Adsorption of Eu^{3+} to smectites and fluoro-tetrasilicic mica

By

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ABSTRACT

The adsorption of Eu^{3+} from aqueous solution to natural Na^{+}-montmorillonite (Kunipia F), synthetic saponite (Sumecton SA) and synthetic fluoro-tetrasilicic mica (Na^{+}-TSM) clay samples was investigated. Adsorption capacities derived from the isotherms were, respectively, 1.02, 0.71 and 1.00 meq / g clay for Kunipia F, Sumecton SA and Na^{+}-TSM. The adsorption capacities were comparable to the cation exchange capacities of the clays, which were, respectively, 1.19, 0.71 and 0.94 meq / g clay. The greater slope of the TSM adsorption isotherm relative to the montmorillonite and saponite isotherms indicates a high affinity of Eu^{3+} for Na^{+}-TSM. The high affinity of TSM for Eu^{3+} was thought to be related to the large electronegativity of the octahedral fluorine groups in TSM. Photoluminescence of adsorbed Eu^{3+} was observed for

saponite and TSM, but not for montmorillonite. Quenching of Eu^{3+} luminescence by iron in the montmorillonite structure is the probable reason for this phenomenon. The luminescence intensity varied with the amount of adsorbed Eu^{3+} for saponite and TSM as a result of self-quenching.

Key Words, Adsorption, Europium (III) ion, Kunipia F, Montmorillonite, Sumecton SA, Synthetic saponite, Fluoro-tetrasilicic mica, Photoluminescence

INTRODUCTION

Adsorption of Eu^{3+} onto layered silicates such as natural hectorite (Bergaya and van Damme, 1983), natural montmorillonite (Bergaya and van Damme, 1983; Takahashi, et al., 1998; Bradbury and Baeyens, 2002; Coppin, et al., 2002; Stumph, et al., 2002; Rabung et al., 2005; Okada et al., 2006) and synthetic magadiite (Mizukami et al., 2002) through cation exchange reactions. The luminescence properties of the resulting Eu^{3+} exchanged layered silicates have been investigated for the basic understanding of the host-guest interactions. It has been pointed out that the iron in a natural montmorillonite quenched the luminescence of Eu^{3+} (Bergaya and van Damme, 1983). On the other hand, relatively intense luminescence has been observed for the magadiite system partly due to the absence of iron in the silicate layer (Mizukami et al., 2002). Based on the variation of luminescence intensity as a function of the adsorbed amount, the interlayer spatial distribution of Eu^{3+} is proposed to affect luminescence intensity (Mizukami et al., 2002). Recently, Eu^{3+}-montmorillonite was successfully used as an adsorbent with luminescence detection ability for 4-nonylphenol (Okada et al., 2006). The adsorptive and sensing properties of various rare earth ions adsorbed layered materials is worth further investigating to optimize materials' performance. In the present study, the adsorption and the photoluminescence of Eu^{3+} on smectites (a natural montmorillonite [Kunipia F], a synthetic saponite [Sumecton SA]) and synthetic fluoro-tetrasilicic mica (Na^{+}-TSM) were investigated.

Kunipia F and Sumecton SA have extensively been investigated for the construction of clay-based advanced materials (Ogawa and Kuroda, 1995; Ogawa and Kuroda, 1997; Shichi and Takagi, 2000; Ogawa, 2004). It has been note that the Kunipia F and Sumecton SA smectites behaved differently. This has been shown by differences in the catalytic activity (Urabe et al., 1988), the adsorption of phenols

(Okada and Ogawa, 2003; 2004; Okada et al., 2005ab), separation efficiency for optical resolution of a racemic mixture (Nakamura et al., 1988) and the aggregation of a cationic cyanine dye after adsorption (Ogawa et al., 1996; Miyamoto et al., 2000). The differences have been ascribed to such factors as surface layer charge density (Nakamura et al., 1988; Ogawa et al., 1996; Okada and Ogawa, 2003; 2004; Okada et al., 2005ab) and the location of isomorphous substitution (Urabe et al., 1988; Ogawa et al., 1996). In contrast, there is no report on the effect of structural differences on metal ion adsorption behavior.

