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Spectrophotometric Determination of Cu^{2+} Metal Ions via Complex Formation with Carboxylated Tris(2-aminoethyl)amine

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ABSTRACT

An aminopolycarboxylic acid chelating agent; tris(2-aminoethyl)aminehexaacetic acid (TAHA) was prepared and characterized. TAHA formed stable complexes with Cu(II) ions and other metal ions at pH 10. The complexation behavior was studied by spectrophotometry at the complex maximum wavelength. Mixtures of Cu(II) and other metal ions (M^{2+}; Ca^{2+}, Co^{2+}, Ni^{2+}, Cd^{2+}) were titrated with TAHA at pH 10. The stoichiometry of ligand - to - metal was found to be 1:1. The stability constant of Cu(II)–TAHA complex was determined to be 1.86×10^{5} by using the continuous variation method. Beer's law was obeyed over the concentration range 3.0×10^{-4} M – 1.2×10^{-2} M for Cu(II) solution. The results of the quantitative determination of Cu(II) gave LOD and LOQ values of 7.285×10^{-6} M and 2.428×10^{-5} M respectively. The percent relative standard deviation (%RSD) for five replicate samples was found to be 1.088% and 4.804% for Cu(II) concentrations of 1.2×10^{-2} M and 3.0×10^{-4} M respectively.

Keywords

Tris(2-aminoethyl)aminehexaacetic acid; complexation; spectrophotometry.

Academic Discipline And Sub-Disciplines

Chemical Sciences

SUBJECT CLASSIFICATION

Analytical Chemistry

TYPE (METHOD/APPROACH)

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INTRODUCTION

The detection of transition metal ions in solution and in solid materials is of increased concern, as a result of increased environmental pollution worldwide. Metals play an important role in biological activities of all living organisms in a proper balance [1, 2]. Heavy metals are required for living organisms in very small amounts. Increasing uptake of these metal ions may cause serious health problems and toxicity to humans, animals as well as to plants [3]. Free metal ions cause challenging problems in many industrial processes. Aminopolycarboxylic acid chelating agents (APCAs) are used to interact with metal ions, and restrict them from catalyzing unwanted chemical reactions, or form insoluble metal salt precipitates [4]. Spectroscopic methods of analysis introduce a good choice for detecting metal ions. These methods provide the advantages of simplicity, low cost, time and effort saving, besides the ease with which the data can be manipulated and analyzed.

In a previous study, an optical chemical sensor was developed and stabilized on surface, based on polymer swelling and shrinking, using tris(2-aminoethyl)aminehexaacetic acid attached on PVBC polymer. The response was based on the interaction between the metal cations and the deprotonated carboxylated tris(2-aminoethyl)amine functional group. The complex caused significant changes in the optical properties of the sensing element [5].

In this study, tris(2-aminoethyl)aminehexaacetic acid (TAHA) and its metal complexes were prepared and characterized in solution. TAHA is similar to EDTA and it is expected to have the following properties: high solubility in water, high complex stability with large formation constants, high selectivity, rapid complex formation and intense absorption bands in the infrared region because the carboxylic acid functional groups are strong infrared absorbers [6].

Tris(2-aminoethyl)aminehexaacetic acid is expected to form stable complexes due to high number of chelation sites [7]. Tris(2-aminoethyl)aminehexaacetic acid like other APCAs is important in science and for medical purposes, in both diagnostic and therapeutic applications [8]. TAHA and its metal complexes can be characterized by several techniques, such as potentiometry, NMR [7], FT-IR, spectrophotometry, mass spectrometry, X-ray spectroscopy and elemental analysis.

2. EXPERIMENTAL

2.1 Reagents

Tris(2-aminoethyl)amine, Chloroacetic acid, and $CdCl_2.2H_2O$, were purchased from Sigma-Aldrich. KOH, NaCl, $CuSO_4.5H_2O$, were purchased from Frutarom. $CoSO_4.7H_2O$, $NiSO_4.6H_2O$, $CaCl_2$ anhydride, were purchased from Riedel. All chemicals were of analytical grade. All solutions were prepared with deionized distilled water.

2.2. Instruments

Shimadzu (UV-3101DC) UV-VIS-NIR scanning spectrometer was used for absorption measurements. Quartz cuvettes (1-cm path length) were used. JENWAY (3510) pH Meter was used to measure pH. ATR- Fourier transform infrared spectrophotometer (Necolet Is5 - Id3) was used to obtain IR-Spectra. Heidolph, LABOROTA 4000 - efficient, rotary evaporator was used to remove organic solvents.

2.3. Preparation of TAHA ligand

Potassium chloroacetate was prepared by the addition of dried chloroacetic acid (5.67g, 0.06 mol) to KOH solution (11.2 mL, 0.06 mol). Then tris(2-aminoethyl)amine (1.5 mL, 0.01 mol) was added and the mixture was heated to 90 - 100^{o}C. The pH was adjusted to 10, by the addition of KOH solution and reflux for 10 minutes, and maintained throughout the reaction. This last step was repeated until no consumption of the base was observed [9].

2.4. Acidification of TAHA

The above solution was chilled at 0°C in a freezer for 24 hours. The precipitated potassium chloride was filtered and discarded. The filtrate was acidified to a pH of 3 - 4 with formic acid, cooled in an ice bath while checking the acidity every 15 minutes. Ethanol (equal volume) was added, and the lower aqueous layer was separated and dried under reduced pressure at 70^{o}C [9].

