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Activation Energy for Diffusion of Helium in Water-Saturated, Compacted Na-Montmorillonite

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## Abstract

It is important to clarify the migration behavior of hydrogen gas dissolved in water-saturated, compacted bentonite, which is a promising material for geologic disposal of high-level waste and TRU waste disposal. The diffusion coefficients of helium, which can be detected under extremely low background conditions, in water-saturated, compacted Na-montmorillonite were determined as a function of temperature by a transient diffusion method. The activation energies for diffusion of helium were then obtained. The activation energies were from  $6.9 \pm 4.8$  to  $19 \pm 2.8$  kJ mol<sup>-1</sup> and were regarded to be independent of dry density. The activation energies of helium in water-saturated Na-montmorillonite were roughly equal to those in bulk water, 14.9 kJ mol<sup>-1</sup>, and in ice, from 11 to 13 kJ mol<sup>-1</sup>. It is possible that helium diffuses not only in pore water but also in interlayer water.

## Keywords

helium, diffusion coefficient, activation energy, Na-montmorillonite, transient diffusion method, compacted bentonite, water-saturation, mass spectrometry

## 1. Introduction

In geologic disposal of high-level radioactive waste, glass waste forms may be packed in metallic over-pack (JNC, 2000), which in turn will be surrounded by compacted bentonite. Bentonite is a promising candidate material for retardation of radionuclide migration because it is an ion exchange material with a large surface area, e.g., several tens of square meters per gram. The bentonite has very low hydraulic conductivity. Therefore, it is suitable as an engineered barrier because the migration process is controlled by diffusion with sorption, which is a process that is applicable for long-term assessment. However, because of the impermeability of bentonite, it may be possible that the long-term integrity of the bentonite is affected by the evolution of hydrogen gas resulting from the corrosion of over-pack materials. Similar studies should be carried out for TRU waste disposal. Accordingly, it is important to investigate the migration of this hydrogen gas in the water-saturated, compacted bentonite.

Several reports, in which a breakthrough of gas has been studied using a controlled flow rate gas migration apparatus, are available (Horseman et al., 1999). However, depending on the evolution rate of the hydrogen gas and the migration of the gas under a pressure gradient, the relaxation of pressure by the diffusion of the gas possibly plays an important role in the performance of this buffer material. Few reports are available on gas diffusion in water-saturated, compacted clay for nuclear waste disposal. Eriksen and Jacobsson (1982) and Neretnieks (1985) measured steady-state diffusion of hydrogen gas in water-saturated, compacted bentonite (MX-80) by a through-diffusion method. Their data were examined by Werme and Salo (1991), Wikramaratna et al. (1993) and Platt et al. (1994). The diffusion coefficient values determined from the data by Eriksen and Jacobsson (1982) and Neretnieks (1985) are in the range of  $3.6 \times 10^{-12}$  to  $1.8 \times 10^{-11} \text{ m}^2 \text{ s}^{-1}$ , but the diffusion process of gas in water-saturated, compacted bentonite has not been sufficiently examined. A study is needed to clarify the migration behavior of gas dissolved in water-saturated, compacted bentonite.

In our previous work, diffusion of helium in compacted Na-montmorillonite (Sato et al., 2001) and Ca-montmorillonite (Higashihara et al., 2001) was studied by a transient diffusion method because, in contrast to hydrogen gas, helium can be easily recovered from the montmorillonite at elevated temperatures and detected by mass spectrometric analysis with low background. Quite satisfactory concentration profiles for diffusion of helium were obtained as a function of penetration depth, along with highly reproducible diffusion coefficients (Sato et al., 2001; Higashihara et al., 2001).

The purpose of this present work is to examine the diffusion process of helium dissolved in water-saturated, compacted Na-montmorillonite. The diffusion coefficients of helium in the compacted Na-montmorillonite were obtained at several temperatures by a transient diffusion method; the activation energies for diffusion of helium were determined as a function of dry density.

