

제올라이트 NaA의 수화에 관한 이론적 연구

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Theoretical Study of Hydration of Zeolite NaA

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요 약. Zeolite NaA의 α cage에 있어서의 수화에너지와 그 위치를 결정하였다. Na(1)과 Na(2) 사이의 site selectivity를 에너지 계산으로부터 결정하였는데 Na(1)이 Na(2)보다 선택성이 있는 것을 알 수 있었다. α -Cage에 수화된 물들은 일그러진 정12면체를 형성함을 알 수 있었다. Water(1), water(2), water(3)의 평균수화에너지는 각각 -29.847, -25.344, -15.888 kcal/mole이다. 이 에너지 계산으로부터 얻어진 수화된 물들의 산소원자의 위치는 X선값과 잘 일치함을 보여준다. 또 수화된 정도에 따른 수화에너지의 그래프를 얻었다. 이 결과는 실험으로부터 얻어진 differential heat of sorption curve와 잘 일치함을 보여준다. α Cage속에서의 유전상수는 3.5가 적합함을 알 수 있었다.

ABSTRACT. Hydration scheme and hydration energy are determined in α cage of zeolite NaA. The selectivity between Na(1) and Na(2) is determined from energy calculation. The waters in α cage form a distorted dodecahedral cage. The average binding energies of water(1), water(2) and water (3) are -29.847, -25.344 and -15.888 kcal/mole respectively. The positions of oxygens of hydrated waters are in good agreement with the X-ray data. The heat of immersion curve is also obtained. This result is in good agreement with the differential heat of sorption curve obtained from differential thermal analysis. It is concluded that theoretical method provides considerable uses in the determination and understanding of the hydration and interaction energy of zeolites sorbate binding.

INTRODUCTION

Synthetic zeolites are well known for their industrial applications as adsorbants and molecular sieves, and very important in fundamental researches because of their adsorbant and catalytic properties¹.

Zeolites are crystalline, hydrated aluminosilicates of group 1 and group 2 element, in particular, sodium, potassium, magnesium, calcium, strontium, and barium. Structurally, the zeolites are consist of the framework of aluminosilicates which are based on the infinitely extending three dimensional network of AlO_4 and

SiO₄ tetrahedra linked to each other by sharing all of the oxygens. Zeolites may be represented by the empirical formula $M_2/nO:Al_2O_3 \cdot xSiO_2 \cdot yH_2O$. The aluminosilicate framework of zeolite A can be described in terms of types of polyhedra; one is simple cubic arrangement of eight tetrahedra; the other is the truncated octahedron of 24 tetrahedra (β cage).

In recent years, there has been a great deal of effort directed toward acquiring and understanding of the structure, nature, and properties of zeolites². The structure and the exact positions of atoms in dehydrated zeolite are obtained by X-ray diffraction³⁻⁶. The potential energy between adsorbed material and zeolite is very important in considering the catalytic behavior and as a function of molecular sieve.

One of important properties of all zeolite-sorb complexes are that water is the guest molecule in the zeolites. Water is essential for the synthesis of zeolites. Accordingly, the binding energy of the water within the crystals is important to understand the nature of water-zeolites complex fully.

The electrostatic field of dehydrated zeolite NaA is calculated by Lara and Tan⁷. Recently, the site selectivity of the cation in dehydrated zeolite NaA is obtained from energy calculations⁸.

In this paper, the positions and binding energies of Na(1) and Na(2) are determined with the use of calculated net charge, and those of waters in α cage are obtained with the use of calculated net charge and dielectric constant.

MODEL COMPOUND

Fig. 1 shows the framework of dehydrated A type zeolite. In the case of hydrated zeolite NaA, the bond angles and the bond lengths are obtained by single crystal X-ray diffraction method⁹. The unit cell of hydrated NaA type

zeolite is Na₁₂Al₁₂Si₁₂O₄₈·27H₂O. In this model, there are three kinds of oxygens which are differ in bond length and bond angle.

In this energy calculation, the radius of model compound is about 11 Å. The positions of oxygens, aluminum and silicon are listed in Table 1. Fig. 2 shows the arrangement of each atoms. As X-ray data predicted⁹, we adopt the dodecahedral cage of water.

CALCULATION OF NET CHARGE

Electronegativity was originally defined as an invariant property of atoms^{10,11}. But several workers^{12,13} have suggested that the electronegativity of an atom depends upon the environment of that atom in a molecule.

