Energy transfer in luminescent complexes of Eu$^{\mathrm{III}}$ and Tb$^{\mathrm{III}}$ with homo- and copolymers of acrylic acid and alkyl methacrylates

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The influence of the composition and structure of a macromolecular ligand on the efficiency of energy transfer in complexes of Eu$^{\mathrm{III}}$ and Tb$^{\mathrm{III}}$ with ligands based on acrylic acid has been studied. It has been found that a decrease in the size of an alkyl group of methacrylic esters and a low content of acrylic moieties of Eu$^{\mathrm{III}}$ complexes with copolymers increase the efficiency of Eu$^{\mathrm{III}}$ concentration quenching. Insertion of noncoordinative alkyl methacrylate into the polymeric chain results in an increase in the efficiency of energy transfer from Tb^{3+} to Eu^{3+}.

Key words: europium, terbium, copolymers of acrylic acid and alkyl methacrylates; luminescence spectra; energy transfer.

The polymeric nature of a ligand in macromolecular metal complexes (MMC)[1,2] makes the formation of coordination bonds between a metal and a chelating fragment difficult, which results in the appearance of coordinationally nonsaturated structures and in the manifestation of new interesting properties of MMC. In particular, the existence of these structures in lathanoid MMC affects substantially the photochemical and luminescent properties of polymeric complexes. Conformational changes in the macromolecular ligand (MML) determine the intensity of luminescence of Eu$^{\mathrm{III}}$ and Tb$^{\mathrm{III}}$ upon UV-irradiation[3] and ultrasonication[4] of polymeric complexes.

This work studied the effect of the composition and structure of MML on the efficiency of energy transfer between ions in complexes of Eu$^{\mathrm{III}}$ and Tb$^{\mathrm{III}}$ with polymers based on acrylic acid.

Experimental

Copolymers of acrylic acid (AA) with esters of the methacrylic acid of methyl (MMAA), ethyl (EMAA), and butyl methacrylate (BMAA) were obtained by radical polymerization according to the procedure described previously.[5] Polyacrylic acid (PAA) was obtained by radical polymerization of a 30 % solution of AA in dioxane at 60 °C for 3 h. Dinitrile azobisisobutyrate (0.5 % of the monomer weight) was used as initiator of the polymerization. The composition of the copolymers was calculated by the content of carboxyl groups, and the molecular weight of the polymer was determined by the Staudinger method.[6] The composition of macromolecular ligands is presented in Table 1.

Polymeric complexes with different contents of europium were obtained by the reaction of a solution of one of the copolymers in dioxane with a solution of $\mathrm{EuCl_3 \cdot 6H_2O}$ in ethanol followed by stirring the mixture for 1 h, and a solution of ammonia in ethanol was preliminary added to pH 7. Then the mixture was poured into a large amount of distilled water, washed with water and ethanol, and dried *in vacuo* for 48 h at 60 °C.

Heterometallic Tb/Eu MMC were obtained by pouring a solution of BMAA in dioxane and a solution of chlorides of the corresponding lanthanides in ethanol together, a solution of ammonia in ethanol was added to the mixture to pH 7, and then as described above. Complexes of Tb and Tb/Eu—PAA were obtained by the procedure described previously.[7]

The content of rare-earth elements in complexes was determined by the following procedure: a weighed sample of metal chelate in a porcelain crucible was heated in a muffle furnace at a rate of 200 °C h^{-1} to 700 °C and calcined at this temperature for 1 h. The content of lanthanide was calculated on the basis of the stoichiometry of $\mathrm{Ln_2O_3}$. In the case of heterometallic MMC, the resulting oxide was dissolved in a small amount of dilute HCl upon heating, the mixture was brought to a certain volume by distilled water, and the content of europium was determined by the atomic adsorption method. The content of the second lanthanide was calculated by the residue of oxide $\mathrm{Ln_2O_3}$, subtracting the content of $\mathrm{Eu_2O_3}$ from the total amount of oxides.

