

A water-soluble fluorescent fluoride ion probe based on Alizarin Red S–Al(III) complex

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Abstract

A new water-soluble fluorescent fluoride ion signaling system has been developed based on the ligand exchange mechanism in aqueous medium. This procedure is based on the exchange of two Alizarin Red S (ARS) molecules coordinated to Al(III) by fluoride ion without interference from other common anions. The binary complex of ARS with Al(III) provides a sensitive signaling system for fluoride ion in the concentration range from 5×10^{-6} to 3×10^{-4} M. The ligand exchange reaction of ARS–Al(III) complex with fluoride ion has been investigated by UV–vis and fluorescence spectroscopies combined with the AM1 semi-empirical quantum chemical calculations. The pale orange fluorescence ($\lambda_{\text{max}} = 575$ nm) exhibited by the complex upon excitation at 435 nm decreases in intensity with fluoride addition with a detection limit of 0.1 mg L^{-1} .

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1. Introduction

Fluoride ion quantification in environmental and industrial wastewaters is important [1] due to its vital health implications [2]. Currently available methods for fluoride detection include ^{19}F NMR [3], electrochemical (ion selective electrodes) [4,5], chromatography [6] and chromogenic sensing systems [7,8] involving spectrophotometry [9,10]. Chromogenic sensors for anions consist of two parts: anion receptors and chromophores [11]. The different types of chromogenic anion sensors are classified based on their non-covalent interactions as, electrostatic [12], NH-based hydrogen bonding [13–15], Lewis acid [1,2,16,17] and combinations of these interactions working together [18]. Only a few of these receptors function in aqueous medium [1,2,17], as water competes with the receptor for fluoride ion [19]. An impetus for the development of alternative strategies has been the use of Lewis acid [2,17] receptors and this led us to explore the known field of ARS and its metal complexes in search of a new fluorescent fluoride sensor.

ARS (Fig. 1) derivatives [15] and its complexes with zirconium [20], lanthanum [6,21], thorium [22] and cerium [23,24]

have been used as reagents for fluoride ion determination with the mention of Al(III) interference. Each of these complexes have their limitations in fluoride binding, requiring either a support or an organic solvent. ARS is known to form a stable 2:1 fluorescent complex with Al(III) [25–29]. In our previous paper [30], we had arrived at a fluoride ion sensitive and selective signaling system using 8-hydroxyquinoline–Zr(IV)–EDTA complex and in continuation of this research program on design of novel fluoride sensors, we present the ARS–Al(III) complex, based on the Lewis acid–base reaction, with no support, a one-pot, completely water-soluble, inexpensive fluoride ion sensing system. The high affinity of Al(III) to fluoride ion [31,32] and the fluorescent characteristics of ARS–Al(III) complex [25] have been successfully utilized for fluoride detection (Fig. 1).

2. Experimental

2.1. Reagents

ARS from Sigma was re-crystallized according to the reported procedure [27]. AlCl_3 , sodium fluoride (NaF) and deionized water were used without further purification. All the other reagents and solvents used in this study were of guaranteed reagent grade.

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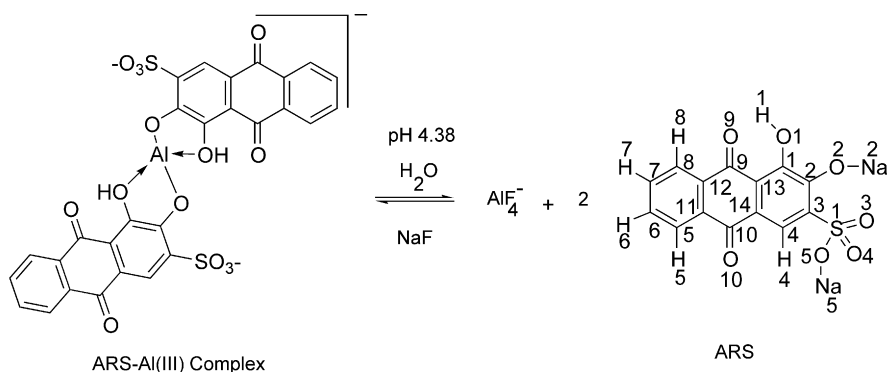


Fig. 1. Ligand exchange reaction of complex upon F^- addition.

