

Influence of pH and Concentration of Complexing Agents on Fluorescence of Samarium(III), Gadolinium(III), and Terbium(III)—Ethylenediaminetetraacetic Acid or Nitrilotriacetic Acid Complexes in Aqueous Solutions

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The fluorescence intensity of aqueous solutions of Sm(III), Gd(III) and Tb(III) complexes with *EDTA* or *NTA* was investigated as a function of complexone concentration over a wide pH range. For Sm(III) and Tb(III) complexes the ratio of intensities of hypersensitive and allowed bands was calculated in order to obtain information about intensity borrowing of the fluorescence bands as a result of vibronic coupling.

[Keywords: Ethylenediaminetetraacetic acid; Fluorescence; Gadolinium(III) complexes; Hypersensitive bands; Nitrilotriacetic acid; Samarium(III) complexes; Terbium(III) complexes]

Einfluß von pH und Konzentration der Komplexbildner auf die Fluoreszenz der Komplexe von Samarium(III), Gadolinium(III) und Terbium(III) mit Ethylendiamintetraessigsäure und Nitrilotriessigsäure in wäßrigen Lösungen

Die Abhängigkeit der Intensitäten der Fluoreszenzbanden wäßriger Lösungen der Komplexe von Sm(III), Gd(III) und Tb(III) mit Ethylendiamintetraessigsäure und Nitrilotriessigsäure von der Konzentration der Komplexbildner wurde in einem weiten pH -Bereich untersucht. Für die Komplexe des Sm(III) und Tb(III) wurde das Verhältnis der hyperempfindlichen und erlaubten Banden berechnet, um Informationen über geborgte Intensitäten der Fluoreszenzbanden infolge vibronischer Kopplung zu erhalten.

Introduction

The fluorescence of some Sm and Tb complexes has been studied previously; however, only over a limited range of ligand concentrations and pH values¹⁻⁷. Fluorescence of Gd complexes has not been investigated at all.

The present work is a continuation of our studies of rare earths metal complexes with *EDTA* or *NTA*⁸. The results on the fluorescence of Sm(III), Gd(III) and Tb(III) complexes in aqueous solution over a wide range of complexone concentration and *pH* values have been obtained. The influence of these parameters on the intensity of the fluorescence bands arising out of different characteristic transitions in the lanthanide ions is discussed.

Experimental

Solutions containing Sm(III), Gd(III) and Tb(III) complexes were made from SmCl₃, GdCl₃ and TbCl₃, obtained by dissolving Sm₂O₃, Gd₂O₃ and Tb₄O₇ (spectroscopically pure, prepared in our laboratory) in hydrochloric acid (AR standard, POCH, Gliwice) and *EDTA* or *NTA* (both AR standard, POCH, Gliwice). The Sm(III), Gd(III) and Tb(III) concentrations were 0.01 mol/dm³ in all experiments.

The following molar ratios Sm(Gd, Tb): complexone were employed: 1:1, 1:2, 1:3, 1:4, and 1:5 with *pH* values of 3.0, 5.5, 7.5, 10.0, and 11.5. The *pH* values of the solutions were brought to the values required by means of additions of ammonia solution (AR standard, POCH, Gliwice) or hydrochloric acid solution and they were measured using a *pH*-meter (26, Radiometer, Copenhagen).

Both complexone solutions and the hydrochloric acid and ammonia solutions did not exhibit any fluorescence under irradiation at the excitation wavelengths and thus were used without any further purification.

The corrected fluorescence spectra were registered using Perkin-Elmer MPF-3 and MPF-44A spectrofluorometers. The radiation source was a xenon lamp, and the exciting wavelengths were 402 nm for Sm(III), 274 nm for Gd(III) and 372 nm for Tb(III).

The registration of fluorescence spectra was carried out using 100-fold amplification of emission for Sm(III) solutions and 3-fold for Tb(III). For Gd(III) solutions the amplification was unity.

