POLAROGRAPHIC STUDIES OF LEAD COMPLEXES WITH THIOUREA IN AQUEOUS MEDIUM

F. Hussain, T. Hussain and M. Hanif

Institute of Chemistry, University of the Panjab, Lahore

Coordination complexes of thiourea with lead(II) ion in aqueous solution have been studied by polarographic method at 10, 25, and 35°C, using Triton-X-100 as maximum suppressor, and 0.1M potassium nitrate as supporting electrolyte. The formation constants were evaluated by applying the DeFord and Hume method.[1] The results, indicated the existence of mono-, bis-, tris-, and tetrakis-coordinated species for lead(II) thiourea complexes.

Introduction

Lane and his co-workers[2] carried out the polarographic studies of coordination complexes of lead (II) ion with thiourea in aqueous solution at only 25°C, using 0.1M potassium nitrate as supporting electrolyte and Triton-X-100 as maximum suppressor, while the concentration of thiourea was varied from 0.05 to 1M. The above authors, applying the DeFord and Hume[1] method to their practical data, proved the formation of four coordinated species such as mono-, bis-, tris-, and tetrakis-, but the work of Federova[3] indicated the existence of three species only. Consequently, the present work was undertaken to reinvestigate this matter of dispute as regards the number of coordination complexes.

Experimental

Materials.—Lead nitrate (E. Merck), potassium nitrate (E. Merck), thiourea (May & Baker), and Triton-X-100 (Rohm and Haas Co., Philadelphia) were used without further purification. The mercury was purified by passing through dilute nitric acid column, containing a little mercurous nitrate, and then by subsequent vacuum distillation. Nitrogen gas of 99.5% purity, supplied by Pakistan Oxygen Company, was further purified according to the method given by Hussain and Amjad.[4] Stock solutions of 0.01M lead nitrate, 1.0M potassium nitrate, and 0.4% X-100 were prepared at frequent intervals.

Procedure.—For each run the required amounts of the stock solutions were taken in 100-ml measuring flask and diluted to a known volume. The concentration of lead nitrate (0.001M), potassium nitrate (0.1M), and Triton-X-100 (0.004%) were kept constant throughout the experimental work while the thiourea concentration was varied from 0.01M to 1M. Current voltage curves were obtained with a pen-recording Cambridge Polarograph. Dropping mercury electrode capillary

characteristics at 25°C were, $m=0.3773$ mg/sec, and $t=6.028$ sec/drop, in 0.1M $KNO_3+0.001M$ $Pb(NO_3)_2$ solution. Capillary constant, $m^{2/3} \times t^{1/6}$ was calculated to be 0.7047. The distance from capillary tip up to the mercury reservoir was 81.5 cm. The polarographic cell used during the experiments was of a type designed by Roe and Nyman.[5] The saturated calomel electrode was prepared as described by Vogel.[6] The same saturated calomel electrode was used throughout the experimental work. Agar-bridge, fresh for each experiment, containing agar-agar one molar with respect to potassium nitrate, was prepared. One arm of this bridge was dipped in saturated calomel electrode and the other in solution under investigation, in the designed cell.

The electrically operated thermostat, in which the saturated calomel electrode and cell containing the sample solution were placed, was controlled within $\pm0.1°C$. The purified nitrogen gas was bubbled through the solution for 20 min. The gas was stopped while obtaining the polarogram.

Results and Discussion

The diffusion currents i_d, (after correction for residual current) and the potentials corresponding to various values of current i, were obtained from the polarograms. The halfwave potentials were obtained by plotting the graps of $(E_{d:e})$ versus log $i/(i_d-i)$ as described by Meites.[7] The zero intercept of such a plot gave the half wave potential of the corresponding curve. The half wave potential, the diffusion current and the DeFord and Hume functions, $F_0(X), F_1(X), F_2(X), F_3(X)$, and $F_4(X)$, at different concentrations of thiourea are given in Tables 1–3, at 10°, 25°, and 35°C, respectively, while the graphs between $F_j(X)$ against the molar concentration X, of thiourea are given in Fig. 1. For the determination of formation constants the method of DeFord and Hume was used. The curved shape of each of the graph drawn by $E_{\frac{1}{2}}$ versus log X indicated

F. Hussain, T. Hussain and M. Hanif

TABLE 1.—Analysis of $E_{\frac{1}{2}}$ of Lead with Thiourea at 10°C.

