help.

TABLE V
Copper formate solutions

| [L] M | E _{1/2} v | I | F ₀ ([L]) | F ₁ ([L]) | F ₂ ([L]) | F ₃ ([L]) | F ₄ ([L]) |
|----------|-----------------------|------|----------------------|------------------------------|--------------------------------|--------------------------------|--------------------------------|
| 0.000 | + 0.061 | 1.66 | | | | | |
| 0.033 | + 0.046 | 1.66 | 3.35 | 71 | — | — | — |
| 0.039 | + 0.045 | 1.66 | 3.62 | 67 | — | — | — |
| 0.045 | + 0.044 | 1.66 | 3.83 | 63 | — | — | — |
| 0.058 | + 0.043 | 1.66 | 4.24 | 56 | — | — | — |
| 0.075 | + 0.038 | 1.66 | 5.88 | 65 | — | — | — |
| 0.092 | + 0.036 | 1.66 | 7.26 | 68 | — | — | — |
| 0.110 | + 0.033 | 1.66 | 8.76 | 70 | 250 | — | — |
| 0.205 | + 0.022 | 1.63 | 21.3 | 100 | 275 | — | — |
| 0.30 | + 0.014 | 1.63 | 40.8 | 133 | 293 | 310 | — |
| 0.40 | + 0.006 | 1.63 | 74.1 | 183 | 345 | 362 | — |
| 0.50 | + 0.000 | 1.63 | 116 | 230 | 370 | 340 | 280 |
| 0.60 | — 0.005 | 1.63 | 179 | 296 | 418 | 363 | 271 |
| 0.70 | — 0.011 | 1.63 | 277 | 395 | 500 | 429 | 327 |
| 0.80 | — 0.015 | 1.57 | 395 | 493 | 560 | 450 | 312 |
| 0.90 | — 0.019 | 1.66 | 532 | 590 | 605 | 450 | 278 |
| 1.00 | — 0.023 | 1.63 | 720 | 719 | 674 | 474 | 274 |
| 1.10 | — 0.027 | 1.68 | 978 | 888 | 767 | 515 | 286 |
| 1.20 | — 0.030 | 1.56 | 1278 | 1064 | 849 | 541 | 284 |
| 1.30 | — 0.033 | 1.63 | 1569 | 1206 | 893 | 533 | 256 |
| 1.40 | — 0.036 | 1.71 | 2088 | 1491 | 1033 | 595 | 282 |
| 1.50 | — 0.039 | 1.68 | 2504 | 1670 | 1084 | 589 | 260 |
| 1.60 | — 0.041 | 1.66 | 3051 | 1906 | 1163 | 603 | 252 |
| 1.70 | — 0.044 | 1.66 | 3717 | 2186 | 1259 | 623 | 249 |
| 1.80 | — 0.047 | 1.57 | 4765 | 2646 | 1445 | 692 | 273 |
| 1.90 | — 0.049 | 1.56 | 5840 | 3073 | 1594 | 734 | 281 |
| 2.00 | — 0.052 | 1.39 | 7227 | 3613 | 1784 | 792 | 296 |
| | | | $\beta_0 = 1$ | $\beta_1 = 45$ $K_1 = 45$ | $\beta_2 = 200$ $K_2 = 4.4$ | $\beta_3 = 200$ $K_3 = 1.0$ | $\beta_4 = 270$ $K_4 = 1.3$ |