Iczkowski and Margrave¹² defined electronegativity as the derivative of ionization energy with respect to charge. The ionization potential and electron affinity obey the relationship

$$E = kq^2 + k'q + k'' \quad (1)$$

where E is the energy of the atom and q is the charge on the atom. When the charge on each atom causes its electronegativity to equal those of the other atoms, the sum of the $I-A$ energies become minimum. Here I and A are a ionization potential and a electron affinity respectively. If the neutral atom is defined as zero energy, the total energy can be written as¹³

$$E = a\delta + \frac{b}{2}\delta^2 \quad (2)$$

where δ is the partial charge resulting from the equalization of electronegativity of each atom and where

$$a = \frac{I-A}{2} \quad (3a)$$

$$b = I+A \quad (3b)$$

Here a and b are defined as the inherent electronegativity and the charge coefficient respectively. And the orbital electronegativity is de-

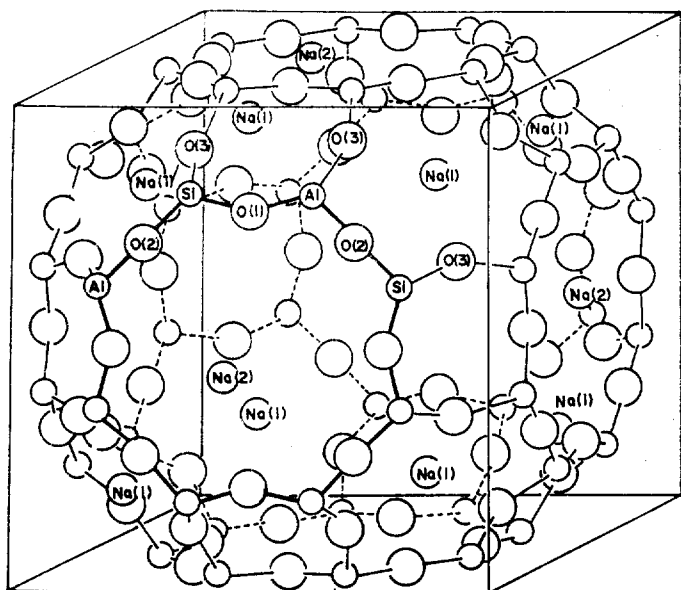
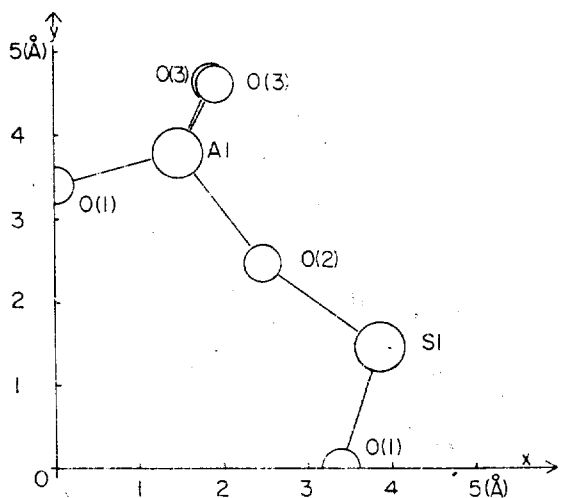


Fig. 1. Structure of dehydrated zeolite NaA.

Table 1. Positions of atoms in A type zeolite framework.

Framework atom	X(Å)	Y(Å)	Z(Å)
Aluminum	3.8687	1.4987	6.0861
Silicon	1.5480	3.7998	6.0861
Oxygen (1)	0.0000	3.3396	6.0861
Oxygen (2)	2.4856	2.4856	6.0861
Oxygen (3)	1.8925	4.6513	4.7620

Fig. 2. Arrangement of a repeating unit (AlO_2SiO_2).

defined¹² as

$$\chi = dE/d\delta = a + b\delta. \quad (4)$$

Huheey¹⁴ applied this method to the calculation of electronegativities and net charges of groups. We apply this method to the calculation of net charges of atoms in NaA type zeolite framework.

A type zeolite has a repeating unit, AlO_2SiO_2 , as shown in Fig. 2. In the calculation of net charge, the large framework of A type zeolite can be reduced into a small system with repeating unit as shown in Fig. 3.

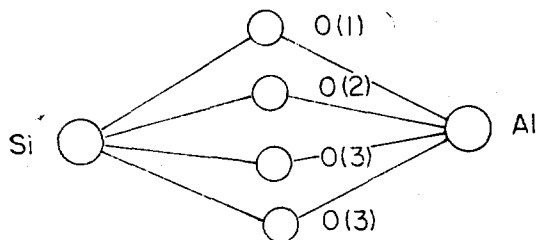
In this small system, each atoms have same environments as those atoms in a real framework.

