AN EBT-BASED "ZINC DIPICOLYL SULFONAMIDE" COMPLEX AS A POTENTIAL COLOURIMETRIC SENSOR FOR INORGANIC PHOSPHATE

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Dipicolylamine (DPA), a tridentate ligand with three nitrogen atoms, is ideal for sensing applications. Its selectivity towards biologically active metal atoms and anions allows for the design of sensors capable of detecting analytes in biological and environmental samples. Our research focuses on designing a sensor that utilizes a zinc complex of a dipicolyl sulfonamide ligand, $Zn(N(SO_2)(1\text{-nap})dpa)Cl_2$ (1-nap = 1-naphthalenyl; dpa = dipicolylamine), to detect inorganic phosphates in water bodies. The sensor employs an indicator displacement method using Eriochrome Black T (EBT) as the indicator. A pure sample of $Zn(N(SO_2)(1\text{-nap})dpa)Cl_2$ complex (ZnDPSA) was used as received to prepare the sensor complex in-solution (H_2O) by mixing the complex and EBT in a 1:4 ratio at pH 9: The exact stoichiometry was obtained by Job's Plot method using UV/Vis spectral data and the optimal pH was determined by monitoring the maximum absorbance at 540 nm. The association constant between ZnDPSA and EBT calculated using the Benesi-Hilderbrand plot is $0.290 \times 10^3 \ mM^{-1}$ while the association constant between ZnDPSA and phosphate ions was calculated to be $1.5781 \times 10^4 \ mM^{-1}$. This ten-fold difference indicates the higher affinity of the ZnDPSA complex towards phosphate ions. Upon the presence of phosphate ions, the designed sensor produces a rapid and distinguishable colorimetric response (the pink colour turns into blue indicating that phosphate ions replace the bound EBT), making it a suitable phosphate detector. However, the lower limit of detection for phosphate ions was established at 0.1751 mM (SD = 0.0169) indicating a moderate level of sensitivity compared to other available Zn-based phosphate sensors. Interestingly, the UV/Vis experiments have demonstrated that the selectivity of the new sensor towards phosphate ions is significant: The interference study shows that the sensor colourimetrically responds only to phosphate ions but not to other common ions such as Cl^-, NO_2^-, SO_4^{2-}, HCO_3^-, and CO_3^{2-}. The sensitivity of the designed sensor could be further improved by modifying the sulfonamide linker of ZnDPSA.

Keywords: Zinc Dipicolyl Sulfonamide complex, Inorganic phosphate detection, UV/Vis studies, EBT indicator

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INTRODUCTION

Zinc Dipicolyl Sulfonamide (ZnDPSA) complexes have generated significant scientific interest due to their unique chemical and physical properties. Its sulfonamide linker can be modified to fine-tune its properties. Dipicolylamine (dpa) is a tridentate ligand with three nitrogen atoms, making it an ideal candidate for sensing applications. Its selectivity towards biologically active metal atoms and anions allows for the design of sensors that can detect analytes in biological and environmental samples. Chelating Zn ions with dpa ligands can increase fluorescence intensity and reduce non-radiative decay rates (Hens, 2015). Zinc (Zn) is a preferred complexing agent due to its high biological activity, sensitivity, and biocompatibility compared to other d-block metal ions. In this study, we have selected the $Zn(N(SO_2)(1\text{-}nap)dpa)Cl_2$ complex, which has been designed, synthesized, and characterized by Darshani et al. in 2020.

High phosphate levels in water can lead to Eutrophication, negatively impacting the environment by reducing water quality and biodiversity. Therefore, monitoring inorganic phosphate levels in water is essential to prevent this phenomenon. In this work, we utilized the novel $Zn(N(SO_2)(1\text{-}nap)dpa)Cl_2$ complex to develop a sensor for detecting inorganic phosphate in water bodies. The sensor operates through an indicator displacement method, using EBT as the indicator. EBT was chosen for its availability and functionality, enhancing the sensor's accuracy and reliability. EBT shows a distinguishable visual change during the displacement with phosphate ions, making it suitable for fluorometric and colourimetric sensing purposes (Vega et al., 2011). As far as my knowledge extends, this $Zn(N(SO_2)(1\text{-}nap)dpa)Cl_2$ complex has not been utilized before for the development of a sensor capable of detecting inorganic phosphate.

METHODOLOGY

Materials: A sample of $Zn(N(SO_2)(1\text{-}nap)dpa)Cl_2$ was received from Prof. Theshini Perera's laboratory. Eriochrome Black T (EBT), Concentrated HCl, NaOH, and other necessary reagents were used as received.

