

# Thermodynamic Study of Complex Formation Between Azamacrocyclic Ligand With $\text{Cu}^{2+}$ and $\text{Fe}^{2+}$ Cations in MeOH- $\text{H}_2\text{O}$ Binary solvents

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**Abstract**— The complex interaction studies involved complex formation reactions between 14-membered tetraaza macrocycle ligand and  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  metal cations in methanol-water (MeOH- $\text{H}_2\text{O}$ ) binary mixtures at different temperatures by applying conductometric method. These are very important due to their role in some analytical applications such as molecular recognition and biological transportation mechanisms. In all cases, the Log  $K_f$  of 1:1 formed complexes between ligand and cations were obtained by fitting the molar conductivity curves using the Genplot computer program. The values of thermodynamic parameters, standard enthalpy ( $\Delta H$ ) and standard entropy ( $\Delta S$ ) for the complexes were obtained from the temperature dependence of the stability constants using the van't Hoff plots. Complexations in every case were found to be entropy stabilized, and the selectivity order of all complexes changes as well as the changes in composition of the solvent mixtures.

**Keywords**— conductometric method, 14-membered tetraaza macrocycle ligand, thermodynamic study.

## 1. Introduction

Azamacrocyclic ligands as the macrocyclic compounds have been shown to be suitable molecules in the field of host-guest chemistry [1-3]. They received great attention due to the existence of donor nitrogen atoms and their applications in medicine and modern chemical techniques such as imaging with radioisotopes, radiotherapy and magnetic resonance imaging, where metal complex with extreme kinetic and thermodynamic stability toward metal release is required [4].

The complexation properties of azamacrocycles are governed mainly by their ring size since N-Functionalization of these compounds may enhance their metal-ion selectivity and the stability of metal complexes based on the coordination properties of the pendant arms [5].

The 14-membered tetraaza macrocyclic ring of 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetra azacyclotetradeca-4,11-diene was reported to make variables complexes with copper [6], cobalt [7] and nickel [8]. Ammonium ions or their derivatives with a partial positive charge are known to be good receptors to make complexes with crown ethers,

calixarenes, cucurbiturils and porphyrins, but they are also able to be used as ligands to make complexes with different metal ions due to the presence of donor groups which can form semi-rigid cone shapes [9-15]. Macrocyclic ammonium salts and their complexation remain competitively under-reported. There exist a variety of techniques to study the complexation reaction of macrocyclic compounds with metal ions, such as potentiometry [16-22], calorimetry [23], NMR spectroscopy [24], polarography [25] and conductometry [26-28]. Among these various techniques, the conductometric technique is a sensitive and inexpensive method with a simple experimental arrangement for such investigations.

One of the main research interests is the influence of solvent properties on the thermodynamics of complexation reactions of macrocyclic ligand with different metal cations. This paper describes the 14-membered tetraaza macrocycle salt of 5,5,7,12,14,14-Hexamethyl-1,8-diaza-4,11-diazoniacyclotetradeca-4,11-diene dibromide (Figure 1) being first synthesized according to the literature method in a one step reaction and obtained in crystalline form. Subsequently, findings of a conductometric study of the complexation reaction of  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  cations with macrocyclic ligand in methanol-water (MeOH- $\text{H}_2\text{O}$ ) binary solution at different temperatures (15, 25, 35 and 45°C) are reported. Consequently, we study the effect of solvent properties and the effect of the composition of the MeOH- $\text{H}_2\text{O}$  binary mixed solvents on stoichiometry and the selectivity between ligand and ions in various systems.

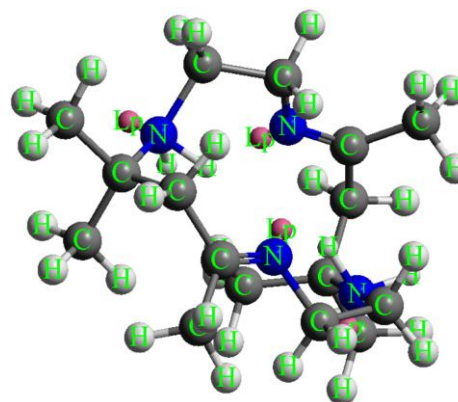


Figure 1: The structure of the ligand (L)

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## Reagents and Apparatus

Copper(II) nitrate hexahydrate and ferrous(II) chloride hexa hydrate were as purchased from Merck and Sigma aldrich with highest purity. Methanol (Sigma aldrich) of the highest purity and bi-distilled de-ionized water were applied throughout the experiment. The weight values of all the MeOH–H<sub>2</sub>O mixtures used were measured and then measurements of conductivity were performed by the thermo scientific orion versastar conductivity meter and connected to the thermostatted water bath (Julabo F12) to keep the temperature constant to within  $\pm 0.01^\circ\text{C}$  during the experiment. A glass conductivity cell dip type composed of the platinum black was used. The cell constant was determined at different temperatures by measuring the conductivity of a 0.1000 M solution of analytical grade potassium chloride produced by E.MERCK in de-ionized water.

