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Molecular Dynamics Simulation Studies of Zeolite-A. II. Structure and Dynamics of Cations in Dehydrated Ca²⁺-Exchanged Zeolite-A

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In a recent paper¹ we reported molecular dynamics (MD) simulation of Na⁺ ions in a rigid dehydrated zeolite-A framework at several temperatures using a simple Lennard-Jones potential plus Coulomb potential with Ewald summation to investigate the structure and dynamics of Na⁺ ions. In this paper the same technique is applied to study the structure and dynamics of cations in dehydrated Ca²⁺-exchanged zeolite-A systems, Ca₆-A and Ca₄Na₄-A. At 298.15 K the calculated positions of Ca²⁺ and Na⁺ ions are in poor agreement with those determined by X-ray diffraction experiments, but this is reasonably explained by large repulsive interactions between cations. A simple harmonic oscillation of Ca²⁺ ions in dehydrated Ca₆-A zeolite and simultaneous random motions for the same kinds of cations in dehydrated Ca₄Na₄-A zeolite due to a positional symmetry are observed in their velocity auto-correlation functions and mean square displacements. MD simulations of the fictitious Ca₈-A zeolite confirm our result for the behavior of Ca²⁺ ions in dehydrated Ca₆-A zeolite.

Introduction

In a previous paper (referred to Ref. 1 throughout this paper), we discussed a molecular dynamics (MD) simulation study of 12 Na⁺ ions in rigid dehydrated zeolite-A framework. This study was carried out by the use of Ewald summation technique for the long-ranged character of Coulomb interaction. Our attention was mainly confined to the determination of a best-fitted set of interatomic potential parameters

which include Lennard-Jones potential parameters and electrostatic charges of Na⁺ ions and framework atoms. The next attention was given in the investigation of dynamic behavior of Na⁺ ions at 298.15 K and 600.0 K using the previously determined interatomic potential parameters. Continuing that study here, we discuss new results in dehydrated, fully and partially, Ca²⁺-exchanged zeolite-A. We have also extended our earlier techniques of MD simulation and Ewald summation to this study of dehydrated Ca₆-A and

$\text{Ca}_4\text{Na}_4\text{-A}$ zeolite systems.

In the crystal structures of dehydrated Ca^{2+} -exchanged zeolite-A, each Ca^{2+} ion displaces two of the monovalent Na^+ cations. The ideal chemical composition of a unit cell is $\text{Na}_{12-2x}\text{Ca}_x\text{Al}_{12}\text{Si}_{12}\text{O}_{48}$ where x is the number of Ca^{2+} ions ($0 \leq x \leq 6$). The exchanged Ca^{2+} ions in dehydrated zeolite-A may occupy a site near the center of the 8-ring (α -cage), that of the 6-ring (β -cage), or the opposite of 4-ring. The site selectivity of various Ca^{2+} ions have been extensively studied.

For the system of dehydrated fully Ca^{2+} -exchanged zeolite-A, $\text{Ca}_6\text{-A}$, Takaishi and co-workers² ion per unit cell is located at an 8-ring site, Firor and Seff^{3,4} also reported that five Ca^{2+} ions are located on threefold axes near the centers of 6-ring sites and one Ca^{2+} ion is located in the plane of an 8-ring site. However, Pluth and Smith⁵ reported that all Ca^{2+} ions lie near the centers of 6-rings and the electron density found in an 8-ring by earlier investigators is attributed to potassium scavenged during ion exchange.

Subsequent work for the same system was made by Kim and co-workers,⁶ and they reported that all cations occupy only near 6-ring sites; the 8-ring and 4-ring sites are empty. This occurs because the ionic radius of Ca^{2+} ion is relatively small. Larger cations such as Cs^+ , K^+ , and Ti^+ ions preferentially occupy the 8-ring sites. These 6-ring sites are classified into three types: Ca_I , Ca_{II} and Ca_{III} . 2.5 Ca^{2+} ions at Ca_I and 1 Ca^{2+} ions at Ca_{III} are recessed by 0.32 Å and 0.97 Å, respectively, into the sodalite cavity (β -cage) from the (111) plane at O_3 (see Table 2 where the distance from the center of α -cage to the center of 6-ring window in 6.672 Å). 2.5 Ca^{2+} ions at Ca_{II} are correspondingly recessed into large cavity (α -cage) by 0.47 Å. The fractional occupancy observed at Ca_I and Ca_{II} indicate the existence of 2 types of unit cells in dehydrated $\text{Ca}_6\text{-A}$ zeolite. About 50% of unit cell has 3 Ca^{2+} ions at Ca_I , 2 Ca^{2+} ions at Ca_{II} , and 1 Ca^{2+} ion at Ca_{III} . The remainder has 2 Ca^{2+} ions at Ca_I , 3 Ca^{2+} ions at Ca_{II} , and 1 Ca^{2+} ion at Ca_{III} .