Confirmation of the purity of $Zn(N(SO_2)(1\text{-}nap)dpa)Cl_2$ complex: A 0.1 mM solution of $Zn(N(SO_2)(1\text{-}nap)dpa)Cl_2$ (**Stock 1**) was prepared by dissolving 5.23 mg of white solid in 100 ml of methanol. UV/Vis and fluorescence spectra of the prepared solution were obtained and compared with the published data. (Darshani et al., 2020)

Preparation of Sensor Solution: A 0.1 mM solution of EBT was prepared by dissolving 4.61 mg of EBT in 100 ml distilled water (**Stock 2**). To determine the optimum pH for the formation of the EBT-based $Zn(N(SO_2)(1\text{-}nap)dpa)Cl_2$ complex, a 1:1 mixture of **Stock 1** and **Stock 2** was prepared by mixing 20 ml of each stock solution. A series of aliquots of the mixture was taken, and the pH of each aliquot was adjusted from pH 2-11 using 0.01 M NaOH and/or 0.01 M HCl solutions. A solution series was prepared using the continuous variation method to determine the stoichiometric ratio between $Zn(N(SO_2)(1\text{-}nap)dpa)Cl_2$ and EBT by Job's Plot method ($\lambda_{max}= 540$ nm). The association constant of EBT-based $Zn(N(SO_2)(1\text{-}nap)dpa)Cl_2$ complex was determined using the Benesi-Hilderbrand method.

Phosphate sensing analysis: 2.5 ml aliquots of the sensor solution were taken (at pH 9) and the UV/Vis absorbance spectra were recorded before and after adding different amounts of phosphate ions. The association constant of phosphate ions to the $Zn(N(SO_2)(1\text{-}nap)dpa)Cl_2$ complex and the limit of detection of phosphate ions were determined using the Benesi-Hildebrand method and OriginPro software, respectively.

Conformation of the selectivity of the sensor towards the phosphate ions: The UV/Vis absorbance spectra of the sensor solution (at pH 9) was recorded before and after the separate addition of anions; HPO_4^{2-}, Cl^-, NO_2^-, SO_4^{2-}, HCO_3^-, and CO_3^{2-}, by keeping the ratio of complex and anion as 1:10. Further, the experiment was repeated for a mixture of equal amounts of mentioned ions. The spectral changes and visual color changes were recorded.

RESULTS AND DISCUSSION

The obtained $Zn(N(SO_2)(1\text{-nap})dpa)Cl_2$ (Figure 1) sample appeared as white powdered crystals. The central metal atom (Zn) binds with two atoms of Cl and two atoms of pyridyl N in the chelating ligand. The chelating ligand is a dipicolyl sulfonamide derivative, functionalized with a 1-naphthanyl group at the central sulfonamide N atom. The compound contains a rare eight-membered chelate ring. (Darshani et al., 2020)
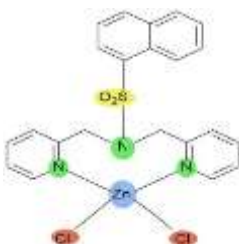

Figure 1-: Structure of $Zn(N(SO_2)(1\text{-nap})dpa)Cl_2$

The UV/Vis and fluorescence spectra of a solution obtained by dissolving the complex in methanol were measured (Figures 2(a) and (b)). The new spectra were compared with the published data (Darshani et al., 2020) to confirm the purity.
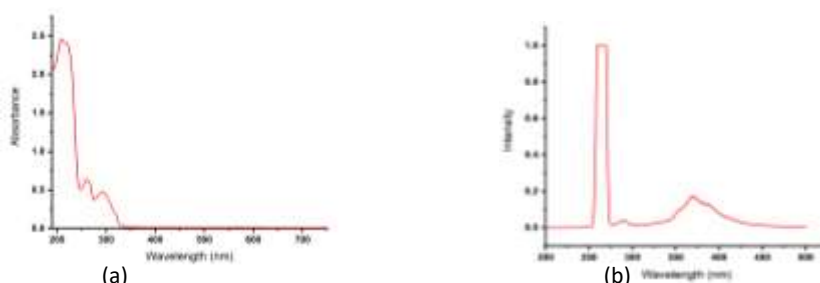

(a)   (b)

Figure 2-: (a) UV/Vis spectrum for $Zn(N(SO_2)(1\text{-nap})dpa)Cl_2$ (b) Florescence spectrum for $Zn(N(SO_2)(1\text{-nap})dpa)Cl_2$

The maximum absorbance for the newly formed EBT-ZnDPSA complex was observed to be at pH = 9. Hence all the other experiments were carried out at pH = 9. Based on the Job's Plot (Figure 3), the stoichiometric ratio between ZnDPSA and EBT was determined to be 1:4.

