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Fluorescence properties of Eu^{3+}–polyacrylic acid derivative and its bimetallic complexes

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Abstract

The copolymer (PAAAB) of acrylic acid (AA) and *N*-acryloyl-*p*-aminobenzoic acid (AAB) was prepared by polymeric reaction. The fluorescence properties of the Eu^{3+}–PAAAB complex were investigated. The fluorescence intensity of Eu^{3+} in the Eu^{3+}–PAAAB complex is strongest when the Eu^{3+} content in the system is 8.0 wt.%, and exhibits concentration quenching with a further increase in Eu^{3+} content.

The fluorescence properties of the bimetallic complexes Eu^{3+}–copolymer–M (M ≡ Sr^{2+}, Co^{2+}, Tb^{3+}, Gd^{3+}, Nd^{3+}, Dy^{3+}, Er^{3+}) were also investigated in detail. Energy transfer occurs between the ions of the systems, i.e. from Gd^{3+} or Tb^{3+} to Eu^{3+} and from Eu^{3+} to Sr^{2+}, Co^{2+}, Nd^{3+}, Dy^{3+} or Er^{3+}. The fluorescence intensities are increased significantly in Eu^{3+}–copolymer–Gd^{3+} and Eu^{3+}–copolymer–Tb^{3+} systems and decreased in the other bimetallic systems.

Keywords: Bimetallic complexes; Eu^{3+}–PAAAB complex; Fluorescence properties

1. Introduction

The fluorescence properties of trivalent europium are of considerable interest with regard to energy transfer processes and the use of europium in laser systems [1–6]. The fluorescence properties of Eu^{3+}–polymer systems in which Eu^{3+} is directly bound to the polymer chain have been widely investigated in recent years because of their potential laser applications [7–9]. The effect of low molecular weight ligands on the fluorescence properties of Eu^{3+}–polyacrylic acid derivative has been investigated previously [10]. The copolymer of acrylic acid (AA) and *N*-acryloyl-*p*-aminobenzoic acid (AAB) was prepared, and the fluorescence properties of Eu^{3+}–copolymer were studied. The fluorescence properties of the bimetallic complexes Eu^{3+}–copolymer–M (M ≡ Co^{2+}, Sr^{2+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Er^{3+} or Nd^{3+}) were also investigated in detail.

2. Experimental details

2.1. Materials

Europia (Eu_2O_3) (99.99%) was purchased from Yue Long Chemical Factory, Shanghai, People's Republic of China, and used as received. $EuCl_3$ was prepared from Eu_2O_3 following the literature method [9]. Other monomeric materials were purchased from Beijing Chemical Factory, People's Republic of China.

2.2. *Poly(acrylic acid-co-N-acryloyl-p-aminobenzoic acid) (PAAAB)*

Acryloyl chloride, prepared according to the literature [11], was polymerized by the free radical initiator azoisobutyronitrile (AIBN) in dioxan (volume ratio of monomer to solvent, 1 : 1) at 50 °C under a nitrogen atmosphere for 12 h. The concentration of acryloyl chloride unit in the solution was 6.15×10^{-3} mol ml^{-1}.

A certain amount of the above solution was hydrolysed, hydrogen chloride was removed by bubbling with nitrogen, the solvent was evaporated and the molecular weight of poly(acrylic acid) (PAA) obtained was determined to be 2.7×10^5 by viscosity measurement.

PAAAB was synthesized by a method similar to that reported in Ref. [12]. The detailed preparation procedure was as follows. Poly(acryloyl chloride) solution (10 ml) was diluted with *N*,*N*-dimethylformamide (DMF) to 25 ml; 50 ml of DMF solution containing 16.87 g of *p*-aminobenzoic acid and 5 ml of pyridine was added with stirring and cooled in an ice bath. After 18 h of reaction, the mixture was poured into a large amount of water; the precipitate was filtered under

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Table 1
Relative fluorescence intensity (RFI) of Eu–PAAAB[a] complex prepared in different solvents at λ_{em} = 616 nm (λ_{ex} = 396 nm)

Solvent		$HCON(CH_3)_2$	H_2O
RFI	73.9	143.8	22.5

[a] Eu^{3+} content was 7.0 wt.% in Eu^{3+}–PAAAB system. Amount of AAB unit in the copolymer was 30.83 mol.%.

reduced pressure and washed with distilled water and ethyl ether several times. The polymer was dried and powdered by grinding.

