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Thermodynamics of CO_2 adsorption on zeolite NaX in wide intervals of pressures and temperatures

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The dependences of the differential molar isosteric heat of adsorption and entropy of adsorption of CO_2 on zeolite NaX were determined in wide temperature (196—423 K) and pressure (0.1 Pa to 5.4 MPa) intervals. In the initial region of adsorption ($a < 1$ mmol g^{-1}), the differential molar heat of adsorption increases from 40 to 43 kJ mol^{-1} and then decreases to 33 kJ mol^{-1}. The heat of adsorption remains virtually unchanged at 3 mmol g$^{-1} < a <$ 6.5 mmol g^{-1} and decreases sharply at high fillings of zeolite micropores ($a >$ 7 mmol g^{-1}). The heat of adsorption was found to be temperature-dependent. The region with the constant heats shrinks with the temperature increase, and the heats begin to decrease at lower fillings of micropores. The dependences of the change in the differential entropy of the adsorption system on the amount adsorbed were calculated at different temperatures. The specific features of the behavior of the thermodynamic functions of this adsorption system in the initial and medium region of fillings are associated with interactions of adsorbate molecules with Na^+ cations and walls of large cavities. For high fillings, an increase in repulsion forces between adsorbed molecules results in a sharp expansion of the adsorbent and a decrease in the heat of adsorption.

Key words: adsorption, high pressures, carbon dioxide, isosteres, heat of adsorption, entropy of adsorption, adsorption deformation, zeolite NaX.

Investigation of the physical adsorption of gases and vapors in wide intervals of pressures and temperatures is important for the development of the theory of adsorption and industrial innovations.

The use of a microporous crystalline adsorbent (zeolite) as an object of studies makes it possible to avoid errors in determination of the adsorbent volume, which is especially significant for measuring adsorption in a region of high pressures.

It has been shown previously[1] for the Xe—zeolite NaX system that a combination of adsorption data with results of adsorbent deformation allows one to introduce proper corrections in calculations of the thermodynamic characteristics of an adsorption system. For instance, the isosteric heat of adsorption is described, in the general form, by the Bakaev equation[2]

$$q_{st} = -RZ[\partial(\ln p)/\partial T^{-1}]_a[1 - (\partial v_1/\partial a)_T/v_g] - (\partial p/\partial a)_T[v_1 - T(\partial v_1/\partial T)_a], \qquad (1)$$

where R is the universal gas constant; $Z = pv_g/(RT)$ is the compressibility factor; p and v_g are the pressure and specific volume of the equilibrium phase, respectively; $v_1 = V_1/m_0$ is the specific reduced volume of the adsorption system; $a = N_a/m_0$ is the absolute amount adsorbed; V_1 is the volume of a crystal with micropores; N_a is the amount of the adsorbate in micropores; m_0 is the weight of the degassed adsorbent.

If adsorption is not accompanied by sorbent deformation ($v_1 \neq f(a, T)$), then

$$q_{st} = -RZ[\partial(\ln p)/\partial T^{-1}]_a - v_1(\partial p/\partial a)_T. \qquad (2)$$

The value of the second term is usually low (<1%) and becomes significant at high pressures[3] ($p \geq$ 8—10 MPa). Therefore, at standard pressures ($p <$ 100 kPa, Z = 1), expression (2) takes the form

$$q_{st} = -R[\partial(\ln p)/\partial T^{-1}]_a. \qquad (3)$$

In Fig. 1, solid curves are used to show the isosteric heats of adsorption of Xe on zeolite NaX calculated by Eq. (1) and dotted lines to show the heats calculated by Eq. (3). Comparing curves *5—7* and *5´—7´*, one can see that the differences between the heat values calculated by Eqs (1) and (3) are 30—70%.[1,4] Consequently, the nonideal character of the gas phase and adsorption deformation of zeolite NaX should be taken into account in a high-pressure region.

