Protonating and Chelating Efficiencies of Some Biologically Important Thiocarbonohydrazides in 60%(v/v) Ethanol -Water System by Potentiometric and Spectrophotometric Methods

S. Sridhar, P. Kulanthaipandi, P. Thillai arasu, V. Thanikachalam and G. Manikandan

1Department of Chemistry, K.G.S. Arts College, Srivaikundam 628 619, India
2Department of Chemistry, Kalasalingam University, Krishnan Koil. 626 190, India
3Department of Chemistry, Annamalai University, Annamalainagar 608 002, India

Abstract: Protonation behaviour of three thiocarbonohydrazides namely benzylidenethiocarbonohydrazide (BTC), p-tolualidenethiocarbonohydrazide(TTC) and p-anisalidenethiocarbonohydrazide(ATC) and their nature of interactions with metal(II) ions [Cd(II), Pb(II) and Zn(II)] have been evaluated in 60% (v/v) ethanol-water mixture by potentiometric method at 30°C and ionic strength at 0.1 M KNO₃. The results were analysed for chelating tendencies in terms of stability constants and distribution nature of the species.

Key words: Schiffbases • Thiocarbonohydrazide • Benzylidenethiocarbonohydrazide
p-tolualidenethiocarbonohydrazide • p-anisalidenethiocarbonohydrazide • Protonation constant• Stability constant • Potentiometric method

INTRODUCTION

A large number of Schiff bases derived from thiocarboxyhydrazide and their complexes are found to be a novel class of antibacterial [1], anticarcinogenic [2], antiviral [3] and antifungal [4] agents. The bioactive properties of Schiff bases of thiocarboxyhydrazide and their metal complexes motivated several researchers to explore their physical and chemical properties. Study on protonation and chelating nature of the Schiff bases derived from thiocarboxyhydrazide are necessary to understand the biological activities. Although much work has been reported on the synthesis and structural characterization of metal complexes of thiocarbonohydrazides [5-9], a literature survey reveals that the protonation and stability constants of Schiff bases prepared from thiocarboxyhydrazide and its metal complexes have not been determined. Interestingly, the metals Zn, Cd and Pb are often recognised by the same gene regulators and membrane transporters. [10] An examination of the inherent chemical properties of these three metal ions is essential in understanding the basis of metal specificity displayed by target proteins responsible for metal homeostasis and resistance. The relationships between the chemical properties of these metals (Zn, Cd and Pb) and similarities in structural responses they may elicit have to be analysed. In this direction thiocarbonohydrazides, Cd(II), Pb(II) and Zn(II) were selected and studied.

It has been supported that drug action by coordination compounds depends upon the existence of stable species in biological media [11]. There exists a strong equilibrium relationship among all the species. This equilibrium is not only sensitive to the standard conditions but also to the biological media. Concentration is one of the basic parameters which affects the existence of the species is observed by earlier workers. [12-14] Hence there is a necessity for not only generating medicinally active species but also establish conditions for the stability. Hence we have undertaken this work to establish different species and optimum conditions for the stability.

Experimental

Preparation of Ligands BTC, TTC and ATC: Thiocarboxyhydrazide was prepared as per the literature method. [15] Benzylidenethiocarbonohydrazide (BTC), p-tolualidenethiocarbonohydrazide (TTC) and p-anisalidenethiocarbonohydrazide (ATC) were prepared by refluxing 1:1 molar ratio of benzaldehyde (0.01 mol dm⁻³) and thiocarboxyhydrazide hydrochloride (0.01 mol dm⁻³) in ethanol medium for 3 hrs and were
recrystallized twice with ethanol. The products were checked with TLC, IR and elemental analysis. Solutions of BTC, TTC and ATC with strength 0.01 mol were prepared in purified hot ethanol.

Solutions of acid and base were prepared using analytical grade nitric acid and sodium hydroxide, respectively. Double distilled water was used for all the studies. Acid solution was standardized by titrating against primary standard sodium carbonate. Solution of carbonate free 0.1 mol dm$^{-3}$ NaOH in 60% (v/v) ethanol-water mixture was prepared and standardized potentiometrically with potassium hydrogen phthalate solution. The strength of acid and base were verified by least squares fit Gran’s plot. [16] All the metal solutions were estimated according to standard procedures. [17] Analytical grade potassium nitrate was used to maintain constant ionic strength.