The copolymer PAAAB containing different contents of AAB unit was obtained by using different molar ratios of *p*-aminobenzoic acid to polyacryloyl chloride, and was characterized by Fourier transform infrared (FTIR) spectroscopy, ^1H nuclear magnetic resonance (NMR) spectroscopy and elemental analysis [10].

2.3. Eu^{3+}-PAAAB-M complexes

The procedure was similar to the preparation of the Eu^{3+}–PAAAB complex [10]. An aqueous solution of a stoichiometric amount of a second metal ion was added to the complex in DMF solution; the mixture was heated at 80 °C with stirring for 8 h. The second metal ions were Co^{2+}, Sr^{2+}, Gd^{3+}, Tb^{3+}, Dy^{3+}, Nd^{3+} and Er^{3+}, which were obtained from their chlorides or nitrates.

2.4. Fluorescence measurements

A Hitachi model MPF-4 fluorescence spectrophotometer was used for the measurement of the fluorescence spectra of the complexes. Dried fine powder samples were used at room temperature.

2.5. Atomic absorption measurements

A Hitachi model 180-70 polarized Zeeman atomic absorption spectrophotometer was used for the measurement of Eu^{3+} atomic absorption.

3. Results and discussion

3.1. Selection of the solvent

In the preparation procedure of the Eu^{3+}–PAAAB complex, the solvents used had apparent effects on the fluorescence intensity of Eu^{3+} (Table 1). The results in Table 1 indicate that DMF is most suitable for sample preparation.

3.2. Chelate structure of the complexes

In order to obtain structural information on the Eu^{3+}–PAAAB complex, X-ray photoelectron spectroscopy (XPS) was used (Table 2).

By comparison of the binding energy (BE), it was found that $BE_{Eu3d5/2}$ in Eu^{3+}–PAAAB was 0.90 eV lower than that in $EuCl_3$, while BE_{O1s} and BE_{N1s} in the complex were 0.8 eV and 1.1 eV respectively higher than those in PAAAB. This shows that Eu^{3+} in the complex is coordinated by both N and O atoms.

The DMF solution of Eu^{3+}–PAAAB after reaction was poured into distilled water and the complex obtained was filtered. The filtrate residue was then ignited. Had the filtrate contained unreacted Eu^{3+}, then after ignition traces of Eu_2O_3 would have been in evidence. As this was not the case, it was evident that Eu^{3+} completely coordinated with PAAAB. Furthermore, the atomic absorption spectrum of the filtrate indicated no absorption of Eu^{3+}. This suggests that Eu^{3+} is completely coordinated with PAAAB, and the content of Eu^{3+} added to the PAAAB solution is equivalent to the content of Eu^{3+} in PAAAB–Eu^{3+}. As an example, XPS of Eu^{3+}–PAAAB–Tb^{3+} was performed (Table 2) in order to study the effect of addition of a second metal ion on the fluorescence properties of Eu^{3+} and the interaction between the ions in the bimetallic system Eu^{3+}–PAAAB–M. $BE_{Eu3d5/2}$ in Eu^{3+}–PAAAB–Tb^{3+} is 1.9 eV lower than that in $EuCl_3$, while BE_{Tb4d} is slightly higher than that in $TbCl_3$. This indicates that some interaction exists between Eu^{3+} and Tb^{3+}.

