

Adsorption of a four-component gas mixture on zeolite NaX

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Adsorption of N_2 , CH_4 , C_2H_6 , C_3H_8 , and their mixture on zeolite NaX was studied by the volumetric method under static conditions at 278 K in the pressure range from 0.1 to 0.8 MPa. Compressibility factors were calculated in order to take into account the nonideal character of the gas phase. Adsorption isotherms of individual gases and partial isotherms were obtained. The adsorption properties of gases in the adsorption of a mixture and its components were compared. The selectivity coefficient of adsorption of propane in the N_2 — CH_4 — C_2H_6 — C_3H_8 —NaX system was calculated, and its dependence on the total pressure was determined.

Key words: nitrogen, methane, ethane, propane, combined adsorption, zeolite NaX, selectivity coefficient.

Studies of adsorption from multicomponent systems are mainly confined to binary systems.

The purpose of the present work is to obtain experimental data on the adsorption of a four-component gas mixture on a microporous adsorbent at elevated pressure. The adsorption of nitrogen, methane, ethane, propane, and their mixture on zeolite NaX was studied at 278 K in the pressure range from 0.1 to 0.8 MPa.

The adsorption of the individual components, which has been studied previously,^{1–3} is investigated in order to compare the adsorption properties of the gases.

Numerous data on the adsorption of binary mixtures of hydrocarbons on zeolites are available^{4–7}, while data on the adsorption of a four-component gas mixture are lacking.

Experimental

Adsorption of N_2 , CH_4 , C_2H_6 , C_3H_8 , and their mixture on zeolite NaX containing ~20 % of a binding additive was measured by the volumetric method under static conditions on the experimental installation shown in Fig. 1.

The installation was made of stainless steel, and individual vessels were connected by valves B1–B4. An adsorber was placed into a cryostat, the temperature was measured by an ESP-01 resistance and maintained with an accuracy of ± 0.05 K, and the pressure was measured by an IPDTs measuring complex (accuracy class 0.1).

According to the procedure of volumetric measurements, working vessels A and C were calibrated by helium.

To obtain adsorption data the measured amount of a gas (or a gas mixture) was injected into the vessel with the adsorbent that has been kept in the cryostat at a specified temperature. After establishment of the equilibrium ($p = \text{const}$, $C = \text{const}$), the pressure, temperature, and composition of the

equilibrium gas phase (for adsorption of the mixture) were measured in the isothermal regime. The value of adsorption (A) was calculated by the formula $A = N - N_a$, where N is the total number of moles of gas in the adsorption volume, and N_a is the number of moles of gas in the equilibrium gas phase. The N and N_a values were determined by the equation of state, taking into account the nonideal character of the gas at elevated pressure. The adsorption value (a) per g of adsorbent is found from the equation $a = A/M$, where M is the mass of the adsorbent. In the case of adsorption of the mixture, the composition of the equilibrium gas phase was analyzed chromatographically according to the literature procedure.⁸

The measure of the nonideal character of a gas is the compressibility factor determined by the correlation $z = pv/RT$, where p is the pressure, v is the molar volume, T is the temperature, and R is the universal gas constant. For nitrogen,

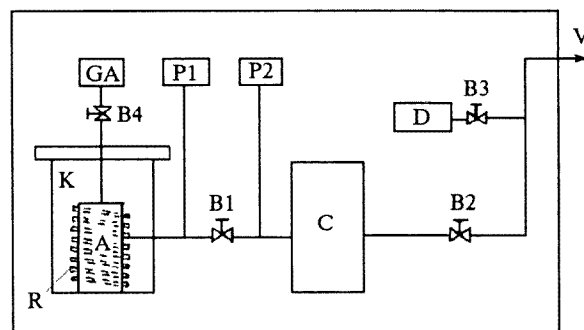


Fig. 1. Block-scheme of the experimental installation for measurement of the adsorption of gases and gas mixtures at elevated pressures: A is adsorber; P1 and P2 are manometers (IPDTs); C is storage vessel; K is cryostat; R is thermoregulator; D is cylinder with the initial gas (mixture of gases); GA is gas analyzer; B1–B4 are valves; and V is vacuum pump.

ethane, methane, and propane, the compressibility factor was calculated by linear interpolation of the tabulated data.^{9–11} Tables of thermodynamic properties of the mixtures studied in this work are absent. Therefore, the deviation from the ideal state for the mixture studied was performed by the computational method. All computational methods are based on the law of corresponding states, which is theoretically valid for all substances, whose p – V – T -properties are described by the two-constant van der Waals equation. The behavior of spherically symmetrical molecules is well described by the two-constant law of corresponding states, and three-parametric correlations are used to enhance the accuracy of calculations. The Pitzer acentricity factor can be used as the third parameter.¹² The compressibility factor can be presented as the following correlation: $z = z^{(0)}(\tau, \pi) + \omega z^{(1)}(\tau, \pi)$, where $\tau = T/T_{cr}$, $\pi = p/p_{cr}$, and ω is the Pitzer acentricity factor of the gas considered.

