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Polarographic Study of Mixed Ligand (*o*-Mercaptobenzoate–Citrate) Complexes of Cadmium(II), Lead(II), and Thallium(I)

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Synopsis. The mixed ligand complex formation of *o*-mercaptobenzoic acid and citric acid with Cd(II), Pb (II), and Tl(I) in aqueous KNO_3 ($\mu = 1.0$ mol dm^{-3}) solutions containing Triton X-100 (0.001%) has been investigated by polarography. It was shown that only one mixed ligand entity MA_iX_j is formed, where *i* is two for Cd (II) and one for Tl(I) *j* is one for all complexes and A and X are the *o*-mercaptobenzoate and citrate ligands respectively. The stability constants have been evaluated.

o-Mercaptobenzoic acid, which figures prominently in the disscussion of sulfur containing ligands has a wide variety of applications in biological, pharmaceutical and analytical fields, such sulfur-containing compounds provide two co-ordination sites *viz.* –COOH and –SH groups. Most of the earlier workers have studied the complexation by using these compounds as simple ligands. Polarography of the *o*-mercaptobenzoic acid in aqueous methanol and dioxone has been studied by K. C. Gupta and Tejinder Kaur.[1] As a part of our investigations on the polarographic study of mixed ligand complexes of sulfur containing organic compounds in combination with several metal ions, the present study of mixed ligand (*o*-mercaptobenzoate and citrate) complexes with Cd(II), Pb(II), and Tl(I), has been initiated, for which no reference could be traced out in the literature. The composition and stability constants of the complexes formed have been studied by polarographic technique.

Experimental

o-Mercaptobenzoic acid (95%, Evan's Chemetics, Inc., New York) and citric acid (B.D.H. AnalaR) as their sodium salts were used as complexing agents. All other reagents used were also of AnalaR (B.D.H.) grade. Stock solutions were prepared in doubly-distilled air-free conductivity-water. Triton X-100 (0.001%) was used as maximum suppressor and KNO_3 ($\mu = 1.0$ mol dm^{-3}) as supporting electrolyte. A southern manual polarograph (Surrey, England) with scalmp galvanometer was used for recording current voltage curves. The capillary characterstics in KNO_3 ($\mu = 1.0$ mol dm^{-3}) at *Ed.e*$= -0.7$ V in conjuction with respect to SCE were $m^{2/3}t^{1/6} = 2.4436$ mg$^{2/3}$ s$^{-1/2}$ ($h = 45$ cm). All measurements were done with the cell immersed in thermostatic bath. Dissolved air was removed by bubbling hydrogen through the cell and the necessory corrections for the IR drop and charging current were made as usual.

Results and Discussion

The formation of each mixed ligand complex was studied at 30 °C by recording polarograms of two different sets.

Set I: 1.0 mM Cd $(NO_3)_2$ or Pb $(NO_3)_2$ or Tl NO_3, 0.001% Triton X-100 and KNO_3 ($\mu = 1.0$ mol dm^{-3}) with constant citrate concentration ($C_X = 40.0 \times 10^{-3}$ mol dm^{-3}) and varying concentration of *o*-mercaptobenzoate ($C_A = 10.0 \times 10^{-3}$ mol dm^{-3} to 80.0×10^{-3} mol dm^{-3}).

Set II: 1.0 mM Cd $(NO_3)_2$ or Pb $(NO_3)_2$ or Tl NO_3, 0.001% Triton X-100 and KNO_3 ($\mu = 1.0$ mol dm^{-3}) with constant *o*-mercaptobenzoate ($C_A = 40.0 \times 10^{-3}$ mol dm^{-3}) and varying concentration of citrate ($C_X = 10.0 \times 10^{-3}$ mol dm^{-3} to 80.0×10^{-3} mol dm^{-3}).

All the plots of log $(i/(id-i))$ *versus* $-$*Ed.e.* yielded straight lines with slopes, which agree with the theoretical value corresponding to $n=2$ for Cd(II) and Pb(II) system and $n=1$ for TI(I) system respectively. The mean values of the slopes for two different series were 0.0302 and 0.0297 for Cd^{2+}, 0.0299 and 0.0301 for Pb^{2+} 0.0589 and 0.0599 for Tl^+ system, showing the reversibility of the reduction. Linear plots of *id versus* $h^{1/2}$ passing through the origin, established the diffusion-controlled nature in each case. The $E_{1/2}$ values from the log plots of the above mentioned c-v curves and corresponding diffusion current values have been recorded (Tables 1a, 1b, and 1c). The $E_{1/2}$ values were found to shift towards more negative values with increasing concentration of complexing agents, showing the complex formation.

Souchay and Faucherre[2] derived an equation where a metal ion complex with two kinds of ligand species simultaneously in solution. If the complexing reaction of the following type is considered.

$$M + iA + jX \rightarrow MA_iX_j \tag{1}$$

With the restriction that single mixed ligand entity MA_iX_j is formed, then the shift in the $E_{1/2}$ of the polarographic wave of the metal ion as a function of the concentration of added reagents A and X is given by

$$\Delta E_{1/2} = \frac{2.303RT}{nF}\log\left(\frac{D_{\text{free}}}{D_{\text{Comp}}}\right)^{1/2} - \frac{2.303RT}{nF}\log K_{MA_iX_j} - i\frac{2.303RT}{nF}\log C_A - j\frac{2.303RT}{nF}\log C_X. \tag{2}$$

The ratio $D_{\text{free}}/D_{\text{Comp}}$ was obtained from the values of the limiting current. From plots of $\Delta E_{1/2}$ *versus* $\log C_A$ with C_X kept constant and $\Delta E_{1/2}$ *versus* $\log C_X$ with C_A kept constant, values for "*i*" and "*j*" can be obtained by intersect method because on differentiation.

