found by the EH calculation.

From the earlier work[1] on the analytic solutions of an f.c.c. metal cluster, it has been assumed that the cluster belong to the point group D_{2h}. Much simplification in a submatrix of nine by nine (a diagonal submatrix) has been made from the symmetry condition. The symmetry, however, may be broken by loosening the restriction on N_A, N_B, and N_C and a new result may be obtained in this case. This symmetry breaking may be one of the efforts to deal with the off-diagonal submatrices (The summation rules[1], then, will change.). Or, the parameters $-E_{z2,z2}(110), S_{z2,z2}(200), \cdots -$ may be replaced by other ones. In these ways, the efforts to treat the off-diagonal submatrices more explicitly will also be continued.

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Encapsulation Characteristics of Gas Molecules in the Cavities of Zeolite A

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Encapsulation capacities (V_{gas}) of, H_2, N_2, CO, CH_4 and CO_2 for $Cs_{2.5}Na_{9.5}$-A (Cs-A) and Na_{12}-A (Na-A) zeolites have been measured in order to understand the effect of molecular properties on the V_{gas}. With appropriate number of large blocking cations on the main windows of cavities in zeolite A, gas molecules can be encapsulated in both the α- and β-cages, resulting in much large V_{gas}. V_{gas} is proportional to the encapsulation pressure (P_e) and is also dependent on the molecular properties of encapsulated gases themselves, especially on intermolecular forces originated from the quadrupole moments of molecules in the molecular-dimensioned cavities of zeolite A. At the low range of P_e, molecules with larger V_{gas} and intermolecular forces apparently have smaller increasing tendencies of V_{gas} upon increases in P_e, showing a linear relationship between the tendencies and intermolecular forces rather than their sizes. Interactions between encapsulated molecules of CH_4 and framework of Cs-A have been estimated and they seem to depend on the number of encapsulated molecules per unit cell. On the basis of calculated density of CO_2, presence of liquid-like phase for the encapsulated molecules in the molecular dimensioned cavities of zeolite A is postulated.

Introduction

For the purposes of storage and transport, gas molecules with kinetic diameters (σ)[1] slightly larger than the diameter of zeolitic windows can be enforced into the molecular-dimensioned cavities of zeolite by heating zeolite with pressured gases around and they can be entrapped by rapid quenching to ambient conditions (encapsulation).[2,3] Unlike chemi- or physisorbed gas molecules, the encapsulated gas molecules in the zeolitic cavities can sustain high pressure without leakage even at room temperature and they can be controllably released by the relaxation of window blocking such as by reheating the zeolite or by exposing the zeolite to small polar molecules (decapsulation).[4-9]

The entrance of gas molecules into the openings at the surface of microcrystals of the zeolites can be controlled by relative sizes of gas molecules and zeolitic windows modified by pore-size engineering.[5,10-14] En- and decapsulation of molecules in the zeolitic cavities can then be performed by invoking vigorous thermal vibrations of zeolite framework in order to widen windows and/or by inducing mobility and geometric changes of the exchangeable blocking-cations, located on the window of cavities and channels in the zeolites, as well as increased kinetic energy of gas molecules at the elevated temperature of en- and decapsulation process.[2,3]

Since the processes of encapsulation must involve those of adsorption, at least in part or initially, the molecular properties of gases, including size, interactions between molecules themselves, and those between molecules and host zeolites, should play an important role in determining encapsulation capacities at given encapsulation conditions. Although a number of studies have been made on the adsorption properties of various gases, studies on effects of gas molecules themselves on the encapsulation have been limited in a certain type of gases, such as hydrogen, methane, and some rare gases.[8,9,15-18] Furthermore, no systematic study of the encapsulation behaviours of such gases has been appeared in the literature. In this work, we attempted to visualize the encapsulation properties of gas molecules in order to understand details of the encapsulation process and to improve the encapsulation capacities of gas molecules for their storage.

