

# Synthesis & Characterization of New Schiff Bases & Their Complexation with Cadmium—A Polarographic Study

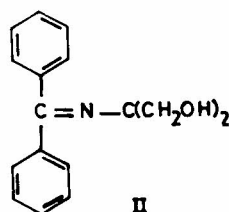
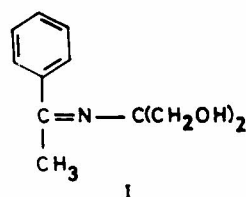
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Synthesis and characterization of new schiff bases, acetophenone-tris(hydroxymethyl)methylamine (APT) and benzophenone-tris(hydroxymethyl)methylamine (BPT) have been described. The complexation of  $\text{Cd}^{2+}$  with these new schiff bases has been investigated polarographically in dimethylformamide-water mixtures. The metal to ligand ratio in these complexes is found to be 1:2. Stability constants of these complexes are  $\beta_1 = 1.0 \times 10^4$ ;  $7.5 \times 10^8$  and  $\beta_2 = 4.4 \times 10^5$ ;  $13.6 \times 10^9$  for Cd-APT and Cd-BPT complexes respectively.

In recent years<sup>1-3</sup>, a number of schiff bases derived from various aldehydes and tris(hydroxymethyl)methylamine have been reported. However, schiff bases derived from ketone and tris(hydroxymethyl)methylamine are unknown. We report here the synthesis of two new schiff bases, acetophenone-tris(hydroxymethyl)methylamine (APT, I) and benzophenone-tris(hydroxymethyl)methylamine (BPT, II). Their relative complexing abilities with  $\text{Cd}^{2+}$  have been studied polarographically.



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

A stock solution (0.1 M) of cadmium(II) was prepared using AR grade cadmium acetate and

standardized<sup>4</sup>. APT and BPT reagent solutions (2.0 M) were prepared in 60% aq. DMF.

## Synthesis of APT or BPT

Equimolar (0.05 M) solutions of tris(hydroxymethyl)methylamine and the ketone (acetophenone or benzophenone) were prepared in ethanol and mixed in 1:1 ratio with constant stirring. The mixture was then refluxed on a water bath for 45 min. On cooling, a white crystalline solid was separated out in each case. The compound was washed with ether and dried. Recrystallization was done from ethanol. The yield and melting point data of compounds are presented in Table 1.

A manual Toshniwal Polarograph model CLO 2A coupled with a 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 in 0.1 M  $\text{KNO}_3$  with open circuit. A Lingane type H-cell and a digital pH-meter (Model LI-120 ELICO) were used in the present study.

The IR spectra (in nujol) of APT and BPT showed peaks in the region  $1660-1650$   $\text{cm}^{-1}$  indicating the presence of azomethine ( $\nu\text{C}=\text{N}$ ) group. The peaks were also observed at  $3340-3330$   $\text{cm}^{-1}$  ( $\nu\text{-OH}$ ) and  $1600$ ,  $1580$ ,  $1500$  and  $1450$   $\text{cm}^{-1}$  (aromatic  $\nu\text{C}=\text{C}$ ). The elemental analyses, yields and melting points and  $pK^{5,6}$  values of APT (I) and BPT (II) are given in Table 1.

A single well defined wave was obtained for cadmium in different concentrations of ligand (APT or BPT) and 0.1 M  $\text{KNO}_3$  at pH 10.5. The ionic strength ( $\mu = 0.1$  M  $\text{KNO}_3$ ) of medium was kept constant. With increase in the concentration of ligand, the half-wave potential is shifted towards more negative values and diffusion current is decreased owing to the complex formation between  $\text{Cd}^{2+}$  and ligand (APT or BPT). The diffusion controlled nature of reduction was