Concentration of thiourea moles/l	$-E_{\frac{1}{2}}(v)$ vs. S.C.E.	i_d (μa)	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.0	0.399	2.25	1.00				
0.01	0.401	2.30	1.086	8.60			
0.02	0.402	2.32	1.241	12.05			
0.05	0.403	2.27	1.46	9.20	44.00		
0.1	0.409	2.27	2.251	12.51	55.00		
0.15	0.415	2.15	3.888	19.25	85.70		
0.2	0.419	2.13	5.442	22.21	76.00		
0.25	0.423	2.10	7.67	27.09	88.00		
0.3	0.429	2.06	13.55	41.50	115.00		
0.4	0.435	2.00	21.54	51.10	110.25		
0.5	0.442	1.96	37.75	73.50	133.00	188.0	360.0
0.6	0.448	1.90	67.68	111.40	174.00	225.0	361.6
0.7	0.454	1.85	110.10	156.70	213.86	249.5	358.1
0.8	0.459	1.83	169.03	210.04	253.8	296.0	360.0
0.9	0.465	1.80	276.54	306.16	332.4	326.0	353.2
1.0	0.470	1.80	411.0	410.0	403.0	364.0	356.0

TABLE 2.—Analysis of $E_{\frac{1}{2}}$ of Lead with Thiourea at 25°C.

Concentration of thiourea moles/l	$-E_{\frac{1}{2}}(v)$ vs. S.C.E.	i_d (μa)	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
0.0	0.388	2.65	1.00				
0.01	0.389	2.80	1.046	4.6			
0.02	0.390	2.84	1.088	4.4			
0.05	0.390	2.625	1.179	3.58			
0.1	0.3925	2.65	1.488	4.88			
0.15	0.399	2.5	1.829	5.526			
0.2	0.396	2.475	2.28	6.40	12.0		
0.25	0.398	2.425	2.382	5.54	6.6		
0.3	0.4025	2.375	3.955	8.183	3.99		
0.4	0.4085	2.325	5.636	11.59	19.0		
0.5	0.415	2.25	9.661	16.562	25.1		
0.6	0.425	2.20	21.52	34.20	50.03	65.05	108.42
0.7	0.431	2.15	35.14	48.771	63.96	75.66	108.1
0.8	0.437	2.10	57.20	70.35	82.94	89.68	112.1
0.9	0.442	2.05	86.98	95.533	101.70	100.78	111.97
1.0	0.447	2.05	128.3	127.3	103.3	112.3	112.5

TABLE 3.—Analysis of $E_{\frac{1}{2}}$ of Lead with Thiourea at 35°C.

Concentration of thiourea moles/l	$-E_{\frac{1}{2}}(v)$ vs. S.C.E.	$i_d(\mu$a)	$F_0(X)$	$F_1(X)$	$F_2(X)$	$F_3(X)$	$F_4(X)$
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
0.0	0.3740	3.025	1.0				
0.01	0.3744	3.036	1.013	1.3			
0.02	0.377	3.035	1.035	1.75			

Table continued:

| (1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
0.5	0.3755	3.0325	1.055	1.1			
0.1	0.3792	3.030	1.243	2.43	1.3		
0.15	0.3818	2.981	1.355	2.367	0.446		
0.2	0.3854	2.936	1.583	2.915	3.075		
0.25	0.3880	2.892	1.772	2.1088			
0.3	0.3906	2.847	1.991	3.3033	3.344		
0.4	0.3958	2.758	2.994	3.735	3.587	1.4687	3.172
0.5	0.4010	2.669	3.127	4.254	3.908	1.814	3.272
0.6	0.4052	2.680	3.946	4.91	4.35	2.250	3.345
0.7	0.4114	2.491	4.928	5.6114	4.7305	2.472	3.274
0.8	0.4166	2.451	6.7295	7.1619	5.2024	2.753	3.216
0.9	0.4218	2.359	7.0139	7.6821	5.869	3.18	3.333
1.0	0.4260	2.220	9.687	8.689	6.387	3.387	3.207
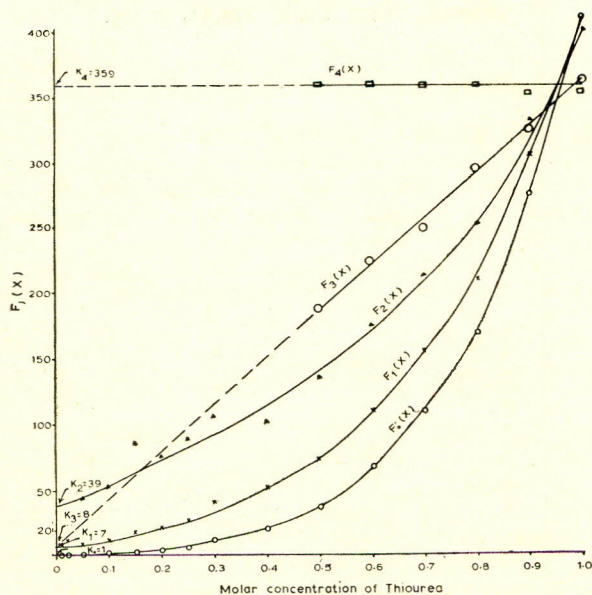
Fig. 1—Formation functions, $F_0(X)$, $F_1(X)$, $F_2(X)$, $F_3(X)$ and $F_4(X)$, as a thiourea concentration at 10°C.

Fig. 2.—Half wave potential versus log X.

the existence of a mixture of lead complexes with thiourea. A typical set of such graphs is shown in Fig. 2.

The plots of $F_j(X)$ against X for the determination of the DeFord and Hume functions $F_0(X)$, $F_1(X)$, and $F_2(X)$, showed curvature, which signifies that there were more complexes of thiourea with lead, having the coordination number up to two. The graphs for $F_3(X)$ versus X at different temperatures were straight lines which indicated the presence of higher complexes than tris species. The graphs for $F_4(X)$ were 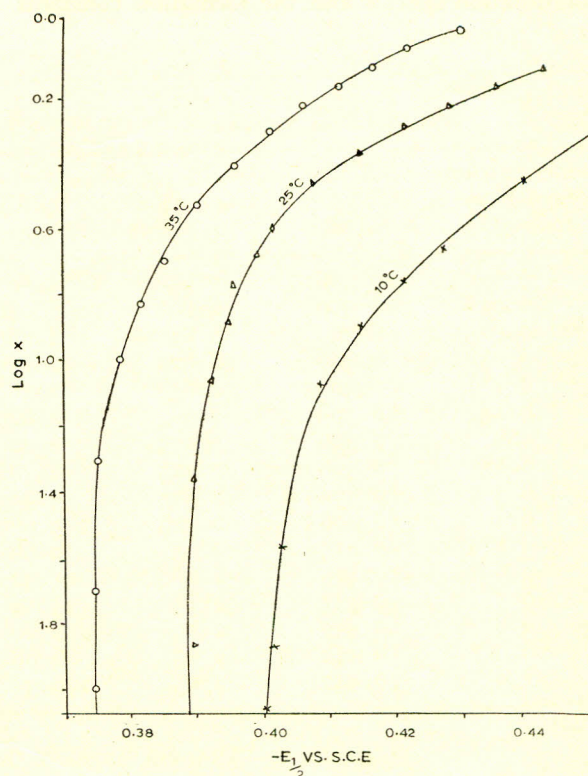straight lines parallel to the concentration axis X, which was taken as an indication of the formation of the last species, namely, tetrakisthiourea lead(II) ion. The experimental results indicated the presence of mono-, bis-, tris-, and tetrakis- lead(II) complexes by varying the concentration of thiourea from 0.01 to 1M. The formation constants K_1, K_2, K_3, and K_4, of lead(II) thiourea complexes were determined at temperature, 10, 25,

and 35°C. The values of these constants are given below.

Temp. °C	K_1	K_2	K_3	K_4
10	7	39	8	359
25	4	11	1.5	111
35	2.3	3	0.18	3.24

It could be observed from these values that the formation constants go on decreasing on increasing the temperature. Moreover, formation constant increases with the increase of coordination number except K_3. This small value for K_3 suggests a very small formation of tris species.

Our experimental data at 25°C regarding the coordination species and the formation constants are in good agreement with that reported by Lane and his co-workers.

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