Ultra Chemistry Vol. 8(3), 377-385 (2012).

Spectrofluorometric Determination of the Stoichiometric and Formation Constant of 8-Hydroxyquinoline Complexes with Aluminium, Cadmium, Magnesium, and Zinc in Aqueous Solution

ZUKI H.M

Department of Chemical Sciences, Faculty of Science and Technology,
University of Malaysia Terengganu, 21030, Kuala Terengganu (MALAYSIA)
hafiza@umt.edu.my

(Acceptance Date 3rd December, 2012)

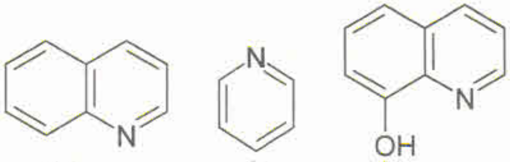
Abstract

The fluorescence spectra of the metal-8-hydroxyquinoline (metal-HQ) complexes were obtained by measuring the fluorescence intensity emitted from the complexes produced by the reaction of metal ions with HQ reagent. The excitation wavelengths for all four Metal-HQ complexes occur at 370 nm. Meanwhile the emission wavelengths for Al-HQ, Cd-HQ, Mg-HQ and Zn-HQ complexes occur at 522 nm, 555 nm, 520 nm and 538 nm respectively. The stoichiometric and formation constant of the metal-HQ complexes were determined by means of Job's method. The stoichiometry evaluated for metal-reagent complexes are 1:3 for Al-HQ and 1:2 for Cd-HQ, Mg-HQ and Zn-HQ respectively. Meanwhile the stability of the complexes are given by the order of $Al^{3-} > Zn^{2-} > Cd^{2-} > Mg^{2-}$.

Key words : 8-hydroxyquinoline, metal-8-hydroxyquinoline complexes, job plots, stoichiometry, formation constant.

1.0 Introduction

Quinoline has been widely used in analytical chemistry. Because of the pyridine group (Figure 1.1b) present in a quinoline molecule (Figure 1.1a), it forms more stable complexes with a metal ion[1]. Recently, there are many types of quinoline derivatives that have been used by researchers for the detection of metal ions[1-4]. Amongst these, 8-hydroxyquinoline is well known to react as a chelating and/or preconcentration agent with several metals because of the presence of basic nitrogen, and a phenolic group in its bonding (Figure 1.1c).



(a) (b) (c)

Figure 1.1 Molecular structure of (a) quinoline (b) pyridine and (c) 8-hydroxyquinoline

In HQ, the hydroxyl group located with respect to the nitrogen atom in the quinoline nuclear allows the formation of the inner complexes by reaction with metals. However, not all metals produce internal complexes with HQ. This is due to the phenomenon of ring closure 'being subordinate to the spatial depositions of the atoms and the direction of their valencies'[5]. Two structures are possible for the formation of complexes with metals (Figure 1.2). Metal may be bound co-ordinately to the nitrogen atom or to the oxygen atom, in either case a five membered ring is formed. The same holds for the HQ derivatives, as all derivatives contain the same reactive group as the parent compounds.

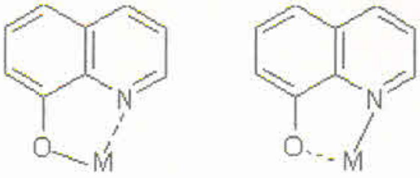


Figure 1.2. Possible structures for complex formation with a metal

Compared to its derivatives, HQ is very unselective. It chelates with many metals (more than 60)[6-10] to form complexes, whereas certain derivatives of HQ only chelate with fewer metals under the same conditions. On its own, HQ is non-fluoresced and sometimes it displays very weak fluorescence due to the intramolecular proton transfer process (from oxygen to nitrogen) in its excited state, which provides a route for non-radiative relaxation[11]. Chelation of metal ions, however, can decrease the p*Ka* values of the hydroxyl proton, and once this proton is lost, HQ becomes highly fluorescent[12]. Consequently, this unique HQ property can provide an on-off sensing response to metal ion binding.

