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POLAROGRAPHIC INVESTIGATION OF THE COMPOSITION AND STABILITY CONSTANTS OF CADMIUM(II) 2-METHYLSUCCINATES

Ivan S. Grozdanov

University "Kiril i Metodij", Institute of Chemistry, Skopje

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Abstract. The complexes of cadmium(II) with 2-methylsuccinic acid in aqueous media at a pH=6.9 and ionic strength of 2.0 mol/dm^3 have been studied polarographically. A model 174 A Polarographic analyser (PAR) with a three-electrode system was used. The experimental polarographic data were treated both with a graphical and a numerical method using a general computer program. The following overall stability constants have been determined: $\beta_1=55\pm5$, $\beta_2=700\pm20$ and $\beta_3=200\pm100$, corresponding to the following complex species: [Cd(MSucc)], $[Cd(MSucc)_2]^{2-}$ and $[Cd(MSucc)_3]^{4-}$ respectively. The influence of the methyl group as a substituent is also discussed.

The complexes of cadmium(II) with some diprotic acids have been studied polarographically by Jain[1] and Gaur[2]. Some substituted diprotic acids have also been studied polarographically under the same experimental conditions[3, 4, 5].

This paper deals with the determination of the composition and stability constants of the complexes formed by cadmium(II) ions in aqueous solutions of 2-methylsuccinic acid. The overall stability constants determined in this work are defined as follows:

$$\beta_1=[ML]/[M]\,[L],$$
$$\beta_2=[ML_2]/[M]\,[L]^2,$$
$$\ldots\ldots\ldots\ldots\ldots\ldots$$
$$\beta_n=[ML_n]/[M]\,[L]^n$$

where M and L stand for metal and ligand concentration, respectively, and ML for the corresponding complex species.

Experimental

Chemicals and solutions. All chemicals were purified and a polarographic check up was performed. The 2-methylsuccinic acid (AR, Aldrich) was recrystallised using a mixture of chloroform and methanol (80:20). Decolorizing charcoal Norit A (Fisher) was used to remove the present yellowish color of the concentrated solutions. Sodium perchlorate (AR, Fisher) was used to adjust the ionic strength constant, after removal of the heavy metal ions by precipitation.

A stock solution of sodium 2-methylsuccinate was prepared by a slow addition of sodium hydroxide and adjusting the pH at 6.9. A constant concentration of cadmium perchlorate of 0.5 mmol/dm^3 was used in all solutions under investigation. Seventeen solutions of a constant cadmium(II) ion concentration and an increasing concentration of 2-methylsuccinate were prepared by dilution of the stock solution, adjusting the ionic strength to 2.0 mol/dm^3 in each one.

Apparatus. A constant temperature of 25±0.05 °C was maintained during the polarographic investigation for all of the solutions, by means of an electronic relay (Precision Scientific). No maximum supressor was used. Purified nitrogen was used for deaeration of all test solutions.

A polarographic cell of a modified H-type[6] with an agar-agar plug, saturated with potassium chloride was used. A saturated calomel electrode was used as a reference electrode and platinum wire as a counter electrode. The dropping mercury electrode used as a working electrode had the following characteristics: m=2.42 mg/s, t=5 s (automatic).

All of the polarograms were recorded on a model 174A polarographic analyser (PAR) and an X – Y Recorder model 0074 (PAR).

Procedure. Each of the test solutions for investigation of complex formation was introduced in the polarographic cell placed in a controlled temperature bath. A thoroughly de-aeration was performed for 15 minutes and the polarograms were run for each of the seventeen test solutions.

Results and discussion

Graphical treatment of the experimental data. DeFord and Hume's[7] graphical method was used for evaluation of the number of complex species in equilibrium and determination of the corresponding overall stability constants. The $F_i(L)$ functions were calculated as follows:

$F_0(L)=\text{antilog}\ \{0.435nF/RT\ [(E_{1/2})_S - (E_{1/2})_C] + \log(I_d)_s/(I_d)_c\}$ where all the symbols have their usual meaning;

$F_1(L)=(F_0(L)-1)/C_L;$

$F_2(L)=(F_1(L)-\beta_1)/C_L;$

....

$F_i(L)=(F_{i-1}(L)-\beta_{i-1})/C_L$

The corresponding overall stability constants were then graphically evaluated as

$\lim_{C_L \to 0} F_i(L)=\beta_i$

The experimental data and the calculated $F_i(L)$ values are presented in Table 1, and the complex species at equilibrium in Table 2.

Numerical treatment of the experimental data. A general computer program for evaluation of stability constants from reversible polarographic data, POLAG[8], was used in this work. The program seems to work well even with relatively poor guesses for the overall stability constants, though it is somewhat slow. The final values obtained numerically, as well as those obtained graphically are presented in Table 3.

The investigations in this work showed that with the increase of the ligand concentration, the half-wave potential shifts towards more negative values, indicating a successive complex formation. A slope of 29±3 mV was obtained for each plot of $\log[(I_d-i)/i]$ versus the potential (E), confirming the reversibility of the reduction process at the dropping mercury electrode.

The values of the overall stability constants determined by the graphical and the numerical method are in good agreement.

