



ISSN No: 0975-7384
CODEN(USA): JCPRC5

J. Chem. Pharm. Res., 2011, 3(6):1022-1027

Spectrophotometric study on stability constants of copper(II) complex with 1-amidino-O-methylurea

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ABSTRACT

The stoichiometries and stability constants of copper(II) ions with 1-amidino-O-methylurea have been determined in aqueous solution at different temperatures 20^oC, 25^oC, 30^oC, 35^oC and 40^oC with constant ionic strength of 0.5 M KNO₃ by using Job's continuous variation method spectrophotometrically. In all cases, the Job's curves displayed a maximum at a mole fraction $X_{metal}=0.5$ indicating the formation of complex with 1:1 metal to ligand ratio. It was observed that metal-ligand stability constant decreases with increasing temperature indicating exothermic nature of the reaction. Plots of thermodynamic stability constants versus 1/T gave linear curves indicating high temperature sensitivity for the -NH group of the ligand. The thermodynamic parameters i.e., ΔG^0 , ΔH^0 and ΔS^0 have also been calculated.

Keywords: Stability constant, spectrophotometrically, 1-amidino-O-methylurea, thermodynamic parameters, copper(II).

INTRODUCTION

Copper is one of the several metal ions that play an important role in biological system. It has a vital role during cell respiration, in the blood of invertebrate animals and in the formation of haemocyanin [1]. Apart from the biological utility of the copper, it also finds applications in industries as fine wires, commutator bars and high conductivity tubes [2].

Metal ions play an important role in all living systems and any malfunctioning of these ions can initiate a number of physiological abnormalities and symptoms of clinical disorders (Wattoo, 2001). Transition metal ions are responsible for proper functioning of different enzymes. Researchers have become increasingly interested in the coordination chemistry of copper complexes as models for the active sites in copper-containing enzymes. This is largely due to the discovery of copper at the centers of many important enzymes [3].

Copper is essential for life but is highly toxic above certain limits to organisms like certain algae, fungi and many bacteria or viruses [4,5]. In addition, the accumulation of copper in the human liver is a characteristic of Wilson's disease which produces neurological and psychiatric defects [6].

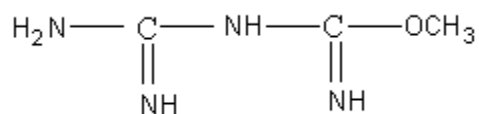
Stable complexes of trivalent and bivalent transition metal ions are found to form with 1-amidino-O-methylurea [7-10]. The ligand 1-amidino-O-methylurea (AMUH) serves as a bidentate ligand satisfying both the primary and secondary valencies with the formation of inner metallic complexes. In view of the significant importance of biguanide, AMUH, we report here, the stability constants of copper(II) complex with AMUH in the ionic strength of 0.5 M KNO₃ at varying temperatures of 20^oC, 25^oC, 30^oC, 35^oC and 40^oC respectively by using Job's method (continuous variation method) spectrophotometrically along with their thermodynamic parameters.

EXPERIMENTAL SECTION

Synthesis of ligand

The ligand 1-amidino-O-methylurea was prepared by published method [11]. The compound was characterized through elemental analysis (Found: C, 23.81; H, 5.98; N, 36.86; Cl, 23.61; calculated for C₃H₈N₄O.HCl: C, 23.61; H, 5.9; N, 36.72; Cl, 23.27); melting point at 160^oC; literature 157^o-158^oC.

Structure of ligand



1-amidino-O-methylurea (AMUH)

