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Spectroscopic study of lanthanide(III) complexes with chosen aminoacids and hydroxyacids in solution

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Abstract

Luminescence spectra and lifetime of Eu(III) and Tb(III) ions in complexes with glycine (AAA), glycolic acid (GA), aspartic acid (ASP) and malic acid (MA) were studied. The effect of the amino–NH_2 and hydroxyl–OH groups on the intensity and lifetime of the lanthanides luminescence were examined. Hydration number for Eu(III) in the systems studied indicated the involvement of carboxyl and hydroxyl groups as well as donor nitrogen atoms in the coordination. The phenomenon of Gd(III) ion emission quenching was analyzed and quantitatively described by determination of the quenching constant K_{SV}.

Keywords: Aminoacid and hydroxyacid complexes; Energy transfer; Hydration; Ln(III) complexes; Luminescence

1. Introduction

A molecule of organic compound can comprise more than one functional group which enhances the chemical activity of the molecule. The majority of such multifunctional compounds are derivatives of carboxylic acid. The coordination properties of trivalent ions [Ln(III)] with aminoacids and hydroxyacids have been the subject of numerous physicochemical studies. Ln(III) complexes with certain aminoacids, as a function of solution pH at a constant ionic strength of the system and stability constants of the complexes, were studied [1]. Legendziewicz et al. thoroughly studied the spectroscopic and structural features of the aminoacids and peptides. The pH dependence of selective coordination of carboxylic groups as well as the presence of dimers in the systems studied have been proved. The proposed mode of coordination was confirmed on the basis of the study of the crystal structures of the complexes [2–4]. Bukietynska et al. [5,6], based on hypersensitive absorption bands of Nd(III), Er(III) and Ho(III), calculated stability constants of lanthanide complexes with monocarboxylic acids and α-hydroxycarboxylic acids. The complexes of rare earth ions with carboxylic and hydroxycarboxylic acids were found effective in separation of rare earth elements [7]. Gadolinium with glycine, alanine and lactic acid in water solution were subjected to NMR studies [8]. The aminoacid molecules were found to form bonds with gadolinium with the involvement of oxygen atoms from the carboxyl group whereas lactic acid forms coordination bonds with the involvement of hydroxyl groups. Katzin et al., on the basis of the electron absorption and CD studies of solutions of Eu(III) and Pr(III) with a number of aminoacids, concluded that the amino group takes part in the coordination [9,10]. Moreover, they established that the stability constant of the complex formed is a function of pK_{NH_2}. Similar were the conclusions drawn by Birnbaum and Darnall who studied lanthanide–aminoacid systems using differential absorption spectroscopy and ^{1}H NMR [11,12], and other researchers [13,14] studied the systems using the potentiometric method, ^{1}H and ^{13}C NMR. Bhutra and Gupta studied the absorption spectra of water solutions of the complexes of Nd(III) and Pr(III) with aminoacids [15,16] and used the results in the discussion of the bond energy, band intensity and nepheloauxetic effect.

2. Experimental

The following amino- and hydroxyacids were used without further purification: aminoacetic acid (glycine, AAA), pure for analysis (POCh Gliwice), aminobutanedioic acid (aspartic, ASP), pure for analysis (Merck), hydroxyacetic acid (glycolic, GA), pure for analysis (Merck) and hydroxybutanedioic acid (malic, MA; Inter. Enzymes Ltd.).

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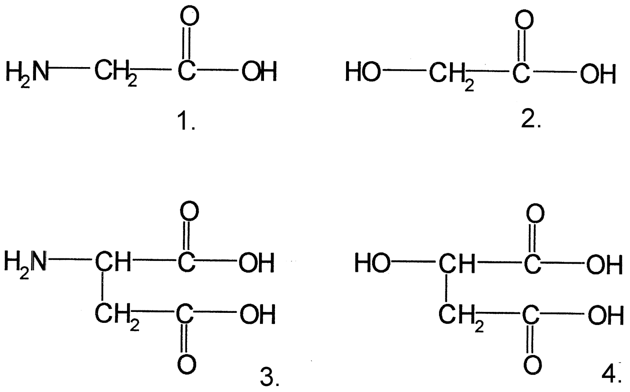

Fig. 1. Schematic presentation of the studied ligands: (1) aminoacetic acid (glycine); (2) hydroxyacetic acid (glycolic acid); (3) aminobutanedioic acid (aspartic acid); (4) hydroxybutanedioic acid (malic acid).

A schematic presentation of the studied acids is shown in Fig. 1.

