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A Selective Chemosensor for Cerium(IV) Based on Hydroxo-functionalized Naphthalenecarboxylic Acid**Amer A. Al Abdel Hamid***Department of Chemistry, Yarmouk University, Irbid 21163, Jordan.**Received on: 13th Jun. 2018;**Accepted on: 29th Jul. 2018*

Abstract: The commercial reagent *3-hydroxo-4-(2-hydroxo-4-sulfo-1-naphthylazo)-2-naphthalenecarboxylic acid* (HCC) was investigated for its potential in metal ions' detection. The interaction of the reagent with a wide spectrum of metal ions was studied using standard analytical and spectroscopic techniques (FTIR, UV/Vis, conductivity measurements and potentiometric titration). The reagent was found to show interesting photochemical properties that promote it to be a selective detector for cerium ions in aqueous solutions. The interaction between HCC and cerium (IV) sulfate was studied by UV/Vis spectroscopy. The effectiveness of HCC reagent as a chemosensor for cerium ions in aqueous matrix was high, where its sensitivity reached a detection limit of < 0.5ppm. The results presented in this report imply a valuable recruitment of an efficient colorimetric detector for cerium ions in aqueous solutions.

Keywords: Cerium(IV), Toxicity, Nanomaterial, Colorimetric chemosensor, Detection.

Introduction

In recent years, rare earth elements have been widely used in industry. Among them, we single out cerium. Cerium is considered one of the most fascinating lanthanide members of the rare earth metals^[1] and continues to attract researchers' attention owing to its remarkable reactivity and oxidability. Its oxidizing tendency is early attributed to the valence change^[1-3] from the trivalent state with one localized 4f-electron to the tetravalent metallic state.

Despite the exceptional importance in many uses^[4], especially in industry, cerium in the form of Ce(IV) has many other environment unfriendly applications. For examples, CeO₂ nanoparticles are predominantly employed as diesel fuel additive (combustion catalyst)^[5,6], where even of the efficient trapping of the CeO₂ particulates, a small amount is still emitted to the environment through the exhaust^[5,7]. Unfortunately, and owing to the dispersive nature of the engineered CeO₂ nanoparticles, there is an ongoing exposure through inhalation

of a large population to the new emissions containing CeO₂ nanoparticles. The high risk of exposure and interactions with the environmental media, thus the public health impacts, the intrinsic toxicity of Ce(IV) and the level of exposure to these novel materials cannot be underestimated. Therefore, the determination of Ce(IV) is paramount and absolutely critical^[8-10] in aqueous relevant environments^[11,12].

As a rule, and in order to determine the Ce(IV) ions, different methods such as inductively coupled plasma atomic emission spectrometry (ICP-AES)^[13], inductively coupled plasma-mass spectrometry (ICP-MS)^[14] and flame atomic absorption spectrometry (FAAS)^[15] are practically applied. However, these methods suffer from a number of disadvantages such as: complexity, expensive equipment and long duration. Additionally, the application of the photometric methods (such as: catalytic kinetic spectrophotometry^[16], chemiluminescence spectrophotometry^[17], UV methods involving chemical changes^[18] and fluorescence spectrophotometry^[19]) generally requires conducting a

multistep chemical reaction, where the inherent use of multiple different chemical reagents and substrates in such multistep reactions usually obstructs controlling the reaction conditions.

Polyaromatics are interesting chromophores, where the assembly of functionalized aromatic rings when interacting with electron deficient metal centers often yields chemical structures that are potentially workable as chemodetectors^[20-22] due to electronic transformations^[23-26]. As an alternative, the complete water soluble/ Ce(IV) sensitive agent (3-hydroxo-4-(2-hydroxo-4-sulfo-1-naphthylazo)-2-naphthalenecarboxylic acid, (HCC)) is here introduced (Figure 1). This agent which is aided by the hydroxo-hydrophilic and acidic carboxylic groups can serve as a Ce(IV) sensitive sensor that operates effectively as a new chemodetector for cerium(IV) ions in aqueous medium. The incorporation of Ce(IV) cations into either or both of the two

functionalities^[27-29] is expected to influence the absorption properties of HCC core, allowing thus access to a new potential chemosensor based on the chromophore-spacer-receptor concept.

