



ENERGETICS OF THE HOST-GUEST INTERACTIONS IN NALTA MOLECULAR SIEVES. THE MOLAR DIFFERENTIAL ENTROPY AND THE ISOTHERM OF ADSORPTION OF (N) CARBON DIOXIDE IN NaA

¹Raxmatkarieva Firuza Gayratovna

Doctor of chemical sciences, professor.

Tashkent Institute of Inorganic Chemistry,

²Davlatova Odina Zakirjonovna

Namangan Institute of Engineering and Technology is a
doctoral candidate.

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ABSTRACT

The paper analyzes The molar differential entropy and the isotherm of adsorption of (N) carbon dioxide in NaA and establishes the molecular host-guest mechanism of interactions in the molecular sieve matrix.

Carbon dioxide is a strategic gas in many industrial processes. Excessive emission of carbon dioxide into the atmosphere leads to a global greenhouse effect [1]. Solving this problem with the help of adsorption techniques is economically advantageous. The most suitable for this purpose are molecular sieves [1,2,3]. The adsorption properties of molecular sieves can be regulated by varying the size and shape of the pores, the Si/Al ratio and the nature of the extraframework cations [4,5]. It has been found that nanoporous molecular sieves NaA [6] and CaA [7] zeolites are good absorbers of carbon dioxide, since the Na⁺ and Ca²⁺ cations [8] provide strong electrostatic interaction with carbon dioxide [9].

The regularities of adsorption of water in NaY molecular sieve were considered in [10] research work. It was found out that an appreciable amount of water is adsorbed in β -cavities. The carbon dioxide

molecule is somewhat larger than the water molecule and therefore at room temperature it is unable to penetrate into the β -cage through six-member oxygen windows with a diameter of 2.6 Å and to form host-guest clusters with sodium cations there. However, cations themselves can migrate from β - to α -cage under the influence of adsorbed molecules [10].

The aim of the study was to establish a stoichiometric relationship between the heats of adsorption of the test carbon dioxide molecule (guest) on homogeneous adsorption sites in NaLTA (host) and number of adsorbed on these sites molecules.

The study was carried out on a universal high-vacuum volumetric set, which allows the dosage of adsorbate to be carried out both with gas-volume and bulk-liquid methods with an accuracy of 0.1% [11, 12]. Differential heats of adsorption were measured using a heat-conducting

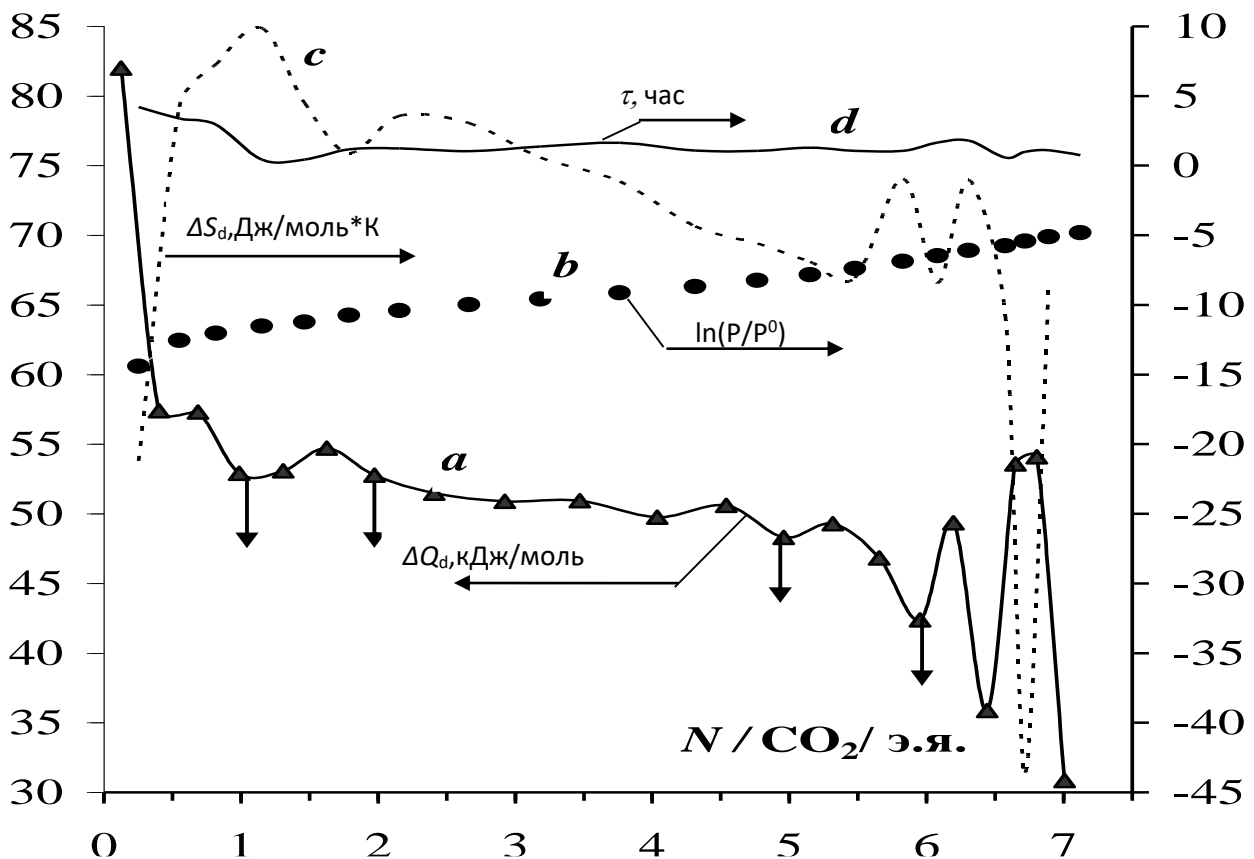


microcalorimeter of the Tianan-Calvet type. The use of the method of heat-flux compensation by the Peltier effect made it possible to increase the accuracy of the detected heat by 10-15 times [12].