3.3. Effect of the content of Eu^{3+} in the complex on the fluorescence intensity of Eu^{3+}

As shown in Fig. 1, the fluorescence intensity of Eu^{3+} is strongly influenced by the Eu^{3+} content in the Eu^{3+}–PAAAB complex and reaches a maximum when the Eu^{3+} content is

Table 2
Binding energy (BE) of the samples

Sample	BE_{O1s} (eV)	BE_{N1s} (eV)	$BE_{Eu3d5/2}$ (eV)	BE_{Tb4d} (eV)
$EuCl_3$	–	–	1137.0	–
$TbCl_3$	–	–	–	158.2
PAAAB	532.2	400.1	–	–
Eu^{3+}–PAAAB	533.0	401.2	1136.1	–
Eu^{3+}–PAAAB–Tb^{3+}	–	400.5	1135.1	158.3

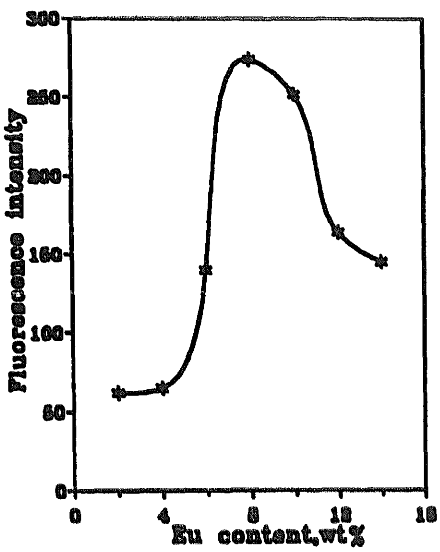

Fig. 1. Relationship between the fluorescence intensity of Eu^{3+} at 616 nm in PAAAB–Eu^{3+} and the Eu^{3+} content. The mole ratio of the nitrogen-containing unit in PAAAB was 45.4%.

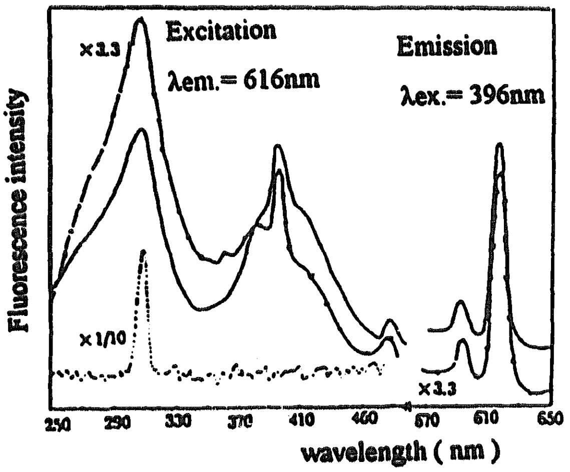

Fig. 2. Fluorescence spectra of Eu^{3+}–PAAAB (– × –), Eu^{3+}–PAAAB–Sr^{2+} (———) and Eu^{3+}–PAAAB–Co^{2+} (- - -).

8.0 wt.%. This result shows that the Eu^{3+}–PAAAB complex contains ionic aggregates in which the metal ions are aggregated together, so that the local concentration of Eu^{3+} ions in these regions is much higher than the overall average concentration. Eu^{3+} is uniformly bound to the copolymer at lower Eu^{3+} content; the fluorescence intensity of Eu^{3+} increases with increasing Eu^{3+} content and reaches a maximum at an Eu^{3+} content of 8.0 wt.%, which is the critical concentration at which Eu^{3+} ions begin to form ionic aggregates. As soon as ionic aggregates are formed, non-radiative energy transfer between Eu^{3+} ions can occur. Thus the fluorescence intensity of Eu^{3+} subsequently decreases with a further increase in Eu^{3+} content; this is a typical concentration quenching pattern.

