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Fluorescence Enhancement of Aluminum(III) 8-Quinolinolate in the Presence of 3,5-Dichlorophenol

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The addition of 3,5-dichlorophenol to carbon tetrachloride solution of tris(8-quinolinolato)aluminum(III) was found to cause considerable enhancement of fluorescence and to suppress the decomposition of the chelate by UV-light irradiation. The fluorescence enhancement was attributed to the association of the metal chelate with the phenol through hydrogen bonding.

Recently, it has been found that various metal chelates of β-diketones and 8-quinolinols form stable hydrogen-bonded complexes with halophenols in nonpolar solvents.[1–4] Such association has potential usefulness in the analytical field: the author and coworkers have reported that the solvent extraction of metal chelates is greatly enhanced in the presence of halophenols due to the formation of more hydrophobic hydrogen-bonded complexes in the organic phase.[4–7] Although the association of metal chelates with phenols may also influence the spectral characteristics of the chelates, no investigations have been made. The fluorescence of metal 8-quinolinolates has been well known and practically applied to fluorometric determination of metal ions.[8] In this study, the effect of 3,5-dichlorophenol (DCP) on the fluorescence of tris(8-quinolinolato)aluminum(III) ([Al(quin)$_3$]) in nonpolar solvents is investigated.

[Al(quin)$_3$] was synthesized in the usual way and its purity was checked by elemental analysis: Found: C, 69.73; H, 3.99; N, 9.00%. Calcd for Al(C$_9$H$_6$NO)$_3$: C, 70.59; H, 3.95; N, 9.15%. DCP of more than 98% purity was purchased and further purified by vacuum sublimation. Organic solvents, benzene and carbon tetrachloride, were of spectroscopic grade. The organic solutions containing 5.1×10^{-6}—2.6×10^{-5} M (1 M = 1 mol dm^{-3}) [Al(quin)$_3$] and 0—0.11 M DCP were prepared and their emission spectra were measured with a Jasco FP-550X spectrofluorometer equipped with a xenon lamp. A 10 nm slit was used in the exciting path and a 5 nm slit in the analyzing path. A cell compartment was thermostated at 25 °C. The obtained spectra were corrected for the differences in sensitivity by reference to known emission of quinine sulfate in 0.5 M sulfuric acid.[9]

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The $\pi \rightarrow \pi^*$ absorption band of [Al(quin)$_3$] had a maximum at 395 nm in both benzene and carbon tetrachloride, and it was shifted to 375 nm in the presence of 0.10 M DCP. The change of molar absorptivity at the absorption maximum was small. The excitation spectra of [Al(quin)$_3$] in the presence and absence of DCP had maxima at the same wavelengths as the absorption maxima.

The emission spectra of [Al(quin)$_3$] always appeared as single and broad bands with flat maxima at 530 nm regardless of the solvents and the presence of DCP. It was confirmed that the solvents and DCP have no fluorescence and the emission intensity is proportional to the concentration of [Al(quin)$_3$]. Figure 1 shows the corrected emission spectra of [Al(quin)$_3$] in carbon tetrachloride in the presence and absence of DCP with an excitation at 365 nm which is one of the most frequently-used excitation wavelengths in fluorometric analysis. The variations of emission intensity with DCP are shown in Table 1. The emission intensity of [Al(quin)$_3$] in carbon tetrachloride is enhanced 2.3-fold by the addition of 0.10 M DCP. Additionally, DCP stabilized the fluorescence of [Al(quin)$_3$] in carbon tetrachloride: after the continuous irradiation of UV-light at 365 nm for 40 min, the emission intensity of [Al(quin)$_3$] in the absence of DCP was decreased to 82% of the initial intensity owing to the photodecomposition of the chelate, whereas the fluorescence in the presence of DCP was not changed. Such enhancing and stabilizing effect of DCP on the fluorescence of [Al(quin)$_3$] should be useful for analytical purposes. The fluorescence in benzene is also enhanced by DCP, but the effect is considerably small compared with that in carbon tetrachloride.

