

A study of the luminescent complexes formed by the dye 1,4-dihydroxyanthraquinone (quinizarin) and Ga(III) and In(III)

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Abstract

Fluorescent species form when Ga(III) and In(III) ions interact with 1,4-dihydroxyanthraquinone (quinizarin), in aqueous and non-aqueous media. Time dependence, temperature, solvent, counterion and pH effects studies have been performed in order to interpret the behaviour of this ligand in the presence of Ga(III) and In(III) ions.

Quinizarin by itself is not fluorescent, but both its absorbance and fluorescence intensity increase proportionally to the complexation with Ga(III) and In(III), thus suggesting the supramolecular nature of these complexes, which could be used as fluorescence sensors.

The fluorescent quantum-yield values of the QNZ complexes with Al(III), Ga(III) and In(III) ions are negatively affected by the increase of the size of M(III) ions, suggesting that the increase in metal size weakens the supramolecular interaction with QNZ.

Potentiometric studies, performed between pH 3 and 6, suggest the formation of 2:1 QNZ/In(III) species, having a high β formation constant.

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1. Introduction

1,4-Dihydroxyanthraquinone (quinizarin, QNZ) is accredited with properties that span from being used as a fungicide and pesticide, to being employed as a dye, a photoinitiator and an additive in lubricants [1]. It also serves as a model for anthracycline antitumour antibiotics [2]. Significantly, the fluorescent complexes of quinizarin with lithium and boron ions are used as spectrophotometric analytical reagents for these metals [3,4].

The literature on the speciation of quinizarin complexes is not mature [5,6]. Early reports suggest the formation of non-polymeric species, having 1:1, 1:2 or 1:3 metal/QNZ stoichiometry [6–8]. In contrast, recent reports cite the formation of polymeric complexes with 1:1 or 2:3 metal/QNZ ratio [1,5,9,10].

Recently, a number of fluorescent sensors and switches have been designed [11–14]. Most of them operate through photo-induced electron-transfer (PET) and consist of two-component systems. For example, an anthracene light-emitting moiety has been linked to an 18-membered

azacrown, the latter acting as a sensor [12]. The uncomplexed system does not fluoresce, the fluorophore being deactivated by an electron-transfer process taking place between the crown and the anthracene. However, the incorporation of K^+ ions in the crown reinstates the typical anthracene emission by means of PET inhibition through the metal–ligand interaction.

In this connection, we have studied the effect of the complexation of QNZ with metal ions that generate fluorescence. Previously, we have investigated the luminescence-producing interaction between QNZ and Al(III) ions [15–17]. Here we report the studies on the systems consisting of QNZ and the trivalent metal ions Ga(III) and In(III).

2. Results and discussion

2.1. Preliminary solution studies

The effect of Ga(III) ions was determined mainly using Ga(acac)₃. This was found to be the best compound for solubility reasons. The use of GaCl₃ was restricted to those alcohols where no interaction between GaCl₃ and the solvent itself occurred.

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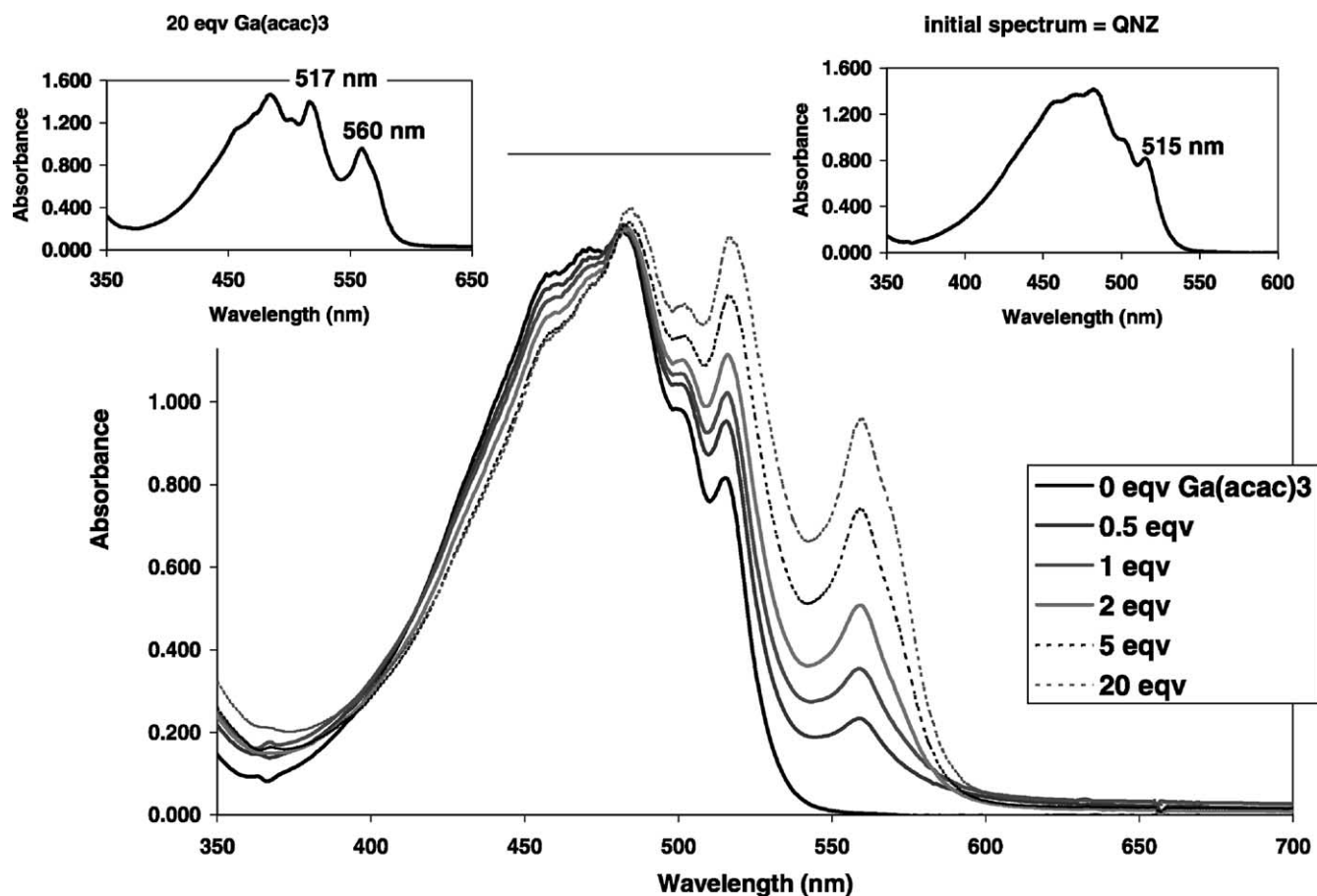


Fig. 1. UV-Vis spectra of solutions of quinizarin and QNZ/Ga(acac)₃ at different molar ratios in *t*-BuOH.

Fig. 1 shows the UV-Vis spectra of solutions of QNZ and of QNZ/Ga(acac)₃ at various molar ratios. The QNZ solutions have a yellow-orange colour that is solvent dependent, and the UV-Vis spectra are characterised by a broad band centred at ca. 480 nm. Upon progressive addition of Ga(III) ions to QNZ, the development of a fluorescent pink/orange species occurred.

The QNZ/Ga(acac)₃ solutions have solvent-dependent UV-Vis spectra. With the alcohols from MeOH to *n*-BuOH, the spectra are characterised by the slow disappearance of the broad band at 480 nm, that becomes a shoulder, and with the appearance of two bands having maxima at ca. 520 and 570 nm, the latter band showing structure even at high QNZ/Ga(III) ratios. In the case of *t*-BuOH, instead, the band at 484 nm is still predominant in the QNZ/Ga(III) spectra together with the band at ca. 560 nm forms. Fig. 2 shows the UV-Vis spectra for QNZ/Ga(acac) at 1:1, 1:3, 1:5 and 1:10 ratio in different solvents.