Prior to the introduction of carbon dioxide, the sample was heated and subjected to high vacuum evacuation at 723 K for 10 hours. Figure (curve a) shows the differential heats of adsorption (Q_d) of CO_2 in NaA at 303 K. The intermittent line is the heat of condensation of carbon dioxide at

$CO_2/u.c.$ with Q_d varying from 52.91 to 52.78 kJ/mol. Next is an extended step extending from 2.0 to 5.0 $CO_2/u.c.$ followed by another step with a length of 1.0 $CO_2/u.c.$ (from 5.0 to 6.0 $CO_2/u.c.$). The process is completed by passing the curve through 2 maxima with a length of 1.0 $CO_2/u.c.$ In total, NaA zeolite contains 7 $CO_2/u.c.$

Fig. Adsorption of carbon dioxide in NaA at 303 K: a - is the differential heats; b - isotherm; c - entropy; d - thermokinetics.



303 K ($\Delta H_v = 27$ kJ / mol). For NaA Q_d begins at ~ 82 kJ / mol and decreases to 57.4 kJ/mol at 0.4 CO_2 per pseudo-elementary cell (u.c.) (the real unit cell is 8 times larger) Further Q_d forms a step, decreasing from 57.4 to 52.91 kJ/mol at 1 $CO_2/u.c.$ Further adsorption is accompanied by the formation of one more step (wave) with a length of 1.0 $CO_2/u.c.$ in the range of adsorption (N) from 1.0 to 2.0

Figure (curve b) depicts the isotherm of adsorption of (N) carbon dioxide in NaA at 303 K in the coordinates N - f (p/p^0) (p^0 is the pressure of CO_2 , at 303 K; $p^0 = 54806$ Torr [15]). The water adsorption isotherm in NaA is initially slightly concave to N ~ 2 $CO_2/u.c.$, then increases rectilinearly to ~ 5 $CO_2/u.c.$, after which it bends toward the axis of ordinates and increases linearly. Isotherm of CO_2 adsorption in NaA is



satisfactorily described by the two-term equation of the theory of volume occupancy of micropores (VOMT) [16].

$$N=6,634\exp[(A/25,17)^5]+0,550\exp[(A/24,57)^3],$$

where N is adsorption in micropores, $(\text{CO}_2)/\text{u.c.}$, $A = RT\ln(P^\circ/P)$ is the work of transferring 1 mmol of vapor from the surface (pressure P°) to the equilibrium gas phase (pressure P), kJ/mol.

Figure (curve c) shows the molar differential entropy of adsorption (ΔS_d) of carbon dioxide in NaA. For zero, the entropy of liquid carbon dioxide is adopted. In general, the curve ΔS_d is located above the entropy of liquid carbon dioxide with the exception of a small portion at the end of the curve.

In accordance with the form of the differential heat of adsorption curve, the entropy of adsorption of carbon dioxide in NaA in the initial region increases rapidly to 31.5 J/mol*K, then passes through a maximum and a minimum in the first two sections, in the third section decreases almost linearly. At the end of the adsorption process, the entropy decreases sharply, crossing the zero line and reaching -22 J/mol*K and also sharply increasing to the positive region.

The deep minimum at the final stage indicates a strong localization of a four-dimensional cluster of four adsorbed carbon dioxide molecules and five Na^+ cations along the ends of the CO_2 molecules. The average integral entropy of adsorption of carbon dioxide in NaA zeolite is 19 J/mol*K, whence it follows that the mobility of adsorbed CO_2 molecules is noticeably higher than that of carbon dioxide molecules in the liquid.

Figure (curve d) shows the time dependence of the establishment of

adsorption equilibrium (τ) on the adsorption of carbon dioxide in NaA. In the first section, the curve sharply decreases, beginning at 4 hours and 15 minutes up to 30 minutes, passes through a minimum, then rises in the second section and passes a series of maxima during the adsorption process, while the time changes from 1 hour to 1 hour 40 minutes, and at the end drops to 30 minutes.

The wave-like character of the curve τ is due to the displacement of cations from its equilibrium positions to form a of full value bond with carbon dioxide. The displacement of cations from equilibrium positions causes charge redistribution. To form the first complex, there is no need to shift the cation. However, further adsorption requires correction of the position of the cation. On the curve τ , each displacement of the cation is accompanied by its passage through a maximum.

Conclusion. Thus, when saturated, NaA zeolite contains 7 molecules of carbon dioxide per u.c. All of them are located in α -cages. β -cages do not participate in the adsorption process. Of the seven adsorbed molecules, four form a cluster at the center of which the H^+ or Na^+ cation is located (initially located at position SIII), surrounded by four molecules of carbon dioxide, whose opposite ends are closed on Na^+ cations at position SI. The three remaining carbon dioxide molecules form three bidentate complexes with cations in positions SII and SI. To form the eighth complex in NaA, there is enough space, but for a monodentate complex, the last cation in the SI position, which is not involved in adsorption, does not have enough strength to retain the carbon dioxide molecule.

The mobility of CO_2 molecules adsorbed in the NaA matrix is much higher than that of



the carbon dioxide molecules in the liquid. The rate of adsorption in the formation of a monomeric adsorption complex is slowed down and reaches 4-5 hours. At higher

fillings, the process is accelerated and the establishment time of adsorption equilibrium is stabilized in the interval from 1 to 1 hour 40 minutes.

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