Results and Discussion

The fluorescence spectrum of uncomplexed aqueous Sm(III) exhibits three characteristic maxima at 563, 596, and 640 nm, corresponding to transitions $^4G_{5/2} \rightarrow ^6H_{5/2}$, $^4G_{5/2} \rightarrow ^6H_{7/2}$, and $^4G_{5/2} \rightarrow ^6H_{9/2}$, respectively⁹. The last one is a hypersensitive transition ($\Delta J = 2$).

Complexes of Sm(III) with *EDTA* and *NTA* show the same maxima, but with an increased intensity. The fluorescence of solutions complexes Sm/*EDTA* and Sm/*NTA* is influenced in a different manner for each complex, by both the complexone concentration and the *pH* of the solution (Figs. 1 and 2), similarly as in the case of Eu(III) complexes⁸.

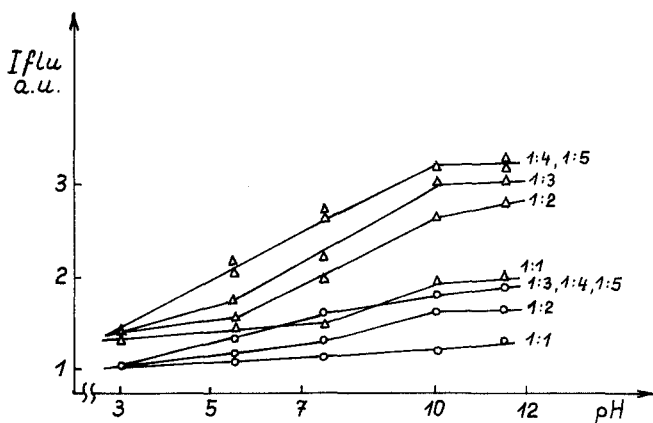


Fig. 1. The intensity of the fluorescence bands at $\lambda = 596$ nm ($-\triangle-$) and 640 nm ($-\circ-$) for Sm : EDTA = 1 : 1, 1 : 2, 1 : 3, 1 : 4, and 1 : 5 as a function of the pH

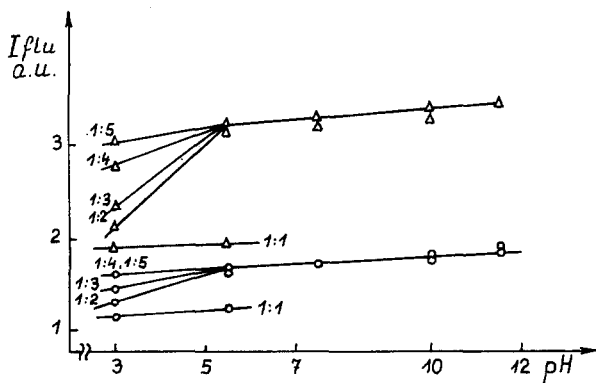


Fig. 2. The intensity of the fluorescence bands at $\lambda = 596$ nm ($-\triangle-$) and 640 nm ($-\circ-$) for Sm : NTA = 1 : 1, 1 : 2, 1 : 3, 1 : 4, and 1 : 5 as a function of the pH

The 563 nm band is omitted from further considerations because its intensity is low and little affected by the experimental conditions. The intensity of the 596 nm band is much greater than that of the 640 nm band over the whole range of experimental conditions.

For solutions of Sm/EDTA the intensity of fluorescence of both these bands increases with increasing pH. This effect is slight for solutions with Sm : EDTA = 1 : 1 for pH over 7.5, but in the presence of

an excess of the complexing agent it becomes more marked. For pH values above 10 the fluorescence intensity reaches a steady level. On increasing the complexone concentration, the fluorescence intensity increases most noticeably on changing the $Sm : EDTA$ ratio from 1 : 1 to 1 : 2. Complexone excesses beyond two-fold have less effect.