Table 1 reports the wavelengths of the bands with highest absorbance for the QNZ complexes with Ga(acac)₃, In(NO₃)₃·5H₂O and Al(acac)₃. These compounds have been selected because they give the highest fluorescence quantum-yield values. The 1:40 QNZ/Ga(acac)₃, in MeOH, produces a band at 521 nm having higher absorbance than

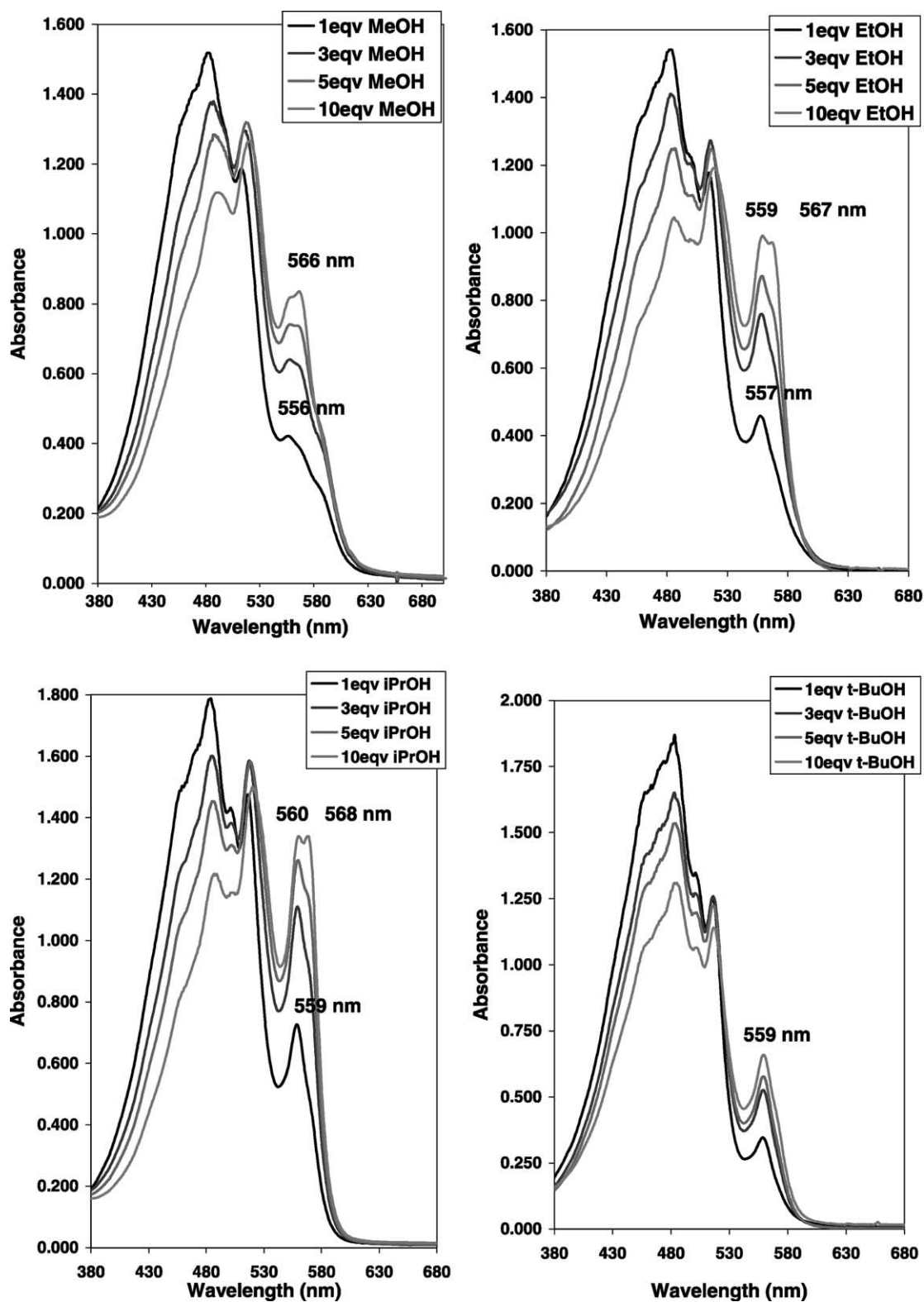
that at 570 nm. Table 1 also contains the data for the QNZ/In(acac)₃ complexes. Their UV-Vis spectra are, in all solvents, consistent with uncomplexed QNZ.

Typical fluorescence spectra of the QNZ/Ga(III) species that formed in solution while increasing the metal molar ratio, are given in Fig. 3. The formation of the pink colour was coincident with the formation of two bands and a shoulder centred, respectively, at ca. 580, 620 and 665 nm when λ_{exc} was 560 nm.

The effect of In(III) ions, and any influence of counterion in determining speciation and fluorescence, was

Table 1
Comparison of the maximum wavelengths of absorbance and emission for QNZ/M(III) compounds 1:40 in different alcohols

Solvent	Ga(acac) ₃	In(NO ₃) ₃ ·5H ₂ O	Al(acac) ₃ [15]	In(acac) ₃
MeOH	521	516	570	481
EtOH	569	517	569	483
PrOH	570	519	571	485
<i>i</i> -PrOH	570	518	571	484
BuOH	571	519	572	483
<i>t</i> -BuOH	484	Sparingly soluble	571	Sparingly soluble

Fig. 2. Solvent effect on the UV-Vis spectra of QNZ/Ga(acac)₃.

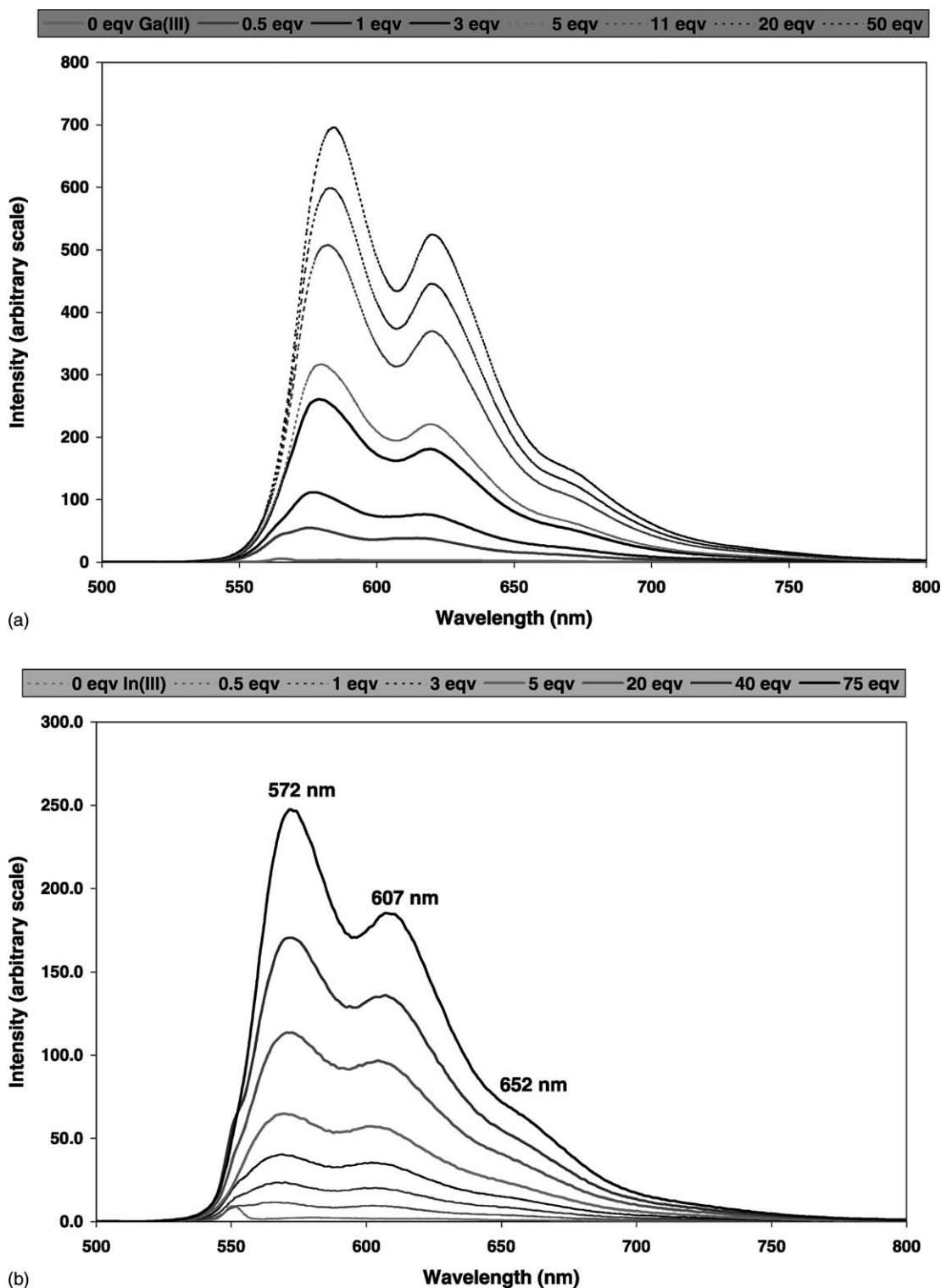


Fig. 3. Fluorescence spectra from the titration of QNZ with (a) Ga(acac)₃ ($\lambda_{\text{exc}} = 565 \text{ nm}$); and (b) In(NO₃)₃·5H₂O ($\lambda_{\text{exc}} = 551 \text{ nm}$).

determined through the use of the following compounds: In(acac)₃, In(NO₃)₃·5H₂O and InCl₃·4H₂O. The choice of the In(III) precursors necessarily limited the range of solvents that could be used due to solubility problems.

