

Multiplets in Polymer Gels. Rare Earth Metal Ions Luminescence Study

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ABSTRACT: Luminescent properties of chemically cross-linked gels of europium, terbium, and neodymium salts of poly(methacrylic acid) swollen in methanol were investigated by steady state and time-resolved fluorescence. The obtained results demonstrate the aggregation of rare earth metal ions bound to the network with the formation of multiplets. The energy transfer $\text{Eu}^{3+} \rightarrow \text{Nd}^{3+}$ in the gel shows that multiplets consist of three to four rare earth metal ions (together with the gel countercharges). This is one of the first observations of multiplet formation in ion-containing polymer gels.

Introduction

The properties of polyelectrolyte gels depend on the state of network counterions. The most striking effect is a collapse induced by gel ionization in media of sufficiently low polarity, where some of the gel counterions form ion pairs with the network ions.^{1,2} When the concentration of ion pairs is sufficiently high, they can aggregate to multiplets due to dipole–dipole attraction. Theoretical considerations suggest that at some critical degree of ionization of the gel the electrostatic energy released when ion pairs and multiplets are formed overcomes the entropy losses caused by ion binding, and a collapsed gel with a multiplet structure becomes thermodynamically favorable.¹

Collapse induced by ionization was observed experimentally for poly(acrylic acid) (PAA) and poly(methacrylic acid) (PMAA) gels neutralized by sodium methoxide in methanol and methanol/water and methanol/dioxane mixtures.² The gel collapse is accompanied by a significant drop in the conductivity of the gel, i.e., by ion binding. Some swelling experiments indicate that ion pairs in the collapsed gel are aggregated to multiplets which effectively cross-link the gel chains.²

The ion aggregation inside polymer gels can be studied on a molecular scale using a fluorescence probe method. This technique allows one to determine the number of ions in the aggregate, their mobility, and their accessibility by various reagents. The small fluorescent rare earth metal (RE) ions are particularly useful as fluorescent probes for this purpose, because their fluorescence properties, in particular the f – f transitions, depend on their coordinative environment.^{3,4} These transitions in free RE ions are forbidden in electro-dipole approximation, and the corresponding energetic states are degenerate. The asymmetric microenvironment causes the polarization of the RE ion under the influence of the electric field of the surrounding ligands, which increases the probability for electro-dipole transitions. In contrast to forbidden bands of electro-dipole transitions, the peaks of allowed magnetodipole transitions show small intensity variations with

the change of the microenvironment of the probe. Thus, the symmetry of microenvironment of RE ions and the strength of their interaction with ligands can be characterized by the ratio of intensity of the forbidden and the allowed fluorescence band.⁵ The energy transfer between different kinds of RE ions,^{5–7} which can act as donors and acceptors, yields an estimate of the inter-ion distances.

Eu(III) and Tb(III) ions are the most frequently used as RE metal fluorescent probes. Eu^{3+} has characteristic luminescence in the range ~ 570 – 800 nm due to ${}^5\text{D}_0$ – ${}^7\text{F}_J$ transitions and Tb^{3+} luminesces in the range ~ 480 – 660 nm due to ${}^5\text{D}_4$ – ${}^7\text{F}_J$ transitions ($J = 6, 5, \dots, 0$).^{5,8} The advantage of these ions is a rather high value of the potential energy of the first metastable state relative to the closest ground state which reduces the quenching of the luminescence of these ions by solvent molecules.

RE ions have been used as fluorescent probes to study ionic interactions in linear polyelectrolytes^{3,4,9–12} and ionomers.^{13–16} To the best of our knowledge, a fluorescence probe method has not been employed for the investigation of ionomeric structures, i.e., ion pairs and multiplets, in polymer gels.

In this paper, the luminescence of Eu^{3+} and Tb^{3+} in PMAA gels swollen in methanol has been investigated to test the ion binding of RE cations to the network anions and the subsequent ion aggregation into multiplets inside the gel. The size of the multiplets has been estimated from data on the energy transfer $\text{Eu}^{3+} \rightarrow \text{Nd}^{3+}$.

Experimental Part

Materials. Lanthanides. Europium nitrate hexahydrate, 99.9% (Acros), terbium nitrate hexahydrate, 99.9% (Acros), and neodymium nitrate hexahydrate, 99.9% (Fluka), were used without further purification.

Gels. PMAA gels were prepared by free-radical polymerization of methacrylic acid in *N,N*-dimethylformamide at a monomer concentration of 3.06 mol/L with 2,2'-azobis(isobutyronitrile) (1.53×10^{-2} mol/L or 0.5 mol %) as initiator and *N,N*-methylene(bisacrylamide) (4.6×10^{-2} mol/L or 1.5 mol %) as cross-linker. The gels were prepared in cylindrical glass tubes with inner diameter of 0.40 cm under a nitrogen atmosphere at 63 °C for 24 h and were washed with a large amount of methanol for 3 weeks to remove unreacted components and sol fraction.

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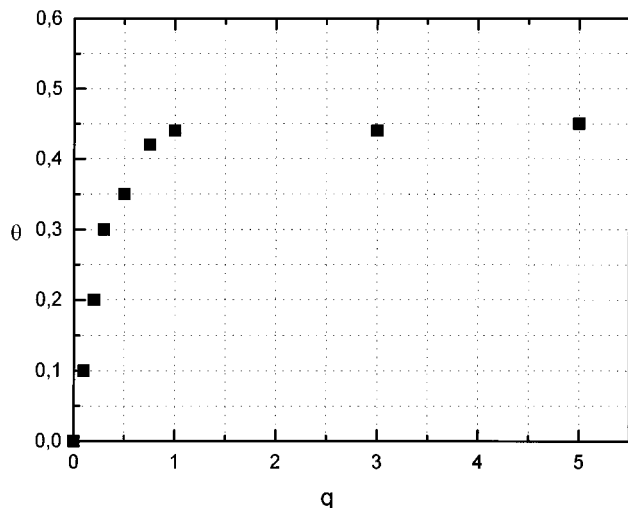


Figure 1. Dependence of the equilibrium composition PMA–Eu complexes Θ on the initial molar ratio q between $\text{Eu}(\text{NO}_3)_3$ and carboxylate groups of the gel.

The PMA–Na gels were obtained by neutralization with sodium methoxide of PMAA gels swollen in methanol.

To exchange the Na ions for RE ions in PMA–Na gels, the samples of PMA–Na gel swollen in methanol were placed in methanol solutions of RE nitrates. After equilibrium was established, the content of RE^{3+} in the gel was evaluated by the decrease of RE^{3+} concentration in the external solution. The concentration of Eu^{3+} and Tb^{3+} in the solution was determined by fluorescence spectroscopy using the emission bands 616 nm ($\lambda_{\text{ex}} = 395$ nm) for Eu^{3+} and 542 nm ($\lambda_{\text{ex}} = 368$ nm) for Tb^{3+} . The equilibrium composition of PMA–RE gels, Θ , was calculated as a molar ratio between RE ions absorbed by the network and PMA carboxy groups.

The degree of swelling of the gel samples was characterized by the $(m - m_0)/m_0$ ratio, where m is the mass of the swollen gel and m_0 is the mass of the dry gel.

Spectral Measurements. Steady-state fluorescence spectra were measured on a Shimadzu RF-5000 fluorimeter using 1.5-nm band-pass settings for excitation and emission. Unless otherwise specified, the emission spectra of Eu(III) were obtained under excitation at 395 nm, while the emission spectra of Tb(III) were obtained under excitation at 368 nm.

Time-resolved fluorescence measurements were performed on an apparatus assembled for this purpose. The samples were excited by the 350- or 530-nm outputs of a pulsed neodymium laser, the duration of the laser pulse being ~ 20 ns. The resulting emission was monitored at 542 nm for Tb^{3+} or 616 nm for Eu^{3+} by a MRD-2 grating monochromator and detected by a photomultiplier tube.

Results and Discussion

Characterization of Polyelectrolyte Gels Containing Rare Earth Metal Ions. RE ions were incorporated into PMA–Na gel through ion exchange reaction with network counterions. The immersion of PMA–Na gel in methanol solution of $\text{RE}(\text{NO}_3)_3$ leads to an absorption of RE ions by the gel. A typical dependence of the equilibrium composition of PMA–RE gel on the initial molar ratio between RE salt and carboxylate groups of the network q is presented in Figure 1. It is seen that at $q < 0.3$ all RE ions are absorbed by the gel; at higher q , the fraction of RE ions inside the gel slightly increases reaching a limiting value ($\Theta = 0.42 \pm 0.04$). The limiting value of Θ is somewhat higher than that expected for a complex containing 1 RE^{3+} per ca. 3 network charged units ($\Theta = 0.33$). Thus, the gel absorbs more RE ions than is necessary to neutralize the network charges. Probably,

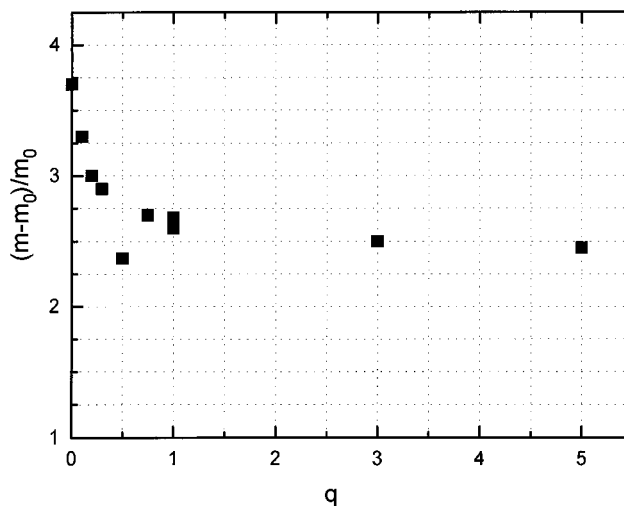


Figure 2. Dependence of the degree of swelling of poly-methacrylate gel in methanol as a function of the initial molar ratio q between $\text{Eu}(\text{NO}_3)_3$ and carboxylate groups of the gel.

this is related with the difficulty of the PMAA chains in adopting a conformation in which each RE ion is surrounded by three carboxylate groups. In the ref 11 it was demonstrated that linear PMAA cannot easily form the tris-coordinate complex with Eu^{3+} because of the steric hindrance of the polymer chain. The analogous high values of Θ ($\Theta = 0.40$ – 0.41) were obtained previously for the complexes of RE ions with linear copolymer of styrene and acrylic acid.¹³

Figure 2 illustrates a typical dependence of the degree of swelling of the gel in methanol on the initial molar ratio between the RE salt and carboxylate groups of the network q . From this figure it is evident that the ion exchange $3\text{Na}^+ \rightarrow \text{Eu}^{3+}$ inside the network leads to a relatively moderate contraction of the gel immersed in methanol. This can be related to the fact that the gel with Na^+ counterions is already in the collapsed state where most of the ion pairs are incorporated in multiplets.

Thus, the results of macroscopic swelling experiments suggest that in methanol most cations are bound to the network charges and that these ion aggregates may attract each other forming multiplets. These phenomena can be characterized on a molecular level by fluorescence measurements.

Steady-State Luminescence. The luminescence spectra of PMA–Eu and PMA–Tb gels swollen in methanol show characteristic RE ion fluorescence and the wavelengths of peaks are practically unaffected by the gel (Figures 3 and 4). This useful information can be obtained from the ratios of intensity of fluorescence bands. In the spectra of Eu(III) (Figure 3) the 579- and 616-nm bands, corresponding to ${}^5\text{D}_0 \rightarrow {}^7\text{F}_0$ and ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$ electro-dipole transitions, are forbidden in the magnetodipole approximation and their intensities are fully determined by the symmetry of the electric field around the probe.^{5,9} The intensity ratios of the forbidden to the allowed 591-nm band I_{579}/I_{591} or I_{616}/I_{591} are usually used to estimate the symmetry of the arrangement of ligands around the Eu^{3+} probe and the strength of their interaction.^{5,11}

In the luminescence spectrum of $\text{Eu}(\text{NO}_3)_3$ in water the allowed 591-nm band is more intense than the forbidden 616-nm band (Figure 3).⁵ In methanol the ratio I_{616}/I_{591} is reversed: the relative intensity of the forbidden 616-nm band is much higher than that of the

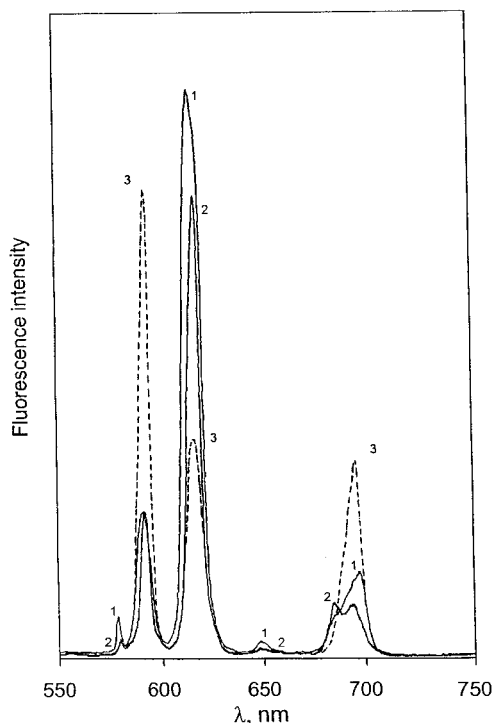


Figure 3. Fluorescence emission spectra of PMA-Eu gel, swollen in methanol, (1) and of solutions of $\text{Eu}(\text{NO}_3)_3$ in methanol (2) and in water (3), obtained under excitation at 395 nm (in all cases the concentration of Eu^{3+} was 0.6 mol/L). The spectra in methanol are normalized to the intensity of the allowed 591-nm band.

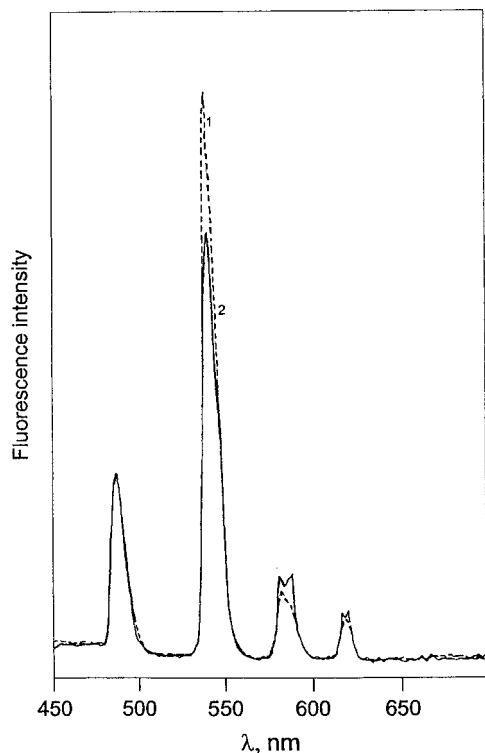


Figure 4. Fluorescence emission spectra of PMA-Tb gel, swollen in methanol (1), and of a methanol solution of $\text{Tb}(\text{NO}_3)_3$ (2), obtained under excitation at 368 nm (in both cases the concentration of Tb^{3+} was 0.6 mol/L). The spectra are normalized to the intensity of 488-nm band.

allowed 591-nm band (Figure 3). This indicates a much more asymmetric microenvironment of Eu^{3+} in methanol. This effect can be attributed to the crowding of

some counterions in the molecular vicinity of RE ions in a solvent of lower polarity.

The difference between the spectra of the PMA-Eu gel and a methanol solution of $\text{Eu}(\text{NO}_3)_3$ is much less pronounced than that between solutions of $\text{Eu}(\text{NO}_3)_3$ in water and in methanol (Figure 3). This suggests the binding of RE ions to the countercharges both in the gel and in methanol solution. But the extent of the binding may be somewhat different. Indeed, the values of the relative intensities I_{579}/I_{591} and I_{616}/I_{591} were found to be equal to 0.09 and 3.3 for a methanol solution of $\text{Eu}(\text{NO}_3)_3$ and to 0.27 and 4.2 for the PMA-Eu gel in methanol. Some enhancement in the relative intensity of forbidden bands in the gel as opposed to solution indicates a more asymmetric arrangement of counterions in the vicinity of the RE ion as well as a stronger interaction of RE ions with surrounding countercharges in the gel.

Relaxation Studies. The binding of counterions can lead to the release of solvent molecules coordinated by RE ions. This process can be followed by time-resolved fluorescence.

The emission intensity of RE ions in water or alcohol solutions is usually quite weak, since the coordinated solvent molecules effectively quench the luminescence by nonradiative dissipation of energy on the vibrations of atoms of solvent molecules, mainly on the high energy O-H vibrations.^{4,5,11,17} As far as the quenching decreases the lifetime of the excited state (and the quantum yield of the luminescence), relaxation studies allow us to estimate the presence of solvent molecules in the vicinity of RE ion. Counterions which are tightly bound to RE ion can expel some of the coordinated solvent molecules, thereby decreasing the rate of radiationless decay. Thus, the time-resolved fluorescence measurements offer one more possibility to reveal a close contact between RE ion and counterions, i.e., the ion binding.

The obtained fluorescence decay curves of RE ions in gels and in solutions may be fitted within the experimental error by a single-exponential function. This suggests small variations of parameters characterizing the electric field in the vicinity of RE ions, which indicates that almost all RE ions in the system are experiencing a similar microenvironment. The values of lifetimes, τ , of $\text{Eu}^{3+}({}^5\text{D}_0)$ and $\text{Tb}^{3+}({}^5\text{D}_4)$ in the gel were measured as 440 and 950 ms, which far exceed those obtained for Eu^{3+} and Tb^{3+} in pure methanol solutions of $\text{Eu}(\text{NO}_3)_3$ and $\text{Tb}(\text{NO}_3)_3$ at the same concentrations of RE ions: 280 and 570 ms, respectively. The increase of both the lifetime and the probability of radiative transitions in the gels points to the decreasing probability of nonradiative transitions and to the enhanced quantum yield of luminescence in the gel as opposed to solution. The much larger τ values for RE ion in the gel compared to solution suggest (1) a less mobile microenvironment around the RE ions in the gel and (2) repulsion of methanol molecules from the vicinity of RE ions in the gel due to the site binding of RE ions. This can be connected with a well-known effect of a macromolecular nature of the ligands.¹⁸ The anions carried by a network do not possess their own translational entropy. This makes the site binding with RE ions in a gel more favorable than in a solution of low molecular weight salt. As all RE ions are experiencing similar microenvironment, we can conclude that almost all RE ions are site bound to the gel countercharges.

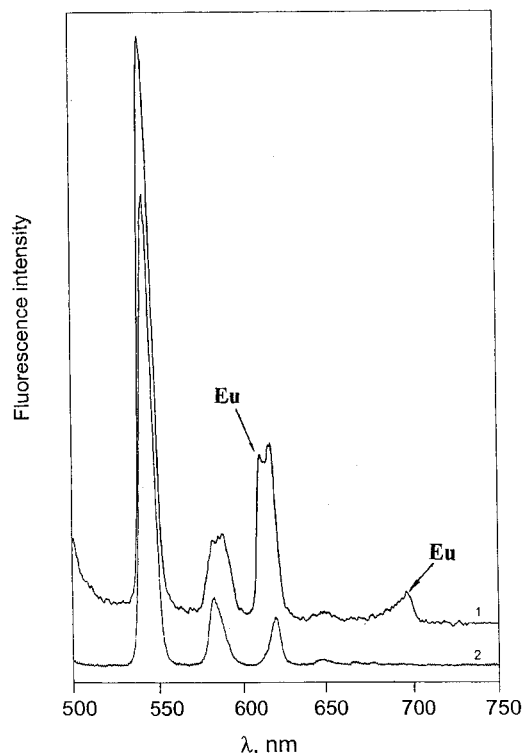


Figure 5. Fluorescence emission spectra of PMA-Eu,Tb gel, swollen in methanol (1), and of a methanol solution of the mixture $\text{Eu}(\text{NO}_3)_3/\text{Tb}(\text{NO}_3)_3$ (2) ($\lambda_{\text{ex}} = 488$ nm, concentrations of Eu^{3+} and Tb^{3+} were 0.3 mol/L).

Energy Transfer. The RE ions bound to the carboxylate groups in PMA-RE gels are expected to aggregate to multiplets due to dipole-dipole attraction. The existence of multiplets can be probed by energy transfer between different fluorescent RE cations simultaneously present in the gel. Multiplets concentrating the ionic species promote the different kind of cations to approach each other enhancing energy transfer.

The energy transfer can be demonstrated, for example, by emission spectrum of PMA-Eu,Tb gel (Figure 5), with excitation at 488 nm (the absorption band of donor-Tb³⁺). A comparison of fluorescence spectrum of PMA-Eu,Tb gel, when only Tb(III) is excited (Figure 5), with that of PMA-Tb gel (Figure 4) shows the appearance of new bands at 698 and ~615 nm, which are identical with those of Eu(III) emission spectrum (Figure 3). Thus, despite the fact that only Tb(III) ions were excited, the emission spectrum of PMA-Eu,Tb gel contains along with the bands of Tb³⁺ some characteristic bands of acceptor-Eu³⁺, which suggests the energy transfer $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ in the gel. It should be noted that at the same concentrations of Eu^{3+} and Tb^{3+} in methanol solution the bands of Eu(III) do not appear, when only Tb(III) is excited.

By time-resolved measurements, a dynamic quenching of Tb(III) fluorescence as a result of radiationless energy transfer from the $\text{Tb}^{3+} {}^5\text{D}_4$ level to the $\text{Eu}^{3+} {}^5\text{D}_1$, ${}^5\text{D}_0$ levels was recorded. The relaxation studies were performed at excitation wavelength 350 nm. The decay curves were monitored at 542 nm. It was found that the rate of decay of the excited state of donor (Tb³⁺) increases in the presence of acceptor (Eu³⁺) (Figure 6). This effect can be attributed to the energy transfer from Tb(III) to Eu(III) ions in the gel. The quantum yield of energy transfer evaluated by the difference in areas

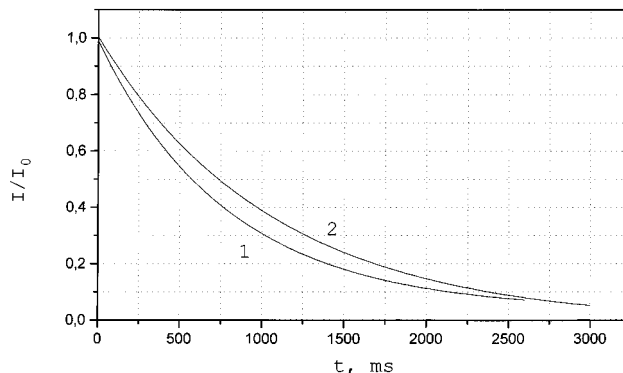


Figure 6. Fluorescence decay profiles for PMA-Eu,Tb (1) and PMA-Tb (2) gels, swollen in methanol, ($\lambda_{\text{ex}} = 350$ nm, $\lambda_{\text{em}} = 542$ nm; concentrations of Eu^{3+} and Tb^{3+} in the PMA-Eu,Tb gel were 0.3 mol/L; concentration of Tb^{3+} in the PMA-Tb gel was 0.6 mol/L).

under the decay curves of $\text{Tb}^{3+} {}^5\text{D}_4$ excited state with and without acceptor Eu^{3+} was shown to be equal to ca. 15%. In methanol solutions under the same conditions the decay curves for the mixture $\text{Eu}(\text{NO}_3)_3/\text{Tb}(\text{NO}_3)_3$ are fairly close to that for $\text{Tb}(\text{NO}_3)_3$ alone. This suggests that in the gel some of the RE cations are held by the polymer network in close molecular-scale proximity to one another indicating on aggregation of RE ions (together with the gel anions) to multiplets. The RE ions bound to the countercharges aggregate to multiplets only in the case of polymer countercharges. This may be explained by the fact that RE ions together with their countercharges are attached to the gel chains, and therefore initially immobilized (in the sense of absence of translational entropy). This fact reduces the entropy losses accompanying the multiplet formation inside the gel.

Size of Multiplets. Fluorescence quenching method is widely used to determine the aggregation numbers of micelles.^{19,20} When donor and acceptor molecules are solubilized in an excess of micelles, the quenching depends on the probability of finding both donor and acceptor in the same micelle, and hence on the total number of micelles.¹⁹

Recently similar technique was applied to estimate the size of ion aggregates in ionomer systems.²¹ The analogous approach is adopted in the present work (see model 1 below). Also, we made a slight modification of the method proposed in ref 21 which should give a more accurate estimation of the multiplet size (model 2). However, it should be mentioned that both models give the results which are rather close to each other.

The description of the fluorescence quenching in the ionomer system should account for two main distinctions from micellar systems: (1) in the ionomer system the aggregation number can be very low;²¹ (2) the ionic aggregates consist mainly of donor and acceptor species and do not contain an excess of "inert" molecules such as detergent in micellar systems.

Model 1. In micellar systems the Poisson statistics is usually used to describe the distribution of donors and acceptors among micelles. As in ionomer system the aggregation number N can be relatively low ($N \sim 2-8$),²¹ the distribution of quenchers among multiplets can be described by Poisson statistics only in the case, when the average number of acceptors residing in a multiplet, \bar{n}_q , is negligibly small compared to unity. In this case there exist only two kinds of multiplets: the multiplets without acceptor and the multiplets containing only one

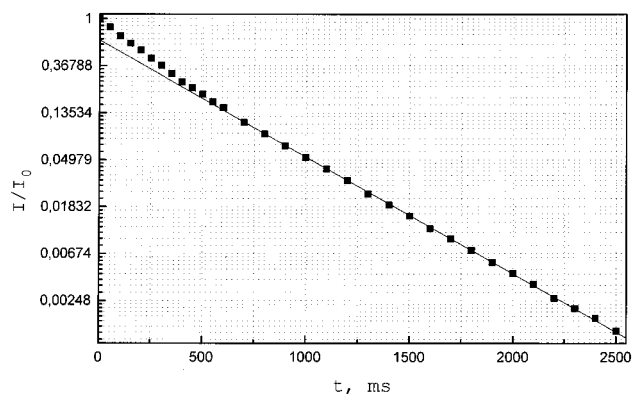


Figure 7. Fluorescence decay curves of PMA-Eu,Nd gel, swollen in methanol ($\lambda_{\text{ex}} = 530$ nm, $\lambda_{\text{em}} = 616$ nm, the concentrations of Eu^{3+} and Nd^{3+} were 0.54 and 0.06 mol/L, respectively).

acceptor. The fractions of these multiplets are $x_0 = 1 - \bar{n}_q$ and $x_1 = \bar{n}_q$, respectively.²¹ In such a case, the kinetics of decay of donors excited with a short light flash can be described by the biexponential equation

$$I = I_0[(1 - \bar{n}_q) e^{-k_0 t} + \bar{n}_q e^{-k_0 t - k_q t}] \quad (1)$$

where I_0 and I represent the fluorescence intensities at zero time and at a time t after the exciting pulse, respectively, k_0 is the intrinsic fluorescence decay rate constant of the donor in the absence of acceptor, and k_q is the quenching rate constant in multiplets containing one acceptor.

For the large t , a plot of the $\ln(I/I_0)$ against t should result in a straight line

$$\ln(I/I_0) \approx -k_0 t + \ln(1 - \bar{n}_q) \quad (2)$$

and the value of \bar{n}_q can be determined from the intercept a with the $\ln(I/I_0)$ axis equal to $a = -\ln(1 - \bar{n}_q)$. Assuming that all RE ions are incorporated in multiplets, the mean aggregation number can be calculated by means of the relation

$$\frac{\bar{n}_q}{N} = \frac{[A]}{[D] + [A]} \quad (3)$$

where $[A]$ and $[D]$ are the molar concentrations of donors and acceptors, respectively.

Experiment. As the efficiency of the energy transfer $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ in the gels is relatively low, especially at a very low concentration of acceptor, which is necessary to realize the above-mentioned approach, another pair of RE donor-acceptor ions ($\text{Eu}^{3+} \rightarrow \text{Nd}^{3+}$) was used to estimate the size of multiplets. In this pair the energy transfer is much more effective. Previously the energy transfer $\text{Eu}^{3+} \rightarrow \text{Nd}^{3+}$ was studied for other systems, for example, in refs 22–24.

Two series of PMA-Eu,Nd gels were prepared with different ratios of Eu^{3+} and Nd^{3+} , keeping the total concentration of RE ions constant. In the first series the total RE^{3+} concentration was equal to 0.6 mol/L, which corresponds to the maximum value of Θ ($\Theta = 0.4$). In the second series the total RE^{3+} concentration was equal to 0.3 mol/L, which corresponds to $\Theta = 0.2$. The excitation of the $\text{Eu}(\text{III})$ ions was relatively weak, such that the number of excited donors was much lower than the number of unexcited donors. Typical fluorescence decay curve is depicted in Figure 7. It is seen that at

Table 1. Multiplet Size N and Related Parameters

Θ	$[A]/([D] + [A])$	a	model 1		model 2	
			\bar{n}_q	N	\bar{n}_q	N
0.4	0.10	0.43	0.35	3.5	0.41	4.1
	0.06	0.17	0.16	2.7	0.21	3.5
	0.05	0.15	0.14	2.8	0.18	3.6
0.2	0.085	0.28	0.24	2.8	0.30	3.5
	0.05	0.16	0.15	3.0	0.19	3.8

large t the curve becomes monoexponential. The values of a , \bar{n}_q and N calculated from the experimental data according to model 1 are presented in Table 1. It is seen that the average aggregation number is equal to 3.

Model 1 suggests the equal probability of the excitation of all multiplets, which is true if the numbers of donors in all the multiplets are the same. This suggestion may be invalid at such a low aggregation number ($N = 3$). Indeed, if we suppose that the total number of RE ions in a multiplet (including both donor and acceptor ions) is constant, the introduction of an acceptor should reduce the number of donors in a multiplet. The probability of excitation of a multiplet will thus depend on the number of donors in it and therefore will be different for the multiplets with and without acceptor. This fact is taken into account in model 2.

Model 2. As in the first model, the system is assumed to contain only two kinds of multiplets: the multiplets without acceptor and the multiplets containing only one acceptor. The number of donors in the first multiplets is N , in the second it is $(N - 1)$ (one place is occupied by an acceptor). The probabilities for exciting donor in these multiplets are proportional to N and $(N - 1)$, respectively. Hence, the fluorescence decay can be described by the following equation

$$\frac{I}{I_0} = \frac{(1 - \bar{n}_q)N e^{-k_0 t} + \bar{n}_q(N - 1) e^{-k_0 t - k_q t}}{N - \bar{n}_q} \quad (4)$$

The function is normalized to the value $(N - \bar{n}_q)$, which is equal to the average number of donors in a multiplet. At large t

$$\frac{I}{I_0} \approx \frac{(1 - \bar{n}_q)N}{N - \bar{n}_q} e^{-kt} \quad (5)$$

$$\ln \frac{I}{I_0} \xrightarrow{t \rightarrow \infty} -kt + \ln \left[\frac{(1 - \bar{n}_q)N}{N - \bar{n}_q} \right] = -kt + \ln \left[\frac{1 - \bar{n}_q}{1 - \frac{\bar{n}_q}{N}} \right] \quad (6)$$

Thus, at large t , the curves $\ln(I/I_0)$ vs t are linear with an intercept a , which gives the values of \bar{n}_q and N :

$$a = -\ln \left[\frac{1 - \bar{n}_q}{1 - \frac{\bar{n}_q}{N}} \right] \quad (7)$$

When treated according to the model 2, the experimental data give the average aggregation number equal to 4 (Table 1). This is somewhat higher than that calculated according to the model 1 (Table 1). The obvious reason for this is as follows. The eq 2 gives higher contribution of multiplets containing acceptors to the total decay curve. As a consequence, the experimental data can be fitted by this equation only with a

value of \bar{n}_q which is lower than according to the more exact model 2.

One more procedure was used to estimate the aggregation number N of multiplets. It considers another extreme case—the excess of acceptor. In this case there are practically no multiplets containing more than one donor. As the multiplets unoccupied by the donor do not contribute to the observed fluorescence, the quenching rate constant will be equal to the product of k_q by the number \bar{n}_a of acceptors in a multiplet. The value of rate constant k_q for quenching of a donor on one acceptor was obtained from the fluorescence decay data at the excess of donor. It equals 4300 s^{-1} .

For the sample with $[A]/([D] + [A]) = 0.9$ ($\Theta = 0.4$) the measured $\bar{n}_a k_q$ value is equal to $13\,000 \text{ s}^{-1}$. This gives an average number of acceptors surrounding one donor $\bar{n}_a \approx 3$. Hence, the multiplet should contain 4 RE ions (3 acceptors and 1 donor). This result is in quite good agreement with that obtained for excess donor (see Table 1). Thus, the aggregation number was shown to be unaffected by the ratio between donor and acceptor.

The close values of the aggregation numbers were obtained by fluorescence quenching method for multiplets in sulfonated polystyrene ionomer in toluene.²¹ In contrast to our data, the quenching was static in nature, which suggests the formation of rigid aggregates. At the same time, it was shown²¹ that at the addition of only 5 vol % of a more polar solvent, methanol, the quenching undergoes a transition from static to dynamic mechanism, indicating the reducing ion pair/ion pair attractions. It should be pointed out that the time scale for the decay of donors used in ref 21, e.g. tris(2,2'-bipyridyl)ruthenium(II) chloride, is much shorter than that of the RE ions.

This paper demonstrates some of the advantages of the use of various kinds of RE ions as donors and acceptors to study the multiplet formation. Being of the same charge and of very close radii, the RE ions can be substituted by one another without appreciable effect on the multiplet structure. This allows one to study the energy transfer at any donor/acceptor ratio. This feature is of particular importance for the investigation of the multiplets, because the latter can be of very small size and therefore could change significantly their structure upon the addition of probe molecules differing appreciably from that constituting an initial multiplet.

Gels with RE Ions as Luminophores. On exposure to ultraviolet light, the PMA–Eu, PMA–Tb, and PMA–Eu,Tb gels exhibited a strong fluorescence of reddish-orange, green, and yellow colors, respectively. The first two colors are characteristic for Eu^{3+} and Tb^{3+} and correspond to their most intensive transitions: $\text{Eu(III)} \ ^5\text{D}_0 \rightarrow \ ^7\text{F}_{2,4}$ and $\text{Tb(III)} \ ^5\text{D}_4 \rightarrow \ ^7\text{F}_{5,5}$. The yellow color of the PMA–Eu,Tb gel seems to be due to the simultaneous luminescence of Eu^{3+} and Tb^{3+} .

The bright fluorescence of the gels doped with RE ions makes these gels promising as new luminescent materials. They can be utilized in numerous technical applications, in particular, for the observation of the spatial arrangement of ionic multiplets in the gel volume by means of fluorescence microscopy. One can also suggest that the simultaneous incorporation in the gel of Eu(III) , Tb(III) , and Gd(III) ions allows one to obtain a gel converting the UV-light, absorbed by Gd^{3+}

and Tb^{3+} , to visible red light by exploiting the energy transfer processes $\text{Gd}^{3+} \rightarrow \text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ and $\text{Gd}^{3+} \rightarrow \text{Eu}^{3+}$.

Conclusions

RE ion luminescence enabled us to find and to characterize the multiplet structures in ion-containing gels. By studying the energy transfer $\text{Eu}^{3+} \rightarrow \text{Nd}^{3+}$ the size of the multiplets was estimated. At the same concentration of RE ions in the solution of low molecular weight salts $\text{RE}(\text{NO}_3)_3$ the formation of multiplets was not detected. Thus, polymer gel promotes the close approach of similarly charged RE ions bound to the network. This is connected with the fact that when the countercharges bounding the RE cations belong to the gel, they are initially immobilized; therefore, the entropy losses accompanying the multiplet formation inside the gel are smaller.

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