Encapsulation of small gas molecules in zeolite A, which is one of the zeolites with largest void volume, can take place either in the α-cage or in the β-cage with 4.2 and 2.2 Å of 8- and 6-ring window openings,[19] respectively, or in both depending on the presence of appropriate blocking cations at the windows of the cages.[16-18] This has been proved by the encapsulations studies of Cs-A with H_2[20,21] and O_2,[22,23] respectively, and by our studies[24-26] on the encapsulation characteristics of MNa-A (M=Cs, Rb, K, and Na) with H_2 and CH_4. We here report our recent results of a study on the encapsulation behavior of gas molecules, H_2, N_2, CO, CH_4 and CO_2, with kinetic diameters of 2.89, 3.64, 3.76, 3.80 and Å[1], respectively, in $Cs_{2.5}Na_{9.5}$-A (Cs-A)[27] and Na_{12}-A (Na-A) systems.[28]

Experimental

Materials. Zeolite 4A ($Na_{12}Si_{12}Al_{12}O_{48}\cdot 27H_2O$: Na_{12}-A·27 H_2O)[28] pellets (1/6″ and 1/8″) were obtained from Union Carbide and they contained about 20 wt% binder (Kaolin) which was considered to be inert throughout the en- and decapsulation processes by acting merely as a diluent. When the zeolite 4A was saturated with the water vapor in a closed vessel at room temperature, it contained 21 wt% of water, measured by TGA (Themal Gravimetric Analysis) method, which agrees well with theoretical value obtained from the formula (22 wt%). The gases (H_2, CH_4, N_2, CO, and CO_2) were purchased from Special Gas Co. and were all purer than 99.9%. Reagents (CsCl and NaCl) for the ion-exchange of the zeolite pellets were obtained from Aldrich and Sigma Chemical Co., respectively, and were all Analytical Grades.

Preparation of $Cs_{2.5}Na_{9.5}$-A (Cs-A). In order to utilize the large cavities (α-cages) of zeolite A as micro containers of gas molecules, at least about 2.5 blocking cations per unit cell are necessary at the centers of 8-rings which construct the main channel system of the zeolite.[27,29] Cs-A was prepared by a static ion-exchange method. The zeolite pellet, 5 g, was placed in a 250 *ml* round-bottomed flask with 25 *ml* of 0.4 N chloride salt solution, a composition of 30 mol% Cs^+ on the basis of previously reported ion-exchange isotherms.[25] The mixture was refluxed at 98℃ for 2 hrs and the supernatant liquid was then decanted. After washing the zeolite with distilled water, a fresh portion of the salt solution was added. This procedure was repeated for a total of 6 times in order to obtain a static equilibrium. The ion-exchanged zeolite was dried at 100℃ for overnight after washing with distilled water until no chloride ion is detected.

Encapsulation and decapsulation. En- and decapsulation of gas molecules in the cavities of above zeolites were carried out in high pressure and vacuum lines, interconnected each other.

High pressure line and encapsulation. The high pressure line is composed of a chamber (Cone Closure Tubing Reactor with dimensions of 11, 18 mm, and 40 cm in ID, OD, and length, respectively), gauge, valves, and pipes (Autoclave Engineering Co.) and an electric heater for the heating of chamber and its temperature-controller. With pre-weighted sample of zeolite inside the chamber, the high pressure line is connected to a high vacuum line (*vide infra*) in order to dehydrate the sample at 350℃ and 1×10^{-3} Torr for overnight.[30] After the complete dehydration of the sample and disconnection from the vacuum line, gas molecules were introduced in the camber from a gas-bomb connected to the high pressure line through a high pressure gas-controller. Encapsulation was then carried out at given temperature (T_e, encapsulation temperature) for a certain period of time (t_e, encapsulation time). After the encapsulation of gas molecules into the cavities of zeolite for t_e, the encapsulation pressure (P_e) is recorded and the chamber was cooled to room temperature. The left-over gas molecules in the chamber were then released by evacuating the chamber at room temperature through the vacuum line until the pressure drops down to 1×10^{-3} Torr.

