Polarographic Studies on the Complexes of Zinc with some Sulphur containing ligands.

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Summary

Polarographic studies have been carried out on irreversible reduction of zinc complexes with thiomalic acid and thiosalicylic acid in acetate buffer (pH 4.8) at the dropping mercury electrode. The measurements reveal a 1:1 (metal : ligand) stoichiometry for zinc thiomalic acid system and 1:2 stoichiometry for zinc-thiosalicyclic acid system. The complexes are reduced irreversibly at the d.m.e. The values of transfer coefficient (α) and forward rate constant K_f^o have been calculated and are 0.289, 3.563×10^{-16} and 0.350, 4.699×10^{-21} respectively for the thiomalic acid and thiosalicylic acid complexes.

The study of sulphur compounds and specially those containing sulphydril group has played a vital role in the field of modern electro-analytical Chemistry as they have found useful applications in medicine, biology and industry. Another distinguishing property associated with the mercaptide group is the ability to react readily with many metals to form complexes containing sulphur bridges. The present study has been undertaken with a view to obtaining more information on the complexing tendencies of mercaptide ion with zinc. Complex formation of zinc (II) with thiomalic acid and thio-salicylic acid (Henceafter abbreviated as TMA and TSH respectively) has been studied using polarographic methods. TMA shows the characteristics of both mercaptans and dicarboxylic acids, and can act as a mono, bi, or tridentate ligand. Similarly TSH may also be regarded as a polyfunctional ligand. Both the ligands form complexes with a number of transition metal ions[1-19]. Cheney et. al.[2] and Martell[3] have done the potentiometric studies of Zn^{+2} and TMA systems, while Nigam et. al.[20] have reported the potentiometric studies on Zn–TSH system. The present paper reveals the polarographic observations, on the reduction of Zn–TMA and Zn-TSH complexes at the dropping mercury electrode in acetate buffer (pH 4.8). Studies reveal that Zinc forms a 1:1 complex with TMA in aqueous medium and a 1:2 complex with TSH in 50% alcoholic medium. Both the complexes are reduced irreversibly with transfer coefficient value $\alpha = 0.289$ and 0.350 respectively. The forward rate constant K_f^o has also been calculated.

Materials and Method

Thiomalic acid and thiosalicylic acid were Evans Chemetics (New York) product of 99.7% purity and only freshly prepared solutions were used whenever needed. Stock solution of zinc was prepared by dissolving Zinc Oxide (B.D.H., AnalaR) in minimum quantity of dil. HCl. All other chemicals were of AnalaR grade and all solutions were prepared in double-distilled water. Polarographic measurements were made with a manual polarographic circuit recommended by Kolthoff and Lingane[73]. All potentials were measured against a Hume and Harris[21] saturated calomel electrode (S.C.E.). Mercury used in the dropping mercury electrode (D.M.E.) was purified by chemical treatment with dilute nitric acid, degreased with O.1N sodium hydroxide and distilled twice

under reduced pressure. Oxygen was removed from the solution with a stream of oxygen–free of vanadous sulphate, sodium hydroxide and distilled water. A trap was used having the same medium as that of the cell to avoid loss of alcohol etc. An atmosphere of nitrogen was maintained over the cell during recording of the polarograms. All the measurements were made at $30° \pm 0.1°C$.

The characteristics of the dropping mercury electrode were : $m = 2\,089$ mg/sec., $t = 3.60$ second, $h = 36.4$ cm and $m^{2/3}\ t^{2/6} = 2.023$ $mg^{2/3}\ sec^{-1/2}$.

All pH measurements were made with a Leeds and Northup pH meter with a general purpose glass electrode.

Results and Discussion

Studies on Zn-TMA System :— Studies were made in aqueous medium and acetate buffer (0.2M $CH_3C00Na + 0.2M$ CH_3C00H), pH 4.8, and at a constant ionic strength, $\mu = 0.2M$ in the presence of $KN0_3$ as supporting electrolyte. Gelatin (0.005%) was used as a maximum suppressor. Zinc (II) gives a single well-defined irreversible wave in this medium. The half-wave potential $E_{\frac{1}{2}}$ of zinc shows a shift to more negative values on the gradual addition of TMA. The results are given in Table I.

