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Enhancement and Quenching of Fluorescence of Metal Chelates of 8-Hydroxyquinoline-5-Sulfonic Acid

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Abstract. Fluorescence enhancement of 8-hydroxyquinoline-5-sulfonic acid complexes of Mg, Ca, Sr, Ba, Al, Zn and Cd were studied in micellar and hydroorganic solvents. Al is extraordinarily amenable to both types of fluorescence enhancement, an order of magnitude to two order of magnitude enhancement of fluorescence intensity has been observed with aqueous hexadecyltrimethylammonium chloride (HTAC) and certain mixed aqueous-organic solvents. Fe(III) appears to be an unusually powerful fluorescence quencher in these systems — the effect is noticeable in low micromolar concentrations and is greatly amplified by cationic surfactants such as HTAC.

Key words: 8-hydroxyquinoline-5-sulfonic acid, sulfoxine, metal chelates, fluorescence, fluorescence quenching.

As chelating reagents of analytical utility, oxine (8-hydroxyquinoline, HQ) and its derivatives are second only to iminodiacetic acid chelants [1]. A unique characteristic of many metal chelates of HQ is their intense yellowgreen fluorescence. The ligand itself is non-fluorescent except in certain concentrated acids and anhydrous polar solvents [2, 3]. It is believed that the fluorescence of the free ligand is quenched by water due to displacement of a prototropic equilibrium which involves the ionization of the hydroxyl proton [3—5]. Excited singlet state pK_a values have been reported [2].

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The intrinsic quantum efficiency for the fluorescence of HQ and its derivatives in absence of quenching is excellent. For example, in concentrated sulfuric acid, ϕ_F is 0.31 for HQ and 0.26 for 8-hydroxyquinoline-5-sulfonic acid (HQS) [2]. A convenient way to rationalize the fluorescence of metal chelates of HQ is that the metal behaves as a "superproton" [6]. However, in simple aqueous solution, the fluorescence of HQS chelates (HQ and its chelates are insoluble in water) do not exhibit nearly as high a quantum efficiency.

A considerable amount of literature exists on the fluorometric determination of metals; several excellent reviews are available [7—10]. For understandable reasons, the vast majority of previous efforts have been focused towards developing specific reagents and conditions for the determination of a single analyte. Preeminent among such fluorogenic ligands (i. e., those that develop fluorescence upon complexation) are morin, salicylaldehydeacetylhydrazone, salicylidene-*o*-aminophenol, kojic acid, 3-hydroxy-2-napthoic acid, benzoin and lumogallion. Because considerable scientific and commercial interests exist in biomedical applications involving intracellular measurement of calcium, significant efforts have been recently devoted to develop high quantum yield fluorogenic ligands for this metal [11]. Generally applicable metal ion indicators that respond via a change in fluorescence upon complexation are typically iminodiacetic acid substituted fluorescent dyes, e. g., derivatives of fluorescein, umbelliferrone, substituted benzidines, etc. These indicators undergo a fluorescent $\rightarrow$ nonfluorescent transition upon complexation, except for alkaline earths at pH > 12. These are of limited value in trace determinations, regardless of the lack of specificity, because of the high blank value.

The advent of metal ion chromatography, specifically the availability of commercial equipment including post-column reactors, now permit sensitive determination of metals by introducing a nonspecific chromogenic reagent such as 4-(2-pyridylazo)resorcinol (PAR) postcolumn, after the desired separation has been achieved [12]. The use of a nonspecific fluorogenic ligand instead of PAR in such applications along with fluorescence detection has the potential to push the detection limits for many metals well beyond the present abilities of atomic spectroscopy, including inductively coupled plasma mass spectrometry [13]. For such an application, HQS, which undergoes a nonfluorescent $\rightarrow$ fluorescent transition upon complexation and forms water soluble complexes, has no parallel. Therefore, we have recently studied the fluorescence behavior of some seventy-eight metal species (this includes oxidation state varia-

tions) in the presence of HQS as a function of pH and found that more than half display usable fluorescence intensities. Further, we have shown, using both in-eluent and post-column introduction of HQS, subpicomole detection limits are easily attainable for a number of metals [14].

