

Plenary Paper—Adsorption and Diffusion

INVESTIGATION OF THE ADSORPTION IN ZEOLITES AT ZERO FILLING

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ABSTRACT

The experimental determination of the thermodynamic characteristics of adsorption (TCA) at low filling and at different temperatures is considered. The data for a few reference systems (low alkanes in types X and Y zeolites) have been used to improve the atom-ion potentials of molecule-zeolite intermolecular interaction. The possibility of using these potentials in the molecular statistical calculations of TCA of other alkanes and nonstrained cyclanes has been investigated. For polar molecules the point moment approximation has been additionally used. Quadrupole moment of cyclopropane was calculated by the chromatoscopic method.

INTRODUCTION

The following trends in experimental and theoretical studies of adsorption in zeolites have been revealed at previous conferences [1,2] (N.B. references have been kept to minimum due to lack of space).

- 1) Directed synthesis of zeolite crystals of a definite composition and size with controlled ion content is carried out [3].
- 2) Not only isotherms but also calorimetric heats of adsorption are measured over a wide range of temperatures [4,5].
- 3) An assumption about the similarity of adsorbate properties in zeolite to those of a liquid is being replaced by a comprehensive analysis of the adsorbate state and its effect on the cation distribution using various methods of optical and NMR spectroscopy [1,2,6-9] and direct calorimetric measurements of heat capacity in adsorbate-zeolite systems [10].
- 4) The method of statistical thermodynamics is being more often used to describe the results of measuring thermodynamic properties of adsorbate-zeolite systems [1,2,11,12].
- 5) A wider use is made of the molecular-statistical method using semi-empirical atom-ion potentials [13-15], which meet the requirement of transference from one molecule to another within a given adsorbate class.

- 6) The idea of adsorption in individual cavities is gradually being replaced by the notion of adsorption in the crystal as a whole.
- 7) An idea of the molecule movement inside a crystal along "potential through" with the smallest barriers of different heights (depending on the zeolite and molecule composition) is associated with self-diffusion coefficients [16].
- 8) Attempts are made to obtain quantum-chemical descriptions of molecule-zeolite systems selecting clusters of different sizes [1,2].
- 9) There is a tendency to distinguish between the applications of the quantitative semi-empirical method of atom-ion and multipole-ion intermolecular interactions and quantum-chemical methods; this is done by analyzing the state of polar adsorbed molecules using the NMR and other spectral methods.
- 10) Distribution of cations in zeolite at different temperatures and in the presence of different adsorbates is now considered as a statistical problem. To solve this problem one must have a more realistic picture of charge distribution in the framework of zeolites of different structure and composition.

As a main topic of this article we have chosen the region of low (zero) filling of zeolite. It deals with basically two of the above listed aspects of the research in this area: 1) selection of reliable experimental data and 2) their interpretation at the molecular level using molecular-statistical adsorption theory which makes use of atom-ion and multipole-ion approximation for a potential function of molecule-zeolite intermolecular interaction.

DETERMINATION OF THERMODYNAMIC CHARACTERISTICS OF ADSORPTION (TCA) FROM EXPERIMENTAL DATA

Extrapolation of static data to zero filling. Due to insufficient sensitivity of static methods used to determine adsorption isotherms, calorimetric heats of adsorption and heat capacities of adsorption systems such measurements are carried out usually starting from rather high fillings of zeolite. To determine TCA for zero filling, i.e. Henry's constants $K_{n^S, c, 1}$ (n^S is the Gibbs adsorption per g of zeolite, c is the gas phase concentration, the index 1 indicates zero filling) the measured isotherm of adsorption has to be extrapolated to $n^S = 0$. The virial expansion [17,18] is convenient for this extrapolation. A very detailed and accurate measurement of the isotherms, however, will be required for a reliable determination of the Henry's constants. The same is true about extrapolation to $n^S = 0$ of calorimetrically obtained heats of adsorption and heat capacities, especially in the case of adsorption of polar substances on cationated zeolites.

Let us consider some examples of the extrapolation of isotherms and heats of adsorption (to $n^S = 0$). Unfortunately, only a limited number of papers present tabulated data in the literature.

Even the nonspecific absorption of alkanes in faujazite is very sensitive to both Si/Al ratio, type of cations and the degree of their exchange. Table 1 gives Henry's constants obtained by extrapolation of such isotherms using the virial expansion. Fig. 1 shows some dependences of the differential heat of adsorption \bar{q} and n^S . From these examples it can be seen that Henry's constants, the heat of adsorption \bar{q}_1 (for $n^S = 0$) the shape of isotherms of adsorption and the heat of adsorption of propane in zeolites X and Y depend on zeolite composition, the nature of alkaline cations and the cations deficit.