**Potentiometric Measurements:** Potentiometric titrations were carried out using combined pH electrode (Ingold) in a thermostated 80 ml glass vessel at 30°C ± 0.1°C. The potentiometric cell was calibrated before and after each experiment. The ionic product of water was calculated at constant ionic strength of 0.1 mol dm$^{-3}$ KNO$_3$ in 60% (v/v) ethanol-water mixture on measuring [OH$^-$] and pH. The pH readings of the 60% (v/v) ethanol-water mixture were corrected according to Van Uitert and Haas relation. [18] Titrations were performed with CO$_2$ free 0.1 mol dm$^{-3}$ NaOH in 60% (v/v) ethanol-water mixture against (a) 4 × 10$^{-3}$ mol dm$^{-3}$ HNO$_3$, (b) a + 1.5 × 10$^{-3}$ mol dm$^{-3}$ ligand (A), (c) b + 5 × 10$^{-4}$ mol dm$^{-3}$ metal,

Minimum mole of metal solution was employed to avoid the probability of multinuclear complexes. Each of the above solutions was brought to a total volume of 30 ml having 60% (v/v) ethanol-water mixture and values of free sodiumhydroxide under the experimental conditions of ionic strength 0.1 mol dm$^{-3}$ KNO$_3$, at 30 ± 0.1°C in ethanol-water mixtures. Owing to the low solubility of ligands A in water, 60% (v/v) ethanol-water mixture was used.

The acid-base behaviour of the ligands A [benzylidenethiocarbonohydrazide (BTC), p-toluaidenethiocarbonohydrazide (TTC) and p-anisalidenethiocarbonohydrazide (ATC)] were studied in 60% (v/v) ethanol-water mixture having 0.1 mol dm$^{-3}$ KNO$_3$ as ionic strength at 30±0.1°C.

All the three ligands A (BTC, TTC and ATC) titrated offered two buffer regions 3.5 to 5 and 9 to 11, suggesting two successive deprotonation steps. Accordingly these compounds are expected to have two ionization constants relevant to the following ionization steps.

$$[H_2A]^+ \rightleftharpoons [HA]^+ + [H]^+$$
$$[HA]^+ \rightleftharpoons [A]^+ + [H]^+$$

The protonation equilibria can be explained by the following equation

The results of proton-ligand constants are tabulated in Table 1. The presence of methyl group in TTC and methoxy group in ATC does not alter appreciably the p$K_a$ and p$K_a$ values. This observation is similar to the observation made in $\alpha$-amino acids [20, 21]. The p$K_a$ values of gly, L-ala, L-phe and L-leu are not changed appreciably due to the presence of various groups like methyl, phenyl, isopropyl, etc.

This is further explained that the p$K_a$ and p$K_a$ can be assigned for the protonation sites of terminal hydrazine amino nitrogen and azomethine nitrogen as shown in the above equilibria equation. The protonation site may not be on thione sulphur. This is evidenced by the fact that at low pH, thione as the predominant one than thiol of thione-thiol tautomerism in ethanol medium as reported by Seleem et al. [22].

The overall protonation constants of the ligands A (BTC, TTC and ATC) are well correlated ($r = 0.989$) with $\sigma$ (Hammett constant; BTC = 0, TTC = -0.17 and ATC = -0.23). Further, the linear correlation of the overall protonation constant can be justified by the fact that...
the electron depletion in benzene ring of aldehyde due to condensation with thioicarboxydrazide are compensated by methyl and more compensated by methoxy group with inductive and mesomeric effects, respectively.