It is of special interest when molecules of an adsorbate capable of specific interacting with an adsorbent are in-

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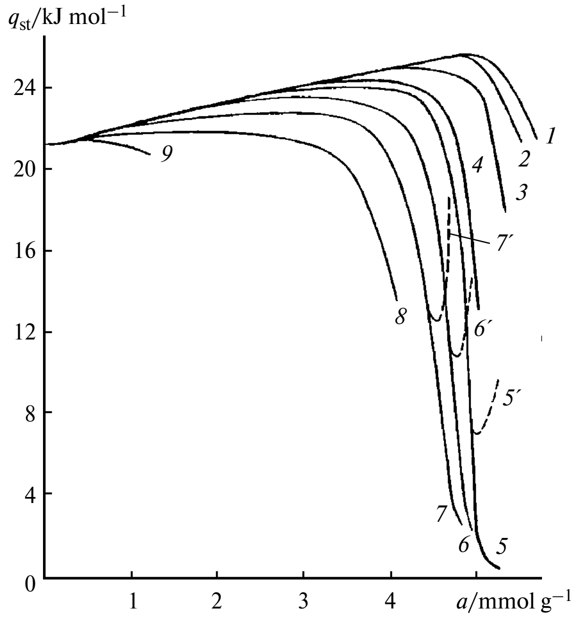

Fig. 1. Differential molar isosteric heat of adsorption (q_{st}) of Xe on zeolite NaX as a function of the amount adsorbed (a) at 150 (*1*), 210 (*2*), 240 (*3*), 280 (*4*), 295 (*5*, *5′*), 310 (*6*, *6′*), 330 (*7*, *7′*), 420 (*8*), and 600 K (*9*). Curves *1*—*8* were calculated taking into account adsorption deformation, and curves (*5′*—*7′*) were calculated ignoring adsorption deformation.

volved in the adsorption process. One of such adsorbates is carbon dioxide, whose molecule possesses a quadrupole moment. In addition, the study of carbon dioxide adsorption on microporous adsorbents over wide pressures is necessary to solve practical problems encountered, for instance, in systems of complex air purification by cryogenic separation, in the areas of ecology, by air purification in life supporting systems in a closed space, *etc.* For these reasons we studied the thermodynamic characteristics of the adsorption of carbon dioxide on zeolite NaX.

Experimental

Completely crystalline zeolite NaX $0.98Na_2O \cdot Al_2O_3 \cdot 2.36SiO_2 \cdot 0.02H_2O$ was used. According to X-ray diffraction data, its unit cell parameter a_0 is 2.496 nm, the density of the zeolite with micropores is 1.429 g cm^{-3}, and the micropore volume is 0.32 cm^3 g^{-1}. Before experiments, the zeolite powder was pelleted under a pressure of 1.5 kbar, which was approximately an order of magnitude lower than the pressure of desintegration of zeolite NaX crystals.

Based on the experimental data[5] obtained earlier by measuring the adsorption isotherms and adsorption deformation in the CO_2—zeolite NaX system in the pressure interval from 0.2 Pa to 5.4 MPa and at temperatures ranging from 196 to 423 K, we calculated the adsorption isosteres, differential molar isosteric heat of adsorption (q_{st}), and differential entropy of the adsorption system. The error of determination of q_{st} was ±3%.

Results and Discussion

Unlike xenon, which cannot interact specifically with adsorbents, carbon dioxide has a considerable quadrupole moment ($4.1 \cdot 10^{26}$ esu),[6,7] which results in the specific ion-quadrupole interaction with Na^+ cations and the unusual behavior of the thermodynamic functions of this adsorption system.

Based on the previously published[5] adsorption isotherms, we calculated the adsorption isosteres of CO_2 on zeolite NaX (Fig. 2). The isosteres in the coordinates $\ln p = f(1/T)$ are linear in a good approximation in the whole pressure region studied. The linearity is retained at temperatures both above and below the critical point, indicating that the properties of the adsorbate in micropores differ substantially from the properties of the phase at equilibrium. From the practical point of view, the linearity of isosteres makes it possible to calculate adsorption equilibria at high pressures avoiding laborous direct measurements and using only experimental data at pressures not higher than the atmospheric pressure.

Figure 3 presents the differential molar isosteric heats as a function of the absolute amount of CO_2 adsorbed on NaX zeolite at 196—423 K calculated by Eq. (1).