Aqueous solutions containing Eu(III), Tb(III) and Gd(III) complexes were prepared from $EuCl_3$, $TbCl_3$ and $GdCl_3$ obtained by dissolving Eu_2O_3, Tb_4O_7 and Gd_2O_3 (spectroscopically pure, made in our laboratory), respectively, in hydrochloric acid (analytical grade) and the appropriate amount of hydroxy- or aminoacids. The concentration of Eu(III) was 0.01 mole l^{-1} in all experiments. All solutions were prepared in scaled flasks of 10 ml volume and had a final ionic strength 0.1 mole l^{-1} $NaClO_4$. The required pH values of the solutions were obtained by addition of NaOH or HCl. For the studies in D_2O the solutions of $EuCl_3$ were evaporated to dryness, and the residue dissolved in D_2O. This procedure was repeated four times. The required pH values of the samples were adjusted with NaOD and DCl. Samples containing D_2O were protected with parafilm to avoid absorption of H_2O from the air.

The emission spectra of the solutions were recorded using a Perkin-Elmer spectrofluorimeter MPF-3, with excitation wavelengths of 394 nm, 368 nm and 274 nm for Eu(III), Tb(III) and Gd(III), respectively.

The luminescence lifetime of Eu(III) excited states were measured with the use of the detection system consisting of a nitrogen laser pumping the LD390 dye (Exciton Chemicals) in methanolic solution in a tunable dye laser, as described earlier [18]. Experiments were conducted at room temperature. The luminescence decay curves observed in this work could be analysed by a single exponential relation (semilogarithmic plots of the luminescence intensity vs. time were linear, providing the decay constants).

The studies were conducted for the metal to ligand ratios of 1:1, 1:2 and 1:10, and for pH values in the range 0.5–7.0.

The optimum experimental conditions were chosen using the diagrams of percentage contents of the complexes studied vs. pH and molar ratio of the solution components. The percentages of the species M, ML, Ml_2 and ML_3 species were calculated with the help of a computer program, written in BASIC, which uses the ligand protonation and complexation stability constants. For instance, Fig. 2 presents the distribution curves of the M–MA complexes formed as a function of the variation of pH and/or metal–ligand ratios.

3. Results

Glycolic acid (GA) and glycine (AAA) form with lanthanide(III) ions complexes of types ML, ML_2 and ML_3, while malic (MA) and aspartic (ASP) acids form complexes of types ML and ML_2.

Changes in intensity of selected bands in the emission spectra of the solutions of Eu(III) and Tb(III) with glycolic acid and glycine vs. pH and molar ratios of the solutions are illustrated in Figs. 3 and 4. As follows from these results, the intensity of luminescence increases with increasing pH of the solution as well as with increasing metal–ligand molar ratio.

The increase in the emission intensity is greater for the complexes of Eu(III) and Tb(III) ions with GA for which the highest value of emission intensity was observed for the system of metal–ligand ratio 1:10 [Fig. 3(b)].

The luminescence intensity of the Eu(III) and Tb(III) with MA and ASP increases both with increasing pH and metal to ligand ratio (Figs. 5 and 6), and the increase is more pronounced for MA acid [Fig. 5(a) and (b)].

From among Ln(III) ions, the Gd(III) ion is characterised by a very high-lying emission level (~32 000 cm^{-1}) — higher than the excited states of most ligands. Therefore, energy transfer from the excited ligands to Gd(III) ion is impossible and no emission from Gd(III) in complexes can be observed. However, the Gd(III) luminescence is quenched by the ligands studied (Fig. 7). The luminescence spectra of Gd(III) ions in the systems with chosen ligands ($\lambda_{exc}=274$ nm) of the complexes were recorded for the emission band at 312 nm ($^6P_{7/2}$–$^8S_{7/2}$). Taking into account the changes in the luminescence intensity of the Gd(III) and the dependence of $I_0/I-1$ on the quenchers concentration (the studied acids), the Stern–Volmer quenching constant K_{SV} values were calculated (Table 1).

4. Discussion

Emission spectra of Eu(III) and Tb(III) with glycine AAA, glycolic acid GA, aspartic acid ASP and malic acid MA were studied for different pH of the solutions and different metal to ligand ratios. In all systems studied the intensity of Eu(III) and Tb(III) emission increases with increasing pH and metal to ligand ratio (Figs. 3–6), which can be explained by the process of complexation.