Upon phosphate addition, the sensor solution produces an immediate colourimetric response as shown in Figure 4(a): There is a bathochromic shift from 560 nm to 575 nm in the sensor solution with phosphate ions compared to the sensor spectrum without phosphate ions (Figure 4(b)). Additionally, the spectrum of the sensor with phosphate ions shows a peak in the 650-700 nm region, attributed to free EBT, providing further evidence of the replacement of phosphate ions with EBT.

The association constant (A_1) between ZnDPSA and EBT calculated using the Benesi-Hilderbrand plot is $0.290 \times 10^3 \, mM^{-1}$. In contrast, the association constant (A_2) between ZnDPSA and phosphate ions was calculated to be $1.5781 \times 10^4 \, mM^{-1}$. A_2 is ten-fold higher than A_1, indicating that the studied ZnDPSA complex has a greater affinity towards the phosphate ions than the EBT (Yilmaz & Oktem, 2018).
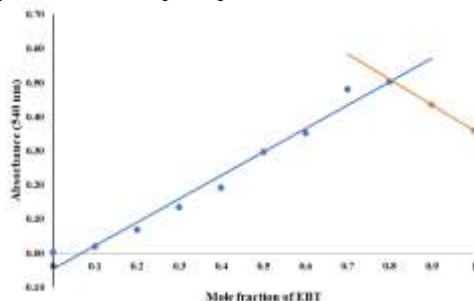

Figure 3-: Job plot for the determination of stoichiometric ratio between Zn(N(SO$_2$)(1-nap)dpa)Cl$_2$ and EBT
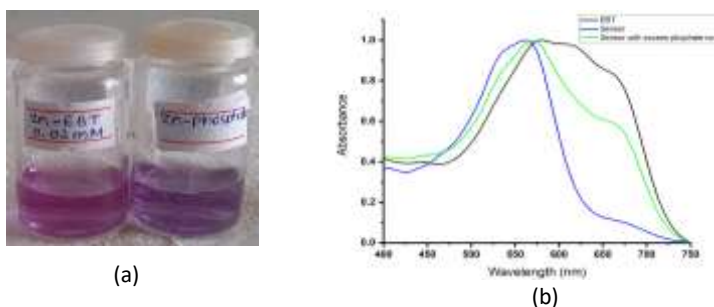

(a)

(b)

Figure 4-: (a) Sensor solution (left), and sensor solution with added phosphate ions (right) at pH 9 (b) UV/Vis spectra of sensor solution (blue), sensor solution with added phosphate ions (green), and free EBT solution (black)

The lower limit of detection for phosphate ion was determined to be 0.1751 mM (Figure 5), which is a moderate result compared to the published data for Zn complexes on phosphate ion detection (Reinke et al., 2021),(Berchmans et al., 2012). However, the selectivity of the studied ZnDPSA complex towards phosphate ion is significantly higher than most similar complexes (Khatua et al., 2009). The alterations in visual appearance exhibited that the solutions that were prepared using phosphate ions permitted Eriochrome Black T (EBT) to remain unbound within the medium, resulting in a discernible shift in colour to blue (Figure 6). The peak, which corresponds to the unbound EBT, was only discernible in the spectra of the solution which contained phosphate ions. These observations prove that phosphate ions have a selectively greater affinity towards the ZnDPSA core than the other anions tested.
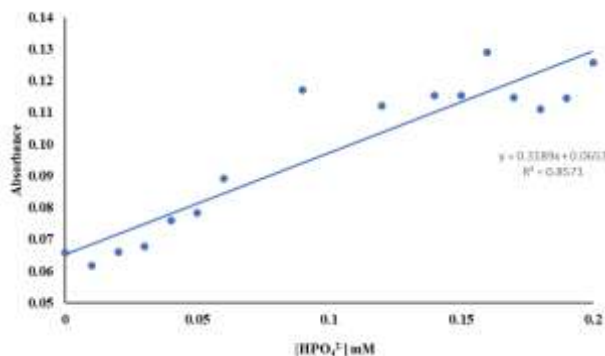

Figure 5-: Linear absorbance plot to obtain the limit of detection

Figure 6-: (a) The solution series of the sensor with different concentrations of ions. From left to right: Sensor, HPO_4^-, Cl^-, NO_2^-, SO_4^{2-}, HCO_3^-, CO_3^{2-}, and a mixture of ions

CONCLUSION/RECOMMENDATIONS

In summary, the results have shown that the novel EBT-based $Zn(N(SO_2)(1-nap)dpa)Cl_2$ sensor can detect inorganic phosphate ions efficiently. The binding affinity of phosphate ions to the complex is considerably higher than that of EBT confirming phosphate ions can immediately replace that bound EBT. This sensor has high selectivity towards phosphate anions over various other anions. The reported sensor can be modified to increase the sensitivity towards the phosphate ions by tuning the functional groups of the ligand. Moreover, the application of the reported sensor for real sample analysis can be investigated.

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