Affinity of finely dispersed montmorillonite colloidal particles for americium and lanthanides

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Abstract

We studied (i) the affinity of the finely dispersed montmorillonite colloidal particles (< 0.45 μm), which originated from Japan, for trace amounts of Am^{3+} and lanthanide ions (Ln^{3+}: Nd^{3+}, Eu^{3+}, Gd^{3+}), and (ii) the differences between the sorption behavior of Am^{3+} and Ln^{3+} onto the colloidal particles and that onto the massive montmorillonite solids. The ion-exchange stoichiometry of sorption reaction of Am^{3+} and Ln^{3+} onto the colloidal particles was 1:3 in the low Na^+ concentration region. In the high Na^+ concentration region, the sorption ratio was constant, and specific for Am^{3+} and each Ln^{3+}. The influence of Na^+ and Ca^{2+} on the sorption of Ln^{3+} onto the finely dispersed Na- and Ca-montmorillonite colloidal particles at different NaCl and $CaCl_2$ concentrations was examined. It was found that the coverage of the sorption sites increased with the Ln^{3+} concentration. The affinity for Ln^{3+} was discussed by selectivity and a Langmuir-type isotherm.

1. Introduction

It has been pointed out that there is a possibility of outflow of bentonite, of which montmorillonite is the main component, from artificial barrier into natural barrier [1]. Finely dispersed montmorillonite colloidal particles are released from the intruding montmorillonite to groundwater. The finely dispersed montmorillonite colloidal particles play an important role in sorption of radionuclides such as Am [2,3].

According to the performance assessment of artificial barrier in high-level radioactive waste disposal, it is found that the hazard from actinides and fission products at outer boundary of artificial barrier is dominated by Am and Cm as well as Pu, especially when the dissolution rate of glass is relatively high [4]. Actinides such as Am are readily sorbed on finely dispersed particles and groundwater colloids, and thus generate actinide-bearing particles and pseudocolloids. Hence, for the performance assessment of high-level radioactive waste disposal system, it is indis-

pensable to understand the formation of finely dispersed Am-bearing montmorillonite colloidal particles.

With regard to sorption and ion-exchange reactions of trivalent cations onto massive montmorillonite solids, many studies have been carried out. Frysinger and Thomas [5] studied the exchange-adsorption of Cs and the tripositive ions of Y and Ce on montmorillonite from Chambers, Arizona, at different concentrations and temperature. The isotherms obtained with the two trivalent ions were closely similar, and the average charge of the sorbed trivalent ions was shown to be nearly three. They also computed the thermodynamic data for the exchange reactions. Bruque et al. [6] described a method for the preparation of Ln–montmorillonite (Ln: lanthanide) that ensured the saturation of the cation exchange capacity using the montmorillonite from La Serrata Bed, Almeria, and discussed the most favorable equilibrium conditions. The H^+–Ln^{3+} exchange rate in the acid montmorillonite and the effect of concentration and pH on the retention of Ln^{3+} ions were investigated. They pointed out a possibility of the precipitation of $Ln(OH)_3$, and also inferred that the ions of smaller hydrated radius were retained to a larger degree. McBride [7] studied the ion-exchange in montmorillonite

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from Upton, Wyoming, over a wide range of surface ionic compositions and ionic strength in Cd^{2+}–Na^+, Cd^{2+}–Ca^{2+}, La^{3+}–Ca^{2+} and La^{3+}–Cs^+ systems. It was found that, when the exchanging ions were of unequal charge, the tactoid structure of the montmorillonite appeared to influence the selectivity for the ions, and that the mass-action might be poor approximation when the adsorbing and desorbing ions had different hydration energies and charge. Miller et al. [8] studied the diffusion of exchanged Yb, Ho and Eu from interlayer positions in montmorillonite from Upton, Wyoming. They found that the dehydration of exchanged montmorillonite between 100°C and 280°C caused the ions to diffuse into the hexagonal rings of surface oxygens and the subsequent migration into the vacant octahedral sites was small. They also obtained the evidence for hydrolysis as a possible mechanism for cation fixation. McBride and Bloom [9] found that the sorption of Al^{3+} on Ca-montmorillonite from Upton, Wyoming, was described by a Langmuir-type isotherm, and pointed out that hydrolysis and precipitation of Al^{3+} at higher pH complicated the exchange behavior.

