Diffusion coefficients of n-heptane in a particle of molecular sieve NaY

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The results of chromatographic measurements of n-heptane diffusion in particles of molecular sieve NaY obtained by the use of nitrogen as carrier gas have been matched by means of two models. The values of effective diffusion coefficients determined at 200—270 °C by means of the model with quasi-homogeneous structure of particles of molecular sieve NaY are 9.83×10^{-10}—$2.12 \times 10^{-9} \, \mathrm{m^2 \, s^{-1}}$ The activation energy of diffusion is $23.6 \, \mathrm{kJ \, mol^{-1}}$. On the other hand, it has been found by using the model with biporous structure of adsorbent particles that the values of D_a/r_0^2 for the diffusion in crystals of molecular sieve are 37.03—$53.58 \, \mathrm{s^{-1}}$.

С использованием двух различных моделей проведена обработка результатов хроматографического измерения диффузии н-гептана в частицах молекулярного сита NaY, используя азот в качестве газа--носителя. С помощью модели, предполагающей квазигомогенную структуру частиц молекулярного сита, были определены значения эффективных коэффициентов диффузии при температурах от 200 до 270 °C: $9,83 \cdot 10^{-10}$—$2,12 \cdot 10^{-9} \, \mathrm{м^2 \, с^{-1}}$. Активационная энергия диффузии равна 23,6 кДж моль$^{-1}$. С помощью модели, в которой предполагается двухпористая структура частиц адсорбента, для диффузии в кристаллах молекулярного сита было найдено, что D_a/r_0^2 равняется $37,03$—$53,58 \, \mathrm{с^{-1}}$

The mass transfer in a particle of molecular sieve due to concentration gradient under isothermal conditions and in the absence of effects of external forces is controlled by diffusion [1]. The complicated porous structure of a particle of molecular sieve consisting of micropores in crystals of zeolites (diameter 0.4—2.2 nm) and pores among crystals of zeolites which are by decimal order larger results in an intricate mechanism of the transport of adsorptive in a particle of adsorbent. In pores the diameter of which is much larger than the mean free path of molecules prevails the transport by molecular diffusion while it is controlled by Knudsen diffusion in pores the diameter of which is much smaller than the mean free path of molecules [2]. The transport of adsorbate in the adsorbed phase is caused by surface diffusion. These mecha-

nisms of transport of adsorptive in a particle of adsorbent simultaneously work in the course of adsorption. In the simplest model, a particle of adsorbent is regarded as a quasi-homogeneous isotropic medium attracting the adsorptive and the transport of adsorptive in pores of the solid phase is governed by diffusion the rate of which is to be characterized by the effective diffusion coefficient [2, 3].

The values of the effective diffusion coefficients can be determined from kinetic curves [2, 4, 5], chromatographic elution curves [6, 7] or by the methods based on NMR [8]. Because of great differences between the values of diffusion coefficient obtained from kinetic or chromatographic measurements and the values of diffusion coefficient determined from NMR measurements, some authors [9, 10] have attempted to present a more adequate description of the structure of adsorbent. The diffusion of substance in a particle of molecular sieve is described as diffusion in biporous structure and its rate is characterized by the diffusion coefficient related to primary pores and the diffusion coefficient related to secondary pores.

The determination of diffusion coefficient of the adsorbed substance in particles of molecular sieve from chromatographic elution curves is based on the theory of gas—solid chromatography developed by *Kučera* [11] and *Kubín* [12]. In this respect, some authors [6, 7] consider the model of simple porous structure of a particle of molecular sieve while other authors [10, 13] adhere to the model of biporous structure put forward by *Ruckenstein* [14] for ion exchangers.

Theoretical

The used relationships and method of calculation of diffusion coefficients

The system of equations characterizing the processes taking place in an adsorption column comprises [15]:

Material balance of adsorptive in column

$$\varepsilon v \frac{\partial C}{\partial Z} + \varepsilon \frac{\partial C}{\partial \tau} + \frac{3(1 - \varepsilon)}{R_0} D' \left(\frac{\partial c}{\partial R}\right)_{R = R_0} = D_L \frac{\partial^2 C}{\partial Z^2} \tag{1}$$

Transport of adsorptive in a spherical particle of adsorbent

$$\beta \frac{\partial c}{\partial \tau} + \varrho_p \frac{\partial a}{\partial \tau} = D' \left(\frac{\partial^2 c}{\partial R^2} + \frac{2}{R} \frac{\partial c}{\partial R}\right) \tag{2}$$

Equilibrium relation

$$a = KC \tag{3}$$

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Boundary conditions

$$D'\left(\frac{\partial c}{\partial R}\right)_{R = R_0} = k_{gc}(C - C_i)$$

$$\frac{\partial c}{\partial R} = 0; \quad R = 0; \quad \tau > 0 \tag{4}$$

Initial conditions

$$C(Z, 0) = 0$$
$$c(R \geq 0, 0) = 0 \tag{5}$$
$$a(R, Z, 0) = 0$$

Injection of adsorptive of concentration C_0 into the column in the time τ_0 is interpreted by

$$C(0, 0 \leq \tau \leq \tau_0) = C_0$$
$$C(0, \tau > \tau_0) = 0 \tag{6}$$

As for eqn (2), it is assumed that the transport of adsorptive in a particle of adsorbent is governed by diffusion in the gaseous phase and the adsorbent represents a quasi-homogeneous isotropic medium.