3.4. Fluorescence properties of Eu^{3+}–PAAAB–M complexes

The fluorescence spectra of Eu^{3+}–PAAAB–M (M ≡ Sr^{2+}, Co^{2+}) are shown in Fig. 2. Compared with the Eu^{3+}–PAAAB complex, the excitation peaks at 379 and 396 nm of Eu^{3+} in Eu^{3+}–PAAAB–Sr^{2+} are reduced; this is more remarkable in Eu^{3+}–PAAAB–Co^{2+}. This indicates that the addition of Sr^{2+} or Co^{2+} to Eu^{3+}–PAAAB facilitates the quenching action of the fluorescence of Eu^{3+}. Fig. 3 shows the relationship between the fluorescence intensity of Eu^{3+} in Eu^{3+}–PAAAB–Sr^{2+} (Co^{2+}) and the Sr^{2+} (or Co^{2+}) content in the system. The fluorescence intensity of Eu^{3+} in Eu^{3+}–PAAAB–Sr^{2+} decreases linearly with increasing Sr^{2+} content, whereas the fluorescence intensity of Eu^{3+} in Eu^{3+}–PAAAB–Co^{2+} decreases exponentially with increasing Co^{2+} content and almost disappears at 2–10 wt.% Co^{2+}.

Although the lanthanide metal ions Nd^{3+}, Gd^{3+}, Tb^{3+}, Dy^{3+} and Er^{3+} have a similar outer shell electronic structure, ionic diameter and certain physicochemical properties to Eu^{3+}, their fluorescence in complexes with PAAAB is very weak (except that Tb^{3+} exhibits strong fluorescence at 545 nm), and the effects of these ions on the fluorescence properties of Eu^{3+} in the complexes are very different (Fig. 5, see below).

The fluorescence excitation spectra of Eu^{3+} in Eu^{3+}–PAAAB–Tb^{3+} and Eu^{3+}–PAAAB are shown in Fig. 4. It can be seen that the fluorescence intensity of Eu^{3+} in the former is higher than that in the latter, while the fluorescence intensity of Tb^{3+} in Eu^{3+}–PAAAB–Tb^{3+} is lower than that in Tb^{3+}–PAAAB (Fig. 4). The results show that energy transfer from Tb^{3+} to Eu^{3+} exists and the fluorescence intensity of Eu^{3+} increases. It can also be seen in Fig. 4 that the shape and position of the peaks of the two spectra of Eu^{3+} in Eu^{3+}–PAAAB and Eu^{3+}–PAAAB–Tb^{3+} are almost the same. This may suggest that energy transfer between Tb^{3+} and Eu^{3+} is probably a non-radiative transfer process.

The effect of the content of the second metal ion on the fluorescence intensity of Eu^{3+} is shown in Fig. 5. Fig. 5

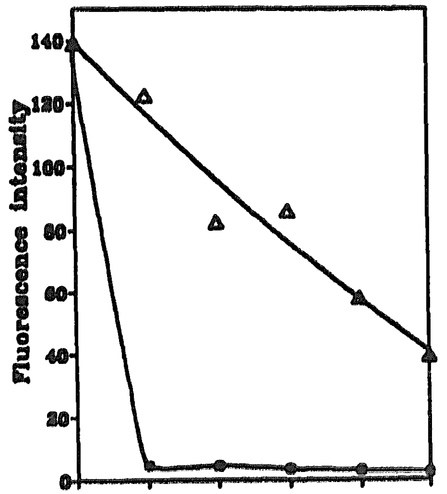

Fig. 3. Fluorescence intensity of Eu^{3+} vs. Co^{2+} (– · –) and Sr^{2+} (– Δ –) content in Eu^{3+}–PAAAB–M^{2+}. For Eu^{3+}–PAAAB–Co^{2+}, the fluorescence intensity was at 616 nm/309 nm, and for Eu^{3+}–PAAAB–Sr^{2+}, it was at 616 nm/396 nm (Eu^{3+} content, 7.0 wt.%).