Inherent electronegativities and charge coefficients are linearly depend on *S*-character¹⁴. The values of ionization potential and electron affinity computed by Jaffé and co-workers¹³ have been used to derive values of inherent electronegativities and electron affinities for appropriate valence states for various atoms. Differences in valence state mean differences in *S*-character. Bond angle, *S*-character, inherent electronegativity, and charge coefficient of atoms in NaA type zeolite are listed in Table 2.

In this work, we assume that negative charge is localized to aluminum atom. Estimation of charge transfer can be obtained by setting the electronegativity functions of one atom equal to those of the others and solving for the values of δ .

$$\delta_{\text{Si}} + \delta_{\text{Al}} + \delta_{\text{O(1)}} + \delta_{\text{O(2)}} + 2\delta_{\text{O(3)}} = 0 \quad (5)$$

$$a_{\text{Si}} + b_{\text{Si}}\delta_{\text{Si}} = a_{\text{O(1)}} + b_{\text{O(1)}}\delta_{\text{O(1)}}$$

Fig. 3. Reduced small system (AlO_2SiO_2).Table 2. Inherent electronegativity (a) and charge coefficient (b).

Framework atom	Bond angle (deg)	S-Character (%)	a	b
Al	109.5	25	7.3	9.04
Si	109.5	25	5.38	5.59
O(1)	145.5	45.18	19.96	20.7
O(2)	159.5	48.36	20.70	21.2
O(3)	144.1	44.75	19.81	20.6

$$\begin{aligned}
 &= a_{\text{O}(2)} + b_{\text{O}(2)} \delta_{\text{O}(2)} \\
 &= a_{\text{O}(3)} + b_{\text{O}(3)} \delta_{\text{O}(3)} \\
 &= a_{\text{Al}} + b_{\text{Al}} \delta_{\text{Al}}
 \end{aligned} \quad (6)$$

The net charges of each atoms are calculated from eq. (5) and eq. (6). The obtained net charge of each atoms are $\delta_{\text{Si}}=0.474$, $\delta_{\text{Al}}=0.109$, $\delta_{\text{O}(1)}=-0.395$, $\delta_{\text{O}(2)}=-0.440$ and $\delta_{\text{O}(3)}=-0.399$ respectively.

ENERGY CALCULATION

The basic formulae and the parametrization used for the potential energy functions follow the general scheme presented by Caillet and Claverie^{15,16}. For hydrogen bonding, new parameter in the dispersion and repulsion term at short distances are used.

Electrostatic Energy. To obtain this term, the net atomic charges of the two interacting molecules must be known. This energy is given by

$$E_{\text{el}}(1-2) = \sum_i^{(1)} \sum_j^{(2)} \frac{\delta_i \delta_j}{\epsilon R_{ij}} \quad (7)$$

where the summations $\sum_i^{(1)}$ and $\sum_j^{(2)}$ run over the atoms of molecules (or fragment) 1 and 2, respectively, and R_{ij} is the distance between atoms i and j ; δ_i and δ_j are the net charges of atom i of molecule 1 and atom j of molecule 2 respectively; ϵ is the dielectric constant of the system. The values of net atomic charges found for water from dipole moment are $\delta_{\text{H}}=0.32$ and $\delta_{\text{O}}=-0.64$ (in electron unit)¹⁷.

The dielectric constant in α cage is determined by comparing the average binding energy of the waters which are bound to Na(1) with the heat of immersion when the degree of pressurization is 0.1. From this comparison, the optimum value of dielectric constant is 3.5.

Polarization Energy. The polarization energy of a molecule in an electric field is calculated as a sum of atomic polarization contributions;

$$E_{\text{pol}}(1) = -1/2 \sum_i \bar{\alpha}_i (\epsilon_i)^2 \quad (8)$$

where ϵ_i is the electric field created at the atom i of molecule 1 by all other molecules (only molecule 2 in the case of a binary complex), and $\bar{\alpha}_i$ is the mean polarizability attributed to atom i .

The contribution of Si and Al atoms to the polarization energy are negligible because they are located in tetrahedra of oxygen. The polarizabilities of atoms in water molecule are obtained from molecular polarizability of water molecule. In order to determine the bond polarizability of O-H bond, the polarizability of lone pair electron must be obtained. When the atom is isotropic, the expression for polarizability of atoms was obtained by Kirkwood¹⁸ as

$$\bar{\alpha} = \frac{4}{9a_0} \sum_i (\bar{r}_i^2)^2 \quad (9)$$

where $\bar{\alpha}$ is the polarizability of atom, a_0 is Bohr radius, and r_i is the radius of i th electron.

$$\bar{r}_i^2 = \left(\frac{n^*}{2(Z-S)} \right)^2 (2n^*+1)(2n^*+2)a_0 \quad (10)$$

where n^* is the effective quantum number and $(Z-S)$ is the effective nuclear charge. From eq. 7 and eq. 8, the polarizability of lone pair electron of oxygen atom is calculated as $0.190 \cdot 10^{-24} \text{cm}^3$. The bond polarizability of O-H bond is $0.345 \cdot 10^{-24} \text{cm}^3$. Using Caillet and Claverie's method¹⁶, the bond polarizability is divided into the atomic polarizability. As a result, the polarizability of oxygen atom in a water molecule is $1.278 \cdot 10^{-24} \text{cm}^3$ and that of hydrogen atom is $0.08 \cdot 10^{-24} \text{cm}^3$.