Table 1. Composition of macromolecular ligands

Ligand	Copolymer	Content of AA (mol. %)	Average molecular weight of polymer, $\bar{M} \cdot 10^4$
1	MMAA	12.6	1.6
2	EMAA	19.7	1.7
3	EMAA	22.6	2.0
4	EMAA	40.1	3.1
5	EMAA	60.9	3.5
6	BMAA	16.8	2.3
7	PAA	100.0	6.5

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Luminescence spectra were recorded on an SDL-1 spectrometer at 300 K. IR spectra were recorded on a Specord-75 IR spectrophotometer as films on KBr plates. The lifetime of the excited state of Tb^{III} (τ) was determined by the analysis of curves of luminescence decay obtained by irradiation of a sample by the pulse of a nitrogen LGI-21 laser (τ = 20 ns, λ = 337 nm).

Signals from a FEU-79 photoelectron multiplier were recorded on the display of an S8-12 oscillograph.

Results and Discussion

Complexes of lanthanides(III) with MML based on AA are white powders that are soluble in cyclohexanone, methyl ethyl ketone, and partially in dioxane; metal polymers with a content of AA higher than 60 mol. % are partially soluble in water. The solubility of the complexes decreases as the content of Ln^{III} increases.

The IR spectra of the samples obtained testify to the chemical binding of the rare-earth ion by the functional groups of MML. The spectra of copolymers based on AA and the spectra of PAA exhibit the absorption band at 1700 cm^{-1} corresponding to stretching vibrations of the nonionized and noncoordinated COOH group. In the spectra of the complexes of Ln^{3+} with MML, the intensity of the band at 1700 cm^{-1} decreases, and the absorption band at 1540—1560 cm^{-1} appears, which corresponds to antisymmetric $\nu_{as}(COO^-)$ stretching vibrations of ionized carboxyl groups.[8]

UV irradiation of MMC of Eu^{III} and Tb^{III} compounds results in their luminescence. The luminescence spectra of the complexes under study are sets of discrete lines corresponding to the Stark f—f-transitions $^5D_0—^7F_j$ (Eu^{3+}) and $^5D_4—^7F_j$ (Tb^{3+}).

The energy transfer between rare-earth ions can result in either luminescence quenching of the ion-donor or sensitization (ignition of luminescence) of ion-acceptors of excitation due to ion-donors of excitation. When the energy is transferred between the same ions, the excitation migration and concentration quenching occur. The main mechanisms of the resonance interaction of lanthanide ions are the electric dipole-dipole and exchange interactions, and the efficiency of migration and relaxation processes in solids depends on the composition and structure of luminescent centers.[9]

The dependence of the intensity of the luminescence of MMC with europium on the metal content in the complex indicates that the structure of polychelate with copolymers (MMAA, EMAA, and BMAA) contain areas with a high local concentration of functional groups and metal ions. Unlike polyacrylates of Eu^{III}, in which the intensity of the luminescence increases monotonically as the europium concentration increases,[2] the intensity of the luminescence in the compounds based on copolymers with AA reaches a maximum at a metal content of 6—18 wt. % and decreases as the content of Eu^{III} further increases (Fig. 1).

The rate of concentration quenching of the luminescence of Eu^{3+} in the complexes with copolymers increases as the size of the alkyl group of esters of methacrylic acid decreases and reaches a maximum for the complex with methyl methacrylate. The europium com-