TABLE VI
Copper acetate solutions

| [L] M | $E_{1/2}$ V | I | $F_0([L])$ | $F_1([L])$ | $F_2([L])$ | $F_3([L])$ | $F_4([L])$ |
|----------|----------------|------|---------------|--------------------------------|--------------------------------|---------------------------------|---------------------------------|
| 0.000 | + 0.061 | 2.57 | | | | | |
| 0.006 | + 0.052 | 2.57 | 2.08 | — | — | — | — |
| 0.012 | + 0.048 | 2.57 | 2.73 | — | — | — | — |
| 0.021 | + 0.044 | 2.58 | 3.71 | — | — | — | — |
| 0.04 | + 0.038 | 2.51 | 5.98 | 121 | 600 | — | — |
| 0.06 | + 0.033 | 2.53 | 9.25 | 137 | 616 | — | — |
| 0.08 | + 0.029 | 2.51 | 12.5 | 144 | 515 | — | — |
| 0.10 | + 0.025 | 2.52 | 17.2 | 162 | 620 | 1200 | — |
| 0.20 | + 0.011 | 2.45 | 51.9 | 254 | 770 | 1350 | — |
| 0.40 | — 0.007 | 2.29 | 225 | 560 | 1150 | 1625 | — |
| 0.60 | — 0.020 | 2.25 | 617 | 1026 | 1545 | 1741 | 1235 |
| 0.80 | — 0.029 | 2.11 | 1391 | 1737 | 2046 | 1933 | 1166 |
| 1.00 | — 0.037 | 1.99 | 2792 | 2791 | 2691 | 2191 | 1191 |
| 1.20 | — 0.045 | 1.96 | 4988 | 4156 | 3380 | 2400 | 1170 |
| 1.40 | — 0.052 | 1.94 | 8751 | 6250 | 4393 | 2852 | 1323 |
| 1.60 | — 0.058 | 1.80 | 14500 | 9062 | 5601 | 3188 | 1368 |
| 1.80 | — 0.063 | 1.83 | 22230 | 12349 | 6805 | 3503 | 1391 |
| 2.00 | — 0.067 | 1.72 | 32580 | 16490 | 8195 | 3747 | 1373 |
| | | | $\beta_0 = 1$ | $\beta_1 = 100$ $K_1 = 100$ | $\beta_2 = 500$ $K_2 = 5.0$ | $\beta_3 = 1000$ $K_3 = 2.0$ | $\beta_4 = 1250$ $K_4 = 1.2$ |

TABLE VII
Copper propionate solutions

| [L] M | $E_{1/2}$ V | I | $F_0([L])$ | $F_1([L])$ | $F_2([L])$ | $F_3([L])$ | $F_4([L])$ | $F_5([L])$ |
|----------|----------------|------|---------------|--------------------------------|--------------------------------|---------------------------------|---------------------------------|--------------------------------|
| 0.000 | + 0.061 | 2.39 | | | | | | |
| 0.005 | + 0.054 | 2.39 | 1.76 | 165 | — | — | — | — |
| 0.012 | + 0.049 | 2.39 | 2.62 | 135 | — | — | — | — |
| 0.021 | + 0.045 | 2.39 | 3.54 | 121 | — | — | — | — |
| 0.04 | + 0.037 | 2.39 | 6.89 | 147 | — | — | — | — |
| 0.06 | + 0.033 | 2.39 | 9.72 | 145 | 583 | — | — | — |
| 0.08 | + 0.029 | 2.35 | 13.2 | 152 | 525 | — | — | — |
| 0.10 | + 0.025 | 2.34 | 18.1 | 171 | 610 | 1600 | — | — |
| 0.20 | + 0.011 | 2.29 | 53.1 | 260 | 750 | 1500 | — | — |
| 0.40 | — 0.008 | 2.19 | 227 | 565 | 1137 | 1717 | 1542 | — |
| 0.60 | — 0.021 | 2.09 | 747 | 1243 | 1888 | 2396 | — | — |
| 0.80 | — 0.031 | 1.99 | 1707 | 2142 | 2540 | 2612 | 1890 | 987 |
| 1.00 | — 0.041 | 1.90 | 3890 | 3889 | 3779 | 3329 | 2229 | 1129 |
| 1.20 | — 0.049 | 1.81 | 7330 | 6108 | 5000 | 3792 | 2243 | 953 |
| 1.40 | — 0.056 | 1.73 | 13290 | 9493 | 6700 | 4464 | 2403 | 931 |
| 1.60 | — 0.062 | 1.64 | 22580 | 14113 | 8752 | 5188 | 2555 | 909 |
| 1.80 | — 0.068 | 1.56 | 37920 | 21066 | 11642 | 6217 | 2863 | 968 |
| 2.00 | — 0.074 | 1.50 | 64050 | 32025 | 15957 | 7753 | 3326 | 1113 |
| | | | $\beta_0 = 1$ | $\beta_1 = 110$ $K_1 = 110$ | $\beta_2 = 450$ $K_2 = 4.1$ | $\beta_3 = 1100$ $K_3 = 1.3$ | $\beta_4 = 1100$ $K_4 = 1.0$ | $\beta_5 = 950$ $K_5 = 0.9$ |

