

Thermodynamic Study of Complex Formation Between Cu(II) and 4-Amino-6-methyl-1,2,4-triazin-3-thione-5-one in Binary Ethanol/Water Mixtures using Conductometric Method

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The stability constant, K_i , for the complexation of copper(II) with 4-amino-6-methyl-1,2,4-triazin-3-thione-5-one (AMTTO) in 0, 20, 40, 60 and 80 (v/v) % ethanol-water mixtures were determined conductometrically at different temperatures. The stability constants of resulting 1:1 complexes were become larger by increasing of temperature and ethanol per cent. 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.

Key Words: Complex, Conductometry, Cu(II), Stability constant, Triazine.

INTRODUCTION

Copper(II) ion is a biologically active, important ion with 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 antiinflammatory agents¹.

On the other hand, numerous compound containing 1,2,4-triazines moiety are well known in natural materials and show interesting biological and antiviral properties²⁻⁴. Many derivatives of 1,2,4-triazine compounds form coloured complexes with different metal ions and can be used as analytical reagents for their determinations⁵⁻⁹. The present study deals with the conductometric determination of the stability constants, stoichiometric ratio and related thermodynamic parameters of 4-amino-6-methyl-1,2,4-triazin-3-thione-5-one (AMTTO) complexes with Cu(II) ion.

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EXPERIMENTAL

The $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and ethanol were purchased from Merck. The ligand of AMTTO was synthesized as reported¹⁰. The conductivity measurements 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 thermostated at the desired temperature $\pm 0.05 \text{ }^\circ\text{C}$ using a ATBIN immersion thermostate.

Procedure: In a typical run, 30 mL of a copper (II) chloride solution ($5 \times 10^{-4} \text{ M}$) was placed in a water-jacketed cell equipped with a magnetic stirrer and connected to the thermostatic circulating water at the desired temperature. The conductance of the initial solution was measured after thermal equilibrium had been reached. Then a known amount of the ligand (L) solution ($5 \times 10^{-3} \text{ M}$) 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 (the ligand solution).

RESULTS AND DISCUSSION

In order to evaluate the influence of adding ligand in the molar conductance of the Cu^{2+} ion used in different (v/v) % ethanol-water mixtures. The conductivity at a constant salt solution ($5 \times 10^{-4} \text{ M}$) was monitored while increasing the ligand concentration ($5 \times 10^{-3} \text{ M}$) at different temperatures. The molar conductance were plotted against $[\text{L}]/[\text{M}]$ mole ratio for reaction of Cu(II) with AMTTO at different temperatures. As an example, the molar conductance vs. $([\text{L}]/[\text{M}])$ curves for Cu(II)-AMTTO complexes in 40 (v/v) % ethanol-water at different temperatures is shown in Fig. 1. The plots (Fig. 1) exhibit one obvious slopes, suggesting that the probable stoichiometric ratio of complexes are M:L. The corresponding molar conductance increased with increasing the temperature (Fig. 1), 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 metal ions (for example M^+) with (L), can be expressed by the following equilibrium¹¹:



The corresponding equilibrium constant, K_f is given by:

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

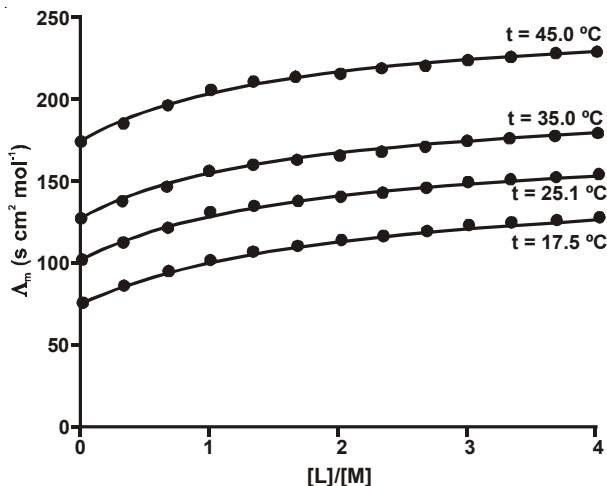


Fig. 1. Molar conductance vs. ($[L]/[M]$) curves for Cu(II)-AMTTO complexes in 40 (v/v) % ethanol-water binary mixtures at different temperatures

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^{11,12}. The use of Deby-Huckel limiting law¹³ lead to the conclusion that $f_{(M^+)} \approx f_{(ML^+)}$, so the activity coefficients in eqn. 2 were canceled. Thus the complex formation constant in term of the molar conductance can be expressed as Takeda¹⁴ and Zollinger *et al.*¹⁵:

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

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 ligand 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 eqns. 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.

Table-1 shows that stability constant values, increases 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 and water are approximately equal¹⁶, if we ignore negligible difference donor number of solvents, it seems to dielectric constant, ϵ , of solvents¹⁶ play an important role in the formation of complexes. The stability constants were become large by increasing of ethanol ($\epsilon = 24.3$) per cent and decreasing of water ($\epsilon = 81.0$) per cent. Therefore, stability constants of Cu(II)- AMTTO complexes vary inversely with dielectric constant of the solvents.