High vacuun line and decapsulation. The high vacuum line is consisted of double stage vacuum pump with Mcleod gauge and an isolated section of known volume whose pressure is continuously measured with computer-controlled pressure transducer. When the release of left-over gas molecules from the encapsulation chamber is completed in the high pressure line, the chamber was only connected to the known volume of vacuum line for subsequent decapsulation. The decapsulation was performed by reheating the chamber with gas-encapsulated zeolite at 400℃ and by measuring the pressure developed in the known volume of vacume line, which is exposed at room temperature, until no additional increase of pressure was observed. Using the pressure data measured from the computer-controlled pressure-transducer, the volume of encapsulated gas molecules per unit weight of zeolite at STP (V_{gas}, *ml*/g-zeolite) was obtained.

Results and Discussion

Encapsulation isotherms of the gases on Cs-A and Na-A are shown in Figures 1 and 2, respectively, in a logarithmic scale with V_{gas}, measured after encapsulation at 350℃ for 30 min, *vs.* P_e (atm), showing the effect of blocking cations in Cs-A with much higher encapsulation capacities. For all gases, the encapsulation capacities are more or less proportional to the P_e with somewhat different degree of increasing tendency. As illustrated in both figures, characteristic strai-

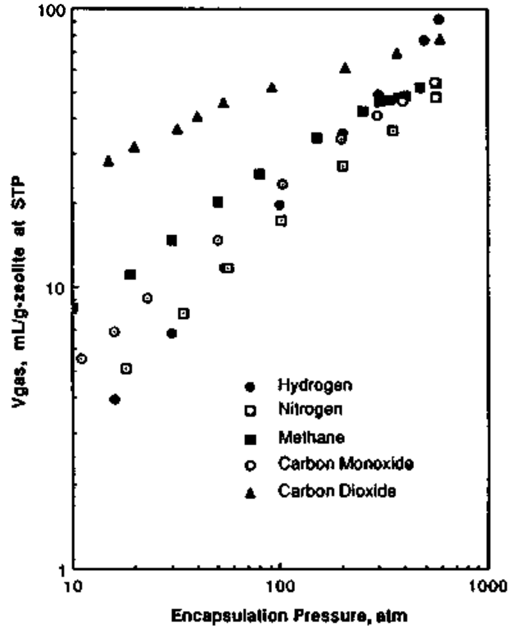

Figure 1. Encapsulation pressure (P_e) dependence of encapsulation capacity (V_{gas}) for various gas molecules in Cs-A at $T_e=350$℃ and $t_e=30$ min.

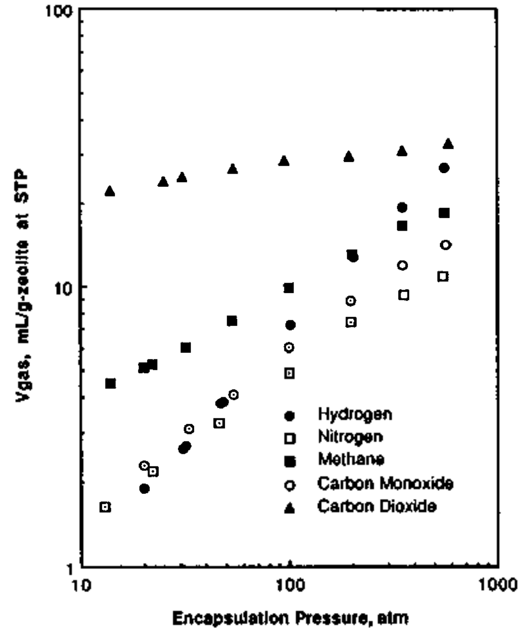

Figure 2. Encapsulation pressure (P_e) dependence of encapsulation capacity (V_{gas}) for various gas molecules in Na-A. See the caption to Figure 1 for other details.

ght lines are noticeable for all gases at lower range of P_e, while some of the gases shows deviations from the linearity at higher range of P_e. This deviation proves that the process of encapsulation should not be treated as a simple adsorption model of Freudlich type. Since the deviation probably originated from the limited volume of zeolite cavities at the final stage of encapsulation with higher P_e, the initial steps of encapsulation, except for diffusion process involved, could be considered as a the normal Freudlich type of adsorption in studying the effects of gas molecules themselves on the encapsulation. Furthermore, as proved in previous work,[24,25] 30 min of t_e for the encapsulation of gases should achieve more than 98% of equilibrium encapsulation capacities, suggesting the V_{gas} under conditions used should be independent from diffusion process.