The crystal structures of dehydrated partially Ca^{2+} -exchanged $\text{Ca}_4\text{Na}_4\text{-A}$ zeolite, determined with the X-ray powder diffraction data,⁷ shows that the eight cations per unit cell occupy the eight 6-ring sites; 4 Ca^{2+} ions move into the large cavity from the (111) plane of the O_3 oxygens by 0.22 Å, and 4 Na^+ ions are displaced into the sodalite unit from the (111) plane of the O_3 by 0.58 Å (see Table VI where the distance from the center of α -cage to the center of 6-ring window is 6.734 Å). These sites are apparently preferred by Ca^{2+} and Na^+ ions, and it was anticipated that all exchangeable cations in dehydrated further Ca^{2+} -exchanged zeolite-A would locate at the 6-ring sites. Subsequent works with Mn^{2+} ,^{8,9} Co^{2+} ,^{9,10} and Zn^{2+} ions^{9,11} which are incompletely exchanged into zeolite-A also show that all divalent cations are located at the 6-ring sites upon vacuum dehydration.

In this paper, we discuss molecular dynamics (MD) simulations (1) of 6 Ca^{2+} ions in dehydrated $\text{Ca}_6\text{-A}$ zeolite framework and (2) of 4 Ca^{2+} and 4 Na^+ ions in dehydrated $\text{Ca}_4\text{-Na}_4\text{-A}$ zeolite framework. The purpose of this work is, first, to test the previously determined potential parameters of both Na^+ ions and framework atoms in Ref. 1 along with the newly determined potential parameters for Ca^{2+} ions. The second is the test of the previously used Ewald summa-

Table 1. Lennard-Jones Parameters and Electrostatic Charges Used in this Work

Ion and atoms	σ (Å)	ϵ (kJ/mol)	Charg (e)
Na^+ ion	1.776	20.8466	0.55
Ca^{2+} ion	1.851	20.8466	1.10
Al (=Si) atom	4.009	0.5336	0.6081
O_1 atom	2.890	0.6487	-0.4431
O_2 atom	2.890	0.6487	-0.4473
O_3 atom	2.890	0.6487	-0.4380

tion technique for the long-ranged interactions such as Coulomb potential. The third is to investigate the dynamic behavior of those cations in both dehydrated Ca^{2+} -exchanged zeolite-A frameworks as well as the site selectivity of those cations.

In Section II we present some briefs of molecular models and the MD simulation in addition to those discussed in detail in Section II of Ref. 1. We discuss our simulation results in Section III and present the concluding remarks in Section IV.

Molecular Models and MD Simulation

$\text{Ca}_6\text{-A}$ and $\text{Ca}_4\text{Na}_4\text{-A}$ zeolite frameworks are modelled by the pseudo cell, $(\text{SiAlO}_4)_{12}$, of the $\text{Pm}\bar{3}m$ space groups ($a = 12.263$ Å and 12.420 Å) which contain 6 Ca^{2+} ions, and 4 Ca^{2+} and 4 Na^+ ions, respectively. The frameworks are assumed to be rigid and the framework atoms are fixed in the space at the positions determined by the X-ray diffraction experiment of Kim and co-workers⁶ for dehydrated $\text{Ca}_6\text{-A}$ zeolite system, and at those of Seff and Shoemaker⁷ for dehydrated $\text{Ca}_4\text{Na}_4\text{-A}$ zeolite system, respectively. The LJ parameters and the electrostatic charges on Si and Al framework atoms are assumed to be equal because the Ewald summation is valid with this assumption. The cation positions obtained from these X-ray diffraction experiments are also used for the initial positions of the cations. For the initial positions of 6 Ca^{2+} ions in hydrated $\text{Ca}_6\text{-A}$ zeolite, there are two possible positions because of the fractional occupancies observed at Ca_I and Ca_{II} as discussed in Section I, and we have chosen 3 Ca^{2+} ions at Ca_I , 2 Ca^{2+} ions at Ca_{II} , and 1 Ca^{2+} ion at Ca_{III} .

The interaction potential for cations and framework atoms is given as a sum of Lennard-Jones (LJ) and Coulomb potentials. The LJ parameters ϵ and σ , and the electrostatic charges, e , for Ca^{2+} and Na^+ ions and framework atoms are given in Table 1. Those for Na^+ ions and framework atoms were already used in Ref. 1, and for Ca^{2+} ion σ is obtained from the ratio of ionic radii of Na^+ and Ca^{2+} ions ($0.95 : 0.99$)¹² with the same ϵ as Na^+ ion and the electrostatic charge is two times of Na^+ ion. The Coulomb potential between electrostatic charges on the cations and framework atoms is treated with the Ewald summation,^{13,14} which was discussed in detail in Section II of Ref. 1.