**Effect of Solvent Composition on Protonation Constant of Ligand A (BTC):** Since the ligands A are neutral, they are not much sensitive with respect to dielectric constant of the medium. As a representative study, the protonation constants of BTC in three different [50, 60 and 70% (v/v)] ethanol-water mixtures are calculated and listed in Table 2. The pK₆₅₆ (protonation of hydrazine amine) value increases slightly as the percentage of ethanol increases, whereas pK₆₁₂ has maximum value at 60% (v/v) ethanol-water mixture. This result suggests that the pK₆₁₂ which stands for the protonation on azomethine nitrogen and not on sulphur of thione. It is observed from the literature that an increase in the protonation constant will result as the dielectric constant of the medium increases if the thiol deprotonation occurs as in the case of carboxylic acid dissociation in amino acids [20]. The deprotonation of protonated azomethine nitrogen can also be supported by the reported study [22] on 2-amino-4-[α-(acetyl)-ethylidinedihydrazine]-6-methylpyrimidine (DHP), where keto form is the predominant one compared to that of enol form in ethanol-water mixture, whereas in dioxane-water medium enol is more predominant than keto form.

The IR spectrum of the ligand BTC(A) does not exhibit absorption at ν_ν(S-H) at ca. 2600 cm⁻¹ but displays strong ν_ν(N-H) band at ca. 3179 cm⁻¹ and ν(C=O) at 1050 cm⁻¹ indicating that in the solid state it remains in the thiketo tautomeristic form. This further supports the protonation sites as azomethine nitrogen and hydrazine nitrogen and not on sulphur of thione. The absence of enolisation in the free ligand is also reported by Wang et al. [24] in the study of thiosemicarbazone ligands.

### Table 1: Proton-ligand constants of ATC, BTC and TTC in 60% (v/v) ethanol-water mixture at 30±0.1 °C and μ = 0.1 mol dm⁻³ KNO₃

<table>
<thead>
<tr>
<th>Stability parameters</th>
<th>ATC</th>
<th>BTC</th>
<th>TTC</th>
</tr>
</thead>
<tbody>
<tr>
<td>log β₆₁₂</td>
<td>10.63 (3)</td>
<td>10.60 (5)</td>
<td>10.69 (4)</td>
</tr>
<tr>
<td>log β₆₁₆</td>
<td>14.54 (2)</td>
<td>14.47 (6)</td>
<td>14.51 (6)</td>
</tr>
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</table>

### Table 2: Proton-ligand and ligand-metals[Cd(II) and Pb(II)] constants of BTC in three different ethanol-water mixtures at 30±0.1 °C and μ = 0.1 mol dm⁻³ KNO₃

<table>
<thead>
<tr>
<th>Stability parameters</th>
<th>50% (v/v)</th>
<th>60% (v/v)</th>
<th>70% (v/v)</th>
</tr>
</thead>
<tbody>
<tr>
<td>log β₆₁₂</td>
<td>10.43 (3)</td>
<td>10.60 (5)</td>
<td>10.79 (4)</td>
</tr>
<tr>
<td>log β₆₁₆</td>
<td>13.78 (2)</td>
<td>14.47 (6)</td>
<td>14.43 (6)</td>
</tr>
<tr>
<td>log β₆₅₆</td>
<td>6.81 (7)</td>
<td>6.76 (20)</td>
<td>6.59 (21)</td>
</tr>
<tr>
<td>log β₆₅₁₂</td>
<td>14.70 (1)</td>
<td>14.77 (2)</td>
<td>14.17 (3)</td>
</tr>
<tr>
<td>log β₆₅₁₆</td>
<td>20.40 (5)</td>
<td>21.05 (6)</td>
<td>19.86 (13)</td>
</tr>
</tbody>
</table>

Stabilities of Single Ligand Complexes: Analysis of complex titration curves of ligands A (BTC, TTC and ATC) with metals(II) [Cd(II), Pb(II) and Zn(II)] show the existence of species like M₄H, M₄A, M₄T and M₄J. Polynuclear complexes have not been found in this present condition, though the ligands A (BTC, TTC and ATC) are having thione as bridging functional group. This should be due to very low ligand: metal ratio i.e., 5:1 and a very low concentration of metal (5 × 10⁻⁴ mol dm⁻³) was employed. This low metal concentration may be the reason for less possibility for the formation of polynuclear complexes [25, 26].

