Journal of Inclusion Phenomena and Molecular Recognition in Chemistry 7: 431–436, 1989.

Energetical Investigation on Water Inclusion in Gd-Exchanged Zeolite X

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(Received: 7 July 1988; in final form: 22 November 1988)

Abstract. A model for water distribution in the supercage of Gd-exchanged zeolite X previously proposed on the basis of structural data is investigated by an energetical calculation. A description of the potential energy acting on the water molecules, which takes into account van der Waals, Coulomb and hydrogen bond contributions, is proposed. The results confirm that the first inclusion shell of water molecules is completely defined by the sites found in the structural analysis. Partial occupany of these sites is discussed in order to simulate real distributions of water in the supercage.

Key words. Zeolite X, water inclusion, energetical calculations.

1. Introduction

Structure analysis of hydrated Gd-exchanged zeolite X [1] performed by single crystal X-ray diffraction showed, in contrast to what is normally observed with other cations [2], a highly ordered water distribution. The presence of most of the Gd in site II facing into the supercage together with its high coordination number results in a forcing of the water molecules to occupy preferentially two sites (O and P) of the supercage. This permitted us to define a schematic model describing the distribution of the water molecules in the supercage as shown in Figure 1. The water molecules are linked forming a complex polyhedron enclosed in the supercage which can be regarded as a first inclusion shell of water. This model, based on structural data, is investigated by energetical calculations in order to verify the experimental deductions and to understand the interaction parameters governing the water ordering.

2. Energetical Investigation

The potential acting on a water molecule in a zeolite cavity can be studied by using a model comprising different contributions. The first one originates from van der Waals and Pauli interactions between framework atoms and water molecules. This potential energy term has been described by the pair 6–12 potential given by:

$$e_1(r_{ij}) = \frac{A_{ij}}{r_{ij}^{12}} - \frac{B_{ij}}{r_{ij}^{6}} \qquad (1)$$

where r_{ij} is the distance between the i- and j-atoms.

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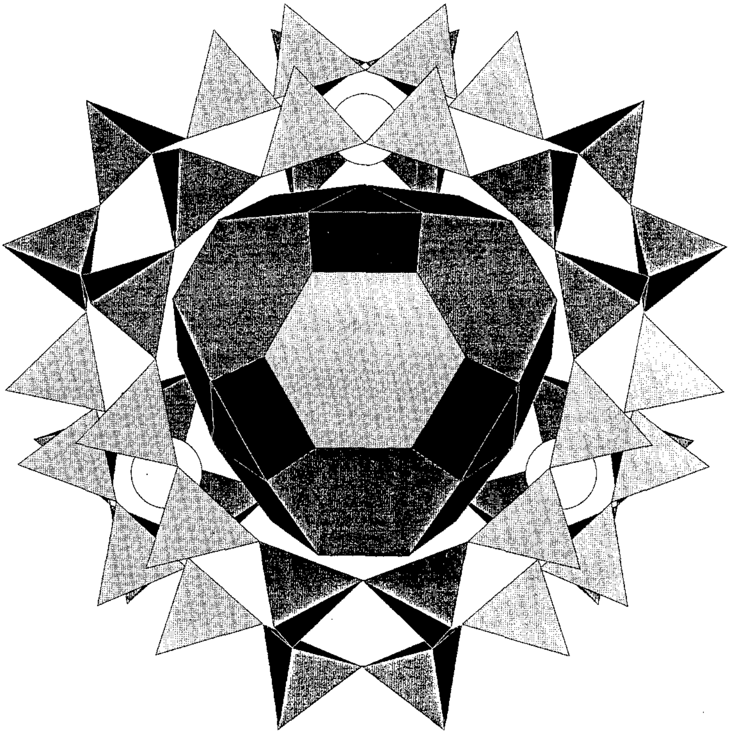

Fig. 1. Schematic model of water distribution in the supercage of zeolite X. The enclosed polyhedron is obtained by connecting oxygen atoms of water molecules in fully occupied P and O sites. Gd atoms in sites II are represented as circles.

