



A thermodynamic Study of complex formation between Cu(II) ion and 4-Amino-3-methyl-1,2,4- triazol-5-thione(AMTT) in binary ethanol / water mixture using conductometric method

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Abstract

The stability constant , K_f , for the complexation of copper (II) ion with 4 -Amino - 3-methyl - 1 , 2 , 4 - triazol - 5 -thione (AMTT) in 0 , 20 , 40 , 60 and 80 (V / V) % ethanol-water mixtures were determined conductometrically at different temperatures . Stability constant of resulting 1:1 complexes were being larger by increasing of temperature and ethanol percent. Stability constants of complexes vary inversely with dielectric constant of solvents .The enthalpy and entropy of complexation were determined from the temperature dependence of the formation constant . In all cases , the complexation were found to be enthalpy unstabilized but entropy stabilized . ΔG° of the studied complexes were evaluated at 25°C using thermodynamic relations , the negative values of ΔG° means that the complexation process is spontaneously .

Keywords: AMTT , Cu(II), Binary mixture, Complex formation, conductometric

Introduction

Copper (II) ion is a biologically active , essential ion and chelating ability and positive redox potential allow participation in biological transport reactions . Cu(II) complexes possess a wide range of biological activity and are among the most potent antiviral , antitumor and anti-inflammatory agents [1] .

On the other hand , Condensed triazoles exhibit a range of pharmacological activities such as : mitotic, hypotensive, CNS stimulant , anti inflammatory and analgesic activities [2-3]. The therapeutic effects of 1,2,4-triazole and 1,2,4- triazol –3-one containing compounds have been well studies for a number of pathological conditions including inflammation , cancer , pain , tuberculosis or hypertension [4-12] .

Triazoles fused another heterocyclic ring has attracted wide spread attention due to their application as antibacterial , antidepressant , antiviral , antitumoral and anti-inflammatory agents , pesticides , herbicides dyes , lubricant and analytical agents [13] .

The present study deals with the conductometric determination of the stability constants, stoichiometric ratio and related to thermodynamic parameters of AMTT complexes with Cu(II).

A large number of physicochemical techniques such as potentiometry, calorimetry, conductometry, NMR spectrometry, spectrophotometry and polarography have been used for study of complexation reactions between crown ethers with different metal cations in solutions [14].

In this paper, we report the results of a conductance study of the thermodynamics of Cu(II) ion complexation with AMTT in ethanol water binary mixture.

Results and Discussion

In order to evaluate the influence of adding (L) in the molar conductance of the metal ion used in different (V/V) % ethanol-water mixtures, the conductivity at a constant salt solution ($5 \times 10^{-4} \text{ mol L}^{-1}$) was monitored while increasing the L concentration ($5 \times 10^{-3} \text{ mol L}^{-1}$) at different temperatures. The molar conductance were plotted against [L] / [M] mole ratio for reaction of Cu(II) with ligand of AMTT at different temperatures. The plots exhibited one obvious slopes, suggesting that the probable stoichiometric ratio of complexes are M : L. Incidentally, as is expected, the corresponding molar conductance increased with increasing the temperature, owing to decrease viscosity of the solvent and consequently, the enhance mobility of the charged species present in the solution. The 1:1 complexes of transition and heavy metal ions (M^+) with (L), can be expressed by the following equilibrium [15]:



The corresponding equilibrium constant, K_f , is given by

$$K_f = \frac{[ML^+]}{[M^+][L]} \times \frac{f_{(ML^+)}}{f_{(M^+)}f_{(L)}} \quad (2)$$

where $[ML^+]$, $[M^+]$, $[L]$ and f represent the equilibrium molar concentration of complexes, free cation, free ligand and the activity coefficient of the species indicated, respectively. Under the dilute condition we used, the activity coefficient of the uncharged ligand, $f_{(L)}$, can be reasonably assumed as unity [15-16]. The use of Debye-Huckel Limiting Law [17] lead to the conclusion that $f_{(M^+)} \approx f_{(ML^+)}$, so the activity coefficients in equation (2) were canceled. Thus the complex formation constant in term of the molar conductance can be expressed as:

$$K_f = \frac{[ML^+]}{[M^+][L]} = \frac{(\Lambda_M - \Lambda_{obs})}{(\Lambda_{obs} - \Lambda_{ML})[L]} \quad (3)$$

where

$$[L] = C_L = \frac{C_M (\Lambda_M - \Lambda_{obs})}{(\Lambda_M - \Lambda_{ML})} \quad (4)$$

