Novel Spectral-Kinetic Methods for Investigation of Ligand Exchange in Labile Metal Complexes in Solutions

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The luminescent spectral-kinetic method using selective complex excitation with short light pulse compared to relaxation reactions is described. The method makes it possible to obtain direct information on the rates of fast chemical reactions of dissociation or addition of ligands to Ln^{3+} ions in solutions. Data are presented on the rates and mechanisms of dissociation reactions for phenanthroline, bipyridile, salicylate, acetate, naphthoate and other complexes of Ln^{3+} ions in water and alcohols.

Introduction

In this article we shall try to show the perspective applications and validity of a spectral-kinetic method suggested by us in 1977 [1] for studying fast complexation reactions of electron-excited lanthanide ions.

The basic idea of our method is similar to a variety of spectral-kinetic methods [2, 3]. A pulse of light with duration shorter than the relaxational process gives rise to the unequilibrium distribution in the ensemble of metal ion excited complexes in solution. When observing the kinetics of establishment of the equilibrium luminescence spectrum of a solution after a flash, one can obtain information about the rates, nature and mechanism of relaxational processes which are responsible for this equilibrium distribution. These processes are the reactions of conformational changes in excited complexes, ligand exchange (particularly association and dissociation reactions), electrophilic replacement, and the migration of excitation energy.

The principal difference from the method of luminescent kinetic spectroscopy for molecules and lanthanide complexes is in the pathways of establishment of unequilibrium distribution in the ensemble of excited centres. In the case of molecules the electronic excitation usually results in considerable changes in equilibrium properties of the system of centers. Therefore, an excitation should be unequilibrium in nature. For lanthanide complexes the equilibrium constants in the ground and excited states differ slightly, so some types of centres must be selectively excited for the establishment of unequilibrium distribution in the excited states.

A mathematical description of the luminescence decay process in metal complex solutions in the presence of fast relaxational processes was made by one of the authors in ref. [4]. Only some basic conclusions should be considered now.

There is a solution with n types of complexes which are differentiated by the number and means of coordination bonds of ligand to metal ions. Equilibrium distribution is maintained due to transformations of one type of complexes into the other during the ligand substitution reactions, conformational changes, electrophilic substitution, and in the case of excited ions due to electronic energy migration between complexes of different types.

Conditions: 1) the rates of complex transitions considerably exceed the rates of deactivation in an excited complex; 2) the intensity of a light pulse is low, *i.e.*, the pumping pulse being discontinued, the concentrations of excited complexes are markedly lower than unexcited ones (in luminescent experiments this condition is practically always fulfilled).

Results: 1) When the pumping pulse is discontinued the behaviour of the system can be described by a system of differential equations linear along the concentrations of excited complexes. The transition rate matrix of this system is independent of time. 2) The intensity of luminescence decay of solution consists of two parts: a sum of $n - 1$ 'fast' relaxational exponents corresponding to the process of equilibrium distribution establishment in the ensemble of excited complexes, and a slower luminescence decay from this equilibrium state. 3) In the experimental curve of luminescence decay the relaxational processes can manifest themselves only under two simultaneous conditions: a) some types of complexes are selectively excited (unequilibrium excitation); b) at least two types of complexes must have different spectral densities of the radiation rate constant at a wavelength of registration of luminescence. 4) Taking into account discrepancies associated with a decomposition of the experimental curves into

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exponential members and with the complicated formulas for the indices of relaxational exponents for a great number of complexes, the following cases are of practical interest: a) no more than three types of complexes take part in relaxation; b) the rates of different stages in a multistage process differ essentially by an order of magnitude; c) one of the stages is markedly slower than the other.

Experimental

When the method of luminescent kinetic spectroscopy is used for the investigation of relaxational processes in solutions of excited lanthanide complexes, the establishment of an effective unequilibrium excitation is a basic experimental problem. It can be resolved either by using varieties in the absorption spectra of a metal ion in different types of complexes or by means of selective sensitization of definite types of complexes. We have used both the selective excitation methods.