Let us consider the course of curve *1* obtained for adsorption at 196 K (see Fig. 3). Under these conditions, the equilibrium gas phase is almost ideal ($Z = 1$), and the interaction of CO_2 with the adsorbent should considerably affect the character of the dependence. In the region of initial adsorption ($a < 1$ mmol g^{-1}), the q_{st} value somewhat increases (from 40 to 43 kJ mol^{-1}) and then (at a = 1—3 mmol g^{-1}) decreases rapidly to ~34 kJ mol^{-1}. In the

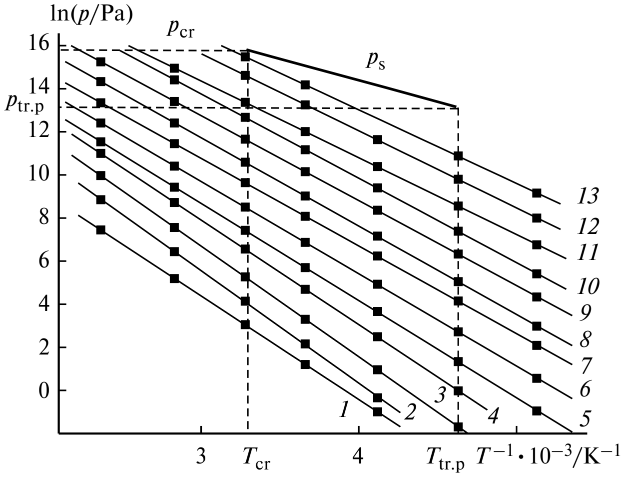

Fig. 2. Isosteres of CO_2 adsorption on zeolite NaX at different amounts adsorbed: 0.2 (*1*), 0.4 (*2*), 0.8 (*3*), 1.5 (*4*), 2.0 (*5*), 3.0 (*6*), 4.0 (*7*), 5.0 (*8*), 6.0 (*9*), 7.0 (*10*), 7.5 (*11*), 8.0 (*12*), and 8.5 mmol g^{-1} (*13*); p_s is the line of saturated vapor pressure; T_{cr}, p_{cr}, $T_{tr.p}$, $p_{tr.p}$ are the temperatures and pressures of the critical and triple points, respectively.

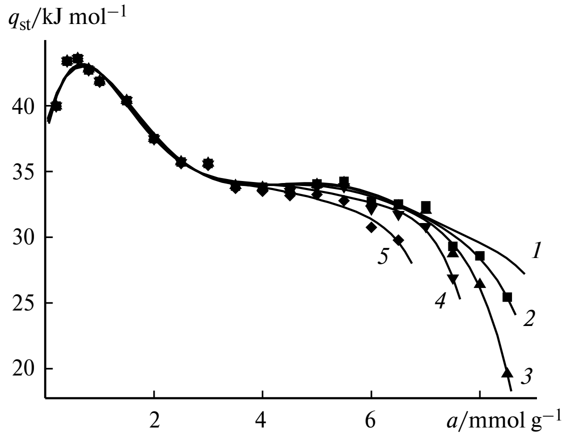

Fig. 3. Differential molar isosteric heat of adsorption (q_{st}) of CO_2 on zeolite NaX as a function of the amount adsorbed (a) at 196 (*1*), 273 (*2*), 305 (*3*), 353 (*4*), and 423 K (*5*).

interval of a varying from 3—3.5 to 5.5—6.5 mmol g^{-1}, the heat of adsorption remains almost unchanged, and then it decreases smoothly in a region of high fillings.

The curve of the dependence of q_{st} on a at 196 K is analogous to the curves obtained at room temperature[8,9] and 333 K.[10] The initial increase in the heat of adsorption at $a < 1$ mmol g^{-1} is of special interest (see Fig. 3). A similar effect has been described previously[8,9]; however, the authors explained it by an experimental error. Our data on adsorption deformation[5] show that the decreased heats at low fillings $a < 1$ mmol g^{-1} are a consequence of two effects. The first effect is related to a decrease in the heat with an increase in the micropore filling that occurs when high-energy adsorption sites are filled. The second effect is the endothermic effect caused by expansion of zeolite. The latter is due to the formation of a CO_2—Na^+ cation adsorption complex by the interaction with the first adsorbed CO_2 molecules with subsequent displacement of the Na^+ cation from the equilibrium state. The formation of the CO_2—Na^+ cation adsorption complexes was assumed in other works[10,11] as well.