Table 1. Henry's constants at 24 C for propane on zeolites X and Y with different cation contents 19.

Zeolite	Average cation content per cell				$K_n^s, \text{c.l}$ $\text{cm}^3 \text{g}^{-1}$
	total	Na^+	Li^+	K^+	
LiNaX-2	80	6	74	-	22500
LiNaX-1	71	27	44	-	1550
LiNaY	50	17	33	-	890
NaX	76	76	-	-	3840
NaY	54	54	-	-	1130
KNaX-3	88	3	-	85	10300
KNaX-2	80	17	-	63	7800
KNaY	57	2	-	55	3070
HY	14	14	-	-	610

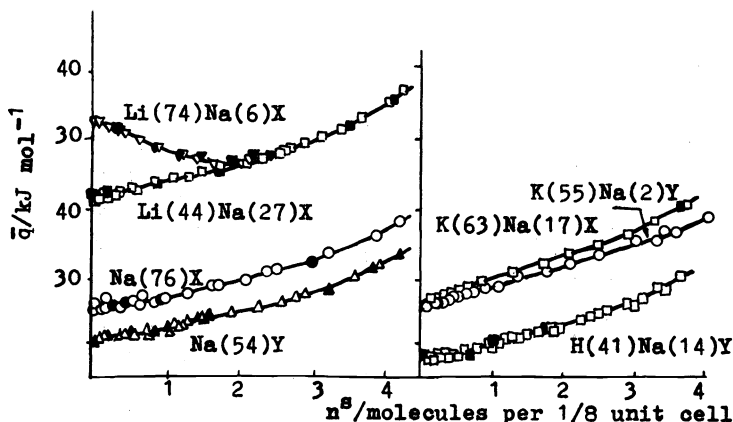


Fig. 1 Heat of propane adsorption \bar{q} vs n^S at 24°C for zeolites with different cation contents (Table 1).

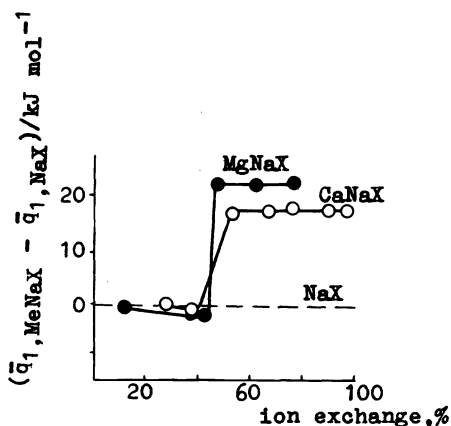


Fig. 2 Dependence of differences between heats of ethylene adsorption in MeNaX and NaX zeolites on the degree of exchange of Me^{2+} for Na^+ .

Replacement of Na^+ in zeolite X by Rb^+ and Cs^+ which possess greater polarizabilities and larger radii increases the adsorption of alkanes (ethane) but sharply reduces the adsorption of ethylene as found with other quadrupole molecules. The effect of Na^+ replacement by Mg^{2+} and Ca^{2+} on the adsorption of alkanes and especially of alkenes depends on the degree of ion exchange. For exchange up to $\sim 40\%$ the heats of adsorption for ethane and ethylene remain almost unchanged and then sharply increase when the double-charged cations appear on the sites accessible for these molecules [20]. This is especially clear for the difference in heats of adsorption of ethylene on zeolites MgNaX (or CaNaX) and NaX (Fig. 2). Similar results were obtained for CO and CO₂ [7.21] when used as probe molecules.

For the small dipolar molecules of water the situation becomes very complicated. The highest values of $\bar{q} \approx 90$ kJ/mol are obtained for LiX zeolite, however, they decrease rapidly with increasing n^S and in the n^S range from 5 to 25 water molecules per 1/8 unit cell, \bar{q} changes insignificantly and is around 65 kJ/mol.