While it was found previously that Al(III) complexes of QNZ all gave a similar UV-Vis spectra [17], in the case of In(III), the UV-Vis spectra were counterion dependent. In the case of nitrate, the broad band typical of QNZ at ca. 480 nm, moves to higher wavelengths and becomes a shoulder while

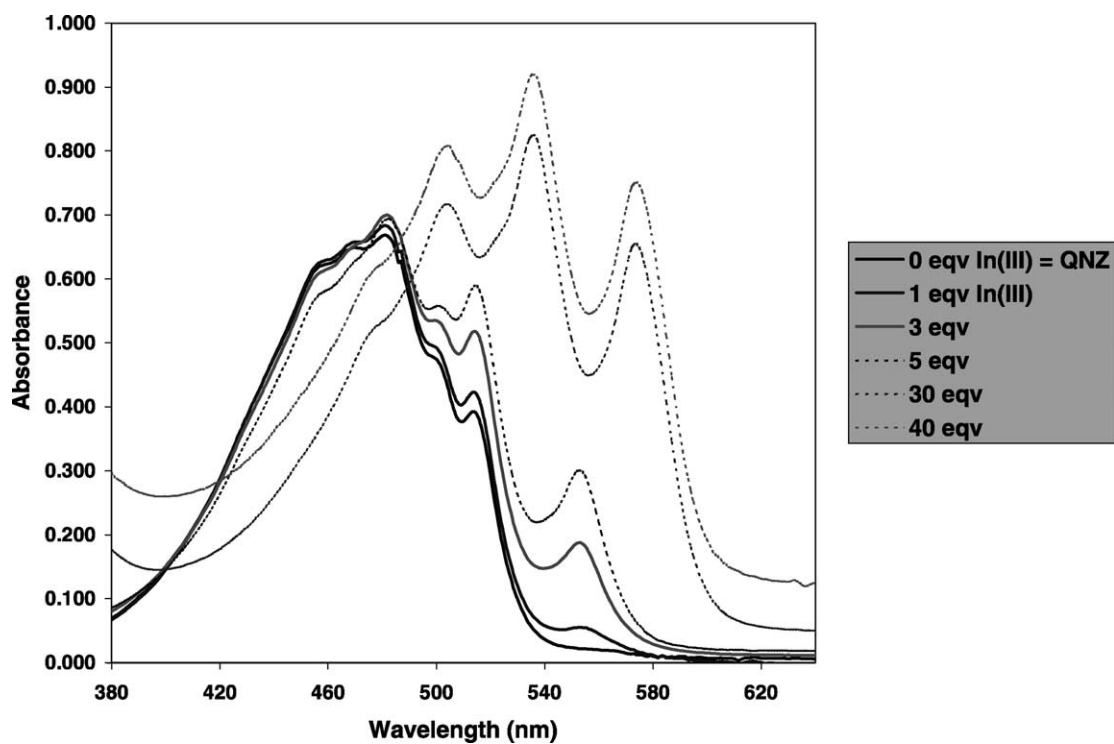


Fig. 4. UV-Vis spectra for quinizarin and In(NO₃)₃·5H₂O at different molar ratios in EtOH.

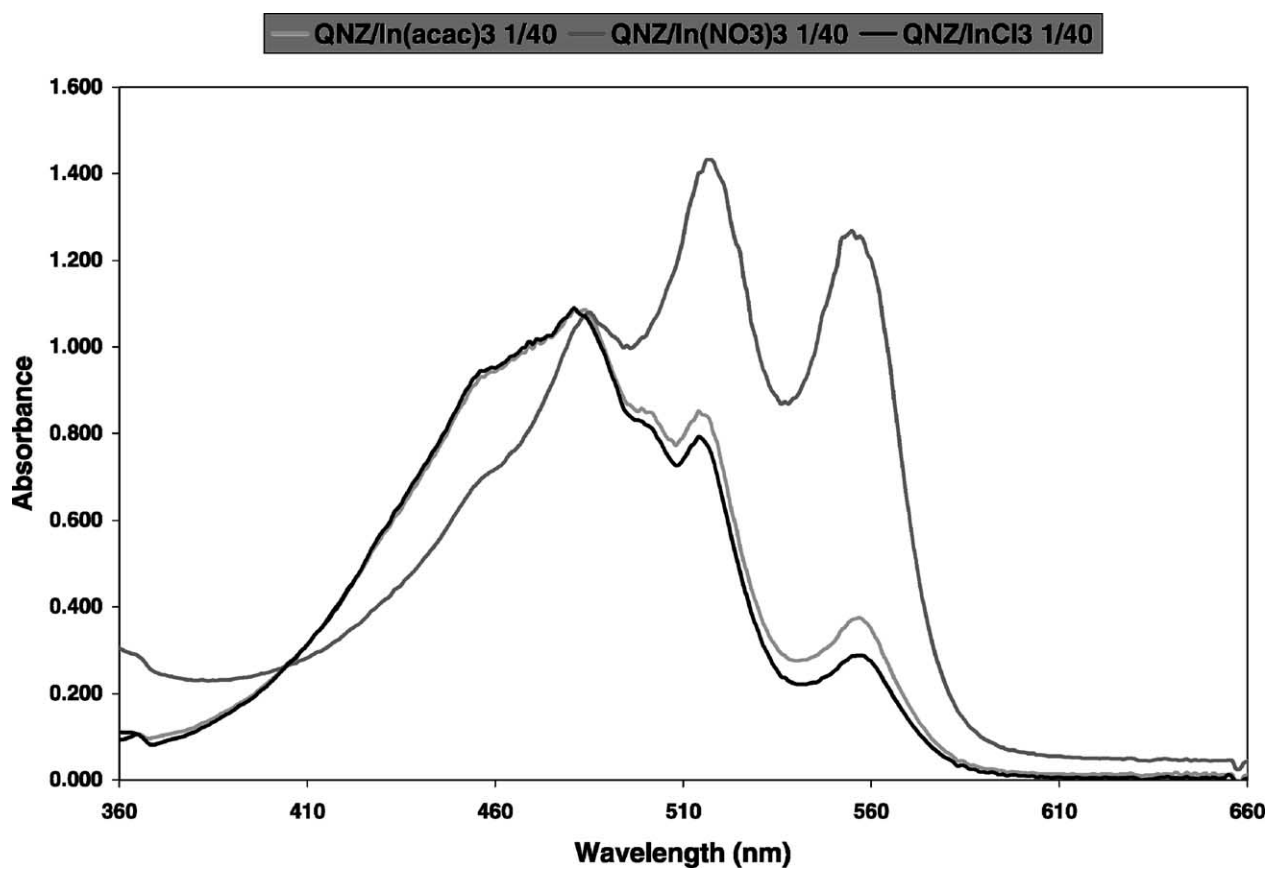


Fig. 5. Comparison of UV-Vis spectra for 1:40 QNZ/In(III)₃ compounds in EtOH.

two other peaks form at ca. 520 and 560 nm. Examples are shown in Fig. 4. The peak at 520 nm has a greater absorbance than that at 560 nm even at high QNZ/In(III) ratios, this being analogous to QNZ/Ga(acac)₃. The UV-Vis spectra of the QNZ solutions with In(acac)₃ and InCl₃·4H₂O, instead, are broadly QNZ in character with an additional peak at ca. 560 nm, of one-fourth intensity of that at 480 nm. A comparison among the spectra of QNZ with different In(III) sources is shown in Fig. 5. The solutions of QNZ/In(NO₃)₃ were pink-coloured while those of QNZ/In(acac)₃ and QNZ/InCl₃ were orange.

Typical fluorescence spectra (not shown) of the QNZ/In(III) species that formed in solution while increasing the metal molar ratio, also show two bands and a shoulder centred, respectively, at ca. 575, 610 and 660 nm when λ_{exc} was 560 nm.

We can conclude that with both Ga(III) and In(III) compounds, the equilibrium of the reaction with QNZ lies less towards the formation of the fluorescent species, responsible for the band at 570 nm, than in the complexes of QNZ with Al(III) compounds. With the latter, at QNZ/Al(III)

molar ratios higher than 1:5, the band at ca. 560 nm was always found to have higher absorbance than that at ca. 520 nm [17].