Double distilled water was used in the preparation of desired concentrations of ligand solutions. The metal ion solution of desired concentration was prepared from the standardized stock solution of CuSO₄.5H₂O. NaOH, HNO₃ and KNO₃ solutions were prepared in CO₂ free double distilled water [12]. By using the usual methods, NaOH and HNO₃ solutions were standardized. All the pH measurements were performed on a Digital systronic μ pH system 362. In all the cases, the pH-meter was calibrated at two pH values i.e., 4.0 and 9.2 \pm 0.05 using (BDH) buffer tablets. All the measurements were carried out at different temperatures by using a thermostat, Haake (Model DC 10) enclosed with the spectrophotometer Shimadzu UV-2450 along with 1 cm quartz cells with an accuracy of \pm 0.1^o C and at the ionic strength of 0.5 M KNO₃. Copper(II) sulphate standard solution of 1.25 \times 10⁻¹ M was pipetted into eleven 25 ml volumetric flasks (0, 1, 2, 3, ..., 9, 10 ml) and an aliquot of 1.25 \times 10⁻¹ M AMUH (10, 9, 8, 7, ..., 1, 0 ml) was added keeping both the number of moles of metal and ligand constant but varying either mole fractions of metal or ligand. Ionic strengths were maintained by adding appropriate quantity of 1.25 M KNO₃. λ_{max} was determined using one of the composition at which there is maximum absorption. The absorption for all the compositions was recorded at a constant wavelength (λ_{max}) [13]. The data of absorption and percentage composition of metal ion and ligand solution at constant pH can be used and curves were constructed. With the help of variable volume Accupipet, Model T200 (20 μ L to 200 μ L), pH values were adjusted with 0.0048 M HNO₃ and 0.0655 M NaOH solutions ranging from 0.02 ml to 0.25 ml. The above reaction mixtures were separately measured with their absorbance values.

RESULTS AND DISCUSSION

The spectral curves of the reaction mixtures of copper(II) with 1-amidino-O-methylurea in the ionic strength of 0.5 M KNO₃ at five different temperatures are shown (Fig.1). The measurements were carried out at 261 nm and pH = 4.6 (Table 1). On plotting measured absorbance against mole fractions of the two constituents of the complex gives a characteristic triangular plot indicating formation of a more stable complex [14]. The composition of the complex was calculated from the point of intersection of the tangents to the curve [15] and was found to be 1:1, metal to ligand ratio at the mole fraction $X_{\text{metal}}=0.5$ (Fig.1). Reaction of copper(II) with 1-amidino-O-methylurea at five different temperatures in the ionic strength of 0.5 M KNO₃ at 261 nm are shown in Table 1. It was observed that the stoichiometric ratio of copper(II) to 1-amidino-O-methylurea in the complex is 1:1.

Table 1: Experimental Data of Copper(II)-1-amidino-O-methylurea by Continuous Variation Method

Sl. No.	Metal Conc. ($\times 10^{-4}$ M)	Ligand Conc. ($\times 10^{-4}$ M)	X_{Cu}	Absorbance at 261 nm				
				20 ⁰ C	25 ⁰ C	30 ⁰ C	35 ⁰ C	40 ⁰ C
1	0	50	0.0	0.755	0.775	0.774	0.790	0.783
2	5	45	0.1	0.784	0.799	0.794	0.804	0.801
3	10	40	0.2	0.807	0.817	0.819	0.824	0.8163
4	15	35	0.3	0.828	0.841	0.838	0.841	0.837
5	20	30	0.4	0.859	0.861	0.862	0.861	0.8546
6	25	25	0.5	0.883	0.881	0.879	0.876	0.869
7	30	20	0.6	0.855	0.852	0.856	0.854	0.8487
8	35	15	0.7	0.826	0.824	0.827	0.831	0.8259
9	40	10	0.8	0.790	0.787	0.803	0.807	0.801
10	45	5	0.9	0.759	0.765	0.772	0.777	0.781
11	50	0	1.0	0.728	0.732	0.746	0.759	0.757

The stability constants of the complexes were calculated from the following relation [16].

$$K_f = \frac{[ML]}{[M][L]} \dots\dots\dots 1$$

$$K_f = \frac{[A_2/A_1]}{[1 - A_2/A_1] \times [C_L - C_M \times A_2/A_1]} \dots\dots\dots 2$$

Here, A_1 = absorbance at break point, A_2 = actual absorbance, C_M = concentration of metal and C_L = concentration of ligand.

