ADSORPTION OF Eu³⁺ TO SMECTITES AND FLUORO-TETRASILICIC MICA

Tomohiko Okada[1,†], Yusuke Ehara[2] and Makoto Ogawa[1,2,*]

[1] Department of Earth Sciences, Waseda University, Nishiwaseda 1-6-1, Shinjuku-ku, Tokyo 169-8050, Japan
[2] Graduate School of Science and Engineering, Waseda University, Nishiwaseda 1-6-1, Shinjuku-ku, Tokyo 169-8050, Japan

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 1.02, 0.71 and 1.00 meq/g of clay, respectively, for Kunipia F, Sumecton SA and Na^+-TSM. The adsorption capacities were comparable to the cation exchange capacities of the clays, which were 1.19, 0.71 and 0.94 meq/g of clay, respectively. 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 Fe 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, Fluoro-tetrasilicic Mica, Kunipia F, Montmorillonite, Photoluminescence, Sumecton SA, Synthetic Saponite.

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; Stumf *et al.*, 2002; Rabung *et al.*, 2005; Okada *et al.*, 2006) and synthetic magadiite (Mizukami *et al.*, 2002) has been examined 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 Fe 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 Fe in the silicate layer (Mizukami *et al.*, 2002). Based on the variation of luminescence intensity as a function of the quantity of adsorbed Eu^{3+}, it was proposed that the interlayer spatial distribution of Eu^{3+} affects 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 layered materials with adsorbed rare earth ions is worth further investigation to optimize the 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 been investigated extensively 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 noted 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.*, 2005a, 2005b), separation efficiency for optical resolution of a racemic mixture (Nakamura *et al.*, 1988) and the aggregation of the 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.*, 2005a, 2005b) 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. As 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, 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 are replaced by F in Na^+-TSM. The difference in the structure of Na^+-TSM

* E-mail address of corresponding author:
makoto@waseda.jp
† Present address: Department of Chemistry and Material Engineering, Faculty of Engineering, Shinshu University, Wakasato 4-17-1, Nagano 380-8553, Japan

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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 of clay, respectively (Ogawa et al., 1992). Europium (III) trichloride hexahydrate (>99.99%) was purchased from Aldrich Co. and was used as received.

Cation exchange with Eu^{3+}

Samples of Na⁺-clays (0.1 g) were allowed to react with 50 mL aliquots of $EuCl_3$ solution (pH̃ 5) in 50 mL polypropylene vessels for 1 day at room temperature. The initial concentrations of aqueous $EuCl_3$ solution were in the range $0.01-2.0$ times as large as the 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 Eu^{3+} adsorbed on clays were determined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) analysis (λ = 381.967 nm) from the difference between the concentration of the remaining Eu^{3+} in the supernatant liquid and that of the blank sample.

Specific surface area

Specific surface areas were determined using the BET equation (Brunauer et al., 1938) from the nitrogen

adsorption isotherms obtained at 77 K. Prior to the adsorption experiments, the adsorbents were dried at 333 K under vacuum (10^{-1} torr) for 3 h. Na⁺-clays were heat treated at 773 K for 1 h under air to determine 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 (XRD) patterns were obtained using a 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. The ICP-AES was performed using a Rigaku Spectro Ciros CCD. Nitrogen adsorption isotherms were obtained at 77 K using 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 to the Giles et al. (1960) classification, the Na⁺-TSM isotherm is type-H and the Sumecton SA and Kunipia F isotherms are type-L. These isotherm types suggest a significant affinity of these clays for Eu^{3+}. Langmuir plots were fitted by linear regression of a graph of C_e/Q vs. 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 of Eu^{3+} adsorbed (Q) in meq of Eu^{3+}/g of clay is plotted vs. the equilibrium concentrations (C_e) in mmol Eu^{3+}/L in Figure 1. The plotted values are the measured 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 amounts of Eu^{3+} adsorbed on Na⁺-TSM, Sumecton SA and Kunipia F were 1.00, 0.71 and 1.02 meq/g of clay, respectively, close to the CECs (0.94, 0.71 and 1.19 meq/g of clay for Na⁺-TSM, Sumecton SA and Kunipia F, respectively). The XRD patterns were recorded under relative humidity of ~20% (Figure 2). The basal spacings of Na⁺-TSM, Kunipia F

