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Synthesis and Characterization of Novel Heterobinuclear Mercury(II)-DTPA-M(II) Complexes: Electrocatalytic and Sensor Applications

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Hg(II) metal complex is synthesized using octadentate ligand diethylene triamine penta acetic acid (DTPA) and the interaction of second metal ions viz. Cu(II), Pb(II), Mg(II) and Ca(II) is studied for the formation of novel heterobinuclear complexes. Heterobinuclear complexes are formed by taking 1:1 ratio of metal ions with Hg(II)-DTPA in aqueous solution at pH above 7. Heterobinuclear Hg(II)-DTPA-M(II) complexes are characterized using electrochemical technique and stability constant is calculated by pH-titration technique. Electroactive and stable Hg(II)-DTPA-Pb(II) complex is found to be suitable for the electrocatalytic application and demonstrated for the detection of glutathione in the wide range of concentration from 10 μ g/L to 10 mg/L.

Keywords diethylene triamine penta acetic acid, electroactive complex, electrocatalysis, glutathione detection, heterobinuclear complex, mixed metal complex

INTRODUCTION

The research on the complexation reactions has always been of great interest because of the numerous applications of the complexes, which have certain properties different from those of its components. Metal complexes find their numerous applications in the area of analytical, environmental, electrochemical chemistry and biological sciences.^[1–5] However, poor stability and solubility limit their extensive and diversified applications. In these developments, macro-ligands, functionalized ligands and mixed ligands complexes with variety of metal ions were synthesized and got intensive interest during the last two decades.^[5–7] However, the studies on mixed metal complexes of multifunctional ligands have been reported to a lesser extent for the technological applications. Apart from EDTA,^[8,9] a few reports are only available for mixed metal complexes, which are mainly based on biofunctional ligands such as glutathionate, Lhistidine and dopamine.^[10-11] Among various polyamino polycarboxylic acid ligands, diethylene triamine penta acetic acid (DTPA) is the most studied for ligands for various applications including detoxification and recently contrast enhancing agent in biomedical magnetic resonance imaging (MRI).^[12] DTPA is an octadentate ligand possessing eight donor atoms (3N and 5O) used for complexation of variety of metal ions.^[13-16] The formation and stability of binary (ML) complexes of some of transition metal ions with DTPA showed its potential towards catalytic applications.^[17] Mercury modified electrode is one of the most popular in the analytical field due to its catalytic property for various chemicals and toxicants. However, its low oxidation potential, poor film stability and toxicity are major limitations for sensor and electrocatalytic applications. In our recent studies, we found that single metal ion complexed DTPA possesses uncoordinated sites that may bind to other metal ions and yield heterobimetallic mixed metal complexes of higher stability and electroactivity with very low solubility. An extensive study on synthesis and characterization of heterobimetallic mixed metal complexes of DTPA is carried out in the view of its potential towards sensor and electrocatalytic applications. Electroactive heterobimetallic mixed metal complexes are used for the development of chemically modified electrodes and demonstrated for the trace analysis of biologically important glutathione protein in aqueous solution.

EXPERIMENTAL

Materials and Instruments

Sodium nitrate, nitric acid, sodium hydroxide and other metal oxides were purchased from Merck, India. DTPA, EDTA and glutathione (GSH MW 307) were purchased from

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Aldrich-Sigma, USA. All other reagents were of A.R. grade and their solutions were prepared in deionized double distilled water.

The absorption spectra were recorded on a Lambda 25 Perkins Elmer UV visible spectrophotometer (obtained from DAAD, Germany under instrument donation program). Titration was carried out using Century Cp 901 S pH meter. Elemental analysis was carried out using atomic absorption spectrophotometer (Varian 250+) equipped with vapor generation assembly (Varian VGA 77). All the electrochemical studies were performed on potentiostat/ Galvanostat, CH Instruments, USA, using a three-electrode system in a single compartment cell. Glassy carbon, gold electrode and platinum disk electrodes, Ag/AgCl reference electrodes and platinum rod counter electrode were obtained from CH Instruments, USA.

