Use of Luminescence of Europium Ions for the Study of the Interaction of Polyelectrolyte Hydrogels with Multivalent Cations

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Europium ions were used as fluorescent probes for examining the interaction of polyanionic hydrogels of chemically cross-linked poly(acrylic acid) and poly(methacrylic acid) with multivalent cations in aqueous medium. The fluorescence data indicate a strong and asymmetric binding of carboxylate groups to Eu^{3+} ions, leading to the expulsion of up to five water molecules from the solvation shell of the ion. The relaxation studies of the nonradiative energy transfer from europium to neodymium ions inside the gel revealed the formation of aggregates consisting of ca. seven rare earth ions (together with the corresponding countercharges of the network chains).

Introduction

Negatively charged polyelectrolyte gels are efficient absorbents of multivalent cations from aqueous media,[1−11] which is promising for various commercial applications, e.g., recovery of precious metal ions, removal of toxic or radioactive ions, concentration of metal ions before analysis.[10,11] Widening the area of practical application of gels can be connected with their activation by trivalent ions of rare earth (RE) elements, which are commonly used as working particles for active media of solid-state lasers. Polymer gels used as a matrix doped with RE ions can serve as a new type of luminofore different from solid-state and liquid ones in their properties. One of the peculiarities of luminofores based on polymer gels with incorporated RE ions consists of the possibility of a wide variation of their mechanical state (from highly swollen to collapsed) in response to small changes of the external parameters (pH, temperature, electric field, etc.).

Luminescent properties of RE ions in the gel are also of interest from a fundamental point of view because they can help to draw insight on the molecular mechanism of the interaction of polyelectrolyte gels with multivalent cations.

The interaction of polyelectrolyte gels with multivalent ions was studied experimentally[1−11] and theoretically.[5,6] It was shown that the absorption of multivalent cations induces the gel collapse because of the decreasing intranetwork osmotic pressure and of the attraction between the gel chains sharing counterions. The experimental studies were mainly devoted to macroscopic swelling behavior of the gels and its correlation with the distribution of multivalent ions between the gel and the exterior solution. At the same time, the data on the molecular mechanism of the binding of ions to the network countercharges remain rather scarce. In the present paper we propose to use fluorescent multivalent cations, Eu^{3+}, as probes to examine the interaction of multivalent ions with the gel chains on a molecular level (RE metal fluorescence probe method). The intensity ratio of forbidden bands (in electrodipole approximation) to allowed ones in the fluorescence spectra of Eu^{3+} (e.g., I_{614}/I_{591}), which depends on the strength and symmetry of electric field around the RE ion, can be used as a measure of the extent of interaction of RE ions with surrounding ligands.[12]

In the case of nonradiative energy transfer from RE^{3+} to ligands, information about the microenvironment of the RE ion can also be obtained from kinetic or steady-state measurements of the probability of this interaction. In particular, the coordinated water molecules are known to quench efficiently the fluorescence of Eu^{3+} ions via energy transfer to OH vibrations. The rate of deexcitation via this process is directly proportional to the number of OH oscillators in the first coordination sphere and does not depend appreciably on the other ligands coordinated around the RE ion.[13−16] This makes the basis of a method of determination of the number of water molecules surrounding RE ions from the fluorescence relaxation data.[16] One more possibility arises when different RE ions, which can act as donors and acceptors (e.g., Eu^{3+} and Nd^{3+}), are introduced simultaneously in the gel. The energy transfer between them[12,17,18] yields an estimate of the interion distances.

The fluorescence of RE ions has been successfully employed to study their interaction with linear polyelectrolytes[19−24] in aqueous solutions. As for the polyelectrolyte gels, their interaction with RE ions was studied only in a nonaqueous medium, methanol, to reveal the ionomer effect.[25]

In the present paper the RE metal fluorescence probe method was applied to the study of the interaction of chemically cross-linked hydrogels of poly(acrylic acid) (PAA) and of poly(methacrylic acid) (PMAA) with multivalent ions in aqueous media. It allowed us to draw insight on the structure and distribution of the metal ion cross-links in the gel.

