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Geometrical structure, molecular docking, potentiometric and thermodynamic studies of 3-aminophenol azodye and its metal complexes

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ABSTRACT

The proton–ligand dissociation constants of 4-(2,3-dimethyl-1-phenylpyrazol-5-one azo)-3-aminophenol (HL) and its metal stability constants with Mn(II), Co(II), Ni(II) and Cu(II) ions have been determined using potentiometric studies. The molecular structure of the ligand is optimized theoretically and the quantum chemical parameters are calculated. The proton–ligand dissociation constants of HL and its metal stability constants with Mn(II), Co(II), Ni(II) and Cu(II) have been determined potentiometrically. The potentiometric studies were carried out in 0.1 M KCl and 20% (by volume) DMF–water mixture. At constant temperature the stability constants of the formed complexes decrease in the order of Cu(II) > Ni(II) > Co(II) > Mn(II). The effect of temperature was studied at 298, 308 and 318 K and the corresponding thermodynamic parameters (ΔG, ΔH and ΔS) were derived and discussed. The dissociation process is non-spontaneous, endothermic and entropically unfavorable. The formation of the metal complexes has been found to be spontaneous, endothermic and entropically favorable. Molecular docking was used to predict the binding between azodye ligand and the receptor of prostate cancer mutant 2q2k-Hormon and receptor of breast cancer mutant 3hb5-Oxidoreductase.

1. Introduction

Azo compounds containing heterocyclic moieties have drawn the attention of many researchers [1–5]. It has been well established that the use of heterocyclic amines with oxygen as the π-excessive hetero atom as diazo component has a marked bathochromic effect compared to analogous dyes derived from benzenoid compounds [6]. Azo derivatives containing antipyrine moiety have many advantages including color depending effect as an intrinsic property leading to better dye ability. The color of these azo derivatives depends on the nature of both the diazo and the coupling components. Majority of the azo compounds are derived from the coupling of diazotized heterocyclic amines with aromatic hydroxyl and amino compounds. The position of azo and hydroxyl groups in these molecules brings into play the azo-hydrazone equilibrium [7]. The use of protein–ligand docking has become a standard method in potentiometric studies. The protein groups surrounding the ligand can highly influence the local pH, so that a different protonation could be favored in the bound state. To account for this effect, the ideal case would be to use multiple protonations in the docking and have the algorithm automatically pick the correct state. Molecular docking is widely used to predict protein–ligand [8,9] and to screen large libraries for molecules that will modulate the activity of a biological receptor.

In this paper, the potentiometric studies are used to determine the dissociation constants of 4-(2,3-dimethyl-1-phenylpyrazol-5-one azo)-3-aminophenol ligand (HL) and the stability constants of its complexes with some divalent transition metal ions such as Mn(II), Co(II), Ni(II) and Cu(II) at different temperatures. The molecular structure of the investigated ligand (HL) is studied and quantum chemical parameters are calculated. Moreover, the corresponding thermodynamic functions are calculated and discussed.

2. Materials and methods

2.1. Preparation of the ligand

4-(2,3-Dimethyl-1-phenylpyrazol-5-one azo)-3-aminophenol ligand (HL) was prepared previously [2–5,10] by coupling an equimolar amount of 1-phenyl-2,3-dimethyl-4-amino pyrazol-5-one and 3-aminophenol as shown in Scheme 1. In a typical preparation, 25 ml of distilled water containing 0.01 mol hydrochloric acid was added to 1-phenyl-2,3-dimethyl-4-amino pyrazol-5-one (0.01 mol). To the resulting mixture stirred and cooled to 0 °C, a solution of 0.01 mol sodium nitrite in 20 ml of water was added dropwise. The formed diazonium chloride was consecutively coupled with an alkaline solution of