METHODS

Synthesis of Complexes

The metal-DTPA complexes were synthesized by mixing the appropriate amount (calculated for 10 mM) of the ligand DTPA and metal oxides viz. mercury oxide (HgO) or other metal oxides (CuO/PbO/CaO/MgO) in 1:1 mole ratio ligand:M(II) in aqueous medium by controlled heating and continuous stirring for 2-3 hours at 50°C. The mixed-metal DTPA complexes were synthesized by introducing the second metal oxide (CuO/PbO/CaO/MgO) in the same mole ratio in the Hg¹¹-DTPA complex solution. The reaction was carried out in aqueous medium by controlled heating and continuous stirring for 2-3 hours at 50°C. The dissolution of DTPA with metal oxides (initially insoluble in water), and appearance of clear solution (with change in color of initial solution) confirmed the formation of a new mixed-metal complex. Volume of reaction mixture was reduced under controlled evaporation by putting it on water bath at below 50°C. Fine crystals of the complexes were appeared at the bottom of the flask, when solution was kept for 1-2 days at room temperature in the dark. Complex precipitates were recrystallized from water and alcohol mixture in 3:1 ratio. Finally complexes were washed with ethanol and dried in an electric oven at 50°C. Air stable, non hygroscopic and crystalline solids were stored in a bottle for further studies.

Calculation of Stability Constant

Irving and Rossotti^[18] pH-titration technique (modified form of the Bjerrum-Calvin^[19]) was used for the calculation of stability constant of the metal-DTPA and mixed metal DTPA complexes. Metal nitrate solutions were standardized by EDTA titrations.^[20] The solution of the diethylene triamine penta acetic acid (ligand) was prepared by dissolving it in two equivalents of alkali in double distilled water. pH was measured with an accuracy ± 0.01 pH at 25°C. Four reaction mixtures viz. acid, ligand, mono metal complex and bimetal complex solutions were made separately as follows:

- (A) $NaNO_3 + HNO_3 + water$.
- (B) $NaNO_3 + HNO_3 + DTPA + water.$
- (C) $NaNO_3 + HNO_3 + DTPA + Hg(II)$ ion solution + water.
- (D) NaNO₃ + HNO₃ + DTPA + Hg(II) ion solution + M(II) ion soln.+ water.

where M(II) = Cu(II), Pb(II), Ca(II) and Mg(II).

Total volume was kept as 50 ml with ionic strength 0.1 M (NaNO₃), free acid concentration 0.02M (HNO₃), metal ion and ligand concentrations 0.01M for each. The molar ratio of M(II):Hg(II):DTPA was kept as 1:1:1 where M(II) = Cu(II), Pb(II), Ca(II) and Mg(II). All these solutions were individually titrated with carbonate free 0.1M NaOH solution.^[18]

The shifts from the pH titration curves were used to calculate the ñ (average number of ligands attached per metal ion), ñH (average number of protons attached per ligand) and pL (the free ligand exponent) values as following:

$$\begin{split} & \tilde{n}H = Y - \{(N_o + E_o) \ (V_2 - V_1)\}/(V_o + V_1)L_o \\ & \tilde{n} = \{(N_o + E_o) \ (V_3 - V_2)\}/ \ \{(V_o + V_1) \ \tilde{n}H \ M_o\} \\ & pL = \log \ \{(K_1[H^+] + K_1K_2[H^+]^2 + -)/(L_o - \tilde{n} \times M_o)\} \\ & \times \ \{(V_o + V_3)/V_o\} \end{split}$$

where,

Y is number of dissociable or replaceable protons attached to the ligand

L_o is the total concentration of the ligand

No is the concentration of alkali

E_o is the total concentration of free acid

Vo is the total volume of reaction mixture

 V_1 is the volume of alkali needed to reach a specified pH for solution "A" (i.e. acid)

 V_2 is the volume of alkali required to attain the same pH in the (acid + ligand) curves

 V_3 is volume of alkali required to attain the same pH in the (acid+ ligand + metal) curves.

