Canadian Journal of Chemistry
Revue canadienne de chimie

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Journal:	<i>Canadian Journal of Chemistry</i>
Manuscript ID	cjc-2017-0163.R1
Manuscript Type:	Article
Date Submitted by the Author:	12-Apr-2017
Complete List of Authors:	Koc, Omer Kaan; Canakkale Onsekiz Mart University Ozay, Hava; Canakkale Onsekiz Mart University, Chemistry
Is the invited manuscript for consideration in a Special Issue?:	N/A
Keyword:	Azo dye, 8-hydroxyquinoline, colorimetric sensor, cyanide ion, aqueous media

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A simple azoquinoline based highly selective colorimetric sensor for CN^- anion in aqueous media

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Abstract

Azoquinoline based sensor **AZQ** was designed and synthesized as a new molecular ion sensor containing an azo group in its structure. The structural characterization of **AZQ** was carried out using FT-IR, NMR, Mass and Elemental analysis. Then, the interaction of **AZQ** with anions was observed visually and UV-Vis measurements were made in EtOH/H₂O (1:1, v/v) solvent mixture. As a result of this investigation, it was determined that **AZQ** is a fast and highly selective sensor for CN⁻ ions. The solution color of **AZQ** changed from light yellow to orange only in the presence of CN⁻ ions. The limit of detection of **AZQ** was calculated as 2.6 μM from anion titration experiments. Also, to identify the interaction mechanism of **AZQ** with CN⁻ ions, ¹H NMR spectra of **AZQ** in the presence of CN⁻ anions were recorded and the structure was proposed for **AZQ**-CN⁻ host-guest complex.

Keywords: Azo dye, 8-hydroxyquinoline, colorimetric sensor, cyanide ion, aqueous media.

Introduction

Anions are one of the most important natural species due to functions in many environmental, chemical and biologically vital processes.¹ Cyanide ions used in many industrial processes are one of the most toxic ionic species. Therefore, the determination of cyanide ions in aqueous environment is a very interesting subject.² In addition, cyanide anions strongly coordinate with transition metals due to their high nucleophilic character. Thanks to these properties, cyanide anions may bind to Fe(III) ions in the active center of enzymes and proteins such as cytochrome-c and hemoglobin when the amount of cyanide in the living organism rises above safe limits. This situation leads to disruption of biological processes such as electron transport chain, oxidative metabolism, oxygen utilization and transport affecting vision, cardiovascular, central nervous system, heart, endocrine and metabolic systems in the living organism. For this reason, cyanide can lead to direct death and is a highly toxic anion.³⁻⁵

Although the cyanide anion is highly toxic, it is still frequently used in many industrial processes/applications such as metallurgy, polymer production, paint, textile, automotive industries and mining sectors. The amount of cyanide waste entering surface waters as a result of these industrial activities increases due to the fact that decomposition is very difficult in nature.⁴⁻⁶ The maximum contaminant level (MCL) for free cyanide is 0.2 mg/L according to United States Environmental Protection Agency (US EPA).⁷ Therefore, the development of simple, inexpensive, highly efficient and sensitive sensors for cyanide anions is extremely important.

In recent years, analysis techniques involving chromatographic, voltammetric and titrimetric methods for cyanide detection have been developed by research groups.⁸ However, these methods have some disadvantages such as requiring expensive equipment and trained personnel as well as involving complex processes and long analysis times.⁶ Therefore, the design of simple, fast and selective chemical sensors with naked-eye properties for cyanide

anions has attracted attention. Designed molecules typically contain two units; the detection unit and the signal unit. In the literature, a large number of molecules have been synthesized urea and thiourea,⁹⁻¹¹ phenol,^{6,12} pirol¹³ and porphyrin¹⁴ nitrofenil,¹⁵⁻¹⁷ anthraquinone,^{18,19} phthalimide-hydrazone²⁰ and naphthopyran derivative²¹ compounds containing the units interacting with cyanide anions.