Na^+-TSM ($Na_2Mg_{2.5}Si_4O_{10}F_2$ (Kitajima and Daimon, 1975; Kitajima et al., 1976; Soma et al., 1990) exhibits swelling, ion exchange and adsorptive properties similar to those of smectites. Since Na^+-TSM does not contain $Fe^{2+/3+}$, some applications as photofunctional materials *(i.e. photoinduced electron-transfer reactions)* have been investigated (Ogawa, et al., 1993; Ogawa et al., 2000; Kakegawa and Ogawa, 2005). The negative charge of Na^+-TSM is derived from octahedral lattice site defects and is not due to isomorphous substitution. The hydroxyl groups in the octahedral sheet in smectites is replaced by fluorine in Na^+-TSM. The difference in the structure of Na^+-TSM relative to the smectites was expected to result in different Eu^{3+} adsorption characteristics.

EXPERIMENTAL

Materials

Na^+-montmorillonite (Kunipia F, supplied by Kunimine Ind. Co., obtained from Aterazawa mine, Yamagata, Japan) and synthetic Na^+-saponite (Sumecton SA, supplied by Kunimine Ind. Co., synthesized by a hydrothermal reaction) are reference clay samples of the Clay Science Society of Japan and were used as received. Na^+-TSM (supplied by Topy Ind. Co.) was used after removing non-expandable impurities by a dispersion-sedimentation method. The chemical compositions of these host materials are summarized in Table 1. Cation exchange capacities (CECs) of Na^+-montmorillonite, Na^+-saponite and Na^+-TSM are 1.19, 0.71 and 0.94 meq / g clay, respectively (Ogawa et al., 1992). Europium (III) trichloride hexahydrate (> 99.99 %) was purchased from Aldrich Co. and was used as received.

(Insert Table 1)

Cation exchanges

Samples of Na^+-clays (0.1 g) were allowed to react with 50-mL aliquots of $EuCl_3$ solution (pH ≈ 5) in 50-mL of polypropylene vessels for 1 day at room temperature. The initial concentrations of aqueous $EuCl_3$ solution were in the range of 0.01 to 2.0 times as large as CECs (7.9×10^{-3} ~ 1.6 mmol L^{-1} for Kunipia F, 4.7×10^{-3} ~ 9.5×10^{-1} mmol L^{-1} for Sumecton and 6.5×10^{-3} ~ 1.3 mmol L^{-1} for Na^+-TSM). Blank samples containing 50-mL of $EuCl_3$ solution, without adsorbents, were also prepared to estimate vaporization losses of solvents and the adsorption of Eu^{3+} on the polypropylene vessel. The resulting solids were separated by centrifugation (25 krpm for 10 min at 293 K). The amounts of the adsorbed Eu^{3+} on clays were determined by ICP-AES analysis (λ = 381.967 nm) from the difference between the concentration of the remaining Eu^{3+} in supernatant and that of blank sample.

Specific surface area

Specific surface areas were determined using BET equation (Brunauer et al., 1938) from the nitrogen adsorption isotherms. Nitrogen adsorption isotherms were obtained at 77 K. Prior to the adsorption experiments, the adsorbents were dried at 333 K under vacuum (10^{-1} torr) for 3 hours. Na^+-clays were heat-treated at 773 K for 1 h under air for the determination of the external surface area. The dehydration was confirmed by the basal spacings of the heat-treated Na^+-clays (1.0 nm).

Equipment

X-Ray diffraction patterns were obtained on Rigaku RAD IB using monochromatic Cu Kα radiation, operated at 20 mA and 40 kV. Steady-state luminescence spectra were recorded on a HITACHI F-4500 fluorospectrophotometer. Inductively-coupled plasma atomic-emission spectroscopy (ICP-AES) was performed using a Rigaku Spectro Ciros CCD. Nitrogen adsorption isotherms were obtained at 77 K on a BELSORP 28 instrument (Bell Japan Inc.).

RESULTS AND DISCUSSION

Figure 1 shows the adsorption isotherms of Eu^{3+} for Kunipia F, Sumecton SA and Na^{+}-TSM from aqueous solution. According the Giles classification (Giles et al., 1960), the Na^{+}-TSM isotherm is type-H and the Sumecton SA and Kunipia F isotherms are type-L. These isotherm types suggest a high affinity of these clays for Eu^{3+}. Langmuir plots were fitted by linear regression of a graph of C_e/Q versus C_e resulting in a linear equation of the form

$$C_e/Q = mC_e + b \qquad (1)$$

where m is the slope and b is the intercept (Langmuir, 1918). The amount adsorbed (Q) in meq Eu^{3+} / g clay and equilibrium concentrations (C_e) in mmol Eu^{3+} / L were extrapolated from Figure 1. The plotted values are the extrapolated data points. The plotted lines are graphs of the Langmuir equation using the fitted parameters for each data set (Figure 1). All Langmuir fits to the extrapolated data had r^2 values of 0.96 or greater.