The need to take into account the nonideal character of the gas phase (according to Eq. (1)), derivative $(\partial p/\partial a)_T$, and adsorption deformation makes the values of heats of adsorption temperature-sensitive in a region of high pressures of CO_2 (see Fig. 3). According to Eq. (1), the influence of the nonideal character of the gas phase on the heat of adsorption is expressed by the compressibility factor of the gas phase Z and its molar volume v_g, the contribution of the noninertness of the adsorbent is expressed by the derivatives $(\partial v_1/\partial a)_T$ and $(\partial v_1/\partial T)_a$, and the influence of the change in the slope of the adsorption isotherm can be described by the term $v_1(\partial p/\partial a)_T$. The contribution of each factor presented above is different. The maximum contribution to the temperature dependence of the heats of adsorption for this system is made by the nonideal character of the gas phase. The contribution of the noninertness of the adsorbent does not exceed 5%, because the maximum pressures were not higher than 6 MPa.

The state of the adsorbate in micropores is characterized by its differential molar entropy (ΔS), which can be determined by the Gibbs—Helmholtz equation[12]

$$\Delta H = \Delta G + T\Delta S, \tag{4}$$

which is written relatively to the standard state: the liquid phase of the adsorptive at a given temperature. The change in the free Gibbs energy of adsorption (ΔG) is

$$\Delta G = RT\ln(f/f_s), \tag{5}$$

where f and f_s are the volatilities of the equilibrium and saturated vapors of the adsorptive, respectively. The change in the enthalpy (ΔH) is equal to the pure differential heat of adsorption

$$\Delta H = -q = q_l - q_{st}, \tag{6}$$

where q_l is the heat of condensation of adsorptive vapors at a given temperature. Taking into account expressions (5) and (6), it follows from Eq. (4) that

$$\Delta S = [q_l - q_{st} + RT\ln(f/f_s)]/T. \tag{7}$$

We used this equation to calculate the change in the differential molar entropy of the adsorbate—adsorbent system.

Figure 4 presents the differential molar entropy of CO_2 calculated from the entropy level of the liquid adsorbate as a function of carbon dioxide adsorbed on zeolite NaX at 217, 243, and 273 K. As follows from the data in Fig. 4, the entropy of the system decreases with an increase in the amount adsorbed, and its decrease slows down only at the highest fillings (~8 mmol g^{-1}).

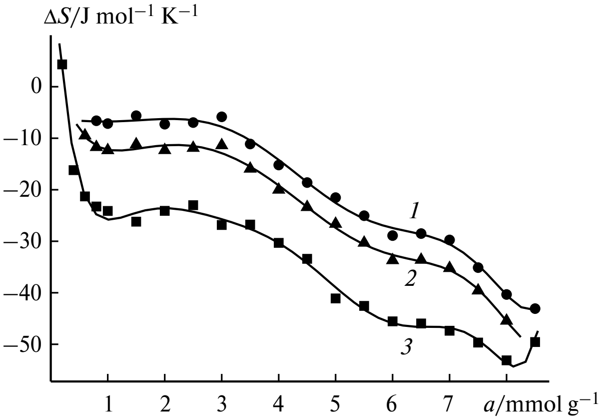

Fig. 4. Change in the molar entropy (ΔS) of the CO_2—zeolite NaX as a function of the amount adsorbed (a) at 217 (*1*), 243 (*2*), and 273 K (*3*).