However, available information on sorption of trivalent actinides still remains scarce whereas only Degueldre et al. have studied the sorption of Am [10]. Furthermore, although the physical, chemical and mechanical properties of montmorillonite are strongly dependent on their origins, few data are available on sorption of not only trivalent actinide ions but also trivalent lanthanide ions onto the montmorillonite produced from Japan. Also, there is a possibility that the sorption of cations onto the finely dispersed montmorillonite colloidal particles is different from that onto the massive montmorillonite solids, because the finely dispersed montmorillonite colloidal particles have large specific surface area, and not only the interlayers but also the edges of surface are considered to contribute the sorption of the cations.

In this paper, we report the sorption affinity of finely dispersed montmorillonite colloidal particles for Am(III) ion (Am^{3+}) and lanthanide(III) ions (Ln^{3+}: Nd^{3+}, Eu^{3+} and Gd^{3+}; Chemical properties of Ln^{3+} is similar to those of actinide(III) ions), and the influence of Na^+ and Ca^{2+} on the affinity for lanthanide(III) ions. In the present work, we used the montmorillonite produced from Tsukinuno, Yamagata Prefecture, Japan.

We, of course, recognize that we have to understand the formation of finely dispersed Am-bearing colloidal particles under environmental conditions (pH = 4 to 10). However, it is difficult to analyze the sorption behavior when hydrolysis and precipitation of Am^{3+} and Ln^{3+} occur. In the present work, as the first step to elucidate the formation mechanism of finely dispersed Am(III)- and Ln(III)-bearing montmorillonite colloidal particles which originate in Japan, we carried out the experiments only at pH 4 where the effect of hydrolysis can be ignored. Moreover, in order to understand the sorption-exchange properties of the montmorillonite, the concentrations of

Am^{3+} and Ln^{3+} were adjusted to the same order of the cation exchange capacity of the montmorillonite.

2. Experimental

2.1. Materials

Americium-241 in HNO_3 was supplied from Amersham. By repeatedly mixing the Am solution with CMPO (n-octyl(phenyl)-N,N-diisobutylcarbamoylmethylphosphine oxide), the daughter nuclides such as [237]Np were removed. Europium-152 in HCl was also purchased from Amersham and was used as received. Stable isotopes of lanthanide chlorides ($NdCl_3$, $EuCl_3$, $GdCl_3$: assay > 99.9%) were supplied from Soekawa Chemicals. We used stable isotopes for Nd and Gd in this work, since the radioisotopes were not available due to relatively short half-life. All other chemicals were analytical reagent grade (Wako Pure Chemical Industries). Water was doubly distilled and ultrafiltered by use of 2 nm ultrafilters (Molecut UFP1, Millipore) immediately before use.

A well purified montmorillonite originating from Tsukinuno, Yamagata Prefecture, Japan was supplied from Nichika, Japan. The montmorillonite was saturated by Na^+ and Ca^{2+} to obtain Na-montmorillonite and Ca-montmorillonite, respectively. The detail description of saturation procedure is given elsewhere [11]. The cation exchange capacity of the montmorillonite was 107.5 meq/100 g.

2.2. Sorption affinity

After distilled water was poured into a polypropylene tube and Na-montmorillonite was added (montmorillonite mass/water volume = 0.5 g/ml), the tube was shaken for 1 month. After centrifugation (3000 rpm, 30 min), a sample was taken from the supernatant and filtered with a 0.45 μm membrane filter (Millipore). This filtrate was used for the solution containing finely dispersed montmorillonite colloidal particles (< 0.45 μm) in this experiment. The amount of montmorillonite in the filtrate was found to be 1.0% of the initial amount, by measuring the mass of the montmorillonite trapped on the 0.45 μm filter and that remaining in the tube. Since the filters used in the present work were washed by a volume of solution, of which the pH was adjusted to the same value as that of the supernatant, and preconditioned according to the experimental procedure described by Nitsche [12], the influence of surfactant in the filter could be considered to be negligibly small and the influence of sorption onto the filter was avoided.