2.2. Time measurements

With all the solvents, the formation of the pink/orange colour upon addition of Ga(III) or In(III) ions to quinizarin occurred after some time. From qualitative kinetic studies, performed using both UV-Vis and fluorescence spectroscopy, it was concluded that the reaction between QNZ and Ga(acac)₃ was approaching equilibrium after 75 min from the mixing of metal and ligand (as shown in Fig. 6a). Therefore, 120 min from the mixing of the reagents was estimated as a reasonable interval of time after which the recording of the spectra was not unduly affected by equilibration.

The QNZ/In(III) solutions in general reached equilibrium faster than that of QNZ/Ga(acac)₃. The fastest reaction was found to be that with In(NO₃)₃·5H₂O: it reaches completion in less than 30 min, as shown in Fig. 6b.

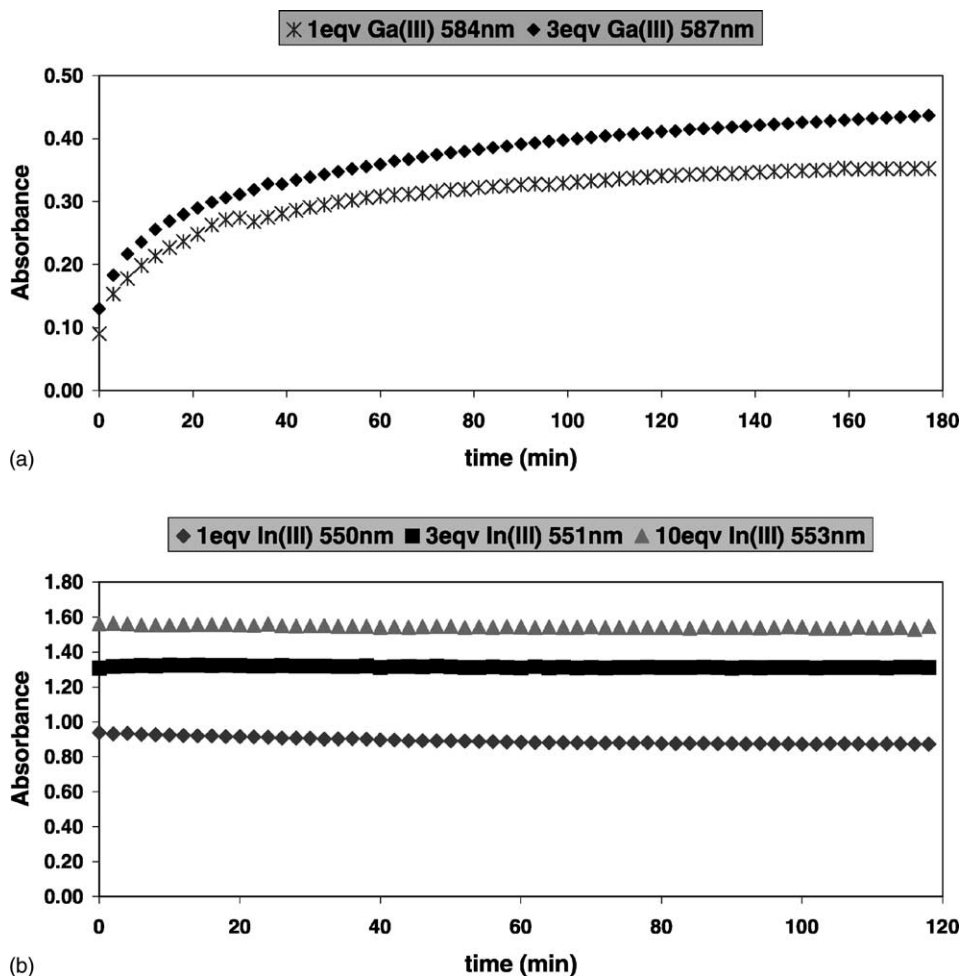


Fig. 6. Studies of the absorbance vs. time of QNZ with (a) Ga(acac)₃ and (b) In(NO₃)₃·5H₂O.

All the spectra reported in this work were recorded after equilibration of the solutions had occurred.

2.3. Speciation studies

The speciation of the fluorescent M(III)/QNZ complexation process was investigated in solution using optical methods such as the continuous variation (Job's method)

and the mole ratio. Examples of these experiments are shown in Figs. 1–4. In titrations, the M(III) ions were added to QNZ up to ratios of 60:1 or 75:1 metal/ligand. These solution studies suggested that the species forming in solution were supramolecular assemblies. In fact, both absorbance and fluorescence intensity were found to increase proportionally with the ratio of metal/quinizarin up to ratios of 60:1, as shown in Figs. 7 and 8 for, respectively, Ga(acac)

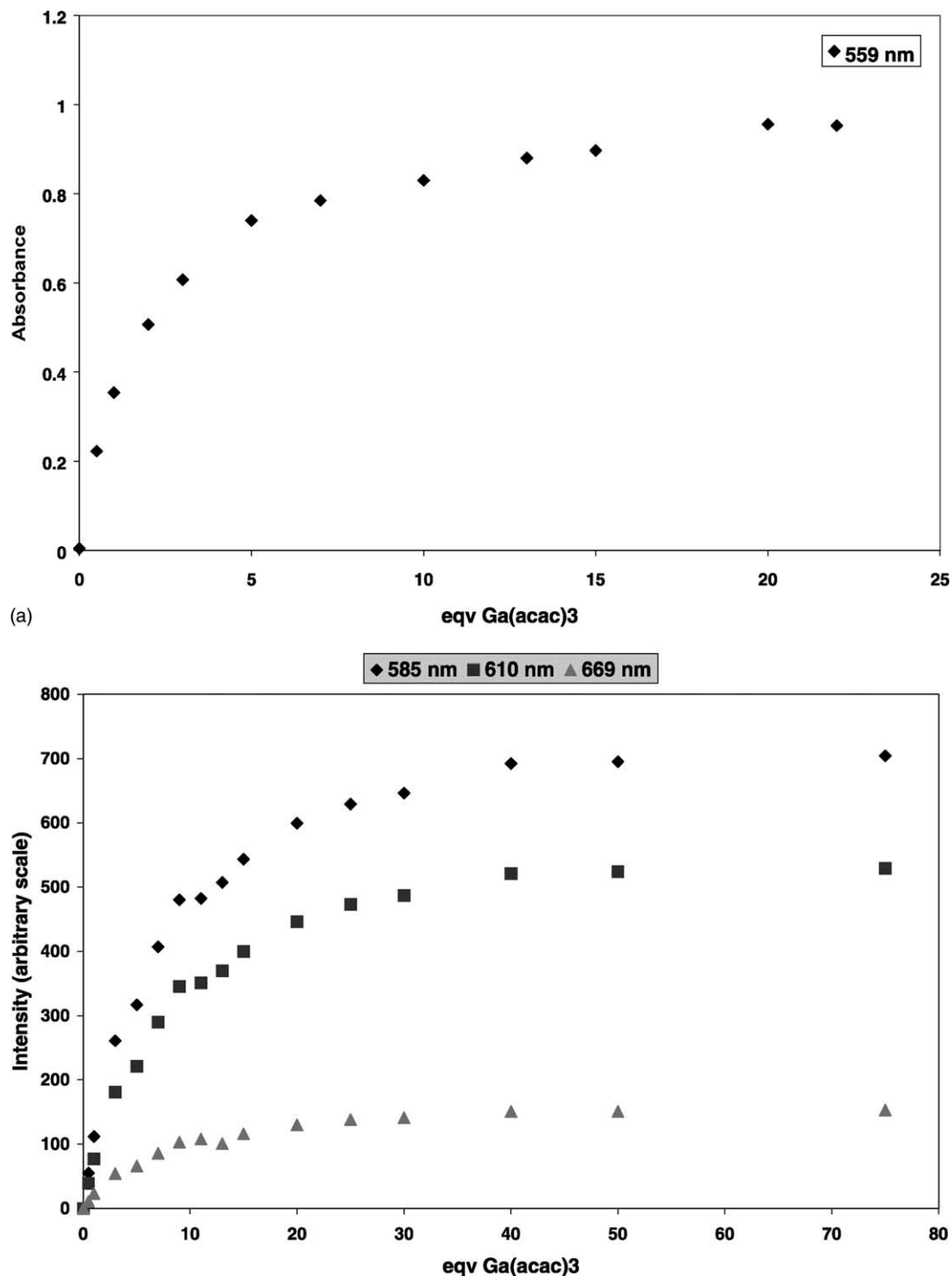


Fig. 7. Titration of quinizarin with Ga(acac)₃ in (a) *t*-BuOH followed by UV-Vis spectroscopy; and (b) *i*-PrOH followed by fluorescence.