It is well known that micellar systems routinely enhance the fluorescence of a variety of fluorescent compounds [15]. In the present paper, we report the enhancement of the fluorescence of metal-HQS complexes in micellar, as well as hydroorganic media for selected metals. An additional aspect is the quenching effect exerted by certain metal ions on the fluorescence of other metal-HQS complexes.

Experimental

A Perkin-Elmer Model LS-5 spectrofluorometer was used for all work. Both excitation and emission slits used were 10 nm, with a 4 s integration time for the readout. An Altex Phi 71 pH meter equipped with a Ross combination electrode (Orion Research) was used for pH measurements, calibrated by the two point method.

8-Hydroxyquinoline-5-sulfonic acid (Aldrich, 98%) was twice recrystallized (as the monohydrate) from large volumes of hot water. Metal salts used were nitrates and were analytical reagent grade. Hexadecyltrimethylammonium chloride (HTAC) was obtained as a 25% (w/v) concentrate (Fisher, HPLC grade). Sodium dodecylsulfate was electrophoresis grade (Bio-Rad); other surfactants were technical grade. Organic solvents used were reagent grade. Potassium hydroxide/hydrochloric acid were used for pH adjustment and were of ultrapure grade (J. T. Baker). Water used in this work was distilled and then deonized; it met or exceeded the specifications of ASTM type I reference reagent water. No explicit efforts were made to determine the nature and concentration of residual trace metals present in the reagents or the solvents. Reagent purity is important in these studies because while certain metal-HQS chelates are intensely fluorescent, others act as powerful quenchers.

Experiments in purely aqueous or surfactant containing solutions were conducted at 10 μM metal concentration level for Al, Cd, Mg and Zn and at 100 μM concentration for Ba, Ca and Sr; the latter two metal-HQS chelates are relatively weakly fluorescent. In all cases, preliminary measurements were also made at lower metal concentration to ensure that the data obtained at the reported concentrations still represent the linear domain of concentration-fluorescence intensity. The HQS concentration in all experiments

was held constant at 1 mM. Experiments were conducted in unbuffered solutions, microaliquots of KOH or HCl were used for pH adjustment. When HTAC is added to a solution containing HQS, the pH decreases due to the deprotonation of HQS to form the HTA^+-QS^- ion pair. Readjustment of pH was therefore necessary. The optimum excitation and emission wavelengths for the fluorescence of the metal-HQS chelates occur around 390 and 510 nm respectively [14]. Small red shifts (≤ 10 nm) were observed in the presence of HTAC; the absorption and emission is broad band and the change in the absolute value of the fluorescence intensity was small ($\leq 5\%$). Consequently, all measurements were made at wavelengths optimal for the purely aqueous system.

For hydroorganic solvent systems, x ml of a 10 μM (Al, Cd, Mg, and Zn) or 100 μM (Ca) aqueous solution of the metal containing 1 mM HQS and adjusted to the optimum pH for fluorescence of the purely aqueous system was diluted to 100 ml with the organic solvent. The composition is reported nominally as (100-x) volume-% of the organic solvent; volume change due to mixing of dissimilar solvents was not taken into account. The reported enhancement factors take into consideration dilution by the organic solvents. The optimal excitation wavelength in the mixed hydroorganic solvents is the same as that in the purely aqueous system; the optimum emission wavelength is red shifted by a small amount (≤ 5 nm). However, the change in fluorescence from that observed for the optimum wavelength for purely aqueous solution was small and once again measurements were made at wavelengths optimum for the aqueous system. It was not considered meaningful to attempt to measure pH in the mixed aqueous solvent systems.

Quenching effects were measured by adding small aliquots of the test quencher ion into metal-HQS solutions (with and without HTAC or organic solvent), the reported quencher concentration is that in the final solution. Measurement wavelengths were as described above.