The variations of quantum yield with DCP were evaluated to elucidate the origin of the fluorescence enhancement. The quantum yield (ϕ) was determined by comparing the integrated emission area of the sample with that of the standard, quinine sulfate in 0.5 M sulfuric acid (ϕ = 0.55 at 25 °C), with making correction for the difference in refractive indexes of the solvents.10) In Table 1, the ϕ values obtained are listed together with the data of molar absorptivity at the excitation wavelength 365 nm and energy difference ($\Delta\nu$) between absorption and fluorescence maximum. In carbon tetrachloride, the quantum yield is obviously enhanced in the presence of DCP. Additionally, the enhanced absorptivity at 365 nm, which results from the shift of the $\pi \rightarrow \pi^*$ absorption band to the shorter wavelength, also makes a considerable contribution to the enhancement of fluorescence. On the other hand, the quantum yield in benzene is not increased by DCP and only the enhanced absorptivity at 365 nm contributes to the fluorescence enhancement. In both solvents, the $\Delta\nu$ value is raised from 6.4×10^3 cm^{-1} to 7.8×10^3 cm^{-1} by DCP.

The association of [Al(quin)$_3$] with DCP was examined by means of infrared spectroscopy. Figure 2 shows the infrared absorption spectra in the O–H stretching vibration region of DCP (0.10 M) in carbon tetrachloride in the presence and absence of [Al(quin)$_3$] (0.013 M). By the addition of [Al(quin)$_3$], the absorption at 3600 cm^{-1} due to a free O–H of DCP is reduced and the broad band around 3100 cm^{-1} due to a hydrogen-bonded O–H11) appears. This result clearly indicates the hydrogen bonding of the hydroxyl hydrogen atom of DCP to [Al(quin)$_3$]. The hydroxyl hydrogen of the phenol is considered to interact with the ligand oxygen atoms

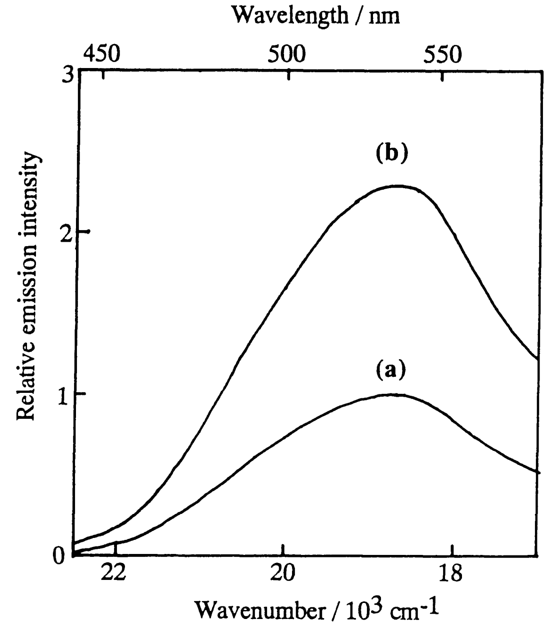

Fig. 1. Corrected emission spectra of 2.55×10^{-5} M [Al(quin)$_3$] in carbon tetrachloride excited at 365 nm: (a) in the absence of DCP; (b) in the presence of 0.10 M DCP.