2.5. Determination of stoichiometry and stability constant of Cu(II)–TAHA complex

Various volumes of 0.025 M Cu(II) solution (0, 1, 2, 3, 4, 5, and 6 mL) were pipetted into seven 25.0 mL volumetric flasks. A 10.0 mL aliquot of ammonia buffer solution was added to each flask. Then different volumes of 0.025 M TAHA (6, 5, 4, 3, 2, 1, and 0 mL) were added respectively to the flasks, then diluted to volume with distilled water. The results are tabulated in Table 2.1. The absorbance was measured for each solution at 736 nm the wavelength of Cu(II)–TAHA complex maximum absorption. One of the above solutions was kept for several weeks, and the absorbance was measured at 736 nm the maximum wavelength of the complex at different time intervals.

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Table 2.1: Data for Cu(II)–TAHA complex (continuous variation method)

Solution No.	Cu^{2+} volume (mL) (0.025 M)	TAHA volume (mL) (0.025 M)	X_{Cu2+}	X_{TAHA}	$[TAHA]_{final}$	$[Cu^{2+}]_{final}$
1	0	6	0	1.000	6×10^{-3}M	0
2	1	5	0.166	0.833	5×10^{-3}M	1×10^{-3}M
3	2	4	0.333	0.666	4×10^{-3}M	2×10^{-3}M
4	3	3	0.500	0.500	3×10^{-3}M	3×10^{-3}M
5	4	2	0.666	0.333	2×10^{-3}M	4×10^{-3}M
6	5	1	0.833	0.1666	1×10^{-3}M	5×10^{-3}M
7	6	0	1.000	0	0	6×10^{-3}M

2.6. Spectrophotometric titrations

2.6.1. Titration of a single metal ion

A 10.0 mL aliquot of a 0.010 M of the required metal solution (Cu^{2+}, Ni^{2+}) was placed in an Erlenmeyer flask. Then 20.0 mL of ammonia buffer solution (pH 10) were added. The resulting solution was titrated with 0.010 M TAHA ligand. Absorbance was measured at 736nm the maximum wavelength of the complex formed as a function of titrant volume.

2.6.2. Titration of Cu(II)–M^{n+} mixture

Two 5.0 mL aliquots of 0.020 M copper(II) solution and 0.020 M solution of another metal (Ca^{2+}, Na^{+}, Co^{2+}, Ni^{2+}, Cd^{2+}) were placed in an Erlenmeyer flask. Then 20.0 mL of ammonia buffer solution (pH 10) were added. The resulting solution was titrated with 0.010 M TAHA ligand. Absorbance was measured at 736 nm the maximum wavelength of Cu(II)–TAHA complex as a function of titrant volume.

2.7. Calibration curve

Different volumes of a standard Cu(II) solution and TAHA were pippetted into seven 25.0 mL volumetric flasks and 10.0 mL buffer solution were added to each flask. The volumes were then diluted to the mark with distilled water. The concentrations of Cu(II) solutions and TAHA were prepared (3.00×10^{-4} M- 12.0×10^{-3} M) in 1:1 ratio. Absorbance was measured for these solutions at 736 nm the maximum wavelength of Cu(II)–TAHA complex against ammonia buffer.

3. RESULTS AND DISCUSSION

3.1. Characterization of the Chelating Agent

3.1.1. FT- IR spectrum of TAHA

The chelating agent was characterized by FT-IR spectroscopy. The most characteristic absorption bands confirming the formation of TAHA appeared at about 1705, 1622 and 1196 cm^{-1}. These absorption frequencies correspond to the stretching vibrations of the carbonyl and the C-O bonds Figure 3.1(a).

3.1.2. FT-IR spectrum of Copper(II)–TAHA complex

Changes in the vibrational modes are expected because of complex formation, especially for the carboxyl group bands [10]. The asymmetric stretching frequency of the COO– group in the TAHA at 1622 cm^{-1} shifted to 1587 cm^{-1} and the symmetric carbonyl band at 1705 cm^{-1} disappeared completely when the complex was formed, Figure 3.1(b).

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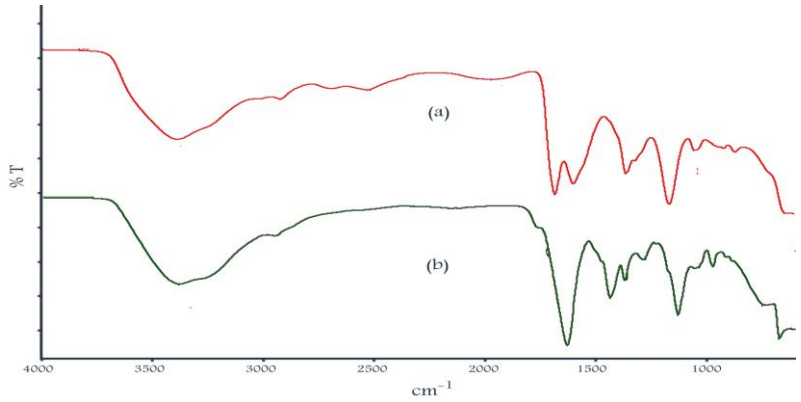

Figure 3.1: IR Spectra of (a) TAHA and (b) TAHA-Cu^{2+} complex

3.2. Absorption spectra

3.2.1. Absorption spectra of $[M(NH_3)_4]^{2+}$ complexes

The wavelengths of maximum absorption were determined to be 641.5 nm and 309 nm for $[Cu(NH_3)_4]^{2+}$ and $[Co(NH_3)_4]^{2+}$ complexes, respectively. The $[Ni(NH_3)_4]^{2+}$ complex had two maxima at 360 nm and 557 nm. As seen in Figure 3.2. $[Ca(NH_3)_4]^{2+}$ and $[Cd(NH_3)_4]^{2+}$ did not absorb within the studied range.