Results and Discussion

Choice of Metal Ions

In the original study [14], seventy-eight metal species were tested and the following were found to exhibit measurable fluorescence over blank: Rb(I), Cs(I), Be(II), Mg(II), Ca(II), Sr(II), Ba(II), Zn(II), Cd(II), Al(III), Ga(III), In(III), Tl(I), Sc(III), Y(III), La(III), Ce(IV), Pr(III), Nd(III), Sm(III), Eu(III), Gd(III), Tb(III), Dy(III), Ho(III), Er(III), Tm(III), Yb(III), Lu(III), Th(IV), Sn(IV), Pb(II), Ti(IV),

Hf(IV), Sb(V), Nb(V), Ta(V), W(VI), Os(III), Ir(IV) and Pt(II). Within the scope of the present study, it was not feasible to test enhancement/quenching of the entire list above. As an utilitarian exercise, we concentrated on the more common metals. The alkaline earth metals were chosen as a group because there is a need to improve the sensitivity currently attainable for these metals by conductimetric ion chromatography. Cadmium was selected because it forms by far the most fluorescent HQS chelate in purely aqueous solution (typically a factor of 5—10 more fluorescent than all others) and zinc was selected because the two metals tend to co-occur in real samples. Aluminium was chosen as a representative of Group IIIA metals. Among the above metals, all except Al form 1 : 2 (metal : ligand) complexes; Al forms a 1 : 3 complex. The surfactant enhancement of the fluorescence of the rare earth-HQS chelates have already been studied [16].

Surfactant Enhancement of Metal-HQS Fluorescence

The enhancement of fluorescence in micellar media reportedly occurs due to increased structural rigidity and microviscosity of the medium as well as due to protection from quenchers like oxygen [15]. The last factor is not likely to be important in the present case because emission at long wavelengths is not susceptible to quenching by oxygen. The emission wavelength above which no oxygen quenching is to be expected is stated to be 530 nm [6]. Although the emission in metal-HQS systems occurs at slightly lower wavelengths, we have not observed any difference in fluorescence intensities with intentional deoxygenation.

Sodium dodecylsulfate forms a negatively charged micelle. A negatively charged ligand such as QS^- is not expected to associate with it and accordingly, no significant enhancement was observed with any of the test metals at any concentration of the surfactant. Small, but discernible (10—15%) enhancement of fluorescence was observed for all the test metals with nonionic surfactants like Triton-X-100 and Brij-78. Because the increases are only marginal, detailed results are not presented. HTAC forms a positively charged micelle and significant increases in fluorescence intensity were observed for all the metals tested. The "control" conditions, i. e., the optimal conditions in aqueous solution and the relative fluorescence intensities are reported in Table I. Relative to these values, the enhancement factors are shown in Fig. 1 for Al, Mg, Sr, Ba, Cd and Zn. In each case, the experiments were conducted at the optimal HTAC concentration for each metal (*vide infra*). Each inset in Fig. 1

shows the fluorescence intensity of the indicated metal as a function of pH (with normalization to unity under the conditions of Table I), with and without HTAC. In terms of practical improvements in detection limits due to enhanced fluorescence intensity, the cases for Al and Ba are the most notable. The situation with Al is dramatic with the enhancement exceeding an order of magnitude.

Table I. Conditions for Maximum Fluorescence in Aqueous Solution[a]

Metal	pH	λ_{ex}, nm	λ_{em}, nm	Relative fluorescence intensity
		Metal concentration 10 μM		
Mg	8	393	506	33
Cd	7	387	522	225
Zn	6	393	506	23
Al	6	395	500	11
		Metal concentration 100 μM		
Ca	8	394	512	48
Sr	8	395	506	27
Ba	8	394	512	14
Blank	8	393	506	1.8

[a] The solutions are unbuffered, HQS concentration is 1 mM, the reported optimal pH values are nearest integer values.