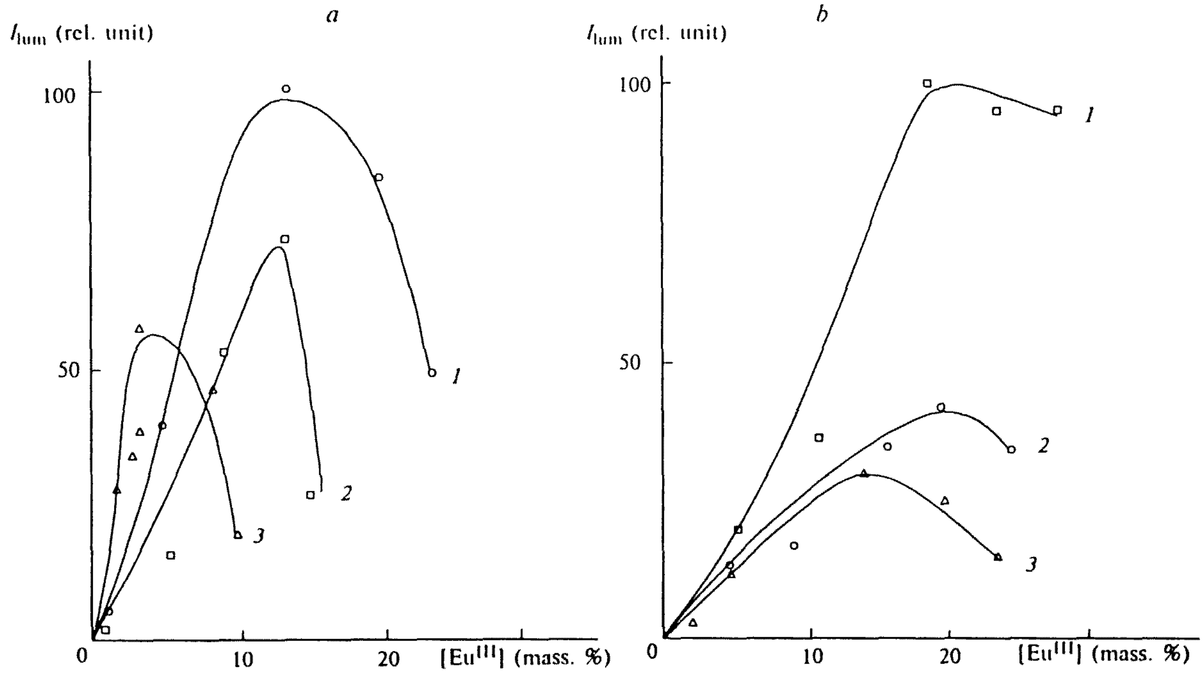

Fig. 1. Dependences of the intensity of luminescence on concentration of Eu^{III} in complexes: *a*, Eu—EMAA **3** (*1*), Eu—BMAA **6** (*2*), Eu—MMAA **1** (*3*); *b*, Eu—EMAA **5** (*1*), Eu—EMAA **4** (*2*), Eu—EMAA **3** (*3*).

plexes with MMAA are characterized by a higher intensity of luminescence of Eu^{3+} compared to the complexes with EMAA and BMAA at the same concentrations of europium(III).

Despite the great number of binding groups, coordinationally nonsaturated structures are formed in the synthesis of complexes with MML.[1] It is likely that in the initial complex more bulky substituents of ethyl and butyl methacrylate create great steric hindrances that prevent the formation of coordination bonds between a metal and a chelating fragment of MML. As a result, a high local concentration of metal ions is achieved faster in the Eu—MMAA complex with a less bulky substituent, and the concentration quenching is observed even at 6—8 wt. % of Eu^{III} (see Fig 1, *a*).

The content of AA in the copolymer also affects the efficiency of the energy migration in the polymers under study: the rate of concentration quenching increases as the content of AA decreases from 60 to 20 mol. % in complexes of europium with EMAA (see Fig. 1, *b*). The observed increase in the efficiency of energy exchange can be explained by the fact that the number of Eu atoms per carboxyl binding group of PAA increases and a higher local concentration of metal ions is achieved as the AA content decreases.

Heterometallic MMC Tb/Eu—PAA and Tb/Eu—BMAA were chosen as model systems for studying the effect of the composition of MML on the efficiency of $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer. The rigid fixation of ion-donors and ion-acceptors on MML eliminates the effects of diffusional approaching in the donor-acceptor pair and allows any required distance, close or far, to be achieved.