Table 1. Slopes (*n*'s) and Intercepts (*k*'s) of Freundlich Type Isotherms of Gas Molecules Encapsulated at Various Encapsulation Pressure for Cs-A and Na-A

Gas	Cs-A		Na-A		VDW constants[a]	
	n	*k*	*n*	*k*	**a**	b
H_2	0.864	0.366	0.806	0.170	0.2444	0.02661
N_2	0.669	0.766	0.548	0.403	1.390	0.03913
CH_4	0.534	2.419	0.397	1.560	2.253	0.04278
CO_2	0.351	11.05	0.131	15.72	3.592	0.04267
CO	0.636	1.215	0.594	0.388	1.485	0.03985

[a] From reference 34.

The constants *k* and *n* derived from an empirical expression, $V_{gas}=kP_e^n$,[31,32] for the straight lines are tabulated in Table 1, together with van der Waals' constants[32] in order to correlate V_{gas} with basic molecular properties of gases. The slopes (n), increasing tendency of encapsulation capacity upon increase of encapsulation pressure, are related with the kinds of gases encapsulated as well as the kind of cages used for the encapsulation. For each gas, Na-A with only β-cages capable of encapsulation shows smaller value of slope than Cs-A with both α- and β-cages (726 and 155 Å per cage,[33] respectively) capable of trapping gas molecules does. This difference in slope gets obvious with molecules of larger polarizability.

Figures 3 and 4 with relationships between the slopes and intercepts of the characteristic lines and molecular properties of encapsulated gases, intermolecular force (a) and molecular volume (b),[34] respectively, show an apparent correlation of the encapsulation capacity with molecular interactions of the gases in the zeolitic cavities. In the case of spherical and diatomic molecules used in this study, smaller molecules with smaller polarizability and dispersion interactions have larger values of slopes, showing compactness of the molecules in the zeolitic cavities. This compactness of small molecules can be seen in both Cs-A and Na-A, but with smaller values of *n* for Na-A due to the smaller size of container (β-cage), illustrating the effect of molecular volume on the slopes. More apparently, considering a relatively small deviation of CO, with a permanent dipole, from the obvious linearity between slopes (*n*'s) and *a*'s of all other non-polar gases (see Figure 3), the intermolecular force that dominates in the encapsulation process seems to be originated from quadrupole moment of the encapsulated molecules, as suggested in many studies of adsorption.[35]

On the other hand, molecules with larger size, interestingly, tend to have larger intercepts (*k*), having much larger encapsulation capacity at lower range of P_e. Regardless of interactions between non-polar molecules and the framework of zeolite, this must related with larger intermolecular interactions of the molecules, suggesting more frequent contacts

