



EFFECT OF PH ON THE FLUORESCENCE QUENCHING OF 5-CHLORO-1, 10 PHENANTHROLINE BY Fe(II)

D. H. Thanippuli Arachchi¹, M. D. P. De Costa¹, R. Senthilnithy^{2*}

¹Department of Chemistry, University of Colombo

²Department of Chemistry, The Open University of Sri Lanka

INTRODUCTION

1,10-Phenanthroline is the parent compound of an important class of chelating agents (Sammes & Yahioğlu, 1994). Due to the high reactivity and short-lived nature, only a very few techniques have been reported in the selective analysis of Fe(II) in contrast to Fe(III). The strong chelating ability of phenanthroline to Fe(II), enables development of phenanthroline based turn-off fluorescence sensors for the analysis of Fe(II). The photophysical properties of phenanthroline structure can be tuned by substitution as well as by varying the pH of the medium. Phenanthroline undergoes mono protonation where one proton is equally shared between the two nitrogen atoms. However, at low acidic conditions, the proton is shared asymmetrically (Listorti et. al., 2007). By substituting the fifth position of the pristine 1,10-phenanthroline with a chlorine (Cl) atom, the chloro derivative is obtained. This study is focused on studying the effect of pH on the fluorescence quenching of 5-chloro-1,10-phenanthroline by Fe(II).

METHODOLOGY

Instrumentation

Fluorescence measurements were made on a Hitachi F 7000 spectrofluorometer with a 150 W xenon lamp using a 1×1 cm² quartz fluorescence cuvette. Slit widths were set to 10 nm on both the excitation and emission monochromators. The excitation and emission wavelengths were 286 nm and 379 nm, respectively.

Reagents and glassware

The AR grade, 98% 5-chloro-1,10-phenanthroline, (NH₄)₂Fe(SO₄)₂·6H₂O, CuSO₄·5H₂O, NiSO₄·6H₂O, NaH₂PO₄·2H₂O, Na₂HPO₄, extra pure 98% H₃PO₄ acid (85% assay), extra pure 98% H₂SO₄ acid, methanol, and freshly double-distilled water were used in preparing the solutions for spectroscopic measurements. All the glassware were cleaned using soap, tap water, and distilled water, respectively, and oven-dried before use in the analysis.

Stock solution of 5-chloro-1,10-phenanthroline

The stock solution of 4.57×10^{-3} M 5-chloro-1,10-phenanthroline was prepared by accurately weighing 10.0 mg of the solid and dissolving it in 10.0 mL of methanol/water 1:1 (v/v) solution.

Fe(II) solutions

The stock solution of 1.27×10^{-1} M Fe(II) was prepared by dissolving an accurately measured amount of 50.0 mg of (NH₄)₂Fe(SO₄)₂·6H₂O in 10.0 mL freshly double-distilled water.

Preparation of aqueous buffers

Buffer solutions (1 M) of pH 3.80 and 4.10 were prepared in deionized water using the appropriate amounts of 98% H₃PO₄ acid, NaH₂PO₄·2H₂O, and Na₂HPO₄.

H₂SO₄ acid solutions

A stock solution of 9.35×10^{-2} M H₂SO₄ was prepared by diluting a volume of 50.0 μL of 98% H₂SO₄ up to 10.0 mL in methanol/water 1:1 (v/v) solution.



Effect of pH on the fluorescence emission of the fluorophores

The variation of the emission spectral characteristics on pH was analyzed by keeping the concentration of 5-chloro-1,10-phenanthroline constant at 1.42×10^{-5} M in methanol/water 1:1 (v/v) solution. The fluorescence emission spectra were obtained upon the addition of 2.0 μL of 1.87×10^{-2} M H_2SO_4 in methanol/water 1:1 (v/v) solution, at each spike. The pH of the resulting solution was recorded concurrently.

Optimization of pH

Aqueous buffer solutions of pH 3.80, 4.10, 4.80, 5.80 and 6.80 were prepared. The solutions for the study were made in methanol/water/buffer 5:4:1 (v/v) ratio by keeping the concentration of the fluorophore constant at 1.42×10^{-5} M. The fluorescence emission spectra were recorded upon the addition of 1.5 μL of 2.55×10^{-4} M Fe(II) working solution, for each value of pH, separately. Stern-Volmer plots were generated and the quenching sensitivity at each value of pH was analyzed.