The maximum adsorbed amounts of Eu^{3+} on Na^{+}-TSM, Sumecton SA and Kunipia F were 1.00, 0.71 and 1.02 meq / g clay, which were close to the CECs (0.94, 0.71 and 1.19 meq / g clay for Na^{+}-TSM, Sumecton SA and Kunipia F, respectively). The XRD patterns were recorded under relative humidity of ca. 20 % (Figure 2). The basal spacings of Na^{+}-TSM, Kunipia F, and Sumecton SA were 1.23, 1.23, and 1.29 nm and increased to 1.52, 1.53 and 1.50 nm after Eu^{3+} adsorption (Figure 2). Judging from the thickness of the silicate layer (0.96 nm), the gallery heights of the Na^{+}- and the Eu^{3+}-forms are 0.3 and 0.6 nm, respectively, indicating the change in the hydration from a monolayer of water molecules to bilayer ones in the interlayer space. The polarizing power is directly related to cation electric-field (ionic charge / ion radii) which is larger for Eu^{3+} (3.2) than for Na^{+} (0.98). As the polarizing power increased, the strength of the interactions between the cations and water molecules surrounding the cations increased. Therefore, it is thought that a larger amount of water was involved in the Eu^{3+}-form.

(Insert Figures 1 and 2)

The type-H adsorption isotherm of TSM indicated a greater affinity for Eu^{3+}

than the type-L isotherms of Kunipia F and Sumecton SA. Difference in Eu^{3+} affinity to clays was also revealed by the Freundlich affinity index (n) values. The calculated values (n) for the present system are listed in Table 2. The Freundlich equation (Freundlich, 1926) is expressed as,

$$Q = K_f C_e^{1/n} \quad (2)$$

where K_f(mmol g^{-1}) and n are constants pertaining to maximum adsorbed amount and a conditional index, which describes the shape of the isotherm (empirical adsorption characteristics), respectively. The n value for TSM system (7.5) was quite larger than those for Kunipia F (1.9) and for Sumecton SA systems (1.5) (Table 2). The high affinity of Sr^{2+} in aqueous solution for a synthetic fluoro-mica was shown previously (Paulus et al., 1992). The high affinity of Eu^{3+} for TSM may be accounted for the structural difference in octahedral sheet (hydroxide or fluoride). The TSM clay contains highly-electronegative fluorine groups instead of the hydroxyls in smectites and this difference might explain the greater Eu^{3+} adsorption by TSM.

The n value for Kunipia F (1.9) was slightly larger than that for Sumecton SA system (1.5). The interlayer expandability of smectites is related to electrostatic interactions between adjacent sheets that depend on the layer charge, cation type, and cation position (van Olphen, 1977). Because the layer change density of Sumecton SA is smaller than Kunipia F, the attractive force between adjacent silicate layers that is mediated by exchangeable cations might be weaker in Sumecton SA. The difference in layer charge might give the relatively higher Eu^{3+} affinity for Kunipia F than for Sumecton SA.

(Insert Table 2)

The Freundlich equations for the Eu^{3+}-TSM and Eu^{3}-Kunipia provided poorer fits to the data than the Langmuir equations, as shown by the r^2 values given in Table 2. In contrast, Freundlich fit to the extrapolated data for the Eu^{3+}-TSM had a larger r^2 value (0.99). We assume that Eu^{3+} stoichimetrically adsorbed to specific adsorption sites of Na^{+}-TSM and Kunipia F, while the Eu^{3+} adsorption occurred on relatively inhomogeneous adsorption sites of Sumecton SA.