In this investigation, a new and simple detection method for the determination of Ce(IV), utilizing the HCC-dye which absorbs energy in the visible region, is presented. Compared to other chemiluminescent dyes, HCC-dye possesses a number of advantages: high absorptivity, good stability, insensitivity to pH levels, wide wavelength range and solubility in water^[30,31]. Interestingly, and in addition to its superior and effective detection of Ce(IV) traces, HCC-Cerium(IV) system has shown, within a good range, a good linearity between the absorption intensity and the Ce(IV) ion concentration. Additionally, and compared with other methods, this method is characterized by a low detection limit.

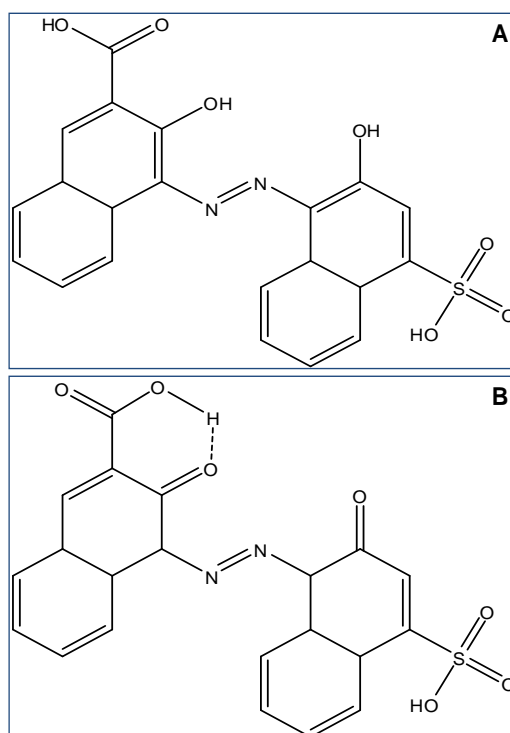


Figure 1. Structure of (a) 3-hydroxo-4-(2-hydroxo-4-sulfo-1-naphthylazo)-2-naphthalenecarboxylic acid, HCC, (b) Simplified structure showing the H-bonding of the COOH proton and keto-tautomeric formation of the phenolic hydrogens.

Materials and Method

All reagents were obtained from commercial sources and were used without further purification. Column chromatography was performed with Silica gel 60A/35–70 μm , Merck

Al_2O_3 90 basic (0.063–0.200mm). UV/Vis spectra were recorded for water solutions on a Shimadzu UV-1800 spectrophotometer using 1-cm quartz cuvettes. Infrared spectra were collected on an ALPHA-Bruker Optics. All IR spectra were recorded as pressed KBr disks.

Typically, for each spectrum, 100 scans were co-added at 4 cm^{-1} resolution.

Conductivity measurements were carried out using JENWAY4010 conductivity meter employing 1.0 mM solutions of HCC agent. Potentiometric titration was carried out using KHP standardized NaOH solution (1.0 mM) employing a Russell RL150 Potentiometer. The pH readings were taken after adding 1.0 mL of the 1.0 mM sodium hydroxide increments allowing 30 seconds to pass to ensure complete mixing before each pH measurement.

Results and Discussion

Potentiometric Titration

The potentiometric titration profile of HCC with 1.0 mM NaOH showed that the carboxylic group lost its proton completely in the pH range from 5.0 to 9.0. This range corresponds to one equivalent of sodium hydroxide (Figure 2). In addition, and as seen in the figure, the deprotonation, interval of the acid group is clear and distinguishable indicating no overlapping with other deprotonation intervals of any acid group.

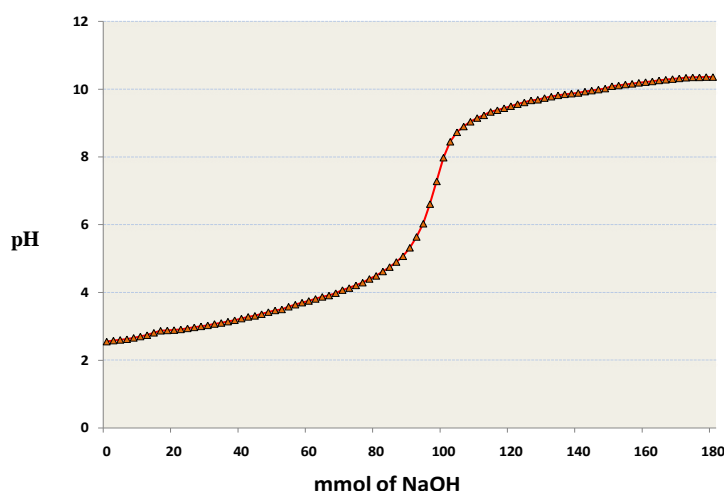


Figure 2. Potentiometric titration of equivalent amounts of HCC with 1.0 mM NaOH aqueous solutions.