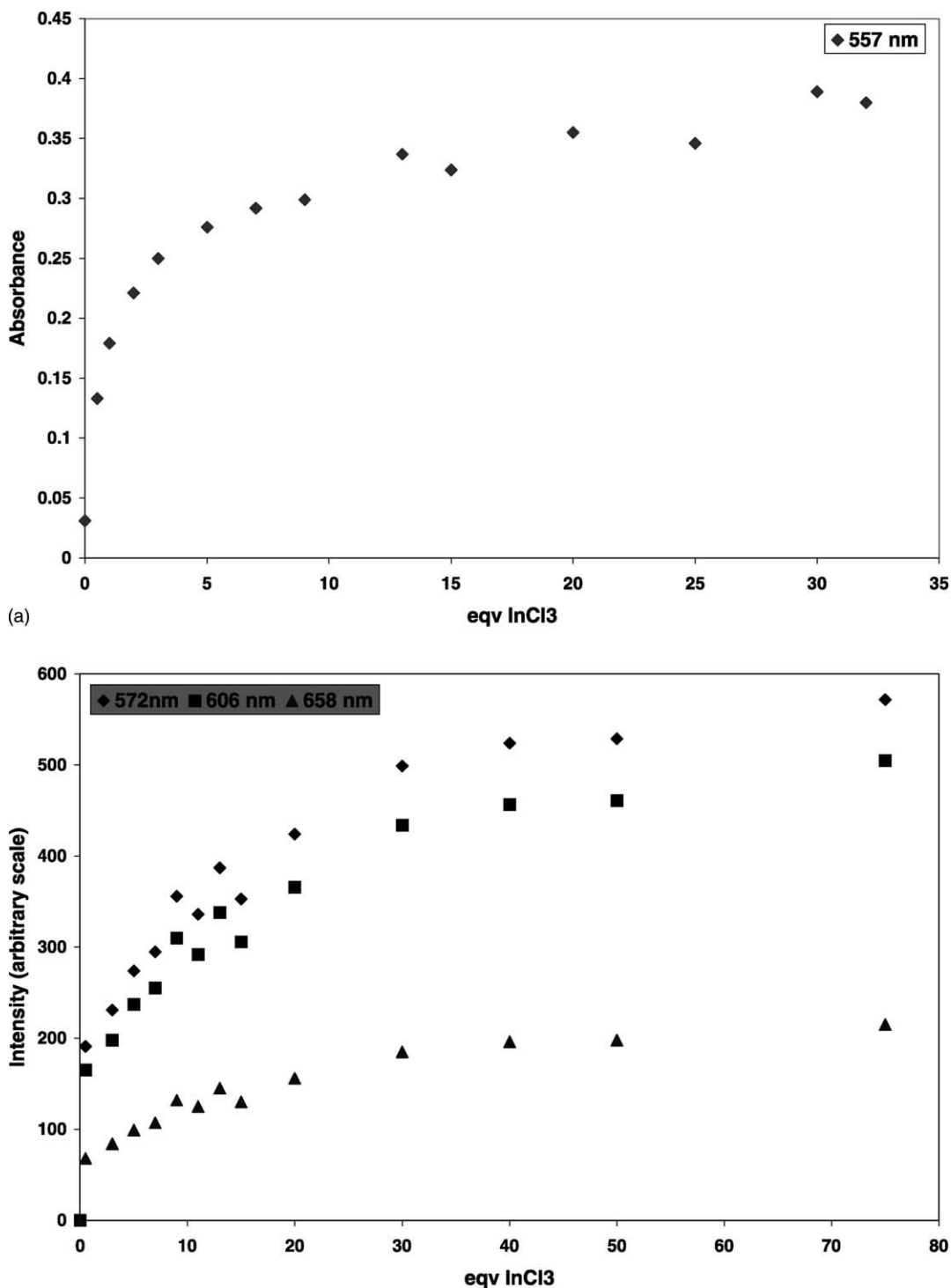


Fig. 8. Titration of quinizarin with $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$ in (a) EtOH followed by UV-Vis spectroscopy; and (b) *i*-PrOH followed by fluorescence.

and $\text{InCl}_3 \cdot 4\text{H}_2\text{O}$. In some instances, enhanced fluorescence was found even at higher ratios.

The difficulty in recovering quinizarin complexes, described in more detail later, and the poor quality of the characterisation data available from the literature make reasonable the hypothesis of supramolecular complexes forming.

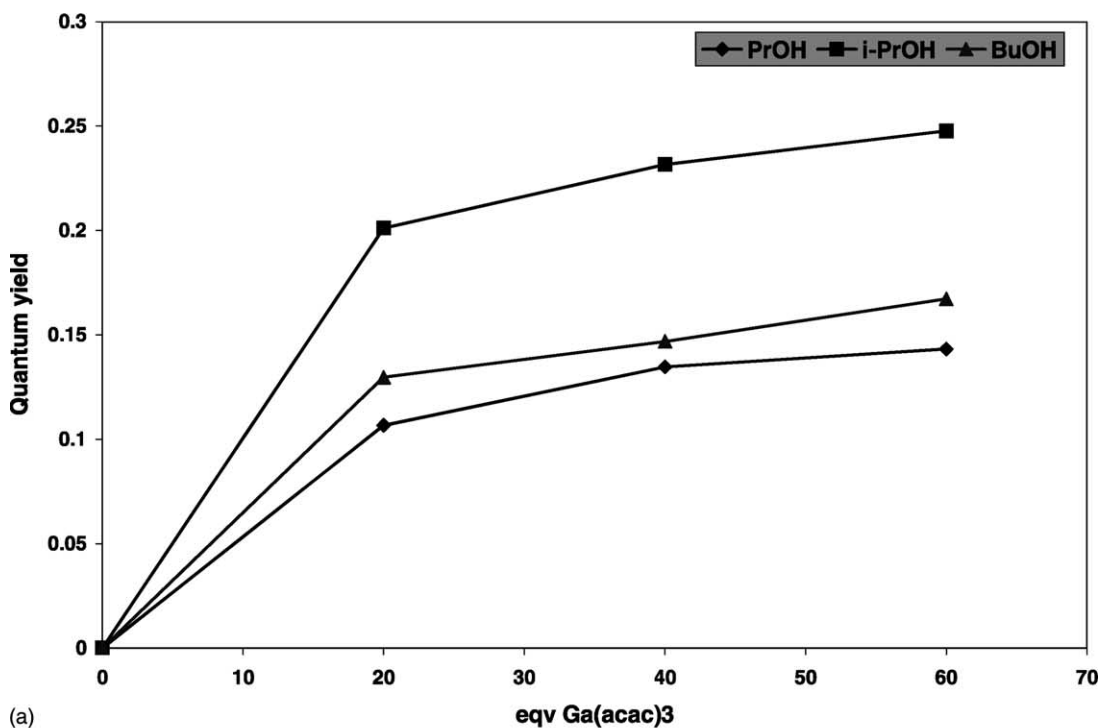
2.4. Temperature effect

UV-Vis studies of 1:1, 3:1 and 5:1 M(III) to QNZ solutions at 298 and 323 K, revealed that temperature does not influence the formation of the fluorescent species.

