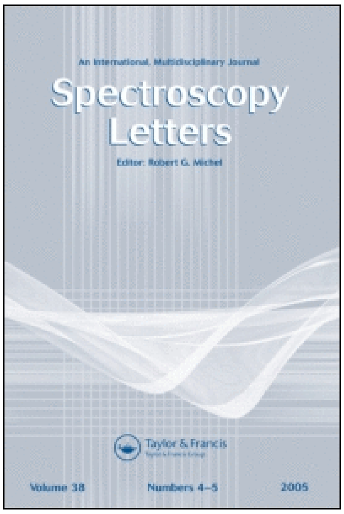

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Secondary Fluorescence Quenching Rate Constants of Eu^{3+} in D_2O by ETOH, CH_3COOD and OH-Groups (H_2O)

by

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It has been shown recently that the fluorescence efficiency of Eu^{3+} in organic solvents is reduced to a different extent by the solvent molecules located in the primary and in the secondary solvation spheres of the ion(1,2). The primary solvation sphere was associated with the nonradiative quenching processes of the rare-earth ion, k_h, whereas molecules located in the secondary solvation sphere were associated with a secondary fluorescence quenching effect i.e. k_{solv}^{sec} or K_Q^{sec}. The structure of the primary solvation sphere was found to exert a marked effect upon the fluorescence efficiency and lifetimes of Sm^{3+} in $POCl_3$: $SnCl_4$(3). Furthermore, a pronounced effect, due to both the primary and the secondary solvation sphere, was observed upon the intensity and the splitting of absorption and emission bands of Eu^{3+} associated with electric-quadrupole transitions(4).

To evaluate this effect, accurate values of fluorescence quenching rate constants are needed, related to molecules both in the primary and the secondary solvation spheres. Such values can be used to test various models for electronic excitation energy transfer from the excited rare-earth ion to the vibrational overtones of the solvent in both spheres.

Enhancement in the fluorescence efficiency of Eu^{3+} in aqueous solutions upon replacing H_2O with D_2O was demonstrated a few years ago(5,6), and it has been attributed to coupling between the electronic levels of the rare-earth ions and some of the vibrational overtones of H_2O and D_2O(7,8). Similar results were observed in solutions of rare-earth ions in alcohols and in deuterated alcohols(9). However, no distinction was made as far as primary and secondary solvation spheres were concerned. In an attempt to obtain more quantitative information regarding this electronic-vibrational energy transfer process, we have employed solutions of $EuCl_3$ and $Eu(NO_3)_3$ in 99.8% D_2O containing small amounts of appropriate quenchers. The chloride was formed by dissolving Eu_2O_3 (99.9 to 99.99%) in DCl and D_2O whereas $Eu(NO_3)_3$ was prepared by dissolving Eu_2O_3 by 70% HNO_3. The latter solutions, $5 \times 10^{-2}M$ in D_2O, contained 0.58M residual water. Furthermore, solutions of $EuCl_3$ and $Eu(NO_3)_3$, $5 \times 10^{-2}M$, were made in ETOH, CH_3COOH and H_2O. Triply distilled water was employed. Absolute ETOH and glacial CH_3COOH were also used. These solutions were used in various combinations resulting in solutions of $5 \times 10^{-2}M$ $EuCl_3$ or $EuNO_3$ in various D_2O quencher systems.

Emission spectra were obtained by using the Aminco-Bowman Spectrophotofluorimeter with a 1P21 phototube and an X-Y recorder. Some typical emission spectra are shown in Figure 1. In each system we show two extreme cases i.e. at [Q]=0 and at fairly high concentration of Q. Figure 1A(a) shows the emission bands of $EuCl_3$ in D_2O in the absence and the presence of 5.20 M ETOH. The change in the composition of the solvation sphere has some effect upon the relative intensities of the emission bands at 591 and 614 mμ. This effect is not observed in the case of $EuCl_3$ in D_2O-H_2O (Figure 1A(b)) despite the addition of 11.7 M H_2O. The reason probably is that these two solvents are so similar in all their properties, that the transition probabilities do not change although the composition of the primary solvation sphere changes.