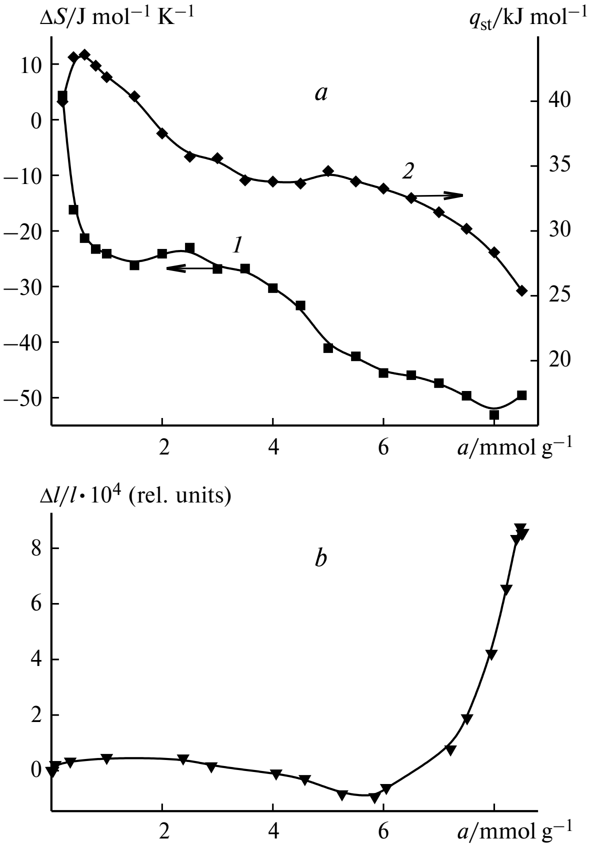

Fig. 5. Changes in the entropy (ΔS) (*1*) and isosteric heat of adsorption (q_{st}) (*2*) at 273 K (*a*) and the relative adsorption deformation ($\Delta l/l$) as a function of the amount adsorbed of CO_2 at 305 K (*b*) on zeolite NaX.

Let us monitor how the amount of CO_2 adsorbed affects the differential molar entropy, isosteric heat of adsorption, and adsorption deformation (Fig. 5). When the first CO_2 molecules are adsorbed ($a < 1$ mmol g^{-1}; on the average, ~1 molecule per zeolite cavity), the heat of adsorption and adsorption deformation increase: the adsorbent is extended. Then, when the filling increases to ~3 mmol g^{-1}, the heat decreases sharply; however, the adsorbent size does not show a measurable change due to gradual filling of high-energy adsorption sites in cavities of NaX. At the same time, at fillings below 1 mmol g^{-1}, the differential entropy of the adsorption system decreases sharply, passes through a minimum at 1.5 mmol g^{-1}, and somewhat increases when the amount adsorbed increases to 2.5 mmol g^{-1}.

The presence of the minimum indicates that the first adsorbed CO_2 molecules form adsorption complexes with the Na^+ cations localized in the position S_{III}. The adsorption system turns to a new energy state, which is indicated, first of all, by the almost constant adsorption deformation of the zeolite and entropy of adsorption in an interval of 1—4 mmol g^{-1} (see Fig. 5). In this state, the adsorbate molecules occupy the remaining centers that are most energetically favorable adsorption sites of zeolite micropores, and the heat decreases.

In the interval from 3—3.5 to 5.5—6.5 mmol g^{-1}, the heat of adsorption remains almost unchanged and reaches a value near 33 kJ mol^{-1}. The reason lies in an increase in the energy of the adsorbate—adsorbate interaction. In this case, the differential entropy of adsorption decreases and the expansion of the zeolite is replaced by contraction. The minimum in the deformation curve at 5—5.5 mmol g^{-1} indicates, most likely, the replacement of effective attraction forces by repulsion forces. This character of the deformation curve is explained by the dependence of the dispersion interaction potential on the average distance between the adsorbed molecules and walls of micropores. At high fillings ($a > 7$ mmol g^{-1}), these distances grow short sharply, and the balance of attraction and repulsion forces in the adsorption system shifts toward the repulsion forces. The latter increase rapidly, resulting in a sharp expansion of the zeolite lattice and a decrease in the heat of adsorption and entropy of the system.

The increase in the differential molar isosteric heat of adsorption of CO_2 on the microporous adsorbent in the initial region of fillings can be caused by the adsorbate—adsorbate cooperative effects and also by a change in the adsorption field of the adsorbent due to the formation of the CO_2—Na^+ cation adsorption complexes at $a \approx 1$ mmol g^{-1}. In the region of moderate fillings of micropores of zeolite NaX (3.5 mmol g^{-1} $< a <$ 6.5 mmol g^{-1}), the effective attraction forces increase gradually. Adsorption deformation turns from the positive (expansion) to negative region (contraction). The entropy of the system decreases. At high fillings, when distances between the adsorbed molecules are short, the attraction forces are replaced by the rapidly increasing repulsion forces, which results in a sharp expansion of the adsorbent and accelerates the decrease in the differential heat of adsorption.

Thus, noninertness of the adsorbent, which is manifested as its deformation upon adsorption and changes in the adsorption field gradient, substantially affects the behavior of the thermodynamic characteristics of the adsorption system.

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