Synthesis and Characterization of Cellulose Ethers/Eu(III)

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ABSTRACT: The coordination complexes of the crystalline structure of cellulose ethers/Eu(III) with fluorescence emission, viz CMC/Eu(III), MC/Eu(III), and HEC/Eu(III), were synthesized and characterized. Results showed the emission spectra of Eu^{3+} ions in these coordination compounds, which originates from electric dipole transition. The main emission peak at 615 nm generated from $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{3+} ions. Their absorption and excitation spectra were different, because the effect of the high polarity of water and having both hydrogen bond donor and acceptor properties on the excited molecule is different from the effect on the ground state of the molecule. Our study demonstrated that the Degree of Substitute (DS) of CMC could influence the fluorescence intensity (FI) of CMC/Eu(III). The emission intensity of CMC/Eu(III) varies with the DS of CMC. For example, when the DS of CMC was 0.89, the FS (fluorescent spectra) of solid CMC/Eu(III) displayed three emission peaks Eu(III): the strongest emission peak at 615 nm ($^5D_0 \rightarrow {}^7F_2$ transition) and other two weaker peaks at 583 nm ($^5D_0 \rightarrow {}^7F_1$ transition) and at 652 nm ($^5D_0 \rightarrow {}^7F_3$ transition), respectively. The concentration of Eu(III) could also affect the FI of these coordination complexes. The FI of the coordination complexes peaked at 615 nm all reached maximum when Eu^{3+} concentration was at 5% (wt/wt). © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 95: 743–747, 2005

Key words: cellulose derivatives; Eu^{3+}; coordination complex; emission spectrum; fluorescence

INTRODUCTION

Cellulose is a chain-like extended linear macromolecule with β-D-glucopyranose units linked by 1,4-glycosidic bonds. The study of cellulose has attracted more and more attention due to its renewable, biodegradable, and biocompatible features. As a polyfunctional alkoxido ligand, cellulose can be used to prepare compounds with optical, electrical, magnetic, or catalytic properties.[1] In the 1980s, Okamoto and coworkers investigated the preparation, characterization, and applications of polymers containing lanthanide–metal ions.[2–5] They observed strong circularly polarized luminescence in the carbxymethylcellulose (CMC)–Tb complexes.[2] As the most important and widely applied cationic ether of cellulose, CMC and other water-soluble ethers of cellulose, including methyl- and hydroxyethyl-cellulose, have attracted considerable attention due to their excellent solution properties and potentially practical applications.[6–8] Especially, fluorescence labeling technique has proved to be available in the investigation of structure of hydrophobically modified cellulose in solution.[9–14] To prepare coatings for specialized paper, we initiated the study on the fluorescence property of Eu salts of water-soluble ethers of cellulose. A series of water-soluble cellulose ethers, including CMC, methyl cellulose (MC), and hydroxyethyl cellulose (HEC), were combined with Eu^{3+} ion to form coordination complexes. The structures of these complexes have been characterized by using FTIR and WAXD and their fluorescence features were investigated.

EXPERIMENTAL

Materials

CMCs (DS = 0.48, 0.67, 0.89, 1.20, 1.56, 2.0, and 2.4, respectively) and HEC were kindly provided by the Laboratory of Cellulose and Lignocellulosics Chemistry, Academia Sinica.

MC (DP = 450, viscosity: 350 ~ 550 cP) was purchased from Pingsha Chemical factory in Kunshan City.

Details of the preparative method

$EuCl_3 \cdot 6H_2O$ solution (A). Eu_2O_3 (2.0800 g) was dissolved in HCl/H_2O solution (1 : 1) and then the solution was diluted in 100-mL volumetric flask.

$EuCl_3$ alcohol solution (B). Eu_2O_3 (2.0800 g) was dissolved in 6 mol HCl aqueous solution. $EuCl_3$ dry powder was first obtained by evaporating the aqueous solution and then dissolved in 100 mL 95% alcohol solution.

CMC(HEC, MC)/Eu(III). The solution A (0.5 mL) was dropped into CMC or HEC or MC (0.0853 g) aqueous

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solutions, respectively. After stirring and refluxing the mixture for 24 h, either the white solids of these coordination compounds were obtained by rotatory evaporating and dried in vacuum or the aqueous solutions of these coordination compounds were obtained by dilution as described above.