Aromatic ligands 1,10-phenanthroline (Phen), 2,2′-bipyridine (Bipy) and anions of 1-naphthoic (Napht$^-$) salicylic (Sal$^-$), 5-sulfosalicylic (SSal$^-$) acids have been used as sensitizers. These ligands form intraspheric complexes with lanthanide ions, absorb UV light effectively, make a rapid transition to the triplet state and during 10^9–10^{10} s^{-1} [5–7] transfer the excitation energy to the lanthanide ion which is associated in the complex. Thus only the rare-earth ions associated with a ligand-sensitizer in the complex can be selectively excited for a short time. In these experiments a N_2-laser was used for excitation (λ = 337 nm, Δt = 20 ns). An experimental set-up for the measurement of the decay kinetics and luminescence spectra has a time resolution of less than 50 ns and is described in ref. [8].

A narrow-band tunable pulsed Rhodamine 6G in ethylenglycole laser excited by a Nd:YAG laser was used for selective excitation of Eu(III) ion complexes in solution with the extremely narrow and sensitive absorption band $^7F_0 \rightarrow {}^5D_0$. The parameters of the laser are as follows: $t_{pulse} \approx 10^{-8}$ s, energy of a pulse is 10^{-3} J, $\Delta\nu_{1/2}$ = 0.5 cm^{-1}, λ_{ex} = 560–620 nm.

The lanthanide ions were injected in solutions as the chemically pure (c.p.) $Ln(NO_3)_3 \cdot 6H_2O$ crystallohydrates, all anions as natrium (c.p.) salts, the Phen and Bipy molecules (also c.p.).

In many cases we used deuterocompounds as solvents in order to increase the lifetime of the excited states of lanthanide ions and to increase the temporal range of spectral relaxations under investigation.

Results and Discussion

The most vivid and simplest results are obtained with only two types of complexes with visible concentration in solution (see above). Therefore in all cases we injected lanthanide ions in solution in great excess compared to ligand-sensitizers. This makes the formation of two-ligand complexes of the ML_2 type unlikely, and in solution there were lanthanide ion complexes with a ligand and solvated complexes in excess. The selective pulsed excitation of the ML complexes through the ligand-sensitizer is followed by the process of equilibrium establishment between the excited complexes and solvates. This process manifests itself in relaxation of the luminescence spectrum of the solution to the equilibrium spectrum which is identical to that of solvated lanthanide ions (Fig. 1). The relaxational kinetic appears at the beginning of the luminescence decay curves measured in the region where the spectral densities of the radiation rate constant are significantly different for complexes and lanthanide solvates. In our experiments the decay curves were always the sum of two exponents. After subtraction of a slow exponential component from the experimental decay curve (the former corresponds to luminescence of the solution during equilibrium distribution of excited complexes and

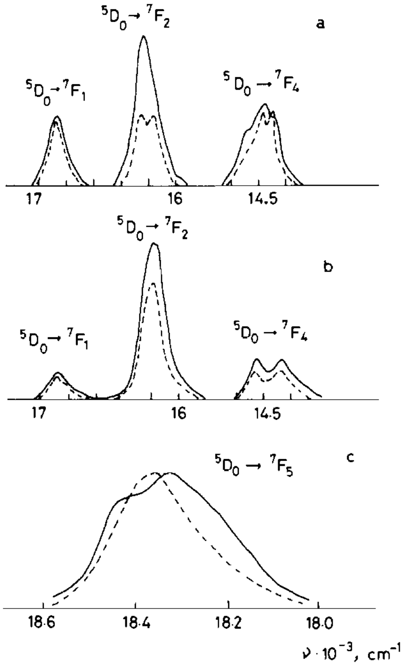

Fig. 1. The luminescence spectra of RE ions sensitized by aromatic ligands measured immediately after the pulsed excitation (solid line) and with delay time when there is one slow ‘equilibrium’ component in decay (broken line). a) The solution consists of $Eu \cdot Phen^{3+}$ complexes and Eu^{3+} solvates in ratio 1:10, the solvent is D_2O, t_{delay} = 1 ms; b) $Eu \cdot Napht^{2+}$ and Eu^{3+} solvates in ratio 1:25, the solvent is methanol-d_4, t_{delay} = 0.8 ms; c) $Tb \cdot Sal^{2+}$ complexes and Tb^{3+} solvates in ratio 1:100, the solvent is methanol-h_4, t_{delay} = 1 ms. T = 295 K, λ_{exc} = 337 nm.

lanthanide solvates) we obtained a 'fast' exponential dependence which described the reaction kinetics

$$M^*L \underset{a_{12}}{\overset{a_{21}}{\rightleftharpoons}} M^* + L \qquad (1)$$

The index of the relaxational exponent is $k_{rel} = a_{21} + a_{12}$. The rate of reaction a_{12} can be neglected as the equilibrium is essentially shifted to solvated ions. Therefore the measured rates of relaxation correspond to the rates of dissociation of the excited lanthanide complexes.