## Methodology

All experiments were conducted using 25 mL of cation solutions ( $5.0 \times 10^{-5}$  M), which were used in the cell titration to obtain the solution conductivities at four desired temperatures. A known quantity of a concentrated solution of ligand ( $2.5 \times 10^{-3}$  M) was added in a stepwise manner by a micropipette calibration and, after each addition, the conductance value of the solution was measured. The ligand solution was added to the cell flask until a suitable value of the  $[L]/[M]$  mole ratio was reached. Molar conductivity,  $\Lambda_m$ , and constant formation,  $K_f$ , for 1:1 complexes in the various MeOH–H<sub>2</sub>O mixtures at different temperatures were measured by fitting the observations of molar conductance,  $\Lambda_{\text{obs}}$ , at various ligand/cation mole ratios. The formation constant, and the limiting molar conductance of the resulting 1:1 complexes, were evaluated by non-linear least squares (curve fitting) using GENPLOT software.

## Results and Discussion

The complexation reaction between a target cation with a ligand in a solution, which is an equilibrium process, can be considered as:



where S is the solvent molecule, and x, y and z are the solvation numbers of the ions, the ligand, and the resulting complex, respectively.

According to Equation 1, the affinity of the ligand and solvent for the metal cation and the affinity of the target ion or the solvent molecules for the ligand result in the change of free energy. Therefore, the solvation of the target cation, ligand, and resulting complex influence the complex formation constant, the Gibbs energy of the complexation process, and its enthalpy in the solutions [2]. These effects are expressed by the Gutman donor number [1]. The changes of molar conductance ( $\Lambda_m$ ) at a constant metallic salt concentration ( $5 \times 10^{-5}$  M) were monitored while increasing the concentration at various temperatures (15, 25, 35 and  $45^\circ\text{C}$ ). This research was conducted in methanol–water (MeOH–H<sub>2</sub>O) binary

mixtures at different temperatures, using the conductometric method. The molar conductance ( $\Lambda_m$ ) versus  $([L]_t/[M]_t)$  mole ratio plots for the complex formation of ligand with  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  cations was studied in (MeOH–H<sub>2</sub>O) binary mixtures at different temperatures, where  $[L]_t$  is the total concentration of the ligand and  $[M]_t$  is the total concentration of the metal cations. Molar conductance values as a function of  $([L]_t/[M]_t)$  for L– $\text{Cu}^{2+}$  complexes in pure methanol is shown in Figure 2. This plot indicates that ligand forms a complex with  $\text{Cu}^{2+}$  cations and these complexes are more mobile than free solvated  $\text{Cu}^{2+}$  cations.

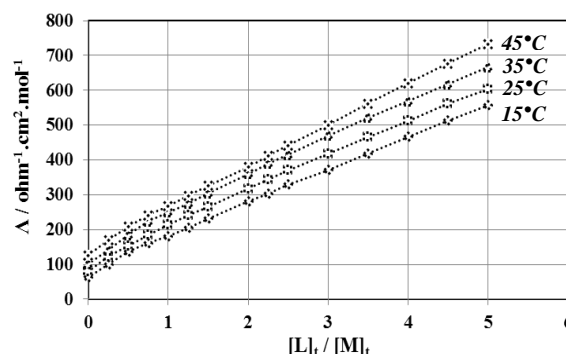


Figure 2: Molar conductance – mole ratio plots for L– $\text{Cu}^{2+}$  complexes in H<sub>2</sub>O–MeOH (% MeOH = 100%) at different temperatures.

Figure 3 shows column plots of all formed complexes in MeOH–H<sub>2</sub>O solvents at various temperatures obtained by computer fitting of the molar conductance–mole ratio data.

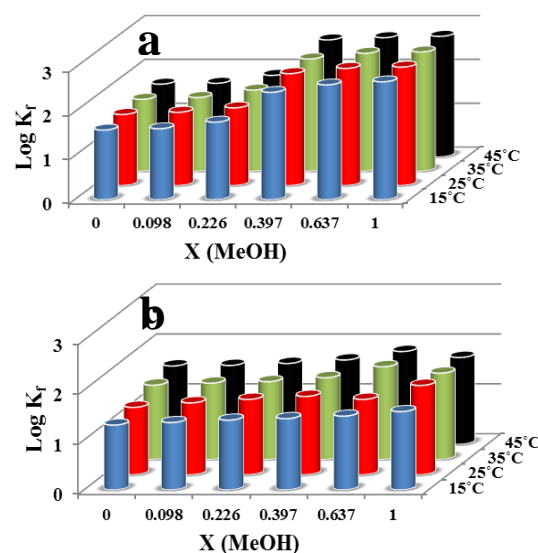


Figure 3: Variation of  $\text{Log}K_f$  of (a) L– $\text{Cu}^{2+}$ , and (b) L– $\text{Fe}^{2+}$  complex with the composition of MeOH–H<sub>2</sub>O binary mixtures at different temperatures.