Here, Λ_M is the molar conductance of the metal ion before addition of the ligand, Λ_{ML} is the molar conductance of the complexed ion, Λ_{obs} is the molar conductance of the solution during titration, C_L is the analytical concentration of the L added, and C_M is the analytical concentration of the metal ion, the complex formation constant, K_f , and the molar conductance of complex, Λ_{ML} , were obtained by computer fitting of equation (3) and (4) to molar conductance – mole ratio data using a non Linear least – squares program Genplot. All calculated stability constants are summarized in Table 1 which shows that stability constant values increase with increasing temperature, meaning that the complexation is an endothermic process.

Comparison of the formation constants (at identical temperature) given in Table 1 revealed that relative stabilities of the complexes increased with increasing ethanol percent. Since, donor numbers of ethanol (19.0) and water (18.0) are approximately equal, if we ignore negligible difference donor number of solvents, it seems to dielectric constant, ϵ , of solvents play an important role in the formation of complexes. Stability constants were become large by increasing of ethanol ($\epsilon = 24.3$) percent and decreasing of water ($\epsilon = 81.0$) percent. Therefore, stability constants of Cu(II)- AMTT complexes vary inversely with dielectric constant of the solvents.

In order to have a better understanding of the thermodynamics of complexation reaction discussed, it is useful to consider the enthalpic and the entropic contributions to these reactions. The ΔH° and ΔS° values for the complexation reaction were evaluated from the corresponding $\ln K_f$ – temperature data by applying a Linear least – squares analysis according to the Van't Hoff equation. The enthalpies and entropies of complexation were determined in the usual manner from the slopes and intercepts of the plots, respectively. ΔG° of the studied complexes were evaluated at 25 °C using the relations:

$$\Delta G^\circ = -RT \ln K_f = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

The computed results were collected in Table 2. The negative values of ΔG° (Table 2) show the ability of the studied ligand to form stable complexes and the process trend to proceed Spontaneously. However, the obtained positive values of ΔH° (Table 2) means that enthalpy is not the driving force for the formation of the complexes. The positive values of ΔS° (Table 2) indicate that entropy is responsible for the complexing process.

For investigating the influence of solvents on the stability constant we drew ($\log K_f$) against (V/V) % of ethanol – water for reaction of Cu(II) with AMTT at different temperatures (Fig 1). Fig. 1 shows that stability constant of complexes were become larger by increasing of ethanol percent and changes of stability constant are become sharper in the mole ratio of 0.4 - 0.6 . According this behavior we can conclude that, there is a considerable interaction between components of solvents in these ranges .

Table1. Stability constant ($\log K_f$) of Cu(II) -AMTT complexes in different (V/V)% ethanol- water solutions at different temperatures.

(V / V)% ethanol-water	$\log K_f$			
	17.5 °C	25.0 °C	35.0 °C	45.0 °C
0	2.52 ± 0.07	2.57 ± 0.07	2.67 ± 0.07	2.68 ± 0.07
20	2.65 ± 0.07	2.71 ± 0.07	2.74 ± 0.07	2.79 ± 0.08
40	2.83 ± 0.07	2.89 ± 0.07	2.97 ± 0.07	3.01 ± 0.08
60	3.20 ± 0.07	3.26 ± 0.07	3.34 ± 0.08	3.42 ± 0.08
80	3.31 ± 0.06	3.37 ± 0.06	3.46 ± 0.07	3.52 ± 0.09

Table 2. The $-\Delta G^\circ$, ΔH° and ΔS° values for Cu (II) – AMTT complexation reactions in (V/V)% ethanol-water binary mixtures.

