

Determination of Aluminum Ion with Morin in a Medium Comprised by Ionic Liquid–Water Mixtures

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Abstract In this study we have employed two ionic liquids (ILs) as a new media for the analysis of aluminum in aqueous solutions by spectrofluorimetric method. ILs are liquid salts and they have no measurable vapor pressure up to their thermal decomposition point, >300 °C. This lack of vapor pressure makes these materials highly attractive for many studies as they can be used as clean solvents. Besides they are promising environments for analysis purposes and optical sensor designs. The results revealed that absorption, excitation and emission spectra of the morin–Al complex exhibited considerable changes in moieties. The morin–Al complex was stable at aluminum concentrations below 9.1 mg L^{-1} in 25% 1-butyl-3-methylimidazolium bromide (IL-I)-water binary mixtures. The higher concentrations of IL ($>25\%$ by volume) was not suitable for the complex formation thus in pure IL media the complex formation even at high aluminum concentrations was not observed. The complex stoichiometry ratio of aluminum: morin was 2:1 in IL-I-water binary mixtures. The linear concentration range was $0.045\text{--}7.2 \text{ mg L}^{-1}$ with a correlation coefficient of $r=0.9909$. The detection limit was found to be 0.036 mg L^{-1} . Cu^{2+} , Mn^{2+} and PO_4^{3-} ions exhibited less interfering effect in presence of IL-I and the tolerance limit of Cu enhanced 10 times when compared with ethanol.

Keywords Aluminum · Morin · Ionic liquid · Fluorescence

Introduction

Anthropogenic activities like refineries, mineral mining, the usage of aluminum-based coagulants and many other reasons increase the dissolved Al^{3+} levels. Apart from this, food additives also contribute substantial amounts of aluminum in the diet. Aluminum is present in many manufactured foods and is added to drinking water for purification purposes [1]. Owing to its toxic effects, it is one of the most important cations in biomedical analytical and environmental chemistry. Al^{3+} ions exert several neurotoxic effects. It has been suspected that aluminum may be an important cause of Alzheimer's disease, bone softening and severe toxic effect to patients with chronic renal failure [2]. For this reason, the determination of trace Al^{3+} is very significant. In the last decade, several methods have been developed for the determination of aluminum including spectrophotometry [3, 4], spectrofluorimetry [5, 6], atomic absorption spectrometry [7], and atomic emission spectrometry [8]. Although most of these are high precision methods, the major drawbacks of these techniques are that they necessitate pre-treatment steps, high instrumentation and operation cost as well as instrumental complexity, large volumes of sample solution and a long period of analysis. Besides they are not totally interference free. Among them, spectrophotometry and spectrofluorimetry were one of the mostly preferred due to their good precision and accuracy, high sensitivity and simplicity with moderately low cost and widespread diffusion of equipments [3–6]. Several reagents such as aluminon, pyrocatechol violet [9], xylol orange [10], 8-hydroxyquinolinesulfonic acid [11] and chlorophosphonazo I [12] have been reported for the spectrophotometric and spectrofluorimetric determination of aluminum.

Morin (3,5,7,2',4'-pentahydroxyflavone) also can form a highly fluorescent complex with aluminum and has been

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used widely for Al^{3+} detection by many researchers. Lian et al. used morin dye in reversed-phase high-performance liquid chromatography with fluorescence detection [13] and Al-Kindy S. et al. used morin in imprinted polymers either in immobilized or in free form [14]. Gupta et al. proposed an Al^{3+} selective potentiometric sensor based on morin in PVC matrix [15]. This method worked over an activity range of 5.0×10^{-7} to 1.0×10^{-1} mol/L of Al^{3+} . Septhum et al. studied the formation of complexes between aluminum with morin and quercetin in aqueous solutions by UV-visible spectroscopy [16].

Yasin et al. have developed a reversed-phase high-performance liquid chromatographic method with fluorescence detection for the determination of labile monomeric aluminum through pre-column complexation using morin as the analytical reagent. The authors said that the most remarkable point of this protocol was that only the most toxic aluminum species that is, free aqua-aluminum ion and its monomeric hydroxo complex ions, selectively forms a complex with morin among various aluminum species [17].

Alonso-Mateos et al. reported a procedure depending on the formation of a complex with morin for the online monitoring of aluminum in drinking water by flow injection analysis. The method allowed the determination of aluminum concentrations higher than $3.1 \mu\text{gL}^{-1}$ [18].