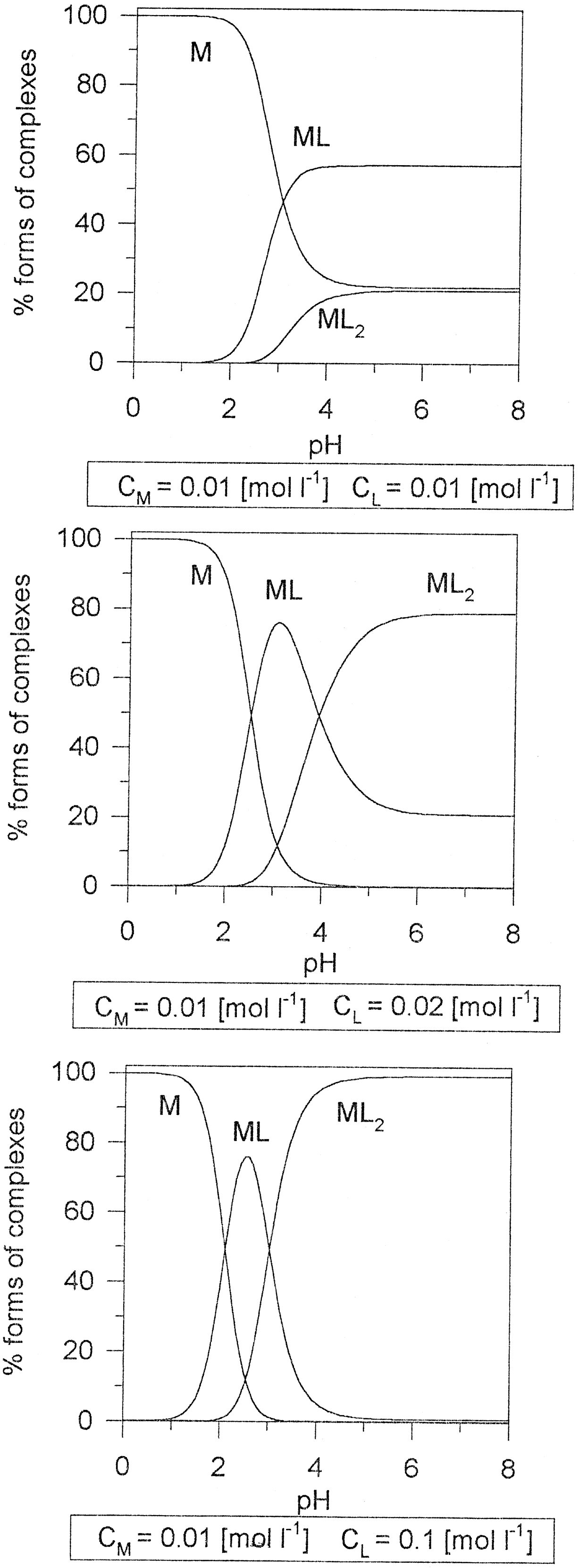

Fig. 2. The distribution curves of the forms of complexes in the systems Eu–MA.