With Sm/NTA complexes, the intensities of both bands increase as the pH is raised from 3.0 to 5.5, but then remain steady up to $pH = 11.5$. For solutions with $Sm : NTA = 1 : 1$ the fluorescence intensity is practically constant in the $pH = 3.0-5.5$ range, unlike the situation when an excess of NTA is present. For this $Sm : NTA$ ratio [as well as $Tb(Gd) : NTA = 1 : 1$] the fluorescence could be studied only up to $pH = 5.5$, since at higher pH values a slight turbidity of the solution is observed as the hydroxide begins to precipitate.

The fluorescence spectrum of uncomplexed $Tb(III)$ exhibits four maxima at 491, 545, 585, and 621 nm, corresponding to transitions ${}^5D_4-{}^7F_6$, ${}^5D_4-{}^7F_5$, ${}^5D_4-{}^7F_4$, and ${}^5D_4-{}^7F_3$, respectively⁹. The 545 and 491 nm bands are strongest; the 585 and 621 nm bands are so weak that they will be ignored in further discussion. The 491 nm band due to the ${}^5D_4-{}^7F_6$ transition is hypersensitive.

Under the same conditions of excitation the fluorescence bands of $Tb(III)$ complexed by $EDTA$ or NTA in aqueous solution appear at the same wavelengths, but are much stronger. Similarly as with Sm , fluorescence intensity generally increases with increasing complexone excess and increasing pH (Figs. 3 and 4).

With $Tb : complexone = 1 : 1$ (for both complexones) there is virtually no fluorescence increase on reducing the acidity. In the presence of at least two-fold complexone excess the fluorescence intensity rises with pH , for $EDTA$ up to $pH = 10.0$, but with NTA only up to $pH = 5.5$.

The fluorescence spectrum of $Gd(III)$ consists of one band, with a maximum at 312 nm, and this band is due to a ${}^6P_{7/2} - {}^8S_{7/2}$ transition⁹. $Gd(III)$ complexes with $EDTA$ and NTA give a fluorescence band with the same maximum, but with an increased intensity. The fluorescence of solutions with $Gd : EDTA = 1 : 1$ is markedly stronger than for other compositions (Fig. 5).

This contrasts with the behaviour of the other lanthanides. The fluorescence intensity decreases slightly but regularly with increasing complexone concentration. For all $Gd/EDTA$ solutions the fluorescence bands increase in intensity between $pH = 3.0$ and 5.5, but beyond $pH = 7.5$ there is a gradual intensity decrease.

For Gd/NTA complexes, the fluorescence band intensity decreases somewhat with complexone excess above three-fold (Fig. 6).

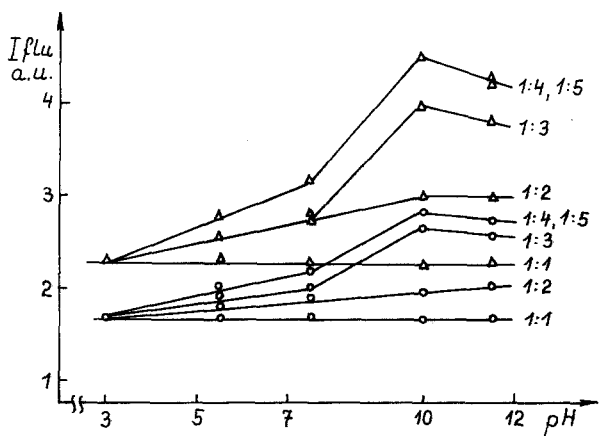


Fig. 3. The intensity of the fluorescence bands at $\lambda = 491 \text{ nm}$ (—○—) and 545 nm (—△—) for $\text{Tb} : \text{EDTA} = 1 : 1, 1 : 2, 1 : 3, 1 : 4,$ and $1 : 5$ as a function of the pH