TABLE VIII
Copper butyrate solutions

| [L] M | E _{1/2} V | I | F ₀ ([L]) | F ₁ ([L]) | F ₂ ([L]) | F ₃ ([L]) | F ₄ ([L]) | F ₅ ([L]) |
|----------|-----------------------|------|----------------------|------------------------------|--------------------------------|---------------------------------|---------------------------------|---------------------------------|
| 0.000 | + 0.061 | 1.53 | | | | | | |
| 0.005 | + 0.057 | 1.49 | 1.41 | 91 | — | — | — | — |
| 0.012 | + 0.052 | 1.49 | 2.08 | 90 | — | — | — | — |
| 0.021 | + 0.049 | 1.46 | 2.76 | 84 | — | — | — | — |
| 0.04 | + 0.041 | 1.40 | 5.23 | 105 | 625 | — | — | — |
| 0.06 | + 0.036 | 1.37 | 8.15 | 119 | 650 | — | — | — |
| 0.08 | + 0.031 | 1.33 | 12.2 | 140 | 750 | — | — | — |
| 0.10 | + 0.027 | 1.26 | 17.3 | 163 | 830 | 2300 | — | — |
| 0.20 | + 0.011 | 1.19 | 63.8 | 314 | 1170 | — | — | — |
| 0.30 | + 0.000 | 1.16 | 154 | 510 | 1433 | 2777 | 2590 | 2966 |
| 0.40 | — 0.009 | 1.10 | 323 | 805 | 1812 | 3030 | 2575 | 2184 |
| 0.60 | — 0.023 | 1.01 | 1062 | 1768 | 2813 | 3683 | 2813 | 1855 |
| 0.70 | — 0.029 | 0.97 | 1773 | 2531 | 3501 | 4144 | 3063 | 1947 |
| 0.80 | — 0.035 | 0.98 | 2736 | 3419 | 4174 | 4467 | 3084 | 1730 |
| 0.90 | — 0.040 | 0.95 | 4248 | 4763 | 5203 | 5115 | 3461 | 1956 |
| 1.00 | — 0.046 | 0.94 | 6653 | 6652 | 6572 | 5972 | 3972 | 2272 |
| 1.10 | — 0.050 | 0.93 | 9199 | 8362 | 7529 | 6290 | 3900 | 2000 |
| 1.20 | — 0.054 | 0.91 | 12870 | 10724 | 8870 | 6892 | 4077 | 1947 |
| 1.40 | — 0.060 | 0.85 | 23470 | 16763 | 11916 | 8083 | 4345 | 1889 |
| 1.60 | — 0.069 | 0.82 | 46660 | 29162 | 18176 | 10985 | 5685 | 2447 |
| 1.80 | — 0.076 | 0.80 | 83450 | 46361 | 25712 | 13951 | 6640 | 2744 |
| 1.90 | — 0.079 | 0.77 | 108400 | 57053 | 29985 | 15466 | 7087 | 2835 |
| | | | $\beta_0 = 1$ | $\beta_1 = 80$ $K_1 = 80$ | $\beta_2 = 600$ $K_2 = 7.5$ | $\beta_3 = 2000$ $K_3 = 3.3$ | $\beta_4 = 1700$ $K_4 = 1.2$ | $\beta_5 = 2000$ $K_5 = 1.1$ |