The system of equations characterizing the processes taking place in a column packed with an adsorbent with biporous structure may be written [16]

Material balance of adsorptive in column

$$w\left(\frac{\partial C}{\partial Z}\right) + \varepsilon\frac{\partial C}{\partial \tau} + \frac{3(1 - \varepsilon)}{R_0} D_i\left(\frac{\partial c}{\partial R}\right)_{R = R_0} = D_L\frac{\partial^2 C}{\partial Z^2} \tag{7}$$

Transport of adsorptive in a particle of adsorbent

$$\varepsilon_i\frac{\partial c}{\partial \tau} + \frac{3(1 - \varepsilon_i)}{r_0} D_a\left(\frac{\partial c_a}{\partial r}\right)_{r = r_0} = D_i\left(\frac{\partial^2 c}{\partial R^2} + \frac{2}{R}\frac{\partial c}{\partial R}\right) \tag{8}$$

Transport of adsorptive in microporous zones of a particle of adsorbent

$$\varepsilon_a\left(1 + \frac{\varrho_p K}{\varepsilon_a(1 - \varepsilon_i)}\right)\frac{\partial c_a}{\partial \tau} = D_a\left(\frac{\partial^2 c_a}{\partial r^2} + \frac{2}{r}\frac{\partial c_a}{\partial r}\right) \tag{9}$$

Equilibrium relation is expressed by eqn (3).
Boundary conditions

$$D_i\left(\frac{\partial c}{\partial R}\right)_{R = R_0} = k_{gc}(C - C_i)$$

$$\frac{\partial c}{\partial R} = 0; \quad R = 0; \quad \tau > 0 \tag{10}$$

$$\frac{\partial c_a}{\partial r} = 0; \quad r = 0; \quad \tau > 0$$

$$c_a(r_0, \tau) = c(R, \tau)$$

Initial conditions

$$\begin{array}{l} C(Z, 0) = 0 \\ c(R, Z, 0) = 0 \\ c_a(r, Z, 0) = 0 \\ a(r, Z, 0) = 0 \end{array} \tag{11}$$

Injection of the sample into the column is expressed by eqn (6).

The moment analysis of the above systems of equations gives the relationships expressing the first simple and the second central statistical moment of elution curve from which the equilibrium adsorption constants and diffusion coefficients are to be determined. According to [15], the following expression may be obtained for the first simple statistical moment

$$\mu_1' = \left[1 + \frac{1 - \varepsilon}{\varepsilon} \beta \left(1 + \frac{\varrho_p}{\beta} K \right) \right] \frac{L}{v} + \frac{\tau_0}{2} \tag{12}$$

The second central statistical moment for the quasi-homogeneous isotropic model of a particle of adsorbent may be written as follows [15]

$$\frac{\mu_2 - \tau_0^2/12}{2\frac{L}{v}} = \delta_i + \delta_e + \frac{D_L}{\varepsilon} \left[1 + \frac{1 - \varepsilon}{\varepsilon} \beta \left(1 + \frac{\varrho_p K}{\beta} \right) \right]^2 \frac{1}{v^2} \tag{13}$$

where

$$\delta_i + \delta_e = \frac{1 - \varepsilon}{\varepsilon} \frac{\beta^2}{15} \left(1 + \frac{\varrho_p K}{\beta} \right)^2 \left(\frac{1}{D'} + \frac{5}{k_{gc} R_0} \right) R_0^2 \tag{14}$$

For the model of a particle of adsorbent with biporous structure we obtain [16]

$$\frac{\mu_2 - \tau_0^2/12}{2\frac{L}{w}} = \delta_i^B + \delta_a + D_L \varepsilon^2 (1 + \delta_0)^2 \frac{1}{w^2} \tag{15}$$

where

$$\delta_0 = \frac{1 - \varepsilon}{\varepsilon} \left[\varepsilon_i + (1 - \varepsilon_i) \varepsilon_a \left(1 + \frac{\varrho_p K}{\varepsilon_a (1 - \varepsilon_i)} \right) \right] \tag{16}$$

$$\delta_i^B = \frac{(1-\varepsilon)\left[\varepsilon_i + (1-\varepsilon_i)\varepsilon_a\left(1 + \frac{\varrho_p K}{\varepsilon_a(1-\varepsilon_i)}\right)\right]^2}{15}\left(\frac{5}{k_{gc}R_0} + \frac{1}{D_i}\right)R_0^2 \qquad (17)$$

$$\delta_a = \frac{(1-\varepsilon)(1-\varepsilon_i)\varepsilon_a^2\left[\left(1 + \frac{\varrho_p K}{\varepsilon_a(1-\varepsilon_i)}\right)\right]^2}{15}\frac{r_0^2}{D_a} \qquad (18)$$

