Monatshefte für Chemie 113, 907—913 (1982)

Monatshefte für Chemie
Chemical Monthly

Influence of *pH* and Concentration of Complexing Agents on Fluorescence of Europium(III) Ethylenediaminetetraacetic Acid and Europium(III) Nitrilotriacetic Acid Complexes in Aqueous Solutions

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(Received 1 February 1982. Accepted 12 February 1982)

The fluorescence of aqueous solutions of Eu(III) complexes with *EDTA* and *NTA* has been investigated. Intensities of the fluorescence bands have been measured as a function of complexone concentrations in the solutions and the *pH*. The results are interpreted in terms of the different forms of Eu(III) complexes and their relative stabilities.

(Keywords: Ethylenediaminetetraacetic acid; Europium(III) complexes; Fluorescence; Nitrilotriacetic acid)

Einfluß von pH und Konzentration der Komplexbildner auf die Fluoreszenz der Komplexe des Europium(III) mit Ethylendiamintetraessigsäure und Nitrilotriessigsäure in wäßrigen Lösungen

Die Fluoreszenz von wäßrigen Lösungen der Komplexe des Europium(III) mit Ethylendiamintetraessigsäure und Nitrilotriessigsäure wurde untersucht. Die Intensitäten der Fluoreszenzbanden in Abhängigkeit von *pH* und Konzentration der Komplexbildner wurden auf der Basis vorkommender Komplexgeometrien und deren Stabilitäten interpretiert.

Introduction

When Eu(III) is complexed, the intensity of fluorescence emitted by its solutions increases. Several types of Eu(III) complexes have been investigated to date, but only over a narrow range of *pH* values and concentrations of complexing solutions[1–5].

0026-9247/82/0113/0907/$ 01.40

The present paper gives an account of an investigation of Eu(III) complexes with ethylenediaminetetraacetic acid (*EDTA*) and nitrilotriacetic acid (*NTA*), as a function of complexone concentrations, over a wide range of solutions *pH* values. The influence of these parameters on the intensities of Eu(III) fluorescence bands at $\lambda = 590$ nm and $\lambda = 615$ nm is discussed. These bands correspond to $^5D_0$—$^7F_1$ and $^5D_0$—$^7F_2$ transitions, respectively.

Experimental

The solutions containing Eu(III) complexes were made from $EuCl_3$, obtained by dissolving Eu_2O_3 (spectroscopically pure, prepared in our laboratory) in hydrochloric acid (AR standard, POCh, Gliwice) and *EDTA* or *NTA* (both AR standard, POCh, Gliwice). The Eu(III) concentration was 0.01 mol/dm^3 in all experiments. The following molar ratios Eu: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, and 1:0 and 1:0.5 with *pH* values 3.0 and 5.5 [higher *pH* values could not be employed here because of the precipitation of $Eu(OH)_3$ under conditions of complexone deficiency]. The *pH* values of the solutions were brought to the values required by means of additions of ammonia solution (AR standard, POCh, Gliwice) or of 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 wavelength and thus they 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 wavelength was $\lambda = 394$ nm. The same conditions were employed for registering the fluorescence spectra in all experiments.

Results and Discussion

The fluorescence spectrum of uncomplexed Eu(III) shows two characteristic maxima at $\lambda = 590$ nm and $\lambda = 615$ nm. These bands arise from transitions $^5D_0$—$^7F_1$ ($\Delta J = 0, \pm 1$), and $^5D_0$—$^7F_2$ ($\Delta J = 2$), respectively. The complexes of Eu(III) with *EDTA* and *NTA* exhibit fluorescence at the same wavelengths, but with increased intensity. The dependences of the intensities of the fluorescence bands on the *pH* and the complexone concentrations are different for the two complexes. For solutions with Eu:*EDTA* = 1:1 the intensity of fluorescence is practically independent of *pH* over the whole range investigated—this is illustrated in Figs. 1 and 2. In the presence of an excess of *EDTA* the intensity of both bands increases with increasing *pH* of the solutions, but the type of curve obtained depends on the Eu:*EDTA* ratio. For solutions with Eu:*EDTA* = 1:2 the intensity of fluorescence begins to increase appreciably when the *pH* reaches 7.5. For solutions with

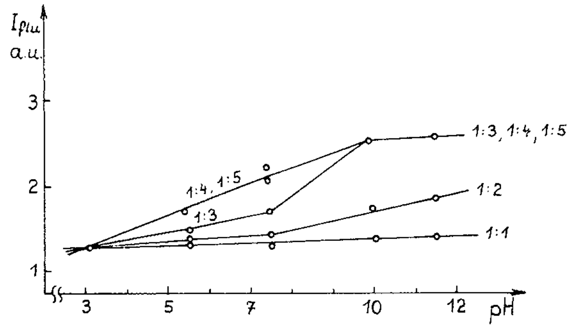

Fig. 1. The intensity of the fluorescence band at $\lambda = 590\,\text{nm}$ for Eu:*EDTA* = 1:1, 1:2, 1:3, 1:4 and 1:5 as a function of the *pH*