A canonical ensemble of fixed N (number of particles), V (volume of zeolite), and T (temperature) is chosen for the simulation ensemble. Gauss's principle of least constraint¹⁵ is used to maintain the system at a constant temperature.

Table 2. Calculated Distances (Å) of Ca²⁺ Ions from the Center of Box and Interatomic Distances

Distance	CB ^a -Ca _I	CB-Ca _{II}	CB-Ca _{III}	Ca _I -O ₃	Ca _I -O ₂	Ca _{II} -O ₃	Ca _{II} -O ₁	Ca _{III} -O ₃	Ca _{III} -O ₁
Exp.	6.992	6.202	7.646	2.098	2.887	2.158	2.882	2.265	3.051
This work	5.923±.152	5.783±.184	7.649±.073	2.224±.176	2.922±.142	2.307±.168	2.969±.197	2.268±.079	3.053±.069

^aCB represents the center of box (or the center of α-cage).

Table 3. Average *x*, *y*, and *z* Coordinates of Ca²⁺ Ions and Distances, *r* (Å), from the Center of Box at 298.15 K for 50,000 Time Steps (10 ps)

Type	Ca _I			Ca _{II}		Ca _{III}
	1	2	3	4	5	6
<i>x</i>	3.417 ± .059	3.516 ± .034	3.443 ± .062	-3.342 ± .046	-3.213 ± .117	-4.518 ± .088
<i>y</i>	3.422 ± .063	-3.458 ± .052	-3.480 ± .078	3.438 ± .022	23.273 ± .186	4.367 ± .027
<i>z</i>	3.470 ± .044	-3.458 ± .050	-3.441 ± .065	3.323 ± .058	-3.438 ± .112	-4.362 ± .010
<i>r</i>	5.952 ± .095	6.024 ± .078	5.984 ± .119	5.834 ± .072	5.732 ± .239	7.649 ± .073
<i>γ</i>	5.923 ± .152		5.783 ± .184		7.649 ± .073	

The ordinary periodic boundary condition in the *x*-, *y*-, and *z*-directions and minimum image convention are applied for the LJ potential. Gear's fifth order predictor-corrector method¹⁶ is used to solve the equations of motion numerically with time step of 2.00×10⁻¹⁶ sec.

Results and Discussion

For both equilibration and sampling procedures of NVT MD simulation of dehydrated Ca₆-A zeolite, we obtained 50,000 time steps runs at 298.15 K using the LJ parameters and electrostatic charges in Table 1. The average distances of Ca²⁺ ions from the center of α-cage and interatomic distances are calculated and compared with those obtained from the X-ray diffraction experiment of Kim and co-workers⁶ in Table 2. The agreements for the position of Ca_{III} type ion-CB-Ca_{III}, Ca_{III}-O₃, and Ca_{III}-O₁ distances are surprisingly good, but those for the positions of Ca_I and Ca_{II} type ions are somewhat poor. The Ca_I and Ca_{II} type ions are recessed by about 1.1 and 0.6 Å, respectively, into the α-cage from their initial positions. Since the Ca_I type ions are initially located inside the β-cage, these ions move into the α-cage across the (111) planes of 6-ring windows during MD simulation for equilibration. This kind of movement is also observed for 8 Na_I type ions near 6-ring sites in dehydrated zeolite-A but the distance is negligibly small (0.06 Å) and the direction is opposite as shown in Table 3 in Ref. 1.

A possible explanation for this recession comes from the competition between the increment of attractive Coulomb interaction between Ca²⁺ ions and framework atoms, and that of repulsive Coulomb interaction between Ca²⁺ ions. The

Table 4. Average Potential (kJ/mol) of Each Ca²⁺ Ion at 298.15 K for 50,000 Time Steps (10 ps)

	Ca _I			Ca _{II}		Ca _{III}
	1	2	3	4	5	6
	-348.0 ± 3.9	-350.9 ± 3.8	-349.4 ± 5.4	-336.3 ± 1.5	-324.2 ± 6.3	-388.7 ± 8.2
	349.4 ± 4.3			-330.3 ± 7.6		-388.7 ± 8.2

Table 5. Diffusion Coefficients (10⁻⁵ cm²/sec) of Three Types of Ca²⁺ Ions Calculated from Mean Square Displacement (MSD)

