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Site Selectivity of Alkaline Earth Metal Cations in Zeolite A

KWANG OH KOH, HAKZE CHON, AND MU SHIK JHON

Department of Chemistry, Korea Advanced Institute of Science and Technology, P.O. Box 150, Cheong Ryang Ri, Seoul, Korea

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Application of a semiempirical potential energy function to calculation of the site selectivity of alkaline earth metal cations in zeolites Na–A and K–A is described. Twenty-seven unit cells were adopted as a model compound. J. E. Huheey's [*J. Phys. Chem.* **69**, 3285 (1965)] electronegativity equalization method was used to calculate the net charge of framework. Although Mg^{2+} and Ca^{2+} ions show site I selectivity, Ba^{2+} ion is distributed over two sites. To study zero-coordinated cations, X-ray data were used for Ca_6–A, Sr_6–A, and K–A. The greater tendency of K^+ ion to occupy eight-ring sites is discussed in terms of site selectivities of the divalent cations.

INTRODUCTION

The molecular sieving action of zeolite A is influenced by the cations on the eight-ring windows. The unit-cell formula of dehydrated Na–A is $Na_{12}[(AlO_2)_{12}(SiO_2)_{12}]$. Zeolite Na–A has the three cationic sites. Sites I are displaced 0.4 Å into the α-cage from the center of six-rings. Sites II are located in the eight-rings displaced about 1.2 Å from the center. Sites III are located opposite the four-rings.

It is well known experimentally and theoretically that smaller cations such as Li^+, Na^+, Ca^{2+}, and Sr^{2+} prefer site I and larger cations such as K^+ and Cs^+ prefer site II (*1–4*). Only Ba^{2+} ion shows mixed occupancy (*5*).

Existence of zero-coordinated cations in zeolite A was claimed by Seff *et al.* (*6–8*). If the distance between two ions exceeds the sum of their corresponding radii by more than 1.0 Å, then those ions may be considered as nonbonded and termed zero coordinated. But Pluth and Smith's new refinements (*9, 10*) of K–A and Na–A showed that all the exchangeable cations are within the bonding distance of framework oxygens. They also claimed that all Sr^{2+} and Ca^{2+} ions in Sr_6–A and Ca_6–A lie near the centers of six-rings (*11, 12*). This does not agree with earlier X-ray data in which one atom was placed in an eight-ring (*6–8*). Earlier X-ray data were supported by a theoretical study (*13*). Recently, Smith *et al.* calculated the crystal energy for Sr^{2+} in zeolite A (*14*). Their result agrees with X-ray data at room temperature for the absence of Sr^{2+} in eight-ring sites (*11*).

When K^+ ions of K–A are exchanged by Ca^{2+} ions, K^+ ions on site I are exchanged in the first place. Hence, the abrupt changes in sieving action occur at 75% exchange in the (K, Ca)–A series.

In the present work, using the semiempirical potential energy functions, we have studied the site selectivity of alkaline earth metal cations in zeolites Na–A and K–A.

MODEL COMPOUND

An ordered arrangement of strictly alternating silica and alumina tetrahedra was used in order to make reliable calculations. For Na–A, the Cartesian coordinates of the pseudocell were obtained from X-ray data (*15*).

For Ca_6–A, Sr_6–A, and K–A, X-ray data were used to study the zero-coordinated cation (*7, 9, 11, 12, 16*). Twenty-seven unit cells were used as a model compound in calculating the interaction energy. The co-

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ordinate origin was taken as the center of the model compound.

For Ca_6–A, Sr_6–A, and K–A, cations near the center of six-rings were considered as site I cations and those in eight-rings as site II cations. Cations occupying neither site I nor site II in K–A were regarded as site III cations.

ENERGY CALCULATION

The potential energy of the cation was calculated in order to find the optimum position of the cation on each axis. Axis I passes through the center of site I and is perpendicular to the plane determined by three oxygen atoms which are located closer to the center of the six-membered oxygen ring. Axis II passes through two oxygen atoms which are located furthest from each other in the eight-membered oxygen ring.