In some studies, it is reported that the addition of cationic and anionic surfactants into the sensing media increase the sensitivity and the selectivity of the proposed method. In most of the sol-gel based sensor designs, the non-ionic surfactant Triton X-100, in which electrostatic interactions are absent, has been intensively used. When the charged surfactants (e.g. sodium dodecyl sulphate (SDS) and cetyltrimethyl ammonium bromide (CTAB)) were used, increased relative signal changes were reported [19, 20]. There are also some studies indicating that the IL type salts may constitute a new class of surfactants with special properties causing some considerable shifts in the spectra [21–23]. ILs are liquid salts and they have no measurable vapor pressure up to their thermal decomposition point, $>300^\circ\text{C}$. This lack of vapor pressure makes these materials highly attractive for many studies as they can be used as clean solvents. They also have high ability to solubilize both organic and inorganic compounds [24–26]. Besides, the solubility and selectivity characteristics of an IL can be tuned by appropriate choice of cations, anions or substituents. By this way, task specific sensors and/or analyse methods can be developed [27]. Merrigan et al. reported the synthesis of four new fluorinated ILs and their action as a fluorous surfactant on an ionic liquid, 1-hexyl-3-methylimidazolium hexafluorophosphate [21]. Miskolczi et al. told that ILs can be used to modify in a controlled fashion the properties of the conventional micelles, if pure micelles do not provide the

desired properties, such as for example, surface tension, viscosity, dispersion stability [23]. Safavi et al. studied the interaction of an imidazolium based IL, namely 1-dodecyl-3-methylimidazolium chloride [C12mim][Cl] with two sulfonated anionic dyes, azocarmine G and methyl orange by spectrophotometric method and concluded that ILs (with some surface active character) can interact with the above dyes and cause considerable shifts in their spectra [28].

In this study, morin was tested for the first time for determination of aluminum ions in presence of ILs in aqueous solutions by spectrofluorimetric method. It is also the first study on the interaction of ILs on the determination of metals by spectrofluorimetric method. The effect of the concentration of IL, pH and the interfering ions were evaluated. The schematic structures of morin and the employed ILs were shown in Fig. 1. It is expected for this study to open a new insight to further expanding and enhancing of the application of green chemistry reagents in analytical chemistry.

Experimental

Materials and method

The commercially available ILs, 1-butyl-3-methylimidazolium bromide (IL-I) and 1-ethyl-3-methylimidazolium tetrafluoroborate (IL-II) were supplied from Fluka. Both ILs are soluble in water and in absolute ethanol. Fluorescent dye morin hydrate (2',3',4',5',7-pentahydroxyflavone) was obtained from Fluka. The stock morin dye solution was prepared as 10^{-3} mol/L in ethanol. Buffer solutions of required pH were prepared either from 1.0 mol/L acetic acid/acetate buffer or from $\text{NH}_4^+/\text{NH}_3$ buffer at the desired pH. The metal solutions were prepared from atomic absorption spectroscopy standards of Al^{3+} , Pb^{2+} , Cu^{2+} ,

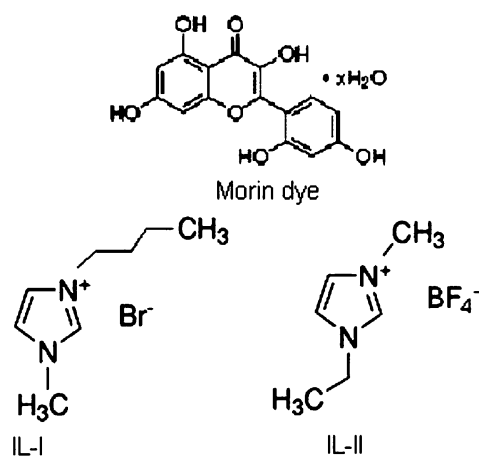


Fig. 1 Chemical structures of the employed ionic liquids and morin dye

Cr^{3+} , Mn^{2+} , V^{3+} and Fe^{3+} (1,000 mg/L, Merck) with 1.0 mol/L sodium acetate buffer at pH 4. The solutions were freshly prepared prior to experiments to contain 10^{-5} mol/L morin and 25% ethanol (Cocktail-I) or 25% IL-I (Cocktail-II), 25% IL-II (Cocktail-III) by volume unless otherwise stated. The solutions were diluted with pH 4 acetic acid/acetate buffer solution, shaken and allowed to stand for 5 min at 25 °C. The absorption and emission based measurements were performed in polymethylmethacrylate semi-micro cuvettes with 10 mm pathlength and 1.5 ml volume. Solvents for the spectroscopic studies were used without further purification. Buffer components or other chemicals were of analytical grade. In all of the studies, ultra pure water of Millipore was used.