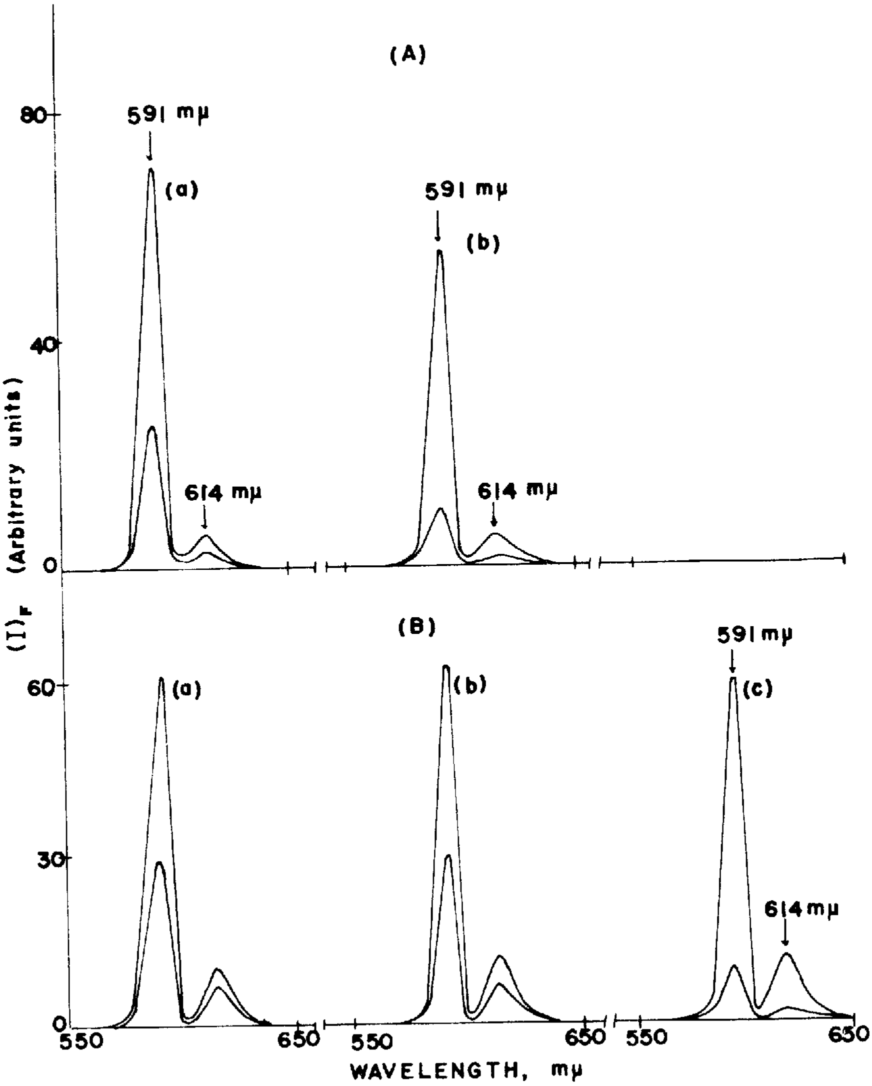

Figure 1. Fluorescence spectra of Eu^{3+} in D_2O and in D_2O-second solvent systems. λ_{exc} = 391 mμ. (A) $EuCl_3$ 5 x 10^{-2} M: (a) in D_2O and in D_2O plus 5.20 M EtOH; (b) in D_2O and in D_2O plus 11.7 M H_2O. (B) $Eu(NO_3)_3$5 x 10^{-2} M: (a) in D_2O + 0.58 M H_2O and in D_2O + 0.58 M H_2O plus 3.42 M CH_3COOH; (b) in D_2O + 0.58 M H_2O and in D_2O + 0.58 M H_2O plus 5.45 M ETOH; (c) in D_2O + 0.58 M H_2O and in D_2O + 0.58 M H_2O plus 15 M H_2O.