## 2. Experimental Materials and Procedure

### 2.1 Specimen

Kunipia-F powder, a product of the Kunimine Industries Co. Ltd., was used to prepare water-saturated, compacted sodium montmorillonite specimens. Kunipia-F contains 99 % montmorillonite. Each Na-montmorillonite powder specimen was dried in air in an oven at 378 K for 24 h and was then compacted in an acrylic cell 20 mm in diameter and 20 mm in height. Sintered stainless-steel filters were placed at both ends of the cell to permit water permeation from both ends. The sintered filters were 2.0 mm in thickness with 2- $\mu$ m-diameter pores. The filters were retained with stainless steel supporting plates 5.0 mm in thickness with a number of holes 2.5 mm in diameter. The dry densities of the Na-montmorillonite specimens were 0.8, 1.0, 1.2, 1.4, and  $1.6 \times 10^3$  kg m<sup>-3</sup>. To avoid helium diffusion by air occluded in the compacted montmorillonite, the specimens were prepared using the following procedure. Each cell was put in a beaker, which was placed in a vacuum desiccator.

After evacuation for half an hour, deionized water was introduced from the side of the desiccator onto the cell, and the beaker was evacuated for another half an hour. Water saturation was carried out for 30 d under atmospheric pressure.

## 2.2 Procedure

The diffusion of helium in the compacted montmorillonite was carried out by a transient diffusion method. Helium dissolved in deionized water by helium bubbling was penetrated into the montmorillonite through a sintered stainless filter in the way of a constant diffusion source.

After 6.0 hours of helium diffusion, each montmorillonite specimen was sectioned into 1.0-mm-thick wafers. The quantities of helium contained in the wafer were analyzed with a quadrupole gas analyzer (QMS, ANELVA AQA-100 MPX). The details of this experimental procedure are given elsewhere (Sato et al., 2001; Higashihara et al., 2001).

## 2.3 Data analysis

The apparent diffusion of helium in the compacted montmorillonite can be described by the equation (Crank, 1975) under the constant concentration of helium source,

$$\frac{C}{C_0} = \operatorname{erfc}\left(\frac{x}{2\sqrt{D_a t}}\right) \quad (1).$$

where,

$C$ : concentration of helium in the compacted montmorillonite ( $\text{mol m}^{-3}$ )

$C_0$ : concentration of helium in the compacted montmorillonite in contact with water containing dissolved helium ( $\text{mol m}^{-3}$ )

$D_a$ : apparent diffusion coefficient ( $\text{m}^2 \text{s}^{-1}$ )

$L$ : thickness of specimen (m)

$x$ : penetration depth (m)

$t$ : diffusion time (s).

In the experimental period, the length of montmorillonite specimens is sufficiently large. So, the specimens are regarded as semi-infinite mediums. The value  $D_a$  was determined by the least-squares fit using  $C/C_0$  and  $D_a$  as variables.

The activation energies for diffusion of helium were obtained from the temperature dependence of the apparent diffusion coefficient of helium, which is described by the Arrhenius equation,

$$D_a = A \exp\left(-\frac{E_a}{RT}\right) \quad (2)$$

where

$A$ : constant (-)

$E_a$ : activation energy for diffusion of helium in water-saturated, compacted montmorillonite (kJ mol<sup>-1</sup>)

$R$ : gas constant (J K<sup>-1</sup> mol<sup>-1</sup>)

$T$ : absolute temperature (K).

Based on Eq. (2), activation energies for diffusion of helium in water-saturated, compacted montmorillonite were determined as a function of dry density.

### 3. Results and Discussion

#### 3.1 Activation energy

Figure 1 gives typical examples of concentration profiles of helium in water-saturated, compacted Na-montmorillonite at a dry density of  $0.8 \times 10^3$  kg m<sup>-3</sup>. The solid lines are the

least-squares-fit curves for the experimental data at the temperatures 278, 298, and 318 K. These profiles are well reproduced by the curves based on Eq. (1), together with the profiles for other specimens. The apparent diffusion coefficients  $D_a$  obtained are summarized in Table 1.