IR Spectral Features

The infrared spectrum^[32] of the azo dye HCC shows intense band appearing at 1665 cm^{-1} (Figure 3). This peak is attributed to the carbonyl group of the acid moiety^[33,34]. The characteristic broad feature in the range $3300\text{--}2500\text{ cm}^{-1}$, that overlaps the CH stretching region, and with a secondary absorption close to $\sim 2600\text{ cm}^{-1}$, is observed for the hydrogen-bonded OH of the carboxylic acid group. The impact of this overlap results in more broadening of the band in this frequency range. Other bands that are associated with the CO and OH components tend to be less pronounced and sometimes may be overlapped with other fingerprint absorptions of the molecule. These are located in the ranges $1287\text{--}1214\text{ cm}^{-1}$ (CO stretch) and 886 cm^{-1} (hydrogen-bonded OH out-of-plane bending).

The free hydroxyl group of phenols commonly absorbs strongly in the $3650\text{--}3584\text{ cm}^{-1}$ region. The absence of these bands from the spectrum of HCC suggests that these phenolic (OH) groups exist in the keto-tautomeric^[33,35] form (Figure 1). The strong C=O absorption at 1665 cm^{-1} supports the suggestion of the existence of the azo dye in the keto-tautomeric state. On the other hand, the peaks appearing at 1566 cm^{-1} and 1444 cm^{-1} are assigned to the N=N stretching vibration of the unsymmetrical substituted aromatic azo compound^[33,36,37]. Furthermore, the vibration frequencies^[38,39] of the groups COO⁻ and S=O of SO₃ appear at 1514 and 1167 cm^{-1} , respectively. This data is in agreement with that previously reported for similar compounds^[33,40-45].

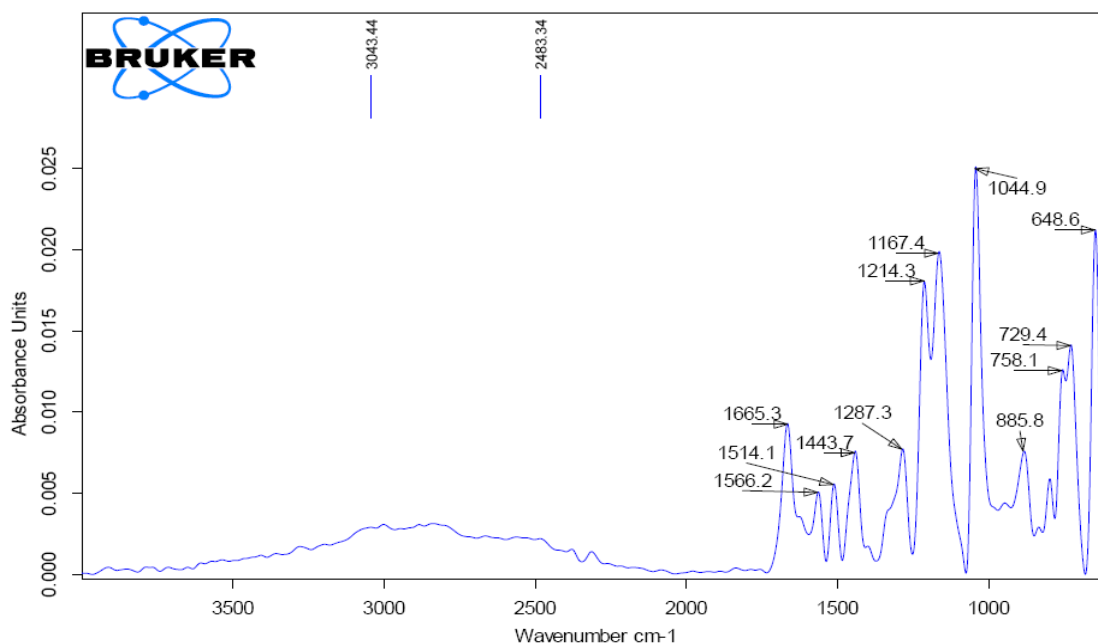


Figure 3. FTIR-spectra of the HCC azo dye.