Since the Ba-complex is not intensely fluorescent (Table I), the enhancement is beneficial in improving detectability. The blank fluorescence with and without HTAC is also shown as a function of pH. Although the blank clearly increases in the presence of HTAC, the absolute value of the blank is sufficiently small (Table I) so as not to cause significant impairment in detectabilities as a result of this increase. It is likely that the increase in the blank is due to the presence of residual adventitious metals, there is perceptible decrease in the blank values if EDTA is added to the system. A relatively general trend is also noticeable in the data represented in Fig. 1: the optimal pH value for maximum fluorescence shift to a slightly lower pH. For some metals, notably Al and Zn, the range of optimal pH is also substantially extended in the presence of the

surfactant. The decrease in the value of the optimal pH is well understood [17] in view of the fact that cationic micelles effectively decrease the pK of weak acids such as HQS.

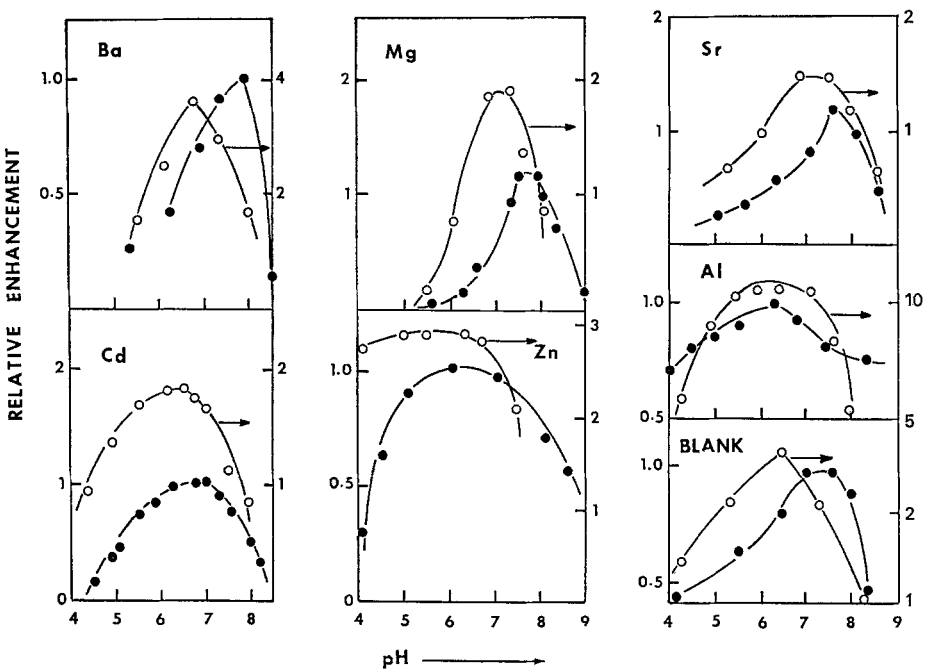

Fig. 1. Relative fluorescence intensities (with respect to fluorescence in purely aqueous solution under optimal conditions) with and without HTAC as a function of pH. Solutions are unbuffered and all solutions contain 1 mM HQS. Al: 10 μM metal, with and without 0.5 mM HTAC; Mg: 10 μM metal, with and without 1 mM HTAC; Sr: 100 μM metal, with and without 0.25 mM HTAC; Ba: 100 μM metal, with and without 0.5 mM HTAC; Cd: 10 μM metal, with and without 0.25 mM HTAC; Zn: 10 μM metal, with and without 0.5 mM HTAC; blank: with and without 0.25 mM HTAC. Open circles: with HTAC, right ordinate; Closed circles: without HTAC, left ordinate

The fluorescence enhancement is dependent on the HTAC concentration and may be acutely so for some metals (Fig. 2). For the majority of the metals tested, the optimal HTAC concentration is at or below 0.5 mM; however, Zn is unique in exhibiting a relative independence of fluorescence enhancement as the HTAC concentration is varied. Although the formal critical micelle concentration (CMC) for HTAC in pure water is 1.3 mM, it is well known that the presence of electrolytes, notably hydrophobic counterions such as that derived from HQS, can drastically lower the CMC