The dependences of the intensity of the luminescence and the lifetime of the excited state of Tb^{3+} (λ_{lum} = 545 nm) on the concentration of Eu^{III} in the Tb/Eu—PAA (7) and Tb/Eu—BMAA (6) complexes are presented in Fig. 2. When the concentration of the acceptor (Eu^{3+}) in the complexes under study increases, the intensity of the luminescence and the lifetime of the excited state of the donor (Tb^{3+}) decreases. As can be seen from Fig. 2, the efficiency of the $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer is substantially higher in the complex with copolymer than in the complex with homopolymer. In fact, in the case of the Tb/Eu—BMAA complex, at equimolar content of Tb^{3+} (donor) and Eu^{3+} (acceptor) ions (C = 0.167 mol L^{-1}), the intensity of the luminescence of Tb^{3+} decreases by 99 %, and the lifetime of the excited state of Tb^{3+} decreases 4.4-fold. For the Tb/Eu—PAA complex under the same conditions, the intensity of luminescence of Tb^{3+} decreases by 28 % only, and the lifetime of Tb^{3+} decreases 1.4-fold.

An important peculiarity of the energy transfer by the inductive-resonance mechanism is the strong dependence of its efficiency on the distance R between the donor and acceptor. The critical distance R_0, at which the probabilities of the energy transfer from Tb^{3+} to Eu^{3+} and deactivation of Tb^{3+*} are equal, was determined by the formula[10]

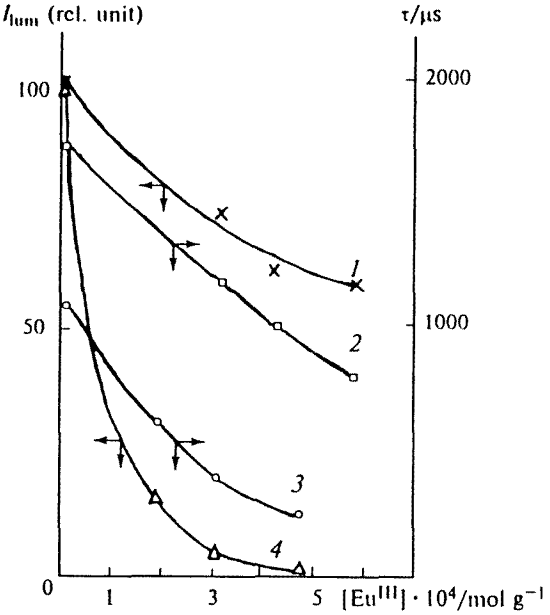

Fig. 2. Dependences of the intensity of luminescence and lifetime of the excited state of Tb^{3+} (λ_{lum} = 545 nm) on concentration of Eu^{III} in complexes Tb/Eu—PAA **7** (*1* and *2*) and Tb/Eu—BMAA **6** (*3* and *4*).

$$R_0{}^3 = 3000/4\pi N\,[Eu^{3+}]_{1/2},$$

where N is the Avogadro number, and $[Eu^{3+}]_{1/2}$ is the concentration of Eu^{3+} ions at which the lifetime of the excited state Tb^{3+*} is twofold lower than that in the absence of the acceptor (determined from the data in Fig. 2).

For the Tb/Eu—BMAA complex, assuming $[Eu^{3+}]_{1/2}$ = 0.24 mol L^{-1}, the following value of the critical distance was obtained: R_0 = 11.8 Å. The average Tb—Eu distance was determined from the data in Fig. 2 using the correlation[11]

$$F/F_0 = [1 + (R_0/R)^6]^{-1},$$

where F_0 is the intensity of luminescence of Tb^{3+} in the absence of Eu^{3+}, F is the intensity of Tb^{3+} in the presence of Eu^{3+}, R is the Eu—Tb distance, and R_0 is the critical distance of energy transfer.

