



Title	Effect of exchangeable cations on apparent diffusion of Ca ²⁺ ions in Na- and Ca-montmorillonite mixtures
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Citation	Physics and Chemistry of the Earth, Parts A/B/C, 35(6-8), 254-258 https://doi.org/10.1016/j.pce.2010.04.006
Issue Date	2010
Doc URL	http://hdl.handle.net/2115/47463
Type	article (author version)
File Information	PCE35-6-8_254-258.pdf



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For Physics and chemistry of the earth

(To be presented at Migration'09)

JPCE-1793

**EFFECT OF EXCHANGEABLE CATIONS ON APPARENT DIFFUSION
OF Ca²⁺ IONS IN Na- AND Ca-MONTMORILLONITE MIXTURES**

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Abstract

Compacted Na-bentonite, of which the major mineral is montmorillonite, is a candidate buffer material for the geological disposal of high-level radioactive waste. A potential alteration of the bentonite in a repository is the partial replacement of the exchangeable cations of Na^+ with Ca^{2+} . The Ca^{2+} cations could be released from cementitious materials and diffuse into the buffer material in the repository. In this study, to evaluate the alteration that could reduce the performance of the bentonite buffer, the apparent diffusion coefficients of HTO and Ca^{2+} ions were determined from non-steady, one-dimensional diffusion experiments using Na- and Ca-montmorillonite mixtures with different ionic equivalent fractions of Ca^{2+} ions. The apparent diffusion coefficient of HTO at a dry density of 1.0 Mg m^{-3} slightly increased with an increase in the ionic equivalent fraction of Ca^{2+} ions. However, the apparent diffusion coefficient of Ca^{2+} and the activation energy for diffusion at the same dry density were independent of the ionic equivalent fraction of Ca^{2+} ions. These findings suggest that unlike HTO, which can be postulated to diffuse mainly in pore water, Ca^{2+} ion diffusion could occur predominantly in interlayer spaces, of which the basal spacing was determined to be constant by the XRD technique.

Keywords: bentonite, montmorillonite, diffusion, exchangeable cation, geological disposal, radioactive waste

Introduction

In the Japanese strategy for geological disposal of high-level radioactive waste, buffer material is used to fill the voids between each carbon steel waste container (so-called “Overpack”) and the host rock (JNC, 2000). Since one important function of the buffer material is to retard the radionuclide transport from the waste form to the surrounding host rock after degradation of the overpack, the most promising candidate for the buffer material is compacted sodium bentonite (Na-bentonite). The major clay mineral in Na-bentonite is Na-montmorillonite, which has a high swelling property together with low hydraulic conductivity and low diffusivity of radionuclides (Pusch and Yong, 2006). However, the large amount of cementitious materials used in waste repository tunnel construction could release Ca^{2+} ions into the groundwater within the tunnel. These released Ca^{2+} ions would be in contact with the buffer material, which could result in the alteration of the clay minerals, i.e., the exchange of Na^+ ions with Ca^{2+} ions. Therefore, the safety assessment of the geological disposal strategy should address the diffusion behavior of radionuclides not only for the compacted Na-bentonite but also for the altered bentonite of which part or all exchange cations are replaced with Ca^{2+} ions. In addition, the degree and extent of the alteration in the repository should be predicted in the safety assessment. These predictions should be based on studies of the diffusivities of Ca^{2+} ions in both the Na-bentonite and the altered bentonite. Although extensive studies have been performed for the diffusion of radionuclides in bentonite (Bourg et al., 2008, Glaus et al., 2007, Gonzalez-Sanchez et al., 2008, Kozaki et al., 2008, Melkior et al., 2009), there are few studies on the diffusivities of Ca^{2+} ions in compacted bentonite (Kozaki et al., 2001a) and the effects of exchangeable

cations on diffusion of radionuclides (Choi and Oscarson, 1996, Kozaki et al., 1999a, 2005).

In this study, therefore, apparent diffusion coefficients of $^{45}\text{Ca}^{2+}$ ions were determined for montmorillonite having different $\text{Na}^+/\text{Ca}^{2+}$ ratios of exchangeable cations. The apparent diffusion coefficients of HTO were also studied since diffusion of HTO can be considered as representative of the diffusion behavior of neutral species in montmorillonite pore spaces. The geometrical changes of the diffusion pathway were evaluated from the viewpoint of the apparent diffusion coefficients of HTO together with the basal spacing of montmorillonite measured by the X-ray diffraction (XRD) technique, while activation energies for the diffusion, which are important parameters for elucidating the diffusion process, were calculated from the temperature dependence of the Ca^{2+} diffusion for each $\text{Na}^+/\text{Ca}^{2+}$ ratio of the exchangeable cations. The diffusion mechanism of Ca^{2+} ions in compacted montmorillonite discussed in this paper is based on these experimental data.