Influence of pH for the selectivity of Fe(II)

The study was carried out at pH 3.80 and 4.10 for the interfering ions: Cu(II) and Ni(II), separately. The fluorescence emission spectra for the ligand alone, for the ligand in the presence of 2.55×10^{-7} M interfering ion, for the ligand in the presence of both Fe(II) and the interfering ion of the same concentration of 2.55×10^{-7} M were recorded. The degree of percentage fluorescence quenching by the interfering ion alone and by both interfering ion and Fe(II) in the same concentration was analyzed.

RESULTS AND DISCUSSION

Effect of pH on the fluorescence emission of 5-chloro-1,10-phenanthroline

Phenanthroline family of compounds usually undergo monoprotonation where one H^+ is shared between the two nitrogen atoms at 1,10 positions. In asymmetric derivatives, protons prefer sitting on one of the two nitrogen atoms than being shared (Listorti et. al., 2007). The variation of the fluorescence emission of 5-chloro-1,10-phenanthroline with the pH of the medium is presented in Fig. 1.

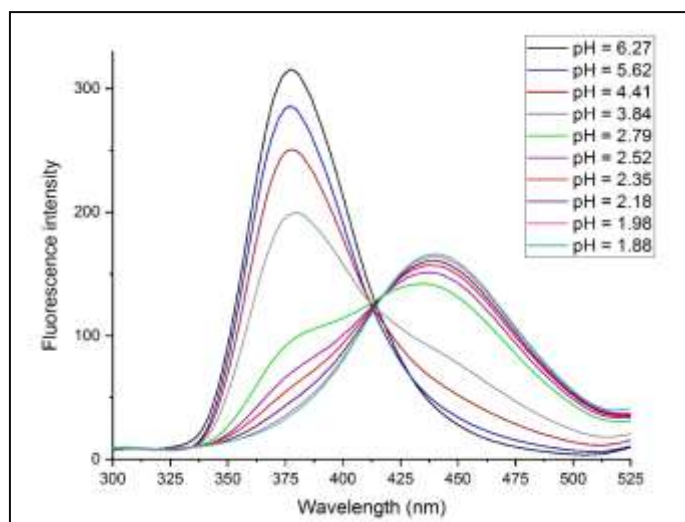


Fig. 1. The effect of pH on the fluorescence emission intensity of 5-chloro-1,10-phenanthroline at $\lambda_{\text{ex}} 286 \text{ nm}$

The appearance of an iso-emissive point suggests that only one chemical equilibrium is under way: the protonation-deprotonation of nitrogen in the phenanthroline structure, resulting in two species,



protonated and unprotonated forms of the ligand. When pH decreases, the fluorescence emission intensity of the peak at 379 nm, corresponding to the unprotonated ligand, was observed to decrease with a concomitant emergence of a broad band at a longer wavelength of 440 nm which corresponds to the protonated ligand. Therefore, pH 2.80 can be suggested as the lowest pH to be used in developing a turn-off sensor to analyze Fe(II) with minimal protonation of the fluorophore.

Optimization of pH

The stability/formation constant of a formed complex depends on the pH of the medium due to by-reactions of the ligand, such as protonation and hydroxide formation. The fluorescence quenching of 5-chloro-1,10-phenanthroline by Fe(II), at different pH, was investigated by examining the magnitudes of the slopes of Stern-Volmer plots generated at each pH. When decreasing the pH of the medium, the magnitude of fluorescence quenching increased, indicating a higher efficiency of metal-ligand complex formation in acidic media, as presented in Table 1.

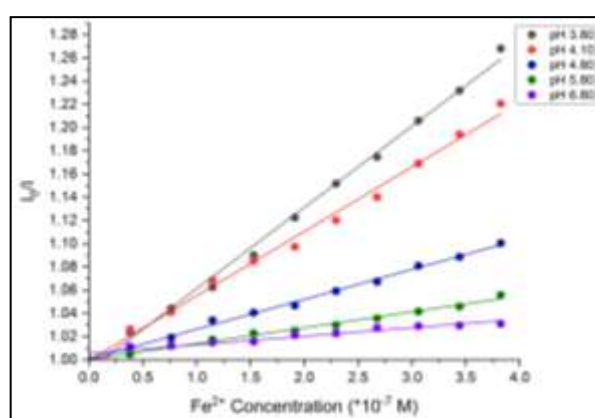


Fig. 2. Stern-Volmer plots indicating the fluorescence quenching of 5-chloro-1,10-phenanthroline with the increasing Fe(II) concentration at different pH.