This paper discusses the solution studies performed involving the investigation of the interaction of the HQ fluorescence reagents with four metal ions (Al^{2+}, Cd^{2+}, Mg^{2+} and Zn^{2+}). The study is focusing on the ability, reactivity and properties of these metal-HQ interactions such as the formation of the complexes, stoichiometry of the complexes, and the formation constant of the complexes. The information obtained will be useful for further analysis and application of the HQ fluorescence reagents as sensing materials for metal ions chemical sensor.

2.0 Experimentation

2.1 Chemical and Reagents :

HQ, and all metal salts used were analytical reagent grade and were used without any further purification. Different pH buffer solutions were prepared from the mixture of phthalate and borax salts. Stock solutions of 0.003 M HQ was prepared by dissolving the reagent into the mixture of distilled deionized water and methanol in 1:1 ratio. Meanwhile, 0.001 M metal ions stock solutions were prepared by dissolving the metal salts into distilled deionised water.

2.2 *Instrumentation and Measurement Procedure :*

The study was performed using the fluorescence technique. All the measurements were recorded by the Perkin Elmer LS55 fluorescence spectrophotometer. The instrument was set to make a measurement at every 0.5 nm interval in the wavelength range of 300 - 650 nm. The excitation and emission slits were set at 10 nm to optimise the fluorescence spectrum. A standard quartz cuvette with a light path of 1.0 cm was used for the entire measurements.

3.0 Results and Discussions

3.1. *Complex Formation and Spectral Features:*

The fluorescence spectra of the metal-HQ complexes were obtained by measuring the fluorescence intensity emitted from the complexes produced by the reaction of metal ions with HQ reagent. The excitation and emission spectra obtained for each metal-HQ complexes are shown in Figure 3.1. The excitation wavelengths for all four Metal-HQ complexes occur at 370 nm. Meanwhile the emission wavelengths for Al-HQ, Cd-HQ, Mg-HQ and Zn-HQ complexes occur at 522 nm, 555 nm, 520 nm and 538 nm respectively.

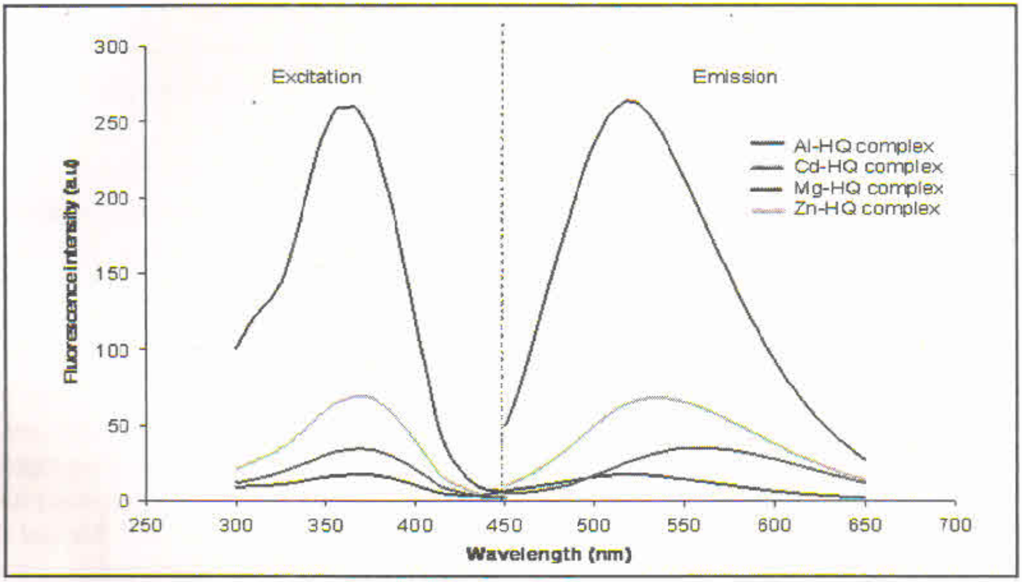


Figure 3.1. Metal-HQ complexes spectra (excitation spectra measured at emission wavelength and emission spectra measured at excitation wavelength)

