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

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Abstract— The complex interaction studies involved complex formation reactions between 14-membered tetraaza macrocycle ligand and Cu$^{2+}$ and Fe$^{2+}$ metal cations in methanol-water (MeOH-H$_2$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 5,5,7,12,14,14-hexamethyl-1,8-diaza-4,11-diazoniacyclotetradeca-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 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-diazeniacyclotetradeca-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 Cu$^{2+}$ and Fe$^{2+}$ cations with macrocyclic ligand in methanol-water (MeOH-H$_2$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–H$_2$O binary mixed solvents on stoichiometry and the selectivity between ligand and ions in various systems.

Figure 1: The structure of the ligand (L)

Reagents and Apparatus

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