Type	Ca _I			Ca _{II}		Ca _{III}
	1	2	3	4	5	6
NSD	.69	.48	.87	.87	4.42	.68

doubled electrostatic charge of Ca²⁺ ions doubles the Coulomb interactions, both attractive and repulsive, between Ca²⁺ ions and framework atoms when compared with Na⁺ ions of dehydrated zeolite-A system. Because Ca²⁺ ions are closer to O₃ and O₂ atoms of 6-ring sites than Al (or Si) atoms (the Ca_I-Al, Ca_{II}-Al, and Ca_{III}-Al distances are 3.232, 3.257, and 3.356 Å, respectively, from the X-ray diffraction experiment⁶ and see Table 2 for Ca-O distances), the interaction energies between Ca²⁺ ions and framework atoms due to the doubled electrostatic charges may be doubled (see Table 5 in Ref. 1 and IV for the average potential energies of cations), even though there is the framework heterogeneity (Al, Si=positive; O=negative charge, see Table 1). On the other hand, the repulsive Coulomb interactions between Ca²⁺ ions increase four times as large as those between Na⁺ ions in dehydrated zeolite-A system. The large repulsion makes to keep the Ca_I and Ca_{II} type ions keeping far away from the Ca_{III} ion which is located inside the β-cage. From this explanation, the results of the X-ray diffraction experiment⁶ seem to underestimate the repulsive Coulomb interaction between Ca²⁺ ions, because there are 4 Ca²⁺ ions inside the β-cage and the distances between them are too short (the Ca(1)-Ca(2) and Ca(2)-Ca(3) distances=4.437 Å; Ca(4)-Ca(6) and Ca(5)-Ca(6)=4.427; Ca(1)-Ca(4) and Ca(3)-Ca(5)=4.690) but the nearest distance between Ca²⁺ ions from our MD simulation results is about 4.9 Å between Ca(5) and Ca(6) ions which can be calculated from Table 3. It is more desirable that 3 Ca_I type ions locate inside the α-cage without changing the Ca_I-O₃ distances, but the inside the β-cage. Note that from both the X-ray diffraction experiment¹⁷ for dehydrated zeolite-A system and our MD

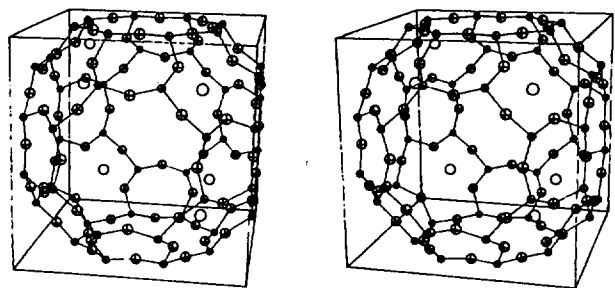


Figure 1. Stereoplot of 6 Ca^{2+} ions in the α -cage of dehydrated $\text{Ca}_6\text{-A}$ zeolite at 298.15 K at the end of 50,000 time steps run for average.

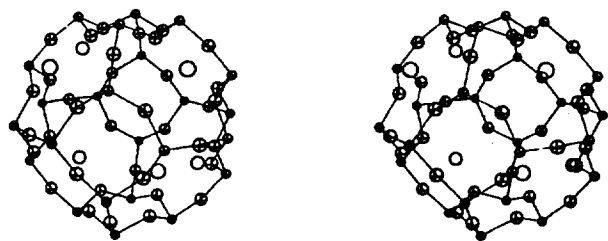


Figure 2. Stereoplot of 6 Ca^{2+} ions in the β -cage of dehydrated $\text{Ca}_6\text{-A}$ zeolite at 298.15 K at the end of 50,000 time steps run for average.

simulation results in Ref. 1, all the 8 Na_I type ions are located inside the α -cage.

Figures 1 and 2 show the stereoplots, by ORTEP,¹⁸ of 6 Ca^{2+} ions and the framework atoms of dehydrated $\text{Ca}_6\text{-A}$ zeolite in the view from the center of α -cage and that of β -cage, respectively, at the end of 50,000 time steps run for average. The average, x , y , and z coordinates of Ca^{2+} ions and distances, r , from CB with the standard deviations are given in Table 3. The large standard deviations of those for Ca(5) ion seem to be due to slightly high potential energy in Table 4 and abnormally huge self-diffusion coefficient in Table 5. Average potential energy of each Ca^{2+} ion at 298.15 K in Table 4 tells us that the Ca_{III} type ion inside β -cage is most strongly bound to the framework atoms and the order of stability is $\text{III} > \text{I} > \text{II}$.