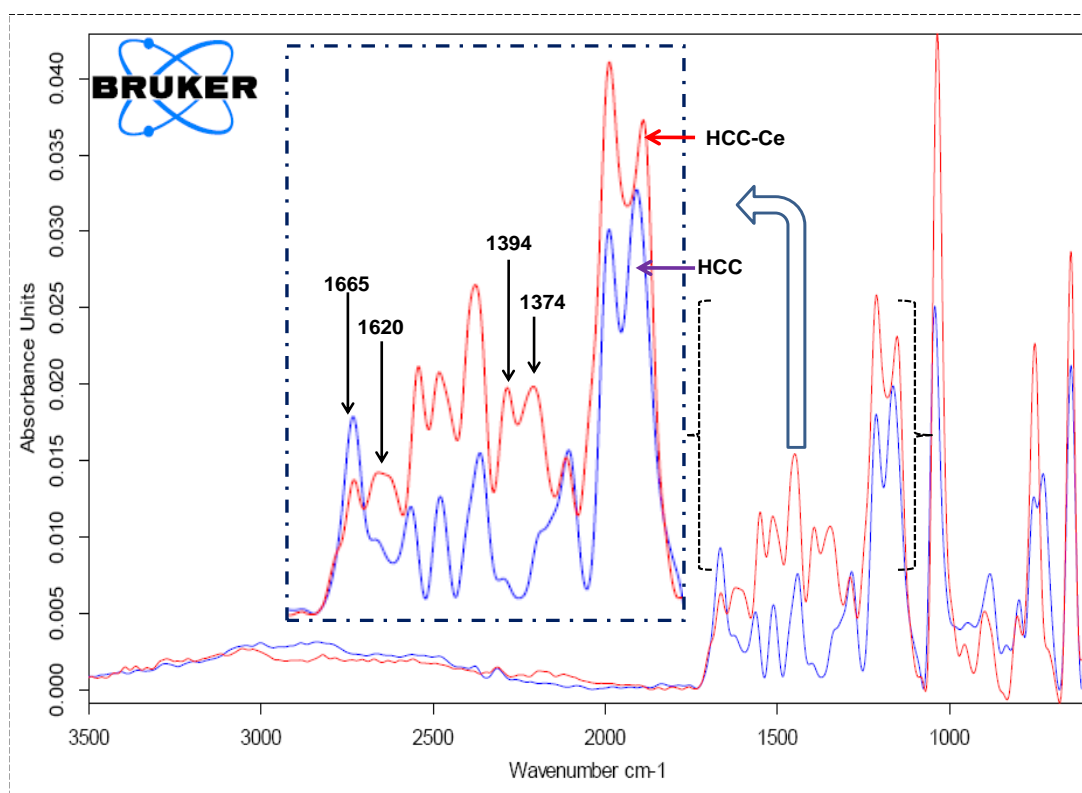


Figure 4. FTIR-spectra of the HCC azo dye interacted with Ce (IV) metal ion.

The interaction of HCC with Ce(IV) leads to spectral changes manifested in the appearance of three new IR bands at the frequencies 1620 cm^{-1} , 1394 cm^{-1} and 1374 cm^{-1} (Figure 4). The appearance of these bands, along with the observed significant reduction in intensity of the 1665 cm^{-1} band, suggest that the $-\text{COOH}$ group

is the active site at which HCC coordinates the incoming Ce(IV) ion. The portion of the IR-spectrum that reflects these spectral changes is shown again in the enlarged inset included in Figure 4. The red shift observed in the carbonyl band from 1665 cm^{-1} to 1620 cm^{-1} , in addition to the appearance of the new two aforementioned

bands, 1394 cm^{-1} and 1374 cm^{-1} , all reveal that the $-\text{COOH}$ group no longer exists in the form of $-\text{C}=\text{O}$ connected to OH . Instead, it does exist in the form of $-\text{COO}^-$ where the two oxygens become equivalent while binding the Ce(IV) ion.

UV/Visible Spectral Features

In aqueous solution, the UV-visible spectra of HCC show three absorption bands: one band in the UV-region and two bands in the visible

region (Figure 5a). The UV-band appears at $\sim 232\text{ nm}$ and is attributed to the $\pi \rightarrow \pi^*$ intra-ligand transitions^[46]. In turn, the first visible band observed at $\sim 348\text{ nm}$ is attributed to $n \rightarrow \pi^*$ electronic transition of the $-\text{N}=\text{N}-$ group^[47], while the second visible band appearing at $\sim 550\text{ nm}$ is assigned to the $\pi \rightarrow \pi^*$ transitions originating from electronic delocalization over the whole HCC (*hydrazone moiety*) electronic system^[47].