The variation of luminescence spectra of the Eu^{3+} exchanged Sumecton SA and Na^{+}-TSM are shown in Figures 3A and 3B, respectively. The luminescence bands ascribable to the $^5D_0$-$^7F_1$ and $^5D_0$-$^7F_2$ transitions of Eu^{3+} were observed at 592 and 614 nm, respectively (Carnall, 1976). On the other hand, the photoluminescence was not observed for the Eu^{3+}-Kunipia F system (data are not shown). The quenching of Eu^{3+} luminescence in Eu^{3+} exchanged Kunipia F was attributed to the 2 wt % structural $Fe^{2+/3+}$ as reported for Eu^{3+} exchanged Wyoming montmorillonite ($Fe^{2+/3+}$: 3 wt%) (Bergaya and van Damme, 1983). The relative luminescence intensity depends on the strength and symmetry of the electric field around Eu^{3+}. The relative intensity of each of the transitions (I_{592}/I_{614}) observed for the Sumecton SA and TSM systems barely changed with greater amounts of adsorbed Eu^{3+}, which suggests Eu^{3+} was adsorbed in a similar manner. In contrast, the ratio differed depending on the clays; the ratio of the intensity (I_{592}/I_{614}) for Sumecton SA system was 0.7, while that for the TSM system was 1.8.

(Insert Figure 3)

Several groups (Takahashi et al., 1998; Stumpf, et al., 2002; Rabung et al., 2005) have discussed the state of the adsorbed Eu^{3+} on smectites by using the I_{592}/I_{614} value. When the I_{592}/I_{614} value is comparable to the value (1.7) for Eu^{3+} aquo ion (Zaitoun et al., 2000), Eu^{3+} has a similar site symmetry (i.e. a highly symmetrical environment). A large amount of Eu^{3+} has been adsorbed as outer-sphere complex between the Eu^{3+} aquo ion on a clay. In contrast, relatively lower I_{592}/I_{614} has been a result of asymmetrical site symmetry of Eu^{3+}, suggesting the formation of inner-sphere complex of Eu^{3+} with the edge hydroxyl groups. Considering to relatively large BET surface area (Table 1) of Sumecton SA (135 m^2/g) compared to that for Na^{+}-TSM (6 m^2/g), the formation of inner-sphere complex with the edge hydroxyls of Sumecton SA is a probable reason to give relatively lower I_{592}/I_{614} value. The lower intensity ratio was also observed for Eu^{3+}-doped silica gel, which was prepared at a basic condition (Selvan et al.,1999; Zaitoun et al., 2000), and magadiite systems (Mizukami et al., 2002). The complexation of surface silanol groups with Eu^{3+} is a possible explanation on the relatively lower I_{592}/I_{614}.

Figure 4 shows the relationship between the intensity of the $^5D_0$-$^7F_2$

luminescence band (at 614 nm) and the amount of the adsorbed Eu^{3+} on Sumecton SA and TSM. Amounts of adsorbed Eu^{3+} were expressed as the amount per ideal surface area (nm^2) in order to examine the effect of Eu^{3+} spatial distribution on the luminescence. Ideal surface areas of clays (S_a) were calculated from the unit-cell dimensions and unit-cell weights of the clays using the equation

$$S_a = (1 / M) \times 6.02 \times 10^{23} \times 2 \times A \times 10^{19}\, m^2 / nm^2 \qquad (3)$$

where "M" equals the unit-cell weight (Table 1) and "A" equals the product of the "a" and "b" unit cell dimensions and 6.02×10^{23} is Avogadro's number (van Olphen, 1977). For example, the ideal surface of Sumecton SA is calculated $S_a = (1 / 810) \times 6.02 \times 10^{23} \times 2 \times 0.514 \times 0.893 \times 10^{19} = 681$ (Table 1). The luminescence intensity was normalized using the amount of adsorbed Eu^{3+} as indicated by the equation $I_n = I_m / m$; where I_n denotes the normalized luminescence intensity, I_m denotes the observed luminescence intensity, and m denotes the amount of adsorbed Eu^{3+}. These symbols were proposed in a previous study on the adsorption of Eu^{3+} to magadiite (Mizukami et al., 2002). In the Eu^{3+}-magadiite system, the luminescence was intensified with increased amounts of adsorbed Eu^{3+} up to 1.0 meq / g; and 0.28 molecule / nm^2. This is based on a surface area of 0.73×0.73 nm^2 for each cell and unit-cell weight of 902 (Brindley, 1969). A further increase in the amount of Eu^{3+} adsorbed to magadiite weakened the luminescence due to concentration quenching at the higher Eu^{3+} loading (Figure 4b). In contrast, a decreased normalized luminescence intensity with increased amounts of adsorbed Eu^{3+} was observed for both the Sumecton SA and TSM systems (Figure 4a). This observation suggests that the concentration quenching occurred even when the loaded amount of Eu^{3+} was quite low compared to that for the magadiite system. Normalized luminescence intensity differences between magadiite and the Sumecton SA and TSM clays might be due to the different nature of the negative sites in these clay minerals. Negative charge sites in smectites are mainly due to isomorphous substitution, whereas, the negative charge sites in TSM are largely due to lattice defects. In contrast, the negative charge sites in magadiite are mostly pH-dependent silanol sites.