In the light of this information, we synthesized an azo dye compound (**AZQ**) as selective sensor for the detection of cyanide anions in EtOH/H₂O (1:1, v/v, pH=6) solvent mixture. The structure of **AZQ** was characterized using spectroscopic techniques. Also, sensor behavior of **AZQ** for cyanide anions was investigated using both colorimetric and spectrophotometric methods in EtOH/H₂O (1:1, v/v, pH=6) solvent mixture. It was determined that **AZQ** has excellent selectivity for cyanide anions.

Experimental

Materials and methods

All chemicals and solvents were purchased from Sigma-Aldrich and used without purification. Distilled water was used in all experimental applications. Fourier Transform Infrared (FTIR) spectrum of **AZQ** was recorded with a Perkin Elmer FT-IR spectrophotometer using ATR apparatus at the range of 4000-650 cm⁻¹. ¹H-NMR and ¹³C-NMR spectra and ¹H-NMR titration experiments were recorded using JEOL NMR-400 MHz instrument. In the NMR measurements, DMSO-d₆ was used as the solvent and tetramethylsilane (TMS) as interval standard. UV-vis spectra were recorded using PG Instruments T80+ spectrophotometer. The pH of the solution was adjusted to pH=6 using NaOH and HCl solution of in the sensor experiments. Mass spectra of **AZQ** were recorded using a SHIMADZU LC-MSMS-8040 instrument. Caution! Nitride and cyanide salts are

potentially toxic compounds. Therefore, even small amounts of these compounds should be used with caution.

Synthesis of AZQ

Aniline (0.56 g; 6.00 mmol) was added dropwise to a solution of 2 mL of hydrochloric acid (37%) in 10 mL water. To this solution was added dropwise 20% NaNO₂ solution (4 mL) for 1 h at 0 °C. During this time, the temperature of the mixture did not exceed 5 °C. The reaction mixture was stirred for 1 h at 0-5 °C. At the end of this time, a solution of 8-hydroxyquinoline (0.88 g; 6.00 mmol) in water containing 0.4 g NaOH (20 mL) was added dropwise to the mixture. The reaction mixture was stirred at 0 °C for 4 hours. Then the reaction mixture was neutralized with hydrochloric acid. The resulting brown solid was filtered and dried. The crude product was crystallized twice from ethyl alcohol and **AZQ** was obtained as a yellow solid (yield 90%; m.p. 190 °C). FTIR-ATR (v_{max}, cm⁻¹): 3378 (O-H), 1570 and 1514 (C=C). ¹H NMR (400 MHz, DMSO-d₆, 25 °C): δ 10.86 (b, 1H, OH), 9.33 (d, J= 8.40 Hz, 1H), 8.97 (m, 1H), 7.96 (t, 3H, J= 7.25 Hz), 7.76 (dd, 1H), 7.57 (t, J= 7.25 Hz, 2H), 7.50 (t, J= 7.25 Hz, 1H), 7.23 (d, J= 8.40, 1H). ¹³C NMR (100 MHz, DMSO-d₆, 25 °C): δ 157.50, 152.97, 148.98, 139.00, 137.09, 133.98, 131.44, 129.99, 128.21, 123.84, 123.04, 115.75, 112.95. LC MSMS m/z: Calcd for C₁₅H₁₁N₃O (M⁺), 249.27. Found: 250.07. Element analysis Calcd. for C₁₅H₁₁N₃O C 72.28, H 4.45, N 16.86 %; Found C 72.19, H 4.58, N 16.81 %.

General procedure of sensor experiments

A stock solution (1x10⁻³) of **AZQ** was prepared in ethanol. The stock solutions (1x10⁻² M) of anions were prepared using the tetrabutylammonium salts of various anions (F⁻, Cl⁻, Br⁻, I⁻, CN⁻, SCN⁻, NO₂⁻, NO₃⁻, HSO₄⁻, H₂PO₄⁻, CH₃COO⁻) in DMSO. The stock solution (1x10⁻² M) of S²⁻ anion was prepared using sodium salt in deionized water. To determine the selectivity of **AZQ**, the stock solutions of **AZQ** and anions were added to 2 ml of EtOH/H₂O (1:1; v/v,

pH=6) solvent mixture. The UV-vis spectra of the prepared solutions were recorded using quartz cuvette with 1 cm light path in the range of $\lambda = 200\text{-}800\text{ nm}$. The concentration of **AZQ** was $25\text{ }\mu\text{M}$ in the selectivity and anion titration experiments. ^1H -NMR titration experiments were carried out by the addition of different amounts of tetrabutylammonium cyanide to the solution of **AZQ** in $\text{DMSO-}d_6$.