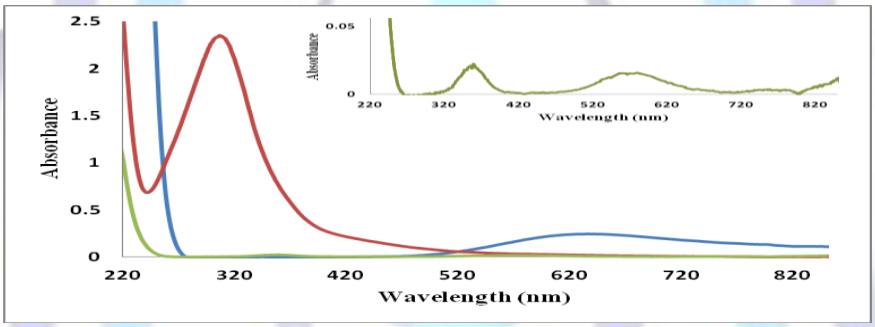

Figure 3.2: Absorption spectra of $[M(NH_3)_4]^{2+}$ complexes at pH 10; A) – Ni^{2+} (10 mL, 0.01 M). B) – Co^{2+} (10 mL, 0.01 M). C) – Cu^{2+} (10 mL, 0.01 M).

3.2.2. Absorption spectra of M(II)-TAHA complexes

The maximum wavelength of Cu(II)-TAHA complex was found to be 736 nm. A small shift in wavelength was observed upon the formation of Co(II)-TAHA complex with strong overlap with the $[Co(NH_3)_4]^{2+}$ maxima. Ni(II)-TAHA complex has almost the same color as $[Ni(NH_3)_4]^{2+}$ complex. Hence, no shift in wavelength was observed as Ni(II)-TAHA complex was being formed. Absorbance was measured at 557 nm during the titration, as seen in Figure 3.3. Ca(II)-TAHA and Cd(II)-TAHA did not absorb within the studied range.

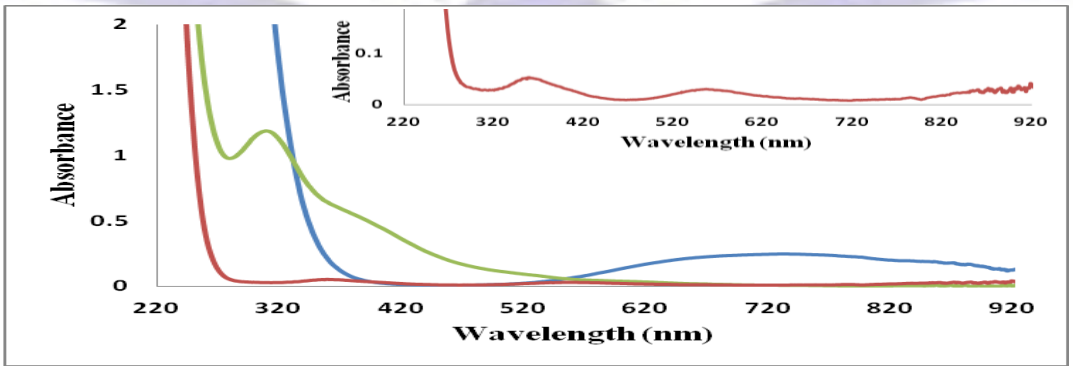

Figure 3.3: Absorption spectra of M(II)-TAHA complexes at pH 10; A) – Ni^{2+} (10 mL, 0.01 M). B) – Co^{2+} (10 mL, 0.01 M). C) – Cu^{2+} (10 mL, 0.01 M).

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3.3. Spectrophotometric titrations

3.3.1. Titration of a single metal ion

Two metal ions (Cu^{2+}, Ni^{2+}) were titrated with TAHA ligand in the presence of ammonia buffer, absorbance was measured at the maximum wavelength of M(II)–TAHA complex.

For each metal ion, correction of absorbance was performed by two ways; in the first method, the measured absorbance was multiplied by the dilution factor (Equation 3.1):

$$\text{Dilution factor} = \frac{(V_{initial} + V_{titrant})}{V_{initial}} \qquad (3.1)$$

Where; $V_{initial}$: initial volume of solution, and $V_{titrant}$: volume of added titrant.

A modified correction method was used in this work to follow the absorption of M(II)-TAHA complex only (Equation 3.2).

$$A'_{corrected} = A'_{measured} - \frac{(\text{Volume metal (mL)} - \text{Volume TAHA (mL)})}{\text{Volume metal (mL)}} \times A_1 \qquad (3.2)$$

Where; $A'_{measured}$ is the measured absorbance corrected for dilution, A_1 is the absorbance of solution containing the other absorbing substance, $A'_{corrected}$ is the corrected absorbance according to a modified correction method.