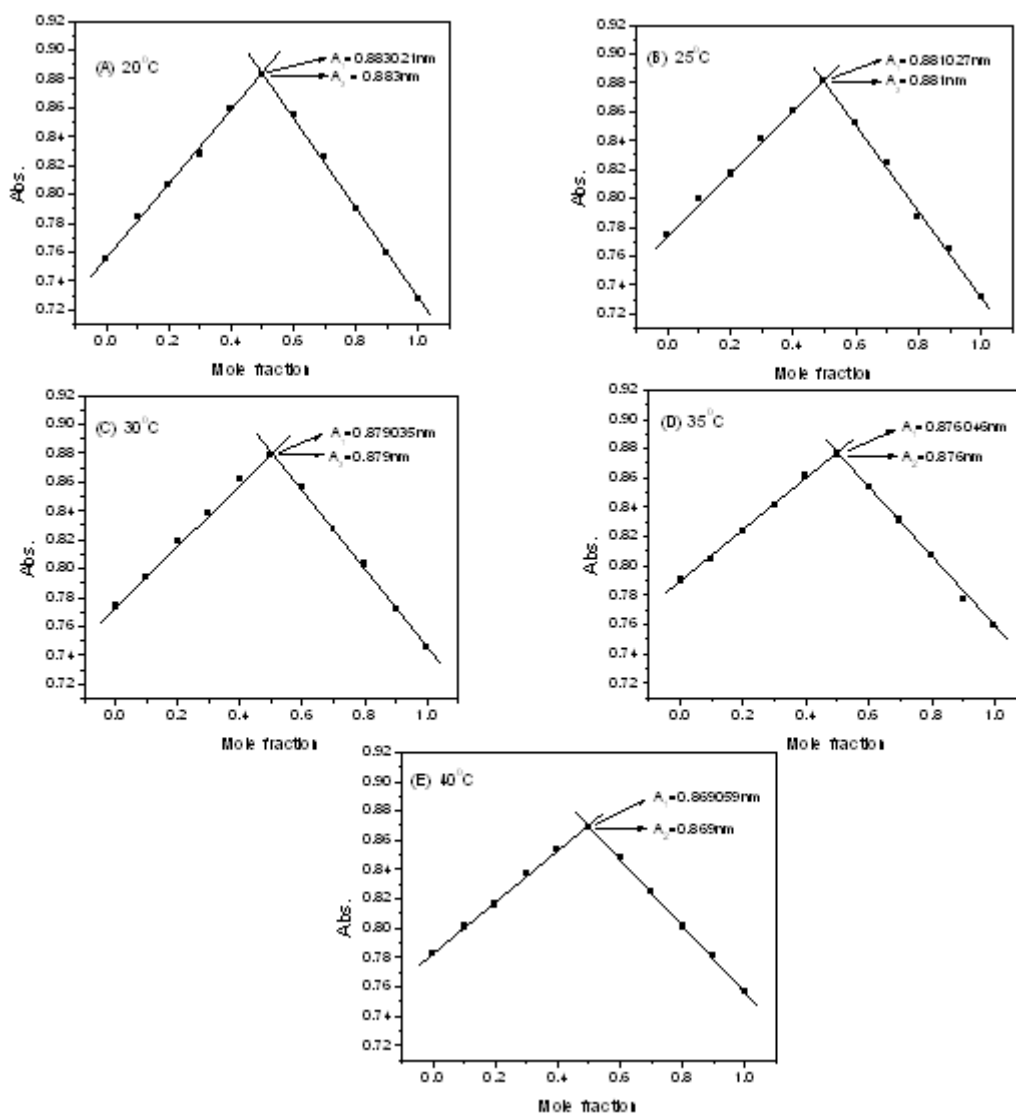
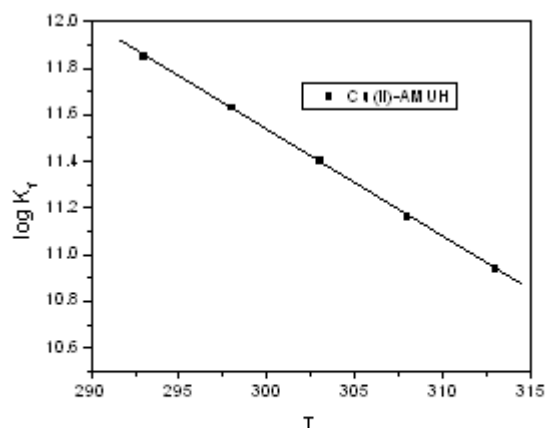
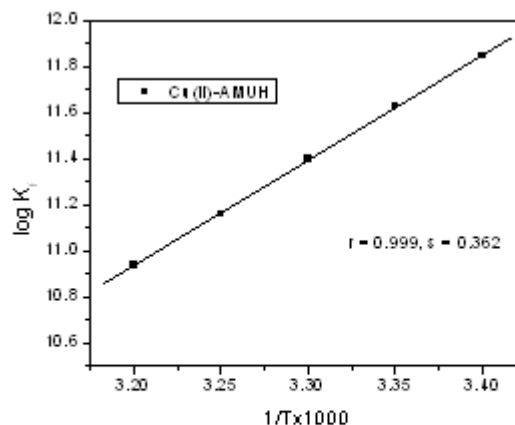