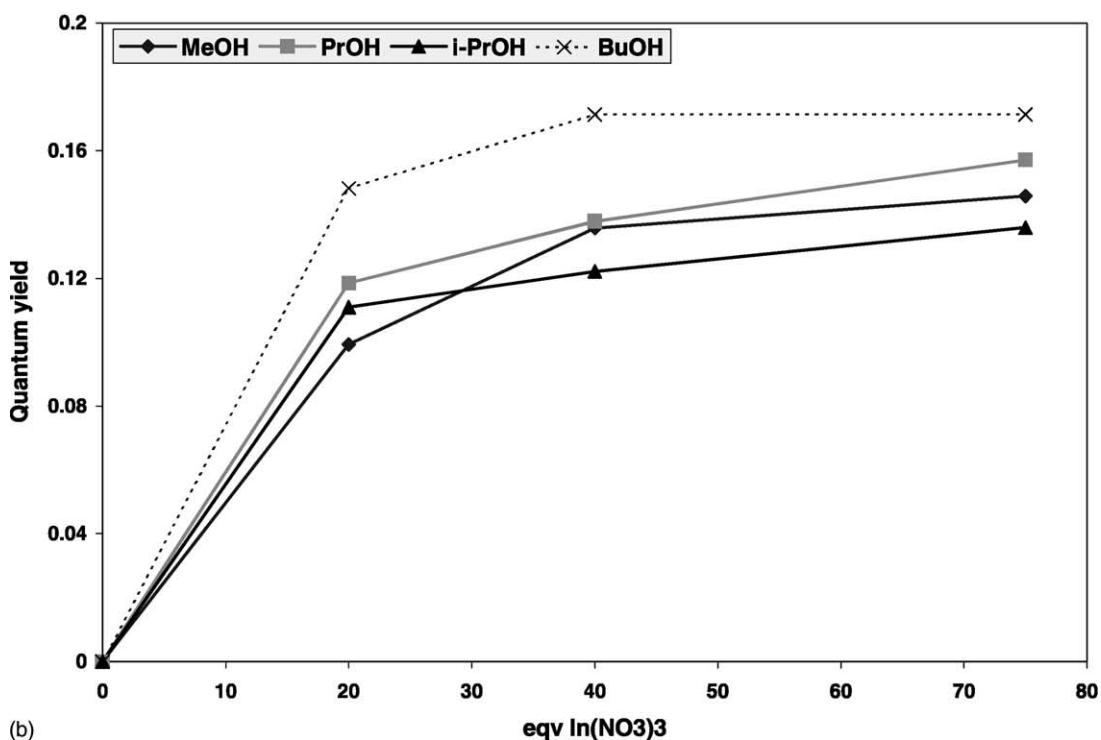
2.5. Solvent effect

In evaluating any solvent effect on fluorescence quantum yields, Ga(acac)₃ was the favoured source of Ga(III) ions and the solvents investigated were methanol, ethanol, propanol, *iso*-propanol, butanol and *tert*-butanol. In analogy with the

investigation of the species formed by QNZ and Al(III) ions [17], attention was mainly focused on the following three M(III)/QNZ ratios: 20:1, 40:1 and 60:1. The trends for PrOH, *i*-PrOH and BuOH are reported in Fig. 9a. Even at these high metal/QNZ ratios, fluorescence quantum-yield values were found to increase proportionally with the M(III) ratio.



(a)



(b)

Fig. 9. Quantum-yield values for different ratios of (a) QNZ/Ga(acac)₃ and (b) QNZ/In(NO₃)₃.

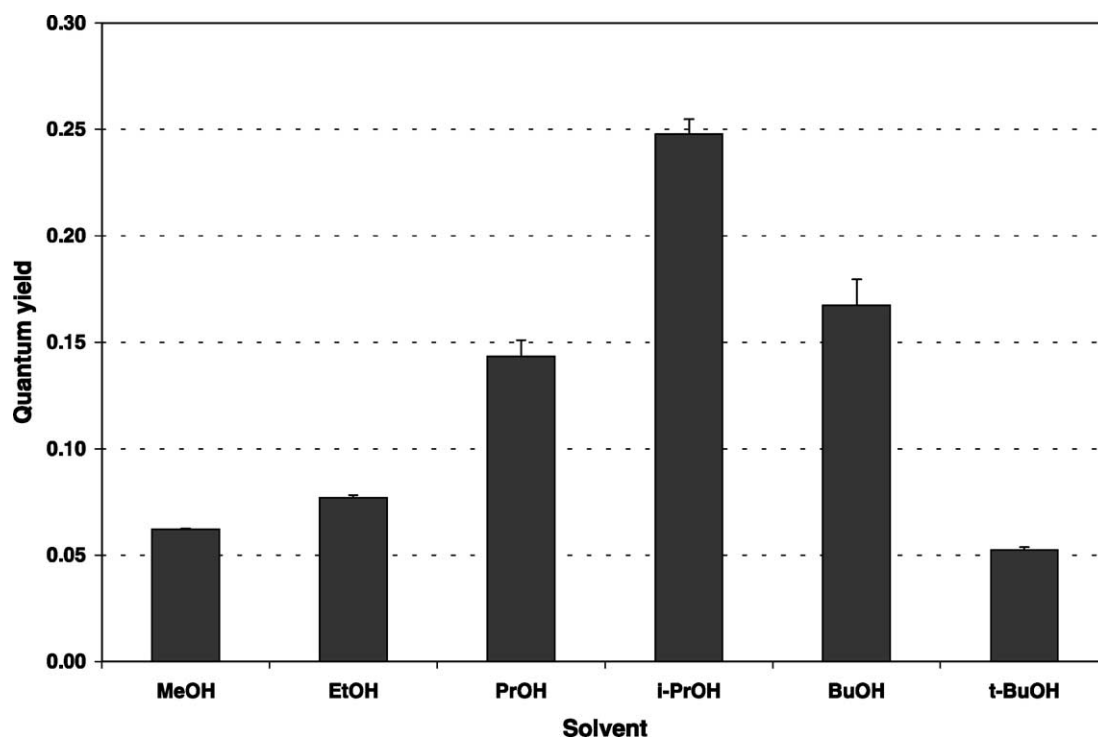


Fig. 10. Quantum-yield values for QNZ/Ga(acac)₃ 1:60 in different alcoholic solvents ($\lambda_{\text{exc}} = 525$ nm). Rhodamine B in EtOH has been used as reference ($\Phi = 0.70$).

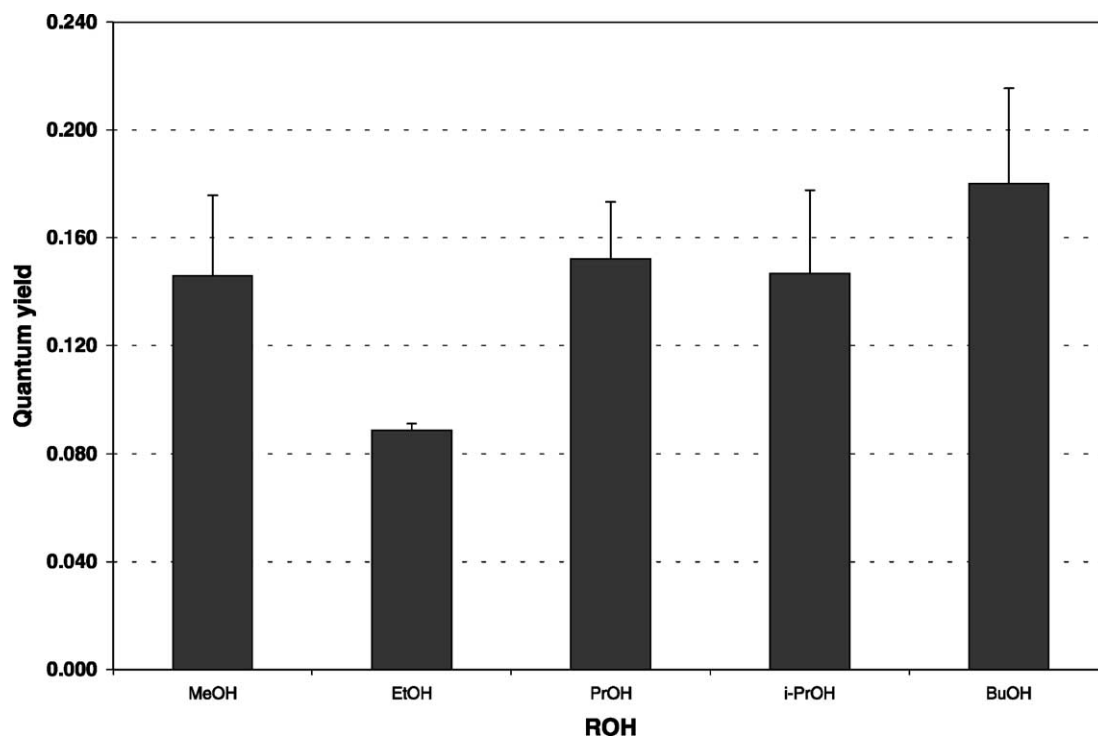


Fig. 11. Quantum-yield values for QNZ/In(NO₃)₃ 1:75 in different alcoholic solvents ($\lambda_{\text{exc}} = 515$ nm). Rhodamine B in EtOH has been used as reference ($\Phi = 0.70$).

Considering the solvent effect, the following trend for the quantum yields was found with all three Ga(III)/QNZ ratios: i -PrOH > BuOH \geq PrOH > EtOH > MeOH > t -BuOH. The values spanned from 0.05 with t -BuOH to 0.25 with i -PrOH. Fig. 10 shows the quantum-yield values of the 60:1 Ga(acac)₃/QNZ ratio in all the alcohols.