The parameters describing the behavior of the Lennard–Jones function are derived from data reported in the literature [3]. In order to improve the efficiency of the model, a second potential term, representing the Coulomb contribution, must be considered. In the point charge approximation, this contribution is described by:

$$e_2(r_{ij}) = \frac{q_i q_j}{r_{ij}} \tag{2}$$

where q_i and q_j are the partial charges on the atoms. Following the same approach reported in [3] the problem of the attribution of the partial charge has been solved by assigning the formal positive charge +3 to Gd atoms and an average, negative charge to the zeolite oxygen atoms as required by the electrostatic neutrality of the system. The fractional charge on the oxygen and hydrogen atoms of water was assumed to be −0.66 and 0.33 units of electronic charge, respectively.

A third and, in these systems a very important term, derives from the presence of hydrogen bonds whose role can be described by a revised Morse potential:

$$e_3(r_{ij}) = D_{ij}\left[1 - \exp\left(\frac{\ln 2(r_{ij} - r_0)}{r_1 - r_0}\right)\right]^2 - D_{ij} \tag{3}$$

where r_0 represents the equilibrium distance, r_1 is the distance at which the Morse potential is zero and D_{ij} is the coupling constant. Values of 1.85 and 1.35 Å have been employed for r_0 and r_1 respectively.

The total energy of the system can be calculated according to the following expression:

$$E=\sum_{ij}\begin{cases} e_3(r_{ij}) & r_{ij}\leqslant R,\ i=H, j=O \\ e_1(r_{ij})+e_2(r_{ij}) & \text{otherwise}\end{cases} \tag{4}$$

where the critical distance R, representing the maximum H—O distance for which hydrogen bonding is considered, is assumed to be equal to 2.6 Å.

In spite of the high symmetry of the zeolite X supercage, calculations have been performed on a spherical environment of radius 9.5 Å surrounding its center and therefore not limited to the asymmetric unit. Studies performed on a single cavity or on a few adjacent cavities in fact require the removal of the symmetry, since for this small structural domain the high symmetry of the zeolite X is retained only for the framework atoms and not for cations and guests which are statistically distributed in the structure.

The potential field related to the water molecules in the cavity was calculated in an opportune set of points defined by imposing the condition that each point represents the center of a sphere of radius 3.3 Å containing a water molecule, in such a way that the interpenetrated van der Waals surfaces along a O—H bond lie on the radius of the sphere. This radius was considered in order to take into account the possible existence of water-framework hydrogen bonds, 3.5 Å being the maximum size of the two interpenetrated van der Waals surfaces. Calculations have been performed for each sphere of the set, with the water molecules being allowed to rotate freely as a rigid body to minimize the potential energy. All calculations have been performed on an IBM RT 6150 computer with the program KABUKI and ALTAMIRA [4]. Graphic structural representations have been obtained with the program VIDEOZEO [5] implemented on an IMB AT personal computer. Extra framework sites have been labeled according to Mortier [2].

3. Results and Discussion

Structural analysis of Gd-exchanged zeolite X revealed the existence of Gd atoms statistically distributed in three-quarters of sites II (general coordinates 0.2364, 0.2364, 0.2364). Each Gd is bonded to framework oxygens and also to three water molecules of the supercage (in sites O with general coordinates 0.0568, 0.0568, −0.2261). In the following calculations it was therefore assumed that a Gd atom in site II involves the presence of the three corresponding WO water molecules.

In a first step the calculations have been limited to a single supercage by considering a full occupation of the sites II by Gd, i.e. without symmetry removal due to partial site occupancy. The potential, calculated for 723 possible water sites within the cavity, shows two pronounced minima corresponding to the site P (0.2728, 0.0487, 0.8382) and to a site, hereafter defined as Q, with coordinates 0.3271, 0.3271, 0.3271. Water in both sites P and Q (WP and WQ respectively) are stabilized by hydrogen bonds with WO. WP can moreover interact with an oxygen atom.