The formation constants of the complexes with ligands BTC, TTC and ATC and metals(II) are tabulated in Table 3, respectively. The mononuclear bis(binary) (M₄A) complexes show the stability order with respect to ligands A (BTC, TTC and ATC) as Pb(II) > Cd(II) > Zn(II). Though three coordination sites are available like hydrazine (-NH-NH₂), azomethine (>C=N-) and thione (>C=S) groups in ligands A, the complexes in general show high stability particularly due to the azomethine nitrogen and reversible binding nature of thione sulphur. With respect to the ligand BTC, all the complexes [M₄H, M₄A, M₄T and M₄J] show the order of stabilities as Pb(II) > Cd(II) > Zn(II). This stability order infers sulphur as one of the donor atoms in vivo as well as in vitro, it is able to form both σ and π bonds [27, 28]. The Zn(II) shows 1 log unit less than Cd(II) and 1.5 log unit less than Pb(II). This is due to the preference of Zn(II) for tetrahedral geometry which in
The log values exhibit the nature of backbonding due to soft Lewis acid. Further, the log values of all the nine binary complexes (M\textsubscript{II}) show the order of stability as Pb(II) > Zn(II) > Cd(II), whereas all the complexes of BTC (M\textsubscript{III}, M\textsubscript{A}, M\textsubscript{A2}, and M\textsubscript{A3}) show the order of stability as Pb(II) > Cd(II) > Zn(II). The methoxy group in the phenyl ring of ATC, increases the electronegative nature of azomethine nitrogen by resonance stabilisation, which will dominate sulphur interaction thereby weakening the softness of the base. Similarly, the methyl group in phenyl ring of TTC, increases electronegative nature of azomethine by inductive effect and thus weakening the softness of the base.

Species distribution plots show the presence of M\textsubscript{AH} species with remarkable percentage (around 60%). From the results it is concluded that though the ligands A are tridentate but act as bidentate in binary systems. The pK\textsubscript{MAH} values in Table 3 demonstrate that in all the protonated binary complexes the nature of protonation is the same. Since azomethine and thiourea are the efficient chelating centres, these will be engaged in chelation with metal ions as demonstrated by Krishna et al. [31] The freely available hydrazine amino group is protonated at lower pH range of 5-5.5 in all the nine protonated binary complexes (M\textsubscript{AH}) of BTC, TTC and ATC with metals(II) [Cd(II), Pb(II) and Zn(II)]. The values of pK\textsubscript{MAH} are smaller than pK\textsubscript{s} of all the three ligands A (BTC, TTC and ATC). This is due to the less basic nature of ligands A in the presence of metal ion. The azomethine nitrogen and thione sulphur as chelating centres is further supported by the study of metal complexes of thiosemicarbazone by Wang et al. [22].

The log K\textsubscript{MAH} values exhibit the nature of backbonding among the three metals with ligands A. The positive \Delta log K\textsuperscript{e} i.e., the higher value of log K\textsubscript{MAH}, than that of log K\textsubscript{MA} for all the nine binary complexes suggest the effective \pi-backbonding [25]. Further, the log K\textsubscript{MAH} of Cd(II) complexes have higher value than the other two metal [Pb(II) and Zn(II)] complexes. This shows the effective \pi-backbonding due to soft Lewis acid behaviour of Cd(II). However, for Pb(II) complex log K\textsubscript{MAH} value is less and for Zn(II) complex it is further less due to borderline Lewis acid nature. The higher value of log K\textsubscript{MAH} is accounted by the enhancement of electropositive nature of metal in MA by the first added ligand. This is due to the ability of sulphur to accept electrons from the orbitals of metal by \pi-backbonding and thus facilitating the addition of second ligand [25, 26].

The values of \Delta log K\textsuperscript{e} are positive with a magnitude of less than 1 log unit. This exhibit the mode of coordination is same in MA and MA\textsubscript{2}, using thione sulphur and azomethine nitrogen as chelating centers as described in M\textsubscript{AH}. Further, the higher values of log K\textsubscript{MAH} of all the nine binary complexes (MA\textsubscript{2}) may be accounted by the trans fashion coordination as shown in Fig. 2. This is in accordance with the results of Braibanti et al. [32]. They suggested the five membered trans arrangement of MA\textsubscript{2} species of M(II)-thiocarbohydrazide at 30 ± 1.0 °C.