2.2. Instrumentation

The fluorescence spectra were recorded on a Perkin-Elmer LS5 Luminescence Spectrometer, at a band path of 5 nm for excitation and emission. Electronic spectra were recorded on a Hitachi U-2001 spectrophotometer with 1 cm quartz cells.

2.3. Procedures

For the fluoride binding study of the ARS–Al(III) complex, ARS, $AlCl_3$ and NaF were dissolved in deionized water to obtain a stock solution of 2×10^{-3} M each and 100 mg L^{-1} fluoride ion, respectively. For the interference study, stock solutions of anions were prepared by dissolving NaCl, Na_2SO_4 , $NaNO_3$, Na_2HPO_4 , KI, KBr in deionized water and each of the stock solutions of cations were prepared by dissolving anhydrous $FeCl_3$ and $CuCl_2$. EDTA stock solution was prepared by dissolving Na_2 EDTA in deionized water. In 10 mL standard flasks, 1 mL of 2×10^{-3} M ARS, 0.5 mL of 2×10^{-3} M $AlCl_3$ solution and 100 μL of 0.08 M acetate buffer solution (pH 4.38) were added to solutions of various fluoride ion concentrations and made up to the mark with deionized water and were used to record the absorption and fluorescence spectra. Complexation equilibrium of each solution was ensured by allowing the solution to stand for 2 h at room temperature (25°C) and then the electronic and fluorescence spectra were recorded.

2.4. Calculations

The current study considered the ARS molecule, the corresponding dianion and its Al(III) complex theoretically in vacuo, using the semi-empirical quantum chemical calculations. Molecular-mechanics [33] MM^+ force field [34] was used for preoptimization of each of the starting geometries, followed by the Austin Model 1 (AM1) semi-empirical method [35] within the spin Unrestricted Hartree-Fock (UHF) formalism [36] to fully optimize the systems geometry. Polak–Ribiere algorithm [37], a conjugate gradient method, was employed for the AM1 geometry optimization with the RMS gradient set to 0.001 kcal/(\AA mol) and the SCF convergency set to 0.0001 kcal/mol. Configuration interaction treatment [38] was used to calculate the electronic absorption spectra. The con-

tribution by singly excited configurations involved the orbital criterion set to 10, i.e. the 10 highest occupied molecular orbitals (HOMO) and the ten lowest unoccupied molecular orbitals (LUMO) have been considered [39]. Hyperchem (version 7.0) program was used to perform all the calculations.

3. Results and discussion

ARS forms a stable 2:1 complex with Al(III) in aqueous medium, without hydrolysis of the aluminum ion [25–29]. The choice of 0.08 M pH 4.38 acetate buffer for the fluoride binding study with the binary ARS–Al(III) complex was two-fold, to avoid precipitation of the aluminum-hydroxy species and to ensure complete complexation between ARS and Al(III) possible only at $\text{pH} > 4$ [27].

3.1. Detection and binding of fluoride ion

A working concentration of 2×10^{-4} M ARS: 1×10^{-4} M $AlCl_3$ in water (pH 4.38) gave a red colored chelate (2:1 composition) with a characteristic band at $\lambda_{\text{max}} = 468 \text{ nm}$, involving a bathochromic shift of 43 nm when compared to the free ARS with a $\lambda_{\text{max}} = 425 \text{ nm}$. Inference drawn from these spectral changes is the complexation of ARS to $AlCl_3$. The solution gave a pale orange fluorescence with a $\lambda_{\text{em-max}} = 575 \text{ nm}$ upon excitation at $\lambda_{\text{ex}} = 435 \text{ nm}$ (isosbestic point). The excitation at the isosbestic point (435 nm) to obtain the fluorescence emission spectra was carried out instead at the band maxima (468 nm), as the fluoride ion fluorescence quenching studies of the complex were monitored better by excitation at 435 nm. For excitation at 468 nm, resulted in spectra where the fluorescence intensity of the free ARS was relatively high compared to the complex, than excitation at 435 nm, where the intensity of the free ARS was very low to that of the complex.

The absorption spectra of a series of solutions having the red colored chelate (2:1 composition) and different fluoride ion concentrations ranging from 0 to 6 ppm were recorded. With a successive increase in the fluoride ion concentration the complex peak at 468 nm showed a decrease in absorbance, while the free ARS peak at 425 nm showed an increase. Distinct isosbestic point at 435 nm (Fig. 2) was obtained from the series of absorbance spectra. A simultaneous and corresponding decrease

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