Twenty-five ml of the filtrate was brought into contact with a small amount of Am solution (100 μl), $NdCl_3$, $EuCl_3$ or $GdCl_3$ in a polypropylene tube, after the pH of filtrate was adjusted to 4 by using HCl in order to mini-

mize hydrolysis of Am and lanthanides. In the experiment using $EuCl_3$, a trace amount of [152]Eu was spiked. The concentrations of Am and lanthanides were 1×10^{-5} M. The tube was closed tightly and shaken gently for 2 weeks to achieve sorption equilibrium. We previously measured the change in the Am and lanthanide concentrations with time, and determined the time required for completion of the Am and lanthanide sorption. The sorption equilibrium was found to be achieved within 7 to 10 days. Hence, we chose an equilibration time of 2 weeks in the present work. During the experiments, we checked the pH of the Am and lanthanide solutions once a day. When the pH shifted to 4.5 where the hydrolysis starts to occur, we readjusted the pH to 4 by the addition of HCl. Since the total volumes of HCl added for the pH adjustment were very small (< 10 μl), the change in the Am and lanthanide concentrations could be neglected. With regard to ionic strength, we adjusted it in the range of 0.04 M to 0.64 M by the addition of NaCl.

After 2 weeks of equilibration, the tubes were centrifuged. A sample was taken from the supernatant of each tube and ultrafiltered with the 2 nm ultrafilter. The activities of [241]Am and [152]Eu in the samples and in the ultrafiltrates were measured by a well type Ge detector. A 2π gas flow counter was also used for the Am activity measurement. The concentrations of Eu as well as Nd and Gd in the samples and in the ultrafiltrates were determined spectroscopically with Arsenazo III [13]. We investigated the sorption of Am and lanthanides onto the tube walls, and checked their mass balance in the separation procedure. It was found that the sorption onto the wall was negligibly small and the mass was balanced. We spectroscopically confirmed [14] that the montmorillonite colloidal particles could be dispersed in the solution at ionic strength of 0.04 M–0.64 M.

All experiments were performed under the aerobic conditions. The temperature was $25 \pm 0.5°C$. All samples were stored in the dark.

2.3. Influence of Na^+ and Ca^{2+} on affinity of finely dispersed montmorillonite colloidal particles for Ln^{3+}

Solutions containing finely dispersed Na- or Ca-montmorillonite colloidal particles (< 0.45 μm) were prepared by the same procedure described in Section 2.2. Twenty-five ml of the solution containing the finely dispersed Na- or Ca-montmorillonite colloidal particles was poured into a polypropylene tube and an amount of $NdCl_3$, $EuCl_3$ or $GdCl_3$ was added to the solution. A trace amount of [152]Eu was also used. The concentrations of lanthanides were in the range of 1×10^{-4} M to 8×10^{-3} M. In order to investigate the influence of Na^+ and Ca^{2+} on the sorption affinity of the finely dispersed montmorillonite colloidal particles for trivalent lanthanide ions, we added NaCl to the Na-montmorillonite solutions and $CaCl_2$ to the Ca-montmorillonite solutions. The concentrations of NaCl and $CaCl_2$ were 0.01 M and 0.1 M. The subsequent experimental procedure was same as that described in Section 2.2. In this study, we obtained the sorption isotherms of lanthanides.

3. Results and discussion

3.1. Sorption affinity

Affinity of finely dispersed Na-montmorillonite colloidal particles for Am^{3+} and Ln^{3+} in NaCl solutions at pH = 4 was investigated in order to confirm whether Am^{3+} and Ln^{3+} are sorbed onto the finely dispersed montmorillonite colloidal particles by ion-exchange. We assumed that the sorption reaction onto the finely dispersed montmorillonite colloidal particles can be described as follows:

$$m\overline{Na^+} + Am^{3+} (\text{or } Ln^{3+}) = mNa^+ + \overline{Am^{3+}} (\text{or } \overline{Ln^{3+}}),$$
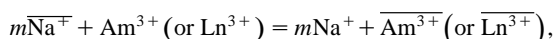
where the bar denotes the sorbed ions. If Am^{3+} and Ln^{3+} are sorbed onto the finely dispersed montmorillonite colloidal particles by ion-exchange, the value of m should be 3, which is the same as that in the sorption onto the massive montmorillonite solids. The apparent equilibrium constant, K_{eq}, for above reaction is given by

$$K_{eq} = \frac{\left[\overline{Am^{3+}} (\text{or } \overline{Ln^{3+}})\right][Na^+]^m}{\left[Am^{3+} (\text{or } Ln^{3+})\right]\left[\overline{Na^+}\right]^m}, \tag{1}$$

where the bracket denotes the concentration. The sorption ratio, K_d (ml/g), of Am^{3+} and Ln^{3+} is expressed as

$$K_d = \frac{\left[\overline{Am^{3+}} (\text{or } \overline{Ln^{3+}})\right]}{\left[Am^{3+} (\text{or } Ln^{3+})\right]}. \tag{2}$$