Dispersion and Repulsion Energy. In this work, we use the sum of atom-atom contribution for evaluating the dispersion energy according to the semi-empirical formula proposed by Kitaigorodskii. The formula for both the dispersion and the repulsion energies is written as

$$E_{\text{disp}} + E_{\text{rep}} = \sum_i^{(1)} \sum_j^{(2)} e(i, j) \quad (11)$$

where each atom-atom contribution $e(i, j)$ is the sum of a dispersion and a repulsion term

$$e(i, j) = k_i k_j \left[-A/Z^6 + (1 - \delta_i/N_i^{\text{val}})(1 - \delta_j/N_j^{\text{val}}) C \exp(-LZ) \right] \quad (12)$$

where

$$Z = R_{ij}/R_{ij}^{0'}$$

and

$$R_{ij}^{0'} = \sqrt{(2R_i^W)(2R_j^W)}$$

R_i^W and R_j^W are the Van der Waals radii¹⁹ of atom i and j . The factors $(1 - \delta_i/N_i^{\text{val}})$ represent the influence of the atomic electron population on the repulsion; δ_i is the net charge of atom i , and N_i^{val} is the number of valence electrons for the neutral atom ($N_{\text{H}}^{\text{val}}=1$, $N_{\text{O}}^{\text{val}}=6$). The multiplicative factors k_i and k_j allow for the variation of the nature of the interacting

atoms ($k_{\text{H}}=1$ and $k_{\text{O}}=1.36$)²⁰. The following values are used for A, C and L ; $A=0.214 \text{ kcal/mole}$, $C=47000 \text{ kcal/mole}$, $L=12.35$.

Van der Waals radius of Na cation is calculated from the polarizability of Na cation. According to Davis²¹, some correlation exist between Lennard-Jones(6-12) diameter σ and the polarizability of a molecule or group as follows.

$$\ln(\sigma^2 - 5.4) = 1.456 + 0.797 \ln(\bar{\alpha}_D \cdot 10^{24}) \quad (13)$$

where $\bar{\alpha}_D$ is polarizability. When $\bar{\alpha}_{\text{Na}^+}$ is $0.190 \cdot 10^{-24} \text{cm}^3$, the diameter of cation is 2.556 \AA . Using the following relationships that the equilibrium distance r_0 equals to $2^{1/6}\sigma$ and the ratio of the equilibrium distance divided by Van der Waals radius equal to $13/11$,²² the Van der Waals radius of Na cation becomes 1.285 \AA .

The multiplicative factor k_{Na^+} is determined from Van der Waals radius of Na cation and experimental data of Na^+ -water binding energy.^{23,24} Minimization of Na^+ -water binding energy at various k_{Na^+} values can determine the optimum k_{Na^+} value which can explain the experimental energy depth of Na^+ -O binding. When k_{Na^+} is 2.86, the calculated equilibrium distance of Na^+ -O binding is 2.26 \AA and the calculated minimum energy depth is in a excellent agreement with experiment. Calculated Na^+ -O equilibrium distance is also in good agreement with the experimental data of Na^+ -O binding distance.

Case of Hydrogen Bond. The equilibrium distance of a hydrogen bond is significantly shorter than the usual intermolecular equilibrium distances. Hence, the simple analytical behavior $(-1/Z^6, e^{-LZ})$ must be refined for such cases.

The distance are divided into two types, R_m and R_M (with $R_m < R_M$); if $R > R_M$, the normal parameters are used for A, C, L ; if $R < R_m$, the modified parameters A', C', L' (with $A' < A$, $C' < C$, $L' > L$) are used; and for $R_m < R < R_M$,

we use the interpolated values of these parameters according to the formula.

$$K(x) = \frac{K+K'}{2} + \frac{K-K'}{2}(0.375x^5 - 1.25x^3 + 1.875x) \quad (14)$$

where K represents one of the symbols A , C , or L and

$$x = \frac{R - 1/2(R_m + R_M)}{1/2(R_m - R_M)} \quad (15)$$

The values $R_m = 1.8 \text{ \AA}$, $R_M = 2.6 \text{ \AA}$, $A' = A/5$, $C' = C/2.7$, $L' = 13.8$ are taken²⁰.