Table I. Characteristics of Zinc Wave in the presence of TMA

(in 0.2M Acetate buffer, pH 4.8 + $KN0_3$)

Conc. of Zn(II) Mx10^3	Conc. of TMA Mx10^2	$E_{\frac{1}{2}}$ Volts Vs S.C.E.
1.00	1.00	1.087
1.00	2.00	1.095
1.00	3.00	1.1015
1.00	4.00	1.105
1.00	5.00	1.108
1 00	6.00	1.109

When the potential of the dropping mercury electrode (Ed.e) was plotted against log $\frac{i}{i_d - i}$, a straight line was obained. The value of reciprocal slopes of the straight lines i, was higher than the values expected for two electron reversible reduction showing thereby the irreversibility of the electrode reaction.

From the stand point of absolute reaction rate theory the current–potential curve for the irrevers.ble reduction of a complex ion is given by

$$E = (E_{\frac{1}{2}})_C - \frac{RT}{\alpha nf} \log \frac{i}{i_d - i} \qquad (1)$$

OR

$$E = (E_{\frac{1}{2}})_C - \frac{.06}{\alpha nf} \log \frac{i}{i_d - i} \qquad (2)$$

at 30°C.

where the symbols have their usual meanings. The value of the transfer coefficient (α) has been calculated from the slope of the

$$E_{dc} - \log \frac{i}{i_d - i}$$

plots and comes out to be 0.289.

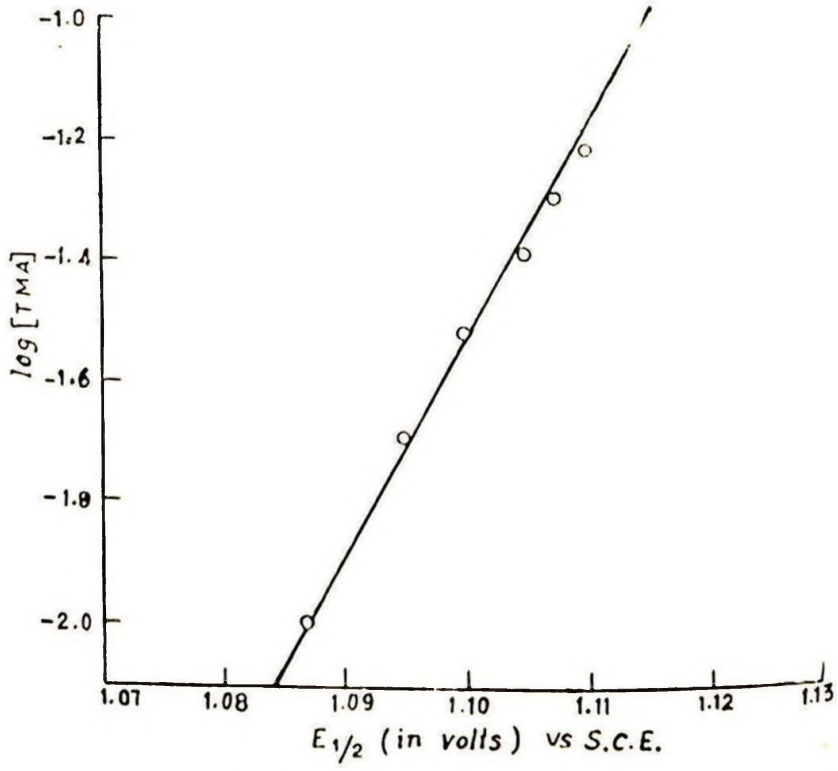


FIG. 1

Plot of logarithm of concentration of thiomalic acid, log TMA (on ordinate) Versus half wave potential ($E_{\frac{1}{2}}$) of the Zn-TMA complex in volts Versus SCE. (on abscissae)