Of special interest are dependences of \bar{q} on n^S shown in Fig. 3 for water adsorption in K-forms of zeolites (calorimetric measurements at 23°C [19]). A curve for the sample which is most rich in K^+ ions is

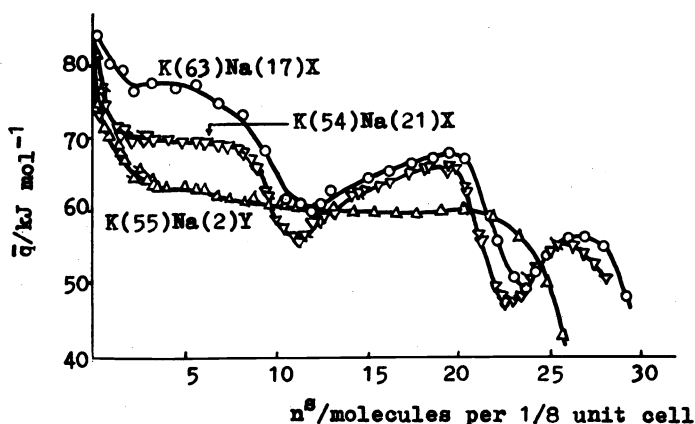


Fig. 3 Heat of adsorption of water vapour \bar{q} vs n^S for K-forms of X and Y zeolites at 23°C.

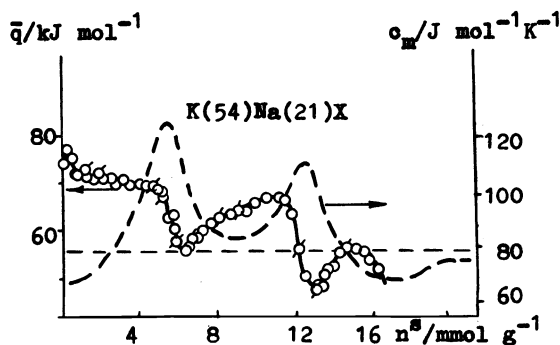


Fig. 4 Heat of adsorption \bar{q} and heat capacity of adsorbed water c_m vs n^S for KNaX zeolite.

similar to the one obtained previously [4]. First, in a large range of fillings (up to $n^S \approx 8$ molecules per 1/8 unit cell) \bar{q} changes little with the increasing n^S , then \bar{q} abruptly drops but resumes its growth, passes through a maximum, drops again and then passes through a second maximum close to the completion of zeolite cavity filling. This type of dependence of \bar{q} on n^S was compared to variations in the average molar heat capacity of adsorbed water c_m (Fig. 4) [10] and its infrared spectrum [22]. Analysis shows that, first, the oxygen of the water molecule gets fixed to a cation and the oxygen ions of the framework interact with a hydrogen atom of this molecule (high \bar{q} , low c_m and "free" valence vibrations of the other OH group of the adsorbed water molecule). This is followed by occupation of K^+ cations by water molecules which is caused by the location, concentration and "hydrophobic" nature of the cations; when these possibilities are exhausted, \bar{q} drops whereas c_m grows due to dissociation of some associates on heating. A further growth of \bar{q} and drop of c_m are caused mainly by the formation of hydrogen-bonded array of associates on the ribs of the zeolite framework. As soon as these associates are formed, \bar{q} drops again, whereas c_m grows. Finally, restructuring of the array when the central parts of zeolite cavities begin to fill again causes growth of \bar{q} and drop of c_m down to a value rather close to that of the heat capacity of liquid water. Variations in the infrared spectrum, contrary to that found in zeolite NaX, show that the growth of n^S does bring about alternate

strengthening and weakening of the hydrogen bonds. For a more accurate interpretation K^+ cations locations increase as n^S must be observed by independent methods. For Li^+ such observations have been started using NMR [1,2,8,9,23]. Important data can be also be obtained using a high resolution infrared Fourier spectrometer (see ref. [2]).

It was shown earlier [4] that the analogous smooth curve of \bar{q} against n^S occurs when the temperature of calorimetric measurements is raised. Here temperature rise acts similar to decationization. A common reason for this is an impossibility to establish in both cases (on zeolite KNaX at 100°C and on zeolite KNaY at 23°C) a well structured array of adsorbed water molecules. In the case of silicalite with no cations [24] water adsorption is much less than found with organic molecules.

From Table 1 and Fig. 1 one can see that in the case of adsorption of n-alkanes onto zeolites extrapolation of the isotherm slope to $n^S = 0$ to obtain $K_{ns,c,1}$ and extrapolation of the dependence of \bar{q} on n^S to obtain \bar{q}_1 does not introduce a significant error, although the adsorption below $n^S < 0.1$ was not measured. In the case of specific adsorption of such strongly polar molecules as water extrapolation to $n^S = 0$ is more difficult.