Arrhenius plots of the apparent diffusion coefficients of helium in water-saturated, compacted Na-montmorillonite are shown at five dry densities in Fig. 2. The solid lines are the regression lines based on the logarithm of Eq. (2). The activation energies for diffusion of helium,  $E_a$ , obtained from the slopes of the lines are listed in Table 1, and plotted in Fig. 3, with those of cesium (Kozaki et al., 1996), sodium (Kozaki et al., 1998a), and tritium in the form of HTO (Nakazawa et al., 1999). The  $E_a$  values of helium in Fig. 2 are smaller than that of water, 18 ~ 19 kJ mol<sup>-1</sup> and look like being scattered ( $\pm 5$  kJ mol<sup>-1</sup>). The discussion of these values is carried out using Fig. 3. The dashed line is the activation energy of helium in bulk water, 14.9 kJ mol<sup>-1</sup> (Wise and Houghton, 1966). The activation energy for diffusion of ions in water-saturated, montmorillonite depends on the dry density and is different from that of ions in bulk water (Parsons, 1959). This indicates that the diffusion process of ions in montmorillonite changes with an increase in dry density (Kozaki et al., 1996; Kozaki et al., 1998; Kozaki et al. 1997; Kozaki et al. 1998b). However, there is little change in the activation energy for the diffusion of helium as is also the case for HTO (Nakazawa et al., 1999), though the activation energy of helium still scatters. This indicates that the diffusion process of helium in water-saturated, compacted Na-montmorillonite does not change in the dry density range from 0.8 to  $1.6 \times 10^3$  kg m<sup>-3</sup>.

### 3.2 Diffusion behavior of helium

Wise and Houghton (1966) reported the diffusion coefficients of several gases dissolved in water ranging between 283 and 333 K. Haas et al. (1971) measured the diffusion coefficients of helium in single-crystalline ice from 173 to 253 K. The former obtained an activation energy of helium of 14.9 kJ mol<sup>-1</sup>, and the latter obtained an activation energy of 11 kJ mol<sup>-1</sup> in the direction parallel to the c-axis

and  $13 \text{ kJ mol}^{-1}$  in the vertical direction. Note that the former and latter values differ little. This indicates that the diffusion mechanism of helium in water is almost that in ice, as can be seen in the following discussion. The diffusion coefficients of several chemical species in water and the activation energies of these species in water, ice, and compacted Na-montmorillonite are summarized in Table 2. The diffusion coefficients of helium in water and hydrogen molecules in water are definitely larger than those of protons and oxygen-18 in the form of  $\text{H}_2\text{O}$  (Eisenberg and Kauzmann, 1969), ions in the hydrated state (Parsons, 1959) and several other larger size gases (Wise and Houghton, 1966), e.g., oxygen, nitrogen, and argon. On the other hand, the activation energies of helium and hydrogen gas dissolved in the water are smaller than those of  $\text{H}_2\text{O}$ , hydrated ions, and other gases. Additionally, the activation energy for diffusion of helium in ice,  $11 \sim 13 \text{ kJ mol}^{-1}$ , is much smaller than that for the self-diffusion of  $\text{H}_2\text{O}$  in ice, 56 or  $66 \text{ kJ mol}^{-1}$ . Therefore, it is very likely that the larger diffusion coefficient and smaller activation energy of helium are results from the size of helium, which is appreciably smaller than  $\text{H}_2\text{O}$ , hydrated ions, and other gases. This is presumably due to the cavity-to-cavity diffusion of helium among water molecules both in the liquid and solid states. Namely, the diffusion behavior of helium in water is analogous to that in ice.

Torikai et al. (1996) studied the water contained in compacted sodium montmorillonite from a thermodynamic aspect. They reported that water adsorbed as single-, two-, or three-layer hydrates in compacted montmorillonite is more stable than that in bulk water. In addition, the water in single-layer hydrate in the montmorillonite is bound as strongly as in ice from the view point of entropy. In the montmorillonite, the values of the activation energies for diffusion of helium are roughly equal to those in water and ice as shown in Table 2. It can be regarded that helium behaves similarly in bulk water, ice, and water-saturated, compacted montmorillonite. Even if the degree of freedom in the motion of water molecule in interlayer spaces is restricted kinetically, as in ice, helium diffusion may occur among water molecules using the cavities. Thus it is possible that helium diffuses not only in pore water but also in

interlayer water. Unfortunately, based on only activation energy, it cannot be concluded whether the diffusion of helium occurs in the pore spaces and/or in the interlayer spaces in the montmorillonite.

