

The influence of excitation of the 4f-orbital of $\text{Eu}(\text{fod})_3$ on complex formation with adamantanone and anomalous enhancement of Eu^{3+} luminescence under the action of H_2O and D_2O molecules in toluene

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The influence of excitation of the 4f-orbital of β -diketonate $\text{Eu}(\text{fod})_3$ (fod is heptafluorodimethyloctanedione) on the formation of the coordination bond with adamantanone (**1**) was studied by the nonradiative energy transfer technique. The kinetic parameters of fluorescence (FL) and the lifetime (τ) of the Eu^{3+} ion in toluene solutions were studied. The increase in the stability of the $\text{Eu}(\text{fod})_3 \cdot \text{1}$ complex when f-f-transitions of the Eu^{3+} ion are excited is related to an increase in the acceptor capability of $\text{Eu}(\text{fod})_3$ due to the increasing fraction of the covalent component determined by the participation of 4f-orbitals. An unexpected effect of enhancement of the $\text{Eu}(\text{fod})_3$ fluorescence under the action of H_2O (D_2O) molecules in toluene solutions was observed. The effect is assumed to be caused by an increase in the negative inductive effect when outer-sphere associates with the fluorinated radical of β -diketonate are formed. The mechanisms of the influence of electron-donating inner-sphere ligands and outer-sphere associates on the quantum yield of fluorescence of $\text{Eu}(\text{fod})_3$ are discussed.

Key words: fluorescence, nonradiative energy transfer; $\text{Eu}(\text{III})$ β -diketonate, adamantanone, complex formation.

Many works^{1,2} have been devoted to studying the factors affecting the intensity of luminescence of f-f-transitions of lanthanide ions (Ln^{3+}), including those concerning mechanisms of nonradiative energy transfer (NET).^{3,4} When the effect of the ligand nature on the quantum yield (Φ) of fluorescence (FL) of Ln^{III} tris- β -diketonates is studied, the main role in the decrease of dissipation excitation energy losses is ascribed to steric or electron-donor properties.⁵ At the same time, the character of the metal-ligand bond, which depends⁶ in many aspects on the donation of the electron density of the unoccupied 4f-orbital to the valence orbitals of the Ln^{3+} ion, is one of the substantial factors determining the quantum yield of FL of Ln^{III} chelates. It is known that an increase in the covalent component of Ln^{3+} -ligand bonds caused by the participation of 4f-orbitals is accompanied by the enhancement of FL of lanthanide ions.⁵ In this connection, it was of interest to study the effect of excitation of the 4f-orbital of the $\text{Eu}(\text{fod})_3$ chelate (fod is heptafluorodimethyloctanedione) on the formation of the coordination bond with monoketone (adamantanone (**1**)) and to study the kinetic parameters and lifetime (τ) of FL of $\text{Eu}(\text{fod})_3$ in toluene solutions containing additives of **1** or water.

Experimental

The lifetime of Eu^{3+} in the excited state was measured on an LIF-200 laser pulse fluorimeter; the radiation intensity (I) and FL spectra of $\text{Eu}(\text{fod})_3$ were measured on a Hitachi MPF-4 spectrofluorimeter; and absorption spectra were recorded on a Specord M-40 spectrophotometer. The intensity of chemiluminescence (CL) was determined on the previously described installation.⁷ Adamantylideneadamantane-1,2-dioxetane (**2**) was synthesized by the known procedure.⁸ Anhydrous $\text{Eu}(\text{fod})_3$ was obtained by heating of the reaction product at 370 K *in vacuo* for 4 h. Toluene was purified by refluxing over Na and distillation. Adamantanone (**1**) (pure grade) was purified by chromatography followed by sublimation. The quantum yield of luminescence of $\text{Eu}(\text{fod})_3$ was determined relatively to $\text{Eu}(\text{tta})_3 \cdot \text{phen}$ (tta is thenoyltrifluoroacetone, phen is 1,10-phenanthroline).⁹

Results and Discussion

The observed increase in both I and τ of FL of $\text{Eu}(\text{fod})_3$ in the presence of **1** is evidence of the higher value of the quantum yield of FL of Eu^{3+} ions in the $[\text{Eu}(\text{fod})_3 \cdot \text{1}]$ complex than that in the starting complex. The possibility of formation of this complex has been