Determination of TCA by gas chromatography. Many papers present \bar{q} values obtained from retention data but few give retention volumes $V_{m,1}$ (per gram of zeolite for zero sample size). $V_{m,1}$ in the case of equilibrium chromatography and a weakly adsorbing carrier gas is close to $K_{ns,c,1}$. Sufficiently accurate gas-chromatographic measurements of $V_{m,1}$ require an equilibrium over all the adsorbent particles, i.e. over all zeolite crystals. Usually particles are obtained by pressing. Hence, while the chromatographic zone moves along the column the establishment of equilibrium is hindered by both intra- and inter-crystalline diffusion.

Decrease in diffusion coefficients down to values considerably less than coefficients of self-diffusion obtained by the NMR method and the effect of crystal size are discussed in [2,25]. Our chromatographic studies revealed that $V_{m,1}$ increases somewhat with a decrease in the size of the pressed particles. Values of $V_{m,1}$ close to those of $K_{ns,c,1}$ obtained by static measurements were found only in experiments with separate crystals.

MOLECULAR STATISTICAL CALCULATIONS OF TCA

The semi-empirical atom-atom potentials and the calculations of Henry's constants for molecules of known structure. The achievements in the molecular statistical theory of adsorption on a homogeneous flat surface of the non-specific adsorbent - graphitized thermal carbon black (GTCB) together with the atom-atom approximation for the intermolecular adsorbate-adsorbent interaction potential enabled us to calculate TCA at zero surface coverage for complex hydrocarbon molecules of known structure (see references in papers [26,27]). For molecules of unknown or uncertain structure it became possible to solve the inverse problem, i.e. on the basis of chromatographic and other adsorption measurements for zero sample size to determine some structural parameters of molecules [26,27]. This method has been termed chromatocopy [28]. Both these possibilities are represented in the scheme below. The aim of moving from right to left is to improve and to check with the aid of

the molecules and of the adsorbent of known structure the working instrument of chromatography, based on the semi-empirical theory of intermolecular interaction, and to update the parameters of the atom-atom potentials.

Structure of molecules, structure of adsorbent	Molecular-statistical theory of adsorption and theory of intermolecular interactions in an atom-atom approximation	Henry's constant (retention volume for zero coverage)
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The molecular statistical calculation of Henry's constant $K_{\Gamma,c,1}$ (Γ is the Gibbs adsorption value per unit surface area) for adsorption on GTCB of non-strained molecules of saturated hydrocarbons needs only two atom-atom potentials: $\varphi_{C(sp^3)} \dots C(GTCB)$ and $\varphi_{H} \dots C(GTCB)$ in the form (6,8,exp). First the theoretical values of φ^* are determined for a reference molecule of known structure (e.g. ethane) and graphite, taken separately. Calculated on the basis of the potential energy of adsorption of the whole molecule $\Phi^* = \sum_{A=C,H} \varphi^*_{A(M)} \dots C(\text{graphite})$ the theoretical $K^*_{\Gamma,c,1}$ were compared with the measured $K_{\Gamma,c,1}$ for the adsorption of these reference molecules on GTCB. From this comparison the correction factor β was found which is to be introduced into the parameters of φ^* so that the molecular statistical calculation may give values coinciding with the measured values of $K_{\Gamma,c,1}$. Thus, $\varphi = \beta\varphi^*$.

The example of solving the inverse problem (from right to left on the scheme) is the chromatographic study of the molecular structure of hexamethylbenzene [26] with the aid of three atom-atom potentials $\varphi_{C(sp^3)} \dots C(GTCB)$, $\varphi_{C(sp^2)} \dots C(GTCB)$, $\varphi_{H} \dots C(GTCB)$. The potential $\varphi_{C(sp^2)} \dots C(GTCB)$ was determined through the adsorption of ethylene and benzene (its parameters are only by 7% higher than those of the $\varphi_{C(sp^3)} \dots C(GTCB)$). The angle of alternate deviation of groups CH_3 in different directions from benzene ring (10°) was determined by chromatography in accordance with electronographic measurements. Furthermore, the barriers of the internal rotation in diphenyl [26], the structure of tetraline [27] and of a number of other hydrocarbons were also determined by chromatography.

The $K_{\Gamma,c,1}$ on GTCB, measured at different temperatures, are especially convenient to be used for chromatographic determination of geometric parameters of molecules. But they are not sensitive to such features of molecules as multipole moments. High sensitivity, however, is found in adsorption in zeolites. Using zeolites we can study both the nonspecific intermolecular interaction of adsorbed molecules with the adsorbent ions and their specific interaction with the electrostatic field generated by the ions (from left to right on the scheme). Besides we can make chromatographic determination of rigid multimoments of adsorbed molecules (from right to left).