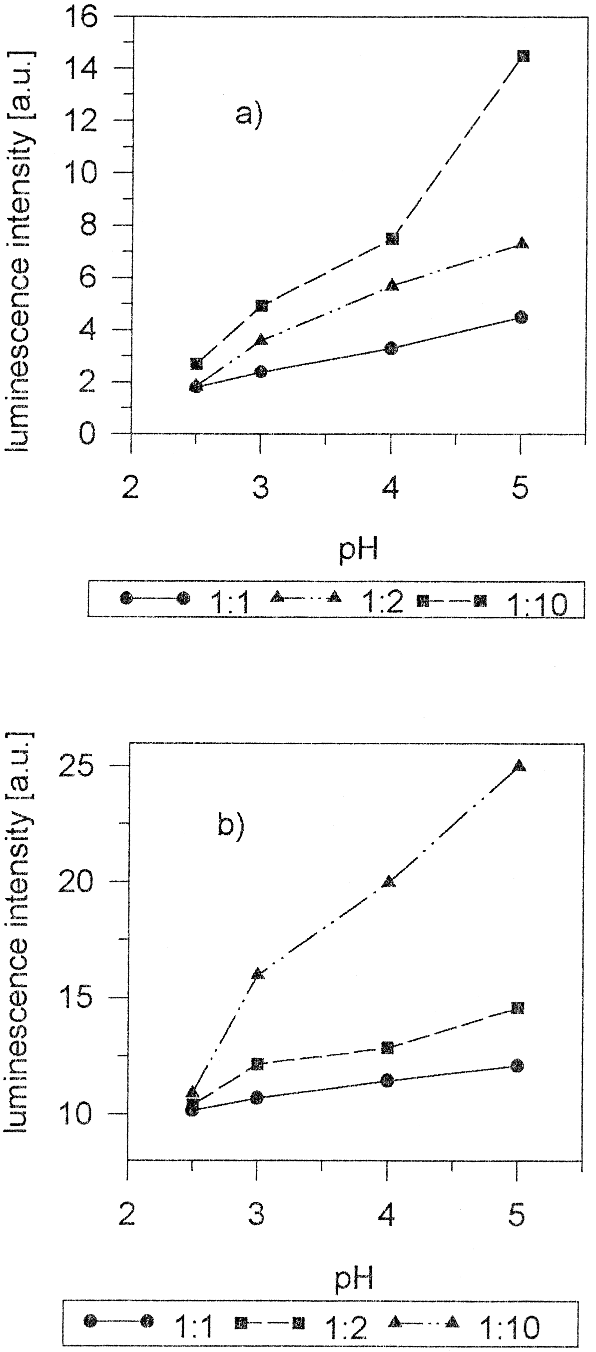

Fig. 3. Intensity of the emission of Eu(III) (a) and Tb(III) (b) ions in solutions of their complexes with glycolic acid as a function of pH and molar ratio (λ_{em} = 615 and 545 nm).

A strong increase in the intensity of the bands studied proves that different forms of the complexes appear, ML, ML_2 and ML_3, which implies a change in the lanthanide coordination sphere. Spectral analysis of the Eu(III) complexes indicates an increase in the values of parameter η with increasing pH and molar ratio (Table 2). The values of this parameter depend on the surrounding of the ion, the ligand field, the symmetry of the complex and vibronic coupling between the bands [19]. In water solutions of

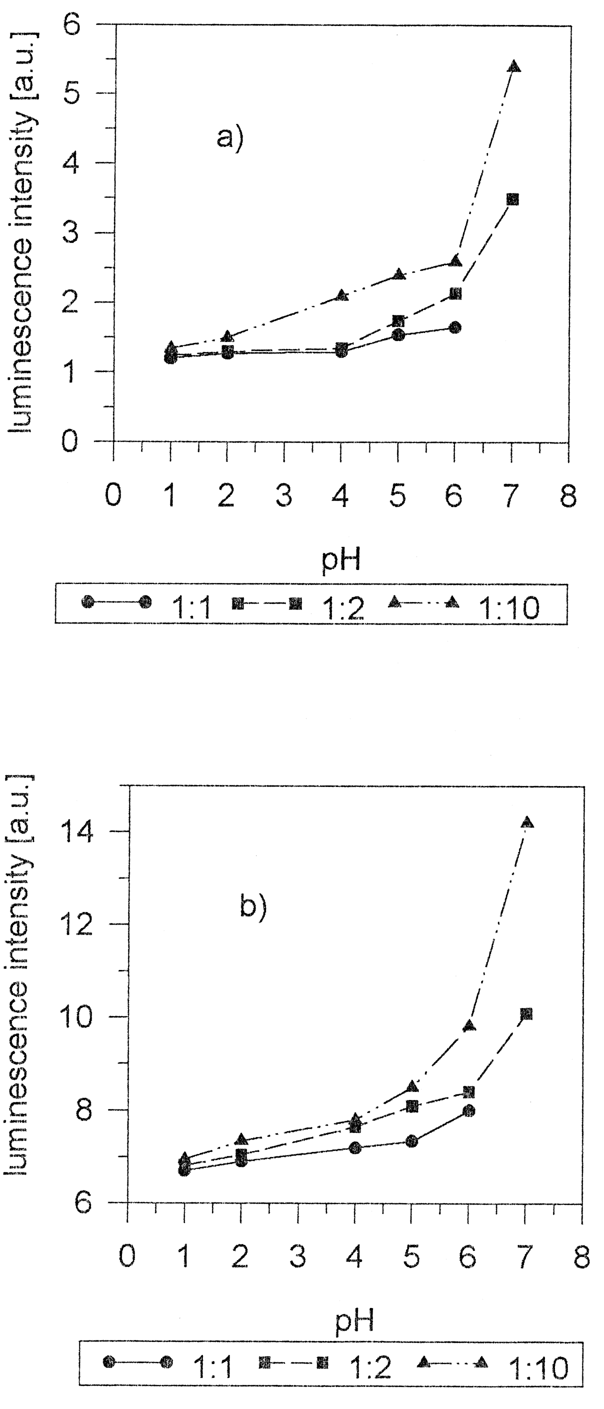

Fig. 4. Intensity of the emission of Eu(III) (a) and Tb(III) (b) ions in solutions of their complexes with aminoacetic acid as a function of pH and molar ratio ($\lambda_{em}=615$ and 545 nm).

$Eu(ClO_4)_3$, the lanthanide ions occur as aqua complexes symmetrically surrounded by 9 molecules of water. For this highly symmetric system η shows the lowest value of 0.39. This value indicates a weak vibronic coupling following from the ligand field influence on the 4*f* orbital of the Eu(III) ion [19]. These changes reflect those in the complex symmetry (Table 2).