Figure 2 represents the luminescence decay curve of Eu^{3+} water (D_2O) solutions with 1,10-phenanthroline and 2,2′-bipyridine after selective excitation of complexes [1, 8]. At the onset of the curves the relaxational process is shown. The dissociative rate constants k_{diss} of the $Eu^*\cdot Phen^{3+}$ and $Eu^*\cdot Bipy^{3+}$ at 295 K are tabulated. The study of the k_{diss} dependence on temperature (the activation energies of the dissociation reaction are 10.6 kcal/*M* for $Eu^*\cdot Phen^{3+}$ and 8.7 kcal/*M* $Eu^*\cdot Bipy^{3+}$) and pH of the solution made it possible to suggest the dissociative mechanism of this reaction. A limiting stage is the output of a nitrogen ion donor (the chelate ring opening) followed by fast complex dissociation.

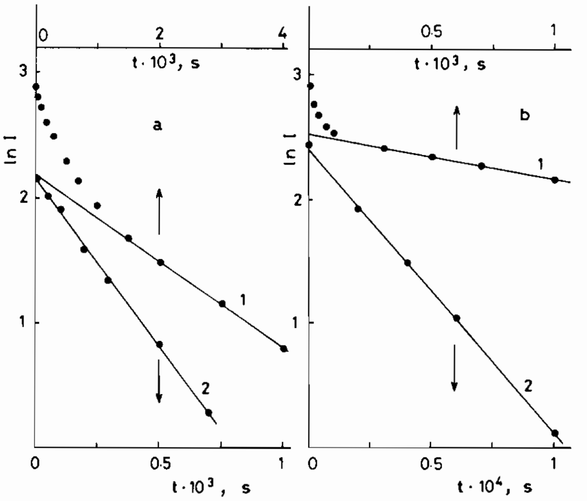

Fig. 2. The curves of intensity decay of luminescence sensitized by 1,10-phenanthroline (10^{-3} *M*) (a) and 2,2-bipyridile (10^{-3} *M*) (b) of Eu^{3+} ($^5D_0$) (10^{-2} *M*) in D_2O at 295 K after pulsed excitation at λ = 337 nm. Points denote the experimental data, straight lines represent the result of decomposition of experimental curves into two exponents; 1) Equilibrium luminescence, 2) Relaxational process.

The investigation of the dissociation of Eu^{3+}-($^5D_0$) and Sm^{3+}($^5G_{5/2}$) complexes with an anion of 1-naphthoic acid ($Napth^-$) [9] showed the strong influence of the solvent on the substitution reaction rate of lanthanide ions. In the methanol/water mixture the dissociation rate increases successively to three orders (see Fig. 3 and Table I) when one passes from pure methanol to water. The $Sm^*\cdot Napht^{2+}$ complex in water is the most short lived one among the investigated complexes with ligands as sensitizers. Its lifetime is $\tau_{diss} = 180$ ns. We showed that the intraspheric complex with an increased coordination number can be an intermediate reactive form during dissociation of $Ln^*\cdot Napht^{2+}$, *i.e.*, most likely the substitution of $Napht^-$ by water molecules in lanthanide ions occurs by the mechanism of associative activation. In pure methanol the $Ln^*\cdot Napht^{2+}$ complex dissociation accelerates with increasing concentration of NO_3^- anions.