Additional variables of composition are introduced to propagate the computational methods of p – V – T -properties over gas mixtures. We have chosen the following rules of mixing:

$$\omega_m = \sum_j \omega_j \cdot y_j,$$

$$T_{pcr} = \sum_j T_{crj} \cdot y_j \quad (\text{Cay rule}),$$

$$p_{pcr} = \frac{R \left(\sum_j y_j \cdot z_{crj} \right) \cdot T_{pcr}}{\sum_j y_j \cdot v_{crj}} \quad (\text{Prausnitz—Gunn rule}),$$

where ω_m is the acentricity factor of the mixture; T_{pcr} and p_{pcr} are the pseudocritical temperature and pressure of the gas mixture; y_j is the molar fraction of the j th component of the mixture; ω_j , T_{crj} , v_{crj} , and z_{crj} are the acentricity factor, critical T , v , and compressibility factor of the j th component, respectively. Using this procedure, we calculated the compressibility factor of the mixture at various pressures within the range from 0.1 to 0.8 MPa at 278 K, which made it possible to determine the partial adsorption of each of the gases under the experimental conditions.

Results and Discussion

1. Adsorption of individual components. The adsorption isotherms of nitrogen, methane, ethane, and propane are presented in Fig. 2. As can be seen, the adsorbability of hydrocarbons increases from methane to propane. This is primarily caused by lengthening of the hydrocarbon chain, which results in a change in the state of molecules. The pressure dependence of adsorption for all gases is significant only at $p \leq 0.3$ MPa, and the adsorption increases insufficiently as the pressure increases further.

2. Adsorption of four-component mixture. The behavior of the component in the adsorption from the mixture cannot always be predicted on the basis of its properties in the individual adsorption. Therefore, information about the behavior of components in the joint adsorption is necessary for development of new methods for calculation of parameters of the adsorption equilibrium of multicomponent mixtures.

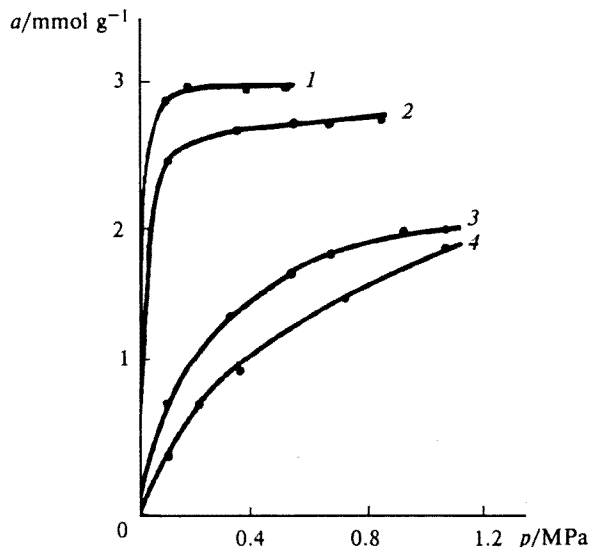


Fig. 2. Adsorption isotherms of propane (1), ethane (2), methane (3), and nitrogen (4) on zeolite NaX; $T = 278$ K.

A mixture of the following composition was used in the experiment: N_2 , 41.57 %; CH_4 , 18.67 %; C_2H_6 , 15.89 %; and C_3H_8 , 23.87 %. The measurements were performed at 278 K with change in pressure from 0.1 to 0.8 MPa. The dependence of the partial adsorption on the total pressure is presented in Fig. 3. As can be seen from the isotherms, the adsorption of each of the components of the mixture noticeably differs from the corresponding values for the individual adsorption (see Fig. 2). Nevertheless, even poorly sorbing components (N_2 , CH_4) under the experimental conditions are not completely displaced from the adsorption volume and, hence, affect the adsorption ability of other components of the mixture. The composition of the equilibrium gas phase depends on the total pressure and the adsorption properties of each of the components. For example, the concentration of propane in the gas phase at $p \leq 0.2$ MPa is low; it mainly contains nitrogen and methane. The concentration of propane and ethane in the gas phase increases as the adsorption volume is filled and the total pressure increases. From the practical viewpoint, such a behavior of the components upon joint adsorption can be used for removal or concentration of propane in complex gas mixtures.