Experimental Part

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

Gels. PMAA and PAA gels were prepared by free-radical polymerization of methacrylic and acrylic acid, respectively, 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*′-methylenebisacrylamide (4.6×10^{-2} mol/L or 1.5 mol %) as cross-linker. The gels were

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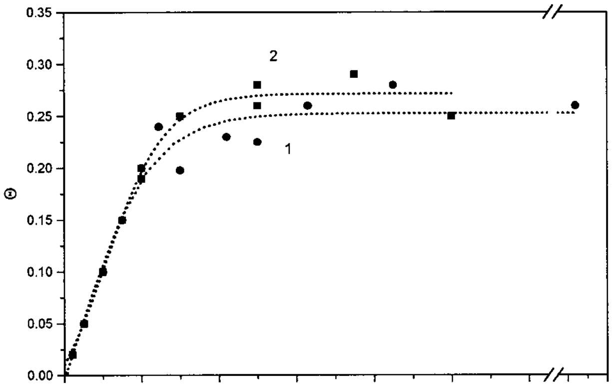

Figure 1. Dependence of the equilibrium composition of PMA−Eu (1) and PA−Eu (2) hydrogels θ on the initial molar ratio q of Eu(NO$_3$)$_3$ to carboxy groups of the gel.

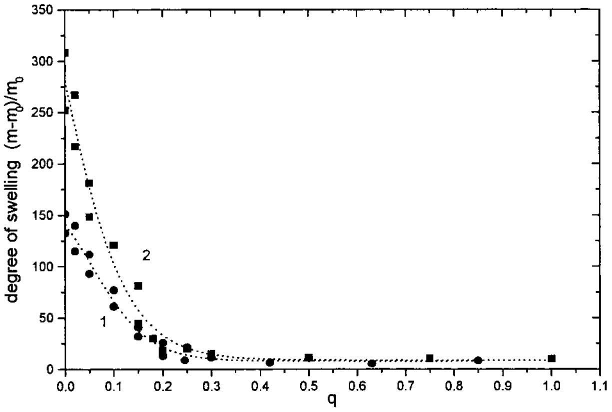

Figure 2. Dependence of the degree of swelling of PMA−Eu (1) and PA−Eu (2) hydrogels on the initial molar ratio q of Eu(NO$_3$)$_3$ to carboxy groups of the gel.

prepared in cylindrical glass tubes with an inner diameter of 0.40 cm under a nitrogen atmosphere at 63 °C for 24 h and were washed at first with ethanol and then with water for 3 weeks to remove unreacted components and the sol fraction.

The poly(sodium methacrylate) (PMA−Na) and poly(sodium acrylate) (PA−Na) gels were obtained by neutralization with sodium methoxide of PMAA and PAA gels swollen in water. The weight fraction of polymer in PMA−Na and PA−Na hydrogels was equal to 0.007 and 0.0036, respectively.

Eu^{3+} ions were incorporated into PMA−Na and PA−Na gels through ion exchange reactions with network counterions. For this purpose the gel samples swollen in water (approximately 0.15 g) were placed in 3 mL of aqueous solutions of Eu(NO$_3$)$_3$. The initial molar ratio of Eu^{3+} salt to carboxylate groups of the gel, q, was varied from 0.1 to 5.0. After equilibrium was established, the content of Eu^{3+} in the gel was evaluated from the decrease of Eu^{3+} concentration in the external solution. The concentration of Eu^{3+} in the solution was determined by fluorescence spectroscopy using the emission band 614 nm (λ_{ex} = 395 nm). The equilibrium composition of PMA−Eu and PA−Eu gels, θ, was calculated as a molar ratio between Eu^{3+} ions absorbed by the network and carboxy groups of the gel.

The PMA−Eu and PA−Eu gels in D$_2$O were prepared in the same way as in water.

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 fluorometer using 1.5 nm band-pass settings for excitation and emission under an excitation wavelength of 395 nm corresponding to the Eu^{3+} upper levels. All spectra were run on air-saturated samples.

Time-resolved fluorescence measurements were performed on an apparatus assembled for this purpose. The samples were excited by the 530 nm output of a pulsed neodymium laser, the duration of the laser pulse being ~20 ns. The resulting emission was monitored at 614 nm by a MRD-2 grating monochromator and detected by a photomultiplier tube.