Figure 1B(a) shows the emission bands of $Eu(NO_3)_3$ in D_2O in the absence and the presence of 3.42 M CH_3COOH. The effect of the change in the composition of the primary solvation sphere upon the relative intensities of the two emission bands is pronounced. This effect is less pronounced in the presence of 5.45 M ETOH (Figure 1B(b)) and it is hardly observed in the presence of 15.0 M H_2O (Figure 1B(c)). The ratio of the intensities of the emission bands at 591 and 614 mμ reflects the ratio in the probabilities of the transitions $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ respectively$^{(10)}$. Therefore, $(I_F)_{591}/(I_F)_{614} \propto {}^5D_0 \rightarrow {}^7F_1/{}^5D_0 \rightarrow {}^7F_2$. Quenching rate constants cannot be determined unless the transition probabilities are kept constant. Some results regarding the dependence of this ratio upon the concentration of the quencher added are shown in Figure 2B for both $EuCl_3$(a) and $Eu(NO_3)_3$(b) in D_2O-Q systems. Addition of H_2O does not seem to alter the ratio. On the other hand addition of either ETOH or CH_3COOH has a marked effect upon the ratio. The effect of the composition of the primary solvation sphere is two fold. First a change in the transition probabilities and second a different efficiency in the radiationless deactivation of the excited rare-earth ion. Both effects have to be avoided in order that accurate quenching rate constants can be determined. It is obvious from Figure 2B that one has to use much less than 3 M of the second solvent to achieve this goal. Furthermore, these rate constants have to be independent of the concentration of Eu^{3+}. The lack of such self-quenching process is illustrated in Figure 2A. Self-quenching according to the process:

$$Eu^{3+}(^5D_0) + Eu^{3+}(^7F_0) \rightarrow 2\ Eu^{3+}(^7F) \qquad (1)$$

is not energetically feasible$^{(10)}$ At very high $[Eu^{3+}]$ the process:

$$Eu^{3+}(^5D_0) + 2\ Eu^{3+}(^7F_0) \rightarrow 3\ Eu^{3+}(^7F) \qquad (2)$$

may become very slightly probable. This is clearly not the case in the systems under study.