[18, 19]. The lowest concentration studied by us in these experiments, 0.25 mM HTAC, therefore probably still represents a micellar system. It is interesting to note that for lanthanide-HQS-HTAC systems, it has been previously reported that the fluorescence enhancement is directly relatable to the formation of 1 : 1 : 1 metal : HQS : HTA aggregates [16]. With trioctylmethylammonium ion as the surfactant, Cd, Zn and Al are reportedly extractable into organic solvents as similar ternary complexes [20, 21]. Several other reports [22—27] exist on the area of micellar enhancement of the

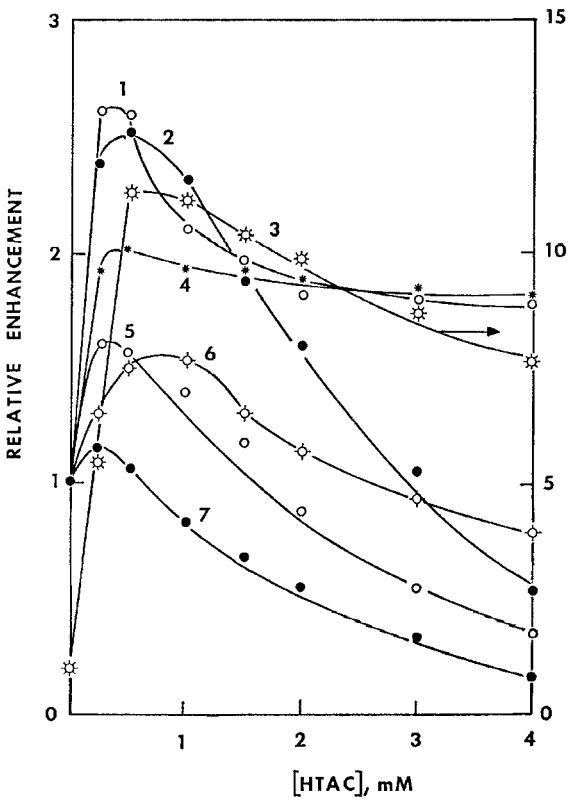

Fig. 2. Fluorescence intensity as a function of surfactant concentration. Metal concentrations same as that in Fig. 1. pH for Al, Cd, Zn: 6, all others: 7. *1*: Blank; *2*: Ba; *3*: Al (right ordinate); *4*: Zn; *5*: Cd; *6*: Mg; *7*: Sr

fluorescence of metal-HQS complexes, in particular by Cui et al. [23—27]. Due to our inability to pursue the original literature in detail, it has not been possible to determine if definitive information exists in these reports regarding the essentiality of micelle forma-

tion for fluorescence enhancement. Clearly, fluorescence enhancement cannot be rationalized by increases in microviscosity or structural rigidity if micelle formation is not necessary. This must therefore remain as an open and important question.

The decrease in fluorescence intensity at high surfactant concentration is a fairly general phenomenon [19]. It is possible that quenchers present as adventitious impurities in the surfactants may, in part, be responsible (*vide infra*). We conducted a limited set of experiments with the bromide salt of HTA^+, fluorescence enhancements were uniformly lower, presumably due to the heavy atom effect. Present theories on micellar effects on chemical equilibria [28—30] suggest, however, a more general explanation which may exist for the observed decrease in fluorescence at high HTAC concentrations. This is that at high micelle concentrations, the cationic micelle effectively competes with the metal ion for binding the anionic ligand. In the case of HQS, it is presumably the sulfonate group that is attached to the stern layer of the micelle. While this leaves the oxygen and nitrogen donor atoms of this particular ligand molecule free to chelate a given metal atom, steric conditions make it impossible for a second ligand molecule, bound to the same micelle, to effectively attach to the same metal atom. Further ligands attached to the same metal atom must therefore either be free or be attached to another micelle. The concentration of the free ligand decreases with increasing micellar concentration and a micelle-ligand-metal-ligand-micelle link is not likely to be thermodynamically favorable. The competitive binding of the ligand by the micelle will be just as effective in reducing fluorescence intensity at increased HTAC concentrations if the ionized phenolate oxygen of HQS were to be attached to the stern layer instead of the sulfonate group. Future experiments will involve the variation of the HQS/HTAC ratio as well as the absolute HTAC concentration and ionic strength for further understanding of these systems.