Normalized velocity auto-correlation (VAC) functions and mean square displacements (MSD) of three Ca^{2+} ions - Ca(1), Ca(5), and Ca(6) - are plotted in Figures 3 and 4. The VAC functions show exact simple harmonic oscillating forms with the same frequency of $(0.2 \text{ ps})^{-1}$ and that of Ca(1) is almost the cosine curve, which indicates that these motions are vibrational rather than translational or diffusive, although the harmonic potential energy term used for the Al(Si)-O bonds in the studies¹⁹⁻²² of non-rigid framework zeolite is not included in our model potential for Ca^{2+} ions and framework atoms. These normal vibrational motions are expected to occur in the real, natural motions of framework atoms. The behavior of the MSD's in Figure 4 is consistent with that of VAC's; the sine curves with the same frequencies of $(0.2 \text{ ps})^{-1}$ but different amplitudes. MSD's of the other Ca^{2+} ions (not shown here) have almost the same frequencies and amplitudes as those of Ca(1) ion. How can we explain this? Since the Ca^{2+} ions with the same mass has a high positional

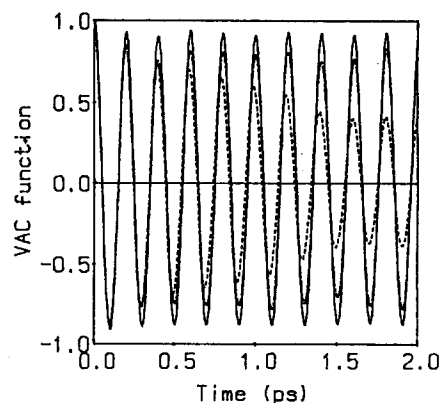


Figure 3. Normalized velocity auto-correlation functions of three Ca^{2+} ions at 298.15 K.—for Ca(1), for Ca(5), and for Ca(6).

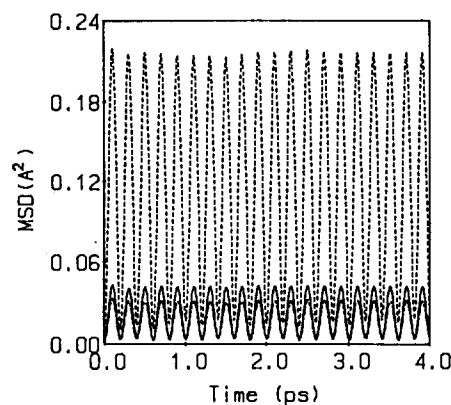


Figure 4. Mean square displacements of three Ca^{2+} ions at 298.15 K.—for Ca(1), for Ca(5), and for Ca(6).

symmetry—due to the occupancy of six among eight 6-ring windows around β -cage (see Figure 2), the thermal motion of a Ca^{2+} ion lets those of other ions have exactly the same frequency. This means that all the ions change the direction of their motions at the same time. The large motion of Ca(5) may correspond to the small motions of the remainder like an air tube connected with several pistons of different diameters. The self-diffusion coefficients of Ca^{2+} ions are calculated from the slopes of the first curves of MSD's using Einstein's relation²³ and are given in Table 5.

MD simulations of this system at different temperature, 100.0 and 600.0 K, are also carried out. The average positions and potential energies of Ca^{2+} ions at both temperatures show almost the same as those at 298.15 K and the "pushing process" of the unstable Na_{III} ion in dehydrated zeolite-A system at 600.0 K, discussed in Ref. 1, is not observed. This is because the Ca^{2+} ions are more strongly bound to the framework atoms than the Na^+ ions and there is no Ca^{2+} ion located at unstable 8-ring or at 4-ring sites. We can see that the average potential energies of Ca^{2+} ions are more than double those of Na^+ ions as shown in Table 5 in Ref. 1 and IV.

Now, we turn our attention to dehydrated $\text{Ca}_4\text{Na}_4\text{-A}$ zeolite system. The analysis of our MD simulation results for this system is almost the same as that of dehydrated $\text{Ca}_6\text{-A}$ system. First, the average distances of Ca^{2+} ions from the center

Table 6. Calculated Distance (Å) of Ca²⁺ and Na⁺ Ions from the Center of Box and Interatomic Distances

Distances	Ca ²⁺ -Ca	CB-Na	Ca-O ₃	Ca-O ₂	Na-O ₃	Na-O ₂
Exp.	6.510	7.318	2.308	2.852	2.370	2.903
This work	5.816 ± .230	6.566 ± .314	2.473 ± .242	2.988 ± .198	2.303 ± .116	2.849 ± .098

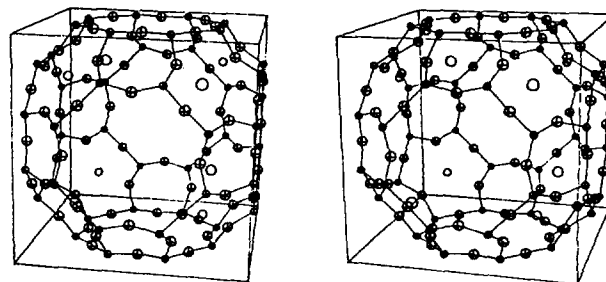
^aCB represents the center of box (or the center of α-cage).