Experimental

The montmorillonite used in this study was Kunipia-F, a commercial product of Kunimine Industries Co. Ltd., Japan. Homoionized Na- and Ca-montmorillonite were prepared by suspending the montmorillonite in fresh solutions of 1 M NaCl three times and 1 M CaCl_2 four times, respectively. Excess salt was removed by rinsing the montmorillonite with distilled water through a dialysis tube. The homoionized montmorillonite was dried in an oven at 378 K, mortared with a pestle, and then sieved to obtain a powder with aggregate sizes between 75 and 150 μm . The Na- and

Ca-montmorillonite mixtures were prepared by mixing the prescribed quantities of each sample. In this study the $\text{Na}^+/\text{Ca}^{2+}$ ratio of exchangeable cations in the mixtures is expressed by the ionic equivalent fraction of Ca^{2+} (-). The detailed procedure for preparation of homoionized montmorillonite was described in a previous paper (Kozaki et al., 2005).

Water-saturation of montmorillonite was accomplished by compaction of the samples into 20 mm-inside-diameter acrylic resin cells at a dry density of 1.0 Mg m^{-3} , followed by exposure of the samples to distilled water through sintered stainless steel filters. The cell lengths were 20 mm for the diffusion experiments and 10 mm for the XRD measurements. The porosity of the compacted montmorillonite at the dry density was estimated to be 0.65 from partial density of the montmorillonite (2.88 Mg m^{-3}). There is a negligibly small difference in porosity between Na- and Ca-montmorillonite.

The basal spacing of the water-saturated, compacted montmorillonite samples was determined from XRD profiles measured from 3 to 8 degrees of 2θ using an X-ray diffraction apparatus (Mac Science MXP³). Flat diffraction planes were obtained by sectioning the surface layer (a few mm in thickness) of the samples just before the measurements.

The apparent diffusion coefficients of HTO or $^{45}\text{Ca}^{2+}$ ions in the water-saturated, compacted montmorillonite samples were determined from concentration profiles of the radiotracer in the samples obtained in the diffusion experiments by the one-dimensional, non-steady diffusion method (the so-called *back-to-back* diffusion method). Using this method, a small amount of HTO or ^{45}Ca

radiotracer was spiked on one end of two compacted montmorillonite samples. The spiked ends of the two montmorillonite samples were placed together, as illustrated in Figure 1. The radiotracer was allowed to diffuse in opposite directions from the junction of the spiked ends. The concentration profiles were obtained from the radioactivity measurements of 0.5-mm-thick montmorillonite slices that were sectioned from the montmorillonite samples after a prescribed period of time for diffusion. The radioactivity measurements were carried out using a liquid scintillation counter (Aloka, LSC-5100). Diffusion experiments were conducted for montmorillonite samples with different ionic equivalent fractions of Ca^{2+} at a constant temperature, which ranged from 288 to 323 K. The detailed procedures of XRD measurement and the diffusion experiment are described elsewhere (Kozaki et al., 1998).

Results and discussion

Apparent diffusion coefficients were determined from the concentration profiles of radiotracers in montmorillonite by assuming each radiotracer to be an infinitely thin source, i.e., the concentration of the diffusing radiotracer, C (counts m^{-3}), can be expressed by the following equation (Crank, 1975):

$$C(x, t) = \frac{M}{2\sqrt{\pi D_a t}} \exp\left(-\frac{x^2}{4D_a t}\right), \quad (1)$$

where D_a is the apparent diffusion coefficient of the radiotracer in the montmorillonite ($\text{m}^2 \text{s}^{-1}$), t is the diffusion time (s), x is the distance from the montmorillonite surface on which the radiotracer was spiked (m), and M is the amount of the applied tracer source per unit area (counts m^{-2}). Figure 2