### Solvent Effect on Single Ligand Complexes of Ligands

**BTC:** The effect of dielectric constant of the medium was studied using BTC(A) as a representative one. The stability results in 50, 60 and 70% (v/v) ethanol-water mixtures of Cd(II) and Pb(II) complexes of BTC(A) are tabulated in Tables 2. The results show that a moderately stable complexes in 60% (v/v) ethanol-water mixture than in 50 and 70% (v/v) ethanol-water mixtures. This may be due to the solvating ability of the solvent with respect to the cation and the ligand. It is obvious that the selective

<table>
<thead>
<tr>
<th>Ligands</th>
<th>Metals</th>
<th>log (\beta\text{MA}_1)</th>
<th>log (\beta\text{MA}_2)</th>
<th>log (\beta\text{MA}_3)</th>
<th>log (\beta\text{MA}_4)</th>
<th>log (K\text{MAH}_1)</th>
<th>log (K\text{MAH}_2)</th>
<th>log (K\text{MAH}_3)</th>
<th>log (K\text{MAH}_4)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BTC</td>
<td>Zn(II)</td>
<td>12.89(6)</td>
<td>6.72(14)</td>
<td>13.85(7)</td>
<td>20.44(6)</td>
<td>6.16</td>
<td>7.13</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cd(II)</td>
<td>13.87(5)</td>
<td>6.76(25)</td>
<td>14.77(2)</td>
<td>21.05(7)</td>
<td>7.11</td>
<td>8.01</td>
<td>1.27</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Pb(II)</td>
<td>14.41(12)</td>
<td>7.80(10)</td>
<td>15.61(8)</td>
<td>22.59(9)</td>
<td>6.61</td>
<td>7.81</td>
<td>0.01</td>
<td></td>
</tr>
<tr>
<td>TTC</td>
<td>Zn(II)</td>
<td>13.63(6)</td>
<td>6.93(10)</td>
<td>14.56(9)</td>
<td>21.88(6)</td>
<td>6.7</td>
<td>7.63</td>
<td>0.70</td>
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</tr>
<tr>
<td></td>
<td>Cd(II)</td>
<td>13.26(6)</td>
<td>7.21(12)</td>
<td>15.31(2)</td>
<td>21.37(8)</td>
<td>6.05</td>
<td>8.10</td>
<td>0.89</td>
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</tr>
<tr>
<td></td>
<td>Pb(II)</td>
<td>13.24(8)</td>
<td>7.56(10)</td>
<td>15.47(2)</td>
<td>5.88(9)</td>
<td>6.79</td>
<td>-0.65</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>ATC</td>
<td>Zn(II)</td>
<td>13.03(2)</td>
<td>7.15(7)</td>
<td>14.24(17)</td>
<td>21.67(6)</td>
<td>5.88</td>
<td>6.79</td>
<td>-0.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Cd(II)</td>
<td>13.25(8)</td>
<td>6.99(7)</td>
<td>15.02(1)</td>
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<td>6.26</td>
<td>8.03</td>
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<td>Pb(II)</td>
<td>14.07(9)</td>
<td>7.92(5)</td>
<td>15.28(8)</td>
<td>21.83(4)</td>
<td>6.15</td>
<td>7.36</td>
<td>-0.56</td>
<td></td>
</tr>
</tbody>
</table>
binding of the cation in solution is a distinctive feature of the solution chemistry [33]. This high stability in 60% (v/v) ethanol-water mixture is the reason for studying all the other studies like protonation, binary and ternary systems in 60% (v/v) ethanol-water mixture.

**Species Distribution of Binary Complexes of Ligands BTC, TTC and ATC with Cd(II), Pb(II) and Zn(II):** The species distributions of all the nine binary Cd(II)/Pb(II)/Zn(II)-BTC/TTC/ATC systems are shown in the Fig. 3-5. All the nine binary systems exhibit free metal ions, MAH, MA, MA₂ and MA₃ species in common with different distribution pattern.