Results and Discussion

Swelling Behavior of Polyelectrolyte Gels in Aqueous Solutions of Eu(NO$_3$)$_3$. The immersion of PMA−Na and PA−Na gels in aqueous solutions of Eu(NO$_3$)$_3$ leads to an effective absorption of Eu^{3+} ions by the gel due to ion exchange reactions with network counterions. Figure 1 presents dependences of the equilibrium content of Eu^{3+} in PMA−Na and PA−Na hydrogels on the initial molar ratio q of Eu(NO$_3$)$_3$ to carboxy groups of the gel. It is seen that the fraction of Eu^{3+} inside the gel increases and reaches a limiting value: $\theta = 0.25$ for PMA−Eu gel and $\theta = 0.27$ for PA−Eu gel. The limiting value of θ is somewhat smaller than that expected for a complex containing one Eu^{3+} per ca. three network charged units ($\theta = 0.33$), which can be due to the steric and connectivity restrictions imposed by the gel chains.

Figure 2 illustrates the dependence of the degree of swelling of the gel on the initial molar ratio q of Eu(NO$_3$)$_3$ to carboxy groups of the gel. From this figure it is evident that the gels shrink upon absorption of trivalent ions. The most pronounced contraction occurs upon almost complete ion exchange 3Na$^+$ → Eu^{3+} inside the network (cf. Figures 1 and 2). These results are consistent with the literature data on the interaction of polyanionic hydrogels with multivalent cations.[1−11]

It should be pointed out that the contraction of the gel induced by the ion exchange 3Na$^+$ → Eu^{3+} in water is more pronounced than in methanol (cf. data of ref 25). This is connected with the fact that in methanol the initial PMA−Na gel is already in a shrunken state with ionomer structure.[25] In more polar medium (water) most of the sodium ions in the gel are free and exert an osmotic pressure that leads to the swelling of the gel. In this case the ion exchange 3Na$^+$ → Eu^{3+} results in a significant contraction of the gel. We can imagine three main effects produced by trivalent cations. First, the exchange of monovalent per trivalent ions leads to a 3-fold decrease of the number of network counterions and hence to the decrease of the intranetwork osmotic pressure. Second, the trivalent counterions should be more strongly bound to the network co-ions because of their high charge. As a result, in contrast to monovalent ions, a significant number of trivalent ions should be site-bound to the network charges, which reduces additionally the input of trivalent ions in the network swelling pressure. Third, the trivalent counterions form bridges between the gel chains. All these effects are favorable for gel collapse.

Steady-State Luminescence. Figure 3 shows a typical emission spectrum of the PA−Eu gel equilibrated in water. This figure depicts also the spectrum of an aqueous solution of europium nitrate at the same concentration of Eu^{3+} ions. It is seen that the relative peak intensities undergo significant perturbations if one compares the low molecular weight salt solution and the gel. First, the ratio of the bands at 614 nm ($^5D_0 \rightarrow {}^7F_2$ transition) and 591 nm ($^5D_0 \rightarrow {}^7F_1$ transition) in the gel is just the reverse of that in water (Table 1). Second, in the gels we detected a band at 578 nm ($^5D_0 \rightarrow {}^7F_0$ transition), which is absent in solution. While significant variations occur in the

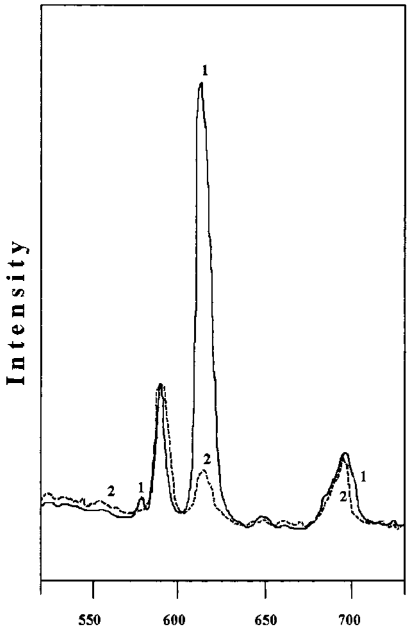

Figure 3. Fluorescence emission spectra of PA−Eu gel (1), equilibrated in water, and of aqueous solution of $Eu(NO_3)_3$ (2), obtained under excitation at 395 nm (in both cases the concentration of Eu^{3+} was 0.011 mol/L). The spectra are normalized to the intensity of the allowed 591 nm band.