Table 1. Kinetic parameters, Φ , and τ of FL upon excitation of Eu³⁺(fod)₃ ($5 \cdot 10^{-3}$ mol L⁻¹) at different concentrations of **1** in toluene at $T = 290$ K

[1] · 10 ³ /mol L ⁻¹	τ_0 /μs	τ/τ_0	I/I_0	Φ (%)	k_{nr} s ⁻¹	k_c s ⁻¹	τ_c /μs
—	200	1.0	1.0	4.3	4800	—	—
2.5	260	1.3	1.2	5.5	3700	—	—
5.0	290	1.4	1.4	6.0	3300	210	4760
10	320	1.6	1.6	7.0	2900	—	—
25	370	1.8	1.8	8.0	2500	—	—
50	400	2.0	2.0	8.6	2300	—	—

Note. $\lambda_{ex} = 465$ nm. Average error $\pm 10\%$.

confirmed previously.¹⁰ The exponential character of FL decay of Eu(fod)₃ in the presence of **1** indicates a fast ligand exchange in the [Eu(fod)₃ · **1**] complex. The position of the bands in the absorption spectra and the ratio of intensities of radiative transitions of FL of Eu(fod)₃ at 298 K remain unchanged when **1** is added. The character of changes in the FL intensity is independent of the wavelength of luminescence excitation (λ_{ex}/nm : 350, 465, and 536).

The quantum yield of luminescence of Eu(fod)₃ in toluene in the absence of **1** (Φ_0) at 290 K is equal to 4.3%. Based on the ratios $\Phi = \Phi_0 I/I_0$ and $\Phi = \Phi_0 \tau/\tau_0$, we determined the values of quantum yields of FL of Eu(fod)₃ at different concentrations of **1**, and the rate constants of radiative ($k_c = \Phi/\tau$) and nonradiative ($k_{nr} = 1/\tau - k_c$) deactivation and the radiative lifetime ($\tau_c = 1/k_c$) of FL of Eu(fod)₃ (Table 1) were calculated from the ratios $\Phi = k_c/(k_c + k_{nr})$ and $\tau = (k_c + k_{nr})^{-1}$. As can be seen in Table 1, k_c remains unchanged as the concentration of **1** increases, and τ_c of FL of Eu³⁺ is close to the value of 5 ms determined previously.¹¹ Thus, the increase in Φ of luminescence of Eu(fod)₃ is caused only by a decrease in nonradiative losses when toluene molecules are displaced by adamantanone from the sphere of the Eu³⁺ ion quenching.

The Φ_1 and k_{nr}^1 values for the [Eu(fod)₃ · **1**]^{*} complex can be obtained by the extrapolation of the Φ and k_{nr} values to [**1**]₀ → ∞. The plots of changes in Φ and k_{nr} can be satisfactorily ($r = 0.999$) linearized in the coordinates $1/(\Phi - \Phi_0)$ and $1/(k_{nr}^0 - k_{nr})$ depending on $1/[**1**]₀$ (here Φ_0 and k_{nr}^0 are the parameters in the absence of **1**, and [**1**]₀ is the initial concentration of **1**) (Fig. 1). $\Phi_1 = 10\%$ and $k_{nr}^1 = 2200$ s⁻¹ were determined from the intercept on the Y-axis, and the lifetime of FL of the [Eu(fod)₃ · **1**]^{*} complex, equal to 410 μs, was determined from the expression $1/\tau_1 = k_c + k_{nr}^1$.

It has been previously proposed¹² to estimate the number of molecular groups added to the Ln³⁺ ion from the change in the τ and I values during complex formation. Then this method has been repeatedly used for determination of the parameters of complex formation of Ln³⁺ and UO₂²⁺ ions with organic substrates^{13–15} and inorganic ions^{16,17} in solutions. The fast ligand