**Distribution of Free Metal Ions M(II) [Cd(II), Pb(II) and Zn(II)]:** The binary systems of BTC, TTC and ATC have free metal ions at low pH region (5-5.5). The equilibrium concentrations of free metal ions in BTC-M(II) binary systems (Fig. 2) with respect to metal ions are in the order Zn(II) > Cd(II) > Pb(II). The availability of high percentage of free Zn(II) might be due to the existence of high percentages of thione sulphur than thiol sulphur in the ligand BTC in the low pH region. It is further reported that in the thione-thiol tautomerism, thione form dominated in ethanol-water mixture [20]. The binding behaviour of thione sulphur with Zn(II) is less than thiol sulphur. Regarding Cd(II) and Pb(II) the thione sulphur
The protonated binary species MAH [M(II)-BTC/TTC/ATC-H] is high for Pb(II) (85%) at the pH of 5.5-5.5, whereas Cd(II) system shows around 65%. The Zn(II) system shows a very low percentage of M4H species. This exhibits the very low binary behaviour of BTC with Zn(II) due to lack of π-backbonding effect of BTC with Zn(II). The possible effective chelating centres might be of azomethine nitrogen and thione sulphur [29].

This indicates that the protonation might be at hydrazine amino nitrogen of BTC. A high percentage of Zn4H (90%) species is observed than Pb4H (25%) and Cd4H (25%) at pH 5.5 in the TTC system. In BTC system only low percentage of Zn4H (20%) and high percentage of Pb4H-AH (85%) and Cd4H-AH (65%) are observed. This observation shows the presence of p-methyl group drastically change the distribution pattern in the low pH region due to a significant change in basicity of azomethine nitrogen in TTC.

Distribution of M4 Species: As the pH increases above 6, the M4 and M42 species co-exists with the domination of M42 species in Cd(II) and Pb(II) systems. In all the nine binary systems the M4 species are less in concentration i.e., below 40%. Particularly for Cd(II) system only 10% of M4 species is formed as a maximum in all the three BTC, TTC and ATC systems. This is due to the effective π-backbonding of the ligands with Cd(II), which leads to the formation of M42 species by making metal ion in M4 more positive [25, 26]. The maximum percentage of Zn4 is shifted slightly at higher pH region than Cd4 and Pb4. This may be due to thiol form domination of BTC at high pH than thione form. Thiol reacts in better way with Zn(II) than thione.

All the three Cd(II)/ Pb(II) /Zn(II)-TTC binary systems show low percentages of M4 species in the TTC system. This is due to high favourable formation of M42 species in all three metals system of TTC. The M42 species formation is restricted in Zn(II)-BTC due to less basic nature of azomethine nitrogen. Presence of p-methyl group enhances the basicity of azomethine nitrogen. This is the reason for high percentage of M4 species in Zn-BTC system, whereas low percentage of M4 species in Zn-TTC system.

The M4 species of M(II)-ATC systems are having higher percentages at the pH of 6.3. A high percentage around 45% of M4 species is observed in Zn(II)-ATC system. This is due to less π-backbonding effect, which restricts the formation of M4 species in this pH range due to thione-sulphur domination than thiol sulphur. In Cd(II)-ATC system the percentage of M4 species is less, due to facilitation of M42 species formation by π-backbonding in M4 species. In the case of Pb(II)-ATC system much change is not observed in M4 species.

Distribution of M42 Species: A very high percentage (75%) of M42 species of Cd(II) exhibits the
effective \(\pi\)-backbonding of thione sulphur in BTC with Cd(II). The Pb(II) system shows a concentration of (50%) \(MA_2\) species at pH of 7 indicates the \(\pi\)-backbonding effect in Pb-BTC is less than in Cd(II)-BTC system. Eventhough the overall stability constants of Pb(II)-BTC system of \(MA_2\) species is higher than the overall stability of \(MA_2\) species of Cd(II)-BTC system, the concentration of \(MA_2\) species in Pb(II)-BTC is less than in Cd(II)-BTC system. This is due to the effective \(\pi\)-backbonding in \(MA\) species of Cd(II) system, which favours the further addition of \(A\) to \(MA\) species. This reason can be explained with the values of log \(K_{MAH}^{MA}\) value is high (8.03) in Cd(II) than in Pb(II) (7.81). Further, in Zn(II)-BTC system \(MA_4\) species concentration is still less and the maximum concentration shifts to high pH region. This strongly supports the thiol form of BTC dominants at high pH and this thiol produce stable \(MA_2\) species in Zn(II)-BTC system.