of α-cage (CB) and interatomic distances are calculated and compared with those obtained from the X-ray diffraction experiment⁷ in Table 6, and the average *x*, *y*, and *z* coordinates of cations and distances, *r*, from CB with the standard deviations are given in Table 7. The same kinds of cations show the same distances from the center of α-cage with *x*, *y*, and *z* coordinates corresponding to four corners of tetrahedral structure. As also observed in the behavior of Ca(5) ion of dehydrated Ca₆-A zeolite system, the large standard deviations of coordinates for Na(3) ion seem to be related to slightly high potential energy in Table 8 and as relatively large self-diffusion coefficient in Table 9. Average potential energy of each cation at 298.15 K in Table 8 shows that Ca²⁺ ions are more strongly bound to the framework atoms than Na⁺ ions.

The Ca²⁺ and Na⁺ ions are recessed by about 0.7 and 0.8 Å, respectively, into the α-cage from their initial positions. Since the Na⁺ ions are initially located inside the β-cage, these ions move into the α-cage across the (111) plane at O₃ (6-ring) during MD simulation for equilibration. The same explanation for the recession in dehydrated Ca₆-A zeolite system is available for that in this system, but the situation is a little different - the repulsive Coulomb interactions between Ca²⁺ and Na⁺ ions. The total repulsive pairwise interaction energies in unit cell (the numerator term of Cou-

Table 9. Diffusion Coefficients (10⁻⁵ cm²/sec) of Ca²⁺ and Na⁺ Ions Calculated from Mean Square Displacement (MSD)

Type	Ca				Na			
No.	1	2	3	4	1	2	3	4
NSD	2.25	1.70	2.53	2.35	2.96	1.24	4.77	.76

**Figure 5.** Stereoplot of 4 Ca²⁺ and 4 Na⁺ ions in the α-cage of dehydrated Ca₄Na₄-A zeolite at 298.15 K at the end of 50,000 time steps run for average.

lomb potential) of both dehydrated Ca²⁺-exchanged zeolite systems are almost the same (6 interaction pairs between Ca²⁺-Ca²⁺, 16 pairs between Ca²⁺-Na⁺, and 6 pairs between Na⁺-Na⁺ in Ca₄Na₄-A, and 15 pairs between Ca²⁺-Ca²⁺ in Ca₆-A), but the number of interactions and the average distance (the denominator term of Coulomb potential) between cations are different (28 and 15) because of the different number of occupancy of eight 6-ring sites (8 and 6). The larger recession of cations in dehydrated Ca₄Na₄-A zeolite system is expected in comparison with that in dehydrated Ca₆-A system (about 6.0 and 4.5 Å totally).

Figures 5 and 6 show the stereoplots, by ORTEP,¹⁸ of 4

Table 7. Average *x*, *y*, and *z* Coordinates of Ca²⁺ Ion and Distances, *r* (Å), from the Center of Box at 298.15 K for 50,000 Time Step (10 ps)

Type	CB				Na			
No.	1	2	3	4	1	2	3	4
<i>x</i>	3.343 ± .128	-3.367 ± .111	3.361 ± .140	-3.370 ± .132	3.803 ± .203	-3.791 ± .121	3.830 ± .222	-3.786 ± .108
<i>y</i>	3.365 ± .141	-3.364 ± .114	-3.342 ± .144	3.356 ± .131	-3.801 ± .204	3.793 ± .122	3.764 ± .274	-3.788 ± .109
<i>z</i>	3.349 ± .142	3.357 ± .125	-3.369 ± .142	-3.351 ± .137	3.805 ± .199	3.794 ± .106	-3.748 ± .268	-3.786 ± .106
<i>r</i>	5.806 ± .237	5.824 ± .202	5.815 ± .246	5.818 ± .231	6.587 ± .350	6.569 ± .201	6.548 ± .441	6.559 ± .187
		5.816 ± .230				6.566 ± .314		

Table 8. Average Potential Energy (kJ/mol) of Each Ca²⁺ and Na⁺ Ion at 298.15 K for 50,000 Time Steps (10 ps)

CB ^a -Ca _i				Na			
1	2	3	4	1	2	3	4
-329.7 ± 10.4	-331.5 ± 9.7	-330.1 ± 12.6	-330.2 ± 11.4	-188.7 ± 3.6	-190.1 ± 2.8	-183.4 ± 7.4	-190.3 ± 2.4
	-330.4 ± 11.1				-188.1 ± 5.3		

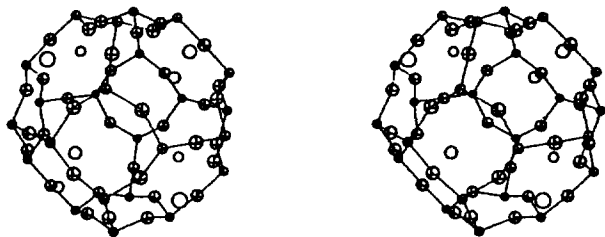


Figure 6. Stereoplot of 4 Ca^{2+} and 4 Na^+ ions in the β -cage of dehydrated $\text{Ca}_4\text{Na}_4\text{-A}$ zeolite at 298.15 K at the end of 50,000 time steps run for average.