Table 1—Analytical Data of the Ligands

| Ligand                                                    | m.p.<br>°C<br>(yield, %) | $pK^{5,6}$   | Found (calc), %  |                |                |
|-----------------------------------------------------------|--------------------------|--------------|------------------|----------------|----------------|
|                                                           |                          |              | C                | H              | N              |
| APT<br>( $\text{C}_{12}\text{H}_{17}\text{O}_3\text{N}$ ) | 139-40<br>(62)           | 8.5†<br>8.2‡ | 64.53<br>(64.57) | 7.59<br>(7.62) | 6.24<br>(6.28) |
| BPT<br>( $\text{C}_{17}\text{H}_{19}\text{O}_3\text{N}$ ) | 138-39<br>(64)           | 8.2†<br>8.8‡ | 71.56<br>(71.58) | 6.63<br>(6.67) | 4.87<br>(4.91) |

†determined polarographically; ‡determined potentiometrically

Table 2—Polarographic Data and Derived Functions for Cd(II)-APT and Cd(II)-BPT Systems

{[Cd<sup>2+</sup>] = 1.0 × 10<sup>-3</sup> M, KNO<sub>3</sub> = 0.1 M, pH = 10.5, Gelatin 0.002 %, Temp. = 25 ± 0.1 °C}

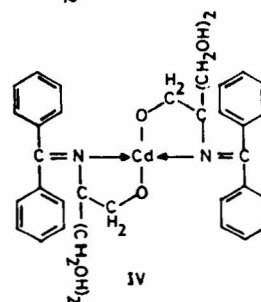
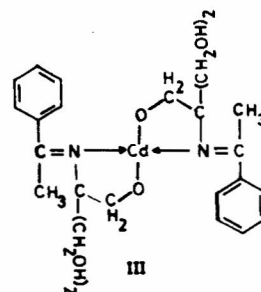
| [Ligand]<br><i>M</i> | <i>i<sub>d</sub></i><br>(μA) | Slope<br>(mV) | - <i>E</i> <sub>1/2</sub><br>(V, SCE) | Δ <i>E</i> <sub>1/2</sub><br>(V, SCE) | Log <i>I<sub>M</sub>/I<sub>C</sub></i> | <i>F</i> <sub>0</sub> [X]<br>× 10 <sup>-3</sup> | <i>F</i> <sub>1</sub> [X]<br>× 10 <sup>-4</sup> | <i>F</i> <sub>2</sub> [X]<br>× 10 <sup>-5</sup> |
|----------------------|------------------------------|---------------|---------------------------------------|---------------------------------------|----------------------------------------|-------------------------------------------------|-------------------------------------------------|-------------------------------------------------|
| APT                  |                              |               |                                       |                                       |                                        |                                                 |                                                 |                                                 |
| 0.00                 | 6.2304                       | 29.24         | 0.590                                 | —                                     | —                                      | 0.001                                           | —                                               | —                                               |
| 0.02                 | 5.9210                       | 31.84         | 0.678                                 | 0.088                                 | 0.0221                                 | 0.973                                           | 4.860                                           | 19.300                                          |
| 0.03                 | 5.6185                       | 31.92         | 0.679                                 | 0.089                                 | 0.0448                                 | 1.100                                           | 3.664                                           | 8.867                                           |
| 0.04                 | 5.5880                       | 31.72         | 0.680                                 | 0.090                                 | 0.0473                                 | 1.203                                           | 3.005                                           | 5.025                                           |
| 0.05                 | 5.5260                       | 31.64         | 0.685                                 | 0.095                                 | 0.0521                                 | 1.795                                           | 3.588                                           | 4.999                                           |
| 0.06                 | 5.4610                       | 31.12         | 0.686                                 | 0.096                                 | 0.0572                                 | 1.964                                           | 3.272                                           | 3.786                                           |
| 0.08                 | 5.5340                       | 30.98         | 0.698                                 | 0.108                                 | 0.0675                                 | 5.146                                           | 6.431                                           | 6.789                                           |
| 0.10                 | 5.2070                       | 30.84         | 0.700                                 | 0.110                                 | 0.0779                                 | 6.108                                           | 6.107                                           | 5.108                                           |
| 0.20                 | 5.0880                       | 30.94         | 0.716                                 | 0.126                                 | 0.0879                                 | 21.620                                          | 10.809                                          | 4.540                                           |
| 0.40                 | 4.0640                       | 30.72         | 0.729                                 | 0.139                                 | 0.1856                                 | 74.230                                          | 18.560                                          | 4.390                                           |
| 0.60                 | 3.6830                       | 30.24         | 0.736                                 | 0.145                                 | 0.2283                                 | 166.700                                         | 27.783                                          | 4.464                                           |
| 0.80                 | 2.7940                       | 29.82         | 0.742                                 | 0.152                                 | 0.3483                                 | 296.000                                         | 36.899                                          | 4.498                                           |
| BPT                  |                              |               |                                       |                                       |                                        |                                                 |                                                 |                                                 |
| 0.00                 | 6.2304                       | 29.24         | 0.590                                 | 0.000                                 | 0.000                                  | 0.001                                           | —                                               | —                                               |
| 0.02                 | 5.4610                       | 30.42         | 0.810                                 | 0.220                                 | 0.0572                                 | 29660                                           | 14829                                           | —                                               |
| 0.03                 | 5.4055                       | 30.85         | 0.814                                 | 0.224                                 | 0.0616                                 | 40980                                           | 13659                                           | —                                               |
| 0.04                 | 5.3340                       | 30.72         | 0.816                                 | 0.226                                 | 0.0675                                 | 48390                                           | 12097                                           | 11492                                           |
| 0.05                 | 5.2865                       | 30.58         | 0.820                                 | 0.230                                 | 0.0713                                 | 66580                                           | 13316                                           | 11632                                           |
| 0.06                 | 5.2070                       | 30.41         | 0.822                                 | 0.232                                 | 0.0779                                 | 79050                                           | 13175                                           | 9458                                            |
| 0.08                 | 5.0800                       | 29.86         | 0.830                                 | 0.240                                 | 0.0886                                 | 150500                                          | 18812                                           | 14140                                           |
| 0.10                 | 4.9530                       | 29.92         | 0.836                                 | 0.246                                 | 0.0996                                 | 245200                                          | 24519                                           | 17019                                           |
| 0.20                 | 4.8260                       | 29.71         | 0.849                                 | 0.259                                 | 0.1116                                 | 694400                                          | 24719                                           | 13609                                           |
| 0.40                 | 3.5740                       | 29.68         | 0.860                                 | 0.270                                 | 0.2413                                 | 2440000                                         | 60999                                           | 13375                                           |

