



Azo linked thiourea based effective dual sensor and its real samples application in aqueous medium



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ARTICLE INFO

Article history:

Received 12 August 2014

Received in revised form 3 November 2014

Accepted 28 November 2014

Available online 9 December 2014

Keywords:

Anions
Schiff base
¹H NMR
Nanomolar
Aqueous medium
Real sample

ABSTRACT

The azo linked thiourea type Schiff base has been synthesized and characterized which is found to sense F^- , AcO^- and Cd^{2+} ions in aqueous medium over other anions and cations. **R1** gave rise to significant changes in the absorption spectrum and ¹H NMR spectroscopic studies upon the titration with F^- , AcO^- . **R1** detects anions and metal ions at nanomolar level. F^- ion detection property of **R1** in aqueous medium was also extended to the real samples like toothpaste and mouthwash.

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1. Introduction

Development of the chemosensors capable of recognizing and sensing both cations and anions is major interest in host–guest chemistry. Dual sensing has considerable attention in recent decades due to the fact that a large number of biological processes involve molecular recognition of anionic and cationic species [1–8]. Nowadays, the development of colorimetric anion sensing is particularly challenging because the color change, in the signalling event detected by the naked eye, without the help of instrument. This method is widely accepted due to the low cost and easy detection. Generally, any chemosensors consist of signaling (chromophore/fluorophore) and binding moieties. Usually N or O donor centers such as imine (CH=N) [9–12] hydroxyl (–OH), [13,14] amide (–CONH), [15–17] urea ((NH₂)₂C=O)) [18–21,22], thiourea ((NH₂)₂C=S) [23–26], pyrrole (–NH) [27,28] and coumarin derivatives [29,30] act as binding sites for both cations and anions. During recent years, there is an upsurge in the field of colorimetric sensing of transition metal ions by organic molecules. Simultaneous sensing of both types of charged analytes has been achieved by integrating cationic and anionic binding sites in a single molecule. Among the cations, special attention is devoted for the colorimetric sensing of toxic and heavy metal ions. Among these metal ions, cadmium is

one of the important natural element and highly toxic. It accumulates in cells, liver and kidneys, thyroid glands and spleen resulting in the physiological disorders or carcinogenic effects. Anions such as fluoride, chloride, bromide, iodide, dihydrogen phosphate and acetate play important roles in biological, industrial, and environmental processes [31,32]. Among various anions, acetate (AcO^-) ion has attracted the interest of chemists since, it is a critical component of numerous metabolic processes and the rate of AcO^- production and oxidation have been frequently used as an indicator of organic decomposition in marine sediments [33]. Fluoride is one of the essential element used in variety of biological processes such as preventing children's dental caries and treating osteoporosis [34–36]. Thus, there is a need to develop receptors which can dually recognize biologically important anions and cations. We have recently concentrated on the system that can sense both biologically active anions and transition metal ions. Upto now, most of the reported chemosensors, the cation and anion analytes were utilized in pure organic medium or in mixed aqueous medium [37–41]. The design and syntheses of chemosensors which can work in pure aqueous analyte solution with high sensitivity, have become more important. Still now, only a few sensors have been designed for anion recognition in the aqueous phase [42,43]. This diversity made an interest to develop anion sensor **R1** that work in DMSO and in H₂O solutions by colorimetric titration and UV–vis spectroscopy. Thiosemicarbazone without azo linkage has been already reported by us as fluorescent chemosensor for transition metal ions [44]. Thiosemicarbazone without azo linkage were not showing any color change towards any anions and Cd^{2+} . It sense

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only cations like Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+} ions though the binding site is same as in **R1**. Therefore, azo group influences the detecting event in **R1**. The group like $-\text{OH}$ present in the **R1**, act as auxochrome.