As follows from the results obtained, propane and ethane are the main competitors in the joint adsorption in this system, while effects of N_2 and CH_4 are insignificant.

Taking this into account, we presented the real four-component mixture as an arbitrary binary system C_3H_8 —X (here X is the arbitrary second component of the $C_2H_6 + CH_4 + N_2$ mixture) and calculated the separation coefficient of the C_3H_8 —X mixture under the experimental conditions. The dependence of the separation coefficient on the total pressure is presented in Fig. 4. As can be seen, the pressure range from 0 to

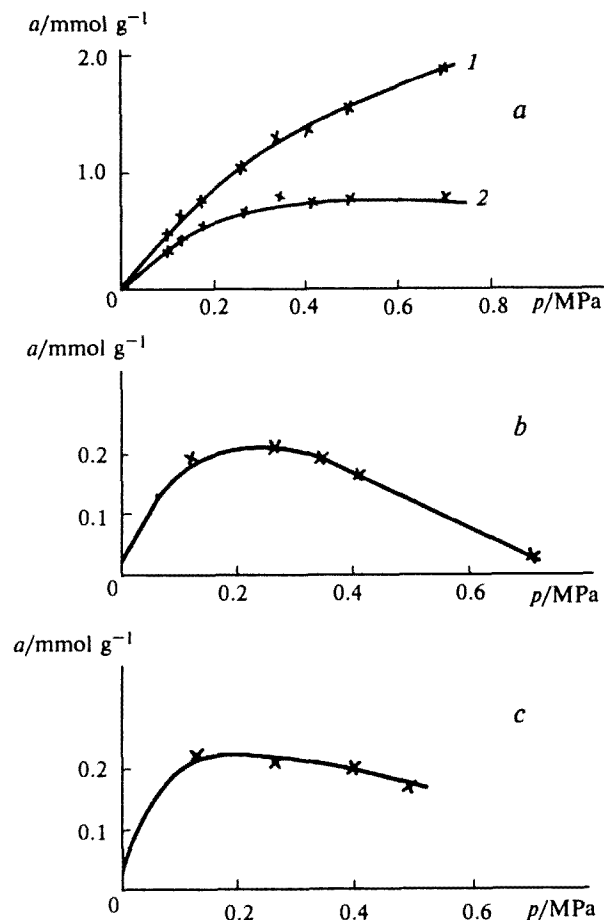


Fig. 3. Experimental dependences $a = f(p)$ for propane (a, 1), ethane (a, 2), nitrogen (b), and methane (c).

0.15 MPa is the most favorable for concentrating propane in the adsorption volume. Information about the adsorption of binary mixtures of components comprising the four-component mixture is necessary for quantitative determination of the degree of mutual effect of the components in the joint adsorption and for checking the possibility of preliminary calculation of the adsorption equilibrium of the four-component mixture, using methods of *a priori* calculation of adsorption equilibria (see, e.g., Ref. 13).

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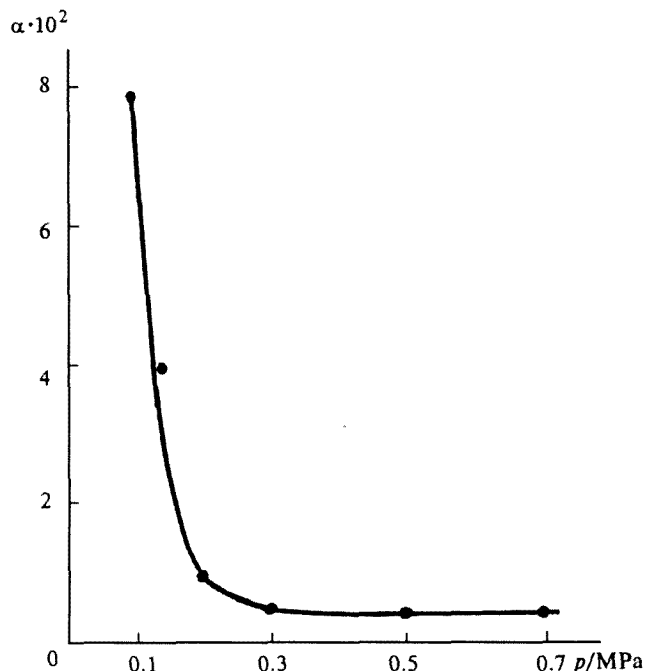


Fig. 4. Dependence of the coefficient of adsorption selectivity of propane on the total pressure of the mixture in the $\text{N}_2\text{-CH}_4\text{-C}_2\text{H}_6\text{-C}_3\text{H}_8\text{-NaX}$ system.

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