



Geometrical structure, potentiometric, molecular docking and thermodynamic studies of azo dye ligand and its metal complexes



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ABSTRACT

The ligand of 6-(4-benzenesulfonic acid azo)-3-aminophenol (HL) is prepared and characterized by elemental analyses, IR, ¹H NMR spectra, mass spectra and X-ray diffraction analysis. The proton–ligand dissociation constants of HL ligand and its metal stability constants with Mn(II), Co(II), Ni(II) and Cu(II) ions have been determined using potentiometric studies as described by Irving and Rossotti. The optimized structure and the calculated quantum chemical parameters of HL ligand were studied. The potentiometric studies were carried out in 0.1 M KCl and 20% (by volume) DMF–water mixture. The effect of different temperatures was studied and the thermodynamic functions (ΔG , ΔH and ΔS) were calculated. 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 azo dye ligand and the receptor of prostate cancer mutant 2q7k-hormone and the receptor of breast cancer mutant 3hb5-oxidoreductase.

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1. Introduction

Azo dyes are compounds containing one or more azo groups of which the nitrogen atoms are sp^3 hybridized imparts color to textile fibers. Aminophenol is an aromatic amino compound and a useful source of diazonium salts for azo coupling reactions. It has found wide applications in the synthesis of mono-azo dyes which are used commercially as dyes [1–3]. However, very limited commercial dis-azo dyes derived from aminophenol were reported in the literature. Also, series of dis-azo dyes which gave good dyeing properties on polyester and nylon substrates have been prepared from *m*-aminophenol [4,5]. A single azo group present in a dye is often insufficient for dye fastness whereas dis-azo compounds with two groups linked to a biphenyl system, provided excellent substantive dyes [6]. Coordination chemistry of quinoline and its azo derivatives has much attention by virtue of their applicability as potential ligands for large number of metal ions [7,8]. The proton–ligand dissociation constants of some azo quinoline derivatives and metal–ligand stability constants of their complexes with the metal ions were determined potentiometrically [9]. The azo quinoline derivatives have one ionizable proton (the enolized

hydrogen ion of the hydroxyl group in the quinoline moiety) and the pK^H values were found to be in the range of 7.83 and 9.62 at different temperatures. 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.

In a more recent study, aminophenol was used as a coupling component in the preparation of 4-(2,3-dimethyl-1-phenylpyrazol-5-one azo)-3-aminophenol azo dye ligand [1]. The proton–ligand dissociation constants of ligand (HL) and its metal stability constants were determined using potentiometric studies. At constant temperature the stability constants of the formed complexes decreased in the order of $Cu(II) > Ni(II) > Co(II) > Mn(II)$. The pK^H values were found to be in the range of 9.01–9.40 at different temperatures [1].

In this paper, the potentiometric studies are used to determine the dissociation constants of 6-(4-benzenesulfonic acid 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. Molecular docking was also studied against the receptor of prostate cancer mutant 2q7k-hormone and receptor of breast cancer mutant 3hb5-oxidoreductase.

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2. Materials and methods

2.1. Preparation of the ligand

6-(4-Benzenesulfonic acid azo)-3-aminophenol ligand (HL) was prepared previously [1] by coupling an equimolar amount of 4-aminobenzenesulfonic acid and 3-aminophenol as shown in Fig. 1. In a typical preparation, 25 ml of distilled water containing 0.01 mol hydrochloric acid was added to 4-aminobenzenesulfonic acid (0.01 mol) and the resulting mixture was stirred and cooled to 0 °C. Solution of 0.01 mol sodium nitrite in 20 ml of water was added dropwise to the above solution. The formed diazonium chloride was consecutively coupled with an alkaline solution of 0.01 mol 3-aminophenol, in 10 ml of pyridine. Immediately, the red precipitate formed was filtered through sintered glass crucible and washed several times by distilled water. The crude product was purified by recrystallization from hot ethanol (yield ~66%) then dried in a vacuum desiccator over anhydrous P₂O₅. Anal.: Calc. for C₁₂H₁₁N₃O₄S: C, 49.15; H, 3.75; N, 14.33. Found: C, 48.09; H, 3.55 and N, 13.18.

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 [10]. Solutions of 0.005 M HCl and 1 M KCl were also prepared in bidistilled water. A carbonate-free sodium hydroxide solution in 20% (by volume) DMF–water mixture was used as titrant and standardized against oxalic acid.