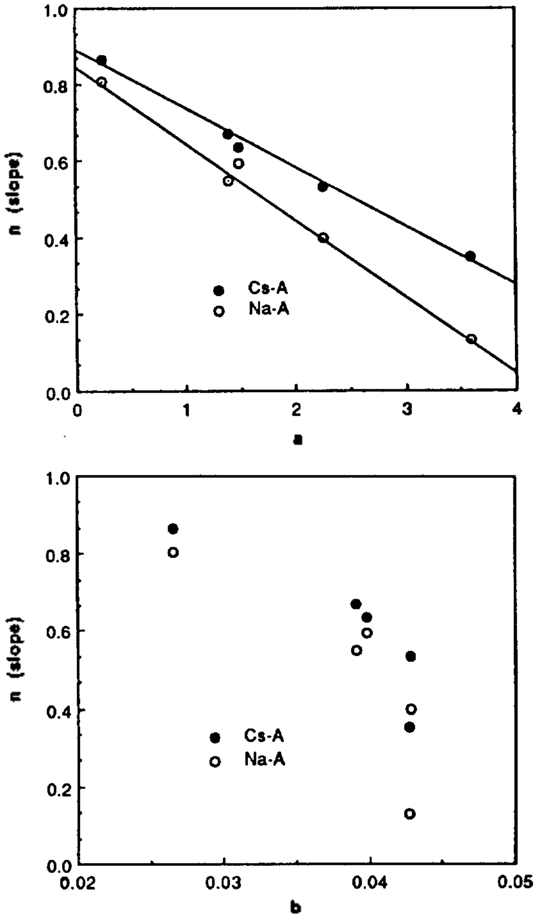

Figure 3. Relationship between slopes (*n*'s) of various gas molecules and molecular properties: intermolecular interaction (van der Waals constant a in l^2 atm/mol^2, above) and molecular volume (*b* in l/mol, below).

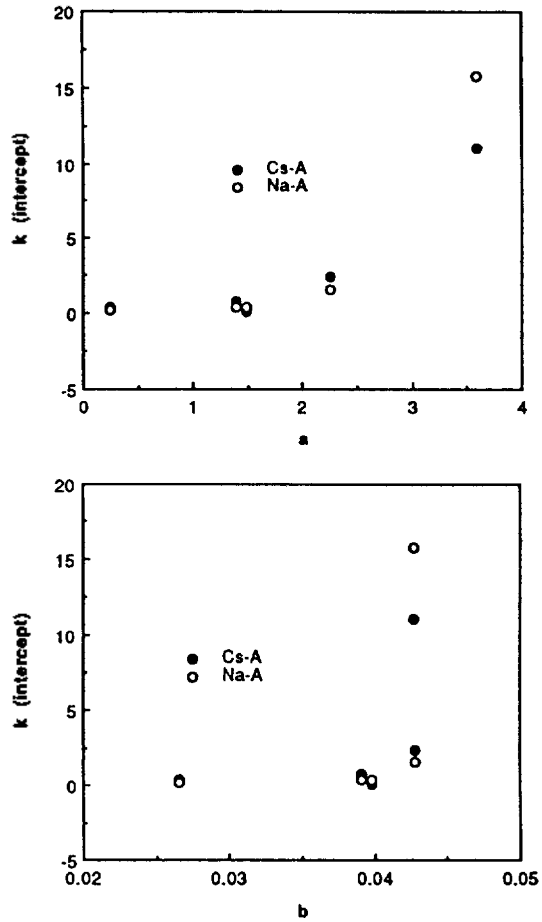

Figure 4. Relationship between intercepts (*k*'s) of various gas molecules and molecular properties. See the caption to Figure 3 for other details.

of the molecules in molecular-dimensioned cavity.

At the range of very high P_e encapsulation capacities of CH_4 and CO_2 begin to show considerable deviation from the linearity (see Figure 1) and seem to follow another linearity, similarly observed in adsorption experiments.[35] In order to keep its state of gas, each encapsulated molecule should keep distances of its kinetic diameter away from centers of neighboring molecules. The volume required for this assumption is that of a sphere with a radius of the kinetic diameter (σ), $4\pi\sigma^3/3$.[36] The maximum numbers of molecules per unit cell for pure gas state, $(775+151)/(4\pi\sigma^3/3)$,[33] correspond to about 6 and 4 for carbon dioxide (3.3 Å) and methane (3.8 Å), respectively, and agree well with the points where deviation from linearity appeared in the experimental observation.[37] This indicates that the state of gas molecules may change with increasing number of the encapsulated molecules, especially when they are cooled to room temperature, for example a phase change from gas to liquid-like or at least partial condensation due to inevitable close contacts in the molecular-dimensioned cavities of the zeolites. This change would be expedited with the gases of larger intermolecular forces, as suggested in the Figure 3 and 4 and insignificant deviations of H_2 and N_2 from the linearity in Figure 1.