confirmed by the proportionality of diffusion current to the square root of effective height of mercury column. The log plots were found to be linear with slopes of 31 ± 1 mV and 29 ± 1 mV for APT and BPT systems respectively indicating reversibility of electrode reaction at d.m.e. with *n* = 2.

The plots of *E*<sub>1/2</sub> versus log [ligand] were found to be smooth curves showing the formation of two or more complex species in equilibrium. Hence, DeFord and Hume's method<sup>7</sup> was employed for the determination of composition and stepwise formation constants of Cd(II)-complexes. The polarographic data and the derived functions of Cd-APT and Cd-BPT systems are given in Table 2. The results show the existence of two types of complex species in each system viz. Cd-L and Cd-L<sub>2</sub> (where L = APT or BPT). The stability constants of complexes are β<sub>1</sub> = 1.0 × 10<sup>4</sup>; 7.5 × 10<sup>8</sup> and β<sub>2</sub> = 4.4 × 10<sup>5</sup>; 13.6 × 10<sup>9</sup> for Cd-APT and Cd-BPT complexes respectively. At higher concentrations (>0.4 M), BPT gives heavy precipitations with cadmium. Hence, the concentration range of BPT for the studies used is 0.02–0.4 M.

The polarographic data clearly indicate the complex formation of Cd(II) with APT and BPT. Based on the previous observations<sup>8–13</sup>, the deprotonation of one of the hydroxyl groups of ligand (APT or BPT) and subsequent coordination through oxygen are

suggested in the alkaline medium used in the present study (pH 10.5). In schiff bases, azomethine nitrogen atom coordinates with the metal ion. Since cadmium(II) is known to form 4-coordinate complexes, structures III and IV are suggested for Cd-APT and Cd-BPT complexes respectively.



## NOTES

Though hyperconjugation and resonance are operative in structure III, the structure IV is more resonance-stabilized, which explains the higher stability of Cd-BPT complex (IV) compound to that of Cd-APT complex(III).

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