RESULT AND DISCUSSION

Comparison of Net Charges of Oxygen Atoms with IR Spectroscopy. The net charge calculated in a previous section explain the IR spectroscopic data of water bound to zeolite. The frequency depend on the type of zeolite and on the cation and the band intensities depend on the degree of the hydration. In hydrated NaA type zeolite, bands at 3500, 3400 and 1660 cm^{-1} correspond to symmetrical adsorbed water molecules, while band at 3280 cm^{-1} correspond to overtone bending vibration of the same molecule²⁵. Bands at 3500 and 3400 cm^{-1} is the O-H stretching band bonded to framework oxygen. These broad two bands probably are due to hydrogen bound to crystallographically different oxygen having different net charge which results in different strengths of interaction (Fig. 4).

As a result, the oxygen atoms in A type zeolite can divided into two classes; one is O(1) and O(3) (net charges are -0.395 and -0.399 respectively), the other is O(2) (net charge is -0.440). The parallel growth of intensities of the broad O-H stretching band increase of hydrated water suggest that none is formed preferentially. If repeating unit of any zeolite is determined then the net charge of atoms in any ze-

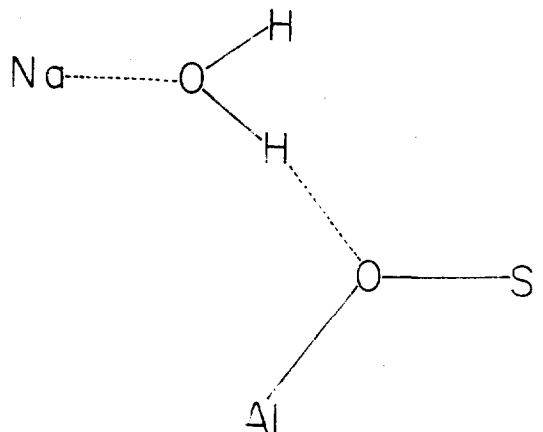


Fig. 4. Hydrogen bond between hydrated water molecule and framework oxygen.

olite framework is evaluated.

Determination of Position of Na Cation and Site Selectivity Between Na(1) Site and Na(2) Site by Energy Calculation. The site selectivity is of great importance in understanding the physicochemical properties of zeolite A, such as adsorption and catalysis. In dehydrated zeolite NaA, the optimum positions and energies of Na(1) and Na(2) are determined by using the net charge and the Van der Waals radius of Na cation (setting $\epsilon = 1$). The dielectric constant is not important in qualitative calculation of selectivity.

As can be seen in Table 3, Na(1) is bound more tightly than Na(2). This is in good agreements with the experimental results of sorption characteristic and ion-exchange behavior, and it has been supported by the results of X-ray diffraction analysis^{26,27}. In Table 4, the calculated optimum position of Na(1) and Na(2) are listed. There is a remarkable agreement between X-ray data⁹ and optimized sodium position.

As shown in the energy map of Na(2), it is evident that there are eight positional degeneracy at eight membered ring window (Fig. 5). Fig. 5 shows one eighth of symmetrical eight

membered ring window. The calculation of the selectivity, optimum position and positional degeneracy of Na cation using obtained net charge and Van der Waals radius of Na cation are in good agreements with experimental data^{9, 26, 27}

Hydration of α Cage. In the determination of the hydration scheme of zeolite NaA, the

Table 3. Binding energy of Na(1) and Na(2) when $\epsilon=1$ (in kcal/mole).

	Na(1)	Na(2)
Electrostatic energy	-103.15	-94.68
Dispersion energy	-0.51	-0.40
Polarization energy	2.55	0.58
Total energy	-101.11	-94.50
Energy difference	6.61	

Table 4. The positions of Na(1) and Na(2) obtained by energy optimization.

		X(Å)	Y(Å)	Z(Å)
Calculated position	Na(1)	3.45	3.45	3.45
	Na(2)	0.87	0.92	6.10
X-Ray data	Na(1)	3.468	3.468	3.468
	Na(2)	0.871	0.871	6.0861

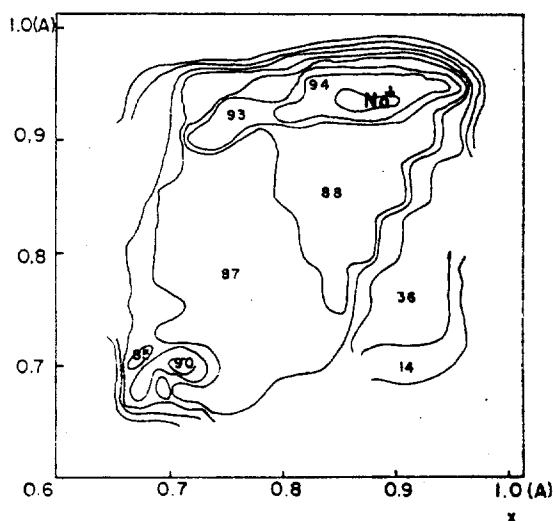


Fig. 5. Energy map of Na(2) at eight membered oxygen ring window (in kcal/mole).