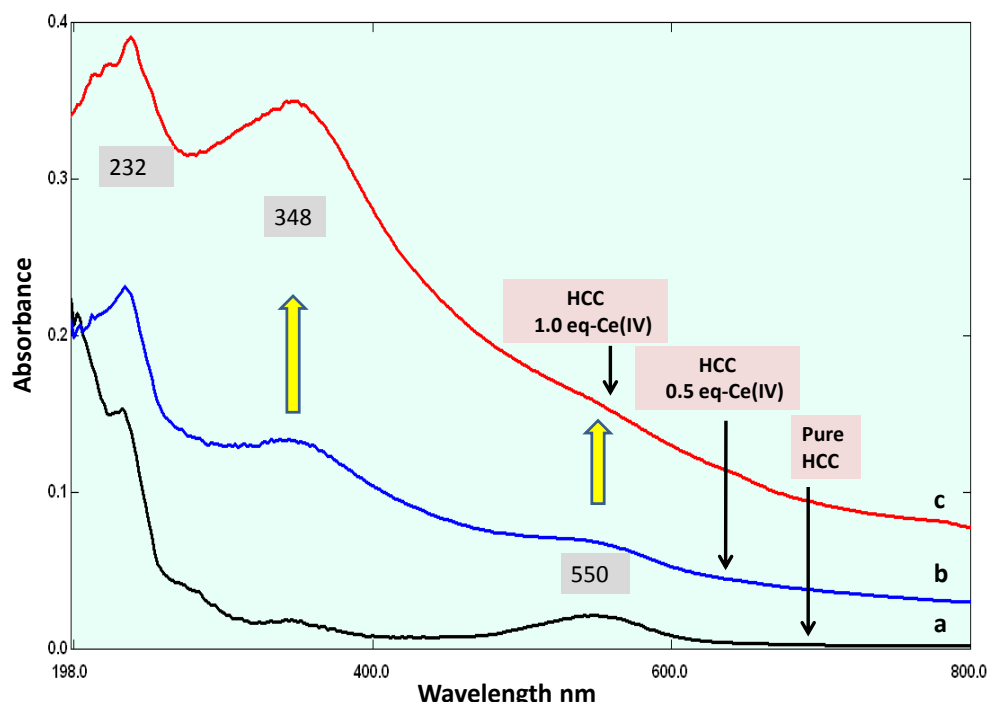


Figure 5. UV-visible absorption spectra of (a) HCC azo dye, (b) HCC treated with 0.5 eq Ce (IV) ions and (c) HCC treated with 1.0 eq Ce (IV) ions.

Interaction of HCC with Ce (IV) ions in aqueous medium has resulted in a pale pink colored solution, indicating that Ce(IV) ions interact efficiently with HCC. This pale pink color was observed to develop instantaneously upon mixing the aqueous solutions of the two species; HCC and Ce(IV). A spectroscopic titration of Ce(IV) was conducted with $1.0\ \mu\text{M}$ aqueous solution of the HCC azo-dye at pH 8. Upon addition of an increased amount of Ce(IV) ions, the peak area under the visible absorption peak corresponding to 550 nm starts to decline; however, the visible band corresponding to 348 nm starts to grow up. This is shown, respectively, in Figures 5b and 5c. The reaction responsible for these changes was observed to be instantaneous and reaches completion very fast,

where the observed reduction in the low-energy 550 nm absorption band was found to respond to Ce(IV) increments and changes proportionally to added Ce(IV) concentrations. Moreover, the color of the HCC solution treated with Ce(IV) was visually observed to change at once from dark violet to pale pink. This change in color was not noticed to take place in the solution unless the amount of the added Ce(IV) reaches the equivalent amount. In addition, this color was found to be stable over time as was observed when the solution was kept on the shelf for more than three weeks. Furthermore, in a control experiment, HCC was found to retain its original color when treated with amounts less than one equivalent of Ce(IV).

Interestingly, the saturation of HCC with Ce(IV) ions was attained after adding ~ 1.1 equivalents of Ce(IV) ions. Beyond this point, further additions of Ce(IV) ions brought no spectral changes in the absorption profile at 550 nm (Figure 6). Furthermore, the potentiometric titration of equivalent amounts of HCC azo dye against Ce(IV) ions in aqueous medium shown in Figure 6 reveals two valuable indications: first, HCC coordinates Ce(IV) in a 1:1 molar ratio, and second, HCC reserves its acidity

despite coordinating the Ce(IV) ion. This is believed to be the case due to the existence of the $-\text{SO}_3\text{H}$ acid moiety. Actually, these two findings were essential in supporting the fact that HCC coordinates Ce(IV) ions via the $-\text{COOH}$ group and not the $-\text{SO}_3\text{H}$ group. Additionally, results of the potentiometric titration profile of HCC(aq) vs. Ce(IV) (aq), shown in Figure 7, go in accordance with the conclusions deduced based on the IR-spectral data introduced in Figures 3 and 4.