Instrumentation

Absorption spectra were recorded using a Shimadzu 1601 UV–Visible spectrophotometer. Steady state fluorescence emission and excitation spectra were measured using Varian Cary Eclipse Fluorescence Spectrophotometer with a Xenon flash lamp as the light source. The pH values of the solutions were checked using a digital pH meter (WTW) calibrated with standard buffer solutions of Merck. All the experiments were carried out at room temperature; 25°C.

Results and discussion

Photocharacterization studies

Spectral characterization of morin and morin–aluminum complex was performed in the three cocktail solutions. Morin and aluminum concentrations of the solutions were 10^{-5} mol/L and 6.74×10^{-5} mol/L, respectively. The UV–visible absorption based data was shown in Table 1. Morin exhibited different maximum absorption wavelengths and molar extinction coefficients in the employed media. By the addition of Al^{3+} into the morin–ethanol– H_2O solution, the peak at 359 nm was decreased and a new absorption band appeared at 414 nm indicating the formation of morin–aluminum complex. The absorption maximum of the complex was blue shifted to 405 nm in both of the IL–water binary mixtures (Table 1). However, the absorption maximum of morin in IL-I (cocktail-II) media was red shifted significantly from 359 to 391 nm (Table 1). Although the dye and IL are individually solvated in water, they can sometimes interact with each other in the employed media by the effect of electrostatic and hydrophobic forces causing the formation of dye–IL complexes [28]. The complex can be an ion-pair involving the cationic part of IL and negatively charged deprotonated morin dye.

Table 1 Absorption based data of morin in presence and absence of aluminum in different mixtures (Morin and aluminum concentrations were 10^{-5} mol/L and 6.74×10^{-5} mol/L, respectively)

| Mixture | Max. abs. wavelength, (λ_{max}^1 , nm) | Max. abs. wavelength, (λ_{max}^2 , nm) | Abs, (A_1) | Abs., (A_2) |
|---------------------------------------|--|--|----------------|-----------------|
| Cocktail-I without Al^{3+} | 359 | | 0,131 | |
| Cocktail-I with Al^{3+} | 359 | 414 | 0,109 | 0,099 |
| Cocktail-II without Al^{3+} | 391 | | 0,240 | |
| Cocktail-II with Al^{3+} | | 405 | | 0,180 |
| Cocktail-III without Al^{3+} | 359 | | 0,180 | |
| Cocktail-III with Al^{3+} | 359 | 405 | 0,178 | 0,120 |

So, a red shift, along with an increase in the intensity of the absorbance, can be seen upon the formation of ion pair. This phenomenon can also increase the solubility of morin in IL–water binary mixtures. However no spectral shift was observed in case of cocktail-III which differs from IL-I with shorter alkyl chain on imidazolium ring and larger anionic group. The molar extinction coefficient of morin in IL-I increased nearly twice with respect to ethanol from $\epsilon = 13100 \text{ M}^{-1} \text{ cm}^{-1}$ ($\lambda_{\text{max}} : 359 \text{ nm}$), to $\epsilon = 24000 \text{ M}^{-1} \text{ cm}^{-1}$ ($\lambda_{\text{max}} : 391 \text{ nm}$).

Figure 2a shows the emission and excitation spectra of morin–Al complex in the three cocktail solutions. The spectra of the complex in all media exhibited broad emission bands ranging from 430 to 650 nm. The emission maximum of the complex exhibited a red shift of 29 nm and an accompanying decrease in fluorescence intensity in IL-I–water mixtures with respect to ethanol–water mixtures. This decrease can be attributed to the competing complex formation of IL both with morin dye and the Al^{3+} ions. Safavi et al. investigated the interactions of an imidazolium based IL with two sulfonated anionic dyes, azocarmine G and methyl orange and showed their resemblance to surfactant interactions [28]. They told that at surfactant concentrations at critical micelle concentration (CMC) values and above, the solubilizing effect of the micelles begins to be important and probably, the ion-association complexes are incorporated into the micelles, and some new changes in spectral responses have been reported [29]. Since ILs can form aggregates with a similar behavior to micelles, it is thus expected that ILs with a large cationic site behave in a similar manner towards anionic dyes. In addition to electrostatic interaction, another kind of interaction can be considered between IL aggregates and the dye moiety (hydrophobic effect), in which the microenvironment of the dye may be changed from that existing in the