shows typical concentration profiles of HTO and Ca^{2+} obtained in this study. The plots of $\ln C(x)$ as a function of x^2 for the HTO and $^{45}\text{Ca}^{2+}$ radiotracers all had good linearity, suggesting that both radiotracers diffused under the condition of being an infinitely thin source as expressed by equation (1). The apparent diffusion coefficients of HTO and $^{45}\text{Ca}^{2+}$ obtained in this study are summarized in Tables 1 and 2, respectively. The uncertainties of the apparent diffusion coefficients were evaluated to be less than 3 % by statistics with a confidence limit of 95% in all cases. Reproducibility of the apparent diffusion coefficient for HTO was evaluated in the previous paper in which the same diffusion experiment was repeated several times (Kozaki et al., 1999b). For HTO in Na-montmorillonite at the dry density of 1.0 Mg m^{-3} , the average value of the apparent diffusion coefficients and the confidence interval calculated from 6 measurements with the confidence limit of 95% were $2.07 \pm 0.25 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$.

The apparent diffusion coefficient of HTO was found to increase slightly as the ionic equivalent fraction of Ca^{2+} increased. This change in HTO diffusivity agrees with the experimental results described in a previous paper by [Choi and Oscarson \(1996\)](#), in which a higher apparent diffusivity of HTO in Ca-bentonite than in Na-bentonite was reported. They also reported that a greater proportion of large pores in Ca-bentonite than in Na-bentonite was determined by Hg intrusion porosimetry, and concluded that higher diffusivity of HTO in Ca-bentonite can be attributed to the different microstructure of the compared bentonite. Considering high porosity of the montmorillonite (0.65 at dry density of 1.0 Mg m^{-3}) and high diffusivity of HTO in the pore water, the same as that in

free water, it can be supposed that HTO predominantly diffuses in the pore water at the dry density of 1.0 Mg m^{-3} . This can be supported by the fact that almost the same diffusion coefficients were reported for HTO and Cl^- in Na-montmorillonite at this dry density (Kozaki et al, 2001b).

Figure 3 shows X-ray diffraction profiles obtained in the present study for montmorillonite samples with different ionic equivalent fractions of Ca^{2+} . No change in the basal spacing (1.88 nm, corresponding to the three-water-hydrate state of the basal spacing) was found when the exchangeable cations of Na^+ were replaced with Ca^{2+} . On the other hand, specific surface areas determined by BET (N_2 gas) and EGME (ethyleneglycol-monoethylether) were reported to be $45 \text{ m}^2 \text{ g}^{-1}$ and $700 \text{ m}^2 \text{ g}^{-1}$, respectively for Na-montmorillonite in a dry powder state, and $34 \text{ m}^2 \text{ g}^{-1}$ and $670 \text{ m}^2 \text{ g}^{-1}$, respectively for Ca-montmorillonite (Kozaki et al., 1999a). The specific surface areas determined by the BET method have a clear difference between Na- and Ca-montmorillonite, whereas there is a small difference in the specific surface areas determined by the EGME method. The BET method measures only the surface area of montmorillonite aggregates, but the EGME method measures the whole surface area including the internal surfaces of the aggregates. Thus, the smaller specific surface area measured by the BET method for Ca-montmorillonite suggests a larger aggregate size in the Ca-montmorillonite than in the Na-montmorillonite. Since there is no difference in the basal spacing between Na- and Ca-montmorillonite, the difference of the aggregate size can be attributed to the number of unit layers making up the montmorillonite aggregate, as pointed out by Choi and Oscarson (1996). That implies that the change in the apparent diffusion coefficient of HTO could be

caused by the structural changes in the pore spaces rather than in the interlayer spaces where the basal spacing was found to remain constant.

The apparent diffusion coefficients of Ca^{2+} ions at each diffusion temperature were found to be independent of the ionic equivalent fraction of Ca^{2+} . It should be noted here that unlike HTO diffusion, Ca^{2+} diffusion is not influenced by the changes in the ionic equivalent fraction of Ca^{2+} . Besides the montmorillonite microstructure, the apparent diffusion coefficient is considered to include the retardation effect caused by the sorption of $^{45}\text{Ca}^{2+}$ on montmorillonite. However, there is no experimental data available on the dependence of K_d values of $^{45}\text{Ca}^{2+}$ on equivalent fraction of Ca^{2+} .