(Insert Figure 4)

CONCLUSIONS

The adsorption of Eu^{3+} from aqueous solution to natural montmorillonite (Kunipia F), and synthetic saponite (Sumecton SA) and synthetic fluoro-tetrasilicic mica (Na^{+}-TSM) was examined. The Eu^{3+} adsorption capacities (1.02, 0.71 and 1.00 meq / g clay for Kunipia F, Sumecton SA and Na^{+}-TSM, respectively) were similar to the cation exchange capacities (1.19, 0.71 and 0.94 meq / g clay for Kunipia F, Sumecton SA and Na^{+}-TSM, respectively), which suggest Eu^{3+} adsorption by cation exchange. Adsorption isotherms indicated a high affinity of Eu^{3+} for TSM relative to the smectites (Kunipia F and Sumecton SA). Luminescence quenching by structural Fe limited luminescence examination of the Kunipia F montmorillonite. The luminescence efficiency decreased with increases in the adsorbed Eu^{3+}, indicating concentration quenching for both Sumecton SA saponite and TSM fluoro-tetrasilicic mica.

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Table 1. Chemical compositions of clays used in this paper. (Okada et al., 2005a)

Adsorbent	Chemical composition	Unit-cell weight	Ideal surface area (m^2/g)	BET surface area (m^2/g)
Na^+-montmorillonite (Kunipia F)	$(Na_{0.53}Ca_{0.09})^{0.71+}$-$[(Al_{3.28}Fe_{0.31}Mg_{0.43})^{oct}(Si_{7.65}Al_{0.35})^{tet}O_{20}(OH)_4]^{0.71-}$	784	704	6
Na^+-saponite (Sumecton SA)	$(Na_{0.49}Mg_{0.14})^{0.77+}$-$[(Mg_{5.97}Al_{0.03})^{oct}(Si_{7.20}Al_{0.80})^{tet}O_{20}(OH)_4]^{0.77-}$	810	681	135
Na^+-TSM	$Na_2Mg_5Si_8O_{20}F_4$	786	702	7

Table 2 Parameters of the adsorption data fitted to Langmuir and Freundlich equations

Host	Maximum adsorbed amount of Eu^{3+} (meq / g)	Type	Langmuir isotherm [a]			Freundlich isotherm [b]		
			m (g/meq)	b (10^3 L/meq)	r^2	K_f (meq g^{-1} $mM^{1/n}$)	n	r^2
Kunipia F	1.02	L	0.90	6.0×10^1	0.99	2.5	1.5	0.93
Sumecton SA	0.71	L	1.1	1.4×10^2	0.96	1.2	1.9	0.99
TSM	1.00	H	0.99	7.3	1.0	1.2	7.2	0.86

a: $C_e/Q = mC_e + b$

b : $Q = K_f C_e^{1/n}$

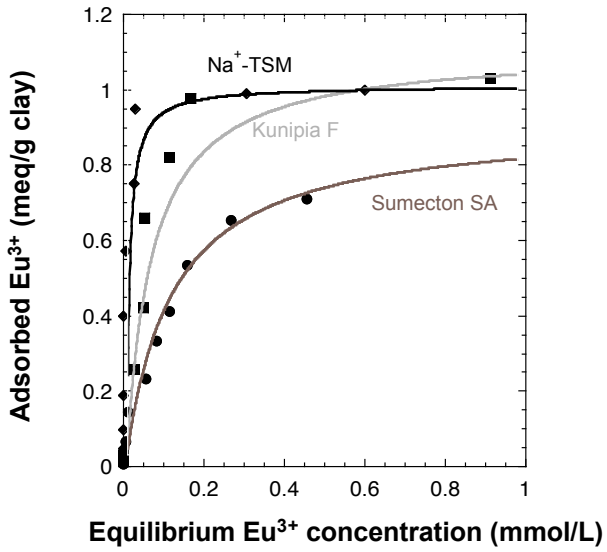

Figure 1. Adsorption isotherms of Eu^{3+} on Kunipia F (square), Sumecton SA (circle) and Na^{+}-TSM (diamond). Solid lines are graphs of the Langmuir equation calculated using the fitted parameters (Table 1) for each data set.