Selection of zeolite model. The theoretical studies of adsorption in zeolites have been conducted according to [29]. Models for zeolites A, X and Y have been developed (see literature in references [13,14]). Most convenient for such studies, for chromatography in particular, are zeolite types with large cavity windows, which allow a study of a variety of molecules, e.g. zeolites X and Y. The assumption about the

uniform distribution of negative charge on the oxygen ions of the aluminium- and silicon-oxygen tetrahedra, is reasonable for zeolite A, but is less valid for zeolites X and especially Y. The absence of data on the distribution of aluminum- and silicon-oxygen tetrahedra force us to assume a uniform distribution for zeolite X and also for zeolite Y [14]. Another flaw of the chosen model may also be connected with the fact, that the proximity of a cation to adjacent O^- ions probably increases their negative charge, while oxygens located further from the cations probably have reduced charge. Cation distribution in a zeolite and the influence of the adsorbed molecules on this distribution introduces a molecular-statistical problem [14], which cannot be solved due to the nonavailability of detailed data on charge distribution in the zeolite skeleton. Therefore it was assumed that singly-charged "non-localized" cations were distributed in sites S_{III} of faujazite equally. Unlike the oxygen ions and cations, aluminium and silicon ions, located within tetrahedrons, possess much lower polarisability. Therefore their influence on the intermolecular interaction potential of adsorption was taken into account only indirectly in the effective charge and polarisability of the oxygen ions, which depend on the Si/Al ratio in the experimentally studied zeolites. Further details of the chosen model of zeolites and of the literature are given in [13,14].

Calculations of Henry's constants for zeolites. The expression for Henry's constant is [13,14]:

$$K_{nS,c,l} = D (e^{-\Phi/RT} - 1) dqd\omega \approx D \int e^{-\Phi/RT} dqd\omega \quad (1)$$

where Φ is the intermolecular interaction potential of the molecule with the entire zeolite, q and ω express correspondingly the sets of coordinates of molecule mass centre and the angles determining its orientation. Coefficient D depends on the symmetry of the molecule and the crystal. The recurrent portion of the zeolite large cavity volume, in which integration is performed, equals $1/24$ of its volume. If B is the number of large cavities in 1 g of zeolite, then D is equal to $24B$, $24B/4\pi$ and $24B/8\pi$ for single-atom, linear and non-linear molecules. Instead of integration, summation was used for a great number of elementary volumes, into which this $1/24$ part of the cavity was divided. It was shown that this approximation does not lead to significant errors [13].

Potential energy of nonpolar molecule. The form of φ has little effect on the results of calculations of the TCA [30]. Therefore, in such a complex case as a zeolite a simple form for φ was chosen (6.12). The calculation for all molecules was carried out in an atom-ion approximation, the contribution of induction interaction between an atom A of the molecule and an ion of type I of zeolite [13] being also taken into account:

$$\varphi_{A,I}^* = -C_{A,I}^* r^{-6} + B_{A,I}^* r^{-12} - (a_A^*/2) \cdot (\rho_I^2 \cdot r^{-4}) \quad (2)$$

where r is the distance between the centres of the atom A and the ion I ; $C_{A,I}^*$ and $B_{A,I}^*$ are the constants of dispersion attraction, and correspondingly, those of repulsion; a_A^* is the molecule polarisability and ρ_I is the charge of the ion I (asterisks are used to indicate that the relevant values are derived from the properties of the adsorbate

and adsorbent taken separately). This equation allows the evaluation of $B_{A,I}^*$ through $C_{A,I}^*$, a_A^* and ρ_I at the minimum of the potential curve using the equilibrium distance r_0 equal to the sum of van der Waals radius of the atom A of the molecule and the radius of the corresponding ion I.

Potential energy of the intermolecular interaction of atom A and the whole of zeolite is:

$$\Phi_{A...Z}^* = - \sum_I C_{A,I}^* \sum_j r_{jI}^{-6} + \sum_I B_{A,I}^* \sum_j r_{jI}^{-12} - (a_A^*/2) [\vec{E}(\vec{r})]^2 \quad (3)$$

where r_j is the distance from the centre of atom A to the centre of j-th ion I, and \vec{E} is the electrostatic field strength near the centre of the atom A which is at a distance r from the centre of the zeolite large cavity. In the case of the adsorption of multiatom molecules, to calculate Φ^* in the atom-ion approximation, the value of $\Phi_{A...Z}^*$ was summed for all atoms of the molecule.