#### 4. Conclusions

The diffusion coefficients of helium were obtained in water-saturated, compacted Na-montmorillonite as functions of temperature and dry density. The activation energies for the diffusion of helium range between 7 to 19 kJ mol<sup>-1</sup>, are independent of dry density, and are roughly equal to those in water, 14.9 kJ mol<sup>-1</sup>, and in ice, 11 ~ 13 kJ mol<sup>-1</sup>. It can be regarded that helium behaves similarly in bulk water, ice, and water-saturated, compacted montmorillonite. Even if the motion of water molecules in interlayer spaces is restricted kinetically, as in ice, helium diffusion may occur among water molecules using the cavities. Thus it is possible that helium diffuses not only in pore water but also in interlayer water.

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Table 1 Apparent diffusion coefficients of helium in water-saturated, compacted Na-montmorillonite  
and activation energies as a function of dry density

Dry density ( $10^3 \text{ kg m}^{-3}$ )	Absolute temperature (K)	Apparent diffusion coefficient ( $\text{m}^2 \text{ s}^{-1}$ )	Activation energy ( $\text{kJ mol}^{-1}$ )
0.8	278	$3.6 \times 10^{-10}$	$14.5 \pm 4.5$
	298	$6.6 \times 10^{-10}$	
	314	$7.3 \times 10^{-10}$	
1.0	281	$2.7 \times 10^{-10}$	$17.2 \pm 5.8$
	291	$3.4 \times 10^{-10}$	
	298	$3.6 \times 10^{-10}$	
	300	$3.4 \times 10^{-10}$	
	306	$5.5 \times 10^{-10}$	
1.2	278	$2.1 \times 10^{-10}$	$6.9 \pm 4.8$
	298	$2.5 \times 10^{-10}$	
	313	$2.9 \times 10^{-10}$	
	287	$1.6 \times 10^{-10}$	
	279	$2.2 \times 10^{-10}$	
1.4	278	$1.1 \times 10^{-10}$	$11 \pm 6.4$
	298	$2.0 \times 10^{-10}$	
	315	$1.9 \times 10^{-10}$	
1.6	278	$9.3 \times 10^{-11}$	$18.5 \pm 2.8$
	298	$1.4 \times 10^{-10}$	
	315	$2.4 \times 10^{-10}$	

Table 2 Diffusion coefficients in water at 298 K and activation energies in water, ice, and water-saturated, compacted Na-montmorillonite

	Diffusion coefficient in water at 298 K ( $\text{m}^2 \text{s}^{-1}$ )	Activation energy ( $\text{kJ mol}^{-1}$ )		
		in water	in ice	in Na-montmorillonite
He	$7.5 \times 10^{-9(a)}$	14.9 <sup>(a)</sup>	11 ~ 13 <sup>(b)</sup>	$6.9 \pm 4.8 \sim 19 \pm 2.8$
H <sub>2</sub>	$6.1 \times 10^{-9(a)}$	16.5 <sup>(a)</sup>	--	--
HTO	$2.4 \times 10^{-9(c)}$	19 <sup>(c)</sup>	56.4, 65.6 <sup>(c)</sup>	18 <sup>(d)</sup>
H <sub>2</sub> <sup>18</sup> O	$2.7 \times 10^{-9(c)}$	18 <sup>(c)</sup>	--	--
O <sub>2</sub>	$2.5 \times 10^{-9(a)}$	18.3 <sup>(a)</sup>	--	--
N <sub>2</sub>	$2.9 \times 10^{-9(a)}$	19.5 <sup>(a)</sup>	--	--
Ar	$2.6 \times 10^{-9(a)}$	21.0 <sup>(a)</sup>	--	--
Na <sup>+</sup>	$1.4 \times 10^{-9(e)}$	18.4 <sup>(e)</sup>	--	14 ~ 25 <sup>(f)</sup>

(a) Wise and Houghton (1966)

(b) Haas et al. (1971)

(c) Eisenberg and Kauzmann (1969)

(d) Nakazawa et al. (1999)

(e) Parsons (1959)

