

Short Communication

Polarographic study of the composition and stability constants of cadmium (II) complexes with new Schiff bases

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Abstract

The synthesis and characterisation of ortho hydroxy acetophenone tris (hydroxymethyl) methylamine (OHAPT) and resacetophenone tris (hydroxymethyl) methylamine (RPT) are described for the first time. The metal to ligand ratio in these complexes is found to be 1:2 in the mixed solvent (30% aqueous DMF) used. Stability constants of these complexes are $\beta_1 = 1.0 \times 10^8$; 4.0×10^5 and $\beta_2 = 14.6 \times 10^8$; 8.1×10^6 for Cd-OHAPT and Cd-RPT complexes respectively. The stability constant order of these complexes is discussed based on the electron density on the donor, azomethine nitrogen and oxygen atoms.

Key words: Polarography, cadmium (II), new Schiff bases, stability constants.

1. Introduction

Schiff bases are important class of compounds since the compounds are tuberculostatically¹ and fungicidally active² and are useful in cancer treatment³ and possess active ingredients of insecticidal⁴ composition. Literature survey revealed that only aldehydes⁵⁻⁷ viz. acetaldehyde, propionaldehyde, isopropionaldehyde, benzaldehyde, 2-hydroxy-1-naphthaldehyde and salicylaldehyde condense with tris (hydroxymethyl) methylamine to give respective Schiff bases. So far no attempt has been made for the preparation of Schiff bases derived from ketone and tris (hydroxymethyl)-methylamine. We report here the synthesis and characterisation of Schiff bases viz. ortho hydroxyacetophenone tris (hydroxymethyl) methylamine (OHAPT) and resacetophenone tris (hydroxymethyl) methylamine (RPT) and their chelating ability towards cadmium in 30% aqueous dimethylformamide medium. The composition and stability constants of Cd-OHAPT and Cd-RPT complexes are determined polarographically.

2. Experimental

Manual Toshniwal polarographic model CLO 2A coupled with Galvanometer type MG-2 was used to record the polarograms. The capillary characteristics of dropping mercury

electrode at constant height of mercury head ($h = 76.5$ cm) were $t = 3.8$ sec; $m = 2.482$ mg/sec at 0 V vs SCE in water. A Lingane type *H*-cell and a digital pH meter (Model LI-120, ELICO) were used in the present study. A Toshniwal thermostat type GL 15 was used to keep the temperature at $26 \pm 0.1^\circ\text{C}$.

A stock solution (0.1 M) of cadmium (II) in a 250-ml volumetric flask was prepared using AR cadmium acetate and standardised gravimetrically⁸. OHAPT and RPT reagent solutions (2.0 M) were prepared in 60% aqueous dimethylformamide.

All reagents used were of AnalaR (BDH) grade and their solutions were prepared in doubly distilled water. All polarographic experiments were done in 30% aqueous dimethylformamide medium. A 0.002% freshly prepared gelatin was used as maximum suppressor.

2.1 Synthesis of OHAPT or RPT

Equimolar (0.5 M) solutions of tris (hydroxymethyl) methylamine and ketone (ortho hydroxyacetophenone or resacetophenone)⁹ were prepared in methanol and equal quantities of both the reactants were taken and mixed with methanol with constant stirring. The mixture was then refluxed on a hot water bath for 45 min. On cooling, white crystalline solid was separated out. The resultant compound was washed with ether and dried. Recrystallisation was done from alcohol.