Considerable changes in the value of η in the same system prove the formation of different forms of complexes. The values of η depend on the kind of acid used as ligand — for the same molar ratio 1:1, they are higher for ASP and MA (characterised by three potential sites of coordination), than for AAA and GA (with two coordination sites).

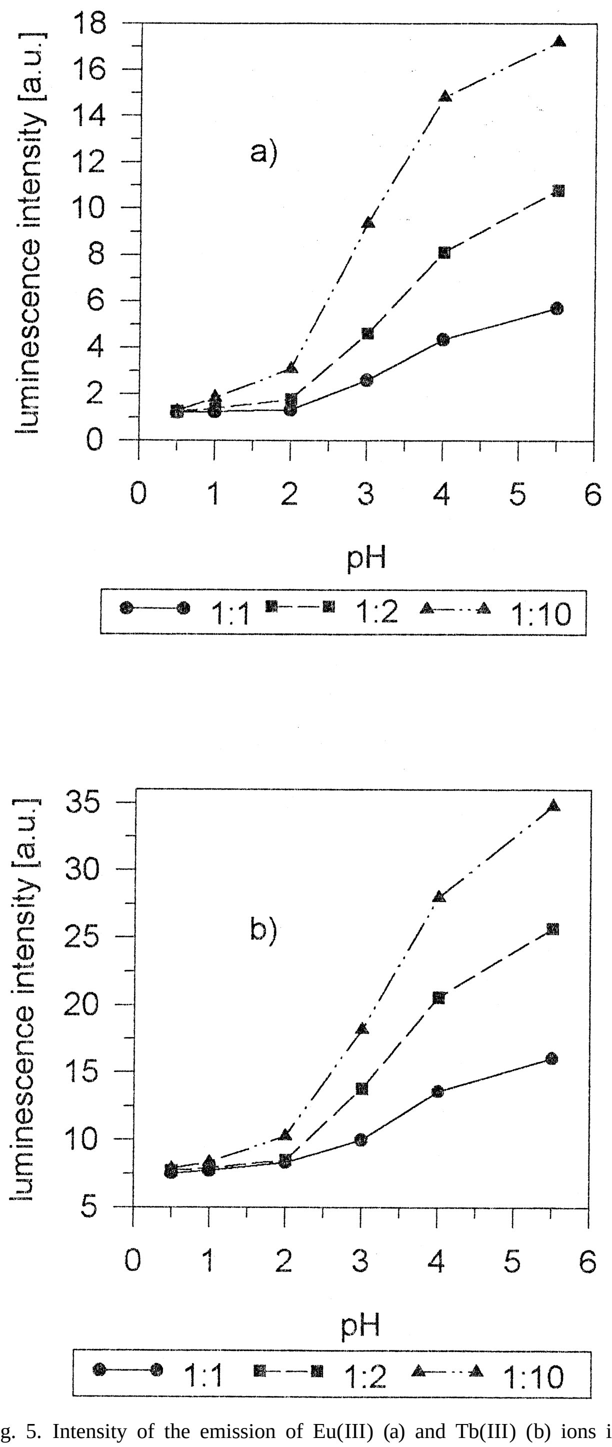

Fig. 5. Intensity of the emission of Eu(III) (a) and Tb(III) (b) ions in solutions of their complexes with malic acid as a function of pH and molar ratio ($\lambda_{em}=615$ and 545 nm).

