

# Fluorescence of Metal Complexes of 8-Hydroxyquinoline Derivatives in Aqueous Micellar Media

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The fluorescence characteristics of 8-hydroxyquinoline derivative complexes of Al(III), Ga(III), In(III), Zn(II), and Be(II) in differently charged micellar media are reported. For most of the chelates studied, large increases are observed in micellar media compared with those obtained in hydroorganic solvents. However, some exceptions are observed, of which the low fluorescence of Zn(II) chelates in anionic sodium lauryl sulfate media is the most noticeable.

**KEY WORDS:** 8-Hydroxyquinoline derivatives; metal chelates; enhanced fluorescence; micellar media.

## INTRODUCTION

The use of aqueous micellar media to increase the molar absorptivity or luminiscence intensity of different solutes, including metal-organic reagent complexes, is well-known [1-3]. Since, in general, enhanced absorbance or fluorescence leads to lower detection limits, micellar media have found numerous successful applications in photometric and fluorimetric analysis.

8-Hydroxyquinoline (HQ) derivatives are extensively used as fluorogenic reagents for metal ions [4,5]. Although several studies have been carried out on the enhancement effect of surfactants on the luminiscence of metal chelates of HQ derivatives, most of the published work is devoted to anionic complexes of 8-hydroxyquinoline-5-sulfonic acid in cationic micellar media [6,7].

The present paper reports a study on the effect of different surfactants, cationic, anionic, and nonionic, on the fluorescent properties of several water insoluble chelates of HQ and some of its derivatives. This is intended to provide useful information for the development of improved analytical determinations, as well as a contribu-

tion to understanding the mechanism of the micellar fluorescence enhancement.

## EXPERIMENTAL

**Apparatus.** Fluorescence was measured on a Perkin-Elmer LS-50 spectrofluorimeter. Slit widths were set to 5 nm in both the excitation and the emission monochromators. For pH measurements a Radiometer pHM64 pH-Meter equipped with an Orion glass combination electrode was used.

**Reagents.** Stock solutions (1 g·L<sup>-1</sup> metal ion) of Al(III), Ga(III), In(III), Zn(II), and Be(II) were prepared from analytical reagent-grade nitrates or oxides (Merck). Stock aqueous solutions of 0.05 M Brij-35 (Fluka), 0.15 M cetyltrimethylammonium bromide (CTAB; Merck), and 0.2 M sodium lauryl sulfate (SLS; Merck) in water were prepared. The ligands used were 8-hydroxyquinoline (HQ; Fluka), 2-methyl-8-hydroxyquinoline (MeHQ; Scharlau), 5,7-dichloro-8-hydroxyquinoline (Cl<sub>2</sub>HQ; Aldrich), 5,7-dichloro-2-methyl-8-hydroxyquinoline (Cl<sub>2</sub>-MeHQ; Fluka), and 5-chloro-7-iodo-8-hydroxyquinoline (ClIHQ; Fluka). Working solutions (5×10<sup>-3</sup> M) in ethanol were prepared daily (except for ClIHQ 2.5×10<sup>-3</sup> M).

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Table I. Relative Fluorescence Intensities

Chelate	Brij-35	SLS	CTAB
Al-HQ	38	42	42
Ga-HQ	26	29	29
In-HQ	35	25	27
Zn-HQ	9	3	15
Al-Cl <sub>2</sub> MeHQ	21	21	
Ga-Cl <sub>2</sub> MeHQ	100	74	100
In-Cl <sub>2</sub> MeHQ	38	12	38
Zn-Cl <sub>2</sub> MeHQ	69	13	65
Be-Cl <sub>2</sub> MeHQ	78	64	
Zn-HQ	9	3	
Zn-MeHQ	9	7	
	1		
Zn-Cl <sub>2</sub> MeHQ	69	13	
Zn-ClIHQ	23	7	

\* $C_{Al} = C_{Ga} = C_{In} = C_{Be} = C_{Zn} = 1.5 \times 10^{-6} M$ ;  $C_{BQ} = C_{Cl_2MeBQ} = 10^{-4} M$ ;  $C_{Brij-35} = 10^{-2} M$ ;  $C_{SLS} = 4 \times 10^{-2} M$ ;  $C_{CTAB} = 3 \times 10^{-2} M$ .

All other reagents used were analytical grade or Suprapur quality. Doubly deionized water, (Culligan Ultra-pure GS;  $18.3 \cdot \Omega \cdot \text{cm}^{-1}$  resistivity) was used. All glassware used for experiments was previously soaked in 10% nitric acid for 24 h and rinsed with this water.

**General Procedure.** A previously diluted aliquot of metal stock solution (containing  $4 \cdot 10^{-7}$  mol of metal) was transferred into a 25-ml calibrated flask. Then 5 ml of stock surfactant solution, 0.5 ml of ligand solution, and 2 ml of buffer solution (acetic acid-NaOH, succinic acid-NaOH, or Tris-HCl) were added. The solution was diluted to volume and the fluorescence was measured at the optimum wavelengths.