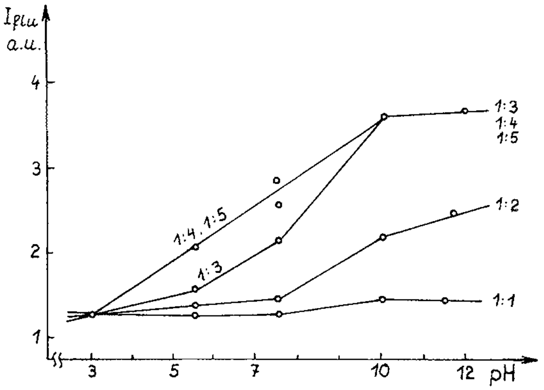

Fig. 2. The intensity of the fluorescence band at $\lambda = 615\,\text{nm}$ for Eu:*EDTA* = 1:1, 1:2, 1:3, 1:4 and 1:5 as a function of the *pH*

Eu:*EDTA* = 1:3, 1:4 and 1:5 the increase is already evident at *pH* = 5.5. The greatest rise in the fluorescence intensity is observed for *pH* values 7.5 to 10. When the *pH* increases further, from 10 to 11.5, the effect is only slight. The observed dependence of the fluorescence band intensities on the *pH* and complexone concentrations can be correlated with the different anionic forms of *EDTA* (H_4Y), with different dissociation constants[6]. Acidic solutions, *pH* = 3.0 and 5.5, contain a mixture of anions, $(HY)^{3-}$, $(H_2Y)^{2-}$ and $(H_3Y)^{-}$; at *pH* = 7.5 the $(HY)^{3-}$ form predominantes and at *pH* = 10.0 and above the ions $(HY)^{3-}$ and Y^{4-} are most important. Increasing concentrations of more highly charged negative ions constitute an important factor contributing to the increased intensity of the fluorescence bands.

Turning now to the changes in fluorescence intensity brought about by solution composition changes showed that for the Eu/*EDTA* system at $pH = 3.0$ the intensity increases with the proportion of *EDTA* for Eu:*EDTA* = 1:0, 1:0.5 and 1:1. Increasing the *EDTA* excess up to 5-fold has no further effect. For solutions at $pH = 10.0$ and 11.5 the fluorescence intensity reaches a steady level for an *EDTA* excess 3-fold and above. The fact that for Eu:*EDTA* = 1:1 the intensities of both fluorescence bands are virtually constant over the whole *pH* range investigated can be taken to indicate that only one form of the complex exists in solution—the most stable one, namely $(\mathrm{Eu}Y)^-$. If the complexone is in excess at $pH > 7.5$, the intensities of both fluorescence bands increase—this may be connected with the existence of new complex forms, e. g. $(\mathrm{Eu}Y_2\mathrm{OH})^{6-}$ (Refs.[3,7]).

For the Eu/*NTA* system, the fluorescence intensities are in general lower than for the Eu/*EDTA* system. Over the whole *pH* range investigated (3.0 to 11.5) the intensity of fluorescence is higher for higher proportions of *NTA* (Eu:*NTA* = 1:2 to 1:5 compared with 1:1). The results for the Eu/*NTA* system are shown in Figs. 3 and 4. For Eu:*NTA* = 1:1 and 1:2 there is only a slight increase in the $\lambda = 590$ nm band intensity when the *pH* rises from 3.0 to 11.5. For the remaining solutions (Eu:*NTA* = 1:3, 1:4, and 1:5), the intensity of this band increases when the *pH* rises from 3.0 to 5.5, but then remains constant when the solutions are made more alkaline. The intensity of the $\lambda = 615$ nm band also increases slightly for all solutions investigated over the *pH* range 3.0 to 5.5. Within this *pH* range the composition of the *NTA* (H_3X) solution changes, as can be inferred from the appropriate dissociation constants[6]. At $pH = 3.0$ two ionic forms $(\mathrm{H}X)^{2-}$ and $(\mathrm{H}_2X)^-$ as well as H_3X are present. At $pH = 5.5$ and 7.5 the ion $(\mathrm{H}X)^{2-}$ predominates, and above $pH = 10.0$ the X^{3-} ion. These ions have less effect on the intensities of the fluorescence bands than the ions derived from *EDTA*.

The intensities of both fluorescence bands increase in acid solutions (*pH* 3.0 and 5.5) as the proportion of *NTA* increases for Eu:*NTA* ratios 1:0, 1:0.5, 1:1, 1:2 and 1:3. Further increases in the *NTA* proportion have no effect. Strongly alkaline solutions ($pH = 10.0$ and 11.5) give constant fluorescence intensities when the excess of *NTA* is two-fold and greater.