Apart from the carboxyl group, these ligands contain an

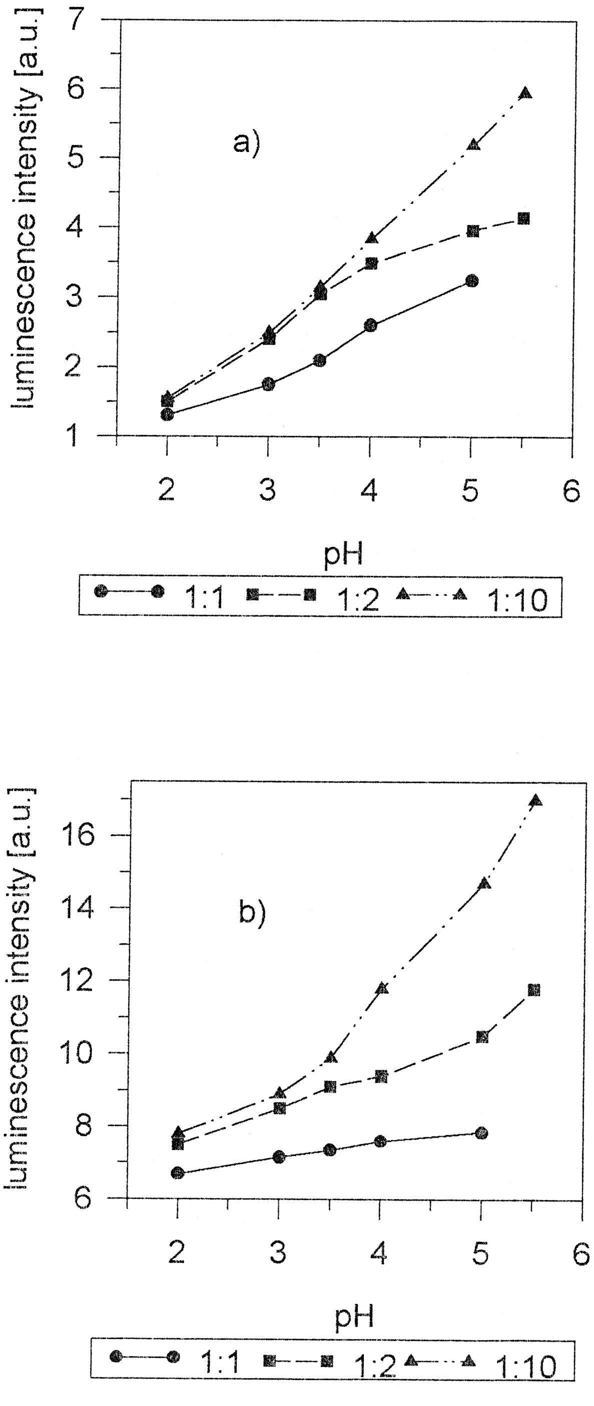

Fig. 6. Intensity of the emission of Eu(III) (a) and Tb(III) (b) ions in solutions of their complexes with aspartic acid as a function of pH and molar ratio ($\lambda_{em}=615$ and 545 nm).

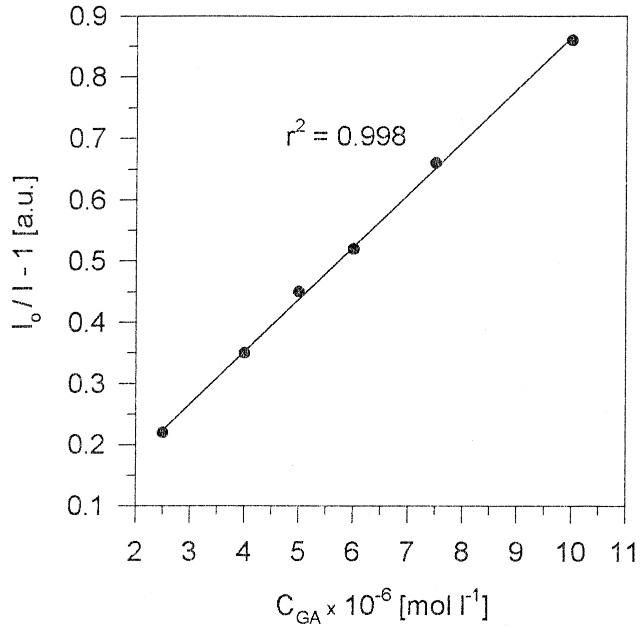

Fig. 7. Intensity of the Gd(III) emission band vs. concentration of the quencher (glycolic acid).

Table 1
Values of Stern–Volmer quenching constant K_{SV}

System	Concentration of quencher (mol l^{-1})	K_{SV}
Gd–AAA	2.5×10^{-8}–10×10^{-8}	2.8×10^{6}
Gd–ASP	2.0×10^{-7}–10×10^{-7}	4.6×10^{5}
Gd–GA	2.5×10^{-6}–10×10^{-6}	8.5×10^{4}
Gd–MA	1.0×10^{-4}–10×10^{-4}	1.2×10^{3}

amine or hydroxyl group which can take part in coordination of the metal ion, repulsing additional water molecules. Involvement of these groups in the coordination was proved by the results of measurements of lifetime and the number of molecules in the inner coordination sphere of the lanthanide (III). This additional site involved in coordination diminishes the symmetry of the system which causes an increase in η. Analysis of the changes in η indicates that in the experimental conditions the symmetry of the systems Eu–AAA, Eu–ASP, Eu–GA and Eu–MA was similar.