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

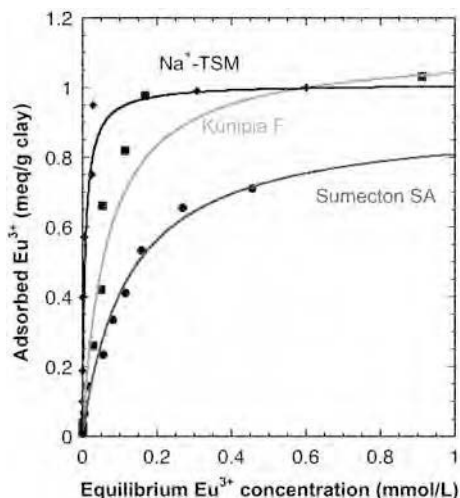| Adsorbent	Chemical composition	Unit-cell weight (amu)	Ideal surface area (m²/g)	BET surface area (m²/g)
Na⁺-montmorillonite (Kunipia F)	$(Na_{0.53}Ca_{0.09})^{0.71+}$-$[(Al_{3.28}Fe_{0.31}Mg_{0.43})^{oct}(Si_{7.65}Al_{0.35})^{tet}O_{20}(OH)_4]^{0.71-}$	784	704	6
Na⁺-saponite (Sumecton SA)	$(Na_{0.49}Mg_{0.14})^{0.77+}$-$[(Mg_{5.97}Al_{0.03})^{oct}(Si_{7.20}Al_{0.80})^{tet}O_{20}(OH)_4]^{0.77-}$	810	681	135
Na⁺-TSM	$Na_2Mg_5Si_8O_{20}F_4$	786	702	7

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.

and Sumecton SA were 1.23, 1.23 and 1.29 nm, respectively 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 were 0.3 and 0.6 nm, respectively, indicating a change in hydration from a monolayer to a bilayer of water molecules in the interlayer space. The polarizing power is directly related to cation electric field (ionic charge/ion radii) which is
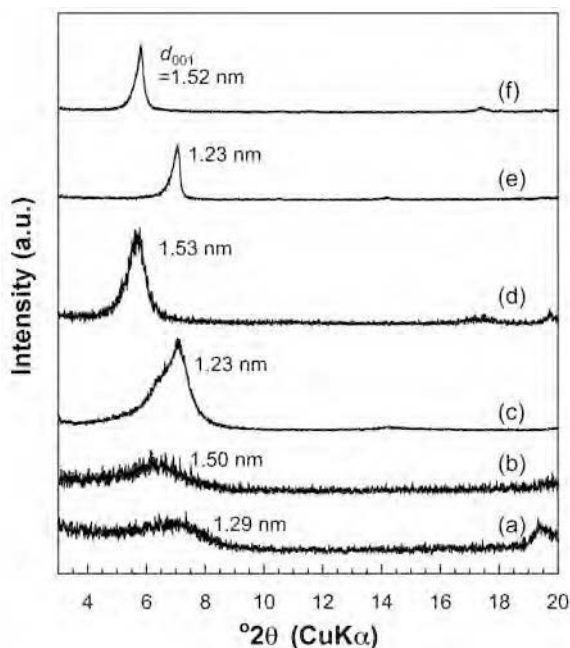

Figure 2. XRD patterns of (a) Sumecton SA, (b) Eu^{3+}-Sumecton SA, (c) Kunipia F, (d) Eu^{3+}-Kunipia F, (e) Na^+-TSM and (f) Eu^{3+}-TSM.

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.

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. Differences in Eu^{3+} affinity to clays were 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

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

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

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, the Freundlich fit to the extrapolated data for the Eu^{3+}-TSM had a larger r^2 value (0.99). We assume that Eu^{3+} adsorbed stoichiometrically 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, luminescence 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.%

Table 2. Parameters of the adsorption data fitted to the Freundlich equation.

Host	Maximum amount of adsorbed Eu^{3+} (meq/g)	Type	Freundlich isotherm[a]		
			K_f (meq g^{-1} $mM^{1/n}$)	n	r^2
Kunipia F	1.02	L	2.5	1.5	0.933
Sumecton SA	0.71	L	1.2	1.9	0.990
TSM	1.00	H	1.2	7.2	0.864

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

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+}, suggesting that 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 the Sumecton SA system was 0.7, while that for the TSM system was 1.8.

