Description of NaX zeolite deformation during adsorption of xenon

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The equation describing the experimental data of NaX zeolite deformation during adsorption of xenon at pressures of 0.001—7 MPa and temperatures of 252—333 K was obtained on the basis of the generalized Lennard-Jones pair interaction potential. The temperature dependences of the constants in the equation were determined.

Key words: adsorption, zeolite, adsorption deformation.

In studies on gas and vapor adsorption on solid adsorbents, a view is adopted that the adsorbent remains unchanged during the adsorption process.[1] At the same time, it is shown[2—5] that not only dimensions, but also the shape of adsorbents, in particular, crystalline solids, are subject to changes during adsorption. Both contraction and expansion of the solid accompany adsorption. These effects are especially pronounced for microporous lamellar adsorbents.[6] With the extension of the pressure and temperature ranges in the adsorption process, the need to take into account the adsorption deformation becomes increasingly important, because the variations in the adsorbent properties can greatly affect the energy parameters of adsorption interaction.

Since the process of adsorption deformation has a substantial effect on the thermodynamic properties and porous structure of the adsorbent, a certain model adsorbate—adsorbent system should be chosen as convenient for experimental studies and calculations. The adsorbent structure in this system should be understood, and it should be susceptible to isotropic deformation, while molecules with the simplest shape and incapability for "specific interactions" are preferred as adsorbates.[7] For example, the behavior of zeolites X and A during adsorption of inert gases satisfies these requirements. The study of these systems allows one to monitor the influence of particular components of the adsorption interaction on deformation of the adsorbent. The purpose of this work is to describe the deformation of crystalline zeolite NaX during adsorption of xenon.

Experimental

The experimental results obtained previously for xenon adsorption[8] served as the initial data for calculations of adsorption deformation. Crystalline zeolite NaX pelleted at 1 kbar with the composition $0.98Na_2O \cdot Al_2O_3 \cdot 2.36SiO_2 \cdot 0.02H_2O$ and a unit cell parameter of 2.496 nm and xenon (spectral purity grade) were used in experiments. Deformation of zeolite pellets was measured on a dilatometer with an inductive detector of linear expansion (the relative error of deformation measurement was $3 \cdot 10^{-6}$).

Adsorption deformation was measured within the pressure range from 1 Pa to 7 MPa and temperature range from 252 to 333 K. The results of dilatometric measurements are presented in Fig. 1 as isotherms of adsorption deformation shown by signs.

Calculation procedure. The description of adsorption deformation based on the principles of phenomenological thermodynamics (see, *e.g.*, Refs., 9 and 10) cannot account for all features encountered in deformation of microporous adsorbents during adsorption. Since it is difficult to consider all components of adsorption interactions in the adsorbate—adsorbent system, studies based on the methods of "numerical experiment" [11—13] treat the solid as an inert carrier of the adsorption field. Accordingly, an attempt is made in this work to describe adsorption deformation of crystalline zeolite NaX during adsorption of Xe on the basis of the generalized potential of molecular interaction, in which both adsorbate—adsorbate and adsorbate—adsorbent interactions are taken into account.[1] The initial equation for the potential energy of the interaction between an adsorbate molecule and the zeolite lattice is based on the generalized Lennard-Jones potential of interaction between two atoms (6-12) with an additional term associated with the induction interaction of the adsorbate with the total electrostatic field created by the framework ions. The equation reads:

$$\Phi(r) = -\sum_i C_{i-a} \sum_j \frac{1}{\left(\left|\mathbf{r}_j^{(i)} - \mathbf{r}\right|\right)^6} + \sum_i B_{i-a} \sum_j \frac{1}{\left(\left|\mathbf{r}_j^{(i)} - \mathbf{r}\right|\right)^{12}} - \frac{\alpha_a}{2}[E(r)]^2, \qquad (1)$$

where the first term is associated with the dispersion attraction of adsorbate molecules by the sites in the framework, the second term is related to the repulsion energy, the third term characterizes the energy of interaction of the adsorbate with the electric field of the framework ions (in our case, Na^+), C_{i-a} and B_{i-a} are constants, α_a is polarizability of the adsorbate molecule (in our case, Xe atom), $E(r)$ is the electrostatic field strength, and $r_j^{(i)}$, r are the radii-vectors that determine the position of interacting particles.