The apparatus, general conditions and methods of calculation were the same as in the previous work [1,2]. The following mixtures (i)–(iii) were prepared and titrated potentiometrically at 298 K against standard 0.02 M NaOH in a 20% (by volume) DMF–water mixture:

- i) 5 cm³ 0.005 M HCl + 5 cm³ 1 M KCl + 10 cm³ DMF.
- ii) 5 cm³ 0.005 M HCl + 5 cm³ 1 M KCl + 5 cm³ 0.01 M ligand + 5 cm³ DMF.
- iii) 5 cm³ 0.005 M HCl + 5 cm³ 1 M KCl + 5 cm³ 0.01 M ligand + 10 cm³ 0.001 M metal chloride + 5 cm³ DMF.

For each mixture, the volume was made up to 50 cm³ with bidistilled water before the titration. These titrations were repeated for the temperatures of 308 and 318 K. All titrations have been carried out between pH 3.5–11.5 and under nitrogen atmosphere.

2.3. Measurements

All the compounds and solvents used were purchased from Aldrich and Sigma and used as received without further purification. Microanalytical data (C, H and N) were collected on Automatic Analyzer CHNS Vario ELIII, Germany. The IR spectra were recorded as KBr discs using a Perkin-Elmer 1340 spectrophotometer. The ¹H-NMR spectrum was obtained with a JEOL FX90 Fourier transform spectrometer with DMSO-d₆ as the solvent and TMS as an internal reference. X-ray diffraction analysis of the ligand (HL) powder form was recorded on an X-ray diffractometer in the range of diffraction angle 2θ = 5–80°. This analysis was carried out using CuK_α radiation (λ = 1.540598 Å). The applied voltage and the tube current are 40 kV and 25 mA, respectively.

This study simulates the actual docking process in which the ligand–protein interaction energies are calculated using a Docking Server [11]. The MMFF94 Force field was used for energy minimization of ligand molecule using Docking Server. Gasteiger partial charges were added to the ligand atoms. Non-polar hydrogen atoms were merged, and rotatable bonds were defined. Docking calculations were carried out on 2q7k-hormone and 3hb5-oxidoreductase protein models. Essential hydrogen atoms, Kollman united atom type charges, and solvation parameters were added with the aid of AutoDock tools [12]. Affinity (grid) maps of 0.375 Å spacing were generated using the Autogrid program [13]. Auto Dock parameter set- and distance-dependent dielectric functions were used in the calculation of the van der Waals and the electrostatic terms, respectively.

The pH measurements were carried out using a VWR Scientific Instruments Model 8000 pH-meter accurate to ±0.01 units. The pH readings in the non-aqueous medium were corrected [1]. The electrode system was calibrated according to the method of Irving et al. [14]. Titrations were performed in a double walled glass cell in an inert atmosphere (nitrogen) at ionic strength of 0.1 M KCl. Potentiometric measurements were carried out at different temperatures. The temperature was controlled to within ±0.05 K by circulating thermostated water (Neslab 2 RTE 220) through the outer jacket of the vessel.

The molecular structure of the ligand was optimized initially with the PM3 semiempirical method so as to speed up the calculations. The resulting optimized structures were fully re-optimized using ab initio Hartree–Fock (HF) [15] with 6-31G basis set. The molecules were built with the Gauss View 3.09 and optimized using Gaussian 03W program [16]. The corresponding geometries were optimized without any geometry constraints for full geometry optimizations. Frequency calculation was executed successfully, and no imaginary frequency was found, indicating minimal energy structures. The molecular geometry for ligand was fully optimized using Density functional theory B3LYP method,

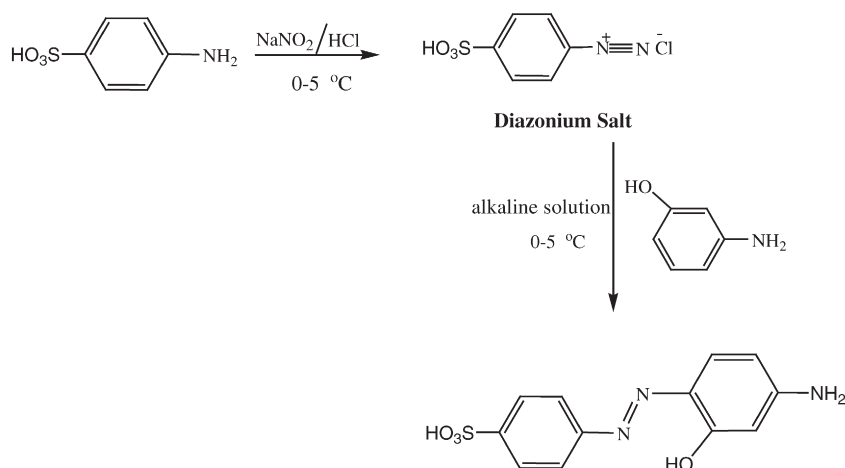


Fig. 1. The formation mechanism of the azo dye ligand (HL).

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