- Mo is the total concentration of metal present in solution
- K1, K2, K3 are the protonation constants of the ligands and

H⁺ is the hydrogen ion concentration

Finally, the stability constants for binary (M(II)DTPA) and bimetal (Hg(II)DTPA M(II)) complexes were evaluated using following formula:

$$\log \mathbf{K} = [\log(\mathbf{L}_0 \times \tilde{n}) - \log\{\mathbf{M}_0 \times (1 - \tilde{n})\} + p\mathbf{L}]$$

 $log(L_o\times \tilde{n})$ represents the amount of complex formed, log $\{M_o\times (1-\tilde{n})\}$ represents the amount of free metal ion and pL the concentration of free ligand (HgDTPA)^{3-}

The stability constants obtained for such binary and ternary complexes were refined with the aid of SCOGS computer program.^[19] The calculated stability constant values as well as literature values^[20,21] were used as preliminary estimates in SCOGS computer programme. Ionic product of water (Kw) and activity coefficient of hydrogen ion under the experimental conditions were obtained from literature.^[21] Computer refined values of the stability constants corresponding to minimum standard deviation in the titer were taken.

Elemental Analysis

Elemental analysis of the metal and mixed metal DTPA complexes were carried out using atomic absorption spectrophotometer equipped with vapour generation assembly. The sample preparation was done as per the standard method keeping in view of volatile nature of mercury complexes.^[22]

Electrochemical Study and Development of Complex Modified Electrode

Electrochemical studies of metal and mixed metal complexes were carried out using CH Instruments, USA, in a single compartment cell equipped with three-electrodes. The cyclic voltammetry and differential pulse voltammetry were carried out either dissolving the complexes in appropriate electrolytes or directly coating over the metal or glassy carbon working electrodes.^[5] Metal or mixed metal complexes were electrochemically coated over the Pt or glassy carbon electrodes by applying -0.6 V vs. Ag/AgCl from1mg/mL complex solution in 0.2M Tris-HCl pH 7.5.

RESULTS AND DISCUSSION

Titration of the pentaprotic acid (H5L) DTPA ligand showed pKH value 1.86, 2.79, 4.29, 8.02 and 10.49 corresponding to successive deprotonation of five -COOH groups. The binary complexes of this octadentate ligand was studied with various metal ions viz. Hg(II), Cu(II), Pb(II), Ca(II) and Mg(II) metal ions in aqueous solution. These metal-DTPA complexes were studied for their stability as discussed under the experimental section. Among these complexes Hg(II)-DTPA showed highest stability and therefore, it can be presumed that in a 1:1, Hg(II):DTPA reaction mixture, Hg(II) remains fully complexed and the reaction mixture mainly contains the species [Hg(II)-DTPA] and [M] at pH lower than 2.5. When pH of the reaction mixture was raised by adding alkali, the dissociable protons of the uncoordinated groups of Hg(II)-DTPA were displaced as per the following equilibria.

$$[H_{3}HgDTPA] + OH^{-} \Leftrightarrow [H_{2}HgDTPA]^{-} + H_{2}O$$
$$[H_{2}HgDTPA]^{-} + OH^{-} \Leftrightarrow [HHgDTPA]^{2-} + H_{2}O$$
$$[HHgDTPA]^{2-} + OH^{-} \Leftrightarrow [HgDTPA]^{3-} + H_{2}O$$

The interaction of other metal ions viz. Cu(II), Pb(II), Ca(II) and Mg(II) with completely deprotonated ligand with rising pH was studied and mixed-metal complexes [Hg(II)-DTPA-M(II)] are formed as:

$$[HgDTPA]^{3-} + M^{n+} \leftrightarrow [MHgDTPA]^{n-3}$$

The Hg(II)-DTPA complex is expected to involve four coordinate tetrahedral arrangement around Hg as this is the most preferred coordination for Hg(II) metal ion.^[23] In the complex species Hg(II)-DTPA, the Hg is expected to bind two amino nitrogen and two carboxylic oxygens in a tetrahedral fashion and

TABLE 1 Stability/formation constant (log β) values for M-DTPA and Hg-DTPA-M (1:1:1) type complexes in aqueous medium. Ionic strength I = 0.1M (NaNO₃), Temp.= 25 +1°C.

