Brief Communications

Fluorescent properties of europium(III) complexes with polyacrylic acid containing grafted *o*-phenanthroline groups

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Fluorescent properties of Eu^{III} complexes with polyacrylic acid containing grafted *o*-phenanthroline groups were studied. The presence of *o*-phenanthroline groups (2%) in the macromolecular ligand provides a 2- to 3-fold increase in the fluorescence intensity as compared to that for Eu^{III} polyacrylates. The effect of concentration quenching of fluorescence, which is observed as the temperature decreases from 300 to 77 K, is explained by the shortening of the average Eu—Eu distances and by the increase in the efficiency of energy redistribution in the complex.

Key words: europium(III), macromolecular complexes, polyacrylic acid, *o*-phenanthroline, luminescence spectra, antenna effect.

Preparation and studies of spectral-luminescent properties of polymeric materials containing rare-earth metal ions chemically bound to the polymeric chain is a challenging problem.[1] The intensity of fluorescence of Ln^{3+} in macromolecular complexes (MMC) is, as a rule, low because of the weak absorption of the lanthanide ions ($\varepsilon \leq 1$) and the absence of effective intramolecular transfer of energy from the levels of the macromolecular ligand (MML) to the Ln^{3+} levels. The transfer of the excitation energy from the chromophore molecule contained in the macromolecule to the resonance levels of Ln^{3+} (the antenna effect)[2,3] is one of the channels of energy transformation in the lanthanide MMC and a possible way of sensitization of fluorescence.

In a continuation of works on studying the effect of composition and structure of MML on fluorescent properties of lanthanide complexes,[4—6] in this work we studied the dependence of the fluorescence intensity and lifetime of the excited state of Eu^{3+} at 300 and at 77 K on the number of metal atoms in europium macromolecular complexes with polyacrylic acid containing *o*-phenanthroline groups. *o*-Phenanthroline and its derivatives are known to form stable complexes with metals.[6] Additionally, being donors of the absorbed energy ($\varepsilon \sim 10^4$), the *o*-phenanthroline molecules favor the increase in the intensity of luminescence of metal complexes.

Experimental

The syntheses of polyacrylic acid (PAA) and of polyacrylic acid with grafted *o*-phenanthroline groups (PAAP) as well as those of their complexes with varied Eu^{3+} content have been described previously.[6] According to spectrophotometry data, the fraction of PAAP units containing the *o*-phenanthroline group is equal to ~2%.

The fluorescence spectra and fluorescence excitation spectra of specimens (powders in quartz ampules) were recorded on an installation assembled on the basis of an SDL-1 spec-

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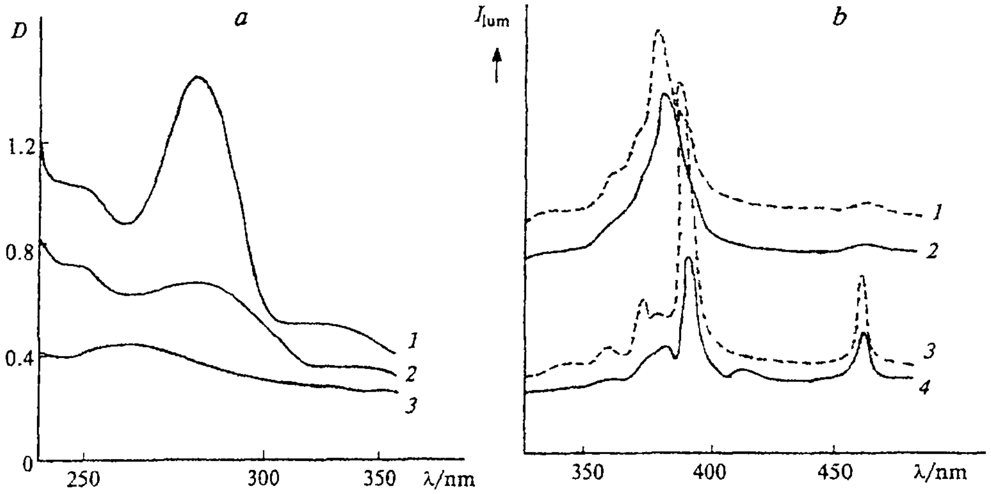

Fig. 1. *a*. Absorption spectra of 5-amino-*o*-phenanthroline (*1*) (dioxane, $C = 4 \cdot 10^{-4}$ mol L^{-1}); PAAP (*2*), PAA (*3*) (films on a quartz support). *b*. Spectra of luminescence excitation of Eu—PAAP MMC ($[Eu^{III}]$ = 17.5 wt.%) at 77 (*1*) and at 300 K (*2*); Eu—PAA ($[Eu^{III}]$ = 17.3 wt.%) at 77 (*3*) and at 300 K (*4*).

trometer and an MDR-23 monochromator at 300 and at 77 K; a Tungsram xenon lamp (2500 W) served as the source of excitation. The electron absorption spectra were recorded on a Specord M-40 spectrophotometer. The lifetime of Eu^{3+} ions in the excited state (τ) was determined by examination of the curves of quenching of the luminescence intensity obtained by irradiating the specimens by pulses of a LGI-21 nitrogen laser (t = 20 ns, λ = 337 nm). The signal of an FEU-79 photomultiplier was recorded on the screen of an S8-12 oscillograph.