3.2 Effect of pH :

Metals react with HQ at specific pH's, so raising or lowering the pH will affect the complexation. Therefore, pH control is important during the complexation process. The intensity of the fluorescence of HQ-metal complexes was measured over a range of pH values obtained by adjusting the pH with sodium chloride and hydrochloric acid. As shown in Figure 3.2, the maximum intensity of Al-HQ complex was obtained at pH 7. Meanwhile, for the Cd-HQ, Mg-HQ, and Zn-HQ complexes, the maximum intensity occurs at pH 6. These optimum pHs (pH 6 and 7) are chosen as the optimum conditions for all experimentations involved.

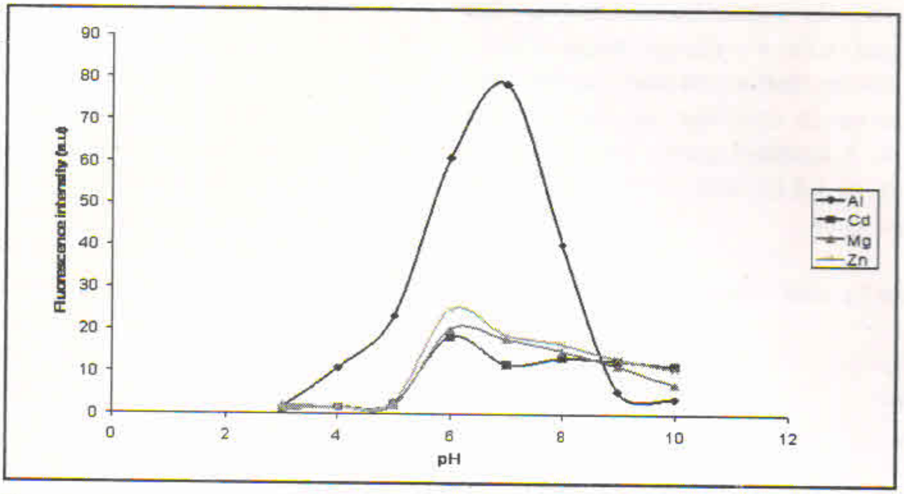


Figure 3.2. Fluorescence plots for Metal-HQ complexes as a function of pH

3.3 Stoichiometry and Formation Constants of the Complexes :

3.3.1 Stoichiometry :

Stoichiometry provides information about the quantitative relationships of the reactants (ligands and metal ions) and products (ligands-metal complexes) in a balanced chemical reaction. This information is useful to determine the complexes formation characteristics and ligand-to-metal ratio of the complexes.

In this study, the stoichiometry of the complexes was determined by means of Job's method[13]. A series of two sets of solutions containing fixed total concentration values of C_1 and C_2 were prepared;

$C_1 = [M] + [L] = 5 \times 10^{-4}$ M and

$C_2 = [M] + [L] = 3 \times 10^{-4}$ M

Job's plots for the formation of complexes of the HQ reagent with Al^{2+}, Cd^{2+}, Mg^{2+} and Zn^{2+} ions are shown in Figures 3.3, 3.4, 3.5 and 3.6 respectively. From these plots, the stoichiometry of the Metal-HQ complexes can be discerned as 1:3 for Al-HQ and 1:2 for Cd-HQ, Mg-HQ and Zn-HQ complexes. These results are complement with metal-HQ stoichiometric reported elsewhere[14,15,16]. The proposed structures of the Metal-HQ complexes are as shown in Figure 3.7. Meanwhile, the proposed geometries of the complexes are square planar for divalent metal complexes (Cd, Mg and Zn) and octahedral for the trivalent metal complex (Al).