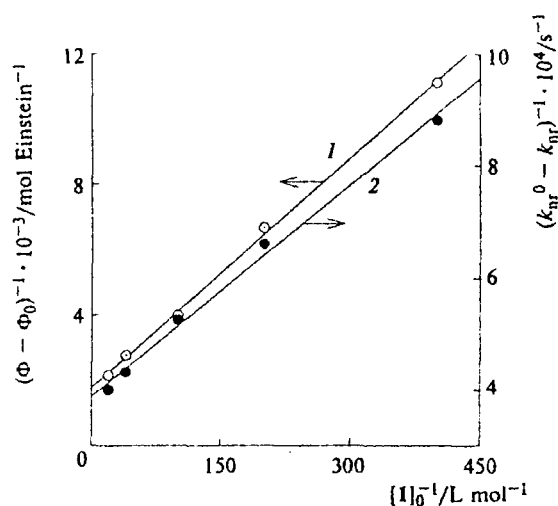


Fig. 1. Dependences of Φ (1) and k_{nr} (2) of FL of Eu(fod)₃ ($5 \cdot 10^{-3}$ mol L⁻¹) on the concentration [**1**]₀ in toluene at 290 K.

exchange and the constant value of k_c are the main conditions for applicability of the NET method.³ As shown above, these requirements are fulfilled in the system studied. When a complex of Eu(fod)₃ with one adamantanone molecule in the excited state is formed, the following equation is fulfilled:^{18,19}

$$\frac{\tau_0}{\tau - \tau_0} = \frac{\tau_1 \tau_0}{\tau_1 - \tau_0} + \frac{\tau_1 \tau_0}{\tau_1 - \tau_0} \cdot \frac{1}{K^* [\mathbf{1}]}, \quad (1)$$

where K^* is the stability constant of the [Eu(fod)₃ · **1**]^{*} complex, τ_0 is the lifetime of Eu³⁺ in the absence of a ligand, τ_1 is the lifetime of FL of the [Eu(fod)₃ · **1**]^{*} complex, τ is the observed time of luminescence decay after the equilibrium concentrations of the complexes in the excited state were established, and [**1**] is the equilibrium concentration of adamantanone. The formation of the 1 : 2 complex of Eu(fod)₃ with **1** can be neglected²⁰ at the initial concentrations [Eu(fod)₃] = $5 \cdot 10^{-3}$ mol L⁻¹ and [**1**] = $2.5 \cdot 10^{-3}$ – $5 \cdot 10^{-2}$ mol L⁻¹.

The equilibrium concentration of **1** was calculated using the values of the stability constant of the Eu(fod)₃ · **1** complex in the ground state. These constants were determined by the method²¹ of studying CL quenching during thermolysis of dioxetane **2**.

$$I_0/I = 1 + K[\mathbf{1}]_0/(1 + K_1 [\text{Eu(fod)}_3]_0) \quad (2)$$

Here I and I_0 are the CL intensities in the presence and absence of **1**, respectively; [Eu(fod)₃]₀ and [**1**]₀ are the initial concentrations of the reagents; and K_1 ($\Delta H = -18.8$ kJ mol⁻¹, $\Delta S = -33.4$ J mol⁻¹ K⁻¹)²² and K are the stability constants of the [Eu(fod)₃ · **2**] and [Eu(fod)₃ · **1**] complexes, respectively. The parameters of complex formation of Eu(fod)₃ in the ground state with **1** in toluene are presented below, and the corre-

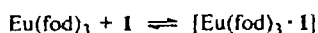
Table 2. Parameters of complex formation of $\text{Eu}(\text{fod})_3$ in the excited state with adamantanone in toluene

$$\text{Eu}^*(\text{fod})_3 + \text{I} \rightleftharpoons [\text{Eu}(\text{fod})_3 \cdot \text{I}]^*$$

T/K	τ_0	τ_1	K^* /L mol ⁻¹
	μs		
280	220	430	360
290	190	410	415
300	160	370	500
310	130	350	625
320	105	320	790
330	90	270	990

Note. $\Delta H_{290}^* = 19.0 \text{ kJ mol}^{-1}$. $\Delta S_{290}^* = 115.0 \text{ J mol}^{-1} \text{ K}^{-1}$. Average error $\pm 10\%$.

sponding parameters in the case of the excited state are given in Table 2.



$$\Delta H_{300} = -22.0 \text{ kJ mol}^{-1}$$

$$\Delta S_{300} = -30.0 \text{ J mol}^{-1} \text{ K}^{-1}$$

T/K	280	290	300	310	320	330
$K/\text{L mol}^{-1}$	310	220	165	120	100	75

The values of K^* and τ_1 of FL of the $[\text{Eu}(\text{fod})_3 \cdot \text{I}]^*$ complex in the excited state were determined from the slope of the linear anamorphosis of Eq. (1), and the thermodynamic parameters of complex formation of **1** with $\text{Eu}(\text{fod})_3^*$ (see Table 2) were determined from the temperature dependence of K^* (Fig. 2).