Interactions between encapsulated molecules and zeolite framework can be theoretically estimated by calculating the intermolecular forces felt by respective encapsulated molecules from the data obtained in this study. A full definition van der Waals constant **a** is[36]

$$\{2\pi A N_A^2(N-1)/3N\}*(1/\sigma^3-1/R^3),$$

where A = *a* constant of proportinality having a different value for each kind of molecules in the expression of interaction energy, $U_1 = -A/$ (distance of separation)^6, N_A = an avogadro number, N = the number of molecules with kinetic diameter, σ, in the container with a radius of R. Therefore, this equation reduces to $\{2\pi A N_A^2/3\}*(1/\sigma^3)$ for a bulk gas in a container with R, much larger than σ of the gas molecules. However, the reduced form of the equations is not valid with the limited number of molecules in the molecular-dimensioned container, as the encapsulated molecules in the zeolitic cavities of this study ($(N-1)/N \neq 1$ and $1/R^3 \neq 0$). In order to evaluate the intermolecular interaction of molecules in the cavities of zeolite *A* ($\mathbf{a}_{zeo}$), calculations for the spherical molecule of CH_4 were carried out by multplying a factor,

$$f_{zeo} = \{(N-1)/N\}*\{(1/\sigma^3-1/R^3)/(1/\sigma^3)\},$$

to **a** calculated from van der Waals (VDW) equation with conditions used in this study and to the bulk value of van

Table 2. Calculated Interatomic Forces ($l^2 \cdot$atm/mol^2) of Encapsulated CH_4 Molecules in the Molecular-Dimensioned Cavities of Cs-A

N[a]	**a**[b]	$\mathbf{a}_{zeo}$[c]	**a**(bulk)[d]	Δ[e]
1.308	16.921	2.997	0.398	2.593
1.794	12.541	4.175	0.749	3.425
2.248	9.926	4.145	0.940	3.204
3.035	7.347	3.706	1.137	2.568
3.802	5.850	3.243	1.247	1.996
4.128	5.448	3.105	1.284	1.820
4.171	5.002	2.860	1.288	1.571
4.283	4.775	2.753	1.299	1.454
4.331	4.475	2.589	1.303	1.285
4.603	4.080	2.402	1.327	1.027
4.802	3.513	2.092	1.342	0.750

[a]Number of encapulated CH_4 molecules per unit cell (those with $n>1$ are listed in this table). [b]Calculated from VDW equation, $\mathbf{a}=V^2RT/n(V-nb)-PV^2/n^2$, where V=void volume, R=gas constant, $T=T_e$, $P=P_e$, $n=V_{gas}$/(molar volume at STP), and b=VDW constant **b**. [c]Calculated by multiplying f_{zeo} (see text) to **a** of column a. [d]Calculated by multiplying f_{zeo} to VDW constant **a**. [e]Differences between values in columns c and d.

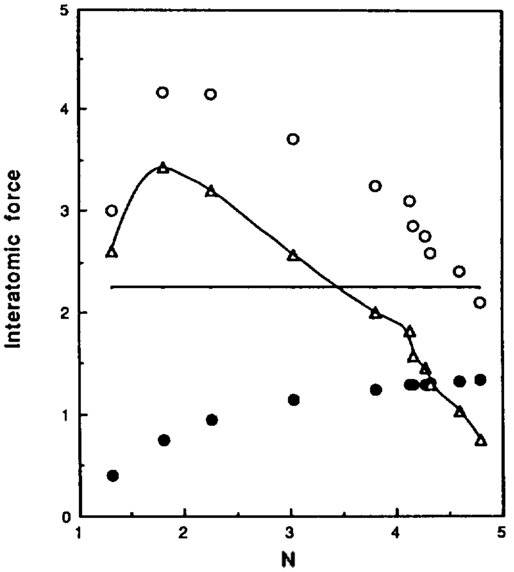

Figure 5. Changes in intermolecular forces ($l^2 \cdot$atm/mol^2) of CH_4 molecules in the molecular-dimensioned cavities of Cs-A upon changes in the number of encapsulated molecules per unit cell (N). (●: calculated from VDW equation, ○: **a** (bulk)*f_{zeo}, —: **a** (VDW), and Δ: differences).