The plot of half wave potential ($E_{\frac{1}{2}}$) versus log (concentration of TMA) gave a straight line with a slope of 0.0285. (fig. 1). The stoichiometry of the complex was found to be 1:1; (metal: ligand). The same stoichiometry has been reported in ammonia buffer earlier[13]. Thus the following electrode reaction may be proposed $Zn(TMA)^{2+} + 2e \rightarrow Zn(Hg) + TMA$ The kinetic parameters of the irreversible wave given by a complex ion can be studied by Matsuda and Ayabe[22] equation.

$$(E_{\frac{1}{2}})_C = \frac{0.06}{\alpha n}\left[\log \frac{K_f^{\circ}}{\sqrt{D_N}} + \tfrac{1}{2}\log\zeta - 0.053 - \log\left(\frac{i_l}{i_d}\right) - (N-P)\log f_x C_x\right] \quad (3)$$

where $(E)_{\frac{1}{2}}$ C = Half wave potential of the complex versus NHE (normal hydrogen electrode)

K_f° = Forward rate constant at potential N.H.E.

D_N = Diffusion coefficient of complex ion in solution

ζ = Drop time at $E_{\frac{1}{2}}$

i_d = Diffusion current

i_l = limiting current

f_n = Activity coefficient of complex ion

f_x = Activity coefficient of ligand.

C_x = Concentration of ligand.

$f_n = f_x = 1$ and $\frac{i_l}{i_d} = 1$

The value of K_f° for this system has been found to be 3.563×10^{-16}.

Studies on Zn—TSH System :— Experiments were done in 50% alcoholic medium and 0.2M acetate buffer (0.2M CH_3COONa + 0.2M CH_3COOH) and at a constant ionic strength $\mu = 0.2M$ in the presence of KNO_3 as supporting electrolyte. Gelatin (0.005%) was used as maximum suppressor. The $E_{\frac{1}{2}}$ for Zn^{2+} shows a shift to more negative values on the addition of increasing amount TSH. The values are shown in Table II.

Table II. Characteristics of Zinc Wave in the Presence of TSH.

(in 0.3M acetate buffer, pH 4.8 + KNO_3).

Conc. of Zn (II) $Mx10^3$	Conc. of TSH $Mx10^2$	$E_{\frac{1}{2}}$ Volts VsS.C.E.
1.00	1.00	1.145
1.00	2.00	1.160
1.00	3:00	1.173
1.00	4.00	1.180
1.00	5·00	1.187
1.00	6.00	1.190

The plot $E_{d.e}$ vs. $\log \frac{i}{i_d - i}$ gives straight lines. The slopes of the lines are higher than that for reversible two-electron reduction. Thus this system is also irreversible. The value of the transfer co-efficient has been calculated from Eqn. (1) and comes out to be 0.350.

When the values of $E_{\frac{1}{2}}$ were plottad against log [TSH] a straight line was obtained (fig.2). The slope of the line was 0.056. The stoichiometry of this complex is 1:2. A stoichiometry of 1:1 was reported in ammonia buffer earlier[14].

The electrode reaction is proposed as

$$Zn(TSH)_2^{2+} + 2e \rightarrow Zn(Hg) + 2TSH$$

The value of forward rate constant K°_f has been calculated from Eqn. (3) to be 5.699×10^{22}.