Figure 4 shows Arrhenius plots of the apparent diffusion coefficients of Ca^{2+} ions in compacted montmorillonite at Ca^{2+} ionic equivalent fractions of 0.28, 0.51, 0.76, and 1.0, together with the least-squares fits of the measured values. Good linearity was obtained at each ionic equivalent fraction. The activation energies for the diffusion of Ca^{2+} in compacted montmorillonite at the different Ca^{2+} ionic equivalent fractions were then determined from the Arrhenius plots. The error bars of the activation energies were evaluated by statistics with a confidence limit of 95%. The values obtained are listed in Table 2, and the dependency of these values on the Ca^{2+} ionic equivalent fractions is shown in Figure 4, along with those of the activation energies for Na^+ diffusion ([Kozaki et al., 2005](#)) and Cs^+ diffusion ([Kozaki et al., 1999a](#)). The activation energy for Ca^{2+} diffusion is found to be independent of the ionic equivalent fractions of Ca^{2+} , although the activation energies for Na^+ and Cs^+ diffusion vary as a function of the Ca^{2+} ionic equivalent fraction. Since the activation

energies in these studies were calculated from temperature dependence of the apparent diffusion coefficient, they can be affected not only by the predominant diffusion process but also by sorption enthalpy. For a montmorillonite suspension, the sorption enthalpy of Ca^{2+} ions on Na-montmorillonite was reported to be $+5.6 \text{ kJ eq}^{-1}$ (Bolt, 1979). If this constant value of the sorption enthalpy is included in the measured activation energy for Ca^{2+} diffusion, the activation energy suggests that unlike for Na^+ and Cs^+ , there would be no change in the dominant diffusion process of Ca^{2+} in montmorillonite even if the exchangeable cation of Na^+ ions in the montmorillonite is partially replaced with a Ca^{2+} cation.

It can be postulated that there are three potential pathways for radionuclide diffusion in solution-saturated, compacted montmorillonite, i.e., pore water, external surfaces of montmorillonite aggregates, and internal surfaces (interlayer spaces) of the montmorillonite aggregates (Kozaki et al., 2008). Pore water is the free water in the relatively large voids between the montmorillonite aggregates (interparticle space), and the external surface is the space on the montmorillonite aggregates where diffuse double layer water forms, whereas the internal surfaces is the space between montmorillonite sheets (TOT-layers).

In the case of Na- and Ca-montmorillonite mixture samples, Ca^{2+} ions were reported to preferentially (compared with Na^+ ions) occupy sites in interlayer spaces of montmorillonite rather than on external surfaces (Dufey et al., 1976). Therefore, for Na- and Ca-montmorillonite mixture samples, the degree of the contribution of each diffusion pathway to the total diffusivity of

radionuclides could vary with the ionic equivalent fraction of Ca^{2+} in the sample. For example, the dependency of the activation energy for Cs^+ diffusion on the ionic equivalent fraction of Ca^{2+} (as indicated in Figure 5) was explained by assuming that the diffusion of Cs^+ in Ca-montmorillonite becomes predominant at the high ionic equivalent fractions of Ca^{2+} (Kozaki et al., 1999a). Similarly, the alterations of the predominant diffusion process among three diffusion pathways were proposed as a possible explanation for the changes in the activation energy for Na^+ diffusion as a function of the Ca^{2+} ionic equivalent fraction (Kozaki et al., 2005). In the case of Ca^{2+} diffusion in Na- and Ca-montmorillonite mixtures, if Ca^{2+} ions preferentially occupy the sites in interlayer spaces in Na-montmorillonite aggregates as previously reported, the $^{45}\text{Ca}^{2+}$ radiotracers would preferentially diffuse in the interlayer spaces of Na-montmorillonite rather than in pore water and external surfaces of the aggregates, and would be accompanied by ion-exchange reactions between Na^+ and Ca^{2+} . In Ca-montmorillonite, the $^{45}\text{Ca}^{2+}$ radiotracer should migrate by self-diffusion, accompanied by isotopic dilution. Since almost all of the Ca^{2+} ions are present in the interlayer spaces as exchangeable cations, the dominant diffusion pathway is expected to be the interlayer spaces, of which basal spacing was determined to be constant by the XRD technique. Therefore, it can be postulated that these diffusion processes could keep the activation energy constant even if the ionic equivalent fraction of Ca^{2+} changed. If this is the case, the geometrical parameter of the diffusion pathway in the pores is not a matter of change in the apparent diffusion coefficient of Ca^{2+} but of HTO, which would predominantly diffuse in the pore water.