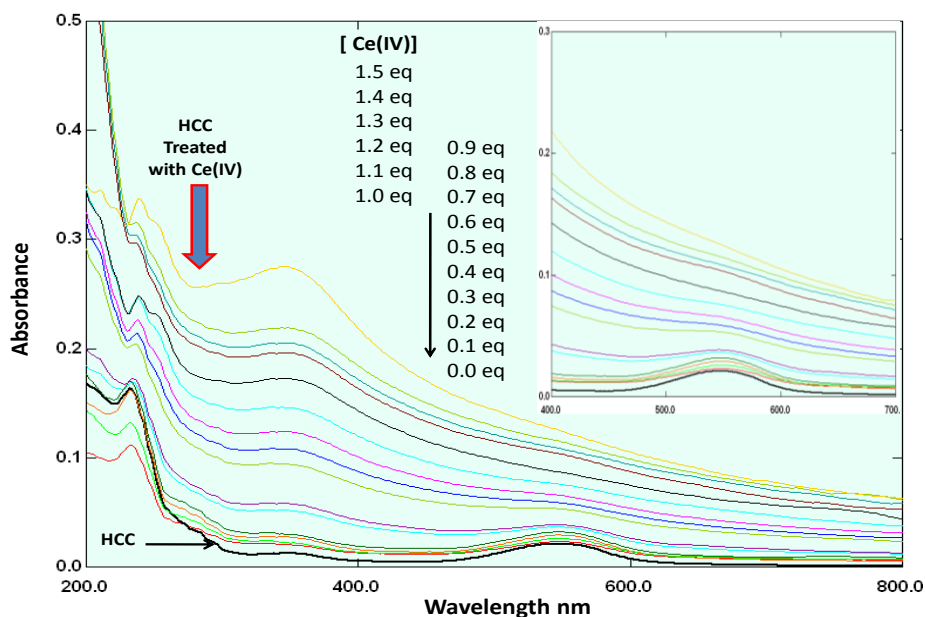


Figure 6. UV-visible absorption spectra of HCC ($1.0 \mu\text{M}$) upon titration with Ce(IV) in water compared to pure HCC. The inset enlarges the absorption within 500-600 nm.

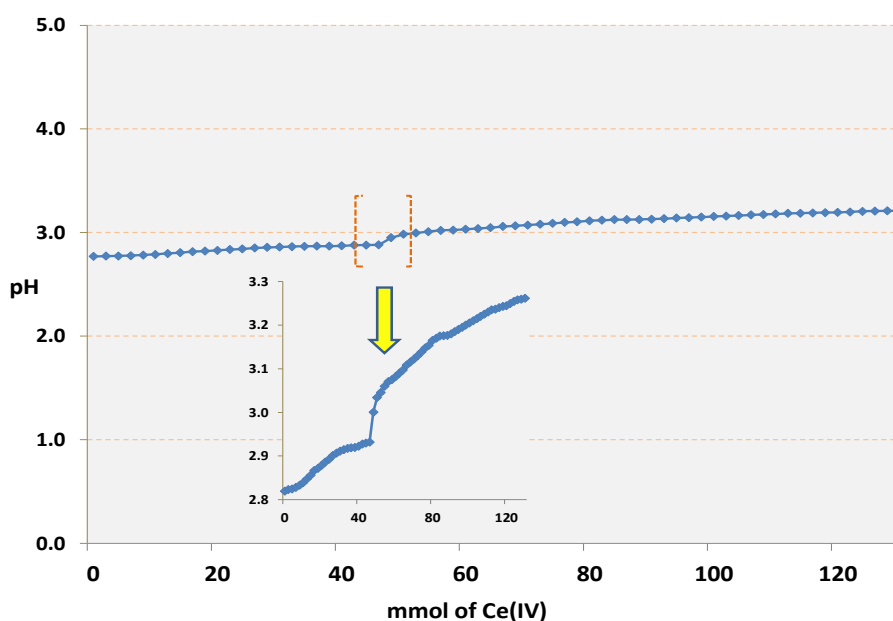


Figure 7. Potentiometric titration of HCC with Ce(IV) in water. The inset shows the pH change corresponding to 50 mmol of Ce(IV) ions.