Complex species	$\log \beta$
[HgDTPA] ³⁻	27.00
[CuDTPA] ³⁻	21.10
[PbDTPA] ³⁻	19.60
[CaDTPA] ³⁻	09.30
[MgDTPA] ³⁻	09.10
[HgDTPACu] ⁻	31.44
[HgDTPAPb] ⁻	29.18
[HgDTPACa] ⁻	27.86
[HgDTPAMg] ⁻	27.49

it has still some vacant coordination sites available for interaction with other metal ions. The complexation equilibria in the pH range 2.5–5.0 for the formation of mixed-metal complexes with Pb(II) may be shown as below:

$$[HgDTPA]^{3-} + Pb^{2+} \leftrightarrow [HgDTPAPb]^{-}$$

Similarly other mixed metal complexes were synthesized and stability constants were evaluated as discussed under the experimental section and shown in Table 1.

The air and thermal stable crystalline complexes showed water solubility, but were insoluble in most of the organic solvents and sparingly soluble in DMSO. The elemental analysis of the complexes also supported the formation of mixed metal complexes in 1:1 mole ratio. The mixed metal complexes showed higher stability in comparison to single metal DTPA complexes. Thermal decomposition temperature of solid complex samples was calculated and it was found to be highest for Pb(II)-DTPA and Hg(II)-DTPA-Pb(II) among all the complexes. Hg(II)-DTPA-Pb(II) complex was used for the development of chemically modified electrodes and the electrocatalytic applications.

Amongst the various chemically modified electrodes, mercury modified electrode is one of most popular in the analytical field due to its unique catalytic property for the electro-oxidation of various chemicals. However, the oxidation at low positive potential and its hazardous nature are the major limitations for its sensor or electrocatalytic applications. Moreover, the mercury film coating is not stable over most of electrode materials. In order to overcome these problems recently, various polymers impregnated mercury electrodes are developed for quantification of the heavy metals in aqueous system.^[23–25]

The electroactivity and the redox properties of the single metal-DTPA and mixed metal complexes were studied in aqueous and non-aqueous solution using a three electrode system. Hg(II)-DTPA-Pb(II) showed best electroactivity and stability



FIG. 1. Differential pulse voltammetric (25 mV/s) study of Hg(II)-DTPA-Pb(II) coated Pt electrode in 0.2M Tris-HCl buffer at pH 7.5.

among all the complexes. Hg(II)-DTPA-Pb(II) complex was coated over Pt or glassy carbon electrodes by applying -0.6 V vs. Ag/AgCl from 1mg/mL solution in 0.2M Tris-HCl buffer (pH 7.5) at room temperature. Hg(II)-DTPA-Pb(II) coated electrode was studied under differential pulse voltammetry in 0.2M Tris-HCl buffer (pH 7.5) at room temperature. Three oxidations peaks at -0.5V due to oxidation of Pb metal, at 0.2 V due to oxidation of mercury metal and a small hump at 0.55 V due to oxidation of DTPA were observed, as shown in Figure 1. The electrochemical stability and redox property of the Hg(II)-DTPA-Pb(II) complex was also studied for several redox cycles and at various scan rates. A typical voltammogram is shown in Figure 2 for Hg(II)-DTPA-Pb(II) coated Pt electrode in 0.2M Tris-HCl buffer (pH 7.5) in the range of -0.2V to 0.5 V vs. Ag/AgCl for scan rates 10, 20, 50, 100, 200 500 and 1000 mV/s. The peaks current are proportional to the scan rate in the scan