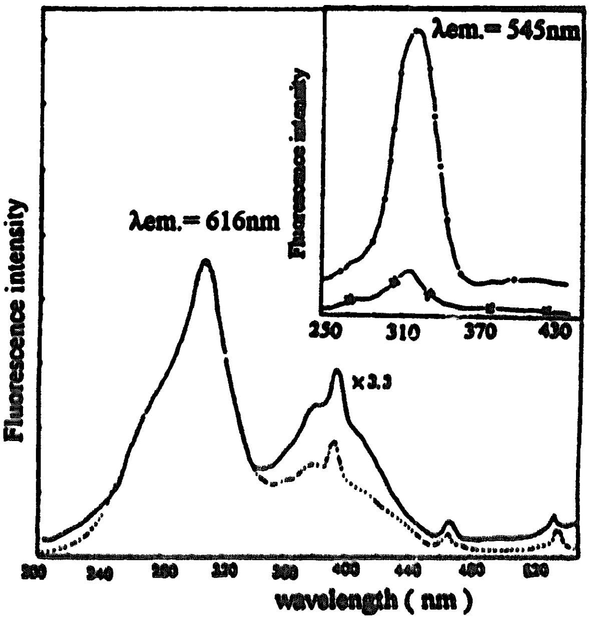

Fig. 4. Fluorescence excitation spectra of Eu^{3+} in Eu^{3+}–PAAAB–Tb^{3+} (——) and Eu^{3+}–PAAAB (- - -), and of Tb^{3+} in Eu^{3+}–PAAAB–Tb^{3+} (– × –) and Tb^{3+}–PAAAB (– · –).

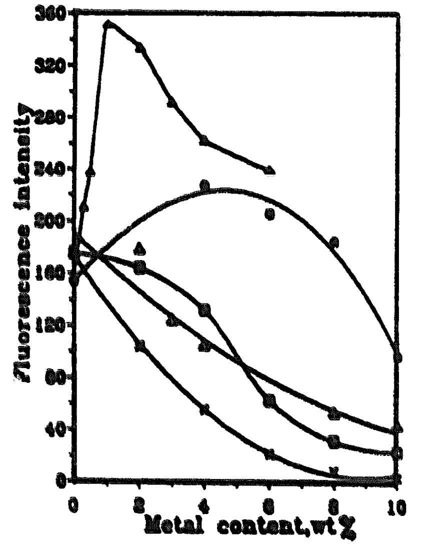

Fig. 5. Relationship between the metal content and fluorescence intensity of Eu^{3+} in Eu^{3+}–PAAAB–M at λ_{em} = 616 nm. The Eu^{3+} content in the systems was 7.5 wt.%. The mole ratio of AAB in PAAAB was 30.83%. – · –, Tb; – △ –, Dy; – □ –, Er; – × –, Nd; – ▲ –, Gd.

shows that the fluorescence intensity of Eu^{3+} is reduced with increasing second ion content in Eu^{3+}–PAAAB–Dy^{3+} (Er^{3+},Nd^{3+}) to a certain extent. This suggests that energy transfer from Eu^{3+} to Dy^{3+}, Er^{3+} or Nd^{3+} exists, and these ions exhibit quenching effects on the fluorescence of Eu^{3+}. In contrast, Gd^{3+} and Tb^{3+} may enhance the fluorescence intensity of Eu^{3+} in the bimetallic systems to different degrees, i.e. energy transfer from Gd^{3+} or Tb^{3+} to Eu^{3+} exists in these complexes. Eu^{3+} exhibits a maximum fluorescence intensity vs. the Gd^{3+} or Tb^{3+} content. This suggests that ionic aggregates exist in both Eu^{3+}–PAAAB–Gd^{3+} and Eu^{3+}–PAAAB–Tb^{3+}. Unlike the single metal system of Eu^{3+}–PAAAB, in which the ionic aggregates are formed only by Eu^{3+}, the ionic aggregates are composed of both Eu^{3+} and Gd^{3+} (or Tb^{3+}) in the bimetallic systems.