Fig.1. Job's curves of equimolar solutions of Copper(II)-1-amidino-O-methylurea at (A) 20°C; (B) 25°C; (C) 30°C; (D) 35°C and (E) 40°C at 261 nm and pH = 4.6.

In all Figures, the mole fraction of the metal ion is represented by abscissa. Very close values of A_1 and A_2 in Fig.1 is due to the formation of more stable copper(II) complex with AMUH [14]. Table 2 shows $\log k_f$ values of copper(II) with 1-amidino-O-methylurea at pH 4.6 with different temperatures along with their thermodynamic parameters. Exothermic nature of the reactions [Fig.2, 3] was also observed from the value of stability constant at different temperatures as the value of stability constant decreases with the rise in temperature.

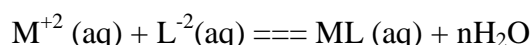
Table 2: Stability constant and Thermodynamic parameters

Sl. No.	Metal ion	Ligand	pH	Temp. (K)	$\log k_f$	ΔG^0 (kJmol ⁻¹)	ΔH^0 (kJmol ⁻¹)	ΔS^0 (kJK ⁻¹ mol ⁻¹)
1	Cu(II)	1-amidino-O-methylurea	4.6	293	11.849	-66.353	-19.214	0.158
				298	11.629			
				303	11.401			
				308	11.161			
				313	10.938			

Fig.2. Variation of $\log k_f$ with T(K)Fig.3. Variation of $\log k_f$ with $1/T(K^{-1})$

$r =$ correlation coefficient,
 $s =$ standard variation

The values of overall change in free energy (ΔG^0), enthalpy (ΔH^0) and entropy (ΔS^0) accompanying complexation reaction have been determined using temperature coefficient and Gibbs-Helmholtz equation. Fig.3 represents the plot of $\log k_f$ vs $1/T$ for Cu(II)-AMUH complex. From the curve the values of ΔG^0 , ΔH^0 and ΔS^0 are evaluated and are given in Table 2. The negative values of ΔG^0 reflect spontaneity of the reaction [17]. The change in enthalpy (ΔH^0) being negative, the reaction occurred is exothermic and formation of complex is favourable. Negative value of enthalpy change also suggests that the metal-ligand bonds are fairly strong [18]. Since the value of ΔS^0 is positive the reaction will tend to proceed spontaneously [19]. Positive entropy changes accompanying a given reaction are due to the release of bound water molecules from the metal chelates [18]. During formation of metal chelates, water molecules from the primary hydration sphere of the metal ion are displaced by the chelating ligand. Thus there is an increase in the number of particles in the system i.e., randomness of the system increases as shown in the following equation.



Williams [20] has pointed out that usually a high entropy value was associated when positively charged cations and negatively charged ligands combined involving the displacement of water molecules, which then become a part of the solvent. Since the water molecules bound to the metal ions are highly distorted and oriented, the entropy is low.

The value of correlation coefficient (r) shows almost perfect positive correlation between $\log k_f$ and $1/T$ which indicates a reproducible one. Standard deviation value of 0.131 and relative standard deviation value of 1.421% for Cu(II)-AMUH complex show within the reproducible limit [21]. The plot of $\log k_f$ vs. $1/T$ yields distinct straight lines (Fig.3) which reflects the high temperature sensitivity for the -NH group of the ligand [22].

CONCLUSION

The value of $\log k_f$ for Cu(II)-AMUH complex at $(25 \pm 0.1)^0C$ in the ionic strength of 0.5 M KNO_3 was found to be 11.629 spectrophotometrically. Exothermic nature of the reactions was

observed from the value of stability constant. The composition of the complex was 1:1 metal to ligand ratio.

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