This new method combines the absorbance dilution correction (Equation 3.1) with a second correction method (Equation 3.3), that was used previously for mole ratio and continuous variation methods to follow only one absorbing species [11].

$$A_{corrected} = A_{measured} - \frac{(\text{Volume metal (mL)} - \text{Volume TAHA (mL)})}{\text{Volume metal (mL)}} \times A_1 \qquad (3.3)$$

Where A_1 is the absorbance of solution containing the other absorbing substance.

Herein, modification of the correction method was made according to the behavior of metal(II)-TAHA and other metal-buffer complexes present in the titration mixture. This correction was used for the titration of a single metal as well as for metal mixtures with TAHA ligand at pH 10. When excess amount of ligand is added, no correction is needed; because there is no excess M(II) to complex ammonia [11].

In the titration of copper(II) ions, Cu(II) forms $[Cu(NH_3)_4]^{2+}$ complex with ammonia (dark blue) at a maximum wavelength of 641.5 nm. Absorption increases with addition of titrant, where $[Cu(NH_3)_4]^{2+}$ complex decomposes in favor of the formation of Cu(II)-TAHA complex. A maximum absorption value was reached at the equivalence point. After that, absorption remained constant as seen in Figure 3.4.

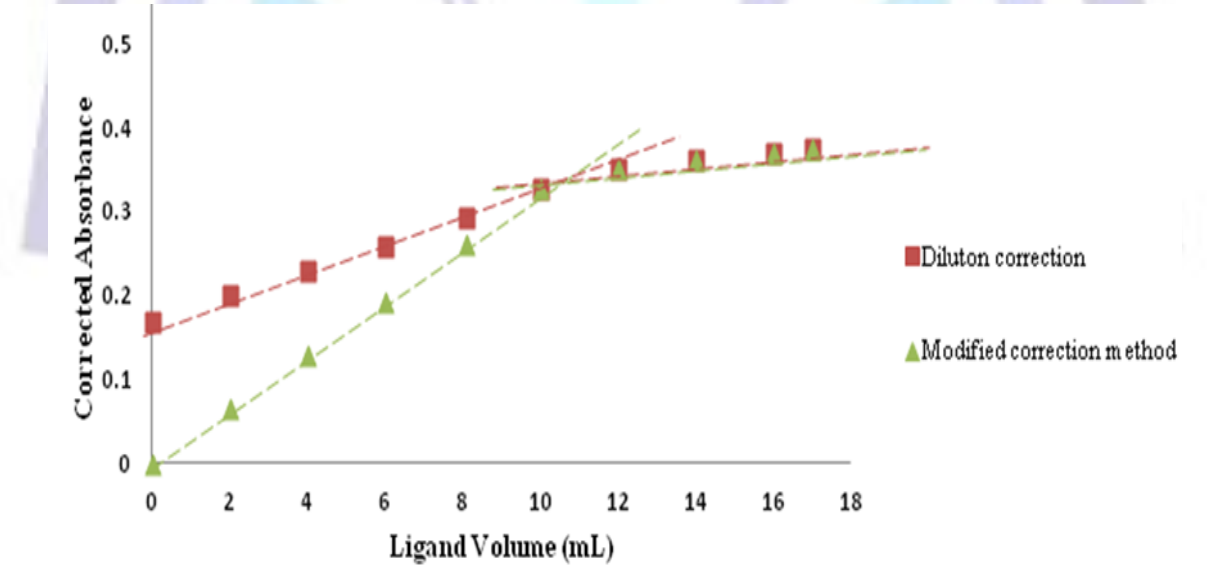

Figure 3.4: Spectrophotometric titration curve for the titration of 10 mL of 0.01 M Cu^{2+} with 0.01 M TAHA. (pH = 10, λ = 736 nm).

A titration curve was constructed for the titration of nickel(II). Ni(II)–TAHA complex has two absorption maxima; 360 nm and 557 nm. Absorbance was measured at the later wavelength, Figure 3.5.

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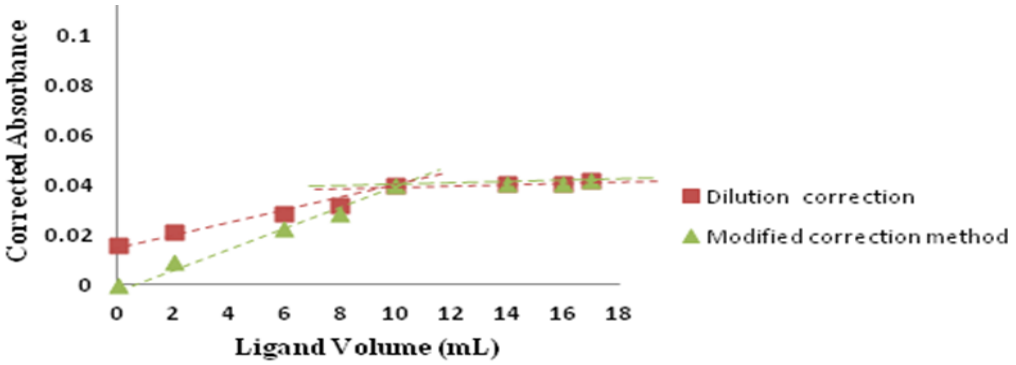

Figure 3.5: Spectrophotometric titration curve for the titration of 10 mL of 0.01M Ni^{2+} with a 0.01M TAHA. (pH = 10, λ = 557 nm).