The theoretical value of constants $C_{A,I}^*$ can be calculated through the convenient approximate quantum-mechanical Kirkwood-Müller formula. This formula yields usually too high values of C^* . This and the inaccuracy of the chosen zeolite models and of the molecules result in the fact, that when calculated on the basis of the properties of the molecule and of the adsorbent taken separately the $K_{ns,c,1}^*$ diverge somewhat from the experimental $K_{ns,c,1}$. As in the case of adsorption on GTCB considered above, this difficulty was overcome by introducing the empirical correction β into the theoretically calculated φ^* ; hence, $\varphi = \beta\varphi^*$, where φ is the atom-atom potential, meeting the experimental values $K_{ns,c,1}$ [after the summation over the molecule atoms and calculations using equation (1)]. It is essential that β should remain constant for atoms of similar electronic configuration in the molecules, i.e. for noble gases and for the sp^3 configuration of C atoms in alkanes and in non- or weakly strained cyclanes (an important property of the transference of atom-atom or atom-ion potential within the given class of molecules on the given adsorbent). β was determined by the same method as in adsorption on GTCB. The complication which arises with zeolites when the induction interaction is taken into account seems to have little effect on the application of the formulae $\varphi = \beta\varphi^*$ and $\Phi = \beta\Phi^*$ [14]. Therefore, we can consider that $\beta = C_{A,I}/C_{A,I}^* = B_{A,I}/B_{A,I}^*$.

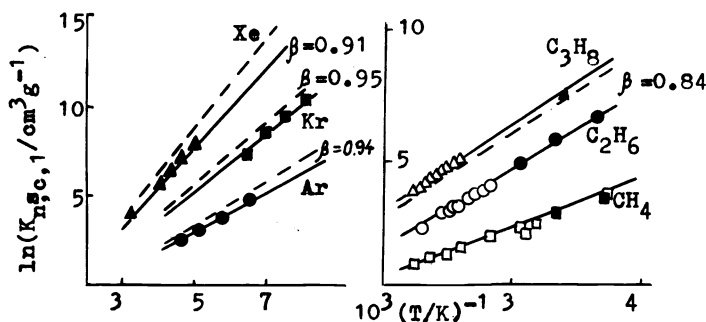


Fig. 5 $K_{ns,c,1}$ vs $1/T$ for adsorption in NaX zeolite: dashed curves are calculated theoretically, solid curves with correction factors β . Open dots are chromatographic, filled dots are extrapolated static data.

Noble gases in zeolites X and Y. For this case eq. (3) expresses the whole potential energy of adsorption at zero filling, and eq. (1) with $D = 24B$ gives $K_{ns,c,1}$. It is shown in Fig. 5a that within the accuracy limits of the experiment and the calculations for Ar, Kr and Xe on the NaX zeolite the β are close to each other and average 0.93. Choosing the system Ar-NaX as the reference system, it is possible to calculate the adsorption of Kr and Xe on NaX, and also Ar, Kr and Xe on KX. In the latter case the correction factor remained the same, $\beta = 0.93$, but a_I^* and other physical properties for the K^+ were introduced into the calculations. Transition to zeolite NaY, as it has been mentioned above, requires finding a new value of β from the comparison of the calculated and measured values of $K_{ns,c,1}$. Because of lack of any reliable experimental data only a rough estimate is obtained for zeolite NaY of $\beta \approx 0.7$ (instead of $\beta = 0.93$ for NaX). Thus, the semi-empirical calculation is sensitive not only to a change in the nature of the cation, but also to the change in their concentration in the zeolite and to changes in the magnitude and distribution of the charge of the oxygen ions in the zeolite lattice.

Alkanes and cyclanes in zeolite NaX. The calculations were performed in an atom-ion approximation. The values of β were determined as for noble gases, that is by comparing theoretically calculated and measured values of Henry's constant for ethane-NaX reference system (Fig. 5b). $\beta = 0.84$ was obtained this way [14]. It was used then in the calculations of $K_{ns,c,1}$ for other alkanes and cyclanes on the same zeolite NaX. Figs. 6 and 7 show that for n-butane, n-pentane, cyclo-

