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Novel colorimetric sensors for cyanide based on azo-hydrazone tautomeric skeletons

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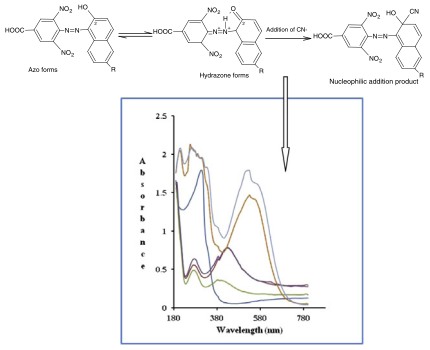
HIGHLIGHTS

- Azo-hydrazone tautomeric switch detected CN.
- Bathochromic shift produced.
- CN detected at low levels.
- Simple methods developed.

GRAPHICAL ABSTRACT



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ABSTRACT

The monoazo dyes, 4-carboxyl-2, 6-dinitrophenylazohydroxynaphthalenes dyes (AZ-01, AZ-03 and AZ-04), were evaluated as a highly selective colorimetric chemosensor for cyanide ion. The recognition of cyanide ion gave an obvious colour change from light yellow to brownish red and upon dilution with acetone produced a purple to lilac colour.

Optimum conditions for the reaction between the azo dyes and cyanide ion were established at 30 °C for 5 min, and different variables affecting the reaction were carefully studied and optimised. Under the optimum conditions, linear relationships between the CN^- concentrations and light absorption were established. Using these azo-hydrazone molecular switch entities, excellent selectivity towards the detection of CN^- in aqueous solution over miscellaneous competitive anions was observed. Such selectivity mainly results from the possibility of nucleophilic attack on the azo-hydrazone chemosensors by cyanide anions in aqueous system, which is not afforded by other competing anions.

The cyanide chemosensor method described here should have potential application as a new family probes for detecting cyanide in aqueous solution.

Introduction

Colorimetric sensors have become very popular in recent years due to their capability to detect and in some instances to semi-quantitate analyte by naked eye detection without resorting to expensive instrumentation [1]. The colorimetric chemosensors are therefore considered as one of the most effective analytical method for environmental monitoring [2–6], particularly detection of major cationic and anionic species whose presence in the environment have deleterious consequences.

Cyanides are naturally occurring substances found in a number of foods and plants and produced by certain bacteria, fungi, and algae. Cyanide can enter the environment as a result of both natural and industrial processes [7]. The primary source of cyanide

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in the air is from car exhaust. Other airborne sources include emissions from chemical processing, other industries and municipal waste incinerators. Cyanide fishing also contributes to pollution of waters in areas used for fishing exotic fish such as the coral reefs areas [8]. Smoking is another important source of cyanide. Cyanide is a component of the tabun, the chemical warfare agent [8]. Cyanide may be found in water from discharges from organic chemical industries, iron and steel works, and wastewater treatment facilities. Exposure to cyanide may also occur in the workplace such as from electroplating, metallurgical, fire fighting, steel manufacturing and metal cleaning industries.

Cyanides are well-known toxic materials and are extremely harmful to the environment and human health. EPA regulates the levels of cyanide that are allowable in drinking water. The highest level of cyanide allowed in drinking water is 0.2 parts cyanide per 1 million parts of water (0.2 ppm). The Occupational Safety and Health Administration (OSHA) has set a limit for hydrogen cyanide and most cyanide salts of 10 parts cyanide per 1 million parts of air (10 ppm) in the workplace [9].

The need to detect and determine cyanides has led to the development of several chemosensor probes based on fluorescence and UV–VIS absorption measurements. Yu et al. [10] gave an excellent review of the various chemical species and their mechanisms of cyanide detection in various media. Some of the compounds that have been used include Zn(II)–porphyrin, Ru(II)–pyridine, boronic acid derivatives, CdSe quantum dots, copper–cyanide affinity, oxazine, pyrylium, squarane, acyltriazene, acridinium, salicylaldehyde, trifluoroacetophenone or trifluoroacetamide derivatives. The trifluoroacetamide derivatives were particularly reported to demonstrate high sensitivity and good selectivity towards cyanide [11–33]. Each of the CN^- chemosensors provided specific advantages; however, many operate using complex systems. The need to devise simple CN^- chemosensor led to the utilization of 4-carboxyl-2, 6-dinitrophenylazohydroxylnaphthalenes [34] as novel CN^- detecting system. Three of the four congeneric monoazo dyes exist principally in the hydrazone tautomeric forms [35]. The mechanism envisaged is that binding of CN^-, if it restores the azo tautomer should give rise to specific absorption changes characterised by bathochromic and/or hyperchromic shifts. These shifts in appropriate solvents should provide a ready, convenient and simple detection system for cyanide ions.