In an attempt to test the selectivity of the HCC agent toward Ce(IV) ions, previous optical measurements were repeated for aqueous solutions of a wide spectrum of cations except Ce(IV) (Figure 8). As noted in the figure, no change in the absorption spectrum of HCC was observed upon interaction with any of the other cations. However, it is worth to mention that higher absorbance was recorded for the 232 nm band when HCC was allowed to interact with high-valent cations, such as Fe(III), Rh(III) and Cr(III). The higher absorption values observed with these cations can be understood in terms of their increased hardness which leads, in consequence, to strong interaction with the electron-rich HCC. Fortunately, in all cases, no spectral changes were induced similar to that witnessed for HCC with Ce(IV) (Figure 6). Therefore, the introduced optical responses demonstrate that HCC neither responds to metal cations other than Ce(IV), nor their accompanied anions. This, in other words, means that HCC has a remarkable selectivity toward Ce(IV) over other metal ions co-existing in aqueous matrix.

In additional control experiments, and when other salts of cerium were used, similar spectral changes were observed. This reveals that counter-anions accompanying the Ce(IV) cation have no effect on the HCC sensing activity. Moreover, the color development of HCC upon contact with Ce (IV) was noticed to be insensitive to the co-existence of other metal ions. This was deduced when HCC was allowed to interact with an aqueous matrix containing submicromolar quantities of Ce(IV) and micromolar quantities of Ag(I), Zn(II), Cu(II), Hg(II), Cd(II), Ni(II), Co(II), Fe(II), Mn(II), Mg, Ca, Ba, Pb(II), Li, K, Na, Rh(III) and Cr(III) cations.

To demonstrate the practical effectiveness of HCC agent as a colorimetric detector for Ce(IV) ions in aqueous solution, the detection limit was estimated graphically depending on the titration profile shown in Figure 6. Based on the plot in Figure 9, HCC was able to sense Ce(IV) ions in less than 0.5 ppm.

