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9-Acridone-4-carboxylic acid as an efficient Cr(III) fluorescent sensor: Trace level detection, estimation and speciation studies

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ABSTRACT

9-Acridone-4-carboxylic acid has been established as an efficient Cr(III) fluorescent sensor. The binding of this ligand with Cr(III) is confirmed by FTIR, thermal and mass spectral analysis of the product. Based on this chelation assisted fluorescence quenching, a highly sensitive spectrofluorometric method is developed for trace level detection, estimation and speciation studies of chromium in DMF-water. The ligand has an excitation and emission maxima at 408 nm and 498.4 nm, respectively. The equilibrium binding constant of the ligand with Cr(III) is 8.1378×10^4 as calculated using Stern–Volmer equation. Up to 9×10^{-6} mol L^{-1} of [Cr^{3+}], linearity has been observed. The interference of foreign ions has been found to be negligible.

1. Introduction

Toxicological studies have indicated that the degree of toxicity of metal ions depends on its chemical form. The toxic nature of the Cr(VI) is attributed to its higher oxidation potential and relatively smaller size, which enables it to penetrate through biological cell membranes. Moreover, in air, chromium particulates play an important role in the oxidation of sulfur dioxide, leading to the formation of acidic aerosols responsible for global acid rain [1]. Cr(VI) has an adverse impact on liver, lung, kidney [2] and causes cancer by oxidizing the biological species such as DNA and some proteins [3].Cr(III) may be considered as an essential trace element for the proper functioning of living organisms (mammals), e.g.: for the maintenance of "glucose tolerance factor"; it is thought to be a cofactor for the insulin action and to have a role in the peripheral activity of this hormone. Metallic chromium or its compounds are widely used in anodizing operation in the surface industry, in making alloys, chrome plating, leather tanning, batteries, refractory, mordant dyeing, paints, welding, catalysis, corrosion control, oxidation, wood preservative and various other industrial applications [4,5]. Chromium species can enter into the environment from their discharge. They can also enter into drinking water supply systems from the corrosion inhibitors used in water pipes and containers. The threshold limit for chromium uptake in air is 0.1 mg m^{-3} and in water is 0.05 mg dm^{-3} [3]. Owing to these two contrasting effects, precise and accurate determination of both species in environmental samples is essential, in addition to the total chromium content [6–8]. Chromium content in natural waters is normally at μg L^{-1} level and there are also severe matrix interferences, which cannot be minimized. Therefore, the direct determination may not be possible with sufficient sensitivity and selectivity even by the methods such as flame atomic absorption spectrometry (FAAS) [9,10], graphite furnace atomic absorption spectrometry (GFAAS) [11,12], inductively coupled plasma atomic emission spectroscopy (ICPAES) [13], X-ray fluorescence spectrometry [14] and electrochemical methods [15,16]. Some forms of preliminary separation and pre-concentration like liquid–liquid extraction [17,18], cloud point extraction [19], ion-exchange [20,21] and solid phase extraction [22–24] are required. Bueno et al. [25] reported direct chromium speciation using X-ray spectrometry allied to chemometrics without separation / preconcentration of Cr species with a detection limits of 17 and 50 μg L^{-1} for Cr(III) and Cr(VI) respectively. X-ray fluorescence spectrometric determination of Cr(VI) after aliquat 336-AC assisted solid phase extraction was carried out by De Vito et al. [26] which required no elution process. Ghaedi et al. [27] reported a new Cr(III) selective electrode based on 1-[(2-hydroxyethyl) amino]-4-methyl-9H-thioxanthen-9-one as a neutral carrier with detection limit of 1.6×10^{-7} mol L^{-1}. Despite having good limits of detection and wide linear ranges, most of these techniques necessitate the use of sophisticated and costly apparatus and complicated operational procedure. Recently, the

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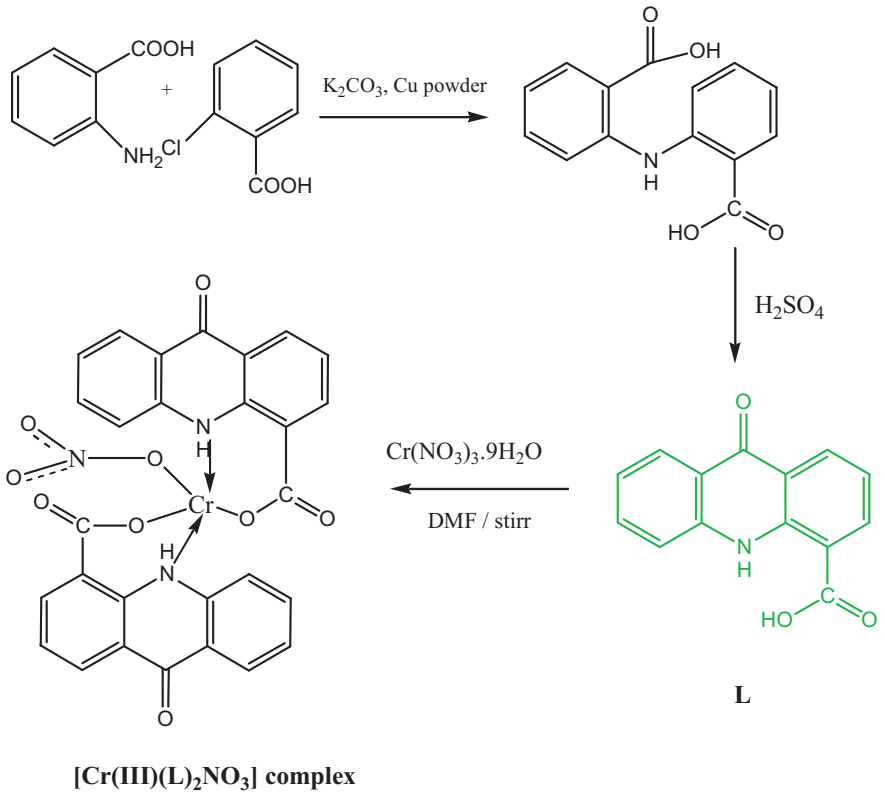