Fluorescence Enhancement in Hydroorganic Media

The fluorescence of the Mg-HQS chelate is significantly higher in pure DMF, compared to that in water [31]. We studied the effect of the solvent composition on the fluorescence of HQS chelates of Ca, Al, Zn and Cd. The results are reported in Table II. The enhancement is not a monotonic function of the DMF content. For Zn and Ca, a small enhancement is observed for Ca and Zn at 10% DMF. This decreases (below unity for Ca) as DMF concentration is increased and finally increases again. The enhancement

for Al is very high and appears to be atypical. It should be noted that blank values remain low and negligible throughout the entire range of solvent composition and optimal wavelengths for fluorescence does not markedly change.

Table II. Fluorescence Enhancement in Aqueous DMF[a]

	% DMF (v/v)								
	10	20	30	40	50	60	70	80	90
Relative enhancement factor									
Ca	1.24	0.60	0.59	0.59	0.82	1.13	1.55	3.10	7.98
Al	2.65	5.80	9.14	14.9	22.3	31.4	41.6	48.1	82.5
Cd	1.71	1.91	1.74	1.65	1.81	2.22	2.79	3.09	2.96
Zn	1.33	1.31	1.39	1.62	2.02	2.77	3.86	5.20	7.05

[a] The relative fluorescence intensity is normalized to unity for the optimal value in aqueous solution under the conditions described in Table I.

Table III. Enhancement Factors Al-HQS Fluorescence in Various Hydroorganic Media[a]

Organic component	Enhancement factor[b]
Methyl acetate	0.25
Acetonitrile	2.06
Ethylene glycol	2.48
Methanol	3.86
Ethanol	4.32
Acetone	5.03
2-Propanol	6.58
Tetrahydrofuran	7.55
1,4-Dioxan	8.01
Dimethylsulfoxide	8.61
Dimethylformamide	9.14
Ethylene glycol dimethyl ether	10.3
Hexamethylphosphoramide	11.9

[a] At a fixed 70 : 30 (v/v) water : organic solvent composition.

[b] With the relative value in purely aqueous media (Table I) set to unity.

It was of interest to determine if the observed enhancement is a fairly general phenomenon for a variety of organic solvents since water is reportedly a quencher for the fluorescence of the free HQS

ligand [3]. Such a study was conducted for a number of water-miscible organic solvents at a fixed water : organic solvent composition of 70 : 30 v/v for the Al-HQS complex; the results are shown in Table III. Enhancement is observed for all but methyl acetate; two solvents actually show better enhancements than DMF, at least at this composition.

Quenching of the Fluorescence of Metal-HQS Chelates

During the original study [14], it was observed that the fluorescence intensities of several metal HQS chelates are consistently below the blank value. Closer examination revealed that these metals not only form nonfluorescent HQS chelates, they effectively quench the fluorescence of other metal-HQS chelates. The fluorescence of the Mg-HQS chelate for example (100 μM Mg, 1 mM HQS, pH 8) is quenched 6%, 38%, 40%, 82% and 99% respectively by 50 μM concentrations of Cr(III), Ti(III), Au(III), Tl(III) and Fe(III). Note that this is in marked contrast to the only other study on the quenching of the fluorescence of metal-HQS chelates in which the quenching effect of various other ions at concentrations an order of magnitude greater than that of the fluorescing chelate (La-HQS) was studied [16]. The very powerful quenching action of Fe(III) on the fluorescence of various metal-HQS chelates is not widely recognized. This is particularly important because of the abundance of this metal in real samples and may indeed limit the usefulness of novel fiber-optic luminescence-based sensors that rely on immobilized HQS [32].