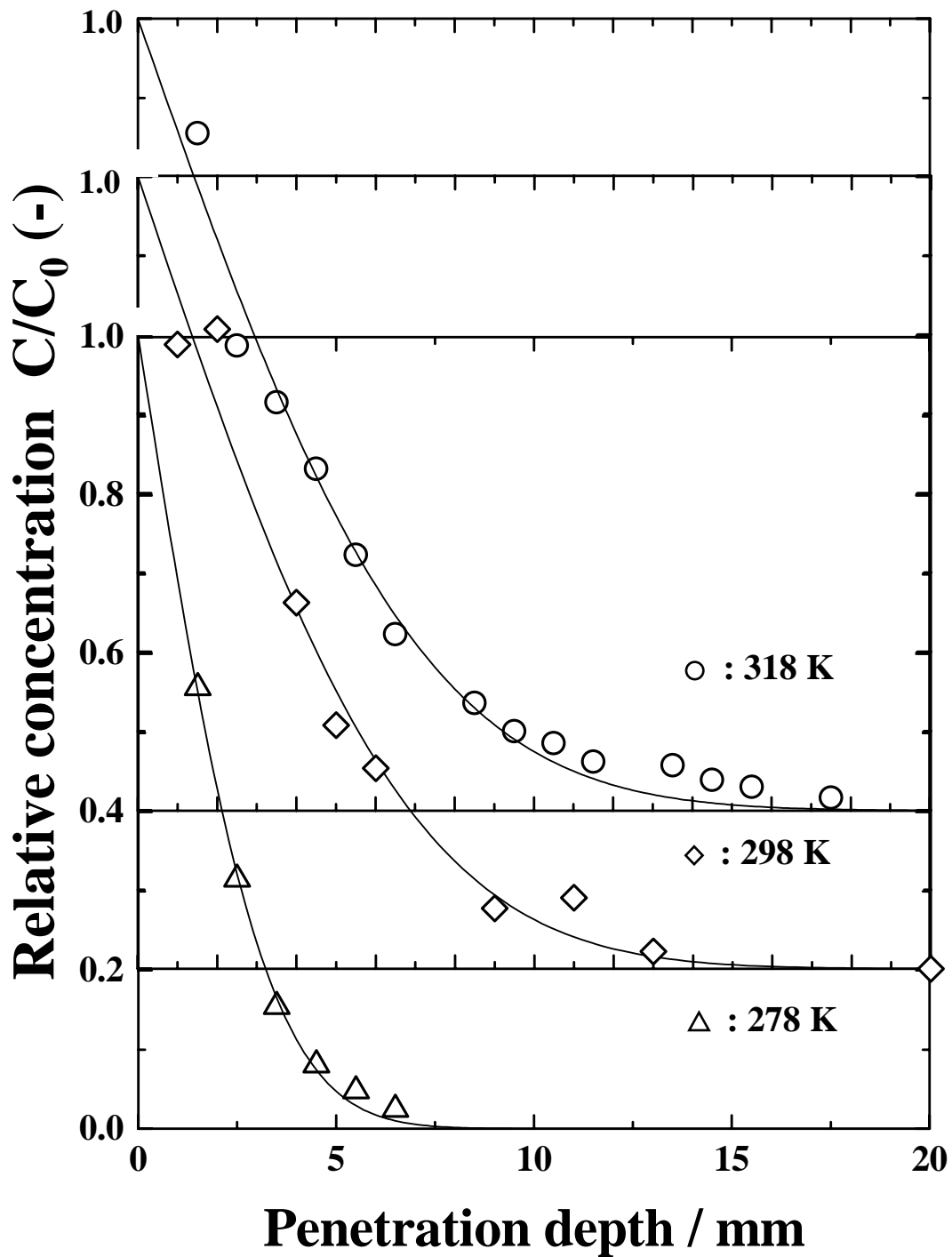
(f) Kozaki et al. (1998a)