TABLE 1: Intensity Ratios of Bands I_{614}/I_{591} in Fluorescence Spectra of Eu^{3+} in Different Media

sample	solvent	C_{Eu}[a] (mol/L)	q[b]	θ[c]	I_{614}/I_{591}
$Eu(NO_3)_3$	H_2O	0.0029			0.41
$Eu(NO_3)_3$	H_2O	0.0292			0.48
$Eu(NO_3)_3$	H_2O	0.0584			0.66
$Eu(NO_3)_3$	H_2O	0.1750			0.63
PA−Eu gel	H_2O	0.0028	0.05	0.05	3.3
PA−Eu gel	H_2O	0.0043	0.10	0.10	3.4
PA−Eu gel	H_2O	0.1220	0.25	0.22	3.5
PA−Eu gel	H_2O	0.1920	1.0	0.25	3.3
PA−Eu linear	H_2O	0.0046			3.5
PA−Eu linear	H_2O	0.1900			4.2
PMA−Eu gel	H_2O	0.0034	0.05	0.05	2.8
PMA−Eu gel	H_2O	0.0086	0.10	0.10	3.2
PMA−Eu gel	H_2O	0.0640	0.25	0.25	3.2
PMA−Eu gel	H_2O	0.2020	0.85	0.28	3.1
$Eu(NO_3)_3$	D_2O	0.0009			0.41
$Eu(NO_3)_3$	D_2O	0.0583			0.52
PA−Eu gel	D_2O	0.0146	0.10	0.10	3.3
PA−Eu gel	D_2O	0.1320	1.0	0.16	3.0

[a] Concentration of Eu^{3+} in solution or in the gel. [b] The initial molar ratio of Eu^{3+} ions to carboxy groups. [c] Molar ratio of Eu^{3+} ions absorbed by the network to carboxy groups of the gel.

relative peak intensities, the positions of fluorescence bands remain unaltered.

Both bands, which are markedly enhanced in the gel (614 and 578 nm), correspond to forbidden f−f transitions. The increases of their relative intensities indicate the fact that Eu^{3+} ions in the gel are in a more strong and asymmetric electric field than in solution. The obvious reason for this is the binding of Eu^{3+} to the network chains.

The site binding of counterions usually leads to the removal of some solvent molecules from the solvation shell of the ion.[26] Since the water molecules are effective quenchers of the Eu^{3+} luminescence, this process can be followed by time-resolved fluorescence.

Time-Resolved Luminescence. The obtained fluorescence decay curves of Eu ions in gels and in solutions may be fitted within the experimental error by a single-exponential function. This suggests the small variations of parameters characterizing the electric field in the vicinity of Eu ions, which indicates that almost all Eu ions in the system are experiencing a similar microenvironment. The values of the fluorescence lifetimes of the Eu^{3+} $^5D_0$ level in PA−Eu and PMA−Eu gels swollen in water are presented in Table 2. For comparison, in this table the fluorescence lifetimes of Eu^{3+} in aqueous solutions of europium nitrate are given as well. It is seen that the Eu^{3+} lifetime in solution is 2-fold shorter than in the gel. This can be a consequence of the expulsion of some water molecules from the vicinity of the cation by a polymer ligand. This supposition is supported by the effects produced by substitution of the solvent from H_2O to D_2O (see below).

Effect of Heavy Water. In D_2O the distribution of the intensities of the 591 and 614 nm bands in the gel as compared to solution is quite similar to that observed in H_2O (Table 1).

The main differences in the fluorescence properties of Eu^{3+} ion in H_2O and in D_2O media are obtained in time-resolved experiments (see Table 2). From these data it follows, first of all, that the lifetimes for the Eu^{3+} $^5D_0$ excited state in D_2O are 1 order of magnitude longer than those in H_2O. This is because the OD vibrations ($\sim$2250 cm^{-1}) are much less effective quenchers of Eu^{3+} luminescence than the OH vibrations ($\sim$3400 cm^{-1}).

