COMPOSITION AND STABILITY CONSTANTS OF LEAD(II) 2-METHYLSUCCINATES

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ABSTRACT

The complexes of lead (II) with 2-methylsuccinic acid in aqueous media at pH = 6.9 and ionic strength of 2 mol/dm³ have been studied polarographicaly. A Model 174 A polarographic analyzer (PAR), with a three-electrode system was used. The 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: $\beta_1 = 270$, $\beta_2 = 7000$, $\beta_3 = 18500$ with a graphical treatment, and $\beta_1 = 294.2$, $\beta_2 = 7118.7$ and $\beta_3 = 17534.8$ with a numerical treatment, corresponding to Pb[Msucc], Pb[Msucc]⁻ and Pb[Msucc]⁻.

In a review /1/ on stability constant determination aided by computer programs published in 1976, it was noted that more than 100 programs or modifications of existing programs have been published and at the same time only two references reported the use of a computer program to calculate stability constants from polarographic data. In this work, a parallel graphical and numerical aproach was applied to calculate the stability constants of lead (II) with 2-methylsuccinic acid.

The complexes of lead (II) with some dibasic acids have been studied by J. N. Gaur and M. M. Palrecha /2/. Some substituted dibasic acid complexes of lead (II) have also been examined /3,4/.

This paper deals with the determination and the composition of the stability constants of the complexes formed by lead (II) in aqueous media of 2-methylsuccinic acid.

EXPERIMENTAL

All chemicals were purified and a polarographic checkup was made The 2-methylsuccinic acid was recrystalized using a mixture of chloroform and methanol (80:20). Decolorizing charcoal Norit A was used to remove the present yellowish color. Sodium perchlorate was used to keep the ionic strength constant, after removal of the heavy metal ions by precipition.

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 5×10^{-4} mol/dm^3 lead perchlorate was used in all test solutions. Sixteen test solutions of a constant metal and increasing ligand concentration were prepared by dilution of the stock solution, adjusting the ionic strength at 2 mol/dm^3 for each one.

A constant temperature of 25 ± 0.05°C was maintained for all the examined solutions by means of an electronic relay (Precision Scientific Co., 62690). No maximum suppresor was used. Purified nitrogen was used for deaeration of all test solutions.

TABLE I

Experimental data and the calculated F [L] values for lead (II) 2-methylsuccinates

[L] mol/dm^3	$E_{1/2}$ v	Id μA	F_0 ([L])	F_1 ([L])	F_2 ([L])	F_3 ([L])
0,00000	—0,3750	2,38	—	—	—	—
0,00625	—0,3880	2,20	2,98	317	—	—
0,01250	—0,3950	2,12	5,34	347	—	—
0,02500	—0,4060	2,05	13,05	482	—	—
0,03750	—0,4130	2,02	22,87	583	—	—
0,05000	—0,4180	1,98	34,48	669	7980	—
0,06250	—0,4240	1,97	55,36	869	9595	—
0,07500	—0,4270	1,96	70,32	924	8724	—
0,10000	—0,4330	1,91	115,27	1142	8727	17270
0,12500	—0,4380	1,88	173,02	1376	8849	14792
0,15000	—0,4434	1,87	265,15	1761	9940	19600
0,20000	—0,4510	1,85	485,07	2420	10751	18755
0,25000	—0,4570	1,80	796,35	3181	11645	18580
0,3000	—0,4620	1,77	1196,47	3984	12383	17943
0,40000	—0,4710	1,75	2443,08	6105	14588	18970
0,50000	—0,4774	1,66	4244,52	8487	16433	18868
0,60000	—0,4830	1,64	6651,70	11084	18023	18372
				$\beta_1 = 270$	$\beta_2 = 7000$	$\beta_3 = 18500$
				$K_1 = 270$	$K_2 = 25,9$	$K_3 = 2,6$

The polarographic cell used was of a modified H-type /5/ with an agar-agar plug saturated with potassium chloride.

A saturated calomel electrode was used as a reference and platinum wire as a counter electrode. The dropping mercury electrode had the following characteristics $m = 2.42$ mg/s, $t = 5$ s (automatic).

All polarograms were recorded on a Model 174 A polarographic analyser, (PAR) and an X .. Y recorder, Model 0074 (PAR).

Graphical tereatment of the experimental polarographic data

DeFord and Hume's /6/ graphical method was used in order to determine the number of the complex species in equilibrium and the overal stability constants. The halfwave potential and the diffusion current for the free (hydratized) lead (II) ions were obtained by graphical extrapolation

The experimentally obtained data and the calculated F [L] values are presented in Table I, and the composition of the complex species in equilibrium in Table II.