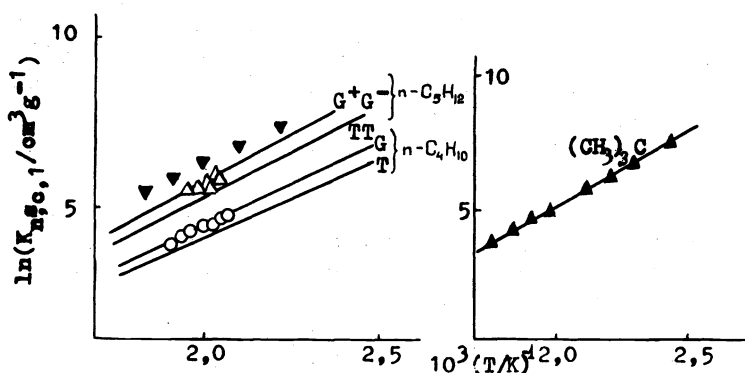


Fig. 6 $K_{ns,c,1}$ vs $1/T$ for $n-C_4H_{10}$, $n-C_5H_{12}$ and $(CH_3)_4C$ in NaX zeolite. Curves are calculated using $\beta = 0.84$. Dots are experimental data.

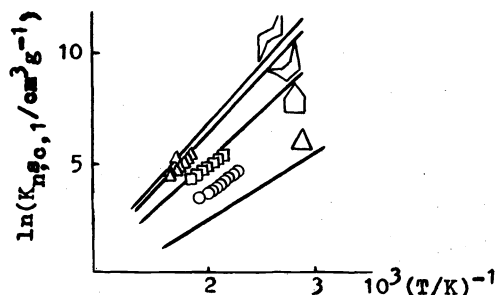


Fig. 7 $K_{ns,c,1}$ vs $1/T$ for cyclohexane, cyclopentane and cyclopropane in NaX zeolite. Curves are calculated using $\beta = 0.84$; dots are experimental data.

pentane and cyclohexane the discrepancy between calculation (lines) and experiment (dots) does not exceed the errors of the measured values of $K_{ns,c,1}$ (more accurate experimental data are needed). Unlike GTCB whose flat surface selects preferentially trans-isomers of n-alkanes the curved surface of zeolite seems to adsorb mainly the gauche-isomers.

A sharp increase in the experimental values of $K_{ns,c,1}$ as compared with those calculated with the help of atom-ion potentials $\Phi_C(sp^3)...Z$ is obtained for the strongly strained molecule of cyclopropane. This question will be considered after the adsorption of polar molecules has been studied.

Polar molecules in zeolite NaX. The consistent application of atom-ion approximation in this case would require a knowledge of the charge distribution in the molecule. Since there are no reliable data of these charge distributions, the contributions of the orientation electrostatic dipole-ion and quadrupole-ion intermolecular interactions were taken into account only in the approximations of the point dipole or the quadrupole Q [17] of the molecule according to the equations

$$\Phi_{\mu} = - \sum_I \rho_I \mu \cos \theta / r^2 \quad (4)$$

$$\Phi_Q = - \frac{1}{4} \sum_I \rho_I Q (3 \cos^2 \theta - 1) / r^3 \quad (5)$$

where θ is the angle between the radius-vector, connecting the molecule mass centre with the ions I of zeolite and the vector defining the molecule orientation in the large cavity of zeolite. The point moments were placed at the molecule mass centre.

Attraction to cations prevails over repulsion from oxygen ions $O^{\delta-}$. The total potential energy of the intermolecular interaction between the polar molecule and zeolite is

$$\Phi = \sum_A \Phi_{A...Z}^* + \Phi_{\mu} + \Phi_Q \quad (6)$$

Let us assume that the somewhat heightened value of $\Phi_{A...Z}^*$ obtained by equation (3) is compensated by the contributions of the orientation interactions into the total energy of repulsion, which were not taken into account. Hence, the correction β was not introduced here.

O_2 , N_2 , CO , CO_2 and NH_3 in zeolite NaX. To the first four of these molecules the corresponding point quadrupole moments were ascribed and to NH_3 both quadrupole and dipole moments [14,31]. The share of Φ_Q in the total Φ_{min} for the adsorption in zeolite NaX of polar molecules O_2 , CO and N_2 is not great (from 8 to ~23 per cent). It is rather considerable for CO_2 (50%), and for NH_3 the sum $\Phi_{\mu} + \Phi_Q$ prevails (~60%). But even the intermolecular interaction of NH_3 molecules with zeolite NaX can be described with the aid of the above-mentioned assumptions concerning Φ^* , Φ_Q and Φ_{μ} . The NMR studies indicate the proximity of the spectra of ammonia adsorbed on zeolite to that of gaseous ammonia [2]. This testifies to the absence of essential changes in the distribution of the electron density in the NH_3 molecule in its intermolecular interaction with zeolite. Thus this interaction can be described in the approximations of equation (6). Fig. 8a shows the results of the calculations of $K_{ns,c,1}$ for these molecules. The calculation gives a