Several groups (Takahashi et al., 1998; Stumpf et al., 2002; Rabung et al., 2005) have discussed the state of the Eu^{3+} adsorbed 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 the 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 an outer-sphere complex between the Eu^{3+} aquo ion on a clay. In contrast, relatively low I_{592}/I_{614} has been a result of asymmetrical site symmetry of Eu^{3+}, suggesting the formation of an inner-sphere

complex of Eu^{3+} with the edge hydroxyl groups. Considering 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 an inner-sphere complex with the edge hydroxyls of Sumecton SA is a probable reason for the smaller I_{592}/I_{614} value. The lower intensity ratio was also observed for Eu^{3+}-doped silica gel, which was prepared under basic conditions (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 for the relatively low 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

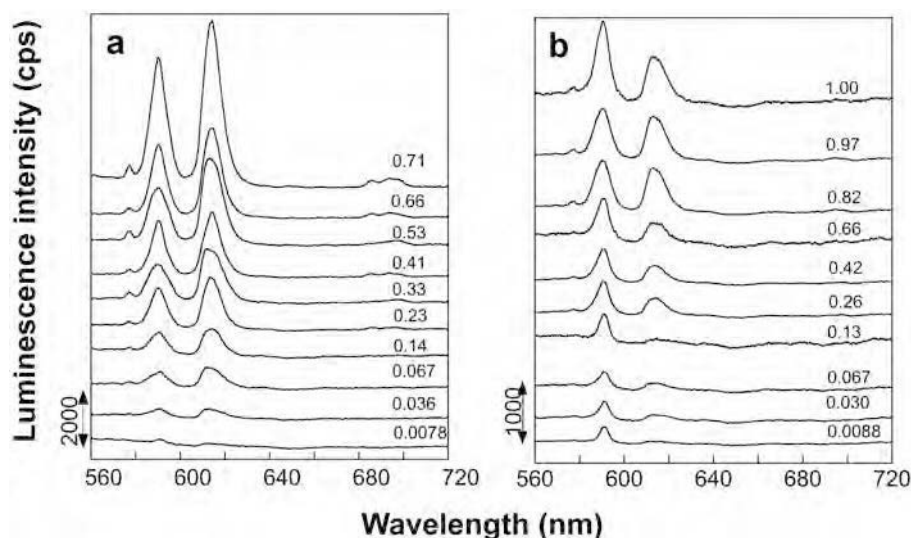$$S_a = (1/M) \times 6.02 \times 10^{23} \times 2 \times A \times 10^{19} \ m^2 \ /nm^2 \qquad (3)$$

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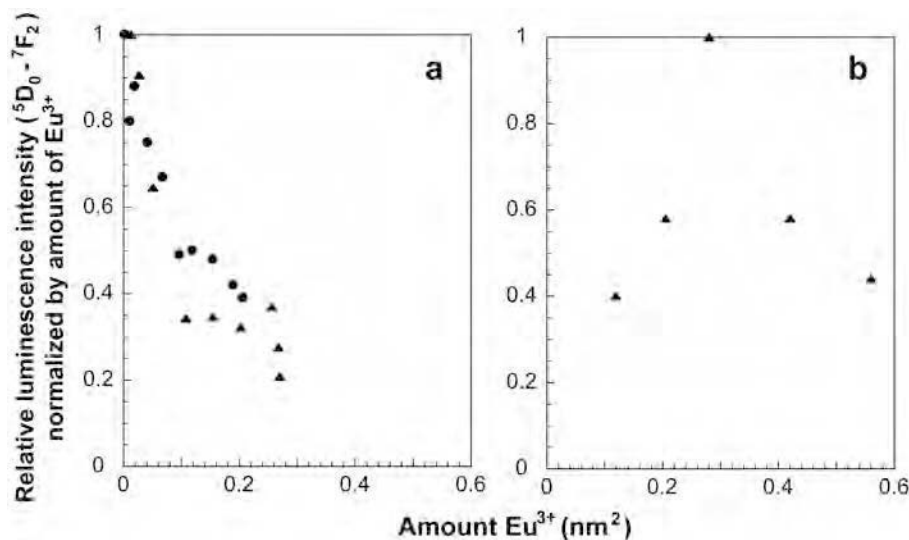
Figure 4. The dependence of luminescence intensity ($^5D_0$-$^7F_2$ transition) on Eu^{3+} concentration for (a) Sumecton SA (circle), Na^+-TSM (triangle) and (b) magadiite (triangle, Mizukami *et al.*, 2002).

where M equals the unit-cell weight (Table 1) and A is 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 given as $S_a = (1/810) \times 6.02 \times 10^{23} \times 2 \times 0.514 \times 0.893 \times 10^{19} = 681$ (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 molecules/nm^2. This is based on a surface area of 0.73×0.73 nm^2 for each cell and a unit-cell weight of 902 atomic mass units (Brindley, 1969). A further increase in the amount of Eu^{3+} adsorbed to magadiite weakened the luminescence due to concentration quenching at the greater 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 amount of Eu^{3+} loaded was quite small 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.

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 of clay for Kunipia F, Sumecton SA and Na^+-TSM, respectively) were similar to the CECs (1.19, 0.71 and 0.94 meq/g of clay for Kunipia F, Sumecton SA and Na^+-TSM, respectively), suggesting 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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