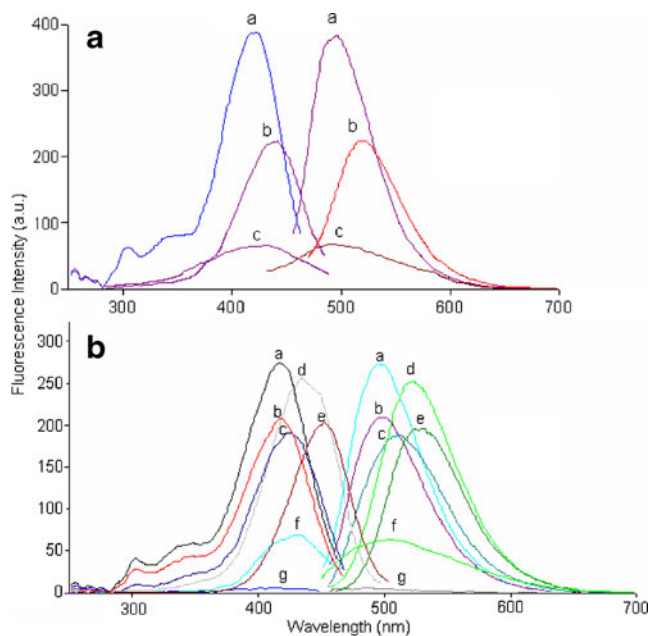


Fig. 2 **a** Emission and excitation spectra of morin aluminum complex in (a) in cocktail-I (b) in cocktail-II (c) in cocktail-III **b** in different concentrations of IL-I containing media (a) 0.1% (b) 2% (c) 10% (d) 25% (e) 50% (f) 75% (g) 100% by volume

bulk aqueous phase, and this change can also be responsible for the spectral shifts.

Effect of variation of ionic liquid concentration

The emission and excitation spectra of morin–Al complex in different concentrations of IL-I are shown in Fig. 2b. The spectra exhibited a decreasing fluorescence intensity together with a slight red shift (14 nm) by the addition of IL-I up to 10% by volume (7.04×10^{-4} mol/L, Fig. 2b(c)). These variations can be related to the interaction of morin with IL-I below the critical aggregation concentration (CAC) value where the morin–IL complex formation takes place. After the addition of 25% IL-I (1.76×10^{-3} mol/L, Fig. 2b(d)), the spectra showed a significant red shift (29 nm) and an enhancement in fluorescence intensity. In submicellar regions a colloidal solution could be formed which will lessen the interaction of dye with IL and the formation of aluminum–morin complex was probably favored with higher fluorescence intensity.

By the increasing amounts of IL (more than 1.76×10^{-3} mol/L of IL-I), the IL concentration was expected to reach the CAC. After this concentration (1.76×10^{-3} mol/L), due to the formation of the dye–IL complexes, the fluorescence intensity of morin–aluminum complex was decreased (Fig. 2b(e),(f),(g)). The observed red shift can be attributed to the enhanced “rigidochromism” related to limited rotational freedom of the molecules in more viscous IL–water mixtures. Additionally, the Stoke’s shift value of

the complex was enhanced from 75 nm to 85 nm in IL-I containing media. Large Stokes shift value is desirable for fluorescence based optical sensor designs because the high Stokes shift values allow the emitted photons to be easily distinguished from the excitation photons, leading to the possibility of very low background signals. For further studies a mixture of 25% of IL-I –75% of buffer solution (cocktail-II) was chosen as optimum working moiety.

Effect of variation of morin concentration

In order to optimize the concentration of the indicator dye, different amounts of morin (from 1.82×10^{-6} mol/L to 10.93×10^{-6} mol/L) were added into the solution at fixed concentration of Al^{3+} ; 6.74×10^{-5} mol/L (Fig. 3). Fluorescence intensity of the morin–aluminum complex had increased considerably up to 9.10×10^{-6} mol/L. At higher amounts of morin, the plot nearly reached a constant plateau and 9.10×10^{-6} mol/L concentration was chosen as optimum for further studies.