(V / V) % ethanol-water	$-\Delta G^\circ$ (25 °C) (Kcal.mol ⁻¹)	ΔH° (Kcal.Mol ⁻¹)	ΔS° (Cal.mol ⁻¹ .°K ⁻¹)
0	3.51 ± 0.99	2.74 ± 0.50	20.96 ± 1.65
20	3.66 ± 0.48	2.09 ± 0.24	19.29 ± 0.79
40	3.98 ± 0.39	2.62 ± 0.20	22.14 ± 0.64
60	4.46 ± 0.28	3.40 ± 0.14	26.35 ± 0.45
80	4.59 ± 0.79	3.42 ± 0.10	26.86 ± 0.34

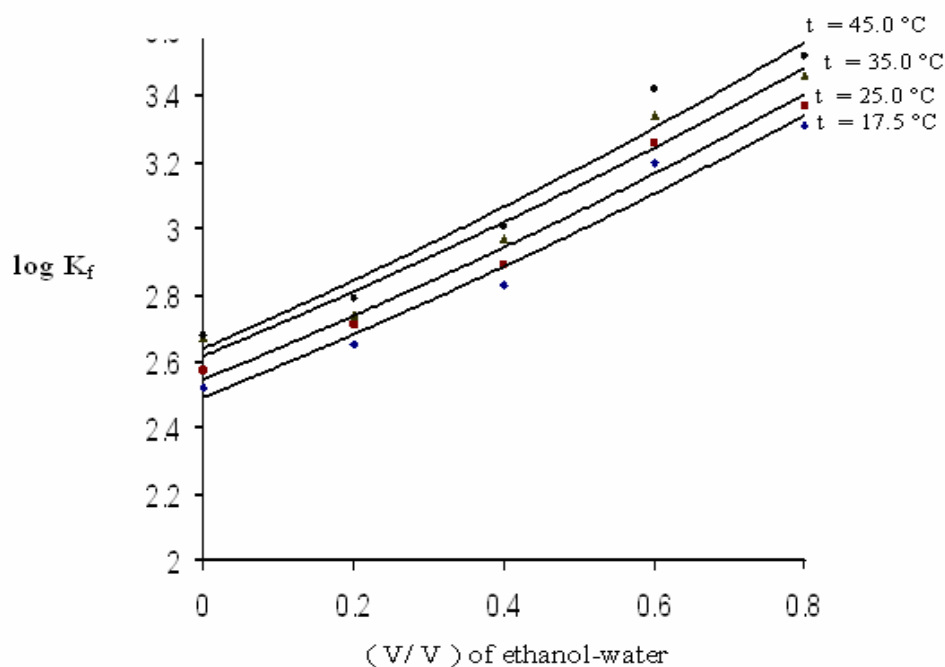


Figure1: LogK_f vs. mole ratio of ethanol for Cu(II) –AMTT complexes at different temperatures

Materials and Methods

Reagents

CuCl₂ · 2H₂O [Merck] and ethanol [Merck] were used as purchased. The ligand AMTT was provided by previously method [18].

Apparatus

Conductivity measurement were carried out with a Metrohm 644 Conductometer. A dip-type conductivity cell, made of platinum black, with a cell constant of 0.69 cm⁻¹ was used. In all measurements, the cell was thermostat at the desired temperature ±0.5 °C using a ATBIN immersion thermostat.

Procedure

In a typical run, 30 mL of a Copper (II) Chloride solution (5 × 10⁻⁴ mol L⁻¹) was placed in a water-jacketed cell equipped with a magnetic stirrer and connect to the thermostatic circulating water at the desired temperature.

Conductance of the initial solution was measured after thermal equilibrium had been reached. Then a known amount of the ligand solution (5 × 10⁻³ mol L⁻¹) was added in stepwise manner using a calibrated micropipette. The conductance of the

solution was measured after each addition, and then corrected to avoid the effect of dilution during the titration by multiplying the measured value by $[(V + v) / V]$, where V is the original volume of the salt (metal ion solution) and v is the volume of titrant (ligand solution).

Conclusion

The stability constants of Cu(II) ion and AMTT show a behavior that depends to the solvent type. The formation constants were being larger by increasing of temperature and ethanol percent. Stability constants of complexes vary inversely with dielectric constant of solvents.

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