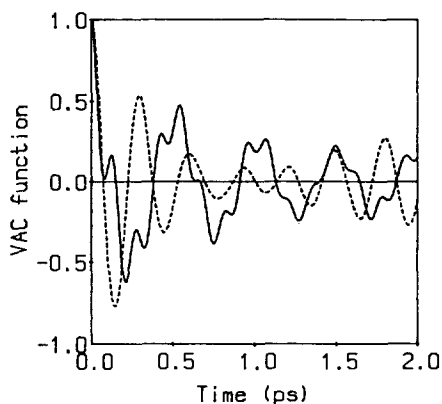


Figure 7. Normalized velocity auto-correlation functions of Ca^{2+} and Na^+ ions at 298.15 K.—for Ca^{2+} and for Na^+ .

Ca^{2+} and 4 Na^+ ions (smaller spheres), and the framework atoms of dehydrated $\text{Ca}_4\text{Na}_4\text{-A}$ zeolite in the view from the center of α -cage and that of β -cage, respectively, at the end of 50,000 time steps run for average.

The average, normalized velocity auto-correlation (VAC) functions of Ca^{2+} and Na^+ ions are plotted in Figure 7, and the individual, mean square displacements (MSD) of 2 Ca^{2+} ions, Ca(2) and Ca(3), and 2 Na^+ ions, Na(1) and Na(4), are plotted in Figure 8. The simple harmonic oscillation behavior which is observed in those functions of Ca^{2+} ions in dehydrated $\text{Ca}_6\text{-A}$ zeolite, is not shown here because of different masses and electrostatic charges of cations, even though this system has a higher positional symmetry than dehydrated $\text{Ca}_6\text{-A}$ zeolite. The MSD's are more like those of Na^+ in the case of dehydrated zeolite-A (Na_1 in Figure 3 in Ref. 1) in which the curve is much broad because of superimposition for average. However, a careful insight into the MSD of the same kinds of cations tells us the simultaneous reandom motions with frequencies of about $(0.35 \text{ ps})^{-1}$ and $(0.5 \text{ ps})^{-1}$ for Ca^{2+} and Na^+ ions, respectively. This might happen because the same kinds of cations are loosely correlated each other with the interference of the other kind of cations.

To confirm our result for the simple harmonic oscillating forms in VAC's and MSD's of Ca^{2+} ions in dehydrated zeolite $\text{Ca}_6\text{-A}$ system, we have created a fictitious zeolite system, $\text{Ca}_8\text{-A}$, which consists of 8 $\text{Ca}^{1.5+}$ ions initially located at the centers of eight 6-ring sites where the zeolite framework atoms are assumed to be the same as those of dehydrated $\text{Ca}_6\text{-A}$ zeolite system, MD simulation of this system shows a perfect positional symmetry. The 8 $\text{Ca}^{1.5+}$ ions are recessed

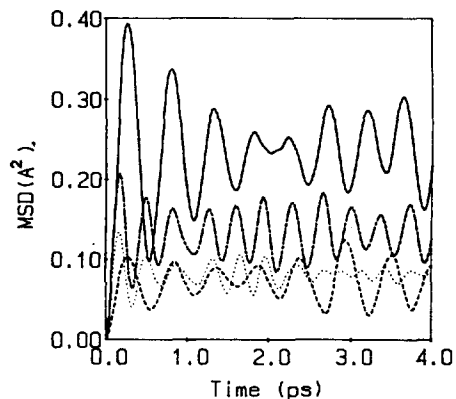


Figure 8. Mean square displacements of Ca^{2+} and Na^+ ions at 298.15 K. for Ca(2), for Ca(3),— for Na(1), and for Na(4).

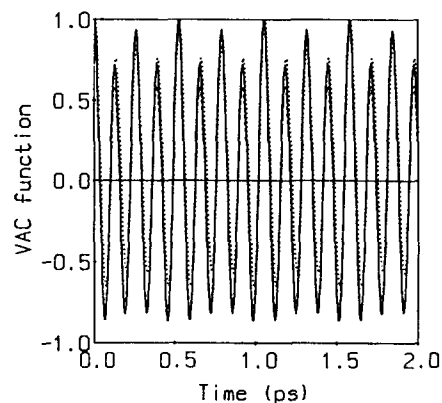


Figure 9. Normalized velocity auto-correlation functions of $\text{Ca}^{1.5+}$ at 298.15 K.—for Ca(1), for Ca(2), and for Ca(3).