## RESULTS AND DISCUSSION

In the first step the fluorescence spectra of the complexes of several metal ions with HQ and Cl<sub>2</sub>MeHQ in different hydroorganic solvents (ethanol, methylethylketone, and dioxane) and in nonionic Brij-35 micellar media were compared. Measurements were made from solutions containing a large excess of ligand and at different pH values to ensure that, in all cases, the data compared corresponded to the maximum complex formation. Although fluorescence intensities ( $I_f$ ) depend on the surfactant concentration, this variable is not critical for the complexes studied: In all cases, relatively high surfactant concentrations (about 10–20 times the cmc) are required to achieve maximum fluorescence, and higher concentration values had no significant effect on

the  $I_f$ . Regardless of the nature of the metal ion, ligand, or solvent, all fluorescence spectra appeared as broad bands with flat maxima. The observed  $I_f$  was almost-independent of the nature of the hydroorganic solvent but increased drastically when Brij was used as solubilizing agent. The enhancement factor was about 5 at a water:organic solvent composition of 50:50 (v/v), and much higher at lower organic solvent contents.

To study the effects of other media, Al(III), Ga(III), In(III), Zn(II), and Be(II) ions were selected. Other metal ions were rejected because of their low fluorescence or poor stability. Table I reports the relative  $I_f$  under optimal conditions, for HQ and Cl<sub>2</sub>MeHQ chelates, whereas Fig. 1 shows the  $I_f$  as a function of pH for some of the chelates studied in the three differently charged micellar media. From these data it can be observed that the influence of the three media is very similar for HQ-metal complexes, whereas the results are more variable for the Cl<sub>2</sub>MeHQ chelates. Nevertheless, some relative general trends can be observed.

(i) The Cl<sub>2</sub>MeHQ chelates are more fluorescent than those corresponding to HQ, except Al. The low fluorescence observed for Al(III)-Cl<sub>2</sub>MeHQ is probably related to the low ability of this ion to form complexes with 2-methyl-8-HQ derivatives [8].

(ii) The optimal pH ranges in SLS medium shifts to higher values compared with Brij medium, whereas no significant differences were observed when Brij and CTAB surfactants were used. This behavior can be explained by data on the solubilization of reagent in the micelles [9,10].

(iii) The fluorescence of Zn(II) chelates in SLS micellar media was low. Data from different HQ derivatives show that this is a general feature of Zn(II) chelates (Table I). Although some authors relate differences in surfactant-enhanced fluorescence to solubilization of chelates in the micelles [11], our current investigations on micellar solubilization equilibria suggest that differences were not significant in the solubilization of Zn(II)-Cl<sub>2</sub>MeHQ in SLS and Brij micelles. Since the molar absorptivities of the complex in both micellar media are very similar, differences in fluorescence should be attributed to differences in quantum yields.

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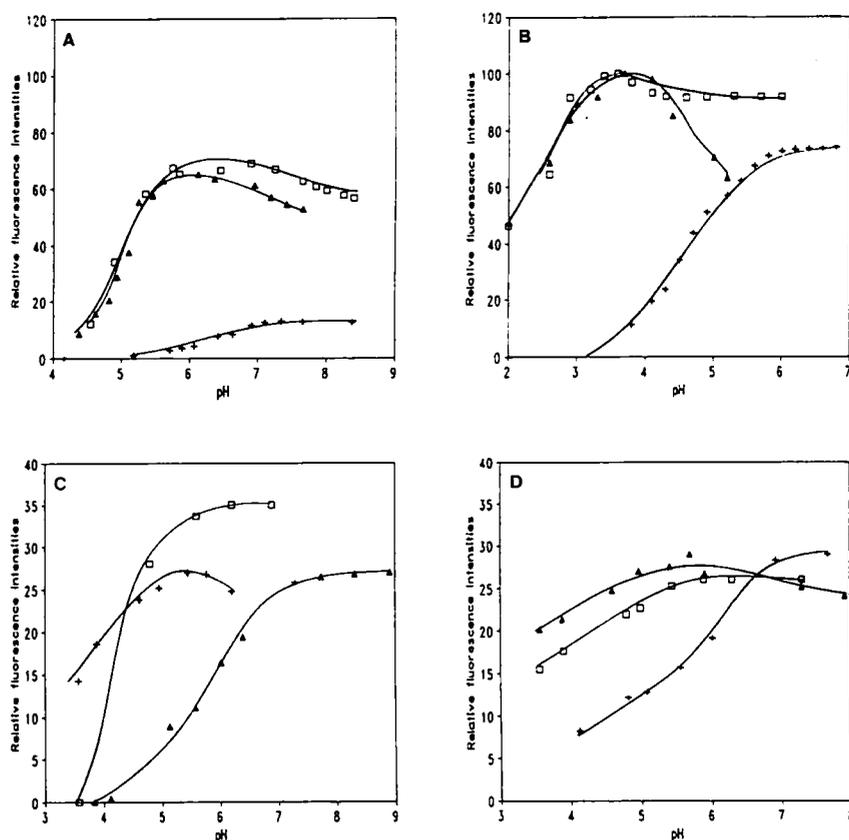


Fig. 1. Effect of pH on the emission of the Zn(II)-Cl<sub>2</sub>MeHQ (A), Ga(III)-Cl<sub>2</sub>MeHQ (B), In(III)-HQ (C), and Ga(III)-HQ (D) chelates in Brij-35 (□), SLS (+), or CTAB (■) media.  $C_{Zn} = C_{Ga} = 1.5 \times 10^{-6} M$ ;  $C_{HQ} = C_{Cl_2MeHQ} = 10^{-4} M$ ;  $C_{Brij} = 10^{-2} M$ ;  $C_{SLS} = 4 \times 10^{-2} M$ ;  $C_{CTAB} = 3 \times 10^{-2} M$ .

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