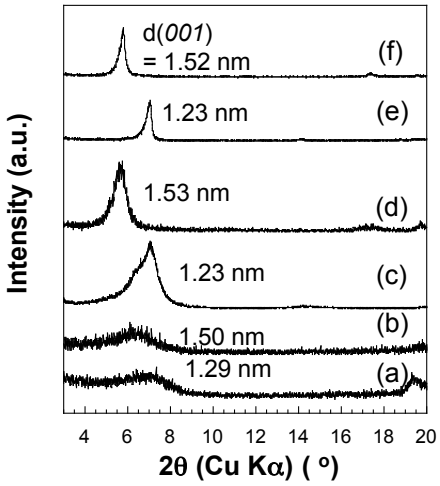

Figure 2. XRD patterns of (a) Sumecton SA, (b) Eu^{3+}-Sumecton SA, (c) Kunipia F, (d) Eu^{3+}-Kunipia F, (e) Na^{+}-TSM and (f) Eu^{3+}-TSM.

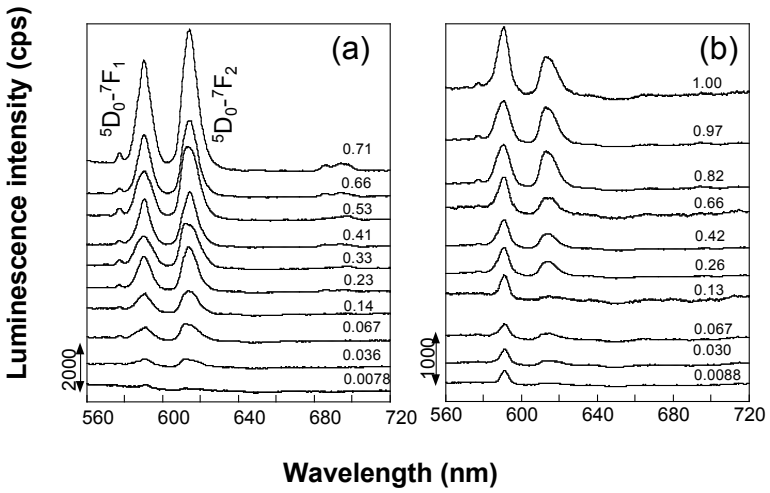

Figure 3. Luminescence spectra of reaction products of $EuCl_3$ with (a) Sumecton SA and (b) Na^+-TSM. The numbers along the right side of each figure designate the amount of Eu^{3+} (meq/g clay).

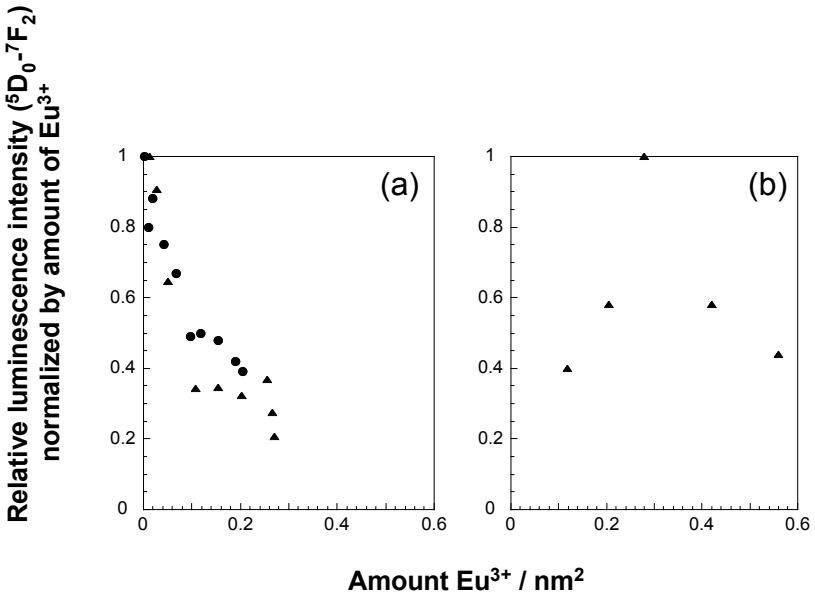

Figure 4. The dependence of luminescence intensity ($^5D_0$-$^7F_2$ transition) on Eu^{3+} concentration for (a) Sumecton SA (circle), Na^+-TSM (triangle) and (b) magadiite (diamond, Mizukami et al., 2002).