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Importance of the Ligand Excess in Investigations of the Fluorescence Intensity of the Lanthanide(III) Complexes of Aminopolyacetic Acids in Aqueous Solutions*

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In the investigations of the fluorescence of Ln(III) (Ln = lanthanide) complexes in solutions, the influence of various experimental factors on the fluorescence intensity (I_{flu}) of the characteristic Ln(III) bands has mainly been discussed [1–5]. Our previous investigations [6–10] have been devoted to studying the dependence of the fluorescence band intensities of Sm(III), Eu(III), Gd(III), Tb(III) and Dy(III) over a wide range of pH values, complexing agent concentrations and temperature of the system. The studies were carried out in solutions of lanthanide complexes with the following aminopolyacetic acids (APA): ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), iminodiacetic acid (IDA), aminoacetic acid (AAA) and acetic acid (AA). The relationship between the intensity of the fluorescence bands and the stability constants of the examined complexes has been demonstrated.

Our previous studies dealt with a relatively slight excess of ligand in the examined complex solutions. These investigations showed that a small ligand excess (a few times), in reference to complex stoichiometry, provided the stabilization of the fluorescence intensity for large ligand molecules. In the case of ligand molecules of small size this effect of 'saturation' is not observed. This fact, important for the theoretical model explaining the mechanism of observed phenomena, has led us to use a large ligand excess in spectrofluorometric investigations.

In this work the influence of the complexing agent excess on the fluorescence band intensities in solutions of Eu(III) complexes with EDTA, NTA, IDA and AAA has been investigated over a wide range.

Experimental

The Eu(III) concentration was kept constant in all solutions and was equal to 1.0×10^{-3} M. The solutions were characterized by molar ratios Eu(III):APA equal to 1:1, 1:5, 1:10, 1:50, 1:100, 1:200 and 1:500 at a pH value of 7.0.

Fluorescence spectra were registered using a Perkin-Elmer MPF-3 spectrofluorometer and an excitation wavelength of 394 nm. The intensity of the fluorescence bands of Eu(III) at $\lambda_{max} = 590$ and 615 nm was studied.

The absorbance of the solutions was measured at $\lambda_{max} = 394$ nm using a Shimadzu 160 spectrophotometer. This value is practically invariable (0.003–0.016) for all the systems investigated.

Results and Discussion

The results presented in Table I indicate the increase in the intensity of the fluorescence bands of Eu(III) in solutions of its APA complexes with the molar ratio Eu:APA greatly increasing (up to 1:500).

TABLE I. Influence of the Ligand Excess on the Eu(III) Fluorescence Intensity in Solution of Complexes with Aminopolyacetic Acids ($[\mathrm{Eu(III)}] = 1 \times 10^{-3}$ M)

Solution composition		I_{flu} (a.u.)		$\eta = \frac{I_{615}}{I_{590}}$
		590 nm	615 nm	
$EuCl_3$		4.5	1.5	0.33
Eu:EDTA =	1:1	35	77	2.20
	1:5	40	116	2.70
	1:10	46	135	2.93
	1:50	68	200	2.94
	1:100	90	285	3.17
	1:200	130	444	3.41
	1:500	135	477	3.53
Eu:NTA =	1:1	39	43	1.10
	1:5	82	78	0.95
	1:10	135	130	0.96
	1:50	143	139	0.97
	1:100	149	151	0.98
	1:200	158	156	0.99
	1:500	167	165	0.99
Eu:IDA =	1:1	18	11	0.61
	1:5	23	28	1.22
	1:10	33	61	1.85
	1:50	64	164	2.40
	1:100	71	172	2.42
	1:200	76	181	2.38
	1:500	81	190	2.35
Eu:AAA =	1:500	26	43	1.65

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The intensity of the fluorescence bands of Eu(III) depends on the complex stability (log β), as in the case of the small ligand excess. The solutions of the Eu/NTA and Eu/EDTA complexes, the most stable ones, are characterized by the greatest fluorescence intensity. Minor values of I_{flu} are observed for the solutions of the Eu/IDA complexes. These values are the smallest for the Eu/AAA complex solutions. In this case the value of I_{flu} is given only for Eu:AAA = 1:500 because of very little differences in I_{flu} among the particular solutions investigated.

On the grounds of the total lack of shift in the position of the bands, an explanation of the observed effects by means of vibronic coupling cannot be expected. We tried to use our data in order to explain the observed phenomena in terms of a theoretical model implying the modification of the transition dipole moment of the central ion by the dipole moments of the ligands. The dipole moment for the electronic transition in the Ln(III) ion depends on the electron cloud moment of the ligand excess, the electric charge of the ligand, and the distance between the lanthanide ion and the ligand [8, 10].

The presented model of phenomena is verified by the intensity of the fluorescence bands obtained (Table I). The resultant dipole moment of the system complex–complexing agent excess is modified by the large ligand excess. This affects distinctly the fluorescence intensity.

The values of the ratio of the hypersensitive transition (forbidden, $^5D_0{-}^7F_2$, $\lambda_{\mathrm{max}} = 615$ nm) band intensity to the allowed ($^5D_0{-}^7F_1$, $\lambda_{\mathrm{max}} = 590$ nm) one have been calculated. This ratio (η) is defined as the degree of intensity borrowing of the band. The values of η obtained indicate the influence of the ligand type and of its excess on the fluorescence intensity of the Eu(III) ion. The values of η are greatest for the Eu/EDTA systems (rising to 3.53 with an increase in the ligand excess), smaller in the case of Eu/IDA solutions, and smallest for Eu/NTA solutions. This fact can be explained by the influence of the ligand molecule symmetry on the degree of intensity borrowing of the band. The higher the ligand molecule symmetry, the smaller the value of η. The ligand symmetry also affects the formation of the resultant dipole moment of the system investigated.

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