REFERENCES

- W. Lossen and G. Voss, *Lieb. Ann.* **266** (1891) 40.
- A. Jaques, *Trans. Faraday Soc.* **5** (1910) 225.
- E. Ferrell, J. M. Ridgeon, and H. L. Riley, *J. Chem. Soc.* **1934**, 1440.
- H. Brintzinger, H. Plessing, and W. Rudolph, *Z. anorg. Chem.* **242** (1939) 197.
- K. J. Pedersen, *Kgl. Danske Videnskaab. Selskab. Math. — Fys. Medd.* **22** (1945) 25.
- I. Leden, *Svensk Kem. Tidskr.* **58** (1946) 129.
- S. Fronaeus, *Acta Chem. Scand.* **3** (1949) 789; Doctoral Diss. Lund, 1948.
- M. Lloyd, V. Wycherley, and C. B. Monk, *J. Chem. Soc.* **1951**, 1786.
- H. M. Hershenson, R. Thompson Brooks, and M. E. Murphy, *J. Am. Chem. Soc.* **79** (1957) 2046.
- P. K. Karmalkar and L. N. Dhoot, *J. Vihram Univ.* **2**, No. 3 (1958) 148.
- D. D. DeFord and D. N. Hume, *J. Am. Chem. Soc.* **73** (1951) 5321.
- I. Filipović, A. Bujak, H. Marač, R. Novak, and V. Vukičević, *Croat. Chem. Acta* **32** (1960) 219.
- I. Filipović, I. Piljac, Z. Crnić, M. Radulović, and Dj. Valente-ković, *Croat. Chem. Acta* **33** (1961) 45.
- S. Ahrlund, *Acta Chem. Scand.* **3** (1949) 789.
- P. Papoff and M. Caliumi, *Gazzetta Chim. Ital.* **84** (1954) 1006.

16. A. Medved, *Diss.*, Zagreb, 1961.
17. J. A. A. Ketelaar, *Chemical Constitution*. Elsevier Publishing Company, Inc., Amsterdam 1953, pp. 29 and 90.
18. C. D. Hodgman, *Handbook of Chemistry and Physics*, Cleveland 1956, pp. 2347 and 2348.

IZVOD

Polarografska istraživanja monokarboksilato-kompleksa nekih metala. III. Kadmijevi i bakreni monokarboksilato-kompleksi

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Određen je sastav i konstante stabilnosti kadmijevih i bakrenih monokarboksilato-kompleksa polarografskom metodom DeForda i Humea. Otopine su bile konstantne ionske jakosti 2, a koncentracija natrijeva monokarboksilata varirana je do 2 M. U svim otopinama bila je konstantna koncentracija odgovarajuće monokarboksilne kiseline od 2 M, da se susvjeti hidroliza kompleksa. Iz polarografskih podataka određene su ove kumulativne konstante stabilnosti kompleksa:

kadmij: formijato-kompleksi $\beta_1 = 20 \pm 2$, $\beta_2 = 50 \pm 5$, $\beta_3 = 40 \pm 8$, $\beta_4 = 36 \pm 8$; acetato-kompleksi $\beta_1 = 40 \pm 5$, $\beta_2 = 110 \pm 10$, $\beta_3 = 110 \pm 15$, $\beta_4 = 215 \pm 20$; propionato-kompleksi $\beta_1 = 30 \pm 2$, $\beta_2 = 80 \pm 20$, $\beta_3 = 400 \pm 50$, $\beta_4 = 290 \pm 30$; butirato-kompleksi $\beta_1 = 17 \pm 2$, $\beta_2 = 160 \pm 20$, $\beta_3 = 400 \pm 50$, $\beta_4 = 480 \pm 60$;

bakar: formijato-kompleksi $\beta_1 = 45 \pm 5$, $\beta_2 = 200 \pm 30$, $\beta_3 = 200 \pm 40$, $\beta_4 = 270 \pm 40$; acetato-kompleksi $\beta_1 = 100 \pm 10$, $\beta_2 = 500 \pm 50$, $\beta_3 = 1000 \pm 100$, $\beta_4 = 1250 \pm 200$; propionato-kompleksi $\beta_1 = 101 \pm 10$, $\beta_2 = 450 \pm 50$, $\beta_3 = 1100 \pm 200$, $\beta_4 = 1100 \pm 200$, $\beta_5 = 950 \pm 200$; butirato-kompleksi $\beta_1 = 80 \pm 10$, $\beta_2 = 600 \pm 100$, $\beta_3 = 2000 \pm 300$, $\beta_4 = 1700 \pm 300$, $\beta_5 = 2000 \pm 300$.

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Primljeno 3. prosinca 1962.