

Complex Formation with Lead and Thiomalic Acid

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With 2 Figures

Abstract

Polarographic and Potentiometric studies of lead and thiomalic acid (TMA) system indicates the formation of a 1:1::Pb(II):TMA complex, in which thiomalic acid behaves as a tridentate ligand. The compound has been isolated and estimated for its lead and sulphur contents which further confirms the above composition of the complex. The bivalent state of lead is confirmed by the measurement of magnetic susceptibility.

Thiomalic acid or mercaptosuccinic acid, which undergoes typical reactions of both, mercaptans, and dicarboxylic acid, can act as mono-, bi-, or tri-dentate ligand. It has been found to form complexes with a number of metal cations¹⁻⁷).

Lead — TMA (thiomalic acid) system has been studied polarographically and potentiometrically. The compound has been isolated and estimated for lead and sulphur contents and its magnetic susceptibility measured. Experimental evidence leads us to believe that thiomalic acid acts as tridentate with Pb²⁺ ions.

Material and Apparatus

Thiomalic acid was obtained as a gift from Evan Chemetics Inc., New York. The material was 99.6% pure and only freshly prepared solutions were used.

All other chemicals used were of analytical grade. The mercury used in d. m. e. was first purified chemically by treatment with nitric acid and subsequently distilled twice.

¹) I. M. KLOTZ, G. H. GERLINSKI and H. A. FIESS, *J. Am. Chem. Soc.* **80**, 2920 (1958).

²) UMA KAPOOR D. PHIL. THESIS, Allahabad University, Allahabad, India (1961).

³) G. E. CHENEY, Q. FERNANDO and H. FREISER *J. Phys. Chem.* **63**, 2055 (1959).

⁴) WAGNER and YOE, *Talanta* **2**, 223 (1959).

⁵) WAGNER and YOE, *Talanta* **2**, 239 (1959).

⁶) R. N. SEN SHARMA, *Science & Culture* **23**, 434 (1958).

⁷) KAPOOR and AGRAWAL, *ICCC*, Stockholm (1962), B, p. 333.

The characteristics of d. m. e. capillary used were

$$m = 2.403 \text{ mg. sec}^{-1}$$

$$t = 3.57 \text{ secs}$$

$$m^{\frac{2}{3}} t^{\frac{1}{3}} = 1.218 \text{ m}^{\frac{2}{3}} \text{ gt}^{\frac{1}{3}}.$$

height of mercury column (h) = 50 cm.

All polarograms were recorded on a Leeds & Northrup Electrochemograph type E. C—V curves were taken at room temperature (33°C). All potentials were measured against a saturated calomel electrode. A Hume & Harris saturated calomel electrode was used as reference electrode in the experiments.

pH titrations were done with a Leeds & Northrup pH meter supplied with all purpose glass electrode operated at 200 volts mains. The usual precautions of the titrations were taken in. KNO_3 was added to each solution to maintain constant ionic strength of the solution. Excess of water was added in each mixture to avoid any volume correction.

The complex was isolated by precipitation. The magnetic susceptibility was measured by Gouy's Method. The assembly consisted of a semi-micro sartorius balance with a LEYBOLD electromagnet. The field obtained was 5500 (approx.) gauss with 1.8 cm pole gap.

Experimental Results

Polarographic investigations were carried out in acetate buffer (0.5 M Acetic acid + 0.5 M sodium Acetate, pH 4.8). Pb (II) in this medium gives a reversible wave with a $E_{\frac{1}{2}}$ value of -0.464 volts versus Saturated Calomel Electrode according to the electrode reaction $\text{Pb (II)} + 2e \rightleftharpoons \text{Pb (Hg)}$. On adding increasing concentrations of TMA, the wave shifted to more negative potential values.

The plot of $E_{\frac{1}{2}}$ versus $\log [\text{TMA}]$ gave a straight line with a slope of 30.0 millivolts (Fig. 1). A plot of $\log \frac{i}{i_d - i}$ versus voltage gave a straight line with a slope of 38.5 millivolts indicating a two electron process at the electrode.

Taking 0.05 M TMA solutions it was found that the limiting current was proportional to the concentration of Pb (II) in the experimental solution in the range studied ($2.5 \times 10^{-4} \text{ M} - 6.83 \times 10^{-4} \text{ M}$). The limiting current of $6.82 \times 10^{-4} \text{ M}$ Pb (II) was found to be diffusion controlled.

For pH titrations three different solutions of metal ion (0.01 M), ligand (0.01 M) and a mixture of metal and ligand (1 : 1) were all titrated with a

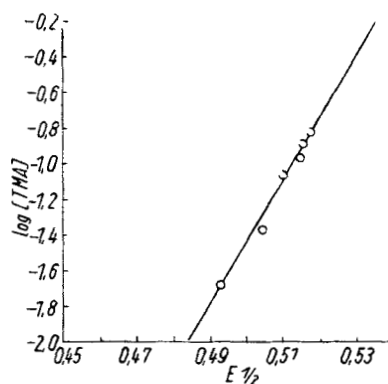


Fig. 1. Polarographic study: Graph of Half wave potential ($E_{\frac{1}{2}}$) in millivolts against logarithm of concentration of Thiomalic acid [TMA.]

standard NaOH solutions. Each solution contained an excess of concentrated KNO_3 solution (0.1 M, 5 ml). Also 100 ml of water to each solution was added to avoid the volume correction. The pH values were plotted against