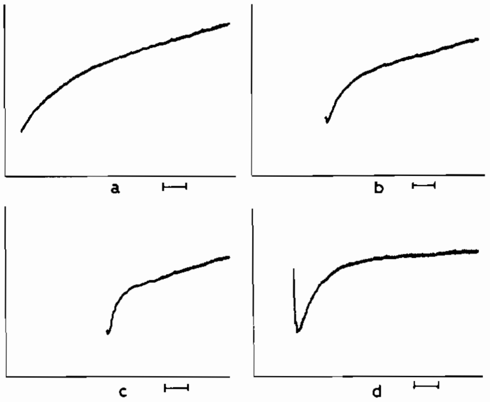

Fig. 3. Decay oscillograms of the Eu^{3+}($^5D_0$) luminescence sensitized by an 1-naphthoic acid anion in methanol-d_4 (a) and in CD_3OD/D_2O mixture with D_2O 3.6% (b), D_2O 10% (c) and (d) measured in total luminescence light. The ratio of Eu^{3+} and $Napht^-$ concentrations is 25:1. Oscillograms (a), (b) and (c) were measured with scan-speed 100 μs/div., oscillogram (d) with 20 μs/div.

Results of particular interest were obtained in the investigation of substitution reactions ligand to solvent in the excited lanthanide complexes with anions of salicylic (Sal^-) and 5-sulfosalicylic ($SSal^{2-}$) acids in water [10, 11]. The rate of dissociation of excited complexes was found to increase linearly with increasing concentration of hydroxonium ions (Fig. 4). Interestingly, a stage limiting the rate of dissociation of $Ln^*\cdot Sal^{2+}$ and $Ln^*\cdot SSal^+$ complexes in water is the reaction of proton addition to the COO^- ligand group. The acid molecule then rapidly leaves the inner sphere of the ion:

$$Ln^*\cdot Sal^{2+} + H_3O^+ \underset{a_{12}}{\overset{k_H[H_3O]^+}{\rightleftharpoons}} \underset{(I)}{Ln^*\cdot HSal^{3+}} \underset{a_{23}}{\overset{a_{32}}{\rightleftharpoons}} \underset{(II)}{} \; Ln^*\cdot Solv^{3+} + HSal \qquad (2)$$

In acid-catalytic dissociation reactions of lanthanide complexes with more dentate ligands ($EDTA^{4-}$ *et al.*) the slowest stage is usually the splitting out of the protonated ligand (stage II in (2)) [12]. In the

TABLE I. The Dissociation Rate Constants of Excited Complexes of Ln^{3+} Ions with Ligand-Sensitizer at 295 K.

Ligand	Ln^{3+}	Solvent	k_{diss}, s^{-1}	τ_{diss}, μs	The mechanism of reaction and limiting stage
1	2	3	4	5	6
1,10-Phenanthroline	Eu^{3+}, $^5D_0$	D_2O	2.7×10^3	370	Dissociative, chelate opening
2,2'-Bipyridile	Eu^{3+}, $^5D_0$	D_2O	2.2×10^4	45	
Anion of 1-naphthoic acid	Eu^{3+}, $^5D_0$	CD_3OD	2.5×10^3	400	
		CD_3OD-D_2O (3:1)	5.5×10^5	1.8	
		CH_3OH-H_2O (3:1)	8.3×10^5	1.2	
	Sm^{3+}, $^4G_{5/2}$	CD_3OD-D_2O (3:1)	6.3×10^5	1.6	
		CD_3OD-D_2O (1:1)	$2 \cdot 10^6$	0.5	
		D_2O	4.4×10^6	0.23	Associative activation
		H_2O	5.5×10^6	0.18	
Anion of salicylic acid	Tb^{3+}, $^5D_4$	CH_3OH	4×10^3	250	
		H_2O	$(1 \pm 0.05) \times 10^{10}\ M^{-1}\ s^{-1}$*		Acid catalysis, proton addition
		D_2O	$(0.76 \pm 0.05) \times 10^{10}\ M^{-1}\ s^{-1}$		
Dianion of 5-sulfosalicylic acid	Tb^{3+}, $^5D_4$	CH_3OH	4×10^3	250	
		H_2O	$(1.05 \pm 0.05) \times 10^{10}\ M^{-1}\ s^{-1}$*		Acid catalysis, proton addition
		D_2O	$(0.79 \pm 0.05) \times 10^{10}\ M^{-1}\ s^{-1}$		
	Dy^{3+}, $^4F_{9/2}$	D_2O	$(0.85 \pm 0.05) \times 10^{10}\ M^{-1}\ s^{-1}$		

*As the limiting stage in dissociation of Ln^*Sal^{2+} and Ln^*Ssal^+ complexes is the reaction of proton addition to ligand, we tabulated the bimolecular rate constants of this reaction k_H ($M^{-1}\ s^{-1}$).