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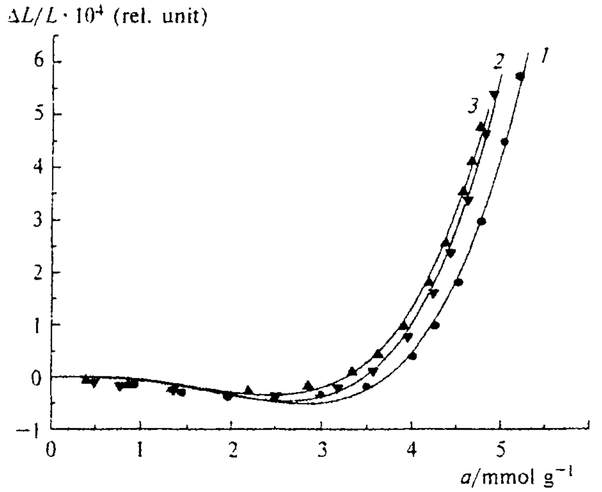

Fig. 1. Calculation of adsorption deformation of the Xe—NaX system on the basis of the generalized Lennard-Jones potential (6-12): points are experimental data obtained at T/K = 272 (*1*); 303 (*2*); and 333 (*3*); solid lines are the calculation by Eq. (7).

It is very difficult to calculate all forces inducing zeolite deformation. Therefore, to describe the adsorption deformation of zeolite NaX, we used the experimental data and the main specific features of the dispersion interaction followed by Eq. (1). Since the force of interaction between two particles is determined as

$$F = -\left(\frac{\partial\Phi}{\partial r}\right)_T,$$

after differentiation of Eq. (1), we obtain the expression for the average force acting on the zeolite crystal when adsorbed molecules are uniformly distributed in its cavities

$$\bar{F} = -C\cdot r^{-7} + B\cdot r^{-13} - D\cdot r^{-5}, \qquad (2)$$

where C, B, and D are constants, and r is the average distance between the nearest atoms involved in the adsorbate—adsorbate and adsorbate—adsorbent interactions when the adsorbed molecules are uniformly distributed in the zeolite cavity. To transform the r distance between interacting adsorbed particles to the adsorption value, it can be accepted in the first, rather rough approximation that $r \sim 1/\sqrt[3]{a}$, and hence,

$$\bar{F} = -C'a^{7/3} + B'a^{13/3} - D'a^{5/3}, \qquad (3)$$

where a is the adsorption in micropores, and C', B', and D' are constants.

A further advance to the expression that determines the relative adsorption deformation was performed using the dependence between the internal pressure, deformation, and the coefficient of all-round contraction. Since zeolite NaX has a cubic symmetry,[14] it can be considered that adsorption deformation of its crystals is isotropic. For the region in which the Hooke law is fulfilled, we have

$$\Delta l/l = \Pi/3k, \qquad (4)$$

where $\Delta l/l$ is the relative linear deformation of zeolite NaX during adsorption, Π is the internal pressure that results in deformation, and k is the module of all-round contraction. Taking into account that

$$\Pi = \bar{F}\cdot s, \qquad (5)$$

where s is the internal surface of pores, which experiences the Π pressure, from Eq. (4) we obtain

$$\bar{F} = 3k/s\cdot\Delta l/l. \qquad (6)$$

Assuming that the internal pore surface and the module of all-round contraction are not affected by adsorption and taking into account Eq. (3), we find the final expression for the relative linear deformation of zeolite during xenon adsorption

$$\Delta l/l = -Aa^{7/3} + Ea^{13/3} - Ga^{5/3}, \qquad (7)$$

where A, E, and G are constants related to the forces of attraction, repulsion, and induction interaction of sorbed xenon molecules with the total electrostatic field, respectively.

Results and Discussion

The results of calculation (solid lines) of the adsorption deformation in the Xe—NaX system by Eq. (7) are presented in Fig. 1. The A, E, and G constants were found by the Newton method as stable solutions of Eq. (7) by approximating the experimental data.

As follows from Fig. 1, the curves calculated by Eq. (7) coincide well with the results of experimental measurements of the adsorption deformation of zeolite NaX during xenon adsorption.

To evaluate whether the choice of the generalized Lennard-Jones potential (6-12) as the initial potential is appropriate, we performed similar calculations in which the Lennard-Jones potential (3-9) for continuum was taken as the initial potential.[15] The curves of deformation isotherms calculated from the initial potentials of two types and the experimental data at 272 K are presented in Fig. 2. As compared with the results of calculation based on the Lennard-Jones potential (6-12), the data obtained on the basis of potential (3-9) deviate considerably from the experimental data. In particular, the average dispersion for different temperatures increased 3 times.