Effect of the pH

The effect of the pH on the emission and excitation spectra of the morin–Al complex both in cocktail-I and cocktail-II was studied over the pH range of 4.0–8.5. Figure 4 shows the dependence of fluorescence intensities of the system on pH. The buffer solutions employed for pH adjustment were not adequate to change the pH of cocktail-II. The IL containing solution strongly resisted pH changes, thus the pH was adjusted by the addition of micro portions of concentrated (1 mol/L) nitric acid or sodium hydroxide solution. This was due to the buffering effect of 1-butyl-3-methylimidazolium bromide. Similar behavior of ILs was reported earlier [30–32]. Formation of such a buffer system enhances the stability of analysis system more than the classical buffer systems and the presence of IL in the analysis solution acts as a sink for acidic or basic species.

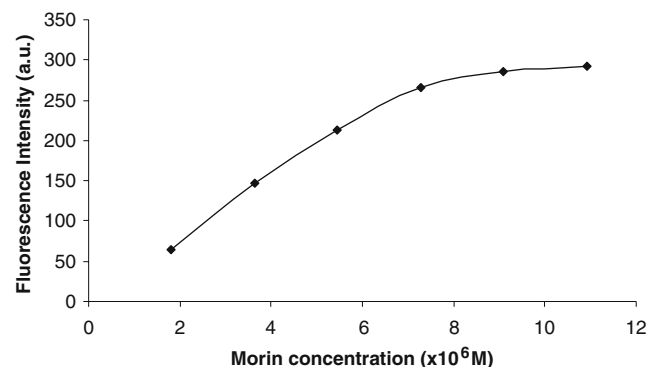


Fig. 3 Effect of morin concentration (1.82×10^{-6} – 10.93×10^{-6} mol/L) to the formation of morin–aluminum complex in IL-I containing media (Al^{3+} concentration was fixed at 6.74×10^{-5} mol/L)

The equilibrium pH of the IL containing solution was 7.0. By the addition of 20 μl portions of concentrated nitric acid (total 100 μl), pH dependent fluorescence signal of the complex decreased by 17%. By the addition of same amount of nitric acid to the ethanol containing solution, the complex had lost nearly its whole fluorescence ($\approx 90\%$).

pH also affects the charge distribution of the morin molecule, the distribution of Al species and the reaction ability of the system. The distribution of the chemical species of aluminum in natural waters at pH 4.0 and pH 7.0 was calculated with chemical equilibrium software (Visual MINTEQ) and shown in Table 2. Figure 4 reveals that the fluorescence intensity of Al–morin–IL system reached the maximum value in neutral condition at pH 7.0, while Al–morin–ethanol system reached its maximum fluorescence intensity in slightly acidic condition at pH 4.0. As the IL system can be thought as a positively charged surfactant containing system due to its imidazolium group, this result is in accordance with the data reported by Long et al [31]. According to Long, with respect to the Al–morin–nonionic surfactant systems whose greatest intensities are all achieved in weak acidic conditions, neutral or alkaline media are more favorable for the reaction of Al, morin and cationic surfactants. The reason was attributed to that when morin reacts with Al^{3+} , Al ions usually bind to the 3-hydroxyl and 4-keto oxygens and to the 5-hydroxyl and 4-keto oxygens. In acidic conditions, other hydroxyls, such as 2'- and 4'-hydroxyls, are labile. By the increase of pH, which will promote the dissociation of these hydroxyls, there are more negative charges on the morin molecules, which not only favor the formation of Al–morin–cationic surfactants ternary complexes, but also favor the electrostatic interaction between morin and cationic surfactants to form larger structures leading to the enhancement of the fluorescence intensity. However in the case of IL-I, as the potential formation of IL–Al and/or IL–morin complex competes with morin–Al complex, at higher pH values than

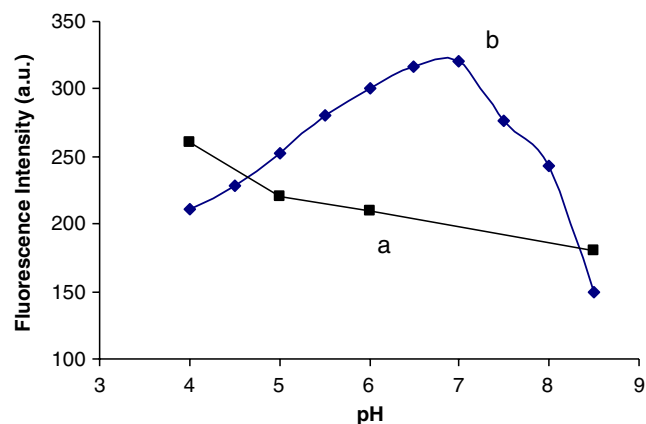


Fig. 4 The fluorescence emission intensity of morin–Al complex at different pH a) Ethanol containing media b) IL-I containing media