Another reason for the increase in the emission intensity is the excess of the ligand. It is known that different ionic forms of the acids studied appear in the solutions [20]. For instance, in AAA solutions (pK of 2.36 and 9.57) the forms HL^- and L^{2-} are observed. ASP gives dissociated forms, i.e. H_2L^-, HL^{2-} and L^{3-} (pK equal to 1.39, 3.70 and 9.63). GA as a result of dissociation forms L^- (pK=

Table 2
Values of η for the studied systems

System	Metal–ligand ratio	$\eta = I_{lum}615/I_{lum}593$
$Eu(ClO_4)_3$		0.39
Eu–AAA	(1:1)	0.98
	(1:10)	1.40
Eu–GA	(1:1)	0.95
	(1:2)	1.41
	(1:10)	2.37
Eu–ASP	(1:1)	1.61
	(1:10)	2.46
Eu–MA	(1:1)	1.57
	(1:10)	2.43

3.63) while MA forms HL^- and L^{2-} (pK of 3.24 and 4.71). In the acid solutions (pH<2) complexes do not form as the process of dissociation of the acids is not strong enough for complex formation. For the solutions of pH at which the dissociation of the acids studied takes place, an increase in the intensity of emission was observed. A change in the intensity of emission occurring at the excess of the ligand results from the change in the dipole moment of the system as the consequence of its modification by the dipole moments of the ligand molecules. The intensity of emission depends on the total dipole moment of the whole system, i.e. the complex and the excessive ligand [21]. For the solutions with complexes, but without the excess of the ligand, e.g. M–MA 1:1, and 1:2, or M–ASP 1:1 and 1:2, the intensity of the emission is practically constant. An increase in the emission intensity, for M–MA of 1:2 (at pH 2–3) and M–ASP of 1:2 (at about pH 6) systems, results from a formation of the 1:2 form of the complex. In the solutions with the ligand in excess, the ligand ions and molecules surrounding the complex change the effective charge of the latter and thus change the resultant dipole moment, leading to the observed increase in the emission intensity of Eu(III) and Tb(III) ions.

The lifetimes of Eu(III) ions were measured in H_2O and D_2O in the solutions with the acids studied. Using the formula $n = 1.05(\tau_{H_2O}^{-1} - \tau_{D_2O}^{-1})$ proposed by Horrocks and Sudnick [22], the number of water molecules in the inner sphere of the lanthanide ion was found (Table 3). Determined hydration numbers, as a function of pH and a molar Ln(III)–ligand ratio indicate that both oxygen atoms of carboxyl and hydroxyl groups as well as nitrogen atoms of amino groups are bonded to the lanthanide(III) ions.

In all the systems studied in the acidic range of pH, the values of the calculated values of the hydration numbers are 8.3–4.8 which means that only the carboxyl groups are involved in coordination of the Ln(III) ions. An increase in the luminescence intensity of Eu(III) and Tb(III) ions, with increasing metal–ligand ratios and pH, resulted from the formation of other complex forms, such as ML_2 and ML_3, and involvement of the hydroxyl groups and of donor nitrogen atoms in the coordination of Ln(III).

This conclusion was confirmed by other authors [2–4,8–15], who reported the involvement of both functional groups of the aminoacids. Brittain [23] studied the process of energy transfer between the complexes Tb(III)–Eu(III) with ASP vs. pH of the solution and proved that for low pH, the Tb–ASP complexes are monomeric, while above pH 6 the associated forms begin to dominate in the solution. Chiral effect on energy transfer from Tb(III) to Eu(III) in monocrystals of aminoacids was studied by Legendziewicz et al. [4]. It was observed in the polymeric compound with glutamic acid, but was not observed in the dimer of the alanine complex.

The intensity of luminescence of Ln(III) ions depends on the number of water molecules responsible for radiationless deactivation of the Eu(III) and Tb(III) ions. Figs. 3(b)–6(b) present the results of measurements of Tb(III) emission intensity ($\lambda_{em} = 545$ nm) on pH and molar ratios of Tb(III) to GA, AAA, MA and ASP. Taking into regard the denticity of the ligands (GA, AAA, MA, ASP) and the percentage contribution of particular forms of complexes (ML, ML_2 and ML_3), in experimental conditions, the number of water molecules coordinated in the inner sphere of the Tb(III) ion was calculated. Dependence of the emission intensity of Tb(III) on the hydration number of Tb(III), in Tb(III)–GA, Tb(III)–AAA, Tb(III)–MA and Tb(III)–ASP complexes, is presented in Fig. 8 as a straight line, assuming the tridentate character of MA and ASP, as

Table 3
Values of hydration number, n, for Eu(III) ion in the complexes with studied acids

Studied system		pH	$\Delta k \times 10^3$	n
Eu–GA	1:1	5.5	7.41	7.8
	1:2	5.5	6.24	6.6
	1:10	8.0	3.54	3.7
Eu–AAA	1:1	6.8	7.88	8.3
	1:2	6.9	6.62	6.9
	1:10	8.9	5.05	5.3
Eu–ASP	1:1	5.5	7.58	8.0
	1:2	5.6	6.49	6.8
	1:10	9.0	3.35	3.5
Eu–MA	1:1	5.4	6.25	6.6
	1:2	5.5	4.55	4.8
	1:10	8.5	2.66	2.8