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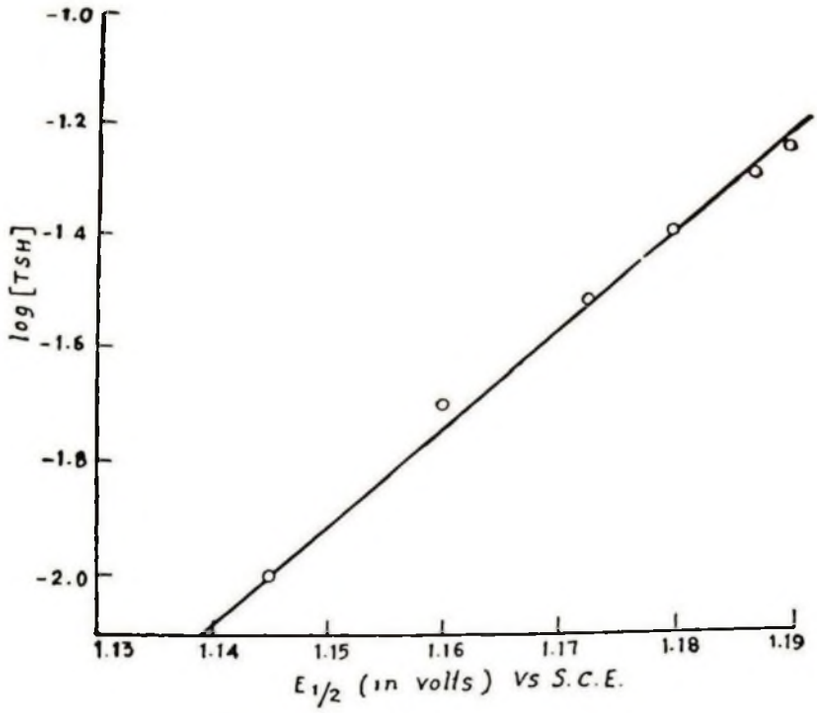


FIG 2

Plot of logarithm of concentration of Thiosalicylic acid, log TSH (on ordinate) Versus half wave potential ($E_{\frac{1}{2}}$) of the Zn-TSH complex in volts vs. SCE. (on abscissae).

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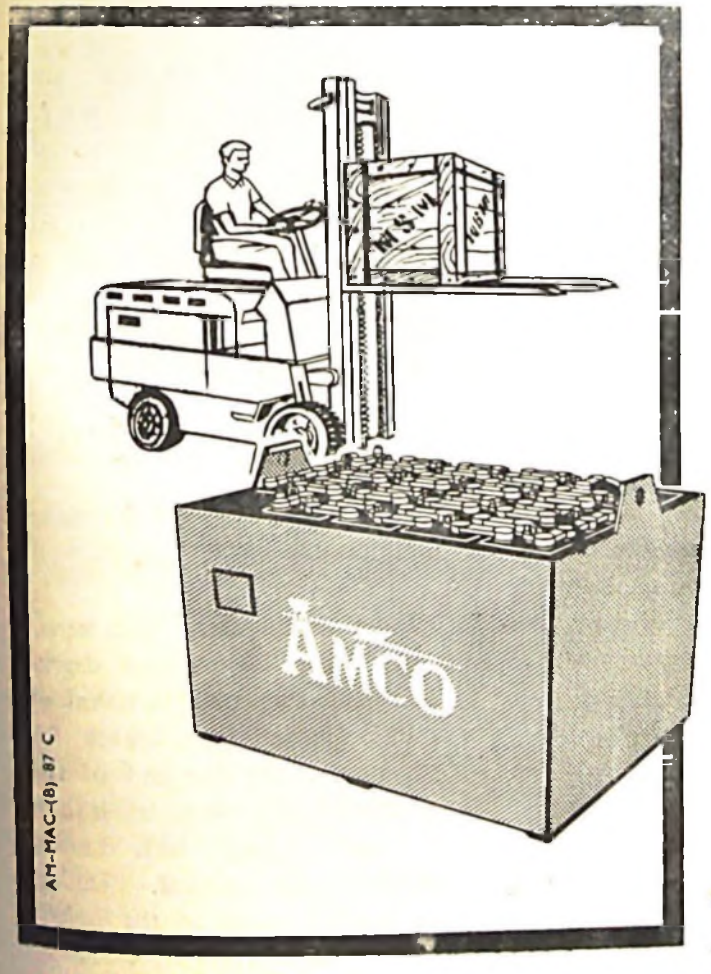
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