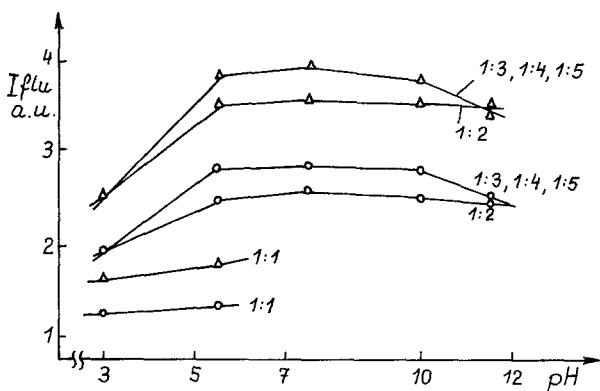


Fig. 4. The intensity of the fluorescence bands at $\lambda = 491 \text{ nm}$ (—○—) and 545 nm (—△—) for $\text{Tb} : \text{NTA} = 1 : 1, 1 : 2, 1 : 3, 1 : 4,$ and $1 : 5$ as a function of the pH

The intensity increases markedly with rising pH in the $pH = 3.0-5.5$ range; above $pH = 5.5$ intensity changes are small. For solutions with $\text{Gd} : \text{NTA} = 1 : 1$, the fluorescence intensity is lower, as with the other lanthanides, and hardly changes over the whole pH range investigated.

In general, the fluorescence intensity of Gd complexes is about 100 times stronger than of Sm complexes and about 3 times stronger than the fluorescence of Tb complexes.

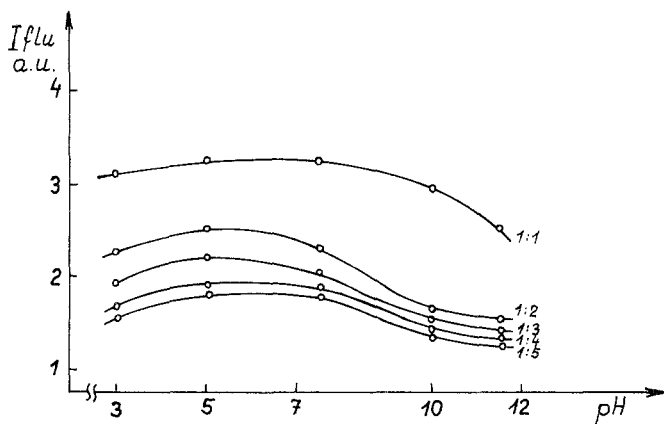


Fig. 5. The intensity of the fluorescence band at $\lambda = 312$ nm for Gd:EDTA = 1:1, 1:2, 1:3, 1:4, and 1:5 as a function of the pH

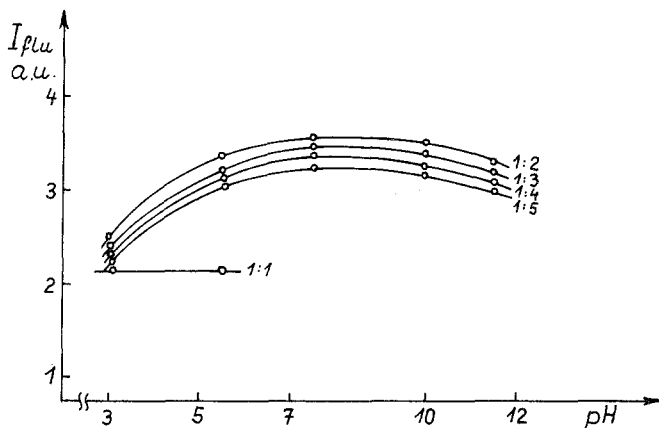


Fig. 6. The intensity of the fluorescence band at $\lambda = 312$ nm for Gd:NTA = 1:1, 1:2, 1:3, 1:4, and 1:5 as a function of the pH

The dependence of the fluorescence intensity of Sm and Tb complexes with EDTA and NTA on solution pH is broadly similar (Figs. 1-4).