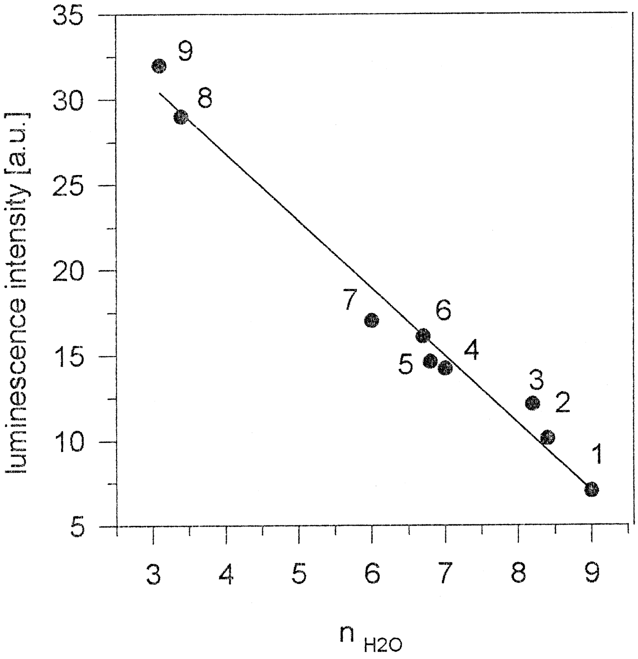

Fig. 8. Intensity of the Tb(III) emission, at 545 nm, vs. the number of water molecules in the inner coordination sphere of Tb(III) complexes: (1) $Tb(ClO_4)_3$; (2) Tb–AAA (1:1); (3) Tb–GA (1:1); (4) Tb–AAA (1:2); (5) Tb–GA (1:2); (6) Tb–ASP (1:1); (7) Tb–MA (1:1); (8) Tb–GA (1:3); (9) Tb–MA (1:2).

well as the bidentate character of AAA and GA. Thus, obtained values of the hydration number are similar to those estimated from the measurements of Eu(III) ion lifetime. The intensity of emission of Eu(III) and Tb(III) was found to depend on the pH of the solution, the excess of the ligand and the type of acid studied. The information on the luminescence properties of Eu(III) and Tb(III) ions and their complexes inferred from the intensity of the emission bands may be misleading, as, for example, the increase in the intensity of the hypersensitive band of Eu(III) at $\lambda_{em} = 615$ nm is much greater than that of the band at $\lambda_{em} = 593$ nm.

The parameter best suited to assessment of luminescence properties is the quantum yield Φ. Its value for Eu(III) in the form of perchlorate and complexes with aminocarboxylic and hydroxycarboxylic acids was found from the formula:

$$\phi = \frac{\tau_{H_2O}}{\tau_{D_2O}}$$

where τ_{H_2O} and τ_{D_2O} are the lifetimes of the excited states [24,25]. Table 4 presents the results of the calculated values of quantum yield of emission and stability constant of the Eu(III) complexes. The quantum yield of emission of the complexes studied is at least twice as high as that of the uncomplexed Eu(III) ion. The quantum yield of emission of the complexes with hydroxycarboxylic acids is higher than those with aminocarboxylic acids. This observation can be explained by the fact that the NH oscillators present in the aminoacid molecule are much more effective quenchers of Ln(III) ions emission than the OH oscillators from the solvent molecules [26,27]. The values of the quantum yield determined in this work are of the same order as the value obtained for the Eu(III) complex with EDTA by Horrocks et al. [24].

Moreover, the process of quenching of the Gd(III) emission was analysed. The quenching constant K_{SV} was determined using the classic Stern–Volmer method. The value of the quenching constant ($K_{SV} = 2.8 \times 10^6$) indicates that the quenching of the Gd(III) luminescence is most effective in the system Gd–AAA. The effectiveness of quenching can be ordered as follows: AAA, ASP, GA and MA. This pattern also confirms that NH oscillators are more effective quenchers of Ln(III) luminescent excited states than OH ones.

Table 4
Values of the quantum yield and stability constant of the Eu(III) ion complexes with studied amino- and hydroxycarboxylic acids

Complex	log β [17]	Φ
EuGA	3.03	0.057
$Eu(GA)_2$	5.07	0.062
$Eu(GA)_3$	6.52	0.084
EuAAA	3.5	0.043
$Eu(AAA)_2$	6.7	0.059
EuMA	4.85	0.061
$Eu(MA)_2$	8.11	0.117
EuASP	5.62	0.049
$Eu(ASP)_2$	9.77	0.096
$Eu(ClO_4)_3$	–	0.028

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