Figure 2 displays the results derived from expression (4) as a function of the coupling constant D for the two sites. For small D values ($D < 16.73$ kJ/mol) the energy of sites P and Q is comparable. Increasing the D values to about 25.10 kJ/mol results in a favoring of the P site, which becomes the absolute minimum of the system's energy. This indicates that coupling constants comparable with those normally observed for hydrogen bonds between water molecules are sufficient to justify the presence of water in site P. Moreover, the unique site in competition with P for accommodating water can be considered to belong to an inner inclusion shell, since it is not able to interact directly with the framework.

A second set of calculations has been performed by taking into account the experimental information on the non-unitary occupancy of sites II by Gd atoms. A

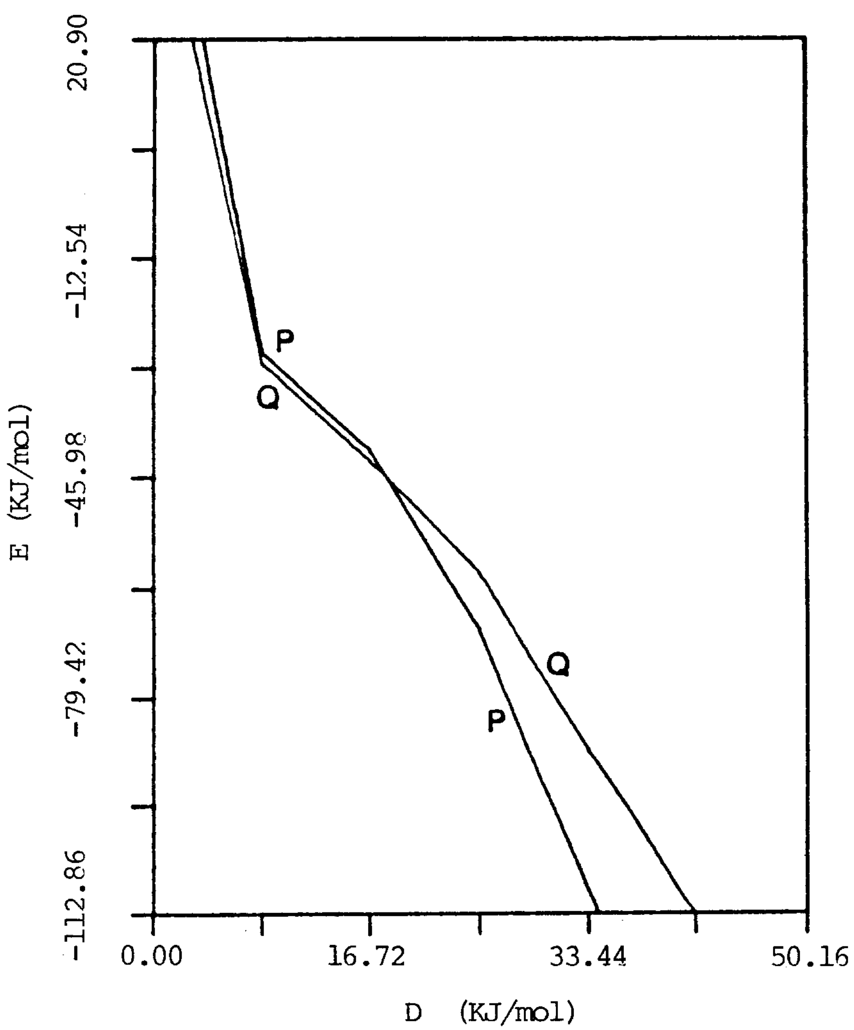

Fig. 2. Potential energy calculated for water molecules in sites P and Q as a function of the coupling constant D.

single supercage containing, in agreement with the structural data, only three II sites occupied by Gd has been considered. A coupling constant $D = 25.10$ kJ/mol led to potential energies of -82.42, -68.62 and -58.99 kJ/mol for sites II, O and P respectively. These values indicate that the water molecules exhibit a strong tendency to fill the Gd vacancy and subsequently the O and P sites, reproducing almost the same distribution observed in the fully occupied model. This result points out the selective effect of the hydrogen bonding system in influencing the water distribution inside the supercage.