Characterization of the coordination complexes

2θ Scanning diffraction curves ranging from 0 to 60° were recorded at room temperature with a Rigaku D/MAX-1200 X-ray diffractometer. The incident X-ray was Cu Kα with a power of 40 kV, 25 mA, passed through a nickel filter.

An Aralect RFX-65 FTIR Spectrometer was used. The studied samples were dried and cut to a powder. The powder samples were mixed with KBr and were pressed, respectively, to form a pellet to be used as the FTIR analysis sample.

UV-Vis absorption spectra of the samples were measured with a UV-2201 UV-Vis Recording Spectrophotometer (Shimadzu).

FS and fluorescence excitation spectra were recorded with a Shimadzu RF5001 PC spectrofluorometer. The fluorescence spectra were taken with excitation at 423 or 310 nm and a bandwidth of 3 nm on both the excitation and the emission sides.

RESULTS AND DISCUSSION

Analyses of WAXD and FTIR spectra of these coordination compounds

Figure 1 shows WAXD curves of water-soluble cellulose/Eu(III). It is clear that they have a high crystalline structure. The crystalline structure of CMC/Eu(III) is hexahedron. Crystallinities of these coordination compounds are higher than those of their ligands, and their insolubility in aqueous solution and many organic solvents are also higher than that of their ligands. By the Scherrer equation: ($L_{hkl}=K\lambda/\beta_{n0}\cos\theta$), crystalline sizes of CMC/Eu(III), MC/Eu(III), and HEC/Eu(III) were calculated to be 27.51, 27.51, and 28.74 nm, respectively.

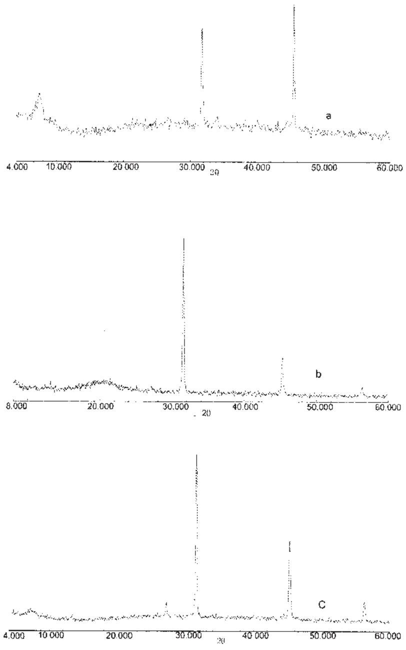


Figure 1 WAXD of CMC/Eu(III), (HEC/Eu(III), and MC/Eu(III). (a) HEC/Eu(III); (b) MC/Eu(III); (c) CMC/Eu(III).

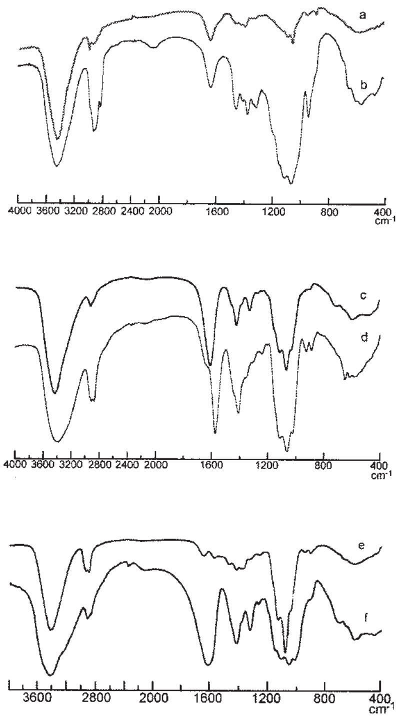


Figure 2 FTIR of CMC/Eu(III), MC/Eu(III), and HEC/Eu(III). (a) MC; (b) MC/Eu(III); (c) HEC/Eu(III); (d) HEC; (e) CMC/Eu(III); (f) CMC.