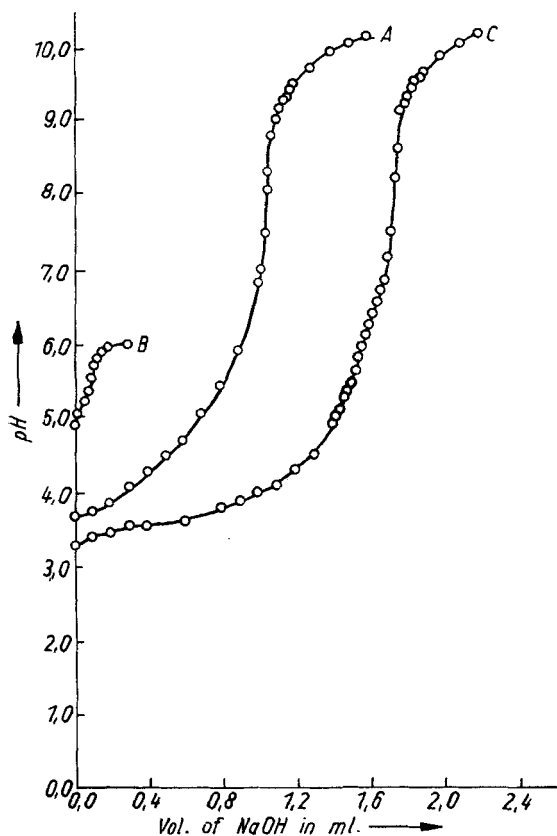


Fig. 2. Potentiometric study: A. Titration of thiomalic acid (0.01M) + KNO_3 (0.1M) with NaOH; B. Titration of $\text{Pb}(\text{NO}_3)_2$ (0.01M) + KNO_3 (0.1M) with NaOH; C. Titration of thiomalic acid (0.01M) + $\text{Pb}(\text{NO}_3)_2$ (0.01M) + KNO_3 (0.1M) with NaOH

the volume of NaOH added (Fig. 2). A shift of 0.56 ml of NaOH, at inflexion point is observed. This shift has been attributed to the release of fresh proton from thiomalic acid due to complex formation.

Two solutions of $\text{Pb}(\text{NO}_3)_2$ and TMA (0.1 M each) were mixed in the 1:2 proportion. An excess of TMA was taken to ensure complete precipitation. The precipitate was slightly warmed, allowed to settle down, and finally filtered through filter pump. After several washing with warm water and alcohol, it was dried carefully in an oven at 30–40 °C. The amount of sulphur was estimated by BaSO_4 method and was found to be 8.2%. 0.1 g of this complex was dissolved in minimum quantity of HNO_3 concentration and

boiled to ensure complete decomposition of the complex. Amount of Pb (II) in this solution was estimated polarographically and was found to be 0.059 g.

The magnetic susceptibility of the complex thus isolated, was determined. It was found to be diamagnetic. The susceptibility and other values are given in the following table:

No.	β	Temp. °C	V in ml.	W in g	ΔW in mg	$\chi_g - 10^6$
1.	0.249	30.5	0.3618	0.21722	- 0.38	- 0.37
2.	0.249	30.5	0.3618	0.22987	- 0.37	- 0.36
3.	0.249	30.5	0.23013	0.23013	- 0.38	- 0.37

Mean: - 0.37

Discussion

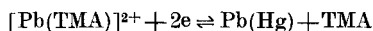
The shift in $E_{\frac{1}{2}}$ values with concentration of TMA clearly indicates the complex formation between Pb (II) and TMA. As the complex Pb (II) ion undergoes two electron reduction at d. m. e., the number of ligand molecules coordinated to the metal atom can be calculated using the equation⁸⁾

$$\frac{dE_{\frac{1}{2}}}{d \log[\text{TMA}]} = - \frac{0.059}{n} \beta$$

where p' is the number of the ligand groups attached to the oxidised form of the metal ion and n' is the number of electrons involved in the reduction. Substituting the different values from graph (Fig. 1), we get $p = 1$. The extrapolated $E_{\frac{1}{2}}$ of Pb - complex at $(\text{TMA}) = 1$ is found to be - 0.542 volts. Substituting this value in the equation

$$E_{1/2at[x]=1} = E_0 + \frac{0.059}{n} \log k_{ox}.$$

where E_0 has been taken at $E_{\frac{1}{2}}$ of uncomplexed⁹⁾ Pb (II), the value of $\log K$ can be calculated. This comes out to be 3.6. The electrode reaction can thus be proposed as follows:



neglecting the charge contribution of TMA.

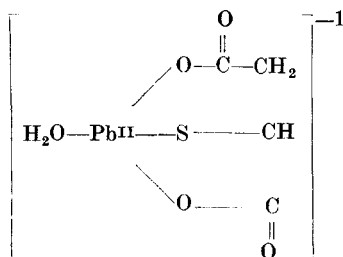
In pH measurements the shift of 0.56 ml (1.70-1.14) of NaOH must be due to the release of third proton from thiomalic acid due to complex formation and this shift must correspond to the strength of the metal ion which is utilised in complexation. The equivalence comes out to be 1 : 1 between metal ion and NaOH. Again since one molecule of NaOH will neutralise one proton of TMA, the equivalence between metal ion and TMA comes out to be 1 : 1. The result is in confirmation with the one, obtained by polarographic measurements (Fig. 2).

From the estimations of lead and TMA in the solid compound isolated, it was further confirmed that it gives the same complex in solution as in the solid state. As the most probable coordination number of lead (II) is four, the fourth valency bond is assumed to be occupied by water molecule. The

⁸⁾ K. ANITA DEMMELER, H. GAYER and M. J. ELKIND, Chem. Education **30**, 557 (1953).

⁹⁾ LINGANE, Ind. Eng. Chem. Anal. **15**, 583 (1943).

bivalent state of lead is confirmed by the measurement of magnetic susceptibility which gives a value of -0.37×10^{-6} . On the basis of all these, the formula of the compound may be assumed as



In polarographic studies, however, the water molecule may be replaced by an acetate ion, which is present in large excess.

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