For a complete discussion of the behavior of water molecules, however, it is necessary to consider the interactions between water molecules in adjacent cavities, since each supercage faces four other supercages through the 12-rings. If a full occupancy of the P sites is hypothesised, the WP water molecules, forming hexagons in the inner side of the 12-rings, face similar hexagons at a distance of 1.7 Å.

Structural data indicate an occupancy factor of 0.5 for these sites. Energy calculations confirm the physical inconsistency of the unitary occupany factor, the most favored distribution being a configuration in which only three non-consecutive P sites are occupied in the hexagons, facing configurations being tilted by 60°. Figure 3 shows the most probable water distribution inside the supercage as derived from energetical calculations when the presence of three Gd atoms and an occupancy of 0.5 for sites P is imposed.

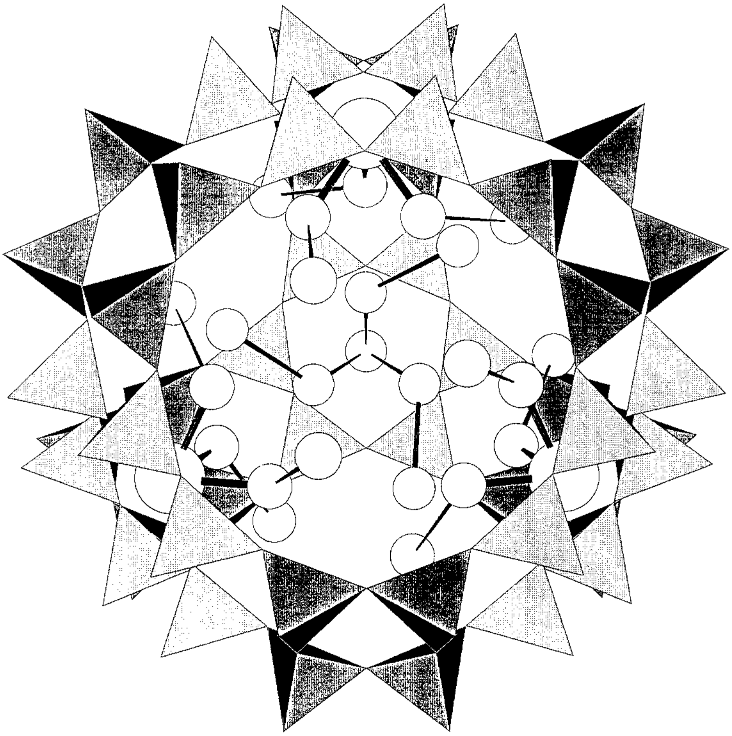

Fig. 3. Schematic model of the most probable water distribution within the supercage obtained by energetical calculations imposing the presence of three Gd atoms and an occupancy of 0.5 for sites P. Gd atoms are represented by large circles.

Within the limits of the partial occupany observed for sites II, P and O, the first water inclusion shell inside the supercage can therefore be considered to be completely defined by the model deduced from the structural analysis. With respect to the ideal fully occupied model, vacancies in sites do not seem to introduce new potential minima. The high ordering of water can be ascribed both to local organization induced by Gd atoms and to the absence in the supercage of cations which can perturb the hydrogen bond system.

The presence of a potential minimum in site Q led us to investigate the possible existence of ordered water within the first coordination shell, as suggested by X-ray analysis. A model containing four Gd atoms and fully occupied O and P sites was considered first. In this case a potential minimum corresponding to site Q has also been demonstrated, the coupling energy being very close to the one reported in Figure 2. Analogous calculations performed with a Gd atom substituted by a water molecule show no substantial changes in the ability of this site to fix a water molecule, permitting us to confirm a possible inner coordination tetrahedron of water stabilized by hydrogen bonds with WO water molecules.

Acknowledgement

One of us, O.O., wishes to thank ENIRICERCHE for financial support for the research.

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