Results and discussion

Synthesis and spectral characterization

AZQ was synthesized as a result of the azo coupling reaction of aniline with 8-hydroxyquinoline in two step (**Scheme 1**). The structure of **AZQ** was characterized by FT-IR, ^1H -NMR, ^{13}C -NMR and MS spectrometry techniques. In the FT-IR spectrum of **AZQ**, an O-H stretching band was observed at 3378 cm^{-1} as a broad band. The characteristic C=C stretching bands for aromatic compounds were observed at 1570 and 1514 cm^{-1} . In the ^1H NMR spectrum (**Fig. 1(a)**) of **AZQ**, the signal of the azomethine (HCN) group 8-hydroxyquinoline was observed at $\delta = 9.33\text{ ppm}$ as a doublet.²² The signals related to aromatic protons of **AZQ** were observed in the range of $9.0\text{-}7.20\text{ ppm}$. The -OH proton of **AZQ** was not observed in $\text{DMSO-}d_6$ at $25\text{ }^\circ\text{C}$.²³ Thirteen carbon signals were observed in the ^{13}C NMR spectrum of the compound (**Fig. 1(b)**). In the mass spectrum of **AZQ** a molecular ion peak was observed at 250.07 . All spectral data support the expected structure of **AZQ**.

3. 2. Anion recognition properties of AZQ

In recent years azo dyes have occupied an important place in anion recognition processes. Quinoline azodyes are important compounds due to their coordination capacity with metal ions.²⁴ 5-(phenylazo)-8-hydroxyquinoline (**AZQ**) was previously synthesized in the literature.²²⁻²⁵ However, the sensor properties of **AZQ** for anion species were not studied. In this study we investigated the sensor behavior of **AZQ** for F^- , Cl^- , Br^- , I^- , CN^- , SCN^- , NO_2^- ,

NO_3^- , HSO_4^- , H_2PO_4^- , CH_3COO^- and S^{2-} ions. As seen in **Fig. 2**, the color of the **AZQ** solution turned from light yellow to orange only in the presence of cyanide anions in an EtOH/ H_2O (1:1; v/v, pH=6) solvent mixture. The response time of **AZQ** was pretty fast. The color change was completed in a few seconds with the addition of cyanide. The determination of cyanide anions with the naked eye was possible thanks to this change in color of the solution. Anions may interact by forming strong hydrogen bonds with the acidic protons on the molecule. Then a lone pair of electrons forms on the heteroatom as a result of the deprotonation process. The formed electron pair delocalizes the host molecule and the conjugation in the molecule increases.²⁵ The change in color of **AZQ** in the presence of CN^- anions is a result of the delocalization of the lone electron pair on the resulting phenoxide oxygen by the deprotonation of -OH groups. Also, the sensor behavior of **AZQ** was investigated spectroscopically using a UV-Vis spectrophotometer. For this purpose, UV-Vis spectra of the solution of **AZQ** in the absence and presence of different anions in EtOH/ H_2O (1:1; v/v, pH=6) solvent mixture were recorded in the range of 200-600 nm. In the UV-Vis spectrum of free **AZQ**, an absorption band was observed at $\lambda = 385$ nm while a new absorption band centered at $\lambda = 480$ nm appeared in the presence of CN^- anions (**Fig. 3**). A slight increase in absorbance at $\lambda = 480$ nm was observed in the presence of S^{2-} ions. However, the addition of other anions did not cause any absorption changes. **AZQ** has excellent selectivity for CN^- anions over other anions in EtOH/ H_2O (1:1; v/v, pH=6) solvent mixture. To in the presence of NaCN in o determined the effect of counter cation, we investigated the sensor behavior of **AZQ** EtOH/ H_2O (1:1; v/v, pH=6) solvent mixture. As can be from the **Fig. 3(c)** and **(d)**, counter cation has no effect on sensor properties of **AZQ**.