The first simple and the second central statistical moment may be determined from the experimental response curve $C(L, \tau)$ by means of the following expressions

$$\mu_1' = \frac{\int_0^\infty \tau C(L, \tau)\,d\tau}{\int_0^\infty C(L, \tau)\,d\tau} \qquad (19)$$

$$\mu_2 = \frac{\int_0^\infty (\tau - \mu_1')^2 C(L, \tau)\,d\tau}{\int_0^\infty C(L, \tau)\,d\tau} \qquad (20)$$

The values of equilibrium adsorption constants may be determined from the relationships $\mu_1' = f(1/v)$ in accordance with eqn (12). In respect of eqns (13) and (15), the relationships $\mu_2 v/2L = f(1/v^2)$ and $\mu_2 w/2L = f(1/w^2)$ enable us to obtain the values of $(\delta_i + \delta_e)$ and $(\delta_i^B + \delta_a)$ for equivalent radii of the used particles. The value of $\tau_0^2/12$ may be neglected with respect to μ_2. The diffusion coefficients are to be determined from the relationships $(\delta_i + \delta_e) = f(R^2)$ and $(\delta_i^B + \delta_a) = f(R^2)$ in consistence with eqns (14), (17), and (18).

Experimental

Materials

Nitrogen of electric bulb industry deprived of oxygen rests by adsorption on a copper catalyst and of humidity on a molecular sieve Nalsit 4 was used.

n-Heptane pure (Jenapharm, Apolda) of the following composition (x/mole %): n-heptane 94.67, n-pentane 0.02, 2-methylpentane 0.02, n-hexane 0.51, 2-methylhexane 1.71, 3-methylhexane 2.32, methylcyclohexane 0.21, n-octane 0.12, higher hydrocarbons 0.42.

Molecular sieve NaY (Research Institute for Oil and Hydrocarbon Gases, Bratislava)

passivated with a 10 % solution of NaOH for 2 h. The properties of particles of the molecular sieve are given in Table 1. The distribution of pores obtained by means of a mercury porosimeter is represented in Fig. 1.

Table 1

Properties of molecular sieve NaY

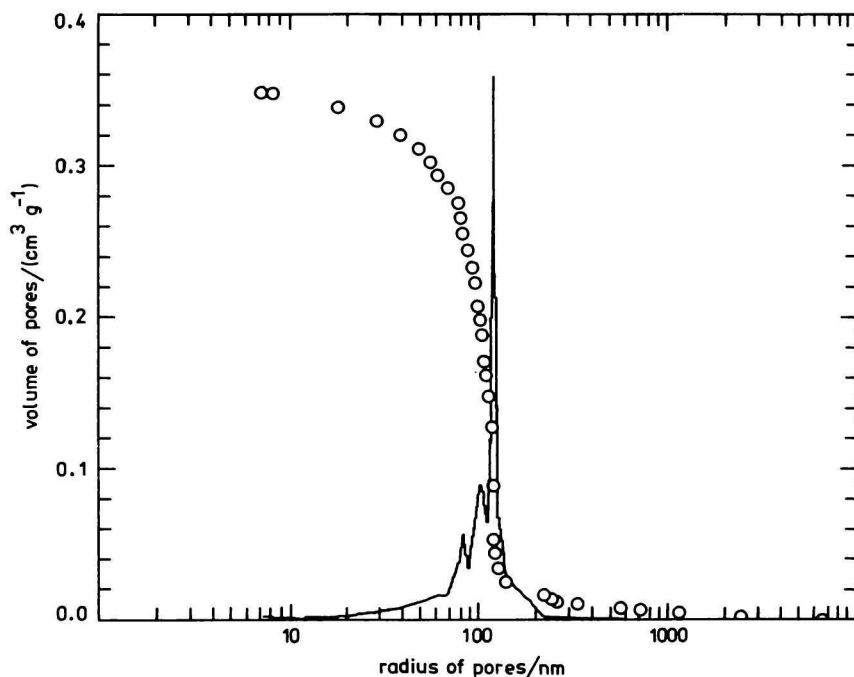|	
Particle density	$1200 \, \text{kg m}^{-3}$
Specific volume of macropores determined by mercury porosimetry	$0.349 \, \text{cm}^3 \, \text{g}^{-1}$
Specific volume of micropores	$0.236 \, \text{cm}^3 \, \text{g}^{-1}$
Specific volume of pores	$0.585 \, \text{cm}^3 \, \text{g}^{-1}$
Specific surface determined from BET isotherm	$485 \, \text{m}^2 \, \text{g}^{-1}$
Primary porosity	$0.2832 \, \text{m}^3 \, \text{m}^{-3}$
Secondary porosity	$0.4188 \, \text{m}^3 \, \text{m}^{-3}$
Particle porosity	$0.7020 \, \text{m}^3 \, \text{m}^{-3}$

Fig. 1. Distribution of pores determined by mercury porosimetry.

Apparatus and measurements

The measurements were carried out on a chromatograph CHROM 41 in which the columns with a bed of molecular sieve NaY particles were used instead of chromatographic column. The characteristics of the bed in individual columns and the working conditions are given in Table 2. In order to eliminate parasite signals, a reference column packed with molecular sieve NaY was used parallel to the measuring column. The flow of the carrier gas was measured with capillary flow meters. Heptane was dosed with a microliter syringe. The apparatus enabled us to dose the vapour of heptane into the column from the stream of gas by means of six-way cock, as evident in Fig. 2.