3.3.2. Titration of Cu(II)–M^{n+} mixtures (M^{n+}; Ca^{2+}, Na^{+}, Co^{2+}, Ni^{2+}, or Cd^{2+})

Titration was carried out for several Cu(II)–M^{n+} mixtures, where M^{n+} represents; Ca^{2+}, Na^{+}, Co^{2+}, Ni^{2+}, or Cd^{2+}.

3.3.2.1. Cu^{2+}– Ca^{2+} mixture

Ammonia acts as a secondary ligand, $[Cu(NH_3)_4]^{2+}$ complex being more stable than $[Ca(NH_3)_4]^{2+}$. As TAHA is a stronger ligand than ammonia, it will complex Ca^{2+} at first by replacing ammonia. When Ca^{2+} had completely finished, TAHA will start the complexation of Cu^{2+}. As seen in the titration curve, Figure 3.7 two equivalence points were produced. The first for Ca(II) (10 mL), and the second for Cu(II) (20 mL). Beyond the second equivalence point, there was no further increase in absorbance because TAHA does not absorb at this wavelength.

The modified correction method was applied to avoid overlap of absorbance that occurs during the formation of Ca(II)–TAHA complex, and the formation of Cu(II)–TAHA complex at 736 nm. Firstly, $[Ca(NH_3)_4]^{2+}$ (colorless) decomposed to form Ca(II)–TAHA complex (colorless) as ligand is added. Since the original solution has a blue color due to $[Cu(NH_3)_4]^{2+}$, this causes an overlap in absorbance reading. So for the first 10 mL of ligand, absorbance was corrected according to Equation (3.2) as follows:

$$A'_{corrected} = A'_{measured} - \frac{(10\ mL\ Cu^{2+} - 0\ mL\ ligand)}{10\ mL\ Cu^{2+}} \times A_1$$

A_1: absorbance for Cu^{2+} solution in ammonia buffer.

Secondly, as $[Cu(NH_3)_4]^{2+}$ decomposes to form Cu(II)–TAHA complex, the two complexes absorbs strongly at 736 nm. Thus, the modified correction method was used to follow the absorption of Cu(II)–TAHA complex only. Absorbance was corrected according to Equation (3.2) as follows:

$$A'_{corrected} = A'_{measured} - \frac{(10\ mL\ Cu^{2+} - (1\ to\ 10)\ mL\ ligand)}{10\ mL\ Cu^{2+}} \times A_1$$

A_1: absorbance for Cu^{2+} solution in ammonia buffer.

When excess amount of ligand is added, no further correction is needed. The titration curve for the same mixture using the modified correction method gives more clear results with sharper end points as shown in Figure 3.6.

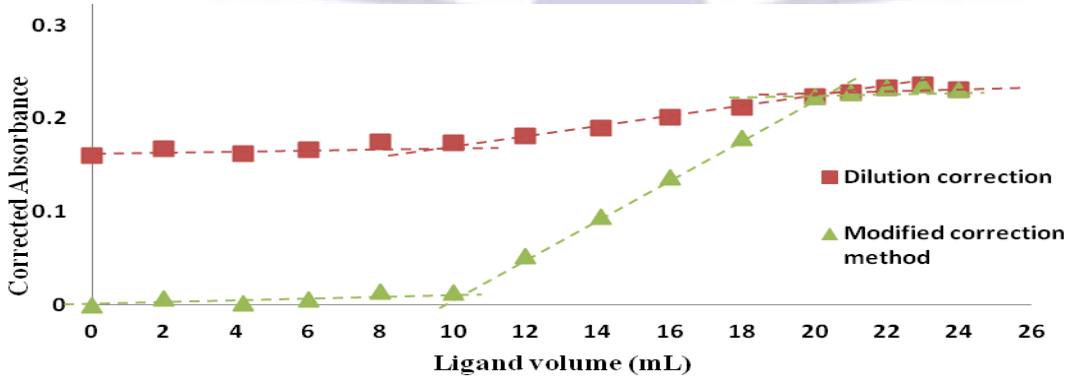

Figure 3.6: Spectrophotometric titration curve for the titration of Cu^{2+}- Ca^{2+} mixture (10 mL of 0.01 M each) with a 0.01 M TAHA. (pH = 10, λ = 736 nm).

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3.3.2.2. Cu^{2+} and Na^{+} mixture

Alkali metal ions do not form complexes at all [12], they are poor complexing agents because they are weak oxidizing agents [13]. Thus, TAHA will form only one stable complex with Cu^{2+}.

In the titration curve for Cu^{2+} and Na^{+} mixture, two straight lines were obtained with one equivalence point. The modified correction method (Equation 3.2) was applied for the two complexes; $[Cu(NH_3)_4]^{2+}$ and Cu(II)–TAHA , because both absorb at 736 nm, Figure 3.7.

3.3.2.3. Cu(II)–M^{n+} mixtures, where M^{n+} represents; Co^{2+}, Ni^{2+}, or Cd^{2+}

Ammonia acts as a secondary ligand, however, $[Cu(NH_3)_4]^{2+}$ is more stable than $[Co(NH_3)_4]^{2+}$, $[Ni(NH_3)_4]^{2+}$ and $[Cd(NH_3)_4]^{2+}$. So TAHA reacts initially with Co^{2+}, Ni^{2+}, Cd^{2+}, by replacing ammonia. When Co^{2+}, Ni^{2+}, Cd^{2+} had completely finished, TAHA starts to react with Cu^{2+}. The titration curves for the titration of the mixtures using the first and the modified correction methods are shown in Figures 3.8, 3.19 and 3.10 respectively.