## Figure Captions

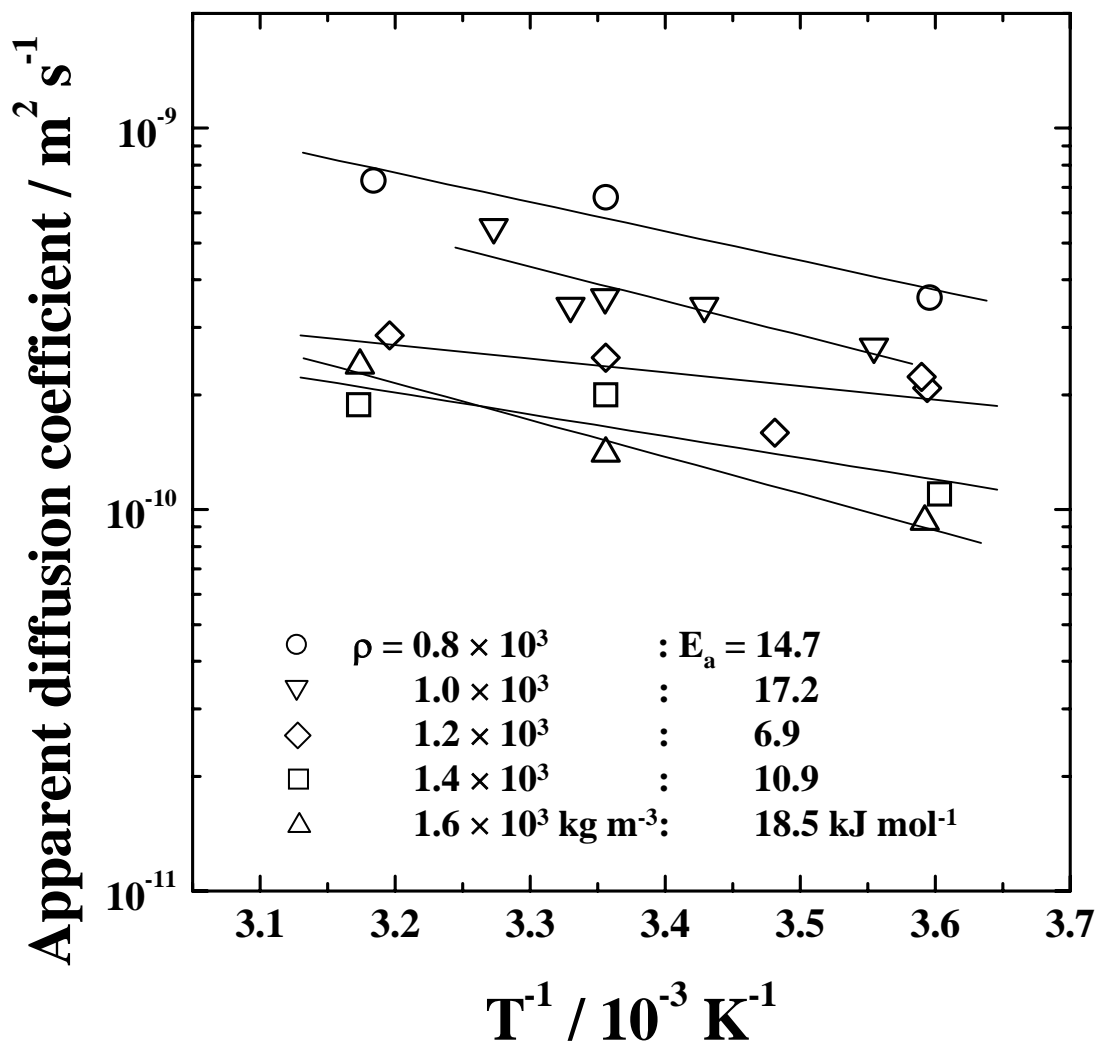
Fig. 1 Concentration profile of helium in water-saturated, compacted Na-montmorillonite at 278, 298, and 318 K; dry density:  $0.8 \times 10^3 \text{ kg m}^{-3}$ , diffusion time: 6.0 h

Fig. 2 Temperature dependence of apparent diffusion coefficients of helium in water-saturated, compacted Na-montmorillonite as a function of dry density