In this article, we report the synthesis of the thiourea based **R1** by simple condensation method. **R1** makes beneficial use of colorimetric and fluorescent sensing for the detection of F^- , AcO^- and cadmium ions in aqueous medium. The sensing ability of **R1** with anions and cations were further investigated by UV–vis and fluorescence spectroscopic method. The interaction of **R1** with F^- and AcO^- also has been evaluated using ^1H NMR spectroscopy. Additionally, the sensing of F^- and AcO^- was confirmed by using fluoride, acetate source of alkali metal ions like sodium fluoride and sodium acetate. It was found that **R1** detects F^- , AcO^- and Cd^{2+} even at nanomolar level. Detection of F^- was further extended to analyse real samples like toothpaste and mouthwash. To the best of our knowledge, for the first time we are reporting the synthesis and dual sensing property of **R1** in aqueous medium.

2. Experimental studies

2.1. Materials and spectroscopic methods

All reagents used for synthesis was obtained commercially and used without further purification. Thiosemicarbazide, salicylaldehyde, aniline were the starting materials used. In the titration experiments, all the anions were added in the form of tetrabutylammonium (TBA) salts, whereas iron, cobalt, nickel, copper, tin and chromium were added as their chlorides. Zinc, cadmium, lead, mercury, manganese and sodium were added as their acetates. Mercury was added as its nitrate. Sodium fluoride and analytical grade solvents such as dimethyl sulfoxide (DMSO) and ethanol (EtOH) were purchased from Sigma Aldrich and used as such. Shimadzu UV-2600 UV–vis spectrophotometer was used to record UV–vis spectra using quartz cell with 1 cm path length. Fluorescence emission spectra were recorded in a Shimadzu RF-5301 PC spectrofluorophotometer at a scan rate of 500 nm/slit width with Ex: 10 nm, Em: 10 nm. Excitation wavelength set was 300 nm. 5×10^{-5} M solution of **R1** in DMSO and 1.5×10^{-5} M solutions of the anions and cations in H_2O were prepared. 0.2 equiv.–2 equiv. of guest solution was added to 3 mL of **R1** taken in the UV cuvette.

2.2. Synthesis and characterization of **R1**

The intermediate for **R1** (Scheme 1) synthesized according to a reported method [45], was used to synthesize **R1** by refluxing with thiosemicarbazide in ethanol for 3 h. The solid precipitated out was filtered and then recrystallized from n-hexane (Scheme 1). Yield: 90%; m.p. 225 °C; IR (KBr, cm^{-1}) ν : (C=N) 1638, (N–H) 3093, (OH) 3467. ^1H NMR (400 MHz, DMSO- d_6 δ_{ppm}) 7.03–7.06 d (Aromatic H), 7.51–7.59 m (Aromatic H), 7.76–7.85 m (Aromatic H), 8.10–8.17 s (NH_2), 8.44 s (NH), 8.570 s (HC=N), 11.48 s (OH). ^{13}C NMR (100 MHz, DMSO- d_6): δ 116.81, 121.03, 122.16, 123.13, 123.93, 129.32, 130.72, 138.54, 145.34, 151.99, 159.34, 177.77. HRMS: Calcd.: 298.0757, found: 298.0759 (Figs. S1–S4).

3. Results and discussion

3.1. Colorimetric sensing studies

The colorimetric sensing ability of **R1** with anions, (F^- , Br^- , Cl^- , AcO^- , H_2PO_4^- and HSO_4^-) transition metal ions (Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} , Hg^{2+} , Mn^{2+} , Sn^{2+} and Cr^{3+}) and fluoride/acetate salts of alkali metal ions (anion sources of Na^+) in aqueous medium was monitored by visual color change method.