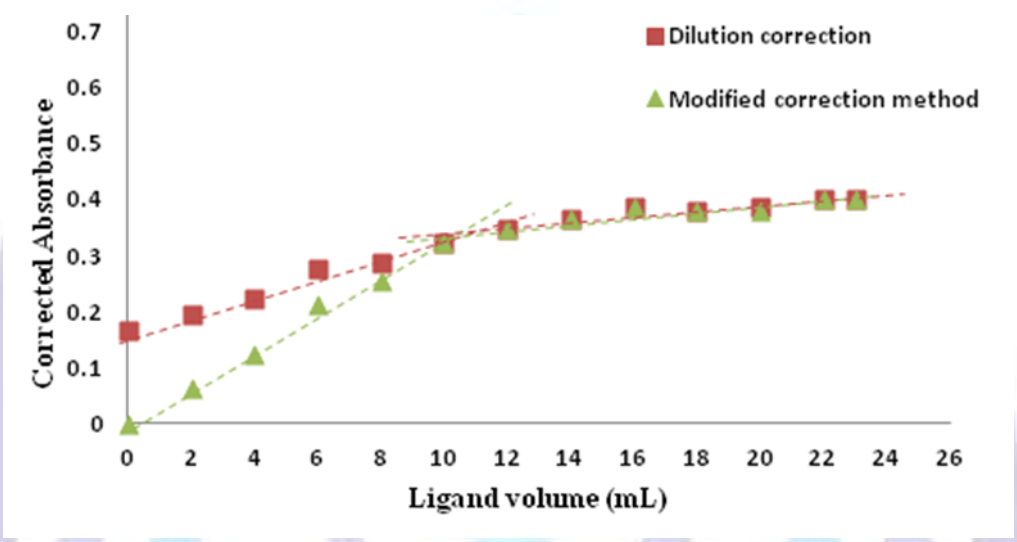

Figure 3.7: Spectrophotometric titration curve for the titration of Cu^{2+} - Na^{+} mixture (10 mL of 0.01 M each) with a 0.01 M TAHA. (pH = 10, λ = 736 nm).

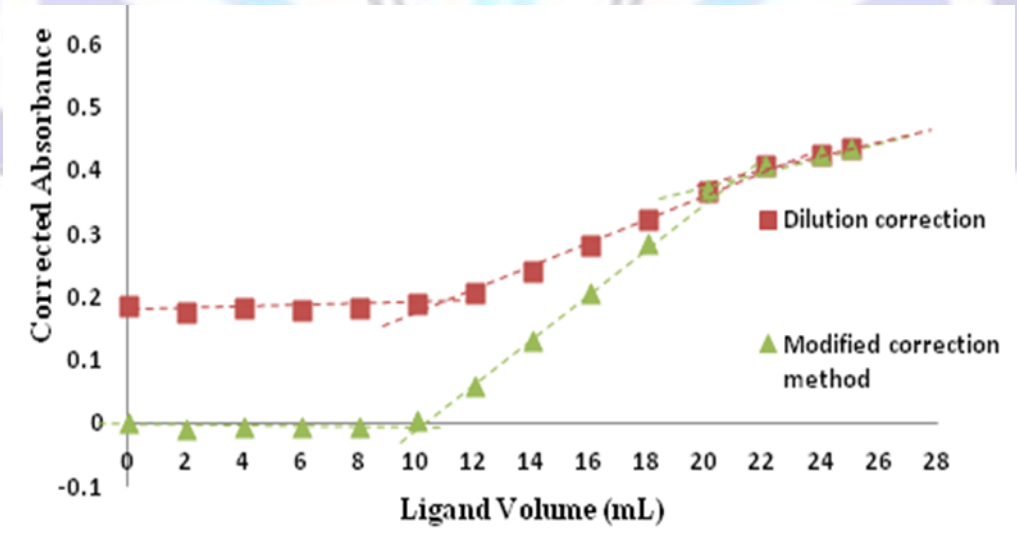

Figure 3.8: Spectrophotometric titration curve for the titration of Cu^{2+}- Co^{2+} mixture (10 mL of 0.01 M each) with a 0.01 M TAHA. (pH = 10, λ = 736 nm).

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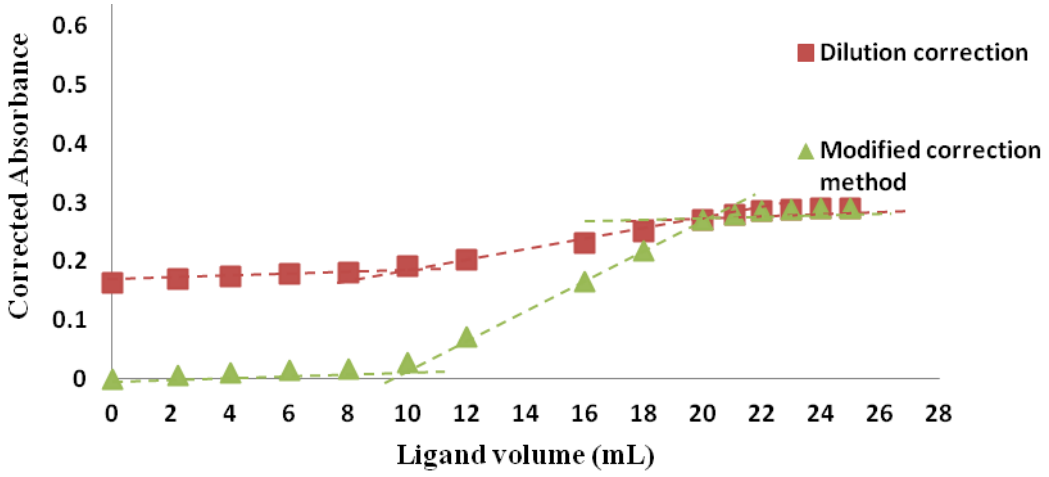