3. Results and discussion

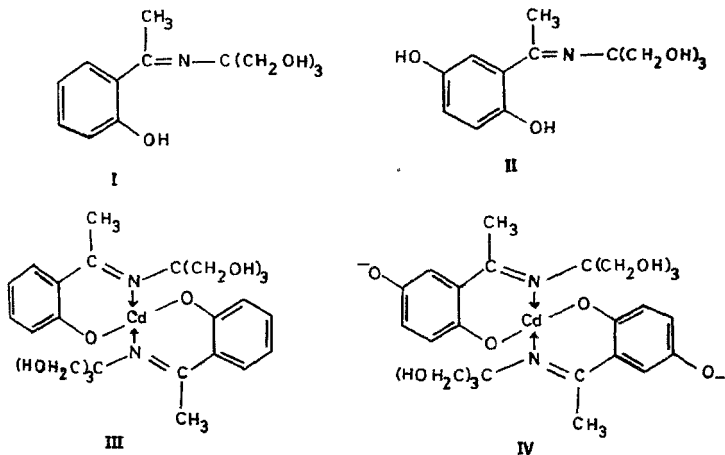
OHAPT and RPT were characterised on the basis of elemental and infrared spectral analysis. The IR spectra (in Nujol) of OHAPT and RPT showed peaks in the region 1630 - 1640 cm^{-1} indicating the presence of azomethine nitrogen ($>C=N$) group. The peaks were also observed at 3340 - 3330 cm^{-1} (broad *S*, *OH* stretching), 3190 - 3180 cm^{-1} (broad, *m*, phenolic *OH*) 1600 , 1580 , 1500 , 1450 cm^{-1} (aromatic *C-C* vibrations). Molecular formula, yield (%) and melting point ($^\circ\text{C}$) of OHAPT and RPT are $\text{C}_{12}\text{H}_{17}\text{O}_4\text{N}$, $\text{C}_{12}\text{H}_{17}\text{O}_5\text{N}$; 142 - 143 , 134 - 135 ; 64 , 66 respectively. The elemental analysis of OHAPT [C%, 60.21 (60.25); H%, 7.08 (7.11); N%, 5.82 (5.86)] and RPT [C%, 56.45 (56.47); H%, 6.64 (6.67); N%, 5.47 (5.41)] confirms the molecular formula of ligands. The calculated values are given in parenthesis. The structures of OHAPT (I) and RPT (II) can be represented as given on page 129.

Cathodic reduction of cadmium (II) was found to be reversible in the presence of ligands (OHAPT or RPT) as revealed by the straight line plots of $E_{d,c}$ vs $\log i/i_d - i$. The diffusion-controlled nature of reduction was confirmed by the proportionality of diffusion current to the squareroot of effective height of mercury column. The concentration of cadmium (1.0 mM) and ligands (0.2 M) was kept constant.

With increase in the concentration (0.02-1.0M) of ligand (OHAPT or RPT) the half-wave potential is shifted towards more negative value and diffusion current is decreased (6.23 to 2.09 μA) owing to the complex formation between Cd^{2+} and ligand (OHAPT or RPT). The $E_{1/2}$ shift in OHAPT and RPT systems are -0.590 to -0.848 V and -0.590 to -0.782 V vs SCE respectively. The log plots were found to be linear with a slope of 29 ± 1 mV and 30

± 1 mV for OHAPT and RPT systems respectively indicating the two-electron reduction. The plots of $-E_{1/2}$ as a function of $-\log[X]$ for Cd-OHAPT and Cd-RPT systems showed the formation of successive complexes and hence DeFord and Hume's method¹⁰ was employed for determining the various complexity functions $F_1[X]$, $F_2[X]$ vs C_x shows a horizontal line parallel to the C_x axis which indicates the formation of 1:2 (Cd: OHAPT or Cd: RPT) metal-ligand complexes. The plots of $F_1[X]$ and $F_2[X]$ vs ligand concentrations when extrapolated to $C_x = 0$ gave values for the stepwise formation constants of cadmium complexes. The stability constants of complexes are $\beta_1 = 1.0 \times 10^8$; 4.0×10^5 and $\beta_2 = 14.6 \times 10^8$; 8.1×10^6 for Cd-OHAPT and Cd-RPT complexes respectively.

The polarographic data clearly indicate the ligational behaviour of OHAPT and RPT towards Cd (II). In alkaline medium the deprotonation of phenolic hydroxyl group and bond formation between metal ion and oxygen¹¹⁻¹³ is expected besides the coordination of azomethine nitrogen atom^{13,14} to cadmium. Since cadmium is known to form 4-coordinate complexes the following structures for Cd-OHAPT (III) and Cd-RPT (IV) complexes are suggested.



The stability constant order of complexes can be represented as follows

$$\beta_1 (\text{Cd} - \text{OHAPT}) > \beta_1 (\text{Cd} - \text{RPT}) \quad (1)$$

$$\beta_2 (\text{Cd} - \text{OHAPT}) > \beta_2 (\text{Cd} - \text{RPT}) \quad (2)$$

In Cd - RPT complex hydroxo group is present in the para position to the oxygen, which is taking part in bond formation with cadmium. The electron withdrawing effect of hydroxo

group decreases the electron density on the latter (oxygen) and azomethine nitrogen atom thereby decreasing the bond strength between cadmium and oxygen; cadmium and nitrogen respectively in Cd-RPT complex. This may be the reason for the low stability constant of Cd-RPT complex in comparison with Cd-OHAPT complex since resonance and hyperconjugation are equally operative in both the structures.

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