The fact that the fluorescence is stronger when the excess of *NTA* is two-fold and greater (compared with the case Eu:*NTA* = 1:1) indicates that two different complex forms are present: at Eu:*NTA* = 1:1, $\mathrm{Eu}X$ and when the complexone is in excess, $(\mathrm{Eu}X_2)^{3-}$—and possibly also others.

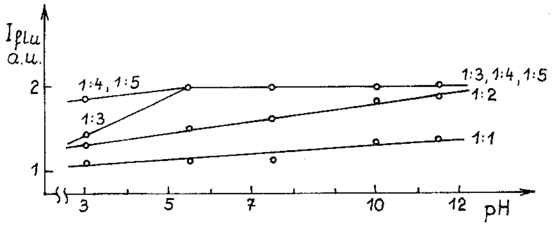

Fig 3. The intensity of the fluorescence band at $\lambda = 590$ nm for Eu:*NTA* = 1:1, 1:2, 1:3, 1:4 and 1:5 as a function of the *pH*

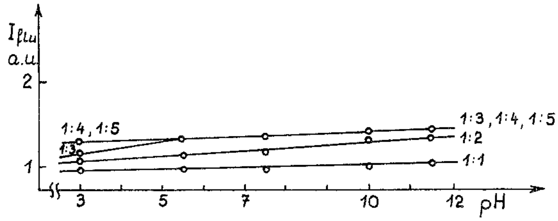

Fig. 4. The intensity of fluorescence band at $\lambda = 615$ nm for Eu:*NTA* = 1:1, 1:2, 1:3, 1:4 and 1:5 as a function of the *pH*

Comparing the two complexones, the intensity of the $\lambda = 615$ nm band increases more with *EDTA*, while the $\lambda = 590$ nm band is favoured by *NTA*. The $\lambda = 615$ nm band is a result of a hypersensitive transition $^5D_0$—$^7F_2$ $(\Delta J = 2)$ and the $\lambda = 590$ nm band is due to an allowed transition $^5D_0$—$^7F_1$ $(\Delta J = 0, \pm 1)$. Because both these bands arise as a result of vibronic coupling[8,9] connected with the influence exerted by the ligand field on the 4f orbitals of Eu, the important quantity is the intensity ratio for the $\lambda = 615$ nm and $\lambda = 590$ nm bands, $\eta = {}^5D_0$—$^7F_2/{}^5D_0$—$^7F_1$, which provides information about the intensity borrowing of these bands which is taking place. The present results have been used to calculate the values of η over the whole range of complexone concentrations and *pH* values employed—they have been collected in Table 1.

The fact that the η values are low indicates that interactions leading to vibronic coupling are weak for both types of complex. For Eu/*EDTA* complexes the values increase with increasing complexone excess and with rising *pH*. For Eu/*NTA* complexes they change only very slightly. The small changes of η for Eu/*EDTA* and its near constancy for Eu/*NTA* over a wide *pH* range indicate that the mechanism leading to a modification of the transition dipole moment which controls the

Table 1. *The ratio of the intensities of the* $\lambda = 615$ *nm and* $\lambda = 590$ *nm fluorescence bands of* Eu(III) *complexes*, $\eta = \frac{^5D_0 - ^7F_2}{^5D_0 - ^7F_1}$

Complex	Ratio Eu:complexone in solution			*pH*		
		3.0	5.5	7.5	10.0	11.5
Eu/*EDTA*	1:0.5	0.69	0.69			
	1:1	0.95	0.95	0.95	1.11	1.07
	1:2	1.00	1.04	1.11	1.40	1.47
	1:3	1.00	1.23	1.38	1.66	1.68
	1:4	1.00	1.47	1.67	1.70	1.78
	1:5	1.00	1.50	1.61	1.78	1.75
Eu/*NTA*	1:0.5	0.40	0.37			
	1:1	0.61	0.61	0.60	0.41	0.44
	1:2	0.59	0.54	0.51	0.51	0.48
	1:3	0.53	0.48	0.48	0.50	0.47
	1:4	0.47	0.54	0.53	0.54	0.52
	1:5	0.46	0.50	0.48	0.48	0.48

intensity changes of the bands is caused by dispersion interactions of the ligands. It should be noted that the η values for $EuCl_3$ (in the absence of complexones) are very low, ca. 0.1. In the presence of complexones, these values are appreciably lower when there is a deficiency of the complexone than when Eu:complexone = 1:1, or when the complexone is in excess.

Work on identifying the forms of Eu(III) complexes and determining their stabilities on the basis of fluorescence measurements of these complex solutions is being continued.

Acknowledgement

We are grateful to Dr. *J. Konarski* for helpful discussion and to Prof. Dr. *J. Koziol* for allowing us to use the spectrofluorimeter in his laboratory.

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