The net charges of framework atoms were calculated by the electronegativity equalization method (*17*). Because zeolite A has the repeating unit $[Na^+(AlO_2SiO_2)]$ and the Al(Si) atoms are bonded tetrahedrally by four oxygen atoms,

$$\delta_{Si} + \delta_{Al} + \delta_{O(1)} + \delta_{O(2)} + 2\delta_{O(3)} = -1 \quad (1)$$

$$\begin{aligned} a_{Si} + b_{Si}\delta_{Si} &= a_{Al} + b_{Al}\delta_{Al} \\ &= a_{O(1)} + b_{O(1)}\delta_{O(1)} \\ &= a_{O(2)} + b_{O(2)}\delta_{O(2)} \\ &= a_{O(3)} + b_{O(3)}\delta_{O(3)} \end{aligned} \quad (2)$$

where a and b are the inherent electronegativity and the charge coefficient. a and b are calculated from O–Al(Si)–O bond angle and s character, because they linearly depend on s character (*17*). The net charges of atoms obtained from Eqs. (1) and (2) are $\delta_{Si} = 0.290$, $\delta_{Al} = 0.812$, $\delta_{O(1)} = -0.520$, $\delta_{O(2)} = -0.550$, and $\delta_{O(3)} = -0.516$.

Potential Energy Functions

Coulombic electrostatic energy. Zeolite lattice atoms are considered as point charges. The Coulombic energy is given by

$$E_{el} = \sum_i \frac{\delta_i \delta_{M^+}}{R_i} \quad (3)$$

where R_i is the distance between the cation and lattice ion, and δ_i and δ_{M^+} are the net charges of the ith atom and cation, respectively. The summation Σ_i is over all atoms in the model.

Polarization energy. The cation becomes polarized by the electric field formed by the framework atom. Thus a force of attraction arises. This energy is given by

$$E_{pol} = -\frac{1}{2} \sum_i \alpha_{M^+} (E_{iM^+})^2 \quad (4)$$

where α_{M^+} is the polarizability of the cation, and E_{iM^+} is the electric field at the cation by the ith atom. The polarizabilities (*18*) of Mg^{2+}, Ca^{2+}, and Ba^{2+} are 0.12×10^{-24}, 0.53×10^{-24}, and 1.69×10^{-24} cm^{-3}, respectively.

Dispersion and repulsion energy. The semiempirical formula proposed by Kitaigorodskii (*19, 20*) is used. This energy is given by

$$\begin{aligned} E_{disp-rep} = k_i k_{M^+} [&-A/Z^6 \\ &+ (1 - \delta_i/N_i^{val}) C \exp(-LZ)] \end{aligned} \quad (5)$$

where $Z = R_i/R_0$,

$$R_0 = [(2R_i^w)(2R_{M^+}^w)]^{1/2}.$$

R_i^w and $R_{M^+}^w$ are the van der Waals radii of atom i and cation M^+. The van der Waals radii of the cations are obtained from Stokes (*21*). The factor $(1 - \delta_i/N_i^{val})$ represents the influence of the atomic electron population to the repulsion. N_i^{val} is the number of valence electrons of the neutral atom. The multiplication factors k_i and k_{M^+} allow for the variation of the nature of interacting atoms ($k_o = 1.36$, $k_{Mg^{2+}} = 0.73$, $k_{Ca^{2+}} = 1.28$, $k_{Ba^{2+}} = 2.03$). The following values are used for A, C, and L: $A = 0.214$ kcal/mol, $C = 4700$ kcal/mol, and $L = 12.35$. The multiplication factors of cations (*22*) are obtained from

$$k_i = 0.234 \alpha_i I_i^{1/2} / (R_i^w)^3 \quad (6)$$

where I_i is the ionization potential of cation *i*. Si and Al are neglected in this energy calculation because they are buried in tetrahedra of oxygens.

RESULTS AND DISCUSSION

Site Selectivity of Divalent Cations in Na–A

When the first divalent cation (Mg^{2+}, Ca^{2+}, Ba^{2+}) enters into the α-cage, two Na^+ ions are exchanged. Because Na^+(III) has the least stabilization energy (*3*), the Na^+ ion on site III and one on either site I or II, which is occupied by the divalent cation introduced, are exchanged (*23*). According to X-ray results, the Na^+ ion on site III was not discovered in Ca_4Na_4–A (*24*).