FIG. 2. Cyclic voltammetry of HgII-DTPA-PbII coated Pt electrode in 0.2M Tris-HCl buffer at pH 7.5 at various scan rates 10, 20, 50, 100, 200, 500 and 1000 mV/s (lower to higher peak current).

range 10 to 1000 mV/s and the peaks potential is also not varying much with scan rate, which shows pseudo reversible redox nature and electroactivity of the complex. The complex modified electrode was used for the electrocatalytic oxidation and estimation of biological important glutathione protein. Glutathione (GSH) is a small protein molecule formed from amino acid, cysteine, glyceine and glutamic acid. It is an antioxidant and acts as immune system and detoxifier in the body. Differential pulse voltammetry technique was used for the detection of GSH (molecular wt. 307) using Hg(II)-DTPA-Pb(II) complex modified electrode in the range of $10\mu g/L$ to 10mg/L in 0.1M phosphate buffer (6.7 pH). When the differential pulse voltammetry was performed for Hg(II)-DTPA-Pb(II) modified electrode in 0.1M phosphate buffer (6.7 pH) in the range of -0.3V to 0.9V vs. Ag/AgCl, two oxidations peaks were obtained as one at 0.22V due to oxidation of Hg(I) to Hg(II) and second a weak peak at 0.5V vs. Ag/AgCl due to ligand DTPA, as shown in Figure 3 of plot A. In addition to a small amount of GSH (to get GSH total concentration of 10 μ g/L), a considerable decease in the Hg oxidation peak current was observed, as shown in Figure 3 plot B. Further addition of GSH a new peak was observed at 0.45V vs. Ag/AgCl. The peak current was found to be proportional as the concentration of the GSH was increased in the solution. The GSH was further estimated for another three more concentrations as 0.1 mg/L, 1 mg/L and 10 mg/L, shown in Figure 3 plot C, D and E. The GSH could not be detected at the bare electrode when present below 10 mg/L. The decrease in the mercury oxidation peak and appearance of a new peak on addition of GSH probably indicates formation of some complex of GSH with the Hg(II)-DTPA-Pb(II). The Hg(II)-DTPA-Pb(II) complex showed a catalytic effect on the oxidation of GSH, which facilitated oxidation of the GSH. The complexation or interaction of the GSH with the Hg(II)-DTPA-Pb(II) modified electrode was also supported as it was observed that the same



FIG. 3. Differential pulse voltammetric (25 mV/s) studies of (A) HgII-DTPA-PbII modified Pt electrode in phosphate buffer 6.7pH (100 mM) as blank and in presence of (B) 10 μ g/L GSH, (C) 0.1 mg/L GSH (D) 1 mg/L GSH and (E) 10 mg/L GSH.

modified electrode after detection of GSH followed by proper washing gave oxidation peak at 0.45 V (with decrease in the peak current).

CONCLUSION

Hg(II)-DTPA and Hg(II)-DTPA-M(II) heterobinuclear complexes are synthesized using Cu(II), Pb(II), Mg(II) and Ca(II) as second metal ions. Stability constants of the crystalline complexes are calculated and Hg(II)-DTPA-Pb(II) complex is found to be most stable among other complexes. Electroactive Hg(II)-DTPA-Pb(II) complex is electrochemically coated over the Pt or glassy carbon electrodes and studied for the electrocatalytic applications for biomaterials. The Hg(II)-DTPA-Pb(II) modified electrode was used for the electrocatalytic oxidation of the biologically important glutathione protein. It was observed that GSH is forming strong interaction with the Hg(II)-DTPA-Pb(II) complex, which catalyzed the oxidation of the GSH. A sensitive detection of GSH was possible in aqueous solution in the range of 10 μ g/L to 10 mg/L using heterobinuclear complex modified electrode.

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