Conclusions

For the safety assessment of the geological disposal of high-level radioactive waste, the degree and extent of the alteration of bentonite buffer caused by Ca^{2+} ions should be studied together with diffusion behavior of radionuclides in the altered bentonite. In this study, the apparent diffusion coefficients of HTO and Ca^{2+} ions were determined from non-steady, one-dimensional diffusion experiments using Na- and Ca-montmorillonite mixtures with different ionic equivalent fractions of Ca^{2+} ions at a dry density of 1.0 Mg m^{-3} . The apparent diffusion coefficient of HTO increased slightly with an increase in the ionic equivalent fraction of Ca^{2+} ions. However, the apparent diffusion coefficients of Ca^{2+} ions at each temperature were almost the same at the range of the Ca^{2+} ionic equivalent fraction from 0 to 1.0. In addition, the activation energy for the Ca^{2+} diffusion was found to be independent of the ionic equivalent fraction of Ca^{2+} . By assuming that a constant value of sorption enthalpy is included in the measured value of the activation energy for Ca^{2+} diffusion, the activation energy suggests that there would be no change in the dominant diffusion process of Ca^{2+} in montmorillonite even if the exchangeable cation of Na^+ ions in the montmorillonite is partially replaced with a Ca^{2+} cation. If Ca^{2+} ions preferentially occupy the sites in interlayer spaces in Na-montmorillonite aggregates, it is likely that, unlike for HTO which can be considered to diffuse in pore water, Ca^{2+} ions could diffuse predominantly in interlayer spaces, the basal spacing of which was determined to be constant by the XRD technique.

Acknowledgements

The authors thank Mr. Yuu Hakozaki for conducting the diffusion experiments using HTO and Mr. Hiroki Sato for conducting the X-ray diffraction experiments. This work has been partly performed in the Central Institute of Isotope Science, Hokkaido University. Financial support was provided by the Ministry of Education, Culture, Sports, Science and Technology (MEXT), Japan (a Grant-in-Aid for Scientific Research (B), No. 20360415), and the Japan Atomic Energy Agency (JAEA).

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Table and figure captions

Table 1 Apparent diffusion coefficients of HTO in Na- and Ca-montmorillonite mixtures at a dry density of 1.0 Mg m^{-3} at 298 K in this study (Ca^{2+} ionic equivalent fractions of 0.5 and 1.0) and the previous study (Ca^{2+} ionic equivalent fraction of 0, Kozaki et al., 1999b).

Table 2 Apparent diffusion coefficients of Ca^{2+} ions in compacted Na- and Ca-montmorillonite mixtures and activation energies for diffusion at a dry density of 1.0 Mg m^{-3} at different ionic equivalent fractions of Ca^{2+} ions in this (Ca^{2+} ionic equivalent fractions of 0.28, 0.51, 0.76 and 1.0) and the previous studies (Ca^{2+} ionic equivalent fraction of 0, Kozaki et al., 2001a).

Figure 1 Schematic of diffusion cell.

Figure 2 Concentration profiles of HTO and Ca^{2+} in compacted Ca-montmorillonite sample; dry density: 1.0 Mg m^{-3} , diffusion temperature: 298 K, diffusion duration and diffusion coefficient: 6.1 h and $2.6 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$ for HTO(left figure), 190.7 h and $1.6 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ for Ca^{2+} (right figure).

Figure 3 XRD profiles of the water-saturated, compacted Na- and Ca-montmorillonite mixtures with different ionic equivalent fractions of Ca^{2+} at a dry density of 1.0 Mg m^{-3} . The dotted line corresponds to a basal spacing of 1.88 nm, i.e., the three-water-hydrate state.

Figure 4 Temperature dependence of apparent diffusion coefficients of Ca^{2+} ions in water-saturated, compacted Na- and Ca-montmorillonite mixtures at a dry density of 1.0 Mg m^{-3} with different Ca^{2+} ionic equivalent fractions in this (Ca^{2+} ionic equivalent fractions of 0.28, 0.51, 0.76 and 1.0) and the previous studies (Ca^{2+} ionic equivalent fraction of 0, Kozaki et al., 2001a).

Figure 5 Activation energies for the diffusion of Ca^{2+} in compacted Na- and Ca-montmorillonite at a dry density of 1.0 Mg m^{-3} as a function of Ca^{2+} ionic equivalent fraction, together with those for the diffusion of Na^+ (Kozaki et al., 2005) and Cs^+ (Kozaki et al., 1999a).