Since the trace amounts of Am^{3+} and Ln^{3+} were used in this work, the concentration of Na^+ in the montmorillonite can be considered to be constant and be equal to the cation exchange capacity, CEC_0 of the montmorillonite. Then, we obtain the following relation,

$$\log K_d = -m \log[Na^+] + \log\left(K_{eq} CEC_0^m\right), \tag{3}$$

indicating that $\log K_d$ is linearly proportional to $\log[Na^+]$. Fig. 1 shows the change in K_d as a function of Na^+ concentration. The experimental errors were within the plotted area. The dependence of K_d on the Na^+ concentration was apparently composed of two distinct regions.

One is the region where the Na^+ concentration is relatively high ($\log[NaCl] > -0.5$). The K_d value in this region was independent of the Na^+ concentration. This is considered to be attributable to the fact that the Na^+ concentration is high enough to prevent Am^{3+} and Ln^{3+} from being sorbed onto the finely dispersed montmorillonite colloidal particles and only the most attractive site, where the negative charges were strongly localized on the surface (for example, surface edges) of the finely dispersed
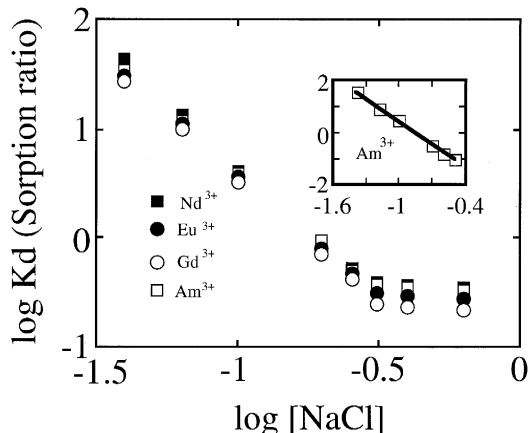
Fig. 1. Dependence of sorption ratio of Am^{3+}, Nd^{3+}, Eu^{3+} and Gd^{3+} on NaCl concentration. Calculated values for Am^{3+} after subtracting constant value in the high Na^+ concentration region are shown in inset (see text).

montmorillonite colloidal particles, would be responsible for the Am^{3+}/Ln^{3+} sorption. Similar phenomenon has been also observed in the sorption of transition metal cations onto the attractive site of layer silicates [15]. It can be considered that the surface edge effect is more marked for the finely dispersed colloidal particles than for the

massive solids. The K_d value was specific for Am^{3+} and each Ln^{3+}, and increased in the following order: $Gd^{3+} < Eu^{3+} < Am^{3+} < Nd^{3+}$. This is in the reverse order of hydration free energy [16,17]. Hydration free energy of Nd^{3+} is the smallest among these four cations. Sorption affinity of massive montmorillonite solids for metal cations (I, II, III) increases with decreasing the hydration free energy [6,18]. This suggests that the sorption of trivalent cations onto the finely dispersed montmorillonite colloidal particles as well as onto the massive montmorillonite solids depends on the hydration energy of the cations.