der Wassls constant **a**, respectively, the results are tabulated in Table 2. In Figure 5, the modified values of **a**, are plotted against the N, the number of molecules in the cavity of Cs-A, with differences between those of calculated from VDW equation and bulk. As expected from the interactions between molecules and the framework of Cs-A, the actual values of **a** calculated from VDW equation are much larger than those of **a** (bulk)*f_{zeo} in all range on N obtained in this study. These interactions are also dependent on the number of molecules encapsulated in the cavity, showing a maximum at about 2 CH_4 molecules per unit cell with about 1.5 times of it bulk value and a rapid decrease at about 4 molecules per unit cell at which repulsion due to inevitable close contact is expected.

The density of encapsulated CO_2 (~18 wt%) in Cs-A, calculated from the number of CO_2 molecules per unite cell, approaches to 0.60 g/cm^3, which is a value almost equal to that of liquid CO_2 (0.599) and much larger than that of saturated vapor at 30℃ (0.337).[38] The calculated value of density actually varies from 0.44 to 0.60 g/cm^3, depending on the void volumes of zeolite A (from 0.235 to 0.345 cm^3/g)[21,33] used in the calculation. A very strong and sharp absorption peak of encapsulated CO_2, appeared at 2345 cm^{-1} in the IR spectrum,[39] possibly suggesting well aligned molecules of CO_2 in the molecular-dimensioned cavities of zeolite A. The shape of this peak, which is assigned to asymmetric stretching mode of CO_2, differs from that of gaseous CO_2 which shows a broad peak at above range.

Conclusion

With appropriate number of large blocking cation on the main window of cavities in zeolite A, gas molecules can be encapsulated in both the α- and β-cages, resulting in much larger V_{gas}. V_{gas} is proportional to the P_e and is also dependent on the molecular properties of the encapsulated gases themselves, especially on intermolecular force originated from the quadrupole moments of molecules in the molecular-dimensioned cavities of zeolite A. At the low range of P_e, molecules with larger V_{gas} and large intermolecular forces apparently have smaller increasing tendencies of V_{gas} upon increases in P_e, showing a linear relationship between the tendencies and intermolecular forces rather than their sizes. Guest-host interactions between encapsulated molecules of CH_4 and framework of Cs-A have been estimated and they seem to depend on the number of encapsulated molecules per unit cell. On the basis of calculated density of CO_2, persence of liquid-like phase for the encapsulated molecules in the molecular-dimensioned cavities of zeolite A is postulated. Finally, V_{gas} of any non-polar gas molecules, such as He, Ar, and Kr, in Cs-A and Na-A system can then be estimated with the relationships obtained in this study.

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Partial Assignment of Heme Groups of Cytochrome c_3 of *Desulfovibrio vulgaris* Miyazaki F by ^{1}H-NMR

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The ^{1}H-NMR signals of the heme methyl, propionate and related chemical groups of cytochrome c_3 from *Desulfovibrio vulgaris* Miyazaki F (*D.v.* MF) were site-specifically assigned by means of 1D-NOE, 2D-DQFCOSY and 2D-TOCSY spectra. They were consistent with the site-specific assignments of the hemes with the highest and second-lowest redox potentials reported by Fan *et al.* (*Biochemistry*, **29**, 2257-2263 1990). The site-specific heme assignments were also supported by NOE between the methyl groups of these hemes and the side chain of Val-18.

Introduction

Cytochrome c_3 is a unique class of heme proteins which contain four hemes in a single polypeptide and show very low redox potentials[1]. Crystal structures of cytochrome c_3 from *Desulfovibrio desulfuricans* Norway and *D. vulgaris* Miyazaki F have been reported[2,3]. Cytochrome c_3 is of great interest not only from a biological point of view but also because of its peculiar physicochemical properties. Redox potentials are one of the important parameters for the electron transfer.

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