Table 1

Ionic equivalent fraction of Ca ²⁺ [-]	Apparent diffusion coefficient of HTO at 298 K [m ² s ⁻¹] (Diffusion period of time)
0	2.07±0.25×10 ⁻¹⁰ (<i>n</i> = 6) [1] (6.3-19.7h)
0.50	2.3×10 ⁻¹⁰ (6.8 h)
1.0	2.3×10 ⁻¹⁰ (7.1 h)
	2.6×10 ⁻¹⁰ (6.1 h)
	2.4×10 ⁻¹⁰ (6.4 h)

[1] Kozaki et al., 1999b, *n* is the number of data)

Table 2

Ionic equivalent fraction of Ca ²⁺ [-]	Apparent diffusion coefficient [m ² s ⁻¹]				<i>E_a</i> [kJ mol ⁻¹]
	(Diffusion period of time)				
	288 K	298 K	313 K	323 K	
0 (*)	1.2×10 ⁻¹¹	1.7×10 ⁻¹¹	2.4×10 ⁻¹¹	2.8×10 ⁻¹¹	18.2 ± 1.1
	(169.7 h)	(43.6 h)	(47.4 h)	(98.4 h)	
	1.2×10 ⁻¹¹	1.7×10 ⁻¹¹	2.2×10 ⁻¹¹	2.9×10 ⁻¹¹	17.9 ± 1.0
	(169.4 h)	(43.8 h)	(47.7 h)	(98.3 h)	
0.28	1.2×10 ⁻¹¹	1.6×10 ⁻¹¹	2.3×10 ⁻¹¹	2.6×10 ⁻¹¹	17.8 ± 0.7
	(237.6 h)	(190.5 h)	(97.6 h)	(74.7 h)	
	1.2×10 ⁻¹¹	1.6×10 ⁻¹¹	2.4×10 ⁻¹¹	2.7×10 ⁻¹¹	17.1 ± 1.0
	(237.8 h)	(190.8 h)	(97.8 h)	(74.9 h)	
0.51	1.1×10 ⁻¹¹	1.6×10 ⁻¹¹	2.1×10 ⁻¹¹	2.6×10 ⁻¹¹	18.8 ± 1.5
	(192.7 h)	(190.3 h)	(119.4 h)	(95.0 h)	
	1.2×10 ⁻¹¹	1.5×10 ⁻¹¹	2.2×10 ⁻¹¹	2.5×10 ⁻¹¹	17.8 ± 0.7
	(192.8 h)	(190.5 h)	(119.5 h)	(95.3 h)	
0.76	1.3×10 ⁻¹¹	1.5×10 ⁻¹¹	2.1×10 ⁻¹¹	2.7×10 ⁻¹¹	17.1 ± 1.0
	(237.9 h)	(191.0 h)	(97.9 h)	(75.0 h)	
	1.1×10 ⁻¹¹	1.5×10 ⁻¹¹	2.1×10 ⁻¹¹	2.5×10 ⁻¹¹	17.1 ± 1.0
	(238.1 h)	(191.2 h)	(98.1 h)	(75.2 h)	
1.0	1.1×10 ⁻¹¹	1.6×10 ⁻¹¹	2.4×10 ⁻¹¹	2.6×10 ⁻¹¹	18.8 ± 1.5
	(192.8 h)	(190.5 h)	(120.0 h)	(72.0 h)	
	1.2×10 ⁻¹¹	1.6×10 ⁻¹¹	2.4×10 ⁻¹¹	2.6×10 ⁻¹¹	18.8 ± 1.5
	(193.0 h)	(190.7 h)	(120.2 h)	(72.2 h)	

(*) Kozaki et al. (2001a)