For Gd complexes the character of the dependence is very different—the effect is particularly marked with Gd/EDTA (Figs. 5 and 6).

The observed changes in the fluorescence intensity of Sm and Tb complexes with EDTA as a function of the pH of the solution and

complexone concentration are associated with the existence of different anionic forms of *EDTA* (H_4Y), with different dissociation constants¹⁰. As the acidity of the solution diminishes, the proportion of more highly charged ions [$(H_3Y)^-$, $(H_2Y)^{2-}$, $(HY)^{3-}$, Y^{4-}] increases, which accounts for the increased intensity of the fluorescence bands.

The fluorescence spectra of complexes solutions, registered under appropriate experimental conditions can be used to obtain information about the different forms of the complexes and about their stabilities. The near constancy of the band intensities over the entire range of *pH* values investigated for both solutions of Sm and Tb complexes with *EDTA* at lanthanide : *EDTA* = 1 : 1 indicates that probably only the most stable form of the complex is present in solution, i.e. $(SmY)^-$ and $(TbY)^-$.

Increasing intensity of fluorescence bands for both metals for lanthanide : *EDTA* \geq 1 : 2, particularly at higher *pH* values may be taken as an indication of the presence in solution of also other complex forms².

The changes in the fluorescence band intensities for the Sm/*NTA* system are associated, in acid solution (*pH* = 3.0), with the occurrence of the 1 : 2 complex, in addition to the 1 : 1 one. The proportion of the 1 : 2 complex increases at greater complexone concentrations. With increasing *pH*, from *pH* = 5.5, the influence of an excess of *NTA* (H_3X) is slight.

With the Tb/*NTA* system, the fluorescence band intensities at *pH* = 3.0 are all the same, except for Tb : *NTA* = 1 : 1. This is most probably due to constant proportions of both known Tb/*NTA* complexes (i.e. 1 : 1 and 1 : 2), independent of the complexone excess.

To generalize, stronger fluorescence for Sm : *NTA* and Tb : *NTA* \geq 1 : 2 compared with 1 : 1 is associated with the existence of different forms of the complexes in solutions : $(SmX_2)^{3-}$, $(TbX_2)^{3-}$, and SmX , TbX .

It is characteristic that with Sm and Tb complexes the fluorescence intensity consistently—though to a different extent—increases when the complexone concentration is raised.

In the case of Gd complexes, the differences in the behaviour of the fluorescence as a function of the *pH* and of the complexone concentration are connected with the fact that the energy level of the excited state of Gd(III) is high—the fluorescence appears in the UV (312 nm).

For Gd/*EDTA* the fluorescence intensity is greatest at Gd : *EDTA* = 1 : 1. The intensity decreases when there is an excess of the complexone and particularly is somewhat more noticeable under

alkaline conditions ($pH = 11.5$)—it is in evidence even at $Gd : EDTA = 1 : 1$.

For Gd/NTA complexes the fluorescence intensity is greatest for solutions with $Gd : NTA = 1 : 2$. If the complexone excess is greater than about three-fold, there is a slight intensity decrease. Solutions with $Gd : NTA = 1 : 1$ gave decidedly the lowest fluorescence intensity, which is associated with only one complex being able to form, GdX . With an excess of NTA , $1 : 2$ complex can form as well.

The hypersensitive bands observed for Sm and Tb (Sm 640 nm, ${}^4G_{5/2} - {}^6H_{9/2}$; Tb 491 nm, ${}^5D_4 - {}^7F_6$) arise as a result of vibronic coupling connected with the influence of the ligand field on the 4f orbitals of Sm and Tb.