The calculated interaction energies of the first-incoming divalent cations are given in Table 1. The cations all show site I selectivity. Although X-ray data show site I selectivity for Ca^{2+} ion (*24*), Ba^{2+} ion in Ba_1Na_{10}–A is distributed over two sites (I and II) (*5*). Because of the small energy difference between sites I and II, Ba^{2+} ion can be considered on the basis of energy calculations to occupy six-ring sites. In Table 1, Ba^{2+} ion on site I is lower in energy than that on site II. The greater tendency of Ba^{2+} ion to occupy six-ring sites is indeed observed in dehydrated $Ba_{3.5}Na_5$–A (*5*). However, partially dehydrated Ba_6–A shows that Ba^{2+} ions prefer to occupy eight-rings (*5*). This implies that Ba^{2+}–Ba^{2+} repulsive energies in the α-cage overcome site energy differences in partially dehydrated Ba_6–A. In Fig. 1, the energies of Mg^{2+}, Ca^{2+}, and Ba^{2+} ions on sites I and II are compared with the hydration energies of these cations. For the three cations, the interaction energies of cations are smaller than the hydration energy. This agrees with the fact that because the framework oxygen atoms are more rigid in the lattice than are the oxygen atoms in water, the ion solvation energy in the lattice is less than the solvation energy in water (*25*). The coordination numbers of the cation on site I and the first hydration numbers of the three cations are 6 (*26*). But secondary and additional hydration shells also pay an important role in the hydration energies. Coordination numbers of cations on site II are smaller than those on site I because of the longer and less symmetrical approaches to the framework. Thus site II is not as energetically favorable as site I. The energies of cations on sites II are nearly constant, whereas those on sites I decrease, as the cationic radii increase. As the size of the incoming cation increases, the Coulombic repulsive energies of the exchanged cation with the remaining Na^+ ions on sites I increase on site I and are nearly constant on site II. Hence Ba^{2+} ion shows the smallest energy difference between sites I and II.

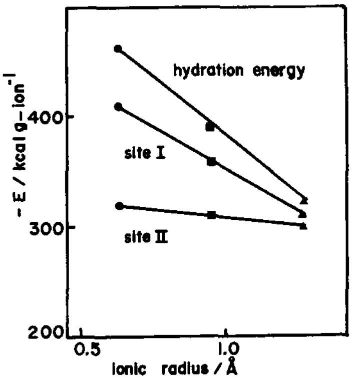

FIG. 1. Comparison of interaction energies of cations with hydration energies for Mg^{2+} (●), Ca^{2+} (■), and Ba^{2+} (▲).

TABLE 1

Interaction Energies of Divalent Cations in Na–A (kcal g-ion^{-1})

Cation	Site	E_{el}[a]	E_{pol}	$E_{disp\text{-}rep}$	E_{tot}
Mg^{2+}	I	−411.1	−0.1	1.1	−410.1
	II	−320.4	−0.1	1.5	−319.0
Ca^{2+}	I	−361.6	−1.3	4.2	−358.7
	II	−308.8	−0.3	1.7	−307.4
Ba^{2+}	I	−307.0	−5.5	3.0	−309.5
	II	−299.4	−0.7	1.2	−298.9

[a] E_{el}, E_{pol}, $E_{disp\text{-}rep}$, and E_{tot} represent the electrostatic, polarization, dispersion–repulsion, and total energies, respectively. 1 kcal g-ion^{-1} = 4.184 kJ g-ion^{-1}.

TABLE 2

Interaction Energies of the Sixth Ca^{2+} in Ca_6^{2+}–A (kcal g-ion^{-1})

X-Ray data	Site	E_{el}	E_{pol}	$E_{disp-rep}$	E_{tot}
Seff *et al.*	I	−459.3	−0.3	12.9	−446.7
	II	−323.6	−0.4	−2.2	−326.2
Pluth and Smith	I	−431.5	−0.3	11.3	−420.5
	II	−268.7	−0.5	−2.2	−271.4

TABLE 4

Interaction Energies of K^+ Ions in K–A (kcal g-ion^{-1})

X-Ray data	Site	E_{el}	E_{pol}	$E_{disp-rep}$	E_{tot}
Seff *et al.*	I	−118.5	−1.2	7.5	−112.2
	II	− 67.8	−0.2	−1.4	− 69.4
	III	1.8	−0.4	−1.8	− 0.4
Pluth and Smith	I	−134.1	−1.9	7.7	−128.3
	II	− 59.7	−0.2	−1.2	− 61.1
	III	− 7.2	−1.5	2.8	− 5.9

Site Selectivity of the Sixth Ca^{2+} and Sr^{2+} in Ca_6–A and Sr_6–A

X-Ray data were used in calculating the interaction energies of the sixth Ca^{2+} and Sr^{2+} ions. According to Pluth and Smith's X-ray data, (*11, 12*) six cations occupy sites I in Ca_6–A and Sr_6–A. Considering five cations on site I and one cation on site II, the interaction energy at site II was calculated. The calculated results are given in Tables 2 and 3. The two cations all show site I selectivity of the sixth cation, in contrast to the calculation of Nitta *et al.* (*13*). Our results agree with those of Smith *et al.* and support the nonexistence of zero-coordinated cation (*11, 12, 14*).