Table 2 pH dependent distribution of aluminum at pH 4.0 (taken from Minteq software)

| Species Name | % of Total Component Concentration | |
|-------------------------------------|------------------------------------|--------|
| | pH 4.0 | pH 7.0 |
| Al^{3+} | 90.795 | 0.000 |
| AlOH^{2+} | 8.772 | 0.080 |
| $\text{Al}(\text{OH})_2^+$ | 0.432 | 4.048 |
| $\text{Al}(\text{OH})_3(\text{aq})$ | 0.000 | 16.219 |
| $\text{Al}(\text{OH})_4^-$ | 0.000 | 79.652 |

7.0, the fluorescence intensity decreases again. Therefore, pH 4 and 7.0 were selected as optimum working pHs for ethanol and IL-I-water binary mixtures, respectively.

Photostability of the complex

The photostability of the morin–Al complex was investigated for selected concentrations of aluminum (relatively diluted and concentrated concentrations of Al; 1.8 mg L^{-1} , 9.1 and 18.2 mg L^{-1}) in cocktail-I, II and III (Fig. 5). The short term photostabilities were recorded as a function of time for 60 minutes. At diluted concentrations, the morin–Al complex was more stable. For 9.1 mg L^{-1} Al^{3+} , the complex have lost its original fluorescence intensity by 40%, 18% and 40% in cocktail-I, II and III, respectively.

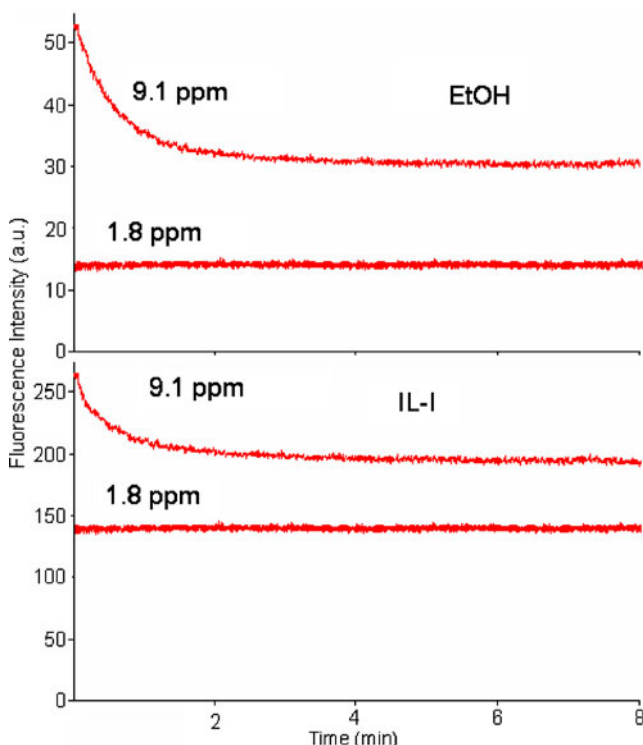


Fig. 5 Fluorescence emission intensity of morin–Al complex as a function of time for different concentrations of Al in different media

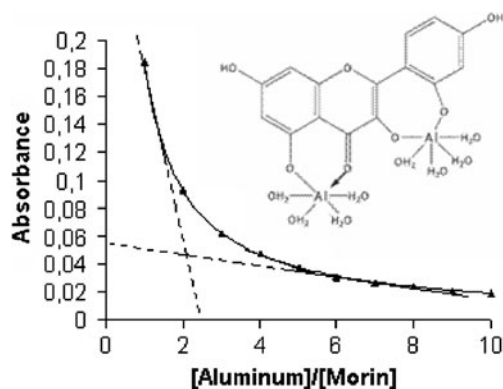


Fig. 6 Absorbance versus [aluminum]/[morin] molar ratios plot in IL-I containing media; inset: possible structure of morin–Al complex

The equilibrium was reached within 4, 4 and 50 min in the employed moieties, respectively. When the Al^{3+} concentration reached to 18.2 mg L^{-1} , the complex have lost its fluorescence intensity by 56% and the equilibrium was attained in 30 min in cocktail-II. Because of the instability of the complex at relatively high concentrations of aluminum in IL, the further experiments were performed with concentrations lower than $9.1 \text{ mg L}^{-1} \text{ Al}^{3+}$ and the solutions were left for 5 min prior to the experiments.