The other is the region where the Na^+ concentration is relatively low ($\log[NaCl] < -0.5$). In this region, $\log K_d$ decreased linearly with increasing $\log[Na^+]$. Two sorption mechanisms seem to be attributable to the K_d values experimentally obtained. One is the sorption onto the attractive site as described above. In order to confirm whether the other mechanism is ion-exchange or not, we corrected the K_d values by subtracting the constant K_d values in the high Na^+ concentration region from the K_d values experimentally obtained. We plotted these corrected K_d values against the Na^+ concentration, and obtained the slopes (m) of 2.94, 2.89, 2.91, 2.86 for Nd^{3+}, Eu^{3+}, Gd^{3+} and Am^{3+}, respectively. This suggests that Am^{3+} and Ln^{3+} are sorbed onto the finely dispersed montmorillonite colloidal particles by ion-exchange, and that the ion exchange stoichiometry of Na^+ for Am^{3+} and Ln^{3+} is close
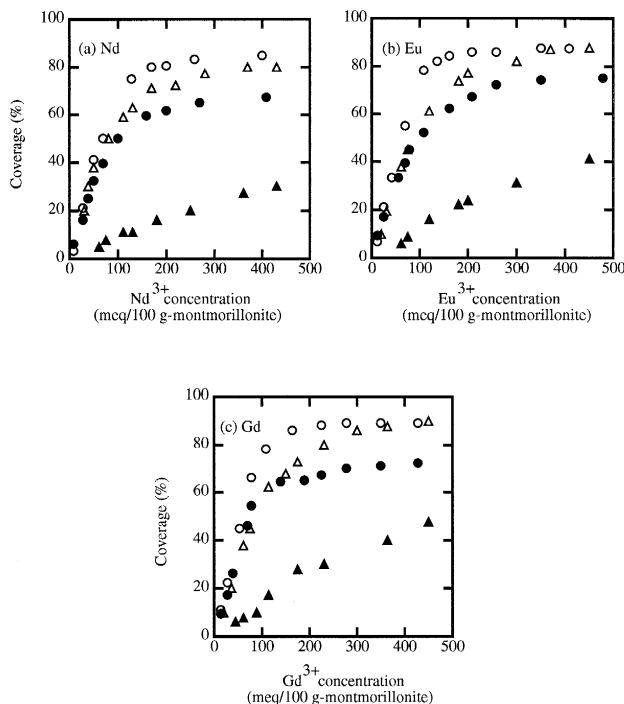

Fig. 2. Sorption isotherms for lanthanides on Na- and Ca-montmorillonites at ionic strengths of 0.01 M and 0.1 M. (a) Nd^{3+}; (b) Eu^{3+}; (c) Gd^{3+}. $\bigcirc$: 0.01 M (NaCl); $\bullet$: 0.1 M (NaCl); $\triangle$: 0.01 M ($CaCl_2$); $\blacktriangle$: 0.1 M ($CaCl_2$).

to the theoretical value, namely 1:3. In Fig. 1, we show the corrected K_d values of Am^{3+} against the Na^+ concentration, as one example.

Thus, we can consider that the sorption behavior of Am^{3+} and Ln^{3+} onto the finely dispersed montmorillonite colloidal particles is basically same as that onto the massive montmorillonite solids.

3.2. Influence of Na^+ and Ca^{2+} on affinity of finely dispersed montmorillonite colloidal particles for Ln^{3+}

Fig. 2 illustrates the sorption isotherms of Ln^{3+} onto the finely dispersed Na- and Ca-montmorillonite colloidal particles. The experimental errors were within the plotted area. At the lower NaCl and $CaCl_2$ concentration (0.01 M), the coverage (θ = amount of sorbed lanthanides/CEC_0) steeply increased in the low Ln^{3+} concentration region, and the increase rate in the coverage decreased in the high Ln^{3+} concentration region. The reason for this decrease in the increase rate is not clear at the present. However, we consider a possible reason as follows. The trivalent cations such as Ln^{3+} are surrounded by large hydration spheres. The hydrated ionic size of Ln^{3+} is larger than that of Na^+ and Ca^{2+}. Hence, it is geometrically difficult for Ln^{3+} to occupy the sorption sites of montmorillonite completely and effectively at the high coverage. The isotherms showing the similar tendency have been also observed for dispersed vermiculite particles (< 5 μm)-Ln^{3+} system [19]. This tendency may be marked for the sorption of highly charged cations onto the dispersed particles.