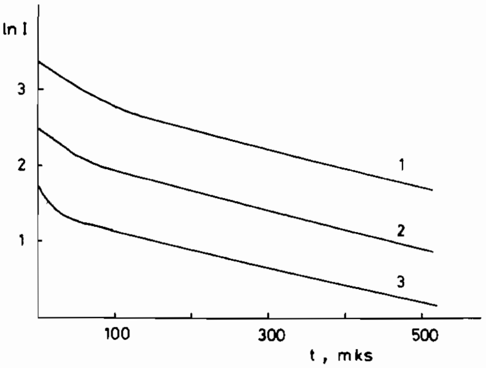

Fig. 4. The decay curves of $Tb^{3+}(^5D_4)$ (10^{-2} *M*) luminescence sensitized by an anion of salicylic acid (10^{-4}) in water at 295 K and at different pH-solutions measured in total luminescence light. 1) pH = 5.7; 2) pH = 5.43; 3) pH = 5.04.

table the bimolecular effective rate constants of dissociation k_H of $Ln^* \cdot Sal^{2+}$ and $Ln^* \cdot SSal^+$ complexes are presented. They are relative to the rate constants of reaction between the proton and anion associated in the lanthanide complex. To obtain the real rate of complex dissociation, k_H should be multiplied by the concentration H_3O^+. The proton being added to the COO^- group of ligands, the great value of k_H enables us to draw the conclusion that Sal^- and $SSal^{2-}$ are associated with lanthanide ions in water *via* an oxygen atom of the COO^- group (and *via* an oxygen atom of the oxy-group).

The selective excitation by sensitized luminescence narrows a variety of ligands and restricts the application of the method. Therefore, using the Eu^{3+} ion solution complexes as an example, we used another more universal method of unequilibrium excitation, that is direct narrow-band excitation by a Rhodamine 6G tunable laser with the $^7F_0 \rightarrow {}^5D_0$ transition in the Eu^{3+} ion through the use of various positions and powers of the oscillator of this transition in Eu^{3+} ions associated in complexes.

Figure 5 represents the luminescence excitation spectra of some solutions with Eu^{3+} ions obtained by means of a tunable laser with registration of luminescence in the $^5D_0 \rightarrow {}^7F_1$ region. As the oscillator strength of the magneto-dipole $^5D_0 \rightarrow {}^7F_1$ transition varies slightly with changes in the immediate surroundings of the Eu^{3+} ion, these spectra are identical to the absorption spectra of solutions in the $^7F_0 \rightarrow {}^5D_0$ transition. The arrows in Fig. 5 show the wavelengths at which the one-ligand complexes $Eu \cdot Ac^{2+}$ (Ac^- is an acetic acid anion), $Eu \cdot Phen^{3+}$, $Eu \cdot EDTA^-$ were then selectively (or advantageously) excited with respect to water Eu^{3+} solvates. The $Eu \cdot Ac^{2+}$ complexes will be advantageously excited due to the fact that the molar extinction coefficient in the $^7F_0 \rightarrow {}^5D_0$ absorption band maximum (Fig. 5a) is approximately five times larger than that of the water solvated Eu^{3+} ion. Figure 6 represents the luminescence decay curves of Eu^{3+} solutions with Ac^- anions (a), Phen (b) molecules, $EDTA^{4-}$ anions (c) in water at 295 K and with the metal to ligand ratio concentrations 5:1. The curves were measured in the region of 'supersensitive' $^5D_0 \rightarrow {}^7F_2$ transition following the advantageous laser excitation of one-