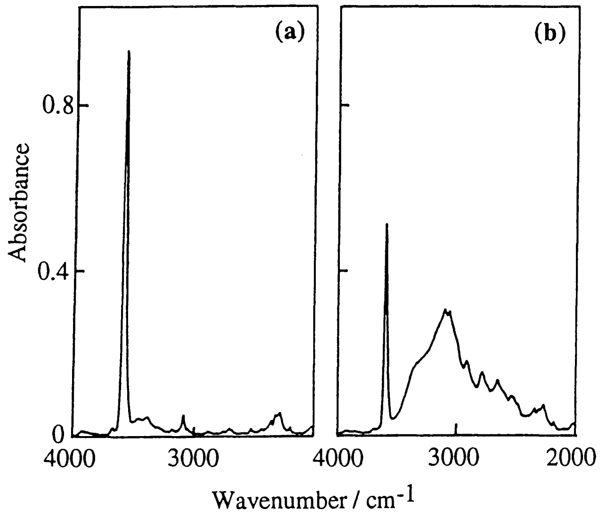

Fig. 2. Infrared absorption spectra of 0.10 M DCP in carbon tetrachloride in a NaCl cell (path length 0.5 mm) at 20 °C: (a) in the absence of [Al(quin)$_3$]; (b) in the presence of 0.013 M [Al(quin)$_3$].

Table 1. Effect of DCP on the fluorescence efficiency of [Al(quin)$_3$]$^{a)}$ excited at 365 nm

Solvent	[DCP] / M	Relative emission intensity at 530 nm$^{b)}$	Absorptivity at 365 nm / M^{-1}cm^{-1}	ϕ $^{c)}$	$\Delta\nu$ $^{d)}$ / 10^3 cm^{-1}
CCl$_4$	0	1.00	3.57×10^3	0.11	6.4
	0.100	2.28	5.88×10^3	0.16	7.8
C$_6$H$_6$	0	1.76	4.51×10^3	0.16	6.4
	0.100	2.03	6.27×10^3	0.14	7.8

a) [[Al(quin)$_3$]] = 2.55×10^{-5} M. b) Maximum in the corrected emission spectra.
c) Quantum yield determined by reference to quinine sulfate in 0.5 M sulfuric acid.
d) Energy difference between absorption and fluorescence maximum.

of the coordinatively saturated chelate.[1-4,6] From the variation of absorbance of the free O–H, the concentration of the hydrogen-bonded phenol is determined to be 0.04 M. In the case of tris(8-quinolinolato)iron(III) ([Fe(quin)$_3$]) under the same conditions, the concentration of the hydrogen-bonded phenol is also estimated to be 0.04 M by using the association constants ($\beta_{\mathrm{ass},n}$) of [Fe(quin)$_3$]•nDCP previously determined, *i.e.*, log $\beta_{\mathrm{ass},1}$ = 3.55, log $\beta_{\mathrm{ass},2}$ = 6.00, and log $\beta_{\mathrm{ass},3}$ = 8.32.[4)] Therefore, it is suggested that [Al(quin)$_3$] forms the association complexes $[Al(quin)_3]\bullet n DCP$ ($n = 1, 2, 3$) similarly to $[Fe(quin)_3]$ and its association constants is comparable to those of $[Fe(quin)_3]$.

It is well-known that halogen-containing solvents such as carbon tetrachloride and chloroform remarkably quench the fluorescence of solutes.[12] Probably, the phenol molecules surrounding the chelate shield the excited singlet state of the chelate from the quenching influence of carbon tetrachloride and consequently enhance the quantum yield of the chelate. This explanation is supported by the fact that there is no enhancement of quantum yield in benzene which has little quenching influence.

Additionally, the dependence of the fluorescence intensity on the concentration of DCP in carbon tetrachloride was investigated. The fluorescence intensity increased with the concentration of DCP and became constant when the phenol concentration was higher than 0.02 M. In the concentration range over 0.02 M, it is expected that more than 80% of $[Al(quin)_3]$ molecules form the 1:3 association complex with DCP, assuming that the association constants of $[Al(quin)_3]$ are comparable to those of $[Fe(quin)_3]$. It is reasonable that the shielding effect described above is larger in the 1:3 association complex than that in the 1:1 or 1:2 association complex.

In conclusion, 3,5-dichlorophenol was found to enhance the fluorescence of tris(8-quinolinolato)-aluminum(III) in carbon tetrachloride by associating with the chelate through hydrogen bonding. Such effect is probably available for many other fluorescent chelates and could be applied to fluorometric analysis.

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