Figure 3.9: Spectrophotometric titration curve for the titration of Cu^{2+}- Ni^{2+} mixture (10 mL of 0.01 M each) with a 0.01 M TAHA. (pH = 10, λ = 736 nm).

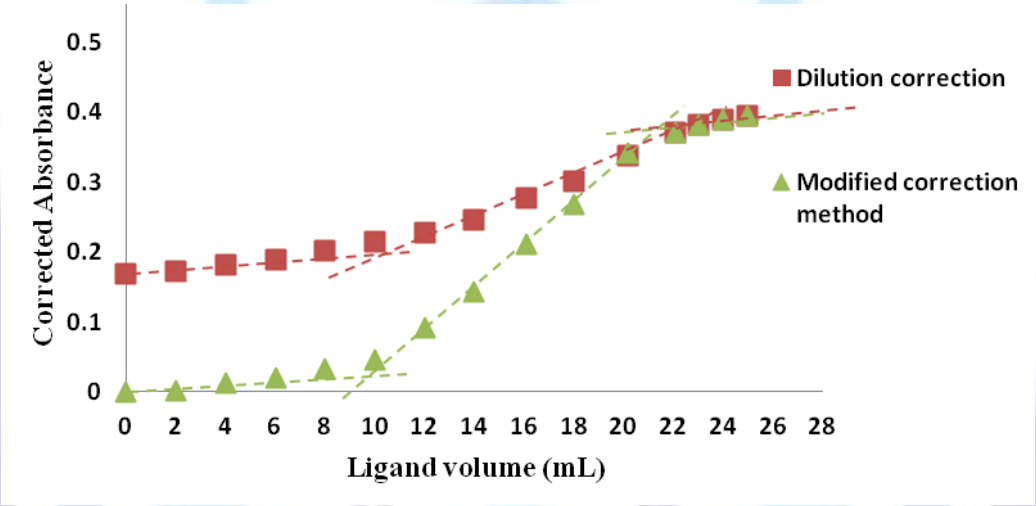

Figure 3.10: Spectrophotometric titration curve for the titration of Cu^{2+}- Cd^{2+} mixture (10 mL of 0.01 M each) with a 0.01 M TAHA. (pH = 10, λ = 736 nm).

3.4. The formula and stability of Cu(II)–TAHA complex

The continuous variation method was used for the determination of the formula and the stability constant of Cu(II)–TAHA complex. A series of solutions were prepared, with constant total moles of metal and ligand. The results are tabulated in Table 2.1. The absorbance was measured for each solution at 736 nm the wavelength of Cu(II)–TAHA complex maximum absorption.

The measured absorbances must be corrected to give the absorbances due to the Cu(II)–TAHA complex alone. This correction should be made for solutions 5, 6, and 7 by using Equation (3.4)

$$A_{corrected} = A_{measured} - \frac{(\text{Volume metal (mL)} - \text{Volume TAHA (mL)})}{\text{Volume metal (mL)} + \text{Volume TAHA (mL)}} \times A_1 \qquad (3.4)$$

where $A_{measared}$ is the absorbance measured, A_1 is the absorbance of solution #7 where only Cu^{2+} and buffer are present in the flask. $A_{corrected}$ is the corrected absorbance. No correction needs to be made for solutions in which sufficient TAHA has been added to complex all the Cu^{2+} [11].

Corrected absorbance was plotted versus the mole fraction of Cu^{2+} to find the complex formula and the formation constant. By extrapolating the two lines, they intersect at a point opposite to mole fraction of Cu^{2+}, that can be used to find the formula using Equation (3.5) [14]:

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$$Y = \frac{X_{Cu2+}}{(1 - X_{Cu2+})} \qquad (3.5)$$

The formation constant can be determined from Equation (3.6) [1]:

$$K_{formation} = \frac{[A_b / A_a]}{[1 - A_b/A_a] \times [C_{ligand} - C_{metal} \times A_b/A_a]} \qquad (3.6)$$

Where A_a = absorbance at break point, A_b = actual absorbance, C_{metal} = concentration of metal, and C_{ligand} = concentration of ligand.

$[Cu(NH_3)_4]^{2+}$ complex absorption peak overlaps with Cu(II)–TAHA complex absorption peak. However, the absorbance correction method solves this problem. The absorbance was measured for each solution at 736 nm. The corrected absorbance was plotted versus the mole fraction of Cu^{2+} as shown in Figure 3.11.