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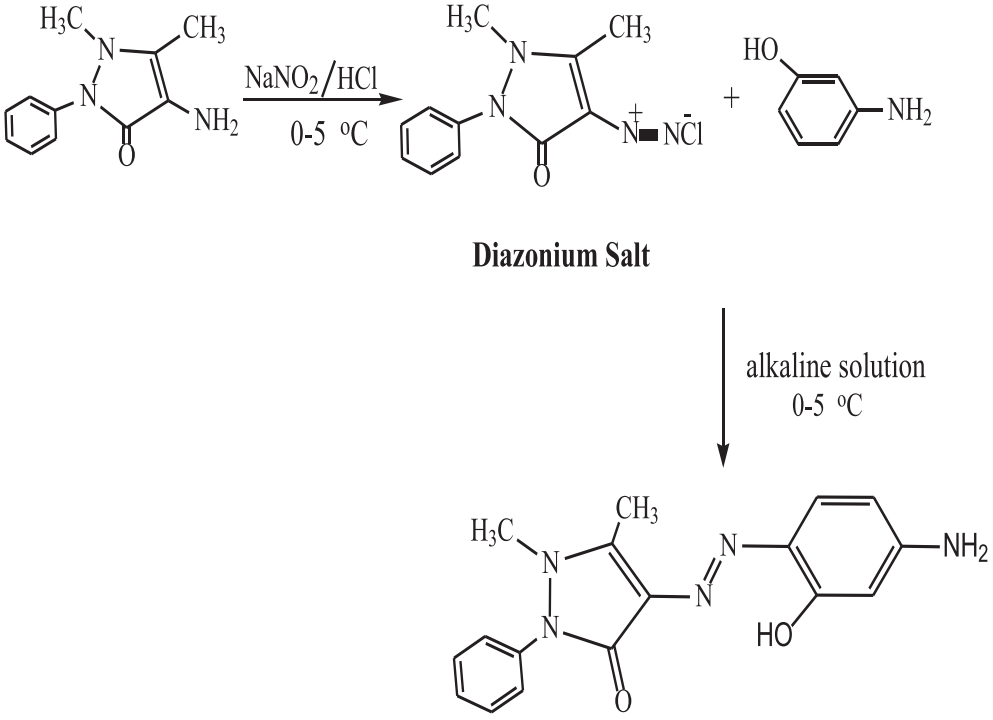

Scheme 1. The formation mechanism of the azo ligand (HL).

0.01 mol 3-aminophenol, in 10 ml of pyridine. Immediately, the deep purple precipitate formed was filtered through sintered glass crucible, washed several times by distilled water. The crude product was purified by recrystallization from hot ethanol, (yield ~68%) then dried in a vacuum desiccator over anhydrous P_2O_5. The structure of the formed ligand (HL) was established by IR, ^{1}H NMR and X-ray spectroscopies.

2.2. Potentiometric studies

A ligand solution (0.01 M) was prepared by dissolving an accurately weighed amount of the solid in DMF. Metal ion solutions (0.001 M) were prepared from metal chloride salts in bidistilled water and standardized with EDTA [11]. Solutions of 0.005 M HCl and 1 M KCl were

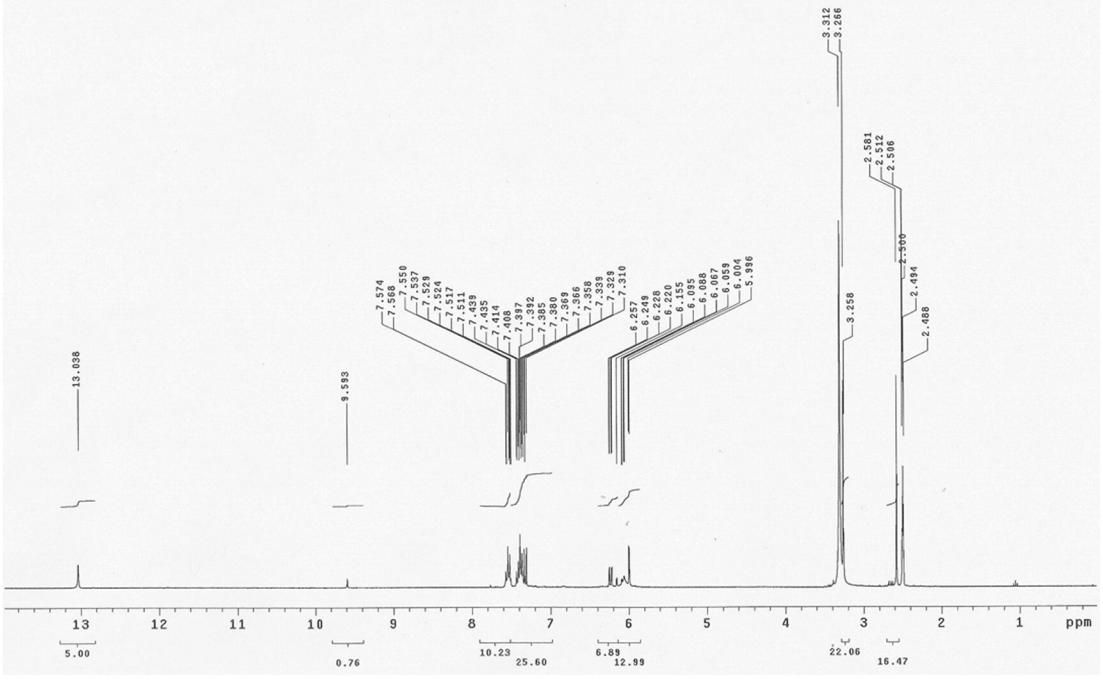

Fig. 1. ^{1}H NMR spectrum of HL ligand