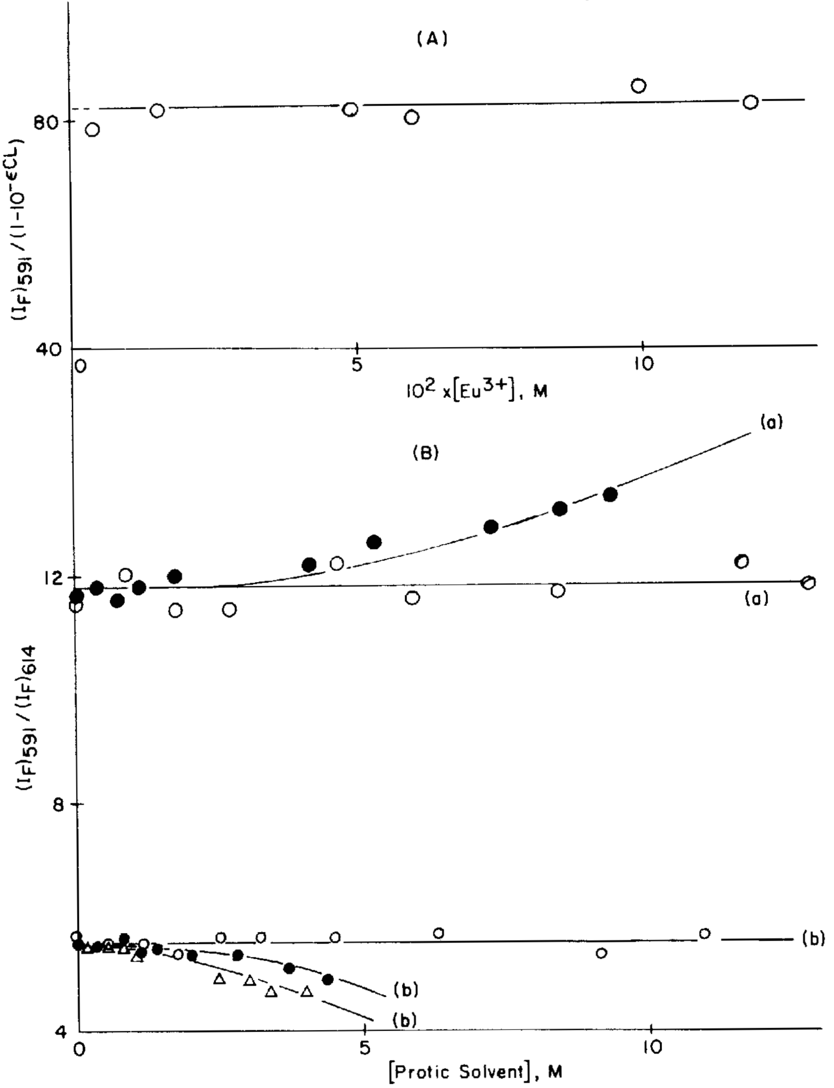

Figure 2. (A) Variation of $(I_F)_{591}/(1-10^{-\varepsilon CL})$ vs $[Eu^{3+}]$ for $EuCl_3$ in D_2O: λ_{exc} = 391 mμ.

(B) Variation of the ratio $(I_F)_{591}/(I_F)_{614}$ vs the concentration of the protic solvent present; λ_{exc} = 391 mμ. (a) $EuCl_3$ 5×10^{-2} M in D_2O: ○ in the presence of H_2O; ● in the presence of ETOH. (b) $Eu(NO_3)_3$ 5×10^{-2}M in D_2O + 0.58 M H_2O: ○ in the presence of H_2O; ● in the presence of ETOH and △ in the presence of CH_3COOH.

The spectroscopy of $EuCl_3$ or $Eu(NO_3)_3$ in D_2O and in the presence of very small amounts of ETOH can be outlined as follows:

$$Eu^{3+}(^7F_0) \xrightarrow{391\,m\mu} Eu^{3+}(^5L_6) \rightsquigarrow Eu^{3+}(^5D_0) \qquad (3)$$

$$Eu^{3+}(^5D_0) \xrightarrow[\text{Sphere}]{\text{Primary Solvation}} Eu^{3+}(^7F) + \text{heat};\ k_h \qquad (4)$$

$$Eu^{3+}(^5D_0) \longrightarrow Eu^{3+}(^7F) + h\nu_{fl}\ ;\ k_{fl} \qquad (5)$$

$$Eu^{3+}(^5D_0) + D_2O \rightarrow Eu^{3+}(^7F) + \text{heat};\ k^{sec}_{D_2O} \qquad (6)$$

$$Eu^{3+}(^5D_0) + ETOH \rightarrow Eu^{3+}(^7F) + \text{heat};\ k^{sec}_{ETOH} \qquad (7)$$

This mechanism gives rise to the following equation:

$$(I_F)_0 / (I_F)_{ETOH} = 1 + k^{sec}_{ETOH}[ETOH] / \{k_{fl} + k_h + k^{sec}_{D_2O}[D_2O]\} \qquad (I)$$

where $(I_F)_0$ refers to the fluorescence intensity at [ETOH] = 0. The lifetimes of $EuCl_3$ and $Eu(NO_3)_3$ were found to be 2.27 and 1.90 msec respectively(11). Therefore,

$$k_{fl} + k_h + k^{sec}_{D_2O}[D_2O] = \tau^{-1} = 4.40 \times 10^2\ sec^{-1}\ (EuCl_3) \qquad (II)$$

and

$$k_{fl} + k_h + k^{sec}_{D_2O}[D_2O] = 5.25 \times 10^2\ sec^{-1}\ (Eu(NO_3)_3) \qquad (III)$$

Results showing the variation of $(I_F)_0/(I_F)_{ETOH}$ vs [ETOH] are illustrated in Figure 3. The effect of the primary solvation sphere becomes very obvious as [ETOH] increases. However, the initial slopes are independent of such an effect. By using these initial slopes, i.e.

$$\text{Slope} = k^{sec}_{ETOH} / \{k_{fl} + k_h + k^{sec}_{D_2O}[D_2O]\} \qquad (IV)$$

and Equations (II) and (III) one can easily obtain:

$$\text{Slope} \leq k^{sec}_{ETOH} / \tau^{-1} \qquad (V)$$

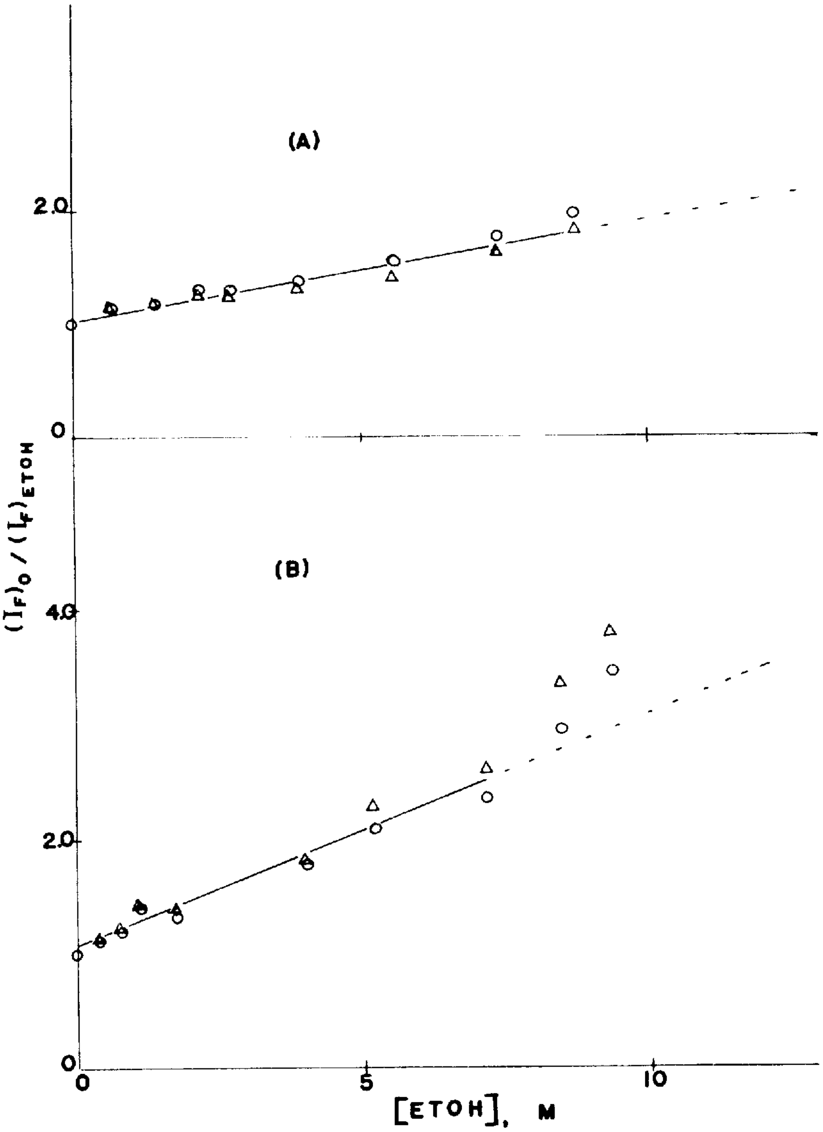

Figure 3. Variation of the ratio $(I_F)_o$ / $(I_F)_{ETOH}$ as a function of [ETOH]; λ_{exc} = 391 mμ; ○ λ_{fl} = 591 mμ; △ λ_{fl} = 614 mμ
(A) $EuCl_5$ 5 x 10^{-2} M in D_2O - ETOH (B) $Eu(NO_3)_3$ 5 x 10^{-2}M in D_2O + 0.58 M H_2O plus ETOH.

The inequality sign is needed because as [ETOH] increases [D_2O] decreases. From Equation (V) we obtain

$$k^{sec}_{ETOH} \geqq 104\ M^{-1}\ sec^{-1} \text{ for } EuCl_3$$

$$k^{sec}_{ETOH} \geqq 80\ M^{-1}\ sec^{-1} \text{ for } Eu(NO_3)_3$$

The spectroscopy of $EuCl_3$ and $Eu(NO_3)_3$ in the systems D_2O-H_2O and D_2O-CH_3COOH is almost similar. One has to consider the isotope-exchange equilibria:

$$D_2O + H_2O \rightleftarrows 2HOD \qquad (8)$$

$$D_2O + CH_3COOH \rightleftarrows HOD + CH_3COOD \qquad (9)$$

At very low [H_2O] or [CH_3COOH] it is obvious that [HOD] = 2 [H_2O] and [OH-group] = [CH_3COOD] = [CH_3COOH]. Of course at higher [H_2O], [OH-groups] < 2[H_2O] and at very high [H_2O] further addition of water will have no net effect upon the concentration of such groups i.e.