FTIR spectra of CMC/Eu(III), MC/Eu(III), and HEC/Eu(III) are shown in Figure 2. In curve (e), –COO$^-$ groups were detected as bands at 1,409 cm^{-1}(ν_s) and 1,565 cm^{-1}(ν_{as}), with the result that CMC/Eu(III) is a saltlike substance; in other words, the bonding forces of CMC/Eu(III) could be treated mainly as electrostatic interactions.[2]

In comparison with curve (d) in Figure 2, curve (c) showed no change at 1,162 cm^{-1} ($\nu_{\text{as}\,C_5-O-C}$) and 1,110 cm^{-1} ($\nu_{\text{as}\ C\text{–}C}$), suggesting the oxygen in C_5–O may not form coordinate bonds with Eu^{3+} in HEC/Eu(III) at all. However, there were some obvious differences at 1,200 ~ 1,500 cm^{-1} (the stretching motion of the –OH group) and a band at 885 cm^{-1} (the stretching motion of –CH_2CH_2OH), completely absent in the spectrum of HEC. These indicated the formation of coordination bonds between Eu^{3+} and oxygen within –CH_2CH_2OH rather than within the anhydroglucose unit of cellulose.

Comparing curve (a) with curve (b), all bands involving ether and aldehyde acetal groups within MC

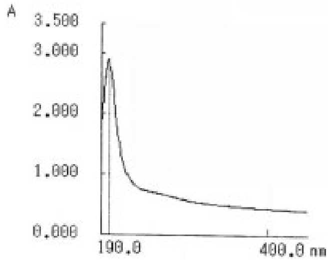


Figure 3 UV-Vis spectra CMC/Eu(III). $C = 4.0 \times 10^{-4}$ g/mL, at room temperature.

changed greatly. This demonstrated that Eu^{3+} forms complexes with the oxygen ligands within both ether and aldehyde acetal groups.

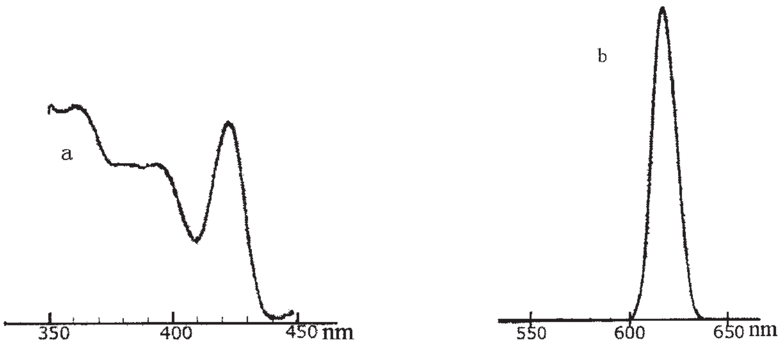
Absorption and fluorescent spectra (FS) of these complexes

In UV-Vis absorption spectra, we observed absorption bands of the coordination compounds of CMC (MC, HEC)/Eu(III), in particular CMC/Eu(III) displayed the strongest band at 190 nm wavelength (Fig. 3). The absorption bands of MC/Eu(III) and HEC/Eu(III) were weaker at about 202 nm.

CMC/Eu(III) is a polar molecule in capable of hydrogen bonding, and water is a solvent of high polarity and having both hydrogen bond donor and acceptor properties. In the ground state the molecule has a solvent cage in which the positive ends of the solvent dipoles will be oriented toward the negative ends of the solute dipole and the negative ends of the solvent dipoles toward the positive ends of the solute dipole. Positively polarized hydrogen atoms of water may be oriented toward lone pairs on the CMC, and acidic hydrogen atoms of the CMC may be oriented toward lone pairs on the water. The solvent cage is in thermal equilibrium with the ground state electronic distribution of the solute. The light absorption process alters the electronic distribution of the solute so that the electronic dipole movement of the excited molecule is different from that of the ground state molecule.

Usually absorptive transitions are more affected by hydrogen bond donor properties of the solvent than by solvent polarity. If a nonbonding pair on the –COOH groups of CMC is bound by a hydrogen atom of water, the hydrogen bonding interaction stabilizes the ground state. Hydrogen bonding solvent also produces a dramatic effect upon intramolecular charge-transfer absorption. Hydrogen bond donors of water interact with functional groups (COOH) that are charge-transfer acceptors in the excited state, enhancing charge-transfer by introducing a partial positive charge into the charge-transfer acceptor group.[15] Finally, solvation of hydrogen atoms on COOH groups, which are charge-transfer acceptors in the excited state, inhibits charge-transfer by leaving a residual negative charge on the functional group. This interaction results in shifting of the absorption spectrum to shorter wavelengths. As a result, there is a great difference between the absorption spectrum and excitation spectrum of CMC/Eu(III) [Figs. 3 and 4(a)].