As can be seen in Fig. 2, the excitation of the Eu^{3+} ion changes the thermodynamics of complex formation. Despite the fact that the complex formation of $\text{Eu}^*(\text{fod})_3$ with **1** is the endothermic process ($\Delta H^* > 0$), the free Gibbs energy is negative in the temperature range stud-

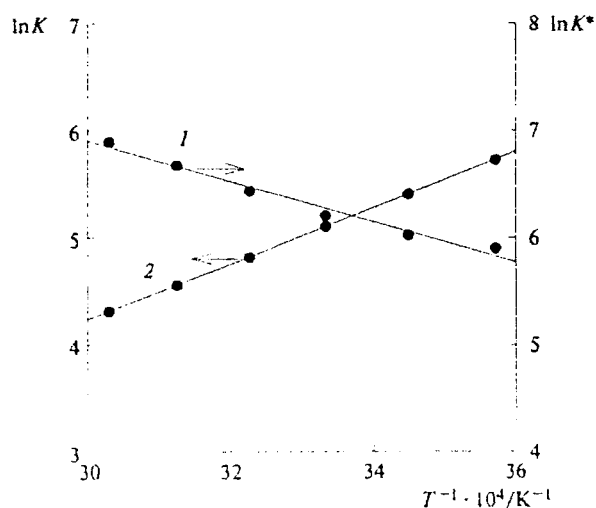


Fig. 2. Temperature dependences of stability constants of complexes with **1** for $\text{Eu}(\text{fod})_3$ in excited (K^*) (1) and ground (K) (2) states in toluene.

ied due to the favorable effect of the entropy factor during the excitation of the Eu^{3+} ion, unlike the $[\text{Eu}(\text{fod})_3 \cdot \text{I}]$ complex in the ground state. An increase in the stability of the $[\text{Eu}(\text{fod})_3 \cdot \text{I}]^*$ complex during excitation of the f-f-transitions of the Eu^{3+} ion is most likely related to enhancement of the acceptor ability of the europium chelate due to an increase in the fraction of the covalent component caused by the participation of the 4f-orbitals. The values of lifetimes τ_1 at 290 K of the $[\text{Eu}(\text{fod})_3 \cdot \text{I}]^*$ complex obtained by different methods coincide (see Table 2), which shows the high accuracy of the NET method for studying complex formation of Ln^{III} chelates in solutions.

The temperature dependences of τ_0 of $\text{Eu}(\text{fod})_3^*$ and τ_1 of $[\text{Eu}(\text{fod})_3 \cdot \text{I}]^*$ (see Table 2) are described satisfactorily by the expression²³

$$\ln(1/\tau^i - 1/\tau_e) = \ln A^i - E_a^i/(RT), \quad (3)$$

where τ^i are the current values of τ_0 and τ_1 at the T temperature, τ_e is the radiative lifetime of Eu^{3+} (4.8 ms), and A^i and E_a^i are the pre-exponential factor and the activation energy of processes of nonradiative deactivation of FL of $\text{Eu}^*(\text{fod})_3$ and $[\text{Eu}(\text{fod})_3 \cdot \text{I}]^*$. The activation parameters of the temperature dependences of τ_0 and τ_1 calculated from Eq. (3) are the following: $E_a^0 = 15.5 \pm 2.0 \text{ kJ mol}^{-1}$ ($\log A^0 = 6.5 \pm 0.8$) and $E_a^1 = 6.7 \pm 1.0 \text{ kJ mol}^{-1}$ ($\log A^1 = 4.6 \pm 0.6$), respectively. The decrease in dissipation excitation energy losses in the $[\text{Eu}(\text{fod})_3 \cdot \text{I}]^*$ complex as compared to that for $[\text{Eu}(\text{fod})_3]^*$ ($E_a^1 < E_a^0$) is most likely due to two reasons: first, a decrease in the number of toluene molecules with a high deactivating ability in the nearest environment of the Eu^{3+} ion; second, an increase in the efficiency of the electron energy transfer to the Eu^{3+} ion due to the coordination of the donating ligand, adamantanone.⁵