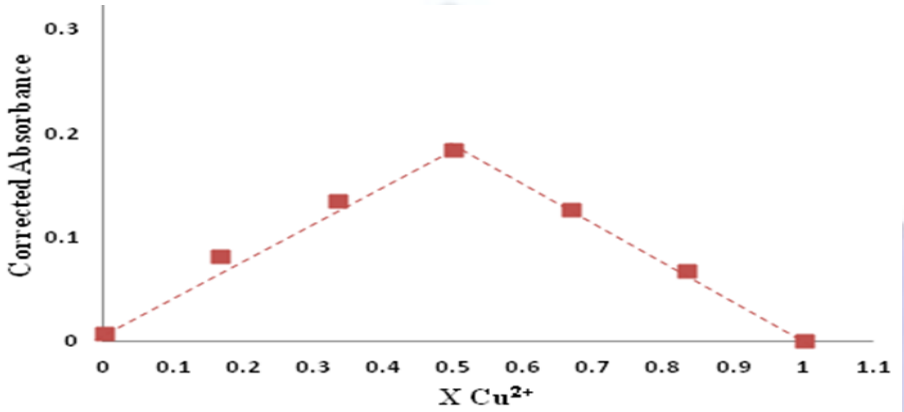

Figure 3.11: Curve for the continuous variation method, for Cu(II)–TAHA Complex at pH 10, λ = 736nm.

The two lines intersect at a point that correspond to a mole fraction of Cu^{2+} = 0.5. Thus, the stoichiometry of Cu(II)–TAHA complex is 1:1. Substituting the following values in Equation (3.6): A_a= 0.193, A_b= 0.185, C_{metal}= 3×10^{-3}M, and C_{ligand} = 3×10^{-3}M, K_f was calculated to be 1.86×10^5.

3.5. Effect of time on complex stability

The Cu(II)–TAHA complex was stable for an extended period of time, with no significant change, Figure 3.12.

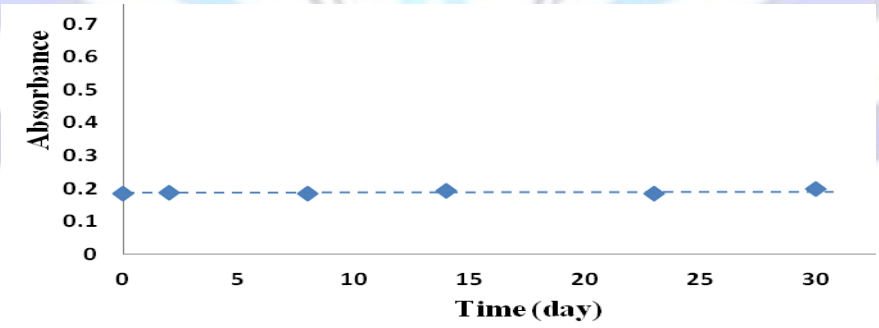

Figure 3.12: Effect of time on Cu(II)–TAHA complex stability, $[Cu^{2+}]$= [TAHA]= 3×10^{-3} M, at pH 10, λ = 736nm.

3.6. The Calibration Curve

A linear relationship was obtained over the studied concentration range. The molar absorptivity, ε was found to be 95.538 $L.mol^{-1}.cm^{-1}$. Beer's law was obeyed over the concentration range 3.0×10^{-4} M – 1.2×10^{-2} M for Cu(II) solution, Figure 3.13.

Conclusion:

In this work, tris(2-aminoethyl)aminehexaacetic acid (TAHA) chelating agent was prepared and characterized. TAHA formed stable complexes with copper(II) and other metal ions. The complexation behavior was studied by

spectrophotometry at the maximum wavelength of metal–TAHA complex. A modified correction method was applied to solve a problem that arose from the fact that more than one complex are formed in the reaction mixture, and absorb at the studied wavelength with a strong overlap. The stoichiometry was found to be (1:1) ligand to Cu(II) mole ratio, by using the continuous variation method. The stability constant of the Cu(II) – TAHA complex (K_f) was determined to be 1.86×10^5. TAHA ligand and its Cu(II) – complex were found to be stable for an extended period of time.

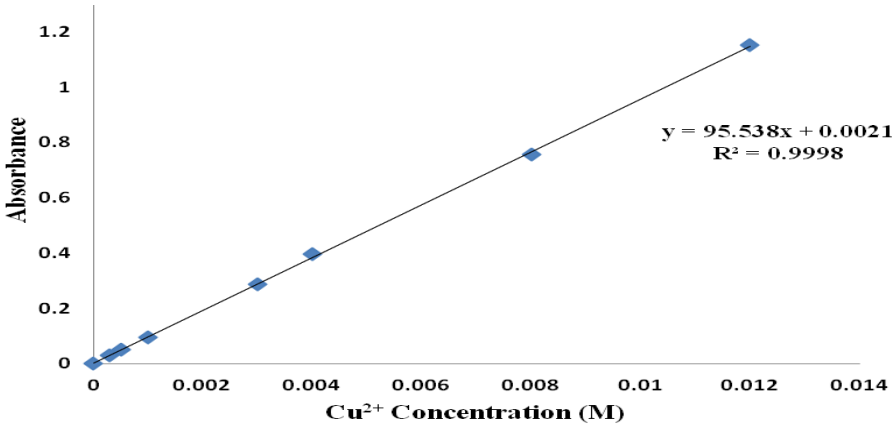

Figure 3.13: Calibration curve for Cu(II) at pH 10, λ = 736 nm.

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