The emission intensity of aquo lanthanide ions is normally quite weak since the coordinated water molecules serve as efficient quenchers of the luminescence. Coordination of a Eu(III) ion by a water-soluble cellulose ether molecule, especially a polyelectrolyte molecule, like a CMC molecule, would result in the expulsion of some or all of the coordinated water molecules and will yield an enhancement in the Eu(III) emission intensity, a phenomenon that has clearly been demonstrated in Table I. It is clear from Table I that the emission of CMC/Eu(III) was the strongest of all and the emission spectra of these coordination compounds all contain emission of Eu^{3+} belonging to electric dipole transition. The main peak at 615 nm was generated from the $^5D_0 \rightarrow {}^7F_2$ transition. In this study, when the DS of CMC was 0.89, there were two other weaker emission peaks at 583 and 652 nm for CMC/Eu(III) in solidity, respectively. The two peaks refer to the magnetic dipole moment transition of



(a) Excitation spectrum, λ_{Em}=615nm; **(b)** Emission spectrum, λ_{Ex}=420nm

Figure 4 FS of CMC/Eu(III) in aqueous solution. $C = 3.2 \times 10^{-3}$ g/mL, pH 6, at room temperature.

TABLE I
Luminescence Characteristics of the Cellulose Derivatives/Eu(III)

	λ_{Ex} (nm)	λ_{Em} (nm)/ Fl	Concentration
CMC/Eu(III)	420	618/90.0	3.2×10^{-3} g/mL (aq)
HEC/Eu(III)	310	618/38.0	3.32×10^{-3} g/mL (aq)
MC/Eu(III)	420	618/42.0	3.32×10^{-3} g/mL (aq)

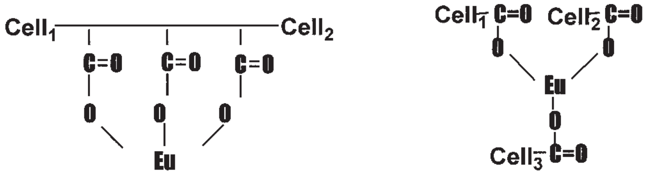
All Eu(III) contents of coordination compounds are 5% (wt : wt) DS of CMC ≠ 0.89; at room temperature.

$^5D_0 \rightarrow {}^7F_1$ for 583 nm and the electric dipole transition $^5D_0 \rightarrow {}^7F_3$ for 652 nm, respectively.

Structures of the coordination complexes

Owing to electrostatic effect, CMC is an equilibrium state in an aqueous dilute solution, in which the distance between the CMC molecular chains is longer and the intermolecular interaction is weak. When Eu^{3+} was added into the solution mentioned above, the CMC molecular chain configuration/conformation and properties would change. Initially, the electrobalance of the solution was broken down and the CMC molecular chains tended to curve. When the Eu(III) bound to carboxylate groups on the CMC chain, the binding sites were at random.[2,16] So the structure of CMC/Eu(III) would be like that shown in Figure 5(a). Random binding of Eu(III) ions to the CMC chains would not be expected to yield strong emission, as the chiralities of the many sites could partially cancel out each other. In contrast, when the solution was heated, the CMC chain motion accelerated and the distance between CMC chains became shorter. Hence, reactions between Eu^{3+} and –COOH groups of intermolecules occur more easily.[16] In other words, the structure of CMC/Eu(III) as shown in Figure 5(b) would be easier to form.

The functional groups on MC and HEC differ from those on the CMC. As a result of electrostatic interactions in CMC/Eu(III), curve (e) is obviously different from curves (b) and (c) (Fig. 2). It appears that the presence of carboxylate groups in the CMC chain produces well-defined binding sites for the Eu(III) ions, and these sites are very chiral. The electrostatic effect has an advantage over intermolecular energy transition,[2] enhances intra- and intermolecular forces, and increases the rigidity of the CMC/Eu(III). Therefore, it explains why the emission intensity of CMC/Eu(III) is the strongest in these complexes (Table I).



(a) (b)

CMC=Cell-COOH

Figure 5 Structures of CMC/Eu(III) in aqueous solution.