It is known^{3,24} that among H- and D-containing solvents, H_2O molecules possess the maximum capability of deactivating FL of Eu^{3+} . However, we discovered that the addition of H_2O to a dehydrated toluene solution of $\text{Eu}(\text{fod})_3$ results in the enhancement of FL of Eu^{3+} rather than quenching. The dependences of I and τ of FL of $\text{Eu}(\text{fod})_3$ on the concentration of H_2O are parallel and have a tendency to saturation (Fig. 3). Similarly to **1**, the decay of FL of $\text{Eu}(\text{fod})_3$ in the presence of H_2O is exponential. At the same time, the addition of H_2O results in a decrease in the molar extinction coefficient of $\text{Eu}(\text{fod})_3$ in the absorption bands of the ligand and Eu^{3+} ion, while the position of the bands and the I ratio in the FL spectra remain unchanged (Fig. 4). The character of changes in I and τ of FL of $\text{Eu}(\text{fod})_3$, unlike **1**, depends on the wavelength of luminescence excitation. When the $^5\text{D}_2$ state of the Eu^{3+} ion is excited (465 nm), the increase in FL is 1.4 times lower than that for excitation of the first singlet level of the ligand (350 nm) (Table 3).

It is known²⁵ that β -diketonate in the $\text{Eu}(\text{fod})_3$ chelate is not hydrolyzed, and the results obtained can most likely be explained by either the change in symmetry of

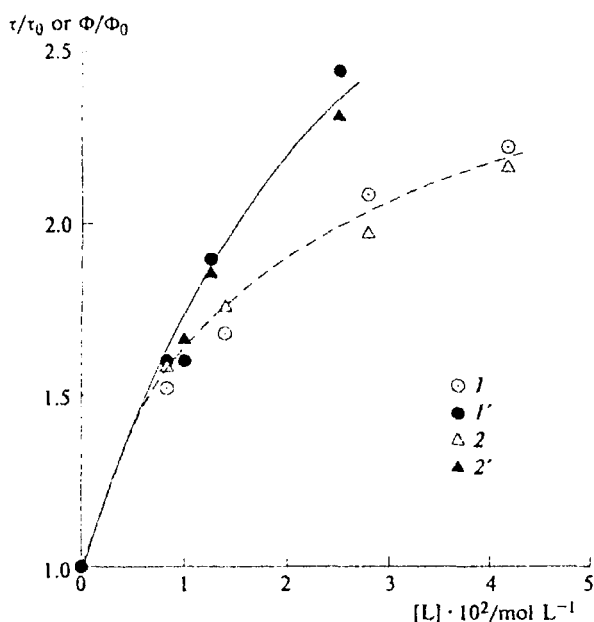


Fig. 3. Dependences of Φ (I , I') and τ (2 , $2'$) of FL of $\text{Eu}(\text{fod})_3$ ($5 \cdot 10^{-3} \text{ mol L}^{-1}$) on the concentrations of H_2O (I , 2) and D_2O (I' , $2'$) in toluene at 338 K. $L = \text{H}_2\text{O}$ or D_2O .

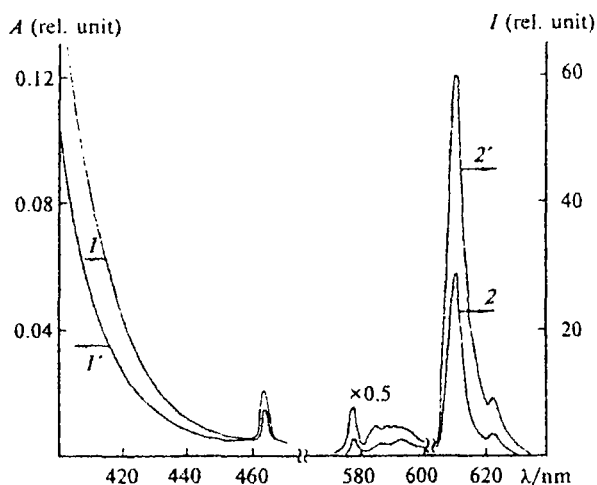


Fig. 4. Absorption (I , I') and FL (2 , $2'$) spectra upon excitation ($\lambda_{\text{ex}} = 350 \text{ nm}$) of $\text{Eu}(\text{fod})_3$ ($5 \cdot 10^{-3} \text{ mol L}^{-1}$) in the absence of H_2O (I , 2) and in the presence of $2 \cdot 10^{-2} \text{ M}$ H_2O in toluene (I' , $2'$) at 338 K.