Complex stoichiometry

The stoichiometry of metal complexes depends on the media. The association of Al^{3+} ion with morin gives rise to two complexes with 1:1 and 1:2 (Al:morin) stoichiometries in methanol solution [33]. In this study, the complex stoichiometry in IL-I containing media was determined by using the molar ratio method. The molar ratio of [aluminum]/[morin] was plotted versus the absorbance at 415 nm (See Fig. 6). The plot exhibited inflection at [aluminum]/

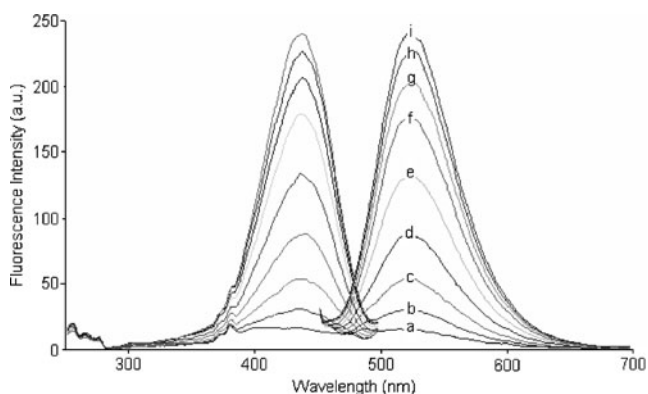


Fig. 7 Emission and excitation based response of morin dye to Al^{3+} in 25% IL-I containing media in the concentration range of 0.0– $7.2 \text{ mg L}^{-1} \text{ Al}^{3+}$ a) 0.0 mg L^{-1} b) 0.045 mg L^{-1} c) 0.16 mg L^{-1} d) 0.39 mg L^{-1} e) 0.84 mg L^{-1} f) 1.75 mg L^{-1} g) 3.11 mg L^{-1} h) 4.93 mg L^{-1} i) 7.20 mg L^{-1}

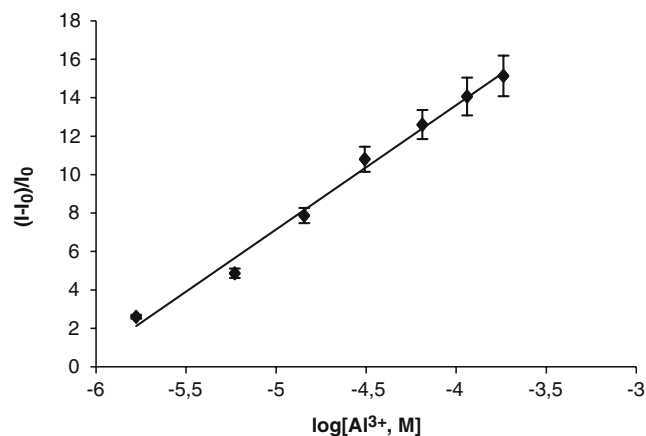


Fig. 8 Linearized emission based response of morin dye to Al^{3+} in cocktail-II

[morin] ratio of 2, indicating only one possible Al^{3+} :morin stoichiometry, 2:1. The proposed structure of $\text{Al}_2(\text{morin})$ is shown in the inset of Fig. 6.

Morin possesses two possible chelating sites, 3-hydroxy-4-oxo and 5-hydroxy-4-oxo. In addition, the 3,2'-dihydroxy system in morin structure is another potential chelating site, which is so placed that a seven-membered chelate ring is formed upon binding Al^{3+} ion. An Al^{3+} ion bridges 2'- and 3-hydroxy groups rather than 4-keto- and 3-hydroxy, and possibly makes another bridge with 5-hydroxy-4-oxo system. Al^{3+} ion has a coordination number of six and forms a complex with an octahedral configuration [2].