TABLE II

Composition of lead (II) 2-methylsuccinate complex species in equilibrium

]L]	β_1[L]	β_2[L]^2	β_3[L[^{3}	$1+\sum_0^i \beta_i[L]^i$	M	ML	ML_2	ML_3
mol/dm^3	—	—	—	—	%	%	%	%
0,00625	1,69	0,21	—	1,96	33,6	56,6	0,1	0,1
0,01250	3,37	1,09	0,036	4,50	18,7	63,2	20,5	0,7
0,02500	6,75	4,37	0,289	11,41	7,7	51,7	33,5	2,2
0,03750	10,12	9,84	0,975	20,94	4,4	44,3	43,0	4,3
0,05000	13,50	17,50	2,312	33,31	2,9	39,1	50,7	6,7
0,06250	16,87	27,34	4,516	48,73	1,8	30,5	49,4	8,2
0,07500	20,25	39,37	7,804	67,43	1,4	28,8	55,9	11,1
0,10000	27,00	70,00	18,500	115,50	0,9	23,4	60,4	16,0
0,12500	33,75	109,37	36,130	179,25	0,6	19,5	63,2	20,9
0,15000	40,50	157,50	62,430	260,43	0,4	15,3	59,4	23,5
0,20000	54,00	280,00	148,000	482,00	0,2	11,1	57,7	30,5
0,25000	67,50	437,50	289,060	794,00	0,1	8,5	54,9	36,3
0,30000	81,00	630,00	499,500	1210,50	0,1	6,8	52,6	41,7
0,40000	108,00	1120,00	1184,000	2412,00	—	4,4	45,8	48,5
0,50000	135,00	1750,00	2312,500	4197,50	—	3,2	41,1	45,5
0,60000	162,00	2520,00	3996,000	6678,00	—	2,4	37,9	60,0

Numerical treatment of the experimental polarographic data

A general computer program for calculation of stability constants from reversible polarographic data POLAG /7/ was used. The program seems to work well even with relatively poor guesses for the overall stability constants, al though it is somewhat slow. The final values and a comparisson with the graphical ones for the overall stability constants are shown in Table III.

TABLE III

The overall stability constants of lead(II) 2-methylsuccinates

Stability constant	Graphical	Numerical
β_1	270	294.2
β_2	7000	7118.7
β_3	18500	17534.8

Standard deviation for the numerical values : S 4.39×10^{-4}

Variance : V 2.51×10^{-6}

RESULTS AND DISCUSION

With the increase of the ligand concentration, the half-wave potential was found to shift towards more negative values, indicating a complex formation. A slope of 29 ± 3 mV was obtained for each plot of log $[(i_d - i)/i]$ vs. E, confirming the reversibility of the reduction process.

The values of the overall stability constants determined graphicaly and numericly, as shown in Table III are in well agreement. Having in mind the differences in the two approaches, this is somewhat supprising. The probable cause for this is the relative simplictiy of the system exammined., i.e. no hydroxyor polynuclear complexes were indicated and only three species in equlibrium were discovered.

By a simple comparisson of the overall stability constants of lead (II) succinates and those of lead (II) 2-methylsuccinates shown in Table IV, more stable complexes of the latter are observed. We beleive that the presence of the methyl group as substituent in succinic acid *influences* greater stability of the formed complexes. The electron-donor characteristics and the positive inductive effect of the methyl group predicts this.

A continuation of the study of the complexes of lead and other metal ions with more methyl-substituted dibasic acids as ligands would certainly bring up a more documented discusion on this subject.

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REFERECES

1. F. Gaizer, Coord. Chem. Rev., 1979, 27, 195.
2. J. N. Gaur and M. M. Parlrecha, J. Polarogr. Soc., (141), 31..35 1968
3. B. Topuzovski and all, Godišen zbornik na PMF na Univerz itetot vo Skopje, Kniga 22 1972, Sekcija A.
4. K. Stojanova. M. S. Thesis, 1978, Faculty of Chemistry, University of Skopje.
5. Kalousek, M., Collection Czechosl. Chem. Communs., 11, 592 1939
6. D. D. DeFord and D. N. Hume, J. Am. Chem. Soc., 73 1951, 5321
7. D. J. Leggett, Talanta, 27 1980 787—793.

ИЗВОД

СОСТАВ И КОНСТАНТИ НА СТАБИЛНОСТ НА ОЛОВО (II) 2-МЕТИЛСУКЦИНАТИ

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Испитани се комплексите на олово (II) со 2-метилкилибарна киселина во водени раствори, при pH=6,9 и јонска јакост 2mol/dm³ со поларографската метода. За снимање на поларограмите беше употребен поларограф модел 174А со триелектроден електрохемиски систем.

Добиените поларографски податоци беа обработени со графичка и нумеричка метода со користење на компјутерски програм. Беа определени следниве константи на стабилност : $\beta_1 = 270$, $\beta_2 = 7000$, и $\beta_3 = 18500$со графичката метода и $\beta_1 = 294{,}2$; $\beta_2 = 7118{,}7$ и $\beta_3 = 17534{,}8$ со нумеричката метода соодветно за: Pb (Msucc), Pb $(Msucc)_2^-$ и Pb $(Msucc)_{3-4}$.