At the higher NaCl and $CaCl_2$ concentration (0.1 M), the coverage was suppressed. This is because the Na^+/Ca^{2+} concentration is high enough to impede the Ln^{3+} sorption. It was also found that the coverage by Ln^{3+} was more significantly reduced by Ca^{2+} than by Na^+. This may be because the strength of montmorillonite-Ca^{2+} bond is stronger than that of montmorillonite-Na^+ bond and Na^+ is more easily exchangeable for Ln^{3+} than Ca^{2+} [20]. Moreover, there is a possibility that the structure of the finely dispersed montmorillonite colloidal particles changed, because a large amount of Ca^{2+}, of which hydrated radius is larger, occupied the narrow interlayer space of the finely dispersed montmorillonite colloidal particles. Consequently, the isotherm for the Ca-montmorillonite/Ln^{3+} system at 0.1 M $CaCl_2$ was very different from the isotherms for the other systems.

Ion exchange of Na^+ or Ca^{2+} by Ln^{3+} in finely dispersed montmorillonite colloidal particles is written as follows:

$$3\overline{M^{n+}} + nLn^{3+} = 3M^{n+} + n\overline{Ln^{3+}},$$
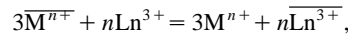
where M = Na or Ca, and $n = 1$ for M = Na and $n = 2$ for M = Ca. We define the selectivity constant, S, for the above equation as follows:

$$S = \frac{[\overline{Ln}][Na(Ca)]}{[Ln][\overline{Na(Ca)}]}, \qquad (4)$$

where the bracket denotes the concentration in (meq/ml) or (meq/g). The variations of the selectivity constants for each system are shown as a function of the coverage in
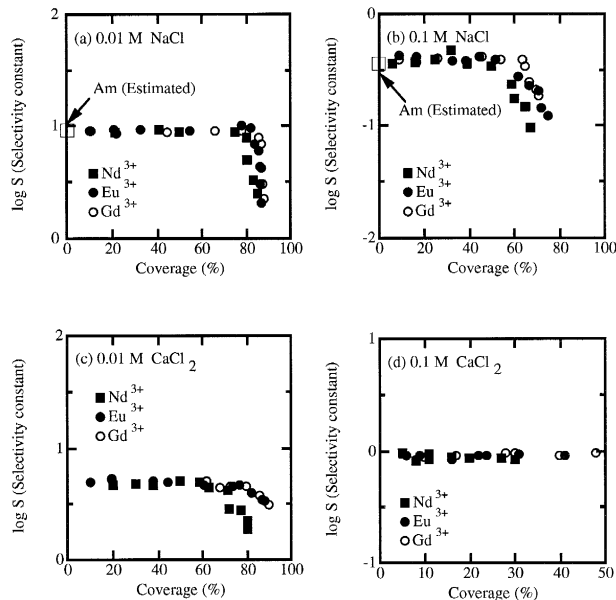

Fig. 3. Dependence of selectivity constant for lanthanides on coverage. (a) 0.01 M NaCl; (b) 0.1 M NaCl; (c) 0.01 M $CaCl_2$; (d) 0.1 M $CaCl_2$. Estimated selectivity constants for Am^{3+} are also shown.

Fig. 3. The selectivity constants for Am^{3+} in the Na-montmorillonite system at 0.01 M and 0.1 M NaCl, which were evaluated from the K_d values in Fig. 1, are also illustrated. In the low coverage region ($\theta < 50\%$), the values of the selectivity constants were found to depend on the NaCl and $CaCl_2$ concentrations and on the type of montmorillonite (Na-type or Ca-type). However, the values of the selectivity constants for three lanthanides in each system did not depend on the coverage and were nearly equal to one another. The values of the selectivity constant for Am^{3+} at 0.01 M and 0.1 M NaCl were also found to be similar to those for Ln^{3+}. This means that differences in the selectivity of finely dispersed montmorillonite colloidal particles for trivalent actinides and lanthanides are quite small in the low coverage region.

We tried to fit a Langmuir-type equation to the sorption results:

$$[Ln^{3+}] = K\left(\frac{\theta}{1 - \theta}\right). \tag{5}$$

The results are shown in Fig. 4. The slopes of lines were approximately unity for all systems. This indicates that the sorption of Ln^{3+} onto the finely dispersed montmorillonite particles is dominated by the Langmuir-type sorption and is coincident with the ion-exchange process discussed in Section 3.1. Since the sorption of cations (I, II) on massive montmorillonite solids has been often discussed by using a Langmuir-type isotherm (Ref. [21] for example), our experimental results suggest that both Ln^{3+} and cations (I, II) are sorbed onto finely dispersed montmorillonite colloidal particles as well as onto massive montmorillonite solids by ion-exchange and their sorption behavior agrees with a Langmuir-type isotherm.