$$HOD + H_2O \rightleftarrows H_2O + HOD$$

The spectroscopy of $EuCl_3$ and $Eu(NO_3)_3$ in these systems will be identical to that in ETOH with the only exception that reaction (7) will be replaced by

$$Eu^{3+}(^5D_o) + H_2O \rightarrow Eu^{3+}(^7F) + \text{heat};\ 2k^{sec}_{OH} \qquad (10)$$

and

$$Eu^{3+}(^5D_o) + CH_3COOH \rightarrow Eu^{3+}\ (^7F) + \text{heat};(k^{sec}_{OH} + k^{sec}_{CH_3COOD}) \qquad (11)$$

Equation (I) can be expressed under these conditions as follows:

$$(I_F)_o\ /\ (I_F)_Q = 1 + 2k^{sec}_{OH}\ [H_2O]\ /\ \{k_{fl} + k_h + k^{sec}_{D_2O}\ [D_2O]\} \qquad (VI)$$

and

$$(I_F)_o\ /\ (I_F)_Q = 1 + \{k^{sec}_{OH} + k^{sec}_{CH_3COOD}\}[CH_3COOH]/\{k_{fl} + k_h + k^{sec}_{D_2O}[D_2O]\} \qquad (VII)$$

for both $EuCl_3$ and $Eu(NO_3)_3$ in the systems D_2O-H_2O and D_2O-CH_3COOH respectively. It should be pointed out that in the case of $Eu(NO_3)_3$ in D_2O-H_2O, $(I_F)_0$ is obtained by extrapolation due to the residual amount of H_2O(0.58M) present.

Results plotted according to Equations (VI) and (VII) are shown in Figure 4. Figure 4A exhibits the variation of $(IF)_0$ / $(IF)_Q$ vs $[CH_3COOH]$ for $Eu(NO_3)_3$ in D_2O. Figure (4B) depicts the variation of the ratio as a function of $[H_2O]$ for $Eu(NO_3)_3$ in D_2O and Figure (4C) depicts a similar variation for $EuCl_3$ in D_2O. Severe deviations from the Stern-Volmer Equation are apparent as the concentration of the second solvent increases. From the initial slopes and the appropriate fluorescence lifetimes(11) we obtain:

$$\text{Slope} \leqq 2k^{sec}_{OH} \,/\, \tau^{-1} \qquad \text{(VIII)}$$

for both $EuCl_3$ and $Eu(NO_3)_3$ in D_2O and

$$\text{Slope} \leqq (k^{sec}_{OH} + k^{sec}_{CH_3COOD}) \,/\, \tau^{-1} \qquad \text{(IX)}$$

for $Eu(NO_3)_3$ in D_2O. Therefore,

$$k^{sec}_{OH} \geqq 117\ M^{-1}\ sec^{-1} \text{ for } EuCl_3;\ k^{sec}_{OH} \geqq 165\ M^{-1}\ sec^{-1} \text{ for } Eu(NO_3)_3$$

$$k^{sec}_{OH} + k^{sec}_{CH_3COOD} \geqq 205\ M^{-1}\ sec^{-1} \text{ for } Eu(NO_3)_3$$

and consequently:

$$k^{sec}_{CH_3COOD} \geqq 40\ M^{-1}\ sec^{-1} \text{ for } Eu(NO_3)_3$$

The values obtained here and appropriate comparative values from the literature are given in Table 1.