$$\left(\frac{\partial(\Delta E_{1/2})}{\partial(\log C_A)}\right)_{C_X} = -\frac{2.303RT}{nF} \tag{3}$$

$$\left(\frac{\partial(\Delta E_{1/2})}{\partial(\log C_X)}\right)_{C_A} = -\frac{2.303RT}{nF} \tag{4}$$

Plots of (I)$\Delta E_{1/2}$ *versus* C_A (C_X kept constant), (II) $\Delta E_{1/2}$ *versus* $\log C_X$ (C_A kept constant) yielded straight lines. Figure 1, curves I and II, for Cd^{2+}, curves I′ and II′ for Pb^{2+}, curves I″ and II″ for Tl^+ systems and thus establish the formation of a single mixed ligand entity MA_iX_j. The coordination numbers *i*

Table 1a. Cd^{2+} Mixed ligand system

Concn C_A/M	0.00	0.01	0.02	0.04	0.06	0.08	0.04	0.04	0.04	0.04
C_X/M	0.00	0.04	0.04	0.04	0.04	0.04	0.01	0.02	0.06	0.08
30 °C $id/\mu A$	6.45	5.64	5.28	5.00	4.58	4.24	5.34	5.12	4.73	4.54
$-E_{1/2}$/V	0.596	0.852	0.870	0.892	0.902	0.910	0.870	0.880	0.898	0.902
$K_{MA_iX_j}$	—	13.929	13.922	14.065	14.077	14.099	13.930	13.962	14.107	14.119

Mean $K_{MA_iX_j}=14.023$, standard deviation $=0.085$.

Table 1b. Pb^{2+} Mixed ligand system

Concn C_A/M	0.00	0.01	0.02	0.04	0.06	0.08	0.04	0.04	0.04	0.04
C_X/M	0.00	0.04	0.04	0.04	0.04	0.04	0.01	0.02	0.06	0.08
30 °C $id/\mu A$	7.10	6.20	6.00	5.60	5.20	4.80	5.90	5.70	5.40	5.22
$-E_{1/2}$/V	0.400	0.654	0.674	0.694	0.706	0.714	0.674	0.684	0.700	0.704
$K_{MA_iX_j}$	—	13.864	13.915	13.984	14.069	14.095	13.929	13.958	14.033	14.043

Mean $K_{MA_iX_j}=13.988$, standard deviation $=0.077$.

Table 1c. Tl^{+} Mixed ligand system

Concn C_A/M	0.00	0.01	0.02	0.04	0.06	0.08	0.04	0.04	0.04	0.04
C_X/M	0.00	0.04	0.04	0.04	0.04	0.04	0.01	0.02	0.06	0.08
30 °C $id/\mu A$	5.80	4.42	4.00	3.34	3.00	2.80	3.60	3.50	3.25	3.17
$-E_{1/2}$/V	0.482	4.498	0.516	0.534	0.544	0.552	0.500	0.516	0.542	0.550
$K_{MA_iX_j}$	—	3.715	3.726	3.764	3.785	3.802	3.793	3.755	3.733	3.741

Mean $K_{MA_iX_j}=3.757$, standard deviation $=0.031$.

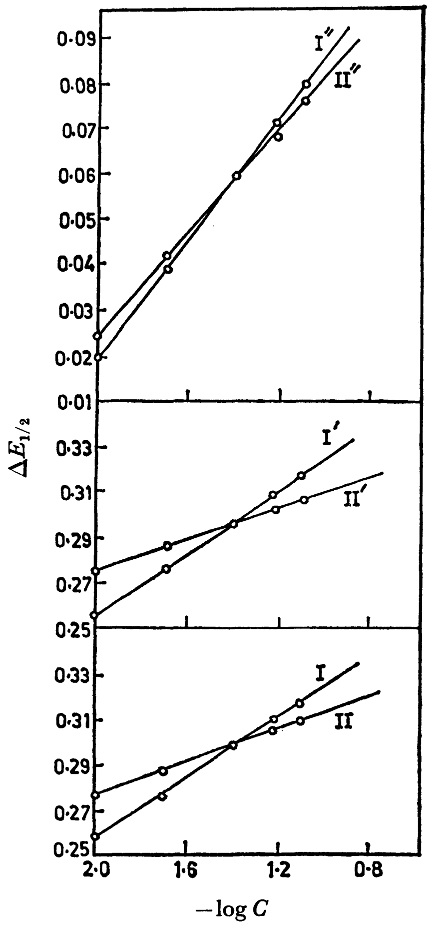

Fig. 1. Plots of $\Delta E_{1/2}$ *versus* $-\log C$.
Curves I and II— for Cd^{2+} system, curves I′ and II′— for Pb^{2+} system, curves I″ and II″— for Tl^{+} system.

and j of ligands A and X were determined from the plot (I) and (II) at 30 °C and found to be i=2.18 for Cd^{2+} 2.05 for Pb^{2+} and 0.94 for Tl^{+} respectively. Integral values of "i" and "j" were used in the calculation of the stability constants $K_{MA_iX_j}$, using Eq. 2 and were found to be 14.023 for Cd^{2+}, 13.988 for Pb^{2+} and 3.757 for Tl^{+} respectively. The present investigation suggests the formation of only one kind of mixed ligand species $[CdA_2X]^{-5}$, $[PbA_2X]^{-5}$, $[TlAX]^{-4}$ with mixed ligand (*o*-mercaptobenzoate–citrate) system.

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