Another interesting fact is that in contrast to H_2O medium, in D_2O the values of τ for Eu^{3+} in the gels are lower than in the europium nitrate solution. This may be caused by the increasing possibilities of emission for the Eu^{3+} ion in the gel, which appear to be due to the stronger interactions and increasing probability of forbidden transitions. In H_2O this effect is masked by strong quenching by solvent molecules.

Evaluation of a Number of Water Molecules in Hydration Shell of Europium Ion. The fact that D_2O is a much less effective quencher of RE emission than H_2O allowed one to develop a method of direct determination of a number of RE metal-coordinated water molecules from the values of RE^{3+} luminescence decay constants. Horrocks and Sudnick have shown[16] that for a wide variety of Eu^{3+} complexes in the solid state and in solution the difference between the rate constants of fluorescence decay in H_2O and D_2O, Δk_{obsd}, is directly proportional to the number of coordinated water molecules n:

$$\Delta k_{obsd} = k_{obsd}(H_2O) - k_{obsd}(D_2O) = cn \qquad (1)$$

Assuming that the same coefficient of proportionality c is valid for our systems, we can determine the values of n from the rates of fluorescence decay of Eu^{3+} in H_2O and in D_2O.

The observed fluorescence decay constant, k_{obsd}, being the reciprocal of the measured fluorescence lifetimes of the $^5D_0$ Eu^{3+} excited state, can be expressed as

$$k_{obsd} = k_{rad} + k_{nonrad} + k_{water} \qquad (2)$$

where k_{rad} is the rate constant for intracenter radiative decay, k_{nonrad} is the rate constant for all nonradiative decay processes excluding deactivation on water, and k_{water} is the rate constant for nonradiative decay on coordinated water molecules. According to eq 1, the value of k_{water} is equal to the difference Δk_{obsd} between k_{obsd} values in H_2O and D_2O, assuming that the quenching of Eu^{3+} fluorescence by D_2O molecules is negligible.

The fluorescence lifetimes of Eu^{3+} measured in both H_2O and D_2O are presented in Table 2. Table 2 summarizes also the calculated values of k_{water} and of the number of water molecules

TABLE 2: Evaluation of the Number of Water Molecules *n* in the First Coordination Sphere of Eu^{3+} Ion on the Basis of Fluorescence Decay Constants

sample	$C_{Eu}{}^{a}$ (mol/L)	τ^{b} (H_2O) (ms)	τ^{b} (D_2O) (ms)	$k_{obsd}{}^{c}$ (H_2O) (ms^{-1})	$k_{obsd}{}^{c}$ (D_2O) (ms^{-1})	$k_{water}{}^{d}$ (ms^{-1})	n
$Eu(NO_3)_3$	0.2	0.115	2.7	8.70	0.37	8.33	9
PA−Eu linear	0.2	0.215		4.65			
PA−Eu gel	0.2	0.210	2.1	4.76	0.48	4.28	4.6
PMA−Eu gel	0.2	0.200	2.0	5.00	0.50	4.50	4.9

[a] Concentration of Eu^{3+} in the solution or in the gel. [b] Lifetime of Eu^{3+} $^5D_0$ excited state in H_2O and in D_2O, respectively. [c] Observed fluorescence decay constant (in water and heavy water, respectively). [d] Rate constant for nonradiative decay on coordinated water molecules calculated as the difference Δk_{obsd} between k_{obsd} values in H_2O and D_2O.

bound to Eu^{3+} ions determined using eq 1. From Table 2 it is seen that the Eu^{3+} aquocomplex contains nine water molecules in a hydration shell, which is consistent with the literature data.[16] In PMA−Eu and PA−Eu gels the average number of water molecules in the first coordination sphere of Eu^{3+} ion is much smaller ($n = 4.9$ and 4.6, respectively). These data imply that about five water molecules are expelled from the vicinity of Eu^{3+} ion upon its binding to the polymer chains. The release of solvent molecules provides a significant gain in entropy favoring the binding of Eu^{3+} to the network countercharges.