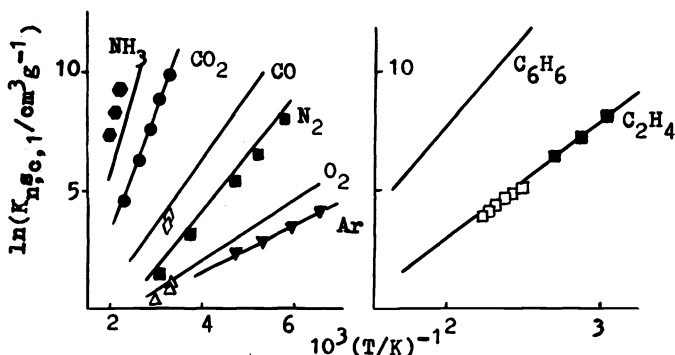


Fig. 8 $K_{ns,c,1}$ vs $1/T$ for polar substances in NaX zeolite. Curves are calculated. Dots are experimental data.

satisfactory estimate and the correct sequence of these values, particularly $Ar < O_2 < N_2$, corresponding to gas chromatographic separation.

Ethylene and benzene in zeolite NaX. In the calculation of Φ^* the properties of the carbon atoms in these particular molecules were taken into account. The quadrupole moments Q were located in the centre of the ethylene double bond and in the centre of the benzene ring. The values of Φ were derived from equation (6) at $\Phi_\mu = 0$. The calculated $K_{ns,c,1}$ [14] are given in Fig. 8b. For ethylene they agree with the measured ones (dots). For benzene it was possible to find by experiment only $\bar{q}_1 = 70$ kJ/mol. The calculation gives 67 kJ/mol. Thus, the chosen approximation of point quadrupole moments for these molecules is satisfactory.

Chromatoscopic determination of the effective quadrupole moment of cyclopropane. The results obtained for ethylene and benzene enable us to explain the increase (Fig. 7) of the measured $K_{ns,c,1}$ (determined by gas chromatography) over those calculated assuming that the carbon atoms in cyclopropane have the configuration sp^3 . This increase shows that in the strongly strained molecule of cyclopropane the electron configuration of the carbon atoms is close to sp^2 , hence, the cyclopropane molecule must have a quadrupole moment. As a matter of fact, even with GTCB the calculation of $K_{\Gamma,c,1}$ using $\varphi_{C(sp^3)} \dots C(GTCB)$ has given somewhat low results, whereas the calculation with the aid of the potential $\varphi_{C(sp^2)} \dots C(GTCB)$ has given $K_{\Gamma,c,1}$ coinciding with the gas-chromatographic measurements. Reference [14] makes use of the above and determines the point quadrupole moment of the cyclopropane molecule by the chromatoscopic method. The $K_{ns,c,1}$ calculated by the molecular statistical method on the basis of equation (6) for the total potential energy of intermolecular interaction of cyclopropane-zeolite is close to the measured one when $Q \approx 4.10^{-26}$ esu.

CONCLUSIONS

In spite of the flaws present in the experimental determinations and the rather crude assumptions made in developing the models for zeolites and molecules and also in the calculations, the chosen molecular

statistical method in the atom-ion approximation and in the approximation of point multipole moments for the potential function of molecule-zeolite intermolecular interaction enables us both to describe the thermodynamic characteristics of adsorption (TCA) at zero filling and, in favorable cases, to determine the multipole moments of molecules by the chromatographic method. The chromatography of molecules with several multipole moments, e.g. of indene molecules is of special interest. The semi-empirical calculations of TCA in zeolites at zero filling and the plotting of the corresponding potential curves and potential charts for more and more complex molecules, and also the obtaining of the atom-atom potentials, necessary for taking into account the intermolecular adsorbate-adsorbate interaction (and first of all of the potentials $\varphi_{H...H}$ for various electronic configurations of atoms H) enable us to calculate both TCA on zeolites at higher filling and to solve the problems of the kinetics of adsorption and diffusion in zeolites on molecular level. For further advance in all these directions it is necessary first of all to increase significantly the accuracy of the experimental determinations of Henry's constant and other TCA as well as to use a variety of physical methods for detailed investigation into the state of adsorbate-zeolite systems.

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