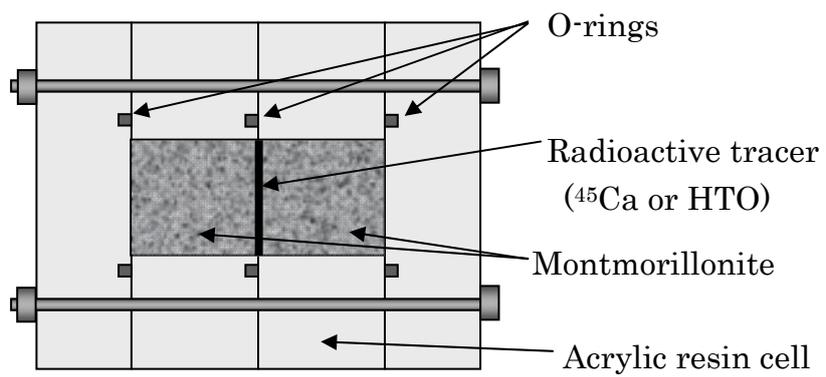


Figure 1

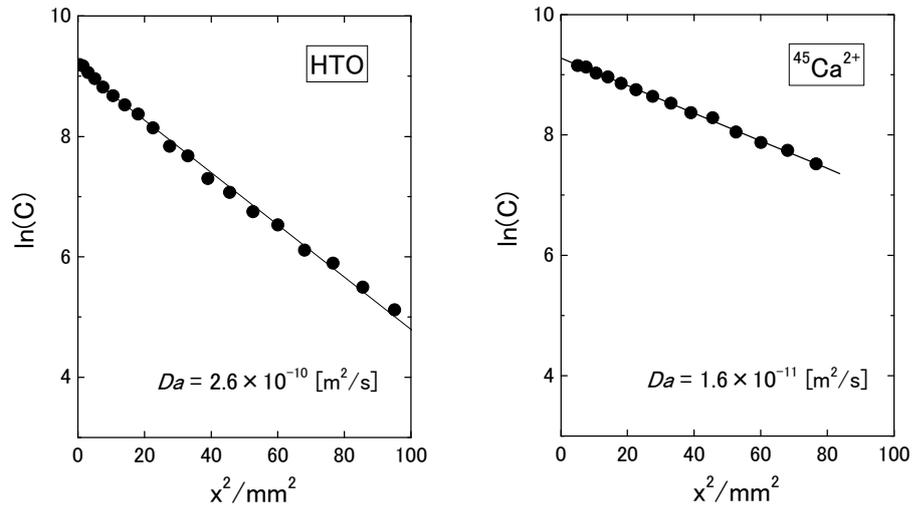


Figure 2

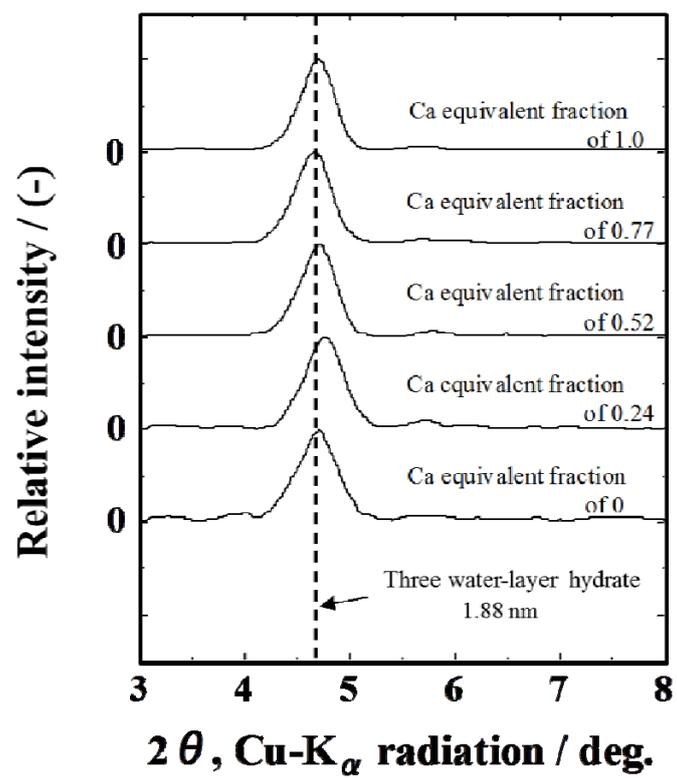