In naked-eye experiments, **R1** (5×10^{-5} M in DMSO) showed dramatic color change from pale orange to red color in the presence of F^- and AcO^- (Fig. 1a). To check the sensing ability of **R1** in organic–aqueous medium, all anions were taken in pure aqueous medium and **R1** was taken in DMSO: H_2O mixture in the ratio of 40:60. In the presence of F^- and AcO^- (1.5×10^{-5} M in H_2O), **R1** (5×10^{-5} M in DMSO: H_2O (40:60, v/v)) shows a color change from pale orange to orange (Fig. 1b). **R1** was found to be insensitive to addition of Br^- , Cl^- , H_2PO_4^- and HSO_4^- . Similarly, fluoride/acetate salts of alkali metal ions (1.5×10^{-5} M in H_2O) also induced the change in color of **R1** from pale orange to red color (Fig. 1c). Color change may occur due to the interaction of anions with **R1** through hydrogen bonding with $-\text{OH}$, $-\text{NH}$ groups. This hydrogen bonding interaction affect the electronic properties of chromophore that results in the color change along with a new charge–transfer interaction between the anion. Similarly the same colorimetric titration was extended to **R1** in DMSO medium with same concentration of **R1** and cations. The addition of transition metal ions (Fe^{3+} , Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Cd^{2+} , Pb^{2+} , Hg^{2+} , Mn^{2+} , Sn^{2+} and Cr^{3+}) to **R1** does not show any visible color change (Fig. S5). The colorimetric responses of the **R1** to other cadmium salts like $\text{Cd}(\text{AcO})_2$, CdCl_2 , $\text{Cu}(\text{NO}_3)_2$, and $\text{Cd}(\text{SO}_4)_2$ was carried out (see supporting information). There is no divergence in color change in the presence of other cadmium salts. From this result it can be inferred that Cd^{2+} ions selectively sense in the presence of counter anions ((Fig. S5).

3.2. UV–vis spectroscopic studies

The sensing behaviour of **R1** towards anions and different transition metal ions was also investigated through spectrophotometric titrations in mixed aqueous medium. The spectroscopic titrations were carried out in DMSO medium. The addition of tetrabutyl ammonium salts of fluoride, bromide, chloride, acetate, dihydrogen phosphate, hydrogen sulphate and hydroxide ions (1.5×10^{-5} M in DMSO) to the solution of **R1** (5×10^{-5} M in DMSO), showed a new and strong absorption band at 480 nm for F^- and AcO^- ions (Fig. 2a). As evident from Fig. 2a, addition of anions, such as Br^- , Cl^- , H_2PO_4^- , HSO_4^- , I^- , NO_3^- , CHO_3^- and CO_3^{2-} did not show any significant change in λ_{max} . Upon the incremental addition of 0–100 μL of F^- and AcO^- ions to **R1**, the absorption band at 480 nm was increased gradually whereas the band at 335 nm was decreased gradually with the isosbestic point at 388 nm (Figs. S6 and S7). The formation of new band at 480 nm is due to the breakage of intramolecular hydrogen bonding and the formation of new complex between anion and **R1**.

As the second experiment, to check the sensing ability of aqueous mediated anions with **R1** was carried out. In general, hydration will terminate the anion sensing behaviour, water the strong competitive solvent in the hydrogen bonding and lead to the leaching of anions and regenerate the receptor molecule. Interestingly, present system displayed the anion recognition process in complete aqueous medium without the regeneration of **R1**. Further 2 equiv. of anions such as F^- and AcO^- ions in H_2O were added to the **R1** (5×10^{-5} M in DMSO: H_2O (40:60, v/v)), it showed a intense absorption band at 500 nm over the other anions like Br^- , Cl^- , H_2PO_4^- , HSO_4^- , I^- , NO_3^- , CHO_3^- and CO_3^{2-} . Upon the incremental addition of F^- and AcO^- (Figs. S8 and S9) ions in aqueous medium, the intensity of the new band at 500 nm was progressively increasing and the band at 330 nm gradually decreasing with an isobestic point at 388 nm (Fig. 2b). Similar absorption spectrum was observed with the addition of sodium salt of acetate and fluoride in aqueous medium (Fig. 2c). In the same way, third experiment was done to check the optical properties of **R1** with different metal cations in aqueous medium. The presence of other cations did not show any optical changes except cadmium (Fig. 2d). From this result, **R1**

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