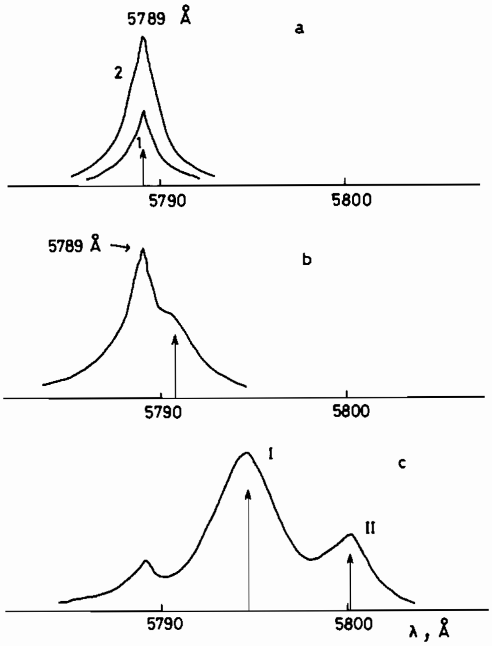

Fig. 5. The excitation spectra of ($^5D_0 \rightarrow {}^7F_1$) luminescence in water solutions with Eu^{3+} ions in the $^7F_0 \rightarrow {}^5F_0$ region measured using a tunable Rhodamine 6G laser. The spectra are identical to the absorption spectra of the $^7F_0 \rightarrow {}^5D_0$ band. a) 1-$Eu(NO_3)_3$ (5.10^{-2} *M*) in H_2O, 2-$Eu(NO_3)_3$ (5.10^{-2} *M*) + NaAc (10^{-2} *M*) in H_2O; b) $Eu(NO_3)_3$ (5.10^{-2} *M*) + Phen (10^{-2} *M*) in D_2O; c) $Eu(NO_3)_3$ (5.10^{-2} *M*) + Na_2H_2EDTA (10^{-2} *M*) in D_2O, pD = 5.5, T = 295 K.

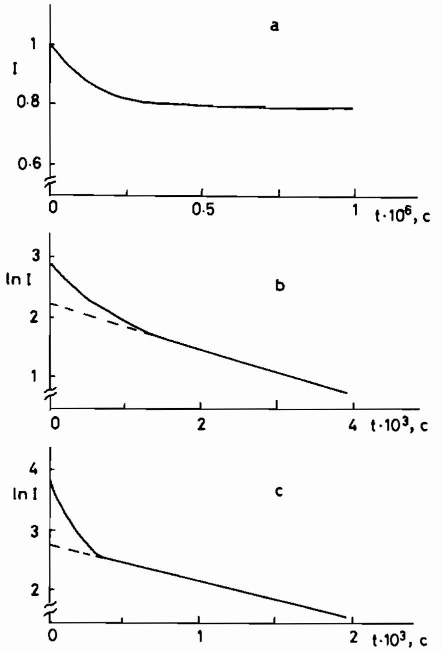

Fig. 6. The decay curves of ($^5D_0 \rightarrow {}^7F_2$) luminescence of solutions containing Eu^{3+} solvates and one-ligand complexes $Eu{\cdot}Ac^{2+}$ (a), $Eu{\cdot}Phen^{3+}$ (b), $Eu{\cdot}EDTA^-$ (c) after pulsed selective (advantageous) laser excitation of complexed Eu^{3+} ions only. The concentrations of solutions are the same as in Fig. 5. The wavelengths of unequilibrium excitation are shown in Fig. 5.

ligand Eu^{3+} complexes. The analysis of these curves shows that as in previous cases they can be described by a sum of two exponents: rapid at initial stages and essentially more slow. The duration of the latter depends on the rate of the $^5D_0$ level deactivation of the Eu^{3+} ion.

Now it should be noted that in all instances we proved that the fast exponents in the decay curves are modified by transitions of lanthanide complexes into solvent ones during the excitation lifetime in a RE ion. Luminescence of the complex with shorter lifetimes of the excited state in the lanthanide ion has no effect. This can be proved by the measurement of the decay times provided that either the spectral densities of radiation rate constants in RE ions associated in complexes and solvates are not different (the $^5D_0 \rightarrow {}^7F_1$ luminescence band in the Eu^{3+} ion) or this value is larger for the solvated lanthanide ion compared to that associated into a ligand complex (some parts of the $^5D_4 \rightarrow {}^7F_5$ band in the Tb^{3+} ion, see Fig. 1). If the 'fast' exponent is really modified by the relaxational process, the decay time is presented in the first case only by a slow 'equilibrium' exponent, and in the second case the 'fast' exponent is released as 'burning' at the onset of the luminescence decay curve following selective excitation.