Experimental

Chemical and reagents

Acetone, methanol, dimethylformamide (DMF), Dimethylsulphoxide (DMSO), Ethanol, KCN, Sodium thiosulphate ($Na_2S_2O_3$), Sodium nitrate ($NaNO_3$), Sodium nitrite ($NaNO_2$), Sodium hypochlorite (NaOCl), Sodium sulphite (Na_2SO_3) (all analytical reagent grade obtained from BDH chemical limited, Poole, England).

Azo dyes utilized

The dyes utilized in this study were as previously synthesised by Adegoke et al. [34] and include the three congeners of 4-carboxyl-2,6-dinitrophenylazohydroxylnaphthalenes that exhibited azo-hydrazone tautomerism namely; AZ01-{6-hydroxyl-5-(4-carboxyl-2,6-dinitrophenylazo)-naphthalene, AZ03-{6-hydroxyl-5-(4-carboxyl-2,6-dinitrophenylazo)-naphthalene-2-(propan-2-oic acid) and AZ04-{6-hydroxyl-5-(4-carboxyl-2,6-dinitrophenylazo)-naphthalene-2-(butan-2-one).

Instrumentation

Mettler analytical balance (Ohaus, USA), thermostated water bath and UV–visible spectrophotometer 6405 (Jenway, UK).

Preparation of stock solutions

For the cyanide stock solution, a 10 mg quantity of potassium cyanide (KCN) was dissolved in 10 mL water to make 1 mg/mL of the cyanide stock solution. Additionally, 10 mg quantity of each dye (AZ-01, AZ-03, and AZ-04) was separately dissolved in 10 mL of DMSO to make 2.616 mM, 2.203 mM and 2.212 mM respectively.

Measurement of UV–VIS spectrum of sample solutions

A 0.5 mL aliquot of the cyanide stock solution was diluted with acetone to 5 mL. The absorbance of the cyanide solution was then recorded from 190 – 800 nm to determine its maximum wavelength. Similarly, a 0.1 mL aliquot of each dye was diluted with acetone to 5 mL and the UV–VIS absorption spectrum was recorded.

Preparation of the azo dye-cyanide adduct

A 0.1 mL quantity of the azo dye was measured into a volumetric flask and 0.5 mL of the cyanide was added. The solution was allowed to stand for 10 min and finally diluted with acetone up to 5 mL final volume. For each dye-cyanide adduct solution, the absorption spectrum was recorded. The effect of other various solvents on the absorptivity of the dye-cyanide adducts were studied using the optimal analytical conditions described above and replacing the acetone as diluting solvent with each of DMF, DMSO, Ethanol, Methanol, and Water and the spectra were recorded from 190–800 nm using the spectrophotometer.

Optimisation of temperature and time required for adduct formation

The optimum temperature required for the formation of adducts between cyanide and the azo dyes and the time required at the optimum temperature were determined using the method of steepest ascent [36] at temperature levels of 30, 50, 60 and 70 °C for 5 and 20 min interval. At the end of the reaction time, the solution was cooled in ice-cold water, and diluted to 5 mL with acetone and the absorbance were recorded at the respective λ_{max} of the adduct.

For the optimisation of time, 0.5 mL quantity of the cyanide stock solution (1 mg/mL) was added to 0.1 mL of each respective (1 mg/mL) dye. The reaction mixture was allowed to stand for varying time interval, 0, 2, 5 10, 15 20, 25, and 30 min respectively at 30 °C. The reaction was terminated by making up to 5 mL with acetone at each of the various time intervals. Each determination was done in duplicate. The absorbance readings of the complex were taken at their respective wavelength maxima and the optimal reaction time was taken as the time corresponding to the maximal absorption of the sample.

Stoichiometric ratio for the azo-cyanide adduct formation

For stoichiometric ratio determination, Job's method of continuous variation [37] was adopted. Equimolar solutions of the cyanide and dye stock solutions were utilized. Various volumes of each dye were made up to 1 mL with the cyanide stock solution. The final solution was allowed to react at 30 °C for 10 min and then processed as done previously.

Calibration curve for the azo dye-cyanide adducts

Calibrations for the determination of cyanide were carried out using the optimal analytical conditions as described above. Linear