Quenching by iron is also important in chromatographic applications of HQS because stainless steel is by far the most common construction material used in modern liquid chromatographic instrumentation. The metal is inevitably leached in trace amounts from the hardware; complexing eluents are commonly used in metal ion chromatography [33] and iron leaching drastically increases. This occurs because the complexation constants for most Fe(III)-chelates are very high and the eluents are rarely deoxygenated. A more detailed investigation on the quenching effect of Fe(III) upon the fluorescence of the HQS-chelates of Mg, Ca, Cd and Al was therefore carried out. The Mg and Al chelates were also studied in the presence of 0.5 mM HTAC and the Al chelate was studied in 70 : 30 water : DMF solvent as well. The results are presented in Fig. 3.

The results in Fig. 3 reaffirm how significant the quenching action of Fe(III) can be, even at trace concentrations. In purely aqueous

medium, the quenching effect decreases in the order Ca > Mg > > Cd > Al; this may very well simply be mirroring the corresponding increase in the respective complexation constants. Although quantitative data are not presented here, we have observed that the susceptibility to quenching for the alkaline earth metals greatly increases along the series. Indeed, if a very small amount of EDTA is added to Sr- or Ba-HQS systems, the fluorescence intensity increases, for the majority of the analytical reagent grade Sr and Ba salts we have studied — showing the presence of adventitious cationic quenchers.

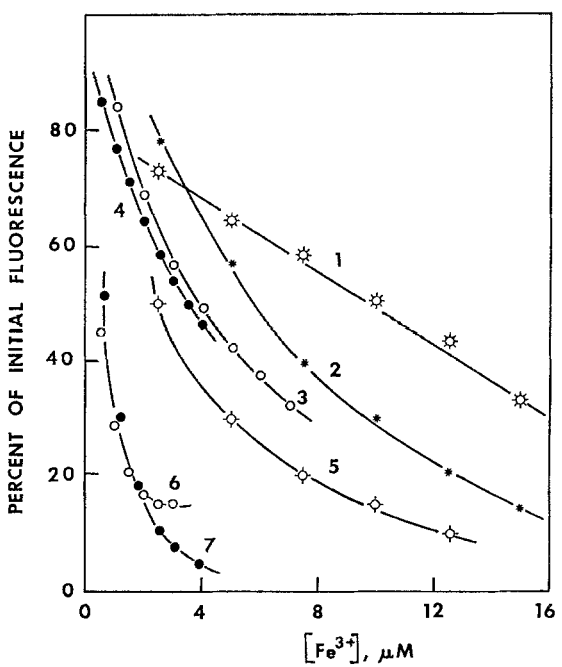

Fig. 3. Quenching of the fluorescence of various metal-HQS chelates by trace amounts of iron. *1*: Al-HQS; *2*: Cd-HQS; *3*: Al-HQS-DMF(aq); *4*: Mg-HQS; *5*: Ca-HQS; *6*: Mg-HQS-HTAC; *7*: Al-HQS-HTAC

The data in Fig. 3 also shows that the presence of the cationic surfactant greatly amplifies the quenching effect. The anionic iron complex is likely concentrated at the positively charged micellar interface. This effect is so large that essentially all gains attainable by surfactant enhancement are wiped out, except at very low quencher concentrations. In a number of analytical applications, this

added susceptibility to quenching in the presence of a cationic surfactant may limit the usefulness of cationic surfactant enhanced metal-HQS fluorescence. It is interesting that hydroorganic enhancement does not make the system as greatly susceptible to quenching, at least for Al. This factor, combined with the very large enhancements attainable in certain hydroorganic media, warrants a more detailed study of the fluorescence of metal-HQS chelates in suitable mixed solvents.

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