Emission based response of morin dye to Al^{3+}

Response of the morin dye to Al^{3+} was tested and evaluated in cocktail-I and cocktail-II in the defined optimum conditions. Figure 7 reveals emission based increasing response of morin dye to Al^{3+} in cocktail-II. Figure 8 shows the normalized calibration plot of aluminum concentration versus relative signal intensity $((I-I_0)/I_0)$, where I was the measured fluorescence intensity at any Al^{3+} concentration and I_0 was the intensity in absence of Al^{3+} . The data on Fig. 8 represent results of five replicate measurements with error bars showing the standard deviations between 4% and 7%. The equation of the normalized calibration plot was $((I-I_0)/I_0) = 6.4728 \log [\text{Al}^{3+}, \text{M}] + 39.502$. The standard deviation of intercept, standard deviation of slope and standard deviation about regression were calculated as 0.3881, 0.2169 and 2.601, respectively according to Miller, 2000 [34]. The morin dye exhibited a linear emission based response to Al^{3+} in the concentration range of 1.5×10^{-6} – $3.7 \times 10^{-5} \text{ mol/L}$ (0.040 – 1.0 mg L^{-1}) in cocktail-I with a correlation coefficient; $r = 0.9947$. The linear concentration range enlarged to 1.7×10^{-6} – $2.7 \times 10^{-4} \text{ mol/L}$ Al^{3+} (0.045 – 7.2 mg L^{-1}) in cocktail-II yielding a correlation coefficient of $r = 0.9909$. The detection

limits (the concentration of the metal ion giving a signal equal to the blank signal plus three standard deviation of the blank) were found to be 0.028 mg L^{-1} and 0.036 mg L^{-1} in cocktail I and II, respectively.

As the IL content of the solution increased, the linear concentration range was shifted to higher values. In pure IL media, the peak of morin–Al complex was not observed indicating that no complex formation was occurred. These results reveal that the increase in IL concentration inhibits the formation of aluminum–morin complex as IL itself competes with morin to form complex with Al. Poor solubility of the complex in IL media can be another reason for the decreasing fluorescence intensity of aluminum–morin complex in presence of ionic liquid.

Selectivity studies

The effect of the most strong interferents (Cu^{2+} , V^{3+} , Cr^{3+} , Pb^{2+} , Fe^{3+} , PO_4^{3-} , Mn^{2+}) on the determination of Al^{3+} (1.82 mg L^{-1}) was examined in both cocktails. The fluorescence intensities of Al–morin complex in the presence and absence of the interferents were recorded. The tolerance limit was expressed as the maximum interferent concentration to be determined within an error of 5%. The results were shown in Table 3. Some species especially present in aqueous samples such as Cu^{2+} , Mn^{2+} and PO_4^{3-} exhibited less interfering effect in IL-I media when compared with ethanol. The tolerance limit of Cu enhanced 10 times in presence of IL-I.

Conclusion

In this study, the determination of aluminum in aqueous solutions was studied in IL and/or ethanol containing moieties using absorption and emission spectroscopy.

The results revealed that both the absorption and the emission based spectra of the morin–Al complex have

differed in the concerned moieties. The emission maximum of the complex exhibited a red shift of 29 nm and an accompanying decrease in fluorescence intensity in IL-I moiety with respect to ethanol. The presence of IL inhibited the formation of aluminum morin complex to some extent. The higher concentrations of IL (>25% for IL-I) were not suitable for the complex formation thus in pure IL media the complex formation even at high aluminum concentrations was not observed. The morin–Al complex was stable at aluminum concentrations below 9.1 mg L^{-1} in IL containing moiety. The complex in IL-I moiety indicated a 2:1 aluminum: morin stoichiometry ratio. This was good news that some species especially present in aqueous samples such as Cu^{2+} , Mn^{2+} and PO_4^{3-} exhibited less interfering effect in IL-I media with respect to ethanol. The tolerance limit of Cu enhanced 10 times in presence of IL-I. This result can open a new insight for further studies with different ILs which can enhance the selectivity of the proposed dye for cation analysis purposes. Besides, the possible inhibition of the formation of metal–dye complexes in IL moieties can be an advantage for anion analysis in presence of interfering metal ions.

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Table 3 The tolerance limit of some selected ions in cocktail-I and II (mg L^{-1})

| Interferent | The tolerance limit of interferent in IL free media (mgL^{-1}) | The tolerance limit of interferent in IL-I containing media (mgL^{-1}) |
|--------------------|---|---|
| Cu^{2+} | 0.91 | 8.18 |
| V^{3+} | 0.45 | 0.18 |
| Cr^{3+} | 0.91 | 0.18 |
| Pb^{2+} | 4.55 | 3.64 |
| Fe^{3+} | 0.09 | 0.09 |
| PO_4^{3-} | 0.45 | 3.18 |
| Mn^{2+} | 0.45 | 1.36 |

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