TABLE-1
STABILITY CONSTANTS ($\log K_f$) OF Cu(II)-AMTTO
COMPLEXES IN ETHANOL-WATER (v/v) % BINARY
MIXTURES AT DIFFERENT TEMPERATURE

Ethanol (v/v) %	$\log K_f \pm$ Standard deviation (n = 3)			
	17.5 °C	25.0 °C	35.0 °C	45.0 °C
0	3.09 \pm 0.08	3.18 \pm 0.08	3.21 \pm 0.09	3.25 \pm 0.09
20	3.17 \pm 0.06	3.25 \pm 0.07	3.31 \pm 0.07	3.35 \pm 0.09
40	3.23 \pm 0.06	3.33 \pm 0.07	3.37 \pm 0.07	3.43 \pm 0.06
60	3.29 \pm 0.05	3.38 \pm 0.06	3.43 \pm 0.06	3.47 \pm 0.07
80	3.32 \pm 0.06	3.42 \pm 0.06	3.48 \pm 0.08	3.54 \pm 0.09

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. Plots of $\ln K_f$ vs. $1/T$ for Cu(II)-AMTTO complexes are shown in Fig. 2. 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:

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

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.

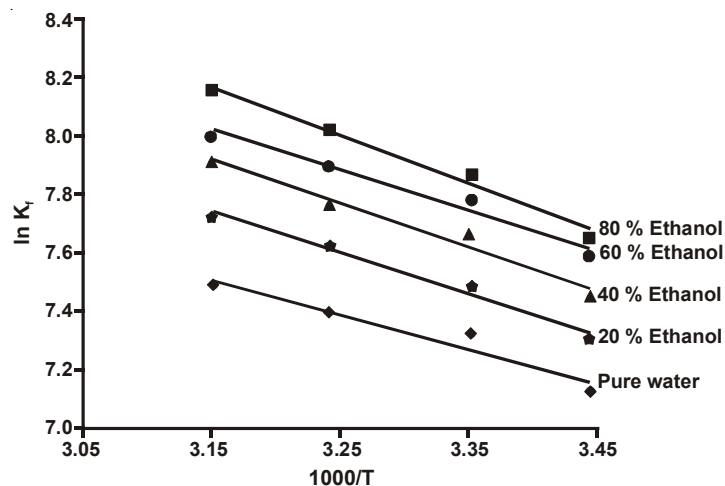


Fig. 2. $\ln K_f$ vs. $1000/T$ for Cu(II)-AMTTO complexes in different ethanol-water (v/v) % binary mixtures

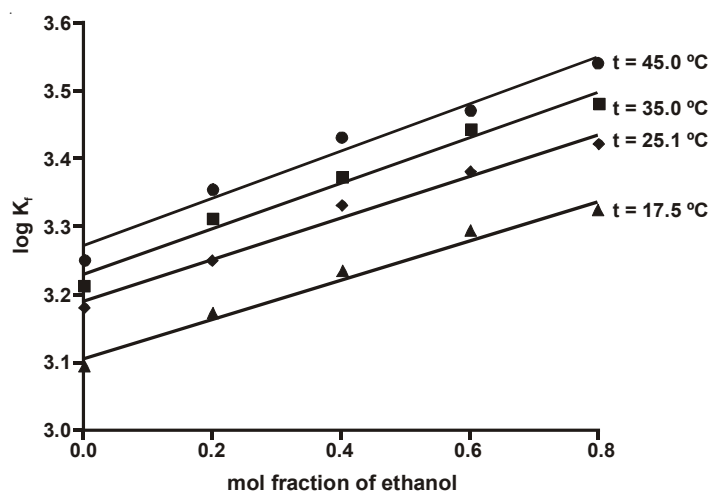


Fig. 3. $\log K_f$ vs. ethanol % for Cu(II)-AMTTO complexes at different temperatures

For investigating the effect of solvents on the stability constants, we draw a plot for ($\log K_f$) against (v/v) % of ethanol-water for reaction of Cu(II) with AMTTO at different temperatures (Fig. 3). These plots were linear and based of this, can get a result that there is not considerable interaction between components of solvents in binary systems of ethanol-water and this components cause to diluted each other in binary systems.

TABLE-2
 ΔG° , ΔH° AND ΔS° VALUES OF Cu(II)-AMTTO COMPLEXATION
 REACTIONS IN ETHANOL-WATER (v/v)% BINARY
 MIXTURES (25 °C)

Ethanol (v/v) %	$-\Delta G^\circ$ (Kcal mol ⁻¹)	$-\Delta H^\circ$ (Kcal mol ⁻¹)	$-\Delta S^\circ$ (cal mol ⁻¹ K ⁻¹)
0	4.29 ± 0.13	2.38 ± 0.49	22.38 ± 1.22
20	4.42 ± 1.67	3.77 ± 0.30	24.10 ± 1.27
40	4.51 ± 0.99	2.96 ± 0.46	25.04 ± 1.52
60	4.58 ± 0.68	2.73 ± 0.39	24.51 ± 0.98
80	4.63 ± 0.86	3.37 ± 0.37	26.85 ± 1.63

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