It was determined from the data presented in Fig. 2 that at equimolar concentrations of $[Eu^{3+}]$ and $[Tb^{3+}]$ F/F_0 = 0.01 and the average distance R_{Tb-Eu} = 5.6 Å. Therefore, it was calculated for the Tb/Eu—PAA complex: $[Eu^{3+}]_{1/2}$ = 0.75 mol L^{-1}, R_0 = 8.1 Å, and R_{Tb-Eu} = 9.5 Å.

The experimental data obtained testify that the composition of MML affects substantially the efficiency of the energy exchange between Tb^{3+} and Eu^{3+} ions: the insertion of noncoordinative alkyl methacrylate into the polymeric chain increases the efficiency of the energy transfer $Tb^{3+} \rightarrow Eu^{3+}$. It is known that the addition of trivalent REE to aqueous solutions of PAA results in the formation of intrachain complexes in which one metal ion corresponds to a fragment of 10—13 monomeric units.[12] It is likely that the insertion of noncoordinative butyl methacrylate into the polymeric chain causes the formation of polymeric areas with a high local density of negatively charged carboxylate groups of PAA and, hence, metal ions. In turn, the formation of ion aggregates facilitates enhancement of the efficiency of energy transfer between lanthanide ions.

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References

1. A. D. Pomogailo, *Polimernye immobilizovannye metallokompleksnye katalizatory* [*Polymeric Immobilized Catalysts*], Nauka, Moscow, 1988, 303 pp. (in Russian).
2. Y. Okamoto, *J. Macromol. Sci.-Chem.*, 1987, **24A**, 455.
3. A. G. Microchnik, N. V. Petrochenkova, and V. E. Karasev, *Spectr. Lett.*, 1995, **25**, 653.
4. J. Kido, Y. Okamoto, N. Yoshioka, H. Nishide, and E. Tsuchida, *Polymer*, 1992, **30**, 2273.
5. N. V. Petrochenkova, A. G. Mirochnik, and V. E. Karasev, *Koord. Khim.*, 1993, **19**, 166 [*Russ. J. Coord. Chem.*, 1993, **19** (Engl. Transl.)].
6. A. M. Toroptseva, K. V. Belogorodskaya, and V. M. Bondarenko, *Laboratornyi praktikum po khimii i tekhnologii vysokomolekulyarnykh soedinenii* [*Laboratory Manual on Chemistry and Technology of High-Molecular-Weight Compounds*], Khimiya, Leningrad, 1972, 416 pp. (in Russian).
7. N. V. Petrochenkova, A. G. Mirochnik, and V. E. Karasev, *Koord. Khim.*, 1991, **17**, 1567 [*Sov. J. Coord. Chem.*, 1991, **17** (Engl. Transl.)].
8. E. Banks, Y. Okamoto, and Y. Ueba, *J. Appl. Polym. Sci.*, 1980, **25**, 323.
9. V. F. Zolin and L. G. Koreneva, *Redkozemel'nyi zond v khimii i biologii* [*Rare-Earth Probe in Chemistry and Biology*], Nauka, Moscow, 1980, 350 pp. (in Russian).
10. A. I. Kryukov and S. Ya. Kuchmii, *Osnovy fotokhimii koordinatsionnykh soedinenii* [*Fundamentals of Photochemistry of Coordination Compounds*], Naukova Dumka, Kiev, 1990, 280 pp. (in Russian).
11. I. Nagato, R. Li, and Y. Okamoto, *Macromolecules*, 1983, **16**, 903.
12. E. V. Anufrieva, R. A. Gromova, E. V. Kondrat'eva, V. D. Pautov, and T. V. Sheveleva, *Vysokomol. Soedin.*, 1976, **18B**, 915 [*Polym. Sci. USSR*, 1976, **18B** (Engl. Transl.)].

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