the environment of the central ion (which should result in an increase in the probability of radiative transitions²) or the formation of associates of H_2O with β -diketonate. The latter assumption is favored due to the stronger increase in Φ for excitation at 350 nm and the unchanged character of k_c . It is most likely that the addition of H_2O leads to hydration of the fluorinated β -diketonate radical to form the hydrogen bond $\text{R}-\text{F}\dots\text{HOH}$. It has been proposed²⁵ that the water

Table 3. Kinetic parameters, F , and τ of FL upon excitation of $\text{Eu}^*(\text{fod})_3$ ($5 \cdot 10^{-3} \text{ mol L}^{-1}$) at concentrations of H_2O and D_2O tending to infinity in toluene at 338 K

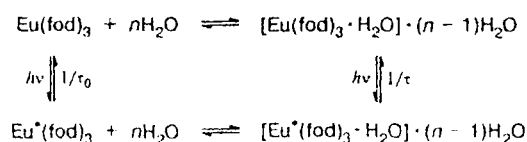
Ligand	τ/τ_0	Φ/Φ_0	Φ (%)	k_{nr} s^{-1}	k_c s^{-1}	τ μs
H_2O	2.5	2.5	4.3	4900	220	190
D_2O	3.0	4.5	7.0	3700	280	250

Note. $\lambda_{\text{ex}} = 350 \text{ nm}$. The values $\Phi_0 = 0.016$ and $k_{\text{nr}}^0 = 12800 \text{ s}^{-1}$ in the absence of H_2O and D_2O (338 K) were calculated from Eq. (3) at the previously determined values of E_a^0 , A^0 , τ_c , and k_c . $\tau_0 = 80 \mu\text{s}$. Average error $\pm 10\%$.

molecules are linked to electronegative groups in the ligand rather than coordinated to the Ln^{3+} ion. We found that the addition of water to a solution of $\text{Eu}(\text{fod})_3$ in toluene at 338 K results in the formation of crystals that are dissolved upon prolonged (30 min) heating of the solution, which points indirectly to the stability of the $n\text{H}_2\text{O}-\text{fod}$ associates. The hydration of fluorinated β -diketonate in $\text{Eu}(\text{fod})_3$ probably results in an enhancement of the negative inductive effect accompanied by a decrease in donation of electrons to O atoms and, as a consequence, by an increase in the ionic character of the $\text{Eu}^{3+}-\beta$ -diketonate bond. On the other hand, it is known⁵ that the enhancement of the ionic extent of the $\text{Eu}^{3+}-\beta$ -diketonate bond results in a decrease in the degradation of the electron excitation of Eu^{3+} to vibrational components of the environment and increases the probability of NET from the triplet level of the ligand to the excited levels of the Eu^{3+} ion. The absence of an increase in Φ and τ of FL of europium(III) trisdipivaloylmethane (DPM) when water is added ($\tau[\text{Eu}(\text{DPM})_3] = \tau[\text{Eu}(\text{DPM})_3 \cdot n\text{H}_2\text{O}] = 325 \mu\text{s}$, toluene, 338 K) is an argument in favor of the fact that the interaction of H_2O molecules with β -diketonate is directed to the fluorinated radical. Thus, the results obtained indicate the possibility of using NET for studying complex formation in the external coordination sphere of Ln^{3+} ions.

In the study of the influence of the character of the chemical Eu^{3+} -ligand bond on the quantum yield of FL of $\text{Eu}(\text{fod})_3$, two competing processes should be taken into account: the inductive-resonance NET on vibrations of the O-H bond in the first coordination sphere of the Eu^{3+} ion and the inductive effect caused by the formation of exosphere associates of H_2O with β -diketonate (Scheme 1).