Site Selectivity of Ca^{2+} in K–A

According to the adsorption experiment, the change in the window size occurs at 33% exchange in the (Ca, Na)–A series and at 75% exchange in the (Ca, K)–A series (*27*). In the case of (Ca, Na)–A series, because the sequence of the interaction energies of Na^+ ions is Na^+(I) > Na^+(II) > Na^+(III), Na^+(II) and Na^+(III) are exchanged in the first place and pore opening occurs at 33% exchange. Because K^+(II) ions of K–A are retained up to 75% exchange, the sequence of the interaction energies of K^+ ions can be anticipated as follows: K^+(II) > K^+(I) > K^+(III). X-Ray data were used in calculating the interaction energy (*9, 16*). Results for dehydrated K–A are given in Table 4. The calculated results all show K^+(I) > K^+(II) > K^+(III) so that K^+(II) ions with smaller interaction energy are not exchanged in the first place, whereas more stable K^+(I) ions are exchanged in the first place.

Because Ca^{2+} ion occupies site I exclusively (*3, 24*), two K^+ ions on sites I and III are exchanged by the first incoming Ca^{2+} ion in K–A. Our results for the reaction

$$\text{K–A} \xrightarrow{Ca^{2+}} Ca_I^{2+}K_{10}\text{–A}$$

are given in Table 5. The site I selectivity of Ca^{2+} ion agrees with the experiment (*24*).

When the second Ca^{2+} ion enters the $Ca_I^{2+}K_{10}$–A system, the coordinates of this system are obtained from K–A. This implies that X-ray data of $Ca_I^{2+}K_{10}$–A are not available and the framework of zeolite is

TABLE 3

Interaction Energies of the Sixth Sr^{2+} in Sr_6^{2+}–A (kcal g-ion^{-1})

X-Ray data	Site	E_{el}	E_{pol}	$E_{disp-rep}$	E_{tot}
Seff *et al.*	I	−445.9	−1.2	26.3	−420.8
	II	−347.8	−1.0	−2.1	−350.9
Pluth and Smith	I	−408.8	−3.1	11.7	−400.2
	II	−316.6	−0.7	−1.6	−318.9

TABLE 5

Interaction Energies of the First Ca^{2+} in K–A (kcal g-ion^{-1})

X-Ray data	Site	E_{el}	E_{pol}	$E_{disp-rep}$	E_{tot}
Seff *et al.*	I	−342.3	−0.1	1.0	−341.4
	II	−241.0	−0.1	3.8	−237.3
Pluth and Smith	I	−326.2	−0.1	1.0	−325.3
	II	−235.0	−0.1	3.8	−231.3

TABLE 6

Interaction Energies of the Second Ca^{2+} in K–A (kcal g-ion^{-1})

X-Ray data	Case	E_{el}	E_{pol}	$E_{disp-rep}$	E_{tot}
Seff *et al.*	I	−405.1	−0.1	1.0	−404.2
	II	−414.2	−0.1	1.0	−413.3
Pluth and Smith	I	−518.3	−0.1	1.0	−517.4
	II	−479.1	−0.1	1.0	−478.2

not changed largely by the small degree of ion exchange. Two cases for two K^+ ions exchanged by Ca^{2+} ion are possible.

Case I. Two K^+ ions on sites I are exchanged.

Case II. K^+ ion on sites I and one on sites II are exchanged.

The results calculated for the reaction

$$Ca_1^{2+}K_{10}\text{–A} \xrightarrow{Ca^{2+}} Ca_2^{2+}K_8\text{–A}$$

are given in Table 6. According to calculations based on the X-ray data of Seff *et al.*, case II is more stable than case I. These results do not agree with the adsorption properties of K–A. But, the calculations based on the X-ray data of Pluth and Smith show case I as more stable, supporting the nonexistence of zero-coordinated cation and explaining the adsorption properties of K–A. Because larger K^+ ions occupy sites different from those occupied by Na^+ ions in zeolite A, the interaction energy of the second-incoming Ca^{2+} ion is larger in case I than case II.

CONCLUSIONS

In Na–A, Mg^{2+} and Ca^{2+} exhibit site I selectivity, but the larger Ba^{2+} ion shows mixed occupancy due to the small energy difference of sites I and II. The sixth Ca^{2+} and Sr^{2+} ions also show site I selectivity. Pore opening at 75% ion exchange in K–A is due to the presence of large K^+ ions on sites different from those on which Na^+ ions are present in Na–A. The calculated results support Pluth and Smith's nonexistence of the zero-coordinated cation.

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