Scheme 1. Synthesis of the fluorescent chemosensor and its Cr(III) complex.

fluorescent method has become very popular due to its operational simplicity, high selectivity, sensitivity, rapidity, nondestructive methodology and direct visual perception [28]. For an efficient fluorescent sensor, in addition to high selectivity towards the ion of interest, a significant change in the fluorescence intensity in presence of the ion and /or a spectral change are required [29,30]. Although, recently a few Cr(III) selective fluorescent sensors [31–33] have been reported but report on trace level speciation and estimation of chromium species without separation of individuals by fluorescence quenching technique are rare [34]. Herein, we report the use of 9-acridone-4-carboxylic acid as an efficient and selective fluorescent sensor for Cr speciation. The developed method is very fast, simple, and inexpensive. The binding of the reagent with Cr(III) is firmly established by the ESI-MS (+) technique and supported by FTIR spectroscopy and binding constant measurement using Stern–Volmer method [35].

2. Experimental

2.1. Materials

2-Chloro benzoic acid (Alfa Aesar, India) and anthranilic acid (SRL, India) were purchased and used as received. All other chemicals and solvents were of analytical grade and used without further purification. Milli-Q 18.2 MΩ cm^{-1} conductivity purification system (Bedford, MA, USA) water was used throughout all the experiments. Cr(III) and Cr(VI) stock solutions were prepared from $Cr(NO_3)_3{\cdot}9H_2O$ and K_2CrO_4 (Merck, Dramstadt, Germany) respectively. The solutions 50 mg L^{-1} for Cr(III) and 5 mg L^{-1} for Cr(VI) were prepared in deionised water respectively. These solutions were standardized against standard stock solutions of Cr(III) (1000 mg L^{-1}) supplied by SOLUTIONS plus inc. (Missouri, USA) which were tested *vs.* NIST SRM # 3108a using AAS. The working solutions of Cr(III) and Cr(VI) were prepared by successive dilution of the stock solutions. The sources of Na^+, K^+, Ca^{2+}, Mg^{2+}, Mn^{2+}, Cr^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+}, Hg^{2+} and Pb^{2+} ions are either their chloride or nitrate salts.

2.2. Apparatus

Absorption and fluorescence spectra were recorded on Shimadzu Multi Spec 1501 absorption spectrophotometer and Hitachi F-4500 fluorescence spectrophotometer, respectively. Mass spectrum was recorded in QTOF Micro YA 263 mass spectrometer in ESI positive mode. IR spectra were recorded on a JASCO FTIR spectrophotometer (model: FTIR-H20). Thermogravimetric analysis was performed on a Perkin Elmer TG/DTA lab system l (Technology by SII). A VARIAN (Spectra AA 55) flame atomic absorption spectrophotometer (FAAS) (Australia) was used for measuring concentration of Cr(III) in the isolated Cr complex to confirm the structure of the L–Cr(III) complex. All measurements were performed using integrated absorbance (peak area). Hollow cathode lamp for Cr was operated at 7.0 mA at wave length 357.9 nm and at a slit width of 0.2 nm. Air and acetylene flow rates were maintained at 3.5 and 1.5 L min^{-1} respectively.

2.3. Synthesis of the ligand (L)

Scheme 1 shows the Ullmann condensation of 2-chlorobenzoic acid and 2-aminobenzoic acid followed by cyclization in the presence of sulfuric acid, produced 9-acridone-4-carboxylic acid [36].

2.4. Synthesis and Isolation of Cr(III) complex with L (Scheme 1)

DMF solution of Cr(III) (55.6 mg, 0.139 mmol of $Cr(NO_3)_3{\cdot}9H_2O$ in 5 mL DMF) was added to a methanolic solution of L (100 mg,0.418 mmol of L in 10 mL methanol) dropwise, and the mixture was stirred for 1 h (Scheme 1). The green reaction mixture