Cartesian coordinates of water molecule are computed as a function of $d_1, \theta_1, \theta_2, \phi_1, \phi_2$ and ϕ_3 in the reference system in which A_1, A_2 and A_3 are fixed (Fig. 6). We used for such computations the method developed by Thompson^{28, 29}.

The hydrated waters are optimized by minimizing the interaction energy of each water molecule through the variation of the six parameter ($d_1, \theta_1, \theta_2, \phi_1, \phi_2$ and ϕ_3) simultaneously using a minimization method in which the derivatives are estimated by differences as described by Fletcher³⁰.

Inside the α cage there appears to be occupied by twenty four water molecules. Because the cavity of A type zeolite is small, the hydrated position is roughly determined by close packing of waters to framework.

In X-ray data of hydrated zeolite NaA, only the positions of oxygen atoms of hydrated water molecule are determined. X-ray data predict that twenty water molecules form the dodecahedral cage, three are bound to Na(2) and one is in dodecahedral cage of water molecule. According to X-ray data of α cage of hydrated zeolite NaA, the binding waters are classified into four classes⁹

- Water(1) ; the water bound to Na(1).
- Water(2) ; the water bound to Na(2).
- Water(3) ; the water bound to the water(1).
- Water(4) ; the water bound to Na(3). (in dodecahedral cage of water molecule)

Fig. 7 shows the dedecadral cage of water molecule adopted in this work. The waters from W1 to W8 are belong to water(1) and from W9 to W20 are belong to water(3). The waters from W21 to W23 are belong to water(2) and W24 is water(4).

Ideally the eight membered ring window may be assumed to hold one Na cation and one water molecule. In X-ray data⁹, the water(4) may be generated by a less symmetrical arrangement

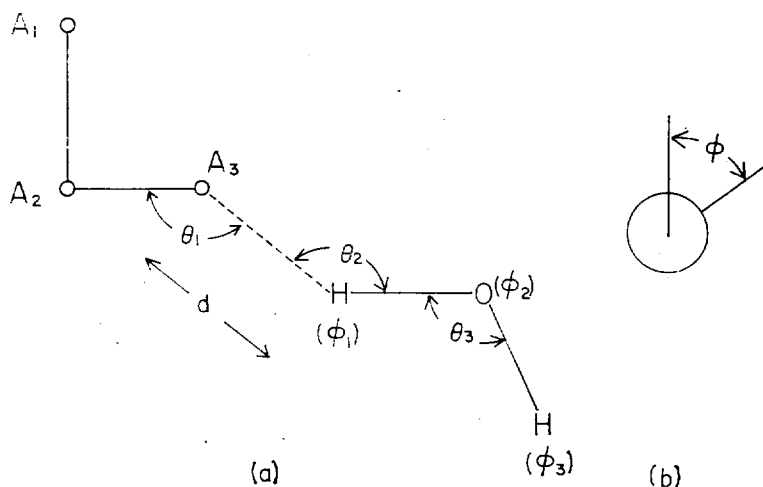


Fig. 6. (a) Variables defining the position of a water molecule with respect to the fixed reference. (b) Positive values of the torsion angle.

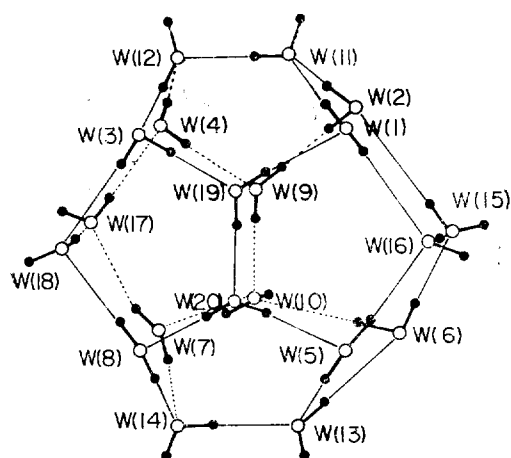


Fig. 7. Proposed dodecahedral cage of water molecules.

involving more than one atom, possibly one H_2O molecule and one Na cation. Na(1) is tetrahedrally coordinated by four nearest neighbors, three framework oxygen atom O(3) and one water(1).