The same behaviour is reported for the interaction of QNZ with In(III) ions. In(NO₃)₃·5H₂O was the chosen source of In(III) ions and the solvents investigated were methanol, ethanol, propanol, *iso*-propanol and butanol. Attention was mainly focused on the following three M(III)/QNZ ratios: 20:1, 40:1 and 75:1 and the trends for MeOH, PrOH, i -PrOH and BuOH are reported in Fig. 9b. Even at these high metal/QNZ ratios, quantum yields were found to increase proportionally with the M(III) ratio, in analogy with what had been found with Ga(III) and Al(III) ions.

Considering the solvent effect, the following trend for the quantum-yield values was found with all three In(III)/QNZ ratios: BuOH \geq i -PrOH \approx PrOH \approx MeOH > EtOH and the values spanned from 0.09 with EtOH to 0.17 with BuOH. Fig. 11 shows the quantum-yield values of the 75:1 In(NO₃)₃/QNZ ratio for all the alcohols.

In Fig. 12, the fluorescence quantum-yield values of QNZ/Al(acac)₃, QNZ/Ga(acac)₃ and QNZ/In(NO₃)₃ are compared in different solvents. With all the solvents the complexes with Ga(III) and In(III) ions give values that are half, or less than those obtained with Al(III) ions. The following trend is found: QNZ/Al(III) > QNZ/Ga(III) \approx QNZ/In(III) which suggests that the size, or the charge den-

sity, of the metal ions influence the formation of fluorescent complexes.

3. Counterion effect

Evidence for any counterion effect was investigated in EtOH comparing the quantum-yield values obtained with In(acac)₃, In(NO₃)₃·5H₂O, and InCl₃·4H₂O. The 1:20, 1:40 and 1:75 QNZ/In(III) molar ratios were investigated and the results are reported in Fig. 13. These data reflect the different acidity of the In(III) materials and their degree of dissociation in solution. The highest quantum-yield values with the first two ratios were given by interaction with In(acac)₃ and InCl₃. When the QNZ/In(III) stoichiometry was 1:75, instead, the quantum-yield values were found to be similar with all the three In(III) compounds, with In(NO₃)₃ giving slightly higher values.

3.1. Stability constants measurements

Quinizarin protonation constants and the stability constants of its In(III) complexes were investigated potentiometrically in dioxane/water 80:20. The ligand protonation constants have been reported previously [17]. Bearing in mind the results obtained previously with Al(III)/QNZ, the conditions chosen for the study with In(III) were M/L 1:2.

The same precipitation problem encountered in the analogous experiment with Al(III) occurred with In(III). A bright

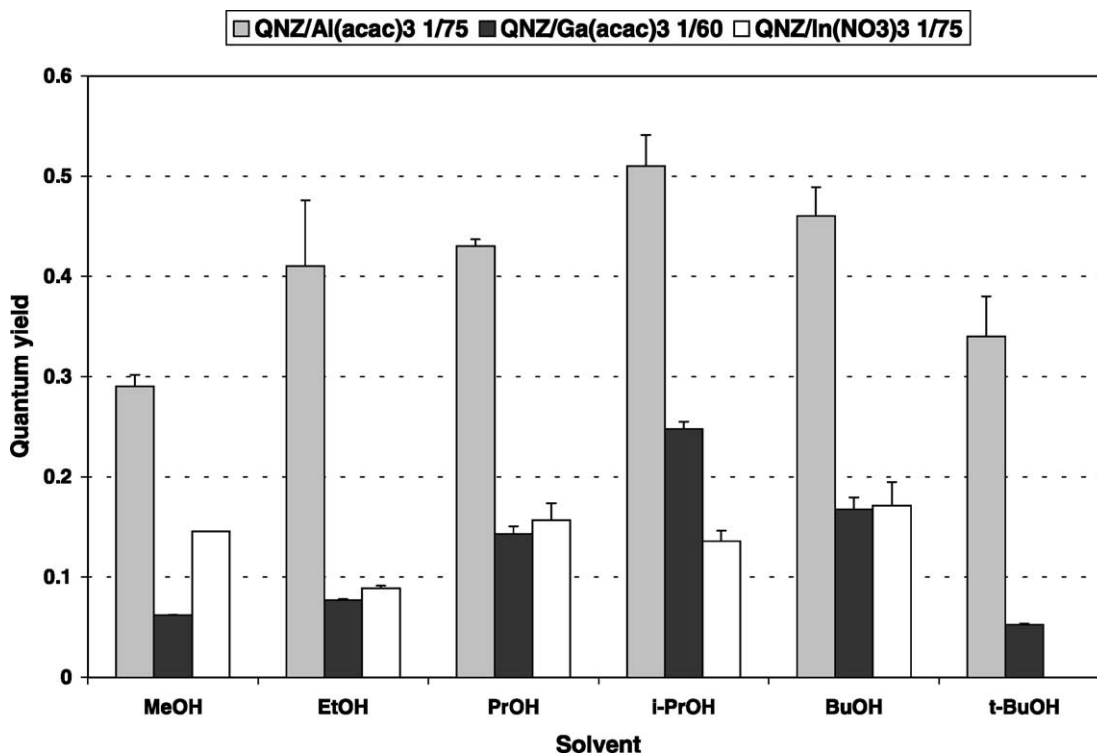


Fig. 12. Comparison of quantum-yield values for QNZ with Al(III), Ga(III) and In(III) ions in different alcoholic solvents.

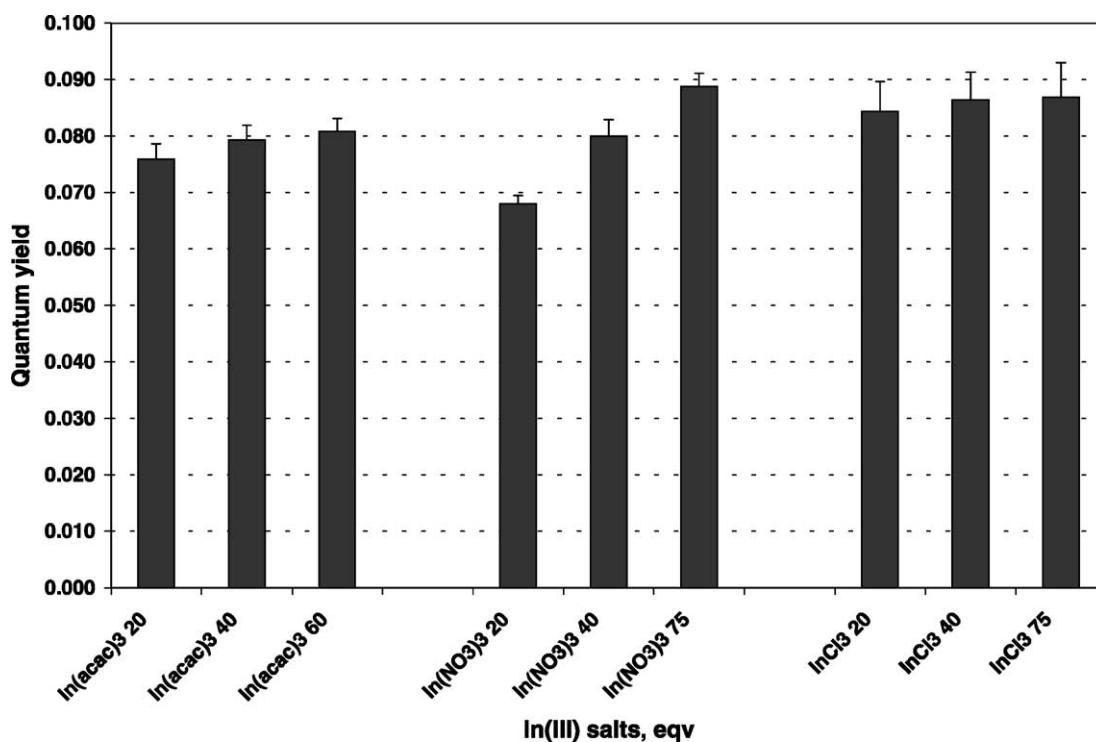


Fig. 13. Counterion effect on the quantum-yield values of QNZ/In(III) compounds in EtOH (Rhodamine B has been used as reference; $\lambda_{\text{exc}} = 515 \text{ nm}$).

pink/red material appeared in the titration beaker even in this case after pH 6. The precipitated material was too scarce to allow successful analysis by mass spectrometry.

The titration curve for the In(III)/QNZ experiment is similar to that obtained in the Al(III)/QNZ experiment as shown in Fig. 14, where the two curves are plotted together.