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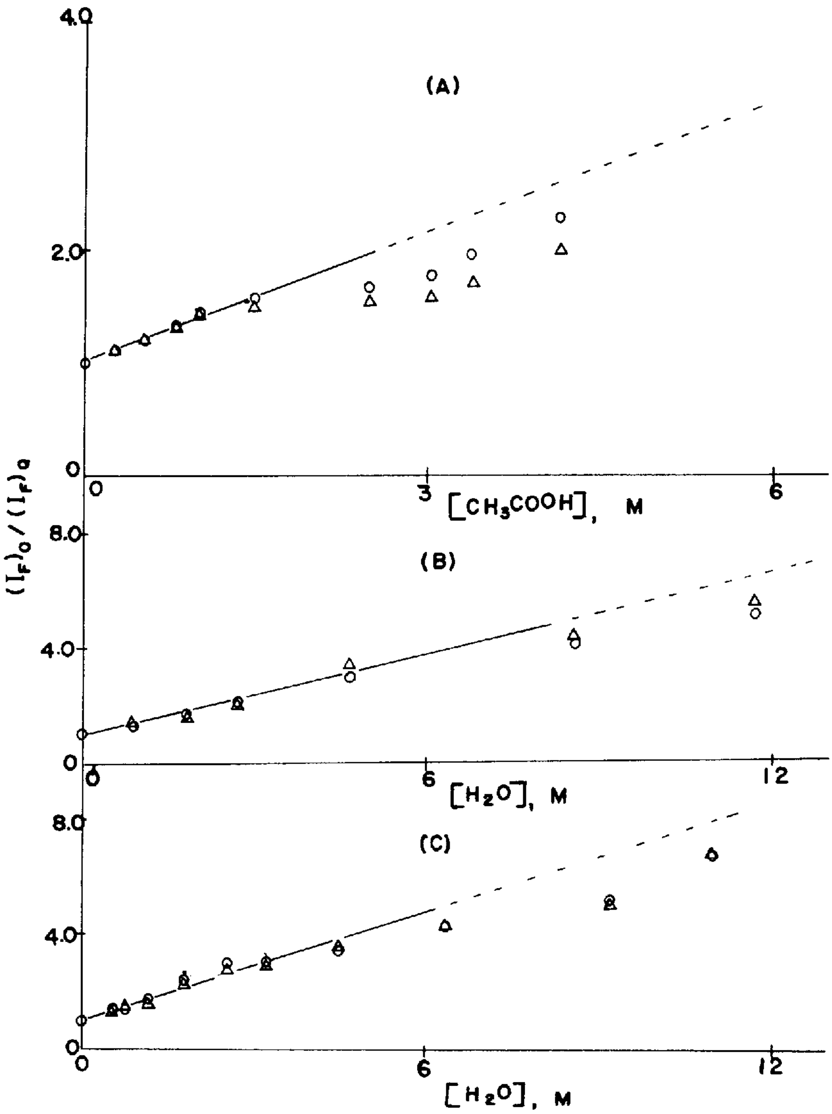

Figure 4. Variation of the ratio $(I_F)_0$ / $(I_F)_Q$ with [Q]; λ_{exc} = 391 mμ; ○ λ_{fl} = 591 mμ; △ λ_{fl} = 614 mμ. (A) $Eu(NO_3)_3$ 5×10^{-2}M in D_2O + 0.58 M H_2O plus CH_3COOH. (B) $EuCl_3$ 5×10^{-2}M in D_2O - H_2O and (C) $Eu(NO_3)_3$ 5×10^{-2}M in D_2O + 0.58 M H_2O plus H_2O.

TABLE 1

SECONDARY FLUORESCENCE QUENCHING RATE CONSTANTS

FOR

Eu^{3+} in SOLUTION

PRIMARY SOLVATION SPHERE			
CH_3COOH	D_2O		Reference
$EuCl_3$	$EuCl_3$	$Eu(NO_3)_3$	
$k^{sec}_{CH_3COOH} \geqq 61\ M^{-1}sec^{-1}$			(1)
	$k^{sec}_{ETOH} \geqq 104\ M^{-1}sec^{-1}$;	$k^{sec}_{ETOH} \geqq 80M^{-1}sec^{-1}$	This Work
$k^{sec}_{CH_3COCl} \geqq 24\ M^{-1}sec^{-1}$			(1)
	$k^{sec}_{OH}(\text{for } H_2O) \geqslant 117\ M^{-1}sec^{-1}$;	$k^{sec}_{OH} \geqslant 165M^{-1}sec^{-1}$	This Work
$k^{sec}_{CF_3COOH} \geqq 14\ M^{-1}sec^{-1}$			(1)
		$k^{sec}_{CH_3COOD} \geqq 40\ M^{-1}sec^{-1}$	This Work
$k^{sec}_{OH}(\text{for } CH_3COOH) \simeq 55\ M^{-1}sec^{-1}$			(2)
$k^{sec}_{C\text{-}H}(\text{for } CH_3COOH) \simeq 57\ M^{-1}sec^{-1}$			(2)

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