The duration of the one-exponential relaxational process caused by an exchange reaction between water and acetate-ions in the first coordination sphere of the excited Eu^{3+} ion is $\tau_{rel} = 1/k_{diss}(1 + K[Ac^-])$ = 120 ns, where K is the constant of monoacetate complex stability. The equilibrium being significantly shifted to Eu^{3+} solvates, the dissociation reaction of the $Eu^*{\cdot}Ac^{2+}$ complex makes an essential contribution into τ_{rel}. Supposing the stability constant (K = 87 M^{-1} [13]) of the $Eu{\cdot}Ac^{2+}$ complex not to be changed during excitation of Eu^{3+}, $k_{diss} = (7 \pm 2) \cdot 10^6\ s^{-1}$ for the dissociation rate constant of $Eu^*{\cdot}Ac^{2+}$.

The same dissociation rate constant (see the Table) is obtained for $Eu^*{\cdot}Phen^{3+}$ complexes on selective excitation in the absorption band $^7F_0 \rightarrow {}^5D_0$ of the Eu^{3+} ion as on sensitized excitation, the coincidence being good. The latter is the evidence of the fact that the dissociation rate of the complex is unaffected by the means of selective excitation, particularly by some energy excess ($\sim 5.10^3\ cm^{-1}$) scattered along the group vibrations in the Eu^{3+} surrounding during energy transfer from the triplet Phen to the $^5D_0$ level.

In neutral and weakly acidic solutions the $Eu{\cdot}EDTA^-$ complexes have two isomeric forms with different positions of the $^7F_0 \rightarrow {}^5D_0$ transition in the Eu^{3+} ion [14–16], *i.e.*, type I ($\lambda_{max}(^7F_0 \rightarrow {}^5D_0)$ = 5794 Å) and type II ($\lambda_{max}(^7F_0 \rightarrow {}^5D_0)$ = 5800 Å) (Fig. 5,c). We tried to measure directly the rate of transition of one isomer into another for the excited $(^5D_0)Eu^{3+}$ ion. For this purpose one of the forms had been selectively excited by a tunable laser pulse in solution with equimolar quantities of Eu^{3+} and $EDTA^{4-}$. Luminescence was registered in the $^5D_0 \rightarrow {}^7F_0$ band which belonged to the other isomeric form of the complex (Stokes shift is very small in lanthanide ions, therefore the absorption and luminescence lines $^7F_0 \rightleftharpoons {}^5D_0$ are not shifted with respect to each other). Luminescence of the isomer which is not excited by a laser appears but we had no success in measuring the rate of the luminescence intensity increase which should be used for definition of the transition rate of one excited isomer into another. This was because of restricted temporal resolution of a set-up during registration of weak signals. (Close situation of lines I and II demanded maximal narrowing of slits of a monochromator). However, we showed the rate of this conformational rearrangement of the $Eu^{*}\cdot EDTA^{-}$ complex to have a low value of $\sim 5.10^5$ s^{-1}.

A sharp non-exponential decay (Fig. 6,c) is observed in solutions containing an excessive amount of water-solvated Eu^{3+} ions in addition to $Eu\cdot EDTA^{-}$ complexes after selective laser excitation of an isomeric form of the complex and registration of luminescence in the $^5D_0 \rightarrow {}^7F_2$ transition. By means of measurement of the time-resolved luminescence spectra (Fig. 7) the 'fast' decay component was shown to correspond to the process of equilibrium distribution establishment between excited complexes $Eu^{*}\cdot EDTA^{-}$ and solvates $Eu^{*}\cdot(D_2O)_n{}^{3+}$. But contrary to previous cases the rate of relaxation is a function of total concentration of Eu^{3+} ions in solution. We proved that equilibrium establishment of distribution of the excited complexes and solvates was a result of excited energy migration between them, the efficiency of the process being essentially associated with conditions of formation of labile dinuclear $[Eu^{*}\cdot EDTA]^{-}Eu^{3+}$ complexes in solution. We succeeded also in determining the stability constant of such a dinuclear complex. However, both the problem and the mechanism of energy migration are out of the limits of this article. These questions had already been considered in detail [17]. It should be noted here that the excited energy migration between identical RE ions in liquid solution was observed by us for the first time.