A very high percentage of Cd(II) species (85%) with high independency is observed in TTC system, which is slightly higher than in BTC system (75%). The same observation is made in Pb(II) system. A very high change in percentage of \(MA_4\) is observed in Zn(II)-TTC system than in BTC and ATC systems. These observations clearly exhibit the involvement of \(p\)-methyl group in increasing basic nature of the ligand TTC.

A very high percentage around 80% of \(MA_4\) species is observed in Cd(II)-ATC system. The \(MA_4\) species in Pb(II)-ATC is 50%. Though the overall stability constants of \(MA_4\) of Pb(II)-ATC is higher than Cd(II)-ATC system, the percentage of \(MA_4\) of Cd(II)-ATC is higher than the percentage of \(MA_2\) of Pb(II)-ATC. The domination of Cd(II)(ATC) might be due to effective \(\pi\)-backbonding. This is further evidenced by the value of log \(K_{MAH}^{MA}\). The value of log \(K_{MAH}^{MA}\) (8.03) is higher than the value of log \(K_{MAH}^{MA}\) (7.36) and log \(K_{MAH}^{MA}\) (6.79). This might be the reason for the low percentage availability of \(MA_2\) species in Zn(II)-ATC system.

**Distribution of \(MA_4\) Species:** As the pH increases, the \(MA_4\) species increases in all the three systems. In Pb(II) and Zn(II) systems high concentration of \(MA_4\) species are noted than that of Cd(II). At high pH range i.e., greater than 7, the thiol form domination favours the high stable \(MA_4\) complex species in Zn(II) - TTC /ATC systems. The other reasons for high stable and high percentage of Zn(II) species of TTC and ATC systems are the inductive and mesomeric effects caused by \(p\)-methyl and \(p\)-methoxy groups.

**UV-Vis Spectra of Binary Systems:** UV-Vis spectra of the ligands BTC, TTC and ATC have been recorded in pH 6 from 200 to 700 nm. The absorption intensity is ATC > TTC > BTC. The absorption intensities are 0.165, 0.160 and 0.140 in the case of ATC, BTC and TTC respectively. The ligand ATC exhibits high intensity which can be ascribed to the presence of methoxy group at \(para\) position to the aldehydic functionality. In the processes of formation of hydrazones the depleted electron density of benzene ring is compensated by mesomeric effect of methoxy group. In the case of TTC, the inductive effect of methyl is less pronounced and hence low absorption intensity is observed. In the case of BTC system no substitution presents in the benzene ring and hence no possibility of compensation of depleted electron density and hence still low intensity of absorption is observed.

The UV-Vis spectra of Zn(II), Cd(II) and Pb(II) with ligands BTC, TTC and ATC were measured in the range of 200 to 700 nm. The UV-Vis spectra of ATC-Zn(II)/Cd(II) / Pb(II) with ligand ATC is presented as a representative spectra in Fig-6. Binary complexes were recorded in the pH of 6.7, where the species \(MA_4\) has maximum concentrations in the distribution plots. From the fundamental chemistry it is known that the electronic energy level diagram \(n-\sigma^*\) and \(n-\pi^*\) are most favourable transitions for compounds which posses
atoms with nonbonding electrons. From the results it is observed that the intensity of $\lambda_{\text{max}}$ follows Pb(II) > Cd(II) > Zn(II). Thus the UV-Vis. Spectra of ligands BTC, TTC and ATC with heavy metals (Cd(II) and Pb(II)) show higher recognition than Zn(II) as observed in the study of tetra(p-t-butyl)tetrathiocalix[4]arene with Cd(II), Pb(II) and Ag(I) [34].

CONCLUSION

The analysis of stability constants and distribution pattern exhibits the different nature of reactivity of the ligands BTC, TTC and ATC with the metals [Zn(II), Cd(II) and Pb(II)]. The presence of p-methyl and p-methoxy groups in TTC and ATC changes the efficiencies of chelation with Zn(II) in a pronounced manner in the physiologically important pH range.

REFERENCES