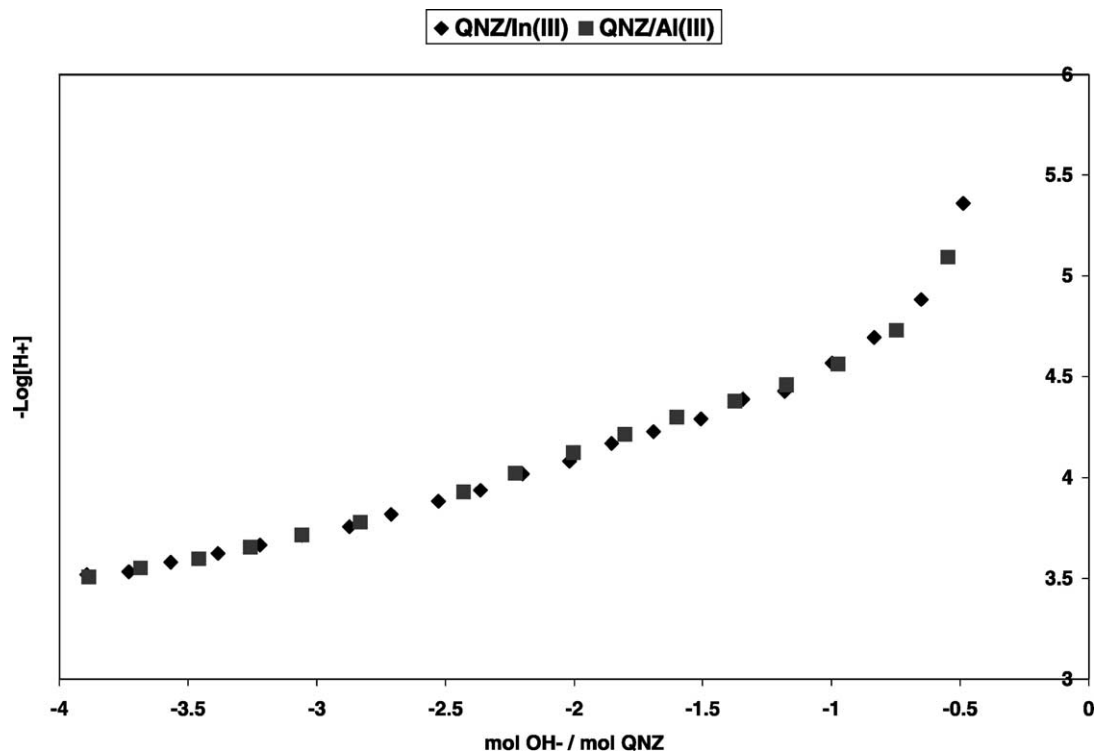


Fig. 14. Comparison among the titration curves of QNZ/In(NO₃)₃ and QNZ/Al(NO₃)₃ with NaOH in dioxane/water 4:1.

Table 2

Comparison of stability constants for the QNZ/In(III) and QNZ/Al(III) species measured potentiometrically in dioxane/water 80:20

Complexation reactions	Stability constants (log β_{LMH})	In(III)/QNZ	Al(III)/QNZ [15]
$M^{3+} + 2QNZ \quad [M(QNZ^{-H})_2]^+ + 2H^+$	log β_{212}	40.86 (0.09)	40.07
$M^{3+} + 2QNZ \quad [M(QNZ^{-2H})(QNZ^{-H})] + 3H^+$	log β_{211}	–	37.13
$M^{3+} + 2QNZ \quad [M(QNZ^{-2H})_2]^- + 4H^+$	log β_{210}	32.27 (0.06)	31.40

pK_a 's for QNZ: pK_1 10.39 and pK_2 9.93 [15]. β_{LMH} represents the overall stability constants for the protonated complexes such that β_{110} indicates the stability for the non-protonated species, ML. The overall stability constants correspond to $K_1 \cdot K_2 \cdot K_3 \cdot K_4 \cdot \dots \cdot K_n$, where K_n are the stepwise protonation constants defined as $K_n = [H_nL^{(n-3)+}]/[H^{+}][H_{n-1}L^{(n-4)+}]$.

The stability constants for QNZ/In(NO₃)₃ obtained in this work are in good agreement with those obtained for QNZ/Al(III), as shown in Table 2. The overall stability constants that resulted from the refinement of the titration data were β_{212} and β_{210} , i.e. the species that form are $[InL_2H_2]^+$ and $[InL_2]^-$. They indicate that highly stable species form in solution.

The speciation data were also calculated [18]. The species $[InL_2H_2]^+$ has its maximum of formation (30%) around pH 4.2. $[InL_2]^-$ is instead the predominant species (80%) at precipitation, at pH 5.36, while 10% of In(III) is still uncomplexed.

3.2. Attempts of isolation of the fluorescent species

Attempts to isolate fluorescent species from a wide range of QNZ/M(III) stoichiometries, in the solid state have proved unsuccessful so far. Experiments have also been set up in the presence of a second ligand, namely py, acac⁻, salicylaldehyde, salicylic acid, pyrophosphate, in order to form mixed-ligand complexes but these have also been proven unsuccessful.

In some instances, single crystals were recovered but they either decomposed by loosing solvent on isolation or they proved to be unsuitable material for X-ray diffractometry.

4. Conclusions

Speciation studies suggest the supramolecular nature of the QNZ/M(III) complexes, where M(III) = Ga, In and Al, as both the absorbance and fluorescence intensity of the complexes increases proportionally to the M(III) equivalents up to 60:1 M(III)/QNZ molar ratio and in certain cases even further.

Potentiometric studies give QNZ/In(III) stability constant values in agreement with those reported for QNZ/Al(III). The 2:1 QNZ/In(III) species were found to form and to have high global stability constants.

From the isolation attempts performed so far it appears that the formation of QNZ/M(III) fluorescent species takes place mainly in solution and it suggests the direct participation of solvents in the stoichiometry of the fluorescent species.

Comparing the fluorescence quantum-yield values obtained with the different M(III) ions, the following trend was

found: QNZ/Al(III) > QNZ/Ga(III) \approx QNZ/In(III) which suggests that the size, or the charge density, of the metal ions are important factor for the efficient formation of fluorescent complexes. The M(III)-ion size increases from 0.535 to 0.800 Å [19] going from Al(III) to In(III), disfavours the formation of the fluorescent species. With both Ga(III) and In(III) ions the equilibrium of formation of the fluorescence complexes with QNZ was found to lie more towards the reactants than with the QNZ/Al(III) complexes. Therefore, among those investigated so far, the Al(III)/QNZ complexes are the most promising to be developed as fluorescent sensors. Further investigation of the interaction between QNZ and In(III) ions are currently under investigation.

5. Experimental

All the solvents and reagents were used as purchased. An interval of time longer than 90 min passed between the preparation of the samples and the recording of UV-Vis and fluorescence spectra. UV-Vis spectra were recorded on a Hewlett-Packard 8453 spectrophotometer. The concentration of the solutions was 3×10^{-5} M in QNZ.

Fluorescence spectra were measured on a Perkin-Elmer LS 55 Luminescence Spectrometer. Relative Φ values were measured at room temperature using 525 nm as excitation wavelength for QNZ/Ga(acac)₃ and 515 nm for QNZ/In(NO₃)₃. Rhodamine B in ethanol was used as reference ($\Phi = 0.70$) [20]. The concentration of the analysed solutions was 5×10^{-6} M in QNZ.

5.1. Potentiometric measurements

The 0.5 M In(III) solutions were prepared from nine hydrated nitrate salt, of analytical grade, with demineralised water. Solution temperatures were maintained at 25.0 ± 0.1 °C using a water-jacketed vessel while CO₂ was excluded by bubbling nitrogen. Ionic strength was maintained 0.10 M with NaClO₄. 50 ml of $\sim 10^{-3}$ M quinizarin, or QNZ/In(III), in dioxane/water 4:1 (v/v) were titrated in the presence of excess HClO₄ (0.20 M) with standard 0.20 M NaOH. The 1:2 In(III)/QNZ molar ratio was used.

Protonation and stability constants were calculated with HYPERQUAD [21]. Differences, in log units, between the values of β provide the stepwise protonation constants. The

species considered were limited to those that could be justified by coordination chemistry. From the stability constants, the distribution curves for the species present at the equilibrium versus $-\log [H^+]$ were calculated with the program DISPLO [18].

Further information on the species that formed during the titrations was obtained with the on-line recording of UV-Vis spectra, using a Hewlett-Packard 8453 spectrophotometer coupled to the titration automatic burette.

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