3.3.2 *Formation constant :*

The formation constant of the complex were also calculated from the Job's plot. At some point x on the Job's plot corresponding to a certain concentration of the complex, the complex reaction can be written as;

$$\begin{array}{ccccc} M & + & L & \leftrightarrow & ML \\ (M-x) & & (L-x) & & x \end{array} \qquad (1)$$

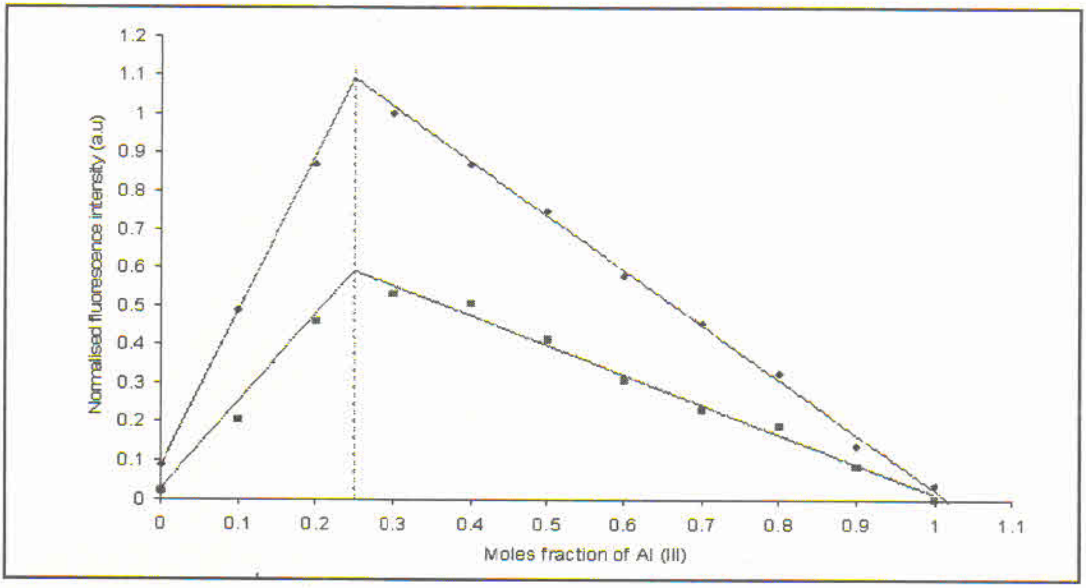