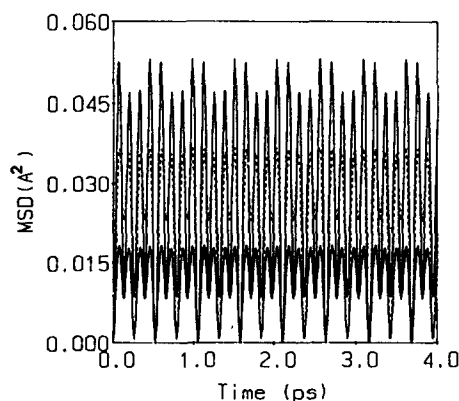


Figure 10. Mean square displacements of $\text{Ca}^{1.5+}$ at 298.15 K. Upper—for Ca(1), for Ca(2), and lower—for Ca(3).

by about 0.85 \AA into the α -cage from their initial positions and the x , y , and z coordinates show that the cations are located on the extended lines from the center of box to the centers of 6-ring sites. The average potential energy of $\text{Ca}^{1.5+}$ ion ($-454.0 \pm 1.6 \text{ kJ/mol}$) is extremely low and also shows the very high positional symmetry Ca_8 zeolite system. In Figures 9 and 10, VAC and MSD of 3 $\text{Ca}^{1.5+}$ ions—Ca(1), Ca(2), and Ca(3)—at 298.15 K are plotted. From the observation of simple harmonic oscillating curves with a frequency

of $(0.13 \text{ ps})^{-1}$, it may be proved that the vibrational motions of Ca^{2+} ions in dehydrated $\text{Ca}_6\text{-A}$ zeolite is a natural phenomenon, and not an artifact of MD simulation.

The temperature effect on the average positions and potential energies for cations in dehydrated $\text{Ca}_4\text{Na}_4\text{-A}$ zeolite system is vanishingly small. Ca^{2+} ions are strongly bound to the framework atoms like in dehydrated $\text{Ca}_6\text{-A}$ zeolite system, and Na^+ ions are still stayed near the 6-ring sites even at 600.0 K in contrast to the Na^+ ions relatively weakly bound, to the framework atoms as in dehydrated zeolite-A system. When the average potential energies of Na^+ ions at the 6-ring sites in dehydrated $\text{Ca}_4\text{Na}_4\text{-A}$ and dehydrated zeolite-A systems are compared, the former Na^+ ion is more stable than the latter because total numbers of cations in unit cell is different. This effect is also found when the average potential energies of Ca^{2+} ions at the 6-ring sites in dehydrated $\text{Ca}_4\text{Na}_4\text{-A}$ and dehydrated $\text{Ca}_6\text{-A}$ zeolite systems are compared.

Concluding Remarks

In this paper, we have studied the local structure and dynamics of cations with molecular dynamics (MD) simulations of rigid dehydrated $\text{Ca}_6\text{-A}$ and $\text{Ca}_4\text{Na}_4\text{-A}$ zeolite systems at 100.0, 298.15, and 600.0 K. The previously determined LJ potential parameters and electrostatic charges were used for the interactions for cations and framework atoms, and the Ewald summation technique was used for the long-ranged character of Coulomb interaction.

From our MD simulations of both systems, the following conclusions may be drawn. (1) At 298.15 K, the average positions of cations in dehydrated $\text{Ca}_6\text{-A}$ and $\text{Ca}_4\text{Na}_4\text{-A}$ zeolite systems are much recessed into the center of α -cage from those determined from the X-ray diffraction experiments.^{6,7} This recession is explained by large repulsive interactions between Ca^{2+} ions and between Ca^{2+} and Na^+ ions. (2) The simple harmonic oscillation behavior of Ca^{2+} ions in dehydrated $\text{Ca}_6\text{-A}$ zeolite due to the positional symmetry is observed in velocity auto-correlation (VAC) functions and mean square displacements (MSD). (3) Simultaneous random motions for the same kinds of cations are also observed in VAC functions and MSD of cations in dehydrated $\text{Ca}_4\text{Na}_4\text{-A}$ zeolite. (4) MD simulations of the fictitious $\text{Ca}_6\text{-A}$ zeolite system show the very high positional symmetry of Ca^{15+} ions. The simple harmonic oscillating behavior of VAC and MSD of Ca^{15+} ions confirms our result for dehydrated $\text{Ca}_6\text{-A}$ zeolite system. (5) The temperature effect on the average positions and average potential energies of cations in both systems is vanishingly small to be ignored. Finally, (6) considering all the results of our MD simulations of both systems, the success of our MD simulation methods with Ewald summation technique is convinced.

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