The ratio of the band intensity for the hypersensitive transition to that of the allowed one, η , gives information about the occurrence of intensity borrowing of these bands. The values of η were calculated for Sm and Tb:

$$\eta_{(Sm)} = \frac{{}^4G_{5/2} - {}^6H_{9/2}}{{}^4G_{5/2} - {}^6H_{7/2}}, \quad \eta_{(Tb)} = \frac{{}^5D_4 - {}^7F_6}{{}^5D_4 - {}^7F_5};$$

the values are presented in Table 1.

Table 1. *The ratio of the intensities of the hypersensitive and allowed fluorescence bands of Sm(III) and Tb(III) complexes*

Composition of complex solution		pH				
		3.0	5.5	7.5	10.0	11.5
Sm : EDTA	1 : 1	0.50	0.48	0.44	0.53	0.53
	1 : 2	0.48	0.44	0.46	0.46	0.47
	1 : 3	0.54	0.43	0.43	0.44	0.44
	1 : 4	0.41	0.43	0.43	0.44	0.43
	1 : 5	0.41	0.45	0.45	0.47	0.44
Sm : NTA	1 : 1	0.28	0.35	—	—	—
	1 : 2	0.41	0.38	0.40	0.37	0.36
	1 : 3	0.39	0.36	0.36	0.37	0.36
	1 : 4	0.30	0.38	0.39	0.42	0.42
	1 : 5	0.36	0.38	0.38	0.40	0.39
Tb : EDTA	1 : 1	0.62	0.60	0.59	0.60	0.59
	1 : 2	0.61	0.60	0.59	0.57	0.57
	1 : 3	0.60	0.59	0.59	0.58	0.57
	1 : 4	0.60	0.59	0.58	0.57	0.58
	1 : 5	0.60	0.58	0.59	0.57	0.60
Tb : NTA	1 : 1	0.58	0.57	—	—	—
	1 : 2	0.66	0.70	0.69	0.69	0.70
	1 : 3	0.64	0.69	0.69	0.71	0.70
	1 : 4	0.64	0.70	0.70	0.69	0.69
	1 : 5	0.64	0.68	0.69	0.70	0.70

The fact that the values of η obtained are low indicates that interactions leading to vibronic coupling are weak for both Sm and Tb complexes. Also, the values of η do not change over the range of experimental conditions employed. This can be taken to indicate that the mechanism leading to a modification of the dipole moment for the transition, which determines the observed band intensities, is caused by dispersion interaction of the ligands.

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References

- ¹ *Poluektov N. S., Kononenko L. I., Bel'tyukova S. V., Gava S. A., Drobyazko V. N.*, Dokl. Akad. Nauk SSSR **220**, 1133 (1975).
- ² *Poluektov N. S., Drobyazko V. N., Meshkova S. B., Bel'tyukova S. V., Kononenko L. I.*, Dokl. Akad. Nauk SSSR **224**, 150 (1975).
- ³ *Brittain H. G.*, Inorg. Chem. **17**, 2762 (1978).
- ⁴ *Bel'tyukova S. V., Poluektov N. S., Kononenko L. I., Kravtshenko T. B.*, Dokl. Akad. Nauk SSSR **247**, 862 (1979).
- ⁵ *Salama S., Richardson F. S.*, Inorg. Chem. **19**, 629 (1980); *ibid.* **19**, 635 (1980).
- ⁶ *Brittain H. G., Konteatis Z.*, J. Inorg. Nucl. Chem. **43**, 1719 (1981).
- ⁷ *Kravtshenko T. B., Bel'tyukova S. V., Nazarenko N. A., Kononenko L. I., Poluektov N. S.*, Dokl. Akad. Nauk SSSR **259**, 151 (1981).
- ⁸ *Elbanowski M., Mąkowska B., Lis S.*, Monatsh. Chem. **113**, 907 (1982).
- ⁹ *Hüfner S.*, Optical Spectra of Transparent Rare Earth Compounds. New York: Academic Press. 1978.
- ¹⁰ *Schwarzenbach G., Flaschka H.*, Die Komplextometrische Titration. Stuttgart: Enke. 1965.