Figure 3

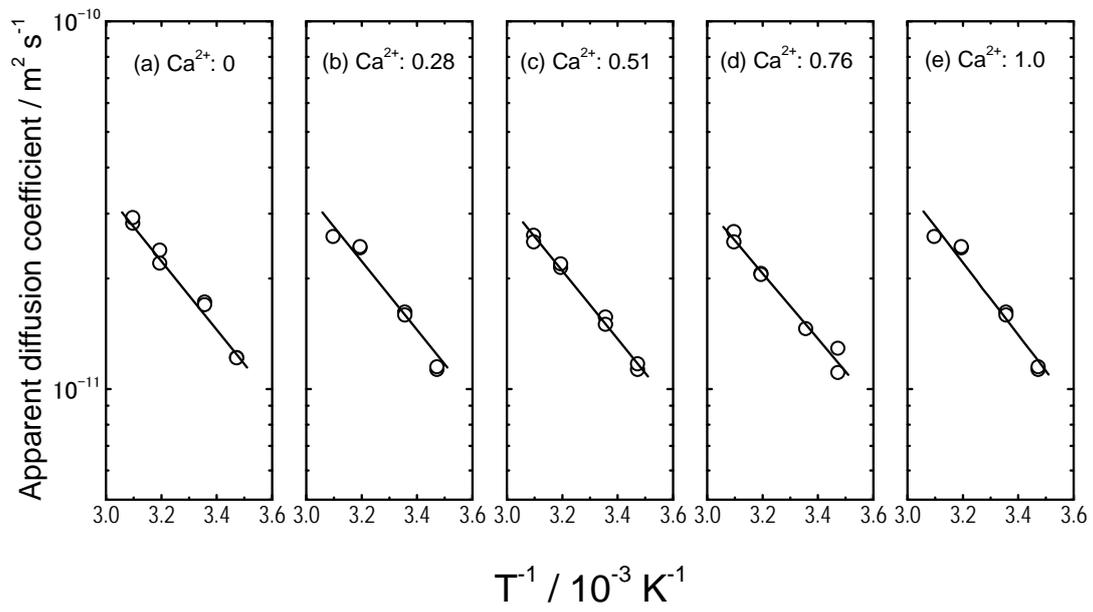


Figure 4

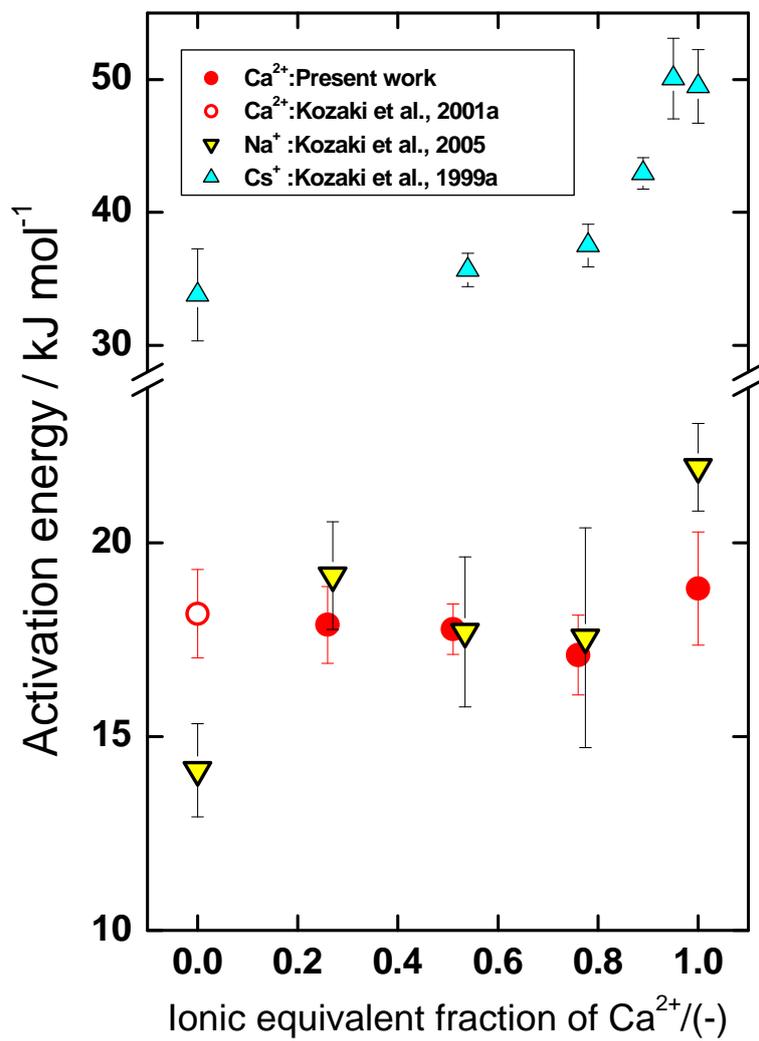


Figure 5