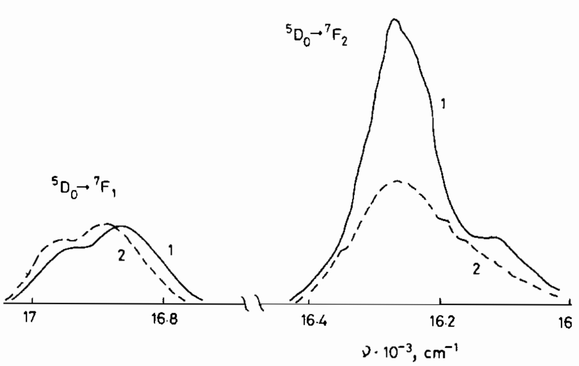

Fig. 7. The 'instantaneous' luminescence spectra (with resolution in time 2 μs) of $Eu(NO_3)_3$ (5.10^{-2} *M*) + Na_2H_2-EDTA (10^{-2} *M*) solution in D_2O (pD = 5.5) in the region of $^5D_0 \rightarrow {}^7F_1$ and $^5D_0 \rightarrow {}^7F_2$ transitions of Eu^{3+} (solid line) and with 600 μs delay (broken line), when only equilibrium luminescence remains.

Unfortunately, we cannot compare our results with those of other authors as there are no literature data on the rates of complexation reactions in excited lanthanides. The comparison can be carried out only for dissociation of the monoacetate Eu^{3+} complex in the ground state. Data on the value of k_{diss} for such a complex are absent from the literature but there are some data for complexes of similar ions, *i.e.*, Sm^{3+} and Gd^{3+}. In ref. [18] the k_{diss} value for acetate complexes in water was evaluated by the method of acoustic absorption. That is $k_{diss} = 3.7 \times 10^7$ s^{-1}. This value is the same for all lanthanides. Using the temperature-jump method it was found that $k_{diss} = 0.7 \times 10^7$ s^{-1} for the Gd^{3+} ion [19]. As can be seen, our data are in rather good agreement with ref. [19]. This fact leads us to believe that the electronic excitation inside the 4f-shell does not change markedly the rates of ligand exchange.

At present there is some information about the kinetics of fast complexation reactions of unexcited lanthanide ions with eight ligands ($SO_4{}^{2-}$ [10–24], $NO_3{}^{-}$ [25, 26], Ac^{-} [18, 19, 27], murexid (1–) [28], antranilate-ion (1–) [19], oxalate-ion (2–) [29], tartrate-ion (2–) [30], malonate-ion (2–) [24]) only in water solutions (we do not mean polydentate lanthanide complexonates in which ligand exchange occurs at a considerably slower rate and is more studied). Some methods were used for this purpose, namely temperature-, pressure-, electric field-jump and acoustic methods. The results obtained by different relaxational methods are often discrepant. This is the result of indirect registration methods of relaxations and by essential differences in the experimental conditions which are specific for each method.

The method of luminescent kinetic spectroscopy which we applied upon pulsed selective excitation is a direct one as the kinetics of equilibrium establishment is registered immediately from variations in the luminescence spectra with time.

Conclusions

Using the method described in this article we studied the kinetics of fast ligand-exchange reactions of excited lanthanide for six ligands not only in water but also in alcohol and mixed alcohol/water solutions. The investigations were carried out for a comparatively short period. We were able to measure within wide limits the dependences of relaxation rates on temperature, pH solution, solvent composition and the ratio of component concentrations as the method of luminescent kinetic spectroscopy makes it possible to obtain high resolution with time and the lifetime of excited states of studied lanthanide ions is rather long. We could also study the mechanisms of fast complexation reactions. The relaxational methods for ground states of ions described above impose more rigid requirements on experimental conditions and in many cases it is impossible to establish the reaction mechanism.

The results of this work show that electronic excitation inside the 4f-shell has no marked effect on the rate of lanthanide complexation, therefore the data on the kinetics of fast complexation reactions of excited lanthanides are probably of great importance for complexes in the ground state as well.

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