The thermodynamic parameters of the complex formation between ligand and  $\text{Cu}^{2+}$  and  $\text{Fe}^{2+}$  cations depends on the nature and composition of the mixed solvents as

expressed by the result of calculated standard enthalpy, ( $\Delta H$ ) and standard entropy, ( $\Delta S$ ) listed in Table 1. As is evident from Table 1, the complexes in all cases are entropy stabilized and entropy acts as the principal driving force for the formation of these complexes in most solvent systems. The experimental values of  $\Delta H$  and  $\Delta S$  show that the enthalpies and entropies of complexation reactions in water–methanol binary solutions do not vary monotonically with the solvent composition. This behaviour may be due to some types of solvent–solvent interactions between these dipolar protic solvents that invoke changes in the structure of solvent when the two chemicals mix. It has been shown that the viscosity of the mixed solvents passes through a maximum, which indicates a strong interaction between water and alcoholic solvents. In addition, the value and the sign of the standard entropy changes are expected to vary with different parameter, such as changes in the flexibility of the macrocyclic ligands during the complicated processes and the extent of cation–solvent, ligand–solvent and complex–solvent interactions.

TABLE 1: Thermodynamic parameters for  $L\text{-Cu}^{2+}$  and  $L\text{-Fe}^{2+}$  in  $\text{MeOH-H}_2\text{O}$  binary solvents at  $25^\circ\text{C}$ .

Medium	$\Delta G \pm \text{SD}$ ( $\text{KJ mol}^{-1}$ )	$\Delta H \pm \text{SD}$ ( $\text{KJ mol}^{-1}$ )	$\Delta S \pm \text{SD}$ J/mol.K
<b><math>\text{Cu}^{2+}</math>- L</b>			
Pure $\text{H}_2\text{O}$	$-6.6 \pm 0.9$	$3.9 \pm 0.4$	$27.2 \pm 2.8$
90.2% $\text{H}_2\text{O}$ -9.8% MeOH	$-8.1 \pm 0.2$	$27.9 \pm 0.4$	$95.7 \pm 7.2$
77.4% $\text{H}_2\text{O}$ -22.6% MeOH	$-9.0 \pm 0.1$	$5.4 \pm 0.5$	$58.6 \pm 7.6$
60.3% $\text{H}_2\text{O}$ -39.7% MeOH	$-9.5 \pm 0.6$	$5.0 \pm 0.8$	$36.5 \pm 7.9$
36.3% $\text{H}_2\text{O}$ -63.7% MeOH	$-13.3 \pm 0.6$	$3.2 \pm 0.2$	$36.7 \pm 2.1$
Pure MeOH	$-10.7 \pm 0.2$	$4.6 \pm 0.5$	$57.1 \pm 12.2$
<b><math>\text{Fe}^{2+}</math>- L</b>			
Pure $\text{H}_2\text{O}$	$-8.9 \pm 0.8$	$9.8 \pm 0.6$	$71.3 \pm 4.6$
90.2% $\text{H}_2\text{O}$ -9.8% MeOH	$-8.9 \pm 0.7$	$15.4 \pm 0.0$	$78.6 \pm 12.4$
77.4% $\text{H}_2\text{O}$ -22.6% MeOH	$-9.6 \pm 0.7$	$28.0 \pm 0.3$	$118.2 \pm 27.4$
60.3% $\text{H}_2\text{O}$ -39.7% MeOH	$-10.2 \pm 0.9$	$7.4 \pm 0.1$	$59.2 \pm 24.0$
36.3% $\text{H}_2\text{O}$ -63.7% MeOH	$-8.3 \pm 0.8$	$15.6 \pm 0.6$	$71.3 \pm 4.7$
Pure MeOH	$-8.7 \pm 0.7$	$13.5 \pm 0.0$	$78.7 \pm 12.4$

The calculated thermodynamic parameters ( $\Delta H$ ,  $\Delta S$  and  $\Delta G$ ) at  $25^\circ\text{C}$  were obtained from the variations of molar conductance as a function of the ( $[L]/[M]$ ) mole ratio using Genplot. All of these calculated thermodynamic parameters for  $L\text{-Cu}^{2+}$  and  $L\text{-Fe}^{2+}$  complexes in pure MeOH, pure  $\text{H}_2\text{O}$  and  $\text{MeOH-H}_2\text{O}$  binary mixtures are summarized in Table 1.

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