Figure 3.3. Job plot for Al-HQ complexes at pH 7

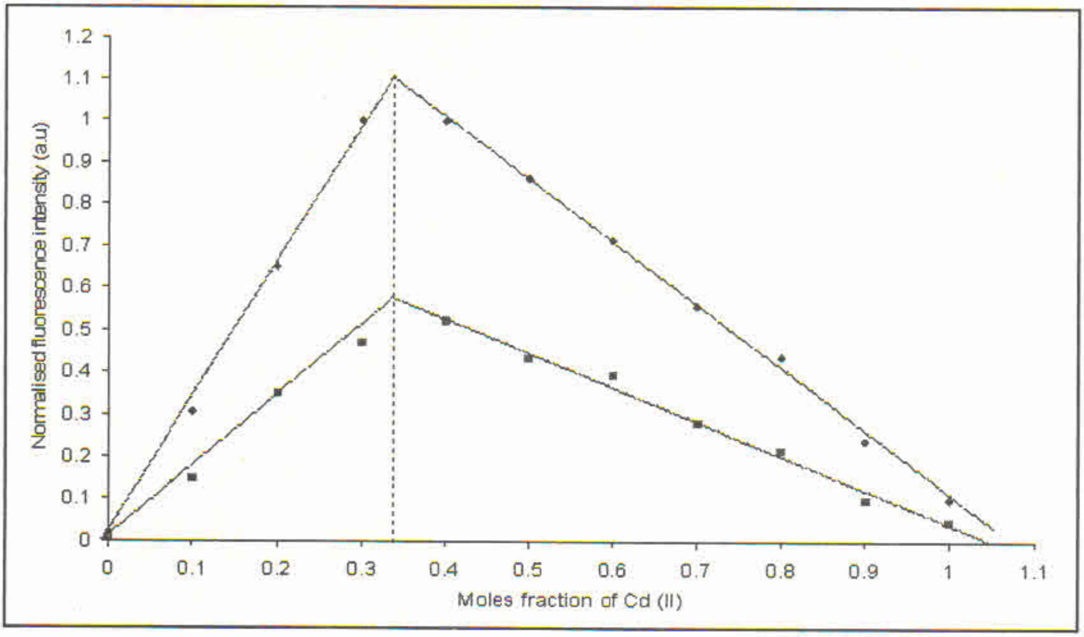


Figure 3.4. Job plot for Cd-HQ complexes at pH 6

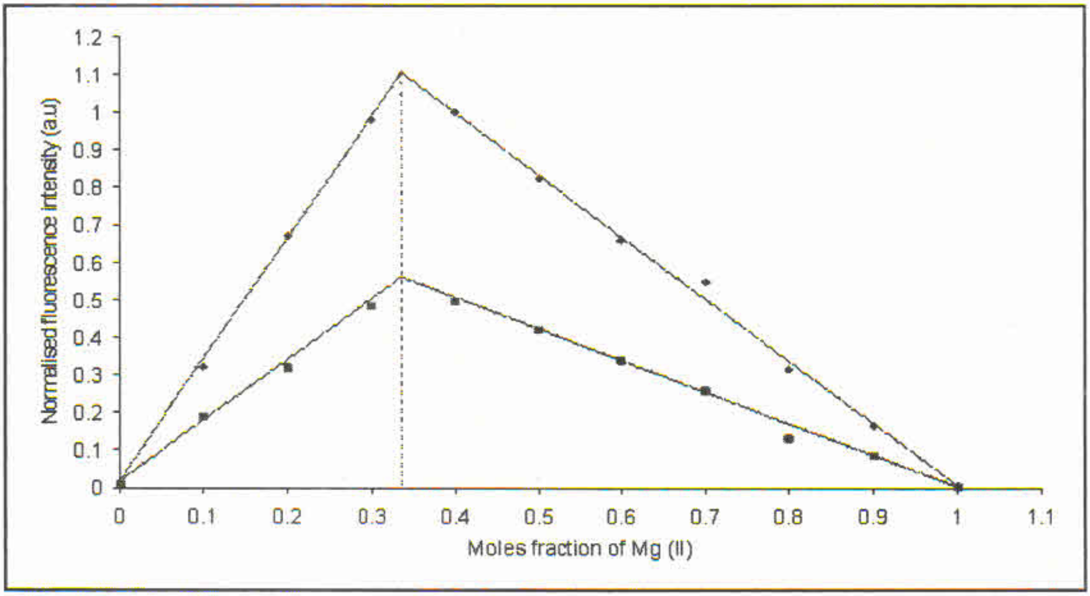


Figure 3.5. Job plot for Mg-HQ complexes at pH 6

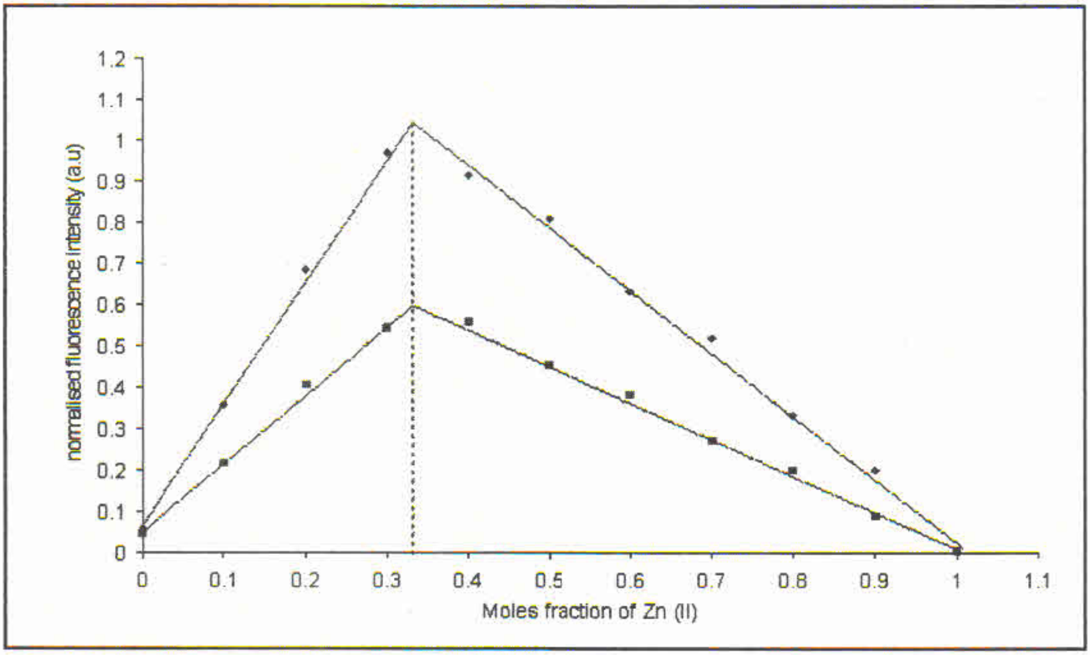


Figure 3.6. Job plot for Zn-HQ complexes at pH 6

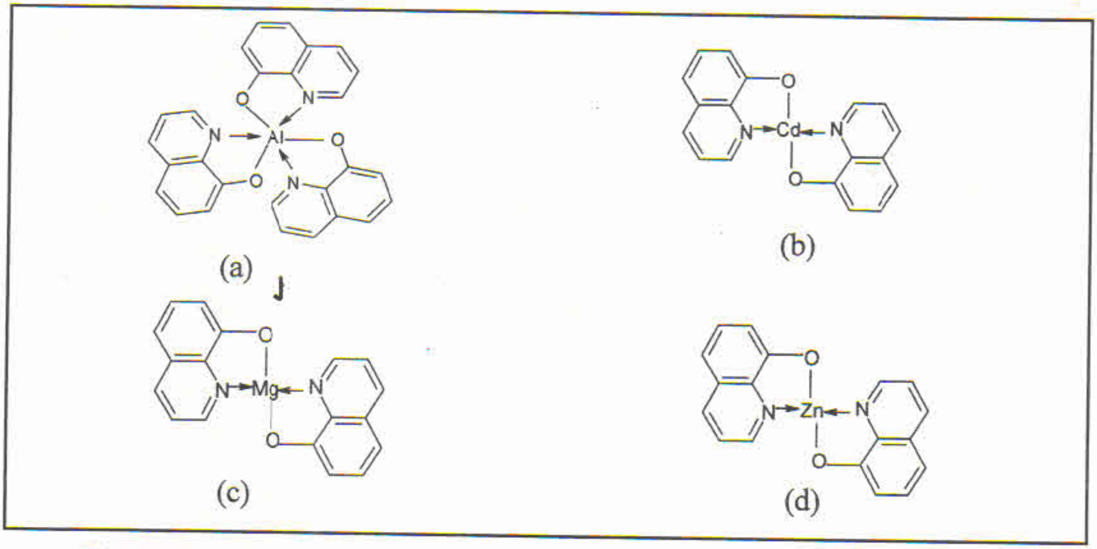


Figure 3.7. Proposed structures of the (a) Al-HQ complex, (b) Cd-HQ complex, (c) Mg-HQ complex and (d) Zn-HQ complex

and if another point x' is chosen on another plot, then;

$$\begin{array}{ccccc} M & + & L & \leftrightarrow & ML \\ (M'-x') & & (L'-x') & & x' \end{array} \qquad (2)$$

where M and M' are the concentration of the metal ions, L and L' are the concentration of the ligands and x and x' are the molar concentration of the complexes obtained from the Job's plots.