As shown in Table 5, in α cage, the binding energy of water(1) in Fig. 6 is nearly same as that of optimized water(1) in the absence of

Table 5. Optimized position and energy of W1 and the energy of W1 in Fig. 6.

	Optimized W1			W1 in Fig. 6		
	X(Å)	Y(Å)	Z(Å)	X(Å)	Y(Å)	Z(Å)
H	1.384	2.236	2.576	1.37	2.15	2.64
O	2.293	2.306	2.287	2.22	2.22	2.22
H	2.232	2.527	1.358	2.14	2.69	1.35
Binding energy	-25.759 kcal/mole			-24.917 kcal/mole		

Table 6 Binding energies of water(1).

Binding water	Electrostatic energy (kcal/mole)	Polarization energy (kcal/mole)	Dispersion & repulsion energy (kcal/mole)	Total energy (kcal/mole)
W1	-25.749	-0.339	1.146	-24.942
W2	-29.144	-0.367	1.034	-28.476
W3	-28.655	-1.102	-0.666	-30.423
W4	-40.965	-0.242	1.457	-39.750
W5	-28.995	-0.365	1.073	-28.287
W6	-25.570	-0.349	1.016	-24.867
W7	-31.554	-0.236	1.646	-30.144
W8	-34.017	-0.159	2.317	-31.859

water(3). The optimized binding energies of water(1) are listed in Table 6. Fig. 8 shows the hydrogen bonding between water(1) and water(3). Dodecahedral cage become favorable when

Table 7. Optimized positions and energies of water(2), water(3), water(4) and Na(3).

Binding water					Binding energy (kcal/mole)
		X(Å)	Y(Å)	Z(Å)	
W11	H	-0.389	1.941	-3.092	-15.060
	O	0.483	2.115	3.464	
W14	H	0.402	2.512	4.316	-18.578
	O	1.776	3.971	0.000	
W16	H	2.402	3.247	-0.001	-13.485
	O	3.260	3.672	0.001	
W21	H	1.743	-3.882	-0.003	-52.147
	O	2.368	-3.157	-0.002	
W22	H	3.226	-3.581	-0.002	-24.436
	O	-1.316	0.401	-1.018	
W23	H	-0.416	0.521	-0.716	-27.194
	O	-0.020	1.425	-0.951	
W24	H	1.112	0.870	4.966	-24.402
	O	0.175	1.068	4.951	
Na(3)	H	-1.004	1.445	4.812	-90.229
	O	-0.953	4.954	-0.832	
	H	0.184	5.160	-1.810	
	O	-1.194	0.506	-5.094	
	H	-0.277	0.779	-5.138	
	O	-0.204	1.237	-5.974	
Na(3)		1.81	-0.38	0.62	-90.229

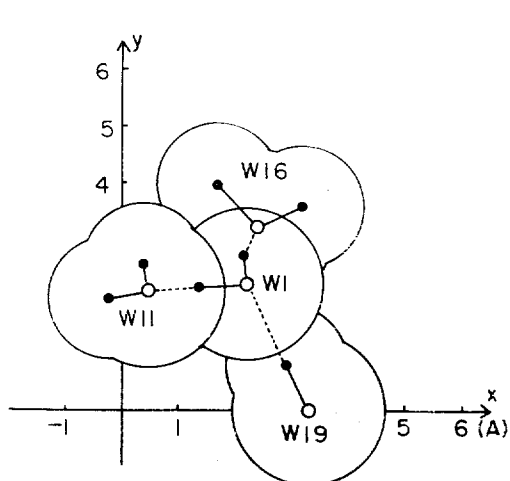


Fig. 8. Hydrogen bonds between water(1) and water(3).

the water(1) form hydrogen bonds with water (3). Because the water(3) are bound loosely,

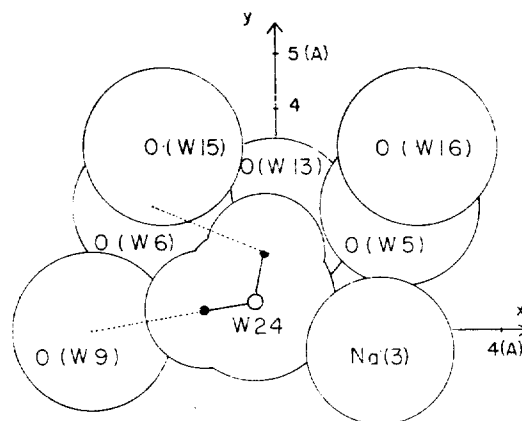


Fig. 9. Hydrogen bonds between water(4) and the waters forming dodecahedral cage.

some of them are selectively optimized in this paper.

