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Stability Studies of Selected Metal Ions Chelates with 2-(4-amino-1,5dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-ylideneamino) Phenol

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Abstract: Acid dissociation and complex stability constants of 2-(4-Amino-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-ylideneamino) phenol (H₂A) with some metal ions chelates have been determined potentiometrically using 0.1 M KCl and 20 % (v/v) ethanol-water mixture. The stability constants of the formed complexes were found to be in the order $Re^{5+} > Ce^{3+} > Pd^{2+} > Th^{4+} > Hg^{2+} > Co^{2+}$. The dissociation constants (pK_a) of H₂A and the stability constants (log K_i) of their complexes were determined at 298, 308 and 318 K. The corresponding thermodynamic parameters (ΔG , ΔH and ΔS) were calculated and discussed. The results indicated that, the dissociation process is non-spontaneous, endothermic and entropically unfavorable. The formation of the metal complexes has been found to be endothermic and entropically favorable.

Keywords: Schiff-base derivative, dissociation and stability constants, thermodynamics.

1 Introduction

Schiff-base coordination complexes have attracted a great attention over the last decades. That is due to their facile syntheses, their wide application, the accessibility of diverse structural modifications and their biological modeling applications, catalysis, design of molecular ferromagnets, and materials chemistry [1, 2]. It is well known that N-atoms play a key role in the coordination of metals at the active sites of numerous metallobiomolecules [3]. The Schiff-bases of 4-aminoantipyrine and their coordination complexes have been extensively investigated because of their biological, clinical, pharmacological, analytical and material applications [4, 5]. In addition, some drugs showed increased activity when administered as metal chelate rather than as free organic compounds [6].

Recently, metal complexes of Schiff base containing pyrazol ligands have been widely studied in the solid state by spectral characterization [7, 8]. However to best of our knowledge, no detailed studies have been carried out on the chelating tendencies of 2-(4-Amino-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-ylideneamino) phenol with bi, tri, tetra and pentavalent transition metal ions. The objective of this study are the potentiometric determination of the dissociation constants of 2-(4-Amino-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-ylidene- amino) phenol (H₂A) and the stability constant of their complexes with Co^{2+} , Pd^{2+} , Rg^{5+} , Th^{4+} and Ce^{3+} at different

temperatures. Furthermore, the corresponding thermodynamic functions of complexation are evaluated and discussed.

2 Experimental

2-(4-Amino-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3ylideneamino) phenol (Figure 1) were prepared by refluxing a mixture of hot solution of 4-aminoantipyrine (10^{-3} M) and 2-hydroxyaniline (10^{-3} M) in 50 ml ethanol for 2 h [9]. The formed solid product was separated by filtration, purified by crystallization from ethanol, washed with diethyl ether, and dried in a vacuum over anhydrous calcium chloride. Then the ligand solution (1.5×10^{-3} M) was prepared by dissolving an accurately weighted amount of the solid in ethanol (Analar).



Fig. 1: Structure of 2-(4-Amino-1,5-dimethyl-2-phenyl-1,2-dihydro-pyrazol-3-ylideneamino) phenol.

Metal ion solutions of Co^{2+} , Pd^{2+} , Hg^{2+} , Th^{4+} and Ce^{3+} were prepared from Analar metal salt samples (BDH) in