4. Conclusions

We studied the sorption affinity of the finely dispersed Na-montmorillonite colloidal particles, which originated from Tsukinuno in Japan, for Am^{3+}, Nd^{3+}, Eu^{3+} and Gd^{3+}, and the differences between the affinity of the finely dispersed montmorillonite colloidal particles and that of the massive montmorillonite solids. We also investigated the influence of Na^+ and Ca^{2+} on the affinity for the lanthanide cations. The following conclusions are drawn.

(1) In the low Na^+ concentration region, $\log K_d$ (sorption ratios) decreased linearly with increasing $\log [Na^+]$, and the ion-exchange stoichiometry of Na^+ for Am^{3+} and Ln^{3+} was 1:3, which is close to the theoretical value for ion-exchange process in the Na-montmorillonite-Am^{3+}/Ln^{3+} system. On the other hand, in the high Na^+ concentration region, the sorption ratios were constant, and specific for Am^{3+} and (also for) each Ln^{3+}, and increased in the following order: $Gd^{3+} < Eu^{3+} < Am^{3+} < Nd^{3+}$, which is in the reverse order of the hydration free energy. These results indicate that the sorption behavior of Am^{3+} and Ln^{3+} onto the finely dispersed montmorillonite colloidal particles is basically same as that onto the massive montmorillonite solids, and that the affinity of the finely dispersed montmorillonite colloidal particles for Am^{3+} and Ln^{3+} is predicted by considering the sorption data of
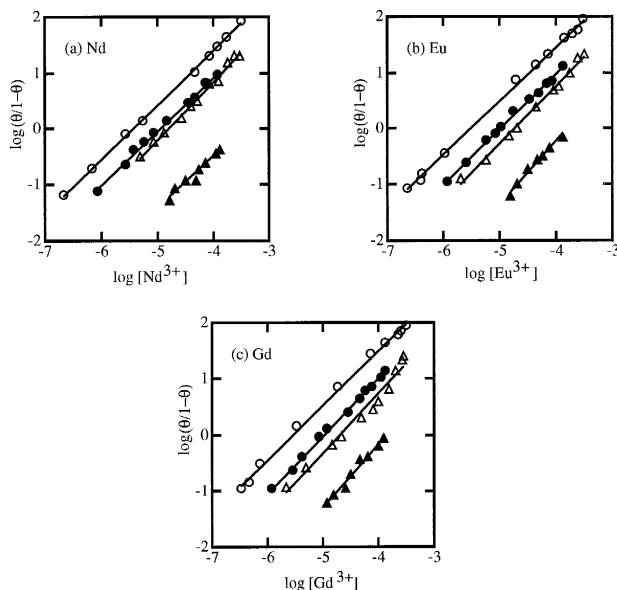

Fig. 4. Fitting of Langmuir-type equation for lanthanide sorption. (a) Nd^{3+}; (b) Eu^{3+}; (c) Gd^{3+}. $\bigcirc$: 0.01 M (NaCl); $\bullet$: 0.1 M (NaCl); $\triangle$: 0.01 M ($CaCl_2$); $\blacktriangle$: 0.1 M ($CaCl_2$).

Am^{3+} and Ln^{3+} onto the massive montmorillonite solids and other information on the environmental conditions (ex. ion concentrations).

(2) The sorption of Ln^{3+} onto the finely dispersed montmorillonite colloidal particles depended strongly on the NaCl and $CaCl_2$ concentration. The coverage by Ln^{3+} was significantly reduced for Ca-montmorillonite/Ln^{3+} system at the higher $CaCl_2$ concentration. The selectivity of the finely dispersed montmorillonite colloidal particles for Ln^{3+} depended on the NaCl and $CaCl_2$ concentrations and the type of montmorillonite, but not on the sorbate ions in the small coverage ($\theta < 50\%$). Furthermore, the sorption of Ln^{3+} onto the finely dispersed montmorillonite colloidal particles was coincident with a Langmuir-type isotherm. This supports that the sorption of Ln^{3+} onto the finely dispersed montmorillonite colloidal particles is basically explained by ion-exchange reaction.

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