Results and Discussion

The examination of the IR spectra of the Eu^{III} complexes with PAAP showed that the macromolecular ligand is coordinated to the nitrogen atoms of *o*-phenanthroline groups if the Eu^{III} content is about 2 wt.%: the characteristic absorption band (AB) of the out-of-plane deformation vibrations of *o*-phenanthroline $\delta(CH)_{Phen}$ at 740 cm^{-1} is split into a doublet at 735 and 750 cm^{-1}. The further increase in the Eu^{III} content in the polymeric complex results in the appearance of ABs of coordinated carboxyl groups $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ (at 1550—1570 cm^{-1} and at 1320—1400 cm^{-1}, respectively) in the IR spectra. This indicates that PAAP is also coordinated to the carboxyl groups of the polymer.[6]

Owing to the high value of molar extinction coefficient of the $\pi\pi^*$ transition in the 230—300 nm region, the molecules of *o*-phenanthroline can transfer a portion of the excitation energy to the Eu^{3+} levels (Fig. 1, *a*). In fact, all the compounds under study luminesce brightly on irradiation by UV light; in this case the intensity of luminescence of the polymeric Eu^{III} complexes with PAAP at 300 and at 77 K is 2—3 times higher than that of the Eu^{III} complexes with PAA (at equal concentrations of metal in compounds).

The most intense bands in the excitation spectrum of europium polyacrylate correspond to the $^5L_6 \leftarrow {}^7F_0$ (395 nm) and $^5D_2 \leftarrow {}^7F_0$ (470 nm) transitions (Fig. 1, *b*). In addition to discrete low-intensity lines corresponding to the f—f transitions of Eu^{3+}, a broad diffuse band in the 350—400 nm region is observed in the spectra of the Eu^{III} polychelates with PAAP. This band indicates that the transfer of the excitation energy occurs from the *o*-phenanthroline levels (donor of the energy of electron excitation) of the PAAP molecule to the resonance levels of Eu^{3+} (acceptor of the energy of electron excitation). It is just the intramolecular transfer of energy (the antenna effect) that may explain the increasing intensity of Eu^{3+} luminescence in polymeric complexes with grafted *o*-phenanthroline groups as compared to those of europium polyacrylates.

The dependences of the luminescence intensities and those of lifetimes of the excited state of Eu^{3+} on the metal content in Eu^{III} complexes with PAAP at 300 and at 77 K are presented in Fig. 2. At 300 K, the fluorescence intensity increases monotonically as the concentration of europium increases, whereas the concentration quenching of fluorescence is observed at 77 K: the fluorescence intensity passes through a maximum at the metal content of about 6 wt.% (see Fig. 2, curves *3* and *4*). It can be assumed that the average Eu—Eu distances are shortened as the temperature decreases to 77 K,[7] which results in a high local concentration of functional groups and metal ions in the structure of polychelate, thus leading to increased efficiency of the energy migration and the fluorescence quenching.

At 300 K, the lifetime τ (Eu^{3+*}) increases monotonically as the Eu^{III} content in the polymer increases, whereas it remains nearly unchanged at 77 K (see Fig. 2, curves *1* and *2*). It is known that dissipation of energy on

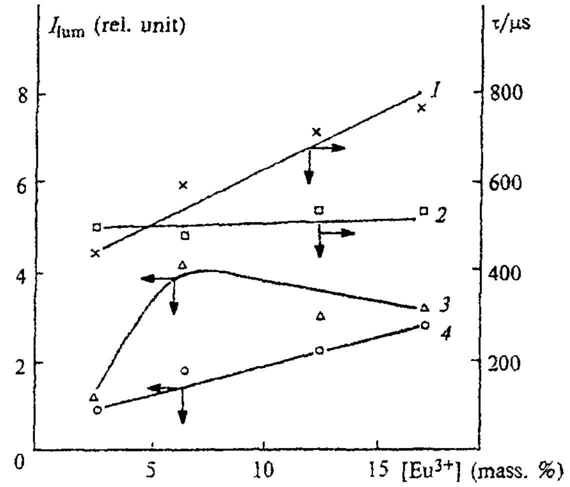

Fig. 2. Dependences of lifetimes of excited state of Eu^{3+} (*1, 2*) and of the luminescence intensity (*3, 4*) (λ_{lum} = 615 nm) on the Eu^{3+} concentration in the Eu—PAAP complexes at 77 (*2, 3*) and at 300 K (*1, 4*).

high-frequency vibrations (in particular, on those of the OH groups) as well as that due to the thermal population of triplet levels close to the $^5D_0$ level of the ligand are the main channels of deactivation of the $^5D_0$ state of Eu^{3+}.[8] The fact that the τ (Eu^{3+}) values remain unchanged as the concentration of the metal changes at 77 K can indicate the low efficiency of these two deactivation channels at low temperature.

At the same time, the average number of OH groups of PAA (quenchers of luminescence) per one europium atom decreases as the metal content in the complex increases. This may explain the decreasing efficiency of deactivation of the $^5D_0$ level of Eu^{3+} at 300 K.

Thus, the presence of 2% of *o*-phenanthroline groups in MML increases the fluorescence intensity by a factor of 2 to 3 as compared to europium polyacrylates. The effect of concentration quenching of fluorescence, which is observed as the temperature decreases from 300 to 77 K, can most likely be explained by the shortening of the average Eu—Eu distances and the increasing efficiency of energy migration in the complex.

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