The stability constants of cadmium(II) complexes with 2-methylsuccinic acid and other related ligands are shown in Table 3. In all these cases cadmium(II) ions form weak complexes in aqueous solutions of the corresponding ligands. Since all of these results were obtained by the same instrumental method (polarography) and the investigations were performed under identical experimental conditions, the

Table 1. The polarographic experimental data and the calculated F(L) values for cadmium(II) methylsuccinates

Tablica 1. Polarografski eksperimentalni podaci i izračunate F(L) vrednosti za komplekse kadmijuma(II) sa metilsukcinatom

C_L mol/dm^3	$-E_{1/2}$ mV	I_d μA	$F_0(L)$ –	$F_1(L)$ –	$F_2(L)$ –	$F_3(L)$ –
0.0000	563.0	2.60	–	–	–	–
0.00625	566.9	2.44	1.44	–	–	
0.01250	569.7	2.35	1.86	68.9	–	–
0.02500	574.4	2.26	2.79	71.8	–	–
0.03755	579.7	2.24	4.28	87.5	–	–
0.05000	583.2	2.17	5.78	95.6	812	–
0.06250	585.9	2.14	7.25	100.12	722	–
0.07500	589.9	2.08	10.26	123.40	912	–
0.10000	595.0	2.03	15.57	145.70	907	2070
0.12500	599.6	2.03	22.33	170.64	925	1800
0.15000	603.6	1.98	31.23	201.56	977	1847
0.20000	611.0	1.94	56.80	279.00	1120	2100
0.25000	616.6	1.88	91.17	360.70	1222	2090
0.30000	621.7	1.88	135.44	448.14	1310	2035
0.40000	629.6	1.80	261.00	850.10	1488	1970
0.50000	636.1	1.74	450.68	899.36	1688	1976
0.60000	642.2	1.69	744.60	1239.0	1974	2123

Table 2. Composition of the complex species in equilibrium for cadmium(II) methylsuccinates at 25 °C

Tablica 2. Sastav kompleksnih vrsta u ravnoteži za komplekse kadmijuma(II) sa metilsukcinatom na 25 °C

C_L mol/dm^3	M mole %	ML mole %	ML_2 mole %	ML_3 mole %
0.00625	69.2	23.8	1.9	0.04
0.01250	53.7	36.9	5.9	0.21
0.02500	35.7	49.2	15.6	1.1
0.03750	23.4	48.2	22.9	2.5
0.05000	17.3	47.6	30.3	4.3
0.06250	13.8	47.4	37.7	6.7
0.07500	9.8	40.2	38.4	8.2
0.10000	6.4	35.3	44.9	12.8
0.12500	4.5	30.8	48.9	17.5
0.15000	3.2	26.4	50.4	21.6
0.20000	1.8	19.4	49.3	28.2
0.25000	1.1	15.1	47.9	34.3
0.30000	0.2	12.2	46.5	39.9
0.40000	0.1	8.4	42.9	49.0
0.50000	0.1	6.1	38.8	55.5
0.60000	–	4.4	33.8	58.0

Table 3. The overall stability constants of cadmium(II) complexes with 2-methylsuccinic acid and other related ligands

Tablica 3. Ukupne konstante stabilnosti za komplekse kadmijuma(II) sa 2-metilćilibarnom kiselinom i drugim srodnim ligandima

Ligand Ligand	β_1	β_2	β_3
Succinate[2] Sukcinat[2]	45	580	1110
Hydroxysuccinate[3] Hidroksisukcinat[3]	25	100	1910
Chlorsuccinate[4] Hlorsukcinat[4]	20	200	1300
Methylsuccinate* Metilsukcinat*	55±5	700±20	2000±100

* this work * ovaj rad

differences in the overall stability constants of these related ligands can be ascribed to the influence of the substituent in the corresponding diprotic acid. In the case of 2-methylsuccinic acid, it is obvious that its complexes with cadmium(II) are slightly more stable compared to the corresponding complexes of succinic acid. This comes as a result of the positive inductive effect of the methyl group. It causes electron repulsion and therefore tends to make the α-carbon atom negatively charged. The positive inductive effect is then transmitted to the carboxylic group, resulting in a decrease of acidity. This, in turn, increases the stability of the methylsuccinate complexes over the corresponding complexes of the unsubstituted succinic acid.

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IZVOD

POLAROGRAFSKO IZUČAVANJE SASTAVA I KONSTANTI STABILNOSTI KADMIJUM(II) 2-METILSUKCINATA

Grozdanov, I.

PMF, Hemiski Institut – Skopje

Izučavani su kompleksi kadmijuma(II) sa 2-metilćilibarnom kiselinom u vodenim rastvorima, kod pH=6,9 i jonske jačine I=2,0 mol/dm^3 ($NaClO_4$). Upotrebljena je DC-polarografija sa troelektrodnim sistemom. Eksperimentalni podaci su obrađivani računskim programom POLAG[8], kao i klasičnom grafičkom metodom DeFord-a i Hume-a[7]. Utvrđeno je prisustvo tri kompleksna jedinjenja u ravnoteži: [Cd(MSucc)], $[Cd(MSucc)_2]^{2-}$ i $[Cd(MSucc)_3]^{4}$ sa odgovarajućim konstantama stabilnosti $\beta_1=55\pm5$, $\beta_2=700\pm20$ i $\beta_3=2000\pm100$.

Uticaj metil grupe kao supstituenta je takođe razmatran u ovom radu.

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