Table 1: Quenching constants derived from Stern-Volmer plots at different pH

pH value	Stern-Volmer quenching constant (*10 ⁻⁹ L/mol)	Correlation Coefficient (r ²)
6.80	0.730	0.9338
5.80	1.37	0.9911
4.80	2.58	0.9966
4.10	5.55	0.9933
3.80	7.00	0.9953

When the pH of the medium is low, the equilibrium between Fe(II) and Fe(OH)_x directs towards producing more free Fe(II), which will then be available for the complexation with 5-chloro-1,10-phenanthroline, enhancing the sensitivity of quenching. If pH of the medium is further decreased up to 2.80, the formation of the metal-ligand complex is expected to be low due to the competition between protonation of the ligand and metal-ligand complexation. Therefore, the lowest pH to be used is not less than 2.80 to avoid the effect from protonation of the ligand. The pH 3.80 - 4.10 could be identified as the optimum range of pH at which the highest quenching sensitivity by Fe(II) is observed for 5-chloro-1,10-phenanthroline.

Influence of pH for the selectivity of Fe(II)



Cu(II) and Ni(II) are two common cations that have been identified in forming complexes with the phenanthroline skeleton. Therefore, this study was carried out to observe the influence of pH for the selectivity of Fe(II) in the presence of Cu(II) and Ni(II), separately. The degree of percentage fluorescence quenching was analyzed at both pH 3.80 and 4.10, for Cu(II) and Ni(II) separately, as presented in Fig. 2. When the emission intensity of the fluorophore alone is 100%, irrespective of the pH, the percentage degree of fluorescence quenching by Fe(II) is higher than that of the amount quenched by the interference ion, indicating a higher selectivity for Fe(II). At pH 3.80, in the presence of Cu(II) and Ni(II), selectivity for Fe(II) is around 3.98 and 5.32 times higher, respectively. At pH 4.10, in the presence of Cu(II) and Ni(II), selectivity for Fe(II) is around 3.79 and 4.02 times higher, respectively. Therefore, a higher selectivity for Fe(II) is observed in the presence of Cu(II) and Ni(II) when the pH is reduced to 3.80. This can be due to the lower stability of the metal-ligand complexes formed between the interfering ion and the fluorophore at lower pH values, which in contrast favours the complex formation between Fe(II) and 5-chloro-1,10-phenanthroline. Therefore, 5-chloro-1,10-phenanthroline can be suggested as a fluorophore that can be used in the accurate determination of Fe(II) at acidic media with minimum interference from foreign ions.

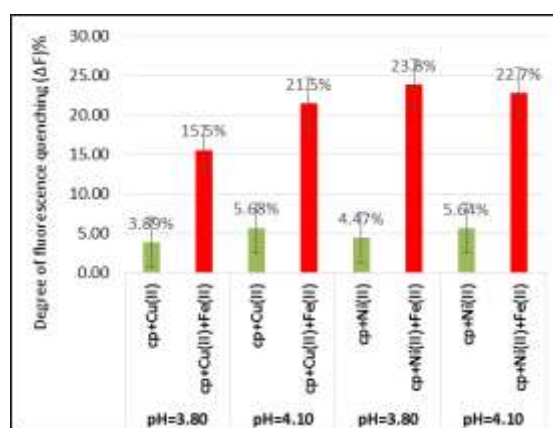


Fig. 3: The degree of fluorescence quenching (ΔF)% in the presence of 2.55×10^{-7} M interfering ion alone, interfering ion and Fe(II) in the same concentration of 2.55×10^{-7} M at pH 3.80 and 4.10, for Cu(II) and Ni(II). (Note: cp = 5-chloro-1,10-phenanthroline ligand)

CONCLUSIONS

The photophysical properties of 5-chloro-1,10-phenanthroline ligand can be effectively tuned through the variation of pH in the medium. The protonation of the ligand occurs at pH below 2.80, and the optimum pH range that can be used in developing the probe was identified as pH 3.80 to 4.10. At acidic pH, the magnitude of fluorescence quenching by Fe(II) is higher, increasing the probe's sensitivity and selectivity due to the stable complex formation between Fe(II) and the ligand. At low pH, 5-chloro-1,10-phenanthroline can be developed as a turn-off fluorescence sensor to analyze Fe(II), with minimum interference from Cu(II) and Ni(II) ions.

REFERENCES

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