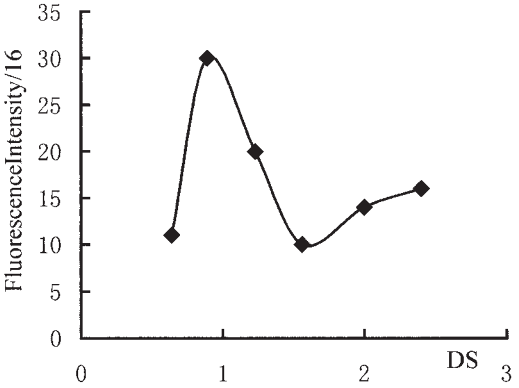


Figure 6 The relationship between fluorescence intensity and DS. λ_{Em} = 615 nm, λ_{Ex} = 394 nm.

Some effects on FS of the coordination compounds

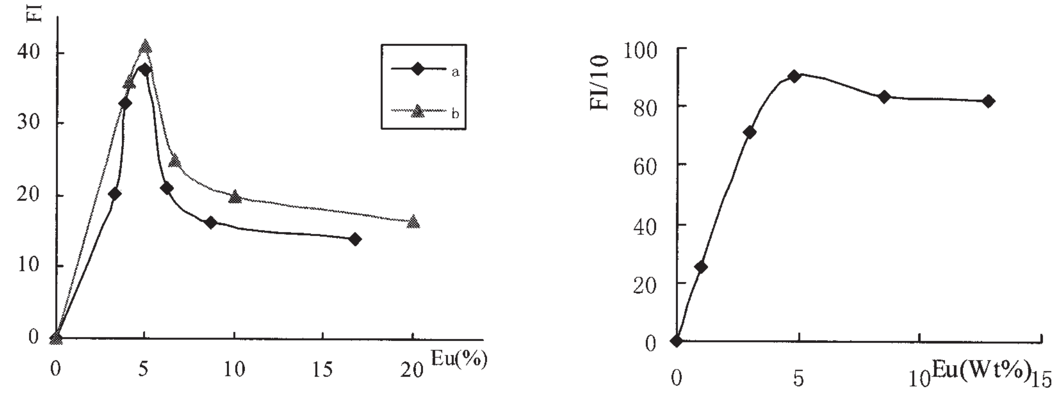
The emission intensity of the Eu(III) species at 615 nm was monitored, yielding the maximum value plotted as shown in Figure 6.

The fluorescence properties of the cellulose ethers were apparent. When DS was different, their CMC/Eu(III) would display different FIs. For example, when DS was 0.89, the FI of CMC/Eu(III) in solid state reaches maximum (Fig. 6). However, the viscosity of CMC showed little effect on the FI of the coordination compounds.

To further investigate the effects of Eu(III) concentration on the emission intensity of cellulose water-soluble ethers/Eu(III) complex system, we measured these complexes' PL spectra with a small range of Eu(III) concentrations (0–5%) and found that the fluorescence intensity increased with increasing Eu(III)concentration. The FI reached a maximum at 5%, and then decreased with a further increase of Eu(III) concentration (Fig. 7). This dependence of fluorescence intensity on increasing Eu(III) content/concentration is a typical fluorescence-quenching pattern[17] and this result provides the evidence that the coordination compounds have ionic aggregates in which metal ions are close together. In other words, the local concentration of the Eu(III) ion in these regions is much higher than the overall aqueous concentration. A similar trend of CMC/Eu(III) in solid state was also observed.

CONCLUSION

Our study demonstrates the formation of the coordination complexes of cellulose water-soluble ethers/



MC/Eu(III), HEC/Eu(III) in aqueous solution
a: HEC/Eu(III), $c=3.32\times10^{-3}$g/mL;
b: MC/Eu(III), $c=3.32\times10^{-3}$g/mL
at room temperature; λ_{Ex}=420nm, λ_{Em}=618nm

CMC/Eu(III) in solidity
at room temperature, D.S of CMC=0.89,
Ex=615nm, λ_{Ex}=394nm

Figure 7 The relationship between FI and the content of Eu^{3+}.

Eu(III) with fluorescence emission. They have a crystalline structure. The emission spectra of these coordination compounds consist of emission of Eu^{3+} in an electric dipole transition. The main peak of 615 nm is originated from the $^5D_0 \rightarrow {}^7F_2$ transition. The property of the ethers and the contents of Eu(III) can influence the fluorescence spectra and intensity.

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