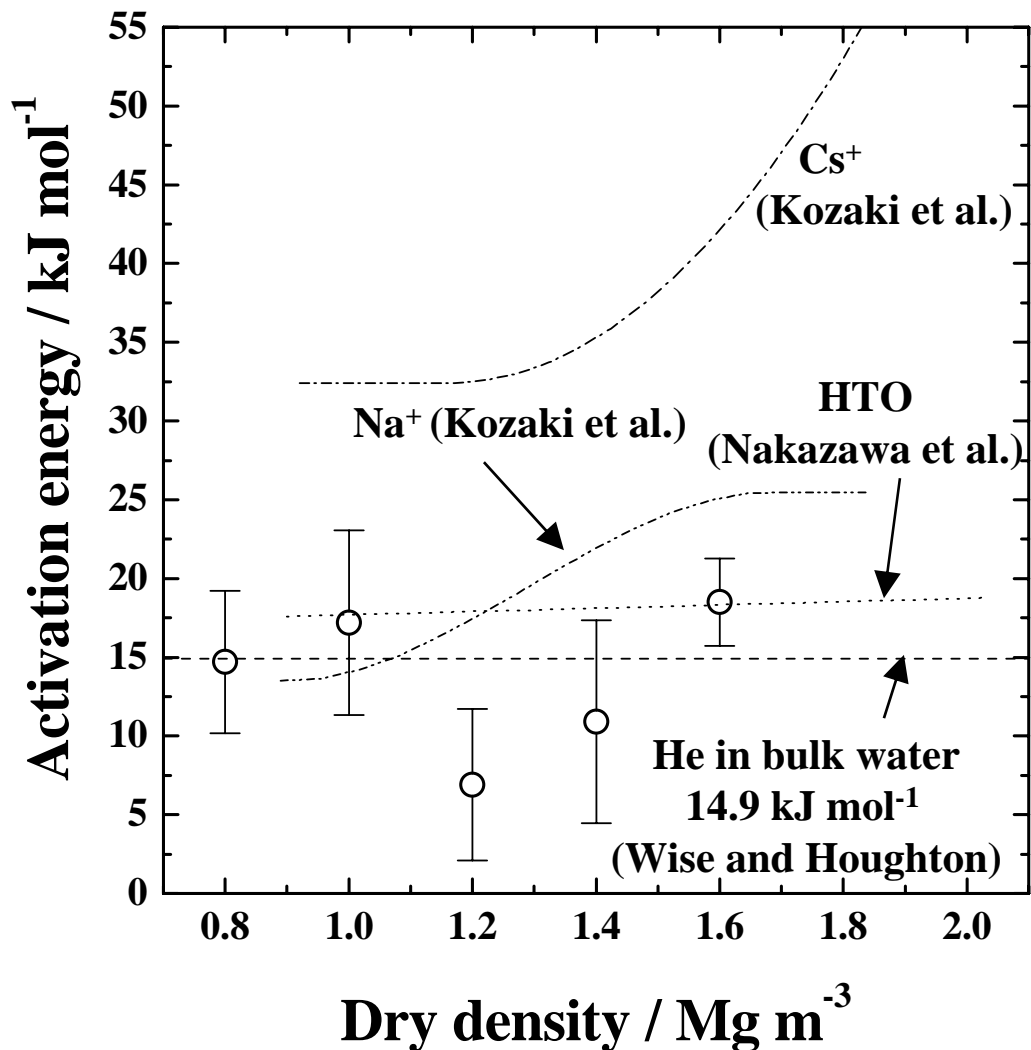
Fig. 3 Dry density dependence of activation energy for diffusion of helium,  $\circ$  ; together with  $-\cdot-\cdot-$  helium in bulk water (Wise and Houghton, 1966),  $-\cdot-\cdot-$  : cesium (Kozaki et al., 1996),  $-\cdot-\cdot-$  : sodium (Kozaki et al., 1998a),  $\cdots$  : HTO (Nakazawa et al., 1999) in water-saturated, compacted Na-montmorillonite



**Fig. 1** Concentration profile of helium in water-saturated, compacted Na-montmorillonite at 278, 298, and 318 K; dry density:  $0.8 \times 10^3 \text{ kg m}^{-3}$ , diffusion time: 6.0 h



**Fig. 2** Temperature dependence of apparent diffusion coefficients of helium in water-saturated, compacted Na-montmorillonite as a function of dry density



**Fig. 3** Dry density dependence of activation energy for diffusion of helium,  $\circ$ ; together with  $- - -$ : helium in bulk water (Wise and Houghton, 1966),  $- \cdot -$ : cesium (Kozaki et al., 1996),  $\cdot - -$ : sodium (Kozaki et al., 1998a),  $\dots\dots\dots$ : HTO (Nakazawa et al., 1999) in water-saturated, compacted Na-montmorillonite