The limit of detection (LOD) is a very important parameter in ion sensing. To determine the detection limit of **AZQ** for CN^- ions, a titration study was performed using a UV-Vis spectrophotometer. For this purpose, UV-Vis spectra of **AZQ** (25 μM) were recorded in the

presence of different amounts of CN^- anions (0–140 μM) (**Fig. 4(a)**). As can be seen from the figure, the absorption intensity at $\lambda = 480$ nm increased with the addition of CN^- anions. Also, the absorbance at $\lambda = 380$ nm simultaneously decreased. A good linear relationship was obtained in the range 0–140 μM for CN^- concentration in the UV-Vis titration curve. The LOD of **AZQ** was calculated as 2.6 μM from $A-A_0$ versus the concentration of CN^- anion curve (**Fig. 4(b)**). The maximum contaminant level (MCL) for free CN^- anions is 0.2 mg/L according to the United States Environmental Protection Agency (US EPA).⁷ The LOD value of **AZQ** is lower than the level determined by the EPA for CN^- anions in drinking water. Also, the LOD value of **AZQ** for CN^- anions was compared with previously reported sensors in the literature (**Table 1**). **AZQ** has some advantages such as simple synthesis procedure, high selectivity and the ability to use in solutions with high water content.

In order to determine the stoichiometric ratio of CN^- ions with **AZQ**, the method of continuous change (Job's plot) was used. The total concentration of **AZQ** and CN^- ions is kept constant at 100 μM while the mole ratio between **AZQ** and CN^- is changed. As seen from **Fig. 5 (a)**, the stoichiometric ratio between CN^- ion and **AZQ** is 1:1. Additionally, the association constant was calculated as 3.33×10^4 ($R^2 = 0.9852$) using the Benesi-Hildebrand relationship in **Fig. 5(b)**.⁶

To examine the interaction mechanism of **AZQ** with CN^- anions, ^1H NMR titration experiments were performed. For this purpose, the ^1H NMR spectra were recorded in the presence of different amounts of tetrabutylammonium cyanide in DMSO-d_6 . In **Fig. 6**, the signal of the aromatic proton at the ortho position of phenolic OH of **AZQ** shifted into a high field region (from $\delta = 7.23$ ppm to $\delta = 6.81$ ppm, $\Delta\delta = -0.42$ ppm). This change in chemical shift is a result of the formation of the phenolate ion as suggested in similar systems.^{25,26} The proposed mechanism is given in **Scheme 2**.

To investigate the effects of other anions on the sensing properties of **AZQ** for CN^- anions, competing anion experiments were carried out. As seen from **Fig. 7**, when the CN^- anions are added to the mixture of **AZQ** (25 μM) and other anions (250 μM) in EtOH/ H_2O (1:1; v/v, pH=6) solvent mixture, the absorbance at $\lambda=480$ nm decreased remarkably in the presence of HSO_4^- and H_2PO_4^- anions. This observation is due to HSO_4^- ($\text{pK}_a=1.92$) and H_2PO_4^- ($\text{pK}_a=7.21$), which include acidic hydrogen, interfering with CN^- as reported in the literature for similar systems.^{3,25}

To investigate the utilization of **AZQ** as test strip in the practical application, test strips were prepared by immersing filter papers into a solution of **AZQ** followed drying in air. **AZQ** impregnated on filter paper strips give yellow color. After, this strips were dipped into anion solutions, orange color is generated only with cyanide ion. The results were given in the **Fig. 8**. As seen from the figure, it can be said that **AZQ** might have potential application as test strip for the detection of cyanide ions.

Conclusions

In summary, **AZQ** was designed and synthesized as a highly selective and sensitive chromogenic sensor for the detection of cyanide ions in highly aqueous media. **AZQ** provided naked eye sensing properties at room temperature. The interaction between **AZQ** and CN^- anions was illuminated using ^1H NMR and UV-Vis spectrometric techniques. The stoichiometric ratio between **AZQ** and CN^- anions was determined as 1:1 by Job's plot. The LOD of **AZQ** for CN^- anion was 2.6 μM and **AZQ** showed good selectivity towards CN^- anions in the presence of other anions. As a result, our new chromogenic sensor providing a simple sensitive analysis for the detection of CN^- anions in aqueous media is added to the literature.