Comparison between PAA and PMAA Gels. The data presented in Table 2 show that PMA chains (in comparison with PA chains) expel somewhat fewer water molecules from the solvation shell of Eu^{3+} ions. This is consistent with the literature data on Tb^{3+} ions interacting with linear PAA and PMAA.[24] As in ref 24, the difference between PA and PMA ligands is quite small. In addition, the values of the I_{614}/I_{591} ratio presented in Table 1 demonstrate slightly less enhancement of the intensity of the forbidden band in the PMA−Eu hydrogel than in the PA−Eu hydrogel. The analogous data were obtained previously for the linear PMA−Eu and PA−Eu.[24] These results indicate that both linear and cross-linked PMA chains possess a weaker binding ability (in comparison with the PA chains) with respect to RE ions. This effect for the linear polymer was attributed to the smaller flexibility of PMA chains, which interferes with the formation of a multidentate metal ion binding site.[24]

Quantum Yield of Luminescence of Eu^{3+}. For the determination of the quantum yield of luminescence of Eu^{3+}, the values of the radiative decay constants k_{rad} of Eu^{3+} ions in the gel and in $Eu(NO_3)_3$ solution in heavy water were evaluated taking into account (a) the values of the observed fluorescence decay constants k_{obsd} (Table 2), (b) the ratio of the areas of the emission spectra of Eu^{3+} in the gel (S_{gel}) and in $Eu(NO_3)_3$ solution in D_2O (S_{sol}) normalized to the intensity of the allowed band at 591 nm ($S_{gel}/S_{sol} = 2.38$), (c) the fact that in the gel the quenching by D_2O vibrations is 2-fold lower than in solution.

The obtained values of k_{rad} in heavy water are equal to 376 and 158 s^{-1} in PA−Eu gel and in $Eu(NO_3)_3$ solution, respectively. From these data the quantum yield of luminescence of Eu^{3+} in heavy water was calculated. It equals ~80% in PA−Eu gel and ~44% in $Eu(NO_3)_3$ solution in D_2O. These values are much higher than in water, 7.5% and 1.6% for the PA−Eu gel and $Eu(NO_3)_3$ solution, respectively.

Distribution of RE Ions Inside the Gel. The character of distribution of RE ions inside the gel was estimated from the data on nonradiative energy transfer between two kinds of RE ions, Eu^{3+} and Nd^{3+}, which can act respectively as donor and acceptor. As Eu^{3+} ions closely spaced to Nd^{3+} ions decay more quickly than those Eu^{3+} ions, which are far apart from Nd^{3+}, the donor fluorescence decay contains information about the distribution of interion distances in the system.

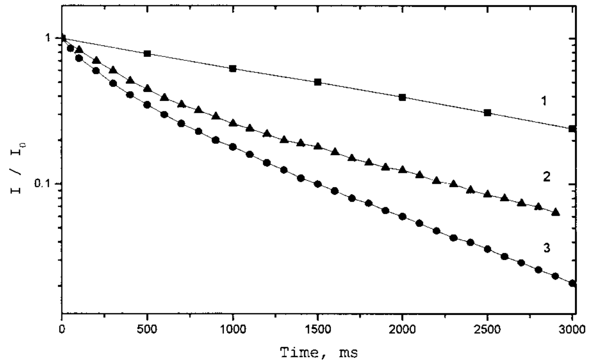

Figure 4. Decay curves of fluorescence from Eu^{3+} ($^5D_0$) level in PA−Eu gel at $\theta = 0.27$ (1) and in PA−Eu,Nd gels at $\theta = 0.05$ (2) and 0.27 (3) at a constant Eu/Nd ratio equal to 9 ($\lambda_{ex} = 530$ nm, $\lambda_{em} = 614$ nm).

In H_2O the decay curve of the PA−Eu,Nd gel is almost a single exponential with a lifetime of 0.2 ms, which is equal to the lifetime of Eu^{3+} in the absence of acceptor (Table 2). This may be due to the fact that the quenching of Eu^{3+} luminescence by Nd^{3+} is masked by the strong quenching by water molecules.

To reveal the quenching produced by Nd^{3+}, the heavy water was used as a solvent. Figure 4 shows the fluorescence decay curves in D_2O of the PA−Eu gel with and without acceptor Nd^{3+}. It is seen that in the absence of acceptor the decay curve is monoexponential, while in its presence the curve deviates from single exponential.