Generally, the formation constant, K_f can be simply written as:

$$K_f = \frac{[ML]}{[M][L]^n} \qquad (3)$$

therefore, the calculations of the formation constant K_f for the metal-HQ complexes are as follows;

i. K_f for the 1:2 stoichiometry complexes (Cd, Mg, Zn)

At some point x on the Job's plot the equation can be written as;

$$K_f = \frac{x}{(M-x)(L-2x)^2} \qquad (4)$$

and, if another point x' (same fluorescence intensity value as x) is chosen on another plot, then

$$K_f = \frac{x}{(M-x)(L-2x)^2} = \frac{x'}{(M'-x')(L'-2x')^2} \qquad (5)$$

Since $x = x'$;

the equation (5) expands to the equation (6);

$$4x^2\{(M+L)-(M'+L')\}+x\{(4L'M'+L'^2) - (4LM+L^2)\}+\{ML^2 - M'L'^2\}=0 \qquad (6)$$

Value of x can be calculated by solving the equation above using a quadratic formula. Two values of x will be obtained but only one would be able to give a positive value of formation constant K_f when substituted in the equation (6).

ii. K_f for the 1:3 stoichiometry complexes (Al)

For the 1:3 metal-ligand complexes, the K_f equation can be written as;

$$K_f = \frac{x}{(M-x)(L-3x)^3} \qquad (7)$$

and,

$$K_f = \frac{x}{(M-x)(L-3x)^3} = \frac{x'}{(M'-x')(L'-3x')^3} \qquad (8)$$

Since $x = x'$;
the equation (8) expands to the equation (9);

$$27x^3\{(M'+L')-(M+L)\}+9x^2\{(3LM+L^2)-(3L'M'+L'^2)\}+ x\{(9L'^2M'+L'^3)-(9L^2M+L^3)\}+\{ML^3-M'L'^3\}=0 \qquad (9)$$

The value of x can be calculated by solving the equation above using a cubic formula. Three values of x will be obtained, however only one would be acceptable, giving a real value to be substituted in the equation (9) for the expression of K_f.

The formation constants of the Metal-HQ complexes evaluated are shown in Table 1.

Table 1. Formation constants for the Metal-HQ complexes

Metal	Fl. intensity (a.u)	Calculated concentration of reactant (x10^{-5} M)				Calculated x / M	Calculated K_f
		M	L	M'	L'		
Al	0.5	1.38×10^{-5}	1.11×10^{-4}	1.65×10^{-5}	5.85×10^{-5}	9.83×10^{-6}	$^{a}9.57\times10^{13}\,M^{-3}$
Cd	0.5	2.50×10^{-5}	1.42×10^{-4}	2.90×10^{-5}	7.10×10^{-5}	2.48×10^{-5}	$^{b}1.27\times10^{10}\,M^{-2}$
Mg	0.5	2.50×10^{-5}	1.42×10^{-4}	3.00×10^{-5}	7.00×10^{-5}	2.47×10^{-5}	$^{b}1.12\times10^{10}\,M^{-2}$
Zn	0.5	2.50×10^{-5}	1.42×10^{-4}	2.70×10^{-5}	7.30×10^{-5}	2.49×10^{-5}	$^{b}2.15\times10^{10}\,M^{-2}$

Note:a- K_f calculated using equation (9) b- K_f calculated using equation (6)