As follows from Fig. 2, the experimental data are better described by the equation obtained from the generalized Lennard-Jones potential (6-12) for the entire deformation isotherm at 272 K.

The numerical values of the A, E, and G constants in Eq. (7) for three temperatures fit the adsorption data:

T/K	$A\cdot10^5$	$E\cdot10^6$	$G\cdot10^6$
272	1.90	0.967	−13.5
303	1.76	1.11	−9.7
333	1.42	1.05	−6.6

The numerical values of the constants correspond to the amounts adsorbed, mmol g^{-1}.

The data presented show that the values of all three constants are temperature-dependent. This is most likely

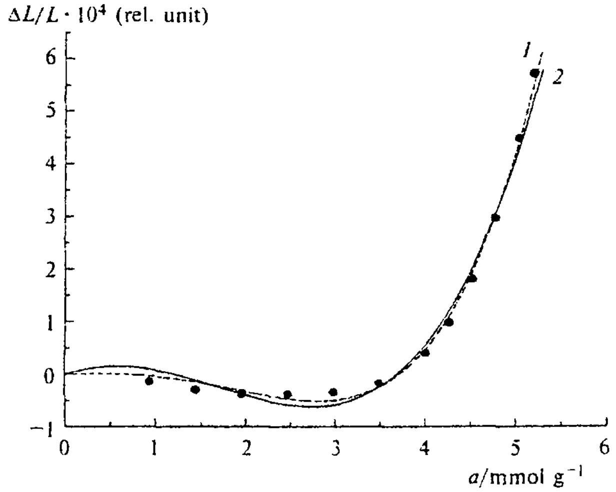

Fig. 2. Calculation of adsorption deformation of the Xe—NaX system on the basis of the generalized Lennard-Jones potential (6-12) (curve *1*) and potential (3-9) (curve *2*) at 272 K; points are experimental data.

related to the contribution of the kinetic component of the internal energy of the adsorption system. The linearity of the temperature dependence can be accepted in the first approximation for all three constants. Then the described method of calculation of the adsorption deformation can be verified as follows. Using the temperature dependences of the *A*, *E*, and *G* constants, we can calculate the deformation isotherm at any arbitrary temperature and then compare the calculated deformation isotherm with the experimental curve. The result of this verification calculation for the isotherm at 252 K is presented in Fig. 3 at $A = 2.08 \cdot 10^{-5}$; $E = 9.72 \cdot 10^{-7}$; and $G = -1.57 \cdot 10^{-5}$. As follows from Fig. 3, the results of calculations agree satisfactorily with the experimental data.

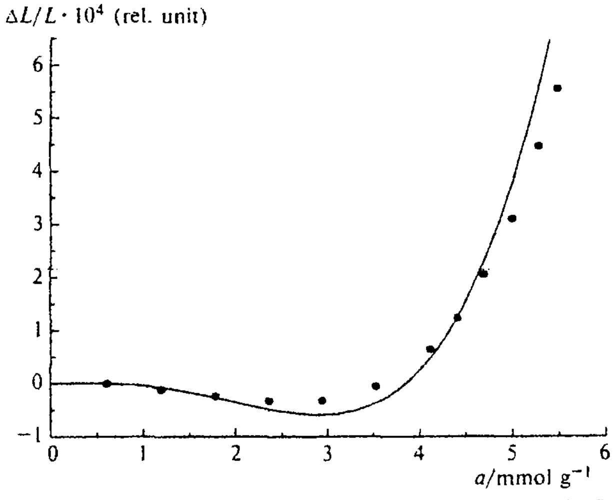

Fig. 3. Calculation of adsorption deformation of the Xe—NaX system from the temperature dependences of the *A*, *E*, and *G* constants for 252 K; points are experimental data.

The proposed approach to the use of the generalized potential corresponds to real energy processes that induce the deformation of zeolite NaX during xenon adsorption. The *A*, *E*, and *G* constants in Eq. (7) reflect, probably, specific forces that are manifested during the interaction of adsorbate molecules with the adsorbent.

Analysis of the results obtained shows that the use of the generalized Lennard-Jones potential of pair interaction (6-12) describes the deformation of zeolite NaX during xenon adsorption in a wide range of micropore filling. The temperature dependence of the constants of the equation of adsorption deformation obtained on the basis of the generalized potential of pair interaction is most likely due to the contribution of the kinetic component of the internal energy of the adsorbate—adsorbent system.

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