The energy transfer from Tb^{3+} to Eu^{3+} in Eu^{3+}–PAAAB–Tb^{3+} occurs at low Tb^{3+} contents. Thus the fluorescence intensity of Eu^{3+} increases with increasing Tb^{3+} content, and reaches a maximum at a Tb^{3+} content of 4.0 wt.%; at this content, the two energy transfer processes between Eu^{3+} and Tb^{3+} and Tb^{3+} and Tb^{3+} are balanced. With a further increase in Tb^{3+} content, the fluorescence intensity of Eu^{3+} decreases gradually, because the energy transfer between Tb^{3+} and Tb^{3+} is more dominant than that between Eu^{3+} and Tb^{3+}. The fluorescence intensity of Eu^{3+} in Eu^{3+}–PAAAB–Gd^{3+} shows a similar tendency. From the curves, it seems that the efficiency of energy transfer from Gd^{3+} to Eu^{3+} is higher than that from Tb^{3+} to Eu^{3+}.

In order to obtain further information about the efficiency of energy transfer in the bimetallic complexes, the relationship between the fluorescence intensity of Tb^{3+} at 545 nm and the Tb^{3+} content in Eu^{3+}–PAAAB–Tb^{3+} is shown in Fig. 6. The fluorescence intensity of Tb^{3+} in Eu^{3+}–PAAAB–Tb^{3+} is strongly decreased compared with that of Tb^{3+} in Tb^{3+}–PAAAB at the same Tb^{3+} content. The maximum fluorescence intensity of Tb^{3+} in Eu^{3+}–PAAAB–Tb^{3+} is only 40% of that in Tb^{3+}–PAAAB. The results support the fact that energy transfer from Tb^{3+} to Eu^{3+} exists in Eu^{3+}–PAAAB–Tb^{3+}. Moreover, the Tb^{3+} content at which the fluorescence intensity of Tb^{3+} reaches a maximum is 6.0 wt.% in Tb^{3+}–PAAAB and 8.0 wt.% in Eu^{3+}–PAAAB–Tb^{3+}. This confirms the result that the energy transfer from Tb^{3+} to Eu^{3+} is more dominant than that from Tb^{3+} to Tb^{3+}

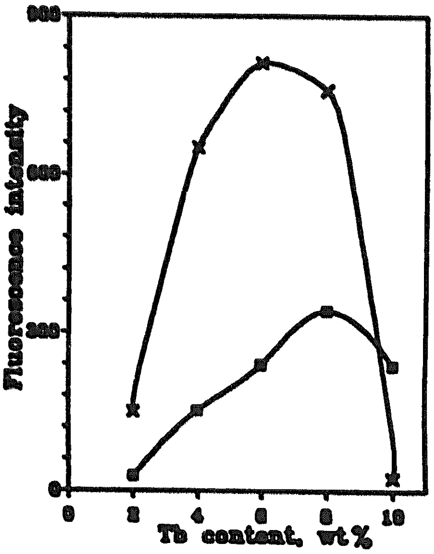

Fig. 6. Relationship between the Tb^{3+} content and fluorescence intensity of Tb^{3+} at 545 nm in Tb^{3+}–PAAAB (– × –) and Eu^{3+}–PAAAB–Tb^{3+} (– ■ –) (Eu^{3+} content, 7.5 wt.%). The mole ratio of AAB in PAAAB was 30.83%.

in Eu^{3+}–PAAAB–Tb^{3+} at low Tb^{3+} contents. From Fig. 5, it can be seen that Dy^{3+}, Nd^{3+} and Er^{3+} facilitate the quenching of the fluorescence of Eu^{3+} to different extents; the fluorescence intensity of Eu^{3+} decreases with increasing content of the ions.

4. Conclusions

Eu^{3+} ionic aggregates exist in the Eu^{3+}–PAAAB system at an Eu^{3+} content of 8.0 wt.% at which the fluorescence intensity of Eu^{3+} reaches a maximum. In ternary complexes of Eu^{3+}–PAAAB–M ($M \equiv Sr^{2+}$, Co^{2+}, Dy^{3+}, Er^{3+} or Nd^{3+}), the second ion has a strong quenching effect on the fluorescence of Eu^{3+}. There is energy transfer from Gd^{3+} or Tb^{3+} to Eu^{3+} in Eu^{3+}–PAAAB–Gd^{3+} (Tb^{3+}); the fluorescence intensity of Eu^{3+} increases in both systems.

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