Formation constant, K_f is also known as the stability constant. Theoretically, the larger the values of the K_f indicate formation of more stable complexes. The calculated K_f values show that the Al-HQ complex ($K_f = 9.57\times10^{13}$ M^{-3}) is more stable compared to other metal-HQ complexes. This is due to the present of chelate effect where the stability increases with the number of attachment points (*i.e.* multiligand complexes are more stable than monoligand). The K_f values obtained for the Cd, Mg and Zn-reagents complexes ranges from 1.12 x10^{10} M^{-2} to 2.15 x10^{10} M^{-2}. The values show that the Zn-reagents complexes are more stable than the Cd and Mg-reagents complexes and the complexes of Cd with HQ reagents are more stable than the complexes of Mg. The overall stability of the complexes are in the order of $Al^{3+} > Zn^{2+} > Cd^{2+} > Mg^{2+}$.

4.0 Conclusion

The complexion ability of HQ reagent with four metal ions (Al^{3+}, Zn^{2-}, Cd^{2+}, Mg^{2+}) in aqueous solutions was investigated experimentally with spectrofluorometric technique. It was found that the stoichiometry evaluated for metal-reagent complexes were found to be 1:3 for Al-HQ and 1:2 for Cd-HQ, Mg-HQ and Zn-HQ. Meanwhile the stability of the complexes calculated from the Job' plots are given by the order of $Al^{3+} > Zn^{2+} > Cd^{2+} > Mg^{2+}$. All the results obtained are useful for the further investigation and development of the HQ reagent as sensing material for metal ions determinations.

5.0 Acknowledgement

MOHE, UMT, RMIC, Uni. Of Manchester and Dr. R. Narayanaswamy are fully acknowledged for their supports.

References

1. T.P. Rao, J.M. Gladis, *Analytical Sciences, 18,* 517, (2002).
2. J.M. Castagnetto, J.W. Canary, *J. Chem. Soc., Chem. Commun., 2,* 203 (1998).
3. O.S. Wolfbeis, W. Trettnak, *Spectrochimica Acta, 43A*, 3, 405 (1987).
4. S.A. Asher, A.C. Sharma, A.V. Goponenko, M.M. Ward, *Anal. Chemistry, 75,* 1676 (2003).
5. R. G. W. Hollingshead, Oxine and Its Derivatives 1, Butterworths Scientific Publications (1954).
6. K. Soroka, R.S. Vithanage, D.A. Phillips, B. Walker, P.K. Dasgupta, *Anal. Chem., 59,* 629 (1987).
7. J.R. Jezorek, H. Freiser, *Analytical Chemistry, 51*, 3, 366 (1979).
8. C.R. Lan, M.H. Yang, *Analytica Chimica Acta,* 287, 101 (1994).
9. R.H. Uibel, J.M. Harris, *Analytica Chimica Acta,* 494,10, (2003).
10. Y. Wang, S. Astilean, G. Haran, A. Warshawsky, *Anal. Chem., 73,* 4096 (2001).
11. J. Fernandez-Lodeiro, C. Nunez, O. N. faza, J. L. Capelo, C. Lodeiro, J. S. S. De Melo, C. S. Lopez, *Inorganica Chimica Acta, 381,* 218 (2012).
12. L. Pondi, M. Montalti, N. Zaccheroni, J. S. Bradshaw, R.M. Izatt, P.B. Savage, *J. Inclusion Phenom. 41,* 123 (2001).
13. G. F. Kirkbright, T.S. West, C. Woodward, *Analytical Chemistry, 37,* 1, 137 (1965).
14. E. Sapelli, T. A. S. Brandão, H. D. Fiedler, F. Nome, *Journal of Colloid and Interface Science, 314,* 214, (2007).
15. E. Ferrada, V. Arancibia, B. Loeb, E. Norambuena, C. Olea-Azar, J. P. Huidobro-Toro, NeuroToxicology 28, 445 (2007).
16. J. He, L. Deng, S. Yang, Spectrochimica Acta Part A 70, 878, (2008).