Acknowledgements

The authors thank to Research Fund of the Çanakkale Onsekiz Mart University for financial support (Project Number: FYL-2016-1060).

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Scheme Captions

Scheme 1. Synthesis scheme of **AZQ**

Scheme 2. Proposed sensing mechanism of **AZQ** for the detection of CN^- ion.

Figure Captions

Figure 1. (a) ^1H NMR and (b) ^{13}C NMR spectrum of **AZQ**

Figure 2. The appearance of the solution of **AZQ** (25 μM) in the presence of different anions (250 μM).

Figure 3. (a) The UV–Vis absorption spectra of **AZQ** (25 μM) with different anions (250 μM) in EtOH/ H_2O (1:1; v/v, pH=6) solvent mixture, (b) The absorption intensity of **AZQ** at $\lambda = 480$ nm in the presence of different anions (1: Free **AZQ**, 2: CN^- , 3: F^- , 4: Cl^- , 5: Br^- , 6: I^- , 7: SCN^- , 8: NO_2^- , 9: NO_3^- , 10: HSO_4^- , 11: H_2PO_4^- , 12: CH_3COO^- , 13: S^{2-}), (c) The UV–Vis absorption spectra and (d) digital camera image of **AZQ** (25 μM) solutions in the presence of TBACN (250 μM) and NaCN (250 μM) in EtOH/ H_2O (1:1; v/v, pH=6) solvent mixture .

Figure 4. (a) The UV–Vis spectra of **AZQ** (25 μM) in the presence of different concentration of CN^- anion (0–140 μM) and (b) The anion titration curve of **AZQ** depending on the absorbance change for CN^- anion in EtOH/ H_2O (1:1; v/v, pH=6) solvent mixture.

Figure 5. (a) Job's plot of the interaction between **AZQ** and CN^- anion, (b) Benesi-Hildebrand relationship for the interaction **AZQ** and CN^- anion.

Figure 6. ^1H NMR spectra of **AZQ** in the presence of different equivalents of tetrabutylammonium cyanide in DMSO-d_6 .

Figure 7. The competitive assay of other anion for the selectivity of **AZQ** for CN^- anion 1: Free **AZQ**, 2 (Blank): **AZQ**+ CN^- , 3: F^- , 4: Cl^- , 5: Br^- , 6: I^- , 7: SCN^- , 8: NO_2^- , 9: NO_3^- , 10: HSO_4^- , 11: H_2PO_4^- , 12: CH_3COO^- , 13: S^{2-} .

Figure 8. The images of test strips of **AZQ** in the presence of different anions

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Graphical Abstract

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Scheme 1.

Figure 1.

Figure 2.

Figure 3.

Figure 4.

Figure 5

Figure 6.

Scheme 2.

Figure 7.

Figure 8.

Table 1.

The LOD values of current chemosensors for CN^- anion.

Sensors	Solvent system	LOD	Linear Range	Reference
Azo Schiff base	$\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (1:9, v/v)	1.9-5.2 μM	- ($R^2=0.9930$)	(12)
Coumarin based sensor	$\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (1:1, v/v)	0.14 μM	0-30 μM ($R^2=0.9950$)	(16)
Azo dye-based colorimetric sensor	$\text{DMSO}:\text{HEPES}$ (8:2, v/v)	10.3 μM	0-16 μM ($R^2=0.9132$)	(25)
Diketopyrrolopyrrole based sensor	THF	0.75 μM	1-10 μM ($R^2=0.9980$)	(13)
Imidazo-anthraquinones	$\text{CH}_3\text{CN}:\text{H}_2\text{O}$ (9:1, v/v)	3.6 μM	-	(19)
Schiff base based sensor	$\text{DMSO}:\text{H}_2\text{O}$ (9:1, v/v)	0.4 μM	-	(2)
Phenothiazine derivative sensor	CH_3CN	3.2×10^{-3} μM	0-6.4 μM ($R^2=0.9913$)	(27)
Azoquinoline derivative sensor	$\text{EtOH}:\text{H}_2\text{O}$ (1:1, v/v)	2.6 μM	0-140 μM ($R^2=0.9926$)	This work