Scheme 1



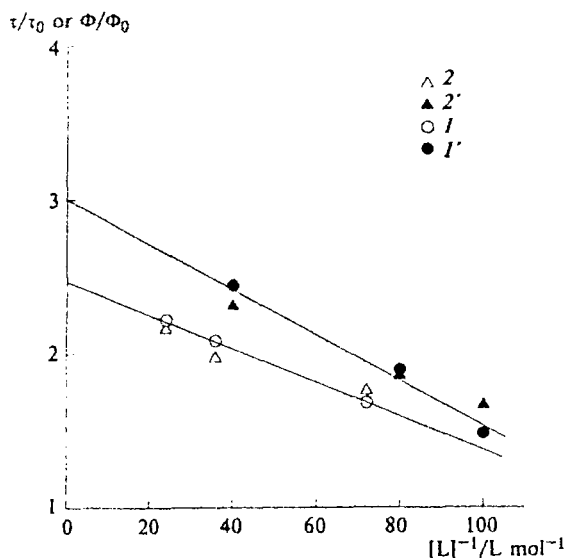


Fig. 5. Dependences of Φ/Φ_0 (I, I') and τ/τ_0 ($2, 2'$) of FL of $\text{Eu}(\text{fod})_3$ ($5 \cdot 10^{-3} \text{ mol L}^{-1}$) on concentrations of H_2O ($I, 2$) and D_2O ($I', 2'$) in toluene at 338 K. $L = \text{H}_2\text{O}$ or D_2O .

Thus, the measured effective rate constant of NET is the sum of the rate constants of both processes ($k_{\text{nr}} = k_{\text{nr}}^1 + k_{\text{nr}}^2$). The transition from H_2O to D_2O should be expected to result in a significant change in k_{nr}^1 due to a decrease in the frequency of stretching vibrations when protium ($\nu_3^{\text{H}} \approx 3400 \text{ cm}^{-1}$) is replaced by deuterium ($\nu_3^{\text{D}} \approx 2250 \text{ cm}^{-1}$).^{3,26} In fact, when D_2O is added, the increase in I and τ of FL of $\text{Eu}(\text{fod})_3$ is higher than that in the case of H_2O (see Fig. 3). In addition, in the presence of D_2O , the intensity and τ of FL of $\text{Eu}(\text{fod})_3$ do not increase in parallel ($\Phi/\Phi_0 \neq \tau/\tau_0$) (see Table 3), which indicates a change in k_{e} .

The plots of changes in Φ and τ of FL of $\text{Eu}(\text{fod})_3$ are satisfactorily ($r = 0.98$) linearized in the coordinates $\Phi(L)/\Phi_0$ and $\tau(L)/\tau_0$ depending on $[L]^{-1}$ ($L = \text{H}_2\text{O}, \text{D}_2\text{O}$) (Fig. 5). The $F, k_{\text{nr}}, k_{\text{e}},$ and τ values at the concentrations of H_2O and D_2O tending to infinity (see Table 3) were obtained from the intercepts on the Y-axis and expressions used in determining the kinetic parameters of luminescence of $\text{Eu}(\text{fod})_3$ in the presence of I . It can be seen in Table 3 that an increase in Φ of $\text{Eu}(\text{fod})_3$ is determined by a decrease in k_{nr} , whereas $k_{\text{e}} = \text{const}$ for H_2O or its changes are incommensurably small as compared to k_{nr} for D_2O . Thus, the deuteration effect $\Phi(\text{D}_2\text{O})/\Phi(\text{H}_2\text{O}) \approx 2$ (see Table 3) is caused to a great extent by a change in the probability of NET in the first coordination sphere of the Eu^{3+} ion rather than an increase in k_{e} . Taking into account the data^{3,26} according to which the partial quenching constant of FL of Eu^{3+} by the O—H bond varies within $400\text{--}550 \text{ s}^{-1}$ and the difference between $k_{\text{nr}}(\text{D}_2\text{O})$ and $k_{\text{nr}}(\text{H}_2\text{O})$ is 1200 s^{-1} (see Table 3), we can reasonably assume the formation of monohydrate $\text{Eu}(\text{fod})_3 \cdot \text{H}_2\text{O}$.

Thus, the data obtained demonstrate the possibilities of the NET technique for studying inner- and outer-sphere complex formation of Ln^{3+} ions in solutions; it was shown that the values of dissipation losses of luminescence can be varied by the selection of ligands differing in electron-donor and steric properties.

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