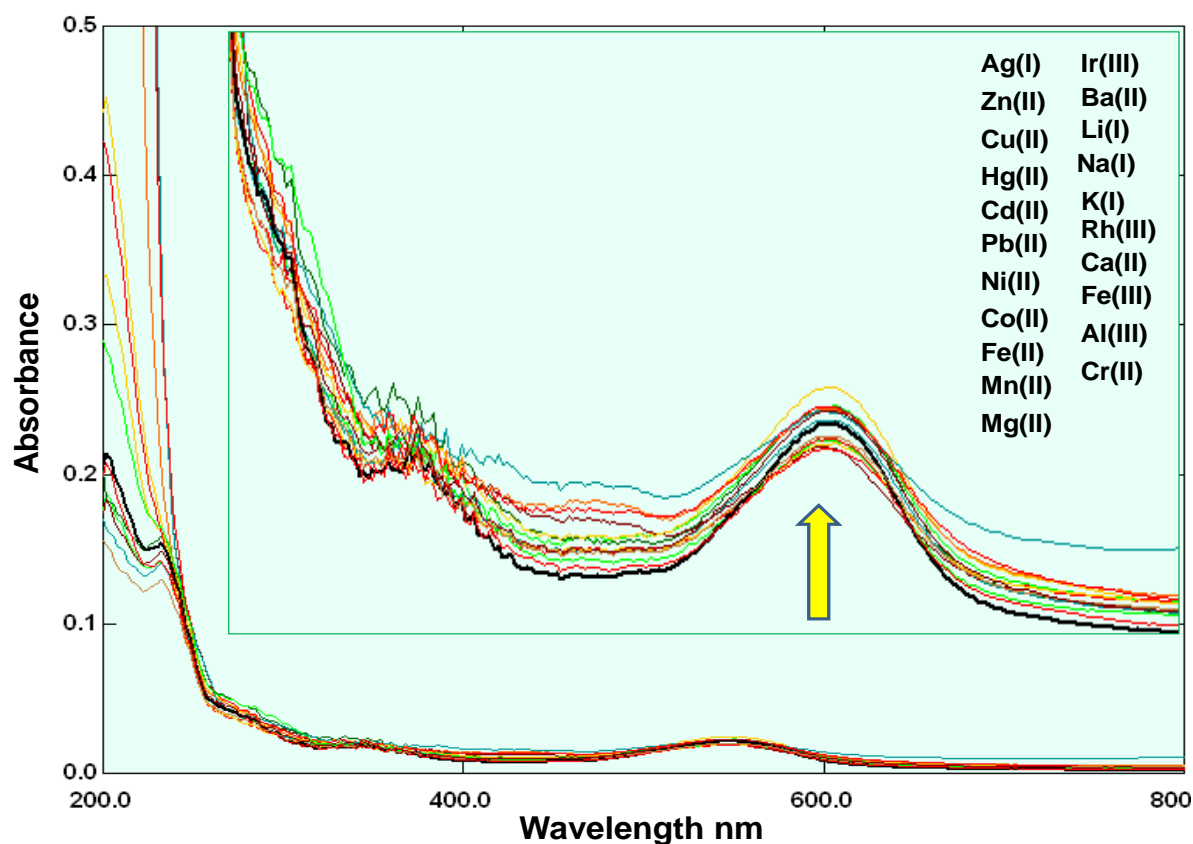


Figure 8. UV-visible absorption spectra of HCC (1.0 μ M) in water upon addition of 1.0 eq of Ag(I), Zn(II), Cu(II), Hg(II), Cd(II), Pb(II), Ni(II), Co(II), Fe(II), Mn(II), Mg(II), Ca, Ba, Li, K, Na, Rh(III), Ir(III), Fe(III), Al(III), Cr(III), but in the absence of Ce(IV).

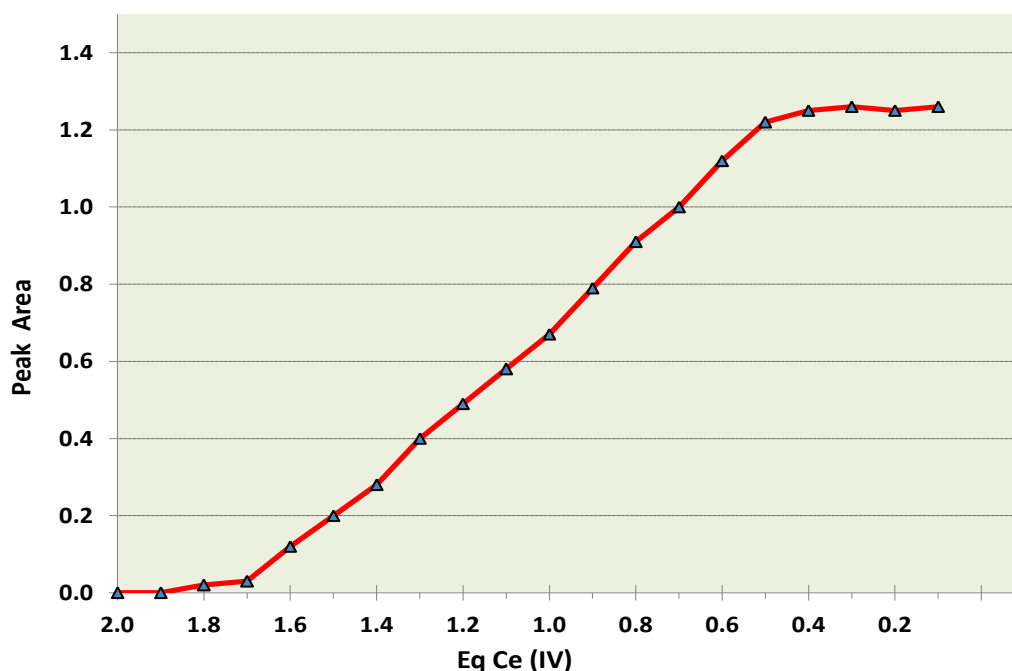


Figure 9. Detection limit of HCC toward Ce (IV) ions in aqueous medium.

Conclusions

The results presented in this report demonstrate that HCC interaction with Ce (IV) ions via the -COOH group was responsible for the observed spectral changes in the UV-visible spectrum of HCC. Interestingly, this study has furnished a highly selective and sensitive chemosensor for Ce(IV) ions in aqueous solution even in the presence of relatively high

concentrations of other potentially competing metal cations. This includes the cations identified by the *U.S. Environmental Protection Agency* as potential environmental water pollutants^[48] such as Zn(II), Cd(II), Pb(II), Ni(II) and Fe(II). Furthermore, and based on UV-vis spectroscopy measurements, the limit of detection of the HCC chemosensor was estimated to be lower than 0.5 ppm, providing a rather high chemosensation for Ce (IV) ions.

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