The optimum position and energy of Na(3) is calculated in dodecahedral cage and then tho-

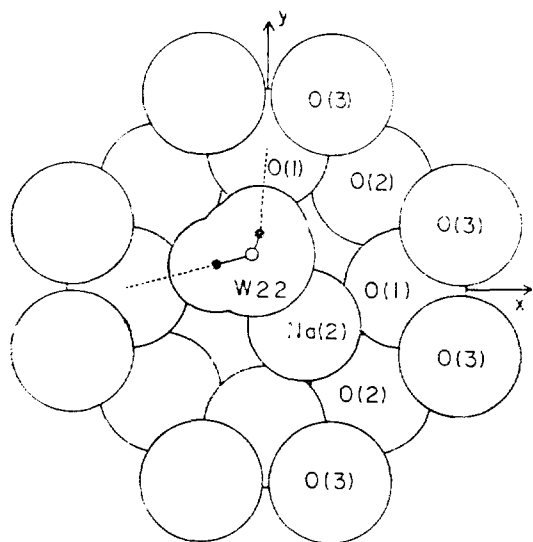


Fig. 10. Hydrogen bonds between water(2) and framework oxygens.

se of all waters are calculated again. In Table 7, the optimum positions and energies of water(2), water(3), water(4) and Na(3) are listed. The average energies of water(1), water(2) and water(3) are -29.847 , -25.344 and -15.888 kcal/mole respectively.

From above calculations, the distorted dodecahedral cage of water molecules is stable and is more stabilized by Na(3) and water(4). Because the water(1) and water(3) form a hydrogen bond with water(4), the distorted dodecahedral cage is stabilized. Fig. 8 shows the hydrogen bonds between water(1) and water(3). Fig. 9 shows the hydrogen bonds between water(4) and the waters forming dodecahedral cage. Fig. 10 also shows the hydrogen bond between water(2) and framework oxygens. As predicted by IR spectra³¹, the hydrogen bond is formed with all kinds of framework oxygens.

Comparison of Calculated Hydration Energy with Experimental Differential Heat of Sorption. Information about binding energy has been obtained from measurement³² by calorime-

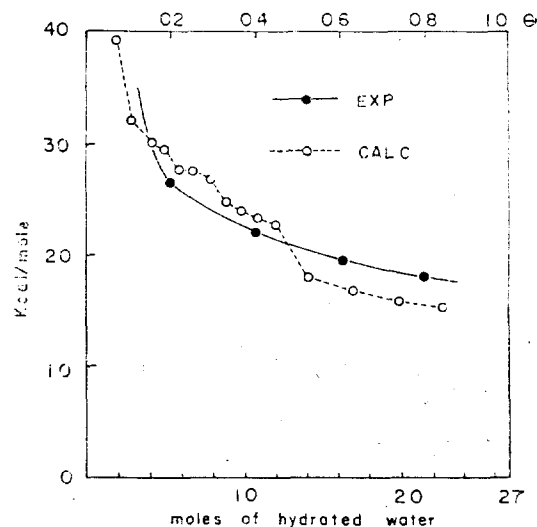


Fig. 11. The differential heat of sorption (●) and the heat of immersion curve obtained by the energy calculation (○).

tric and differential thermal analysis³³. Barrier and Cram^{2b} obtained the heat of immersion curve against degree of presaturation, θ , and in their experiment the saturated water content of zeolite NaA is 21.5 percent. The degree of presaturations defined as $\theta = \text{initial water content} / \text{saturation water content}$. In our calculation, the adopted unit cell contain 22.2 percent of water.

In Fig. 11, the solid line represent the differential heat of sorption obtained from differential thermal analysis^{2b} and the dotted line represent the heat of immersion curve obtained by the energy calculation. In the construction of heat of immersion curve from the binding energies of waters, we assume that the waters bind in order of the binding energy. But the information derived from differential thermal analysis is qualitative or at best only semiquantitative. The differential heat of sorption at $\theta = 0.1$ and $\theta = 0.8$ are 30 kcal/mole and 17.7 kcal/mole respectively.

The calculated hydration energy and the heat

of immersion from experiment show the some energy difference because the calorimetric measurements from the vapor phase deals with the non-equilibrium distributions of water molecules within crystals and through the zeolite bed. The water molecule may stick on sites where they first land.

As a result, the adopted dodecahedral cage of water molecules in α cage is stabilized by distortions. Dielectric constant in α cage is assumed to be about 3.5.

If the X-ray data of framework and the repeating unit are determined then the above method can be used in the energy calculation of the hydrations of any type zeolite.

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