Table 2

Characteristics of column and working conditions

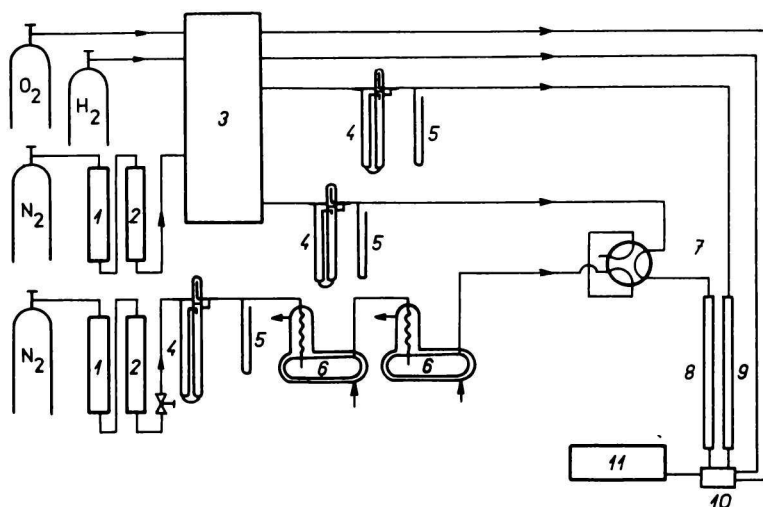| Quantities	Column		
	U_{29}	U_{27}	U_{31}
Length of bed/cm	3.65	3.70	3.90
Inside diameter of column/mm	8.3	8.3	8.3
Fraction of particles/mm	0.40—0.63	0.63—0.71	0.80—1.00
Equivalent radius of particles/mm	0.251	0.334	0.447
Bulk density/(kg m^{-3})	706	636	562
Porosity of bed/(m^3 m^{-3})	0.411	0.470	0.531
Flow of carrier gas (25 °C, 101.3 kPa)/(cm^3 min^{-1})	62—247	70—265	55—243

Fig. 2. Diagram of the used apparatus.

1. Adsorber with Ronge copper; *2.* adsorber with molecular sieve Nalsit 4; *3.* distribution frame of gases with flow control; *4.* flow meter; *5.* manometer; *6.* saturator; *7.* six-way valve; *8.* adsorption column; *9.* reference column; *10.* flame ionization detector; *11.* recorder.

Before measurement, the molecular sieve in columns was activated for 6 h at 380 °C in a stream of dry nitrogen.

Results and discussion

The values of μ_1' found for individual screened fractions of particles of molecular sieve NaY and certain temperatures are plotted as a function of L/v in Fig. 3. In this figure the 95 % and 99 % confidence intervals of the slopes of the investigated relationship are also marked. The confidence intervals of the slope of the straight line $k' - \varkappa_k < k < k' + \varkappa_k$ were calculated according to [17]

$$\varkappa_k = s_k t_a \tag{21}$$

where

$$s_k = \sqrt{\frac{n\left[\sum_{i=1}^{n} y_i^2 - k' \sum_{i=1}^{n} x_i y_i\right]}{(n-1)\left[n \sum_{i=1}^{n} x_i^2 - \left(\sum_{i=1}^{n} x_i\right)^2\right]}} \tag{22}$$
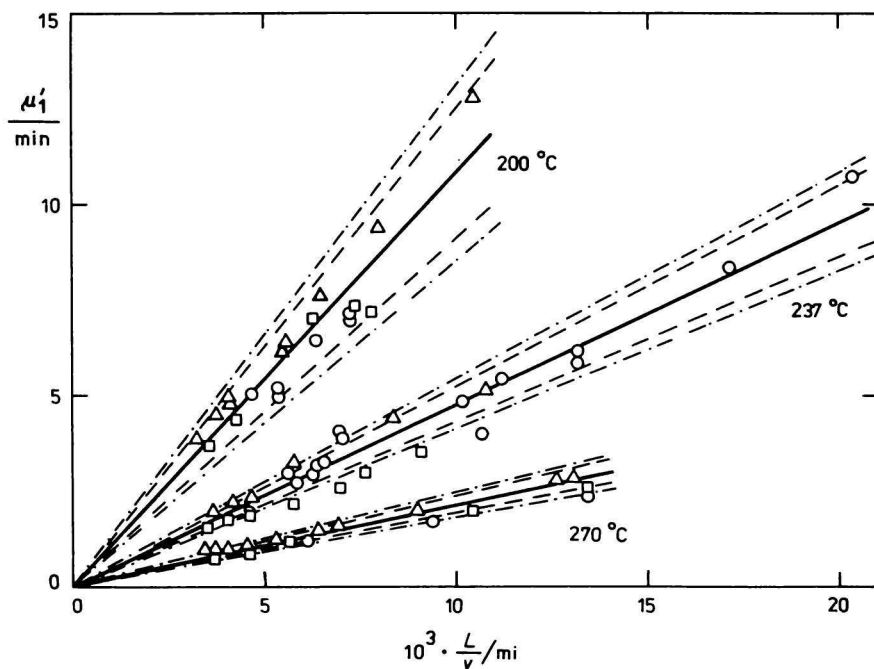

Fig. 3. Relationship $\mu_1' = f(L/v)$.
Particles of molecular sieve with diameter of 0.4—0.63 mm ($\triangle$), 0.63—0.71 mm ($\square$), 0.80—1.00 mm ($\bigcirc$); ——— 95 % confidence interval; —·—·— 99 % confidence interval.

and t_α is the value of the Student distribution t on a chosen level of significance α. The values of equilibrium constants as well as the values of $\varkappa_k$ corresponding to the confidence intervals of slopes of the straight lines in Fig. 3 are presented in Table 3. The retention time of adsorptive in dead volumes of equipment was omitted in statistical calculations because it did not exceed 3 % of the value of the statistical moment similarly as given in paper [18].

Table 3

Values of equilibrium constants of n-heptane on molecular sieve NaY and intervals of reliability

Quantities		Temperature		
		200 °C	237 °C	270 °C
Number of measurements		21	28	19
$K/(m^3\,kg^{-1})$		0.799	0.535	0.140
$\dfrac{\varkappa_k}{m^3\,kg^{-1}}$	95 % interval	0.125	0.035	0.015
	99 % interval	0.170	0.047	0.021
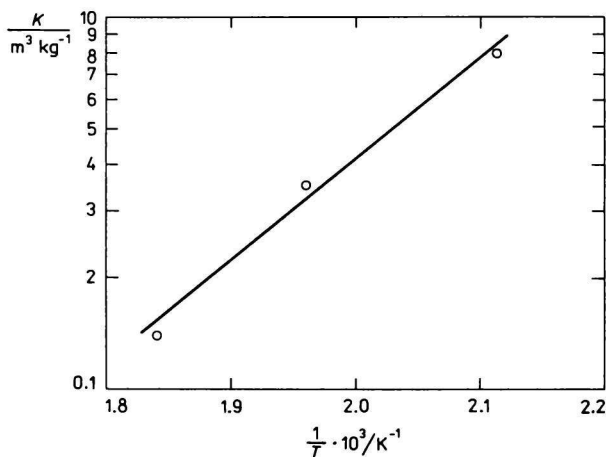
Fig. 4. Relationship $K = f(1/T)$.

According to the van't Hoff equation, the relationship between log K and $1/T$ represented in Fig. 4 enabled us to determine the change in adsorption enthalpy $-\Delta H = 52.4\,\text{kJ mol}^{-1}$.

The values of diffusion coefficients D' determined according to eqns (*13*) and (*14*) on the assumption that a particle of molecular sieve NaY represents quasi-homogeneous isotropic medium are given in Table 4. The corresponding relationships are represented in Figs. 5—8. It results from eqn (*2*) that the values

Table 4

Diffusion coefficients of n-heptane transport in a particle of molecular sieve NaY in the presence of nitrogen and diffusion coefficients of molecular and Knudsen diffusion

Temperature	D' 10^7	D_e 10^9	$D \cdot 10^5$	D_p 10^6	D_k 10^7	D_{kp} 10^8
°C	$m^2 s^{-1}$	$m^2 s^{-1}$	$m^2 s^{-1}$	$m^2 s^{-1}$	$m^2 s^{-1}$	$m^2 s^{-1}$
200	9.23	0.983	1.087	1.907	5.090	8.932
237	5.71	1.38	1.242	2.179	5.285	9.275
270	3.46	2.12	1.386	2.432	5.453	9.570

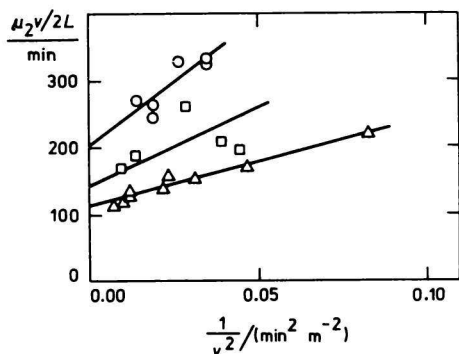*Fig. 5.* Relationship $\mu_2 v/2L = f(1/v^2)$ at 200 °C. Particles of molecular sieve with diameter of 0.40—0.63 mm (△), 0.63—0.71 mm (□), 0.80—1.00 mm (○).

of D' characterize the rate of accumulation of adsorptive in the pores of particle of the adsorbent as well as the rate of adsorption. If we take into consideration that the rate itself of trapping of the adsorptive in the solid surface from immediate proximity is infinitely high [19], we may write

$$\frac{\partial a}{\partial \tau} = K \frac{\partial C}{\partial \tau} \qquad (23)$$

and insert by means of eqn (2)

$$D_e = \frac{D'}{\beta + K \varrho_p} \qquad (24)$$

The values of effective diffusion coefficients thus calculated are also given in Table 4. It results from a comparison of D' and D_e that the greater the equilibrium constant, *i.e.* the lower the temperature, the greater the influence of the rate of adsorption on the value of D' The great change in equilibrium constant with temperature is evidently the reason for that D' decreases with increasing temperature. *Satterfield*[20, 21] describing the processes taking place in particles
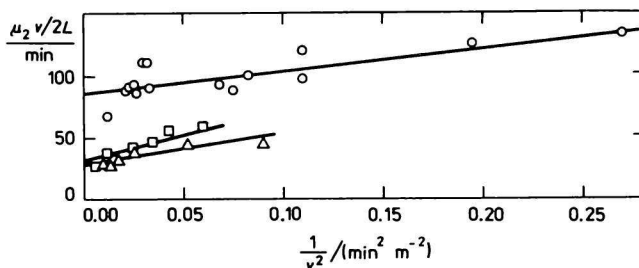
Fig. 6. Relationship $\mu_2 v/2L = f(1/v^2)$ at 237 °C. Denotation is the same as in Fig. 5.
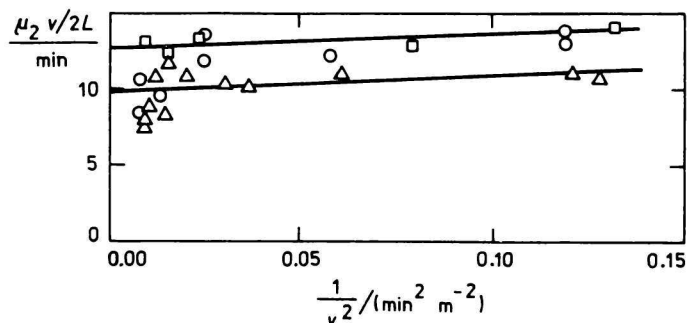

Fig. 7. Relationship $\mu_2 v/2L = f(1/v^2)$ at 270 °C. Denotation is the same as in Fig. 5.

of catalyst used for D' the term effective diffusion coefficient. In papers dealing with the rate of adsorption [2, 22, 23] the effective diffusion coefficient is defined by eqn (*24*).

The activation energy of diffusion of n-heptane in a particle of molecular sieve NaY calculated from the dependence of the effective diffusion coefficient on temperature, as represented in Fig. 9, is 23,6 kJ mol^{-1}.
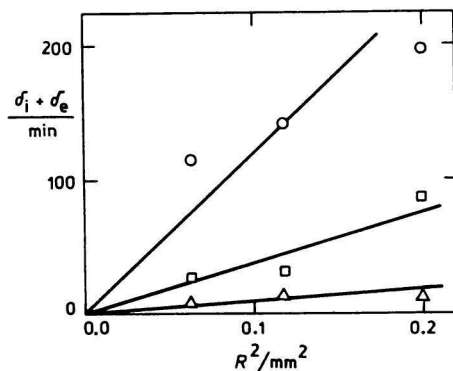

Fig. 8. Relationship $\delta_i + \delta_e = f(R^2)$. ○ 200 °C; □ 237 °C; △ 270 °C.

The coefficients of molecular diffusion of n-heptane in nitrogen calculated according to [24] and the coefficients of the Knudsen diffusion in straight pores calculated for the mean radius of the pores of particle defined according to [20, 21]

$$r_e = \frac{2V}{S} = \frac{2\beta}{S \varrho_p} \tag{25}$$
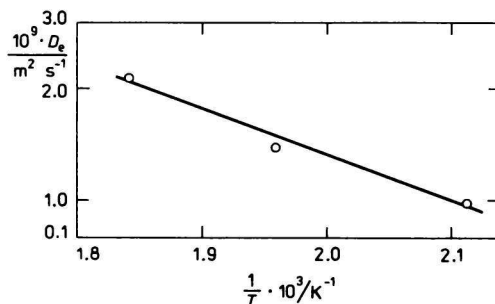
are given in Table 4.

Fig. 9. Relationship $D_e = f(1/T)$.

The mean radius of all pores of a particle of molecular sieve NaY thus defined $r_e = 2 \times 0.585/4850000 = 2.412 \times 10^{-7}$ cm is by two decimal orders smaller than the most frequent radius of the secondary pores presented in Fig. 1. For recalculation of the coefficients of the molecular and Knudsen diffusion for porous medium the following formula was used

$$D_p = \frac{D\beta}{\tau_m} \tag{26}$$

The value of the tortuosity factor $\tau_m = 4$ was chosen in agreement with the data in papers [20, 21].

The calculated values of the diffusion coefficients of the molecular and Knudsen diffusion in solid porous medium are by 2 or 3 decimal orders higher than the found values of the effective diffusion coefficients. That is why we may state that the diffusion in crystal of zeolite significantly manifests itself in the transport of n-heptane in a particle of molecular sieve NaY besides the molecular or Knudsen diffusion.

We have not found the values of diffusion coefficients of n-heptane in particles of molecular sieve NaY in available literature. Nevertheless, the determined values may, to a certain extent, be compared with the values of effective diffusion coefficients of some n-alkanes published in papers [10, 25]. On the basis

of chromatographic measurements, *Hsu* and *Haynes* [10] determined the effective diffusion coefficients of n-butane in molecular sieve NaY and of n-hexane in crystals of molecular sieve NaY. Thus they obtained the values 2.4×10^{-12}—$6.0 \times 10^{-10}\,m^2\,s^{-1}$ for n-butane at 105—240 °C and the value $4.23 \times 10^{-12}\,m^2\,s^{-1}$ for n-hexane at 202 °C. The authors of paper [25] found the value $D_e/R_0^2 = 0.137\,s^{-1}$ for the system n-hexane—particles of molecular sieve NaY at 93 °C by using the gravimetric method which made possible to calculate $D_e = 1.44 \times 10^{-8}\,m^2\,s^{-1}$ for the used radius of particles 0.324 mm. These values of effective diffusion coefficients are consistent with the values determined by us which are presented in Table 4.

Since the structure of a particle of molecular sieve NaY consisting of the crystals of zeolite NaY exhibiting dimensions of μm, entrance openings of 1 nm and diameters of the intracrystalline holes of 1.6 nm irregularly distributed in a particle of adsorbent and joined by the secondary pores is better to describe on the assumption of biporous than on the assumption of quasi-homogeneous medium, the results have also been processed by the use of the relations derived for the diffusion in biporous spherical particles of adsorbent (Table 5).

Table 5

Diffusion coefficients of n-heptane transport in a particle of molecular sieve NaY found on the basis of assumption of biporous structure of this particle

Temperature	$D_i\ 10^7$	D_a/r_0^2	$D_a\ 10^{12*}$	$D_p\ 10^6$
°C	$m^2\,s^{-1}$	s^{-1}	$m^2\,s^{-1}$	$m^2\,s^{-1}$
200	11.62	37.03	9.26	1.14
237	6.20	28.46	9.62	1.30
270	3.68	53.58	13.40	1.45

* For $r_0 = 0.5 \times 10^{-6}\,m$.

The values of diffusion coefficients of the adsorbed substance in transport pores and crystals of zeolite determined by using of relations (*15—18*) and graphs in Figs. 10—13 are listed in Table 5. The values of diffusion coefficients D_i found for transport pores differ from the values of the coefficients of molecular diffusion D_p calculated for the secondary porosity of a particle of molecular sieve less than by one decimal order.

The values of the coefficients of the Knudsen diffusion in the secondary pores calculated for their mean radius $r_e = 2 \times 0.349/(10.88 \times 10^4) = 6.415 \times 10^{-6}\,cm$ are only insignificantly different from the values of the coefficients of molecular diffusion given in Table 4. However, the values of D_i as well as the values of D'
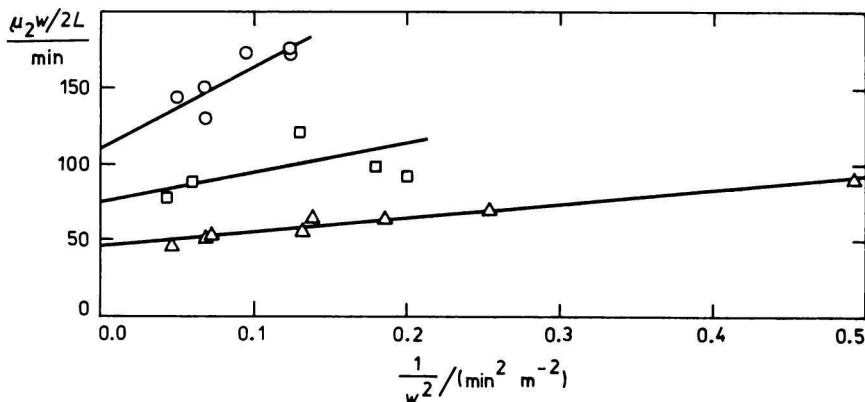
Fig. 10. Relationship $\mu_2 w/2L = f(1/w^2)$ at 200 °C. Screened fraction of particles of molecular sieve NaY with diameter of 0.4—0.63 mm ($\triangle$), 0.63—0.71 mm ($\square$), 0.80—1.00 mm ($\bigcirc$).
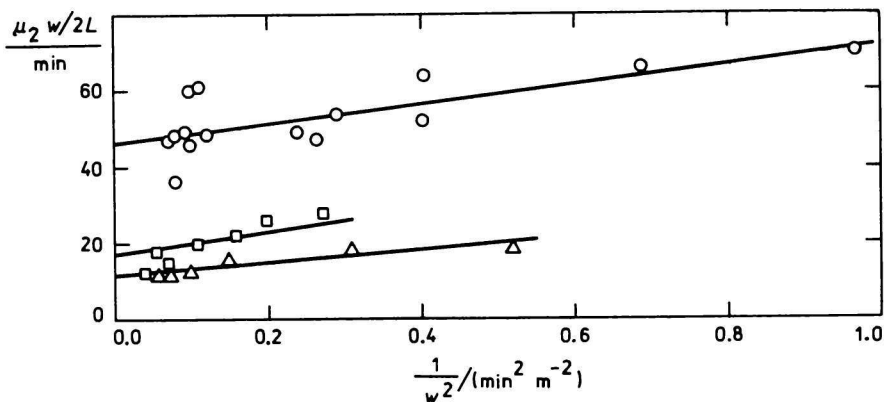

Fig. 11. Relationship $\mu_2 w/2L = f(1/w^2)$ at 237 °C. Denotation is the same as in Fig. 10.

decrease with increasing temperature for the quasi-homogeneous model. The cause of this apparent nonlogic consists in the fact that the experimental values of D_i, in line with eqn (8) comprise the transport of adsorptive in the secondary pores as well as the entrance into the microporous regions of crystal of molecular sieve. The greater the driving force, *i.e.* the greater the equilibrium constant, the higher the rate of entrance of the adsorptive into crystals of molecular sieve. The values of D_a/r_0^2 given in Table 5 correspond to the value of diffusion coefficient of n-hexane $4.23 \times 10^{-12}\,\mathrm{m^2\,s^{-1}}$ found for crystals of molecular sieve NaY and published in paper [10].
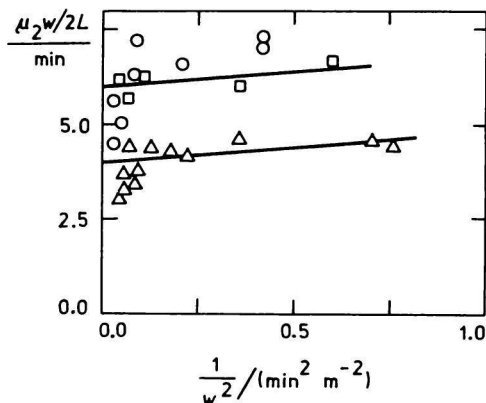
Fig. 12. Relationship $\mu_2 w/2L = f(1/w^2)$ at 270 °C. Denotation is the same as in Fig. 10.
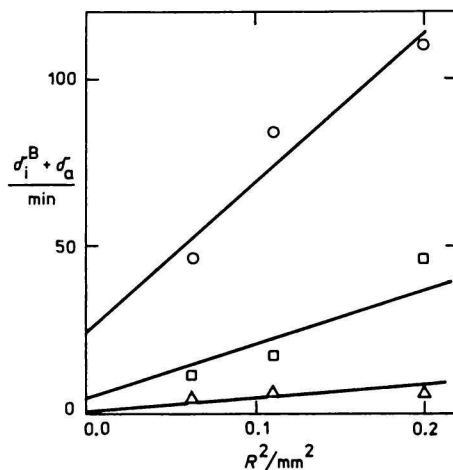
Fig. 13. Relationship $\delta_i^B + \delta_a = f(R^2)$. Denotation is the same as in Fig. 10.

Symbols

a	concentration of adsorbate	$\mathrm{kmol\,kg^{-1}}$
c	concentration of adsorptive in pores of adsorbent referred to the volume of fluid phase	$\mathrm{kmol\,m^{-3}}$
c_a	concentration of adsorptive in the primary pores referred to the volume of fluid phase	$\mathrm{kmol\,m^{-3}}$
C	concentration of adsorptive in the interparticle room referred to the volume of fluid phase	$\mathrm{kmol\,m^{-3}}$
C_i	concentration of adsorptive in interphase	$\mathrm{kmol\,m^{-3}}$
C_0	concentration of adsorptive in a sample injected into column	$\mathrm{kmol\,m^{-3}}$
D	coefficient of molecular diffusion	$\mathrm{m^2\,s^{-1}}$
D'	diffusion coefficient of the adsorbed substance in pores of adsorbent	$\mathrm{m^2\,s^{-1}}$
D_a	diffusion coefficient of the adsorbed substance in the primary pores	$\mathrm{m^2\,s^{-1}}$
D_e	effective diffusion coefficient as defined by eqn (24)	$\mathrm{m^2\,s^{-1}}$
D_i	diffusion coefficient of the adsorptive in the secondary pores	$\mathrm{m^2\,s^{-1}}$
D_k	coefficient of the Knudsen diffusion	$\mathrm{m^2\,s^{-1}}$
D_L	coefficient of the longitudinal diffusion of adsorptive	$\mathrm{m^2\,s^{-1}}$
D_{kp}, D_p	diffusion coefficients calculated for porous medium by means of eqn (26)	$\mathrm{m^2\,s^{-1}}$
k, k'	slope of straight line	

k_{gc}	mass transfer coefficient in fluid phase	$m\,s^{-1}$
K	equilibrium adsorption constant	$m^3\,kg^{-1}$
L	height of a bed of adsorbent	m
n	number of measurements	
r	spherical coordinate in microporous zones	m
r_e	mean radius of pores in a particle of adsorbent as defined by eqn (25)	m
r_0	radius of the microporous zone	m
R	spherical coordinate in a particle of adsorbent	m
R_0	radius of a spherical particle of adsorbent	m
s_k	standard deviation	
S	surface of the pores of adsorbent	m^2
t_a	value of the Student t-distribution	
v	interparticle velocity of gas	$m\,s^{-1}$
V	volume of the pores of adsorbent	m^3
w	superficial velocity of gas	$m\,s^{-1}$
Z	axial coordinate in the bed of adsorbent	m
β	porosity