To reveal the character of the distribution of RE ions inside the gel, let us analyze the decay curves of fluorescence from the Eu^{3+} ($^5D_0$) level in PA−Eu,Nd gels with $\theta = 0.05$, 0.10, and 0.27 at a constant Eu/Nd ratio equal to 9.

Since the efficiency of the energy transfer depends on the density of the acceptors around the donor, in the case of random distribution of ions in the system, it is natural to assume that the decay rate determined from the initial part of the decay curves should be proportional to the overall concentration of acceptors.[27] At the same time, the comparison of the data for the PA−Eu,Nd gel samples at $\theta = 0.05$ and $\theta = 0.27$ shows that the 60-fold increase of the concentration of acceptors is accompanied by a rather slight increase of the rate of energy transfer (by a factor of 2.3) (Table 3). This fact can indicate a strongly inhomogeneous distribution of RE ions in the gel phase such that $RE^{3+}-RE^{3+}$ distances become considerably lower than the average interion distance at random distribution. The close contact between RE ions promotes the fast fluorescence quenching, even at a low average concentration of acceptor.

Another piece of evidence of inhomogeneous distribution comes from the analysis of the values of the microparameter of donor−acceptor interaction C_{DA} ($Eu^{3+} \rightarrow Nd^{3+}$), which characterizes the rate of energy transfer k_{DA} between donor and acceptor (in the case of the dipole−dipole mechanism of donor−acceptor interaction,[28] $k_{DA} = C_{DA}/R^6$, where R is the distance between the particles). If we assume the dipole−dipole mech-

TABLE 3: Parameters of Decay Curves of Fluorescence from $^5D_0$ Eu^{3+} Level in PA−Eu,Nd Gel at Eu^{3+}/Nd^{3+} Ratio of 9:1

no.	θ^a	$C_{Eu}{}^b$ (mol/L)	$A_1{}^c$	$A_2{}^c$	$k_1{}^d$ (ms^{-1})	$\tau_1{}^e$ (ms)	k_2 (ms^{-1})	τ_2 (ms)	χ^2	$k_{initial}{}^f$ (ms^{-1})
1	0.05	0.004	0.54	0.46	3.02	0.331	0.67	1.49	7×10^{-6}	1.20
2	0.10	0.012	0.42	0.58	3.80	0.263	0.85	1.17	2×10^{-5}	1.80
3	0.27	0.250	0.42	0.58	6.00	0.167	1.16	0.86	4×10^{-5}	2.80

[a] Molar ratio of Eu^{3+} ions absorbed by the network to carboxy groups of the gel. [b] Concentration of Eu^{3+} ions in the gel. [c] Preexponential factors in the double-exponential function (eq 4). [d] Rate constant for first (second) decay process. [e] Lifetime for first (second) decay process. [f] Initial rate constant for quenching process.

anism of donor−acceptor interactions and random distribution of RE ions in the gel, the values of C_{DA} can be calculated from the decay curves (Figure 4) by using the eq 3:

$$I = I_0 \exp\left(-\gamma\sqrt{t} - \frac{t}{t_0}\right) \qquad (3)$$

where $\gamma = (^4/_3)\pi^{3/2} n_A C_{DA}{}^{1/2}$, n_A is the concentration of acceptors, and τ_0 is the time of decay of fluorescence of donors in the absence of acceptors.[28]

The values of C_{DA} thus obtained for the gel samples at different θ ($C_{DA} > 10^{-37}$ cm^6/s) are by several orders of magnitude higher than those that are characteristic for the $Eu^{3+} \rightarrow Nd^{3+}$ pair. For example, in a monoclinic crystal of La(Eu,Nd)P_5O_{14} with a rather low symmetry, which ensures the increased probability of forbidden transitions, the value of C_{DA} ($Eu^{3+} \rightarrow Nd^{3+}$) is equal to 2×10^{-41} cm^6/s.[29] The extremely high values of the microparameter of donor−acceptor interaction C_{DA} calculated under the assumption of random distribution of RE^{3+} ions in the gel strongly support the suggestion about the inhomogeneous distribution of RE ions in the gel.

What can be the reason for the inhomogeneous distribution of RE ions within the gel? At first, we can imagine that at small θ RE ions are located mainly in the outer layer of the gel. Increasing the content of RE ions leads to the expansion of this layer to the interior of the gel sample, resulting finally in the uniform distribution of RE ions only at θ close to 0.3. Such a type of inhomogeneous distribution was previously observed for the interaction of polyelectrolyte gels with oppositely charged linear polymers and surfactants.[30] Nevertheless, the separate examination of the outer and inner parts of the gel samples at different values of θ showed that there is no distinction in the fluorescence characteristics of these parts of the gel.

Another possible reason for inhomogeneous distribution of RE ions can be related to the formation of aggregates of RE ions on a microscopic level. Such aggregates can be regarded as multiplets that appear as a result of dipole−dipole attraction between different quadruplets ($RE^{3+} + 3COO^-$ counterions) with asymmetric distribution of charges. The high polarization of quadruplets is evident from a quite significant increase of the forbidden bands of Eu^{3+} ions (Figure 3), indicating an asymmetric arrangement of ligands around Eu^{3+}.

Simple theoretical calculations show that highly polarized quadruplets containing one trivalent cation and three monovalent carboxylic anions, in which oxygen atoms are brought together within the minimum distances equal to their ionic radii, do possess a strong tendency to aggregate with each other due to dipole−dipole attraction, forming multiplet-like ionic structures. Even in highly polar media with a dielectric constant of 80 (water) the gain in energy due to this aggregation will be about (5−6)kT. Therefore, we can expect that in water the asymmetric distribution of charges within quadruplets can lead to their aggregation to multiplets.

We can assume by analogy with ref 25 that at 9-fold excess of donor with respect to acceptor, which was used in the present study, there would exist only two types of multiplets in a system, multiplets without acceptors and multiplets with only one acceptor. In this case the decay curve should consist of two exponents corresponding to the above types of multiplets if decay curves of all multiplets of a given type are the same. Indeed, it was shown that all the fluorescence decay curves can be fitted satisfactorily with a double-exponential function:

$$\frac{I}{I_o} = A_1 \exp(-t/\tau_1) + A_2 \exp(-t/\tau_2) \qquad (4)$$

The calculated values of the preexponential factors A_1 and A_2 and of the fluorescence lifetimes τ_1 and τ_2 are listed in Table 3.

The aggregation number of multiplets N can be estimated from the decay curves (Figure 4) using the approach described in our previous papers.[25,31] The values of N were found to be equal to ca. 7 for all the three PA−Eu,Nd gel samples under investigation, independent of θ (at $\theta = 0.05$, 0.10, and 0.27). It is interesting to note that a close value of N was obtained recently for PA−Eu,Nd gels in a less polar solvent such as methanol.[25]

By application of the value of C_{DA} characteristic for $Eu^{3+} \rightarrow Nd^{3+}$ energy transfer (2×10^{-41} cm^6/s), the average distance between RE ions in a multiplet was estimated to be about 4−5 Å, while the average distance between RE ions in the whole volume of the gel is much higher: ∼20 Å (at $\theta = 0.27$), ∼54 Å (at $\theta = 0.10$), ∼80 Å (at $\theta = 0.05$). Moreover, the RE−RE distance in the gel is almost independent of the average concentration of RE ions.

The existence of multiplets provides an explanation for the fact that with an increase of the average concentration of acceptors more than by 1 order of magnitude the rate of quenching increases only by a factor of 2.3. Indeed, in this case the increase of the concentration of RE^{3+} ions leads simply to the increase of the amount of multiplets, i.e., to the enhancement of the intensity of fluorescence at an almost constant rate of quenching inside each multiplet.

The result of this paper concerning the existence of multiplet-like aggregates of ions in a rather polar medium is nontrivial. The reason for the stability of the aggregates can be a high level of polarization of the quadruplets ($RE^{3+} + 3COO^-$), ensuring an enhanced electrostatic attraction between them.

Conclusions

The gel significantly perturbs the Eu ion emission properties, enabling these properties to be used in studies of the interaction of polyelectrolyte network chains with counterions. The fluorescence data obtained provide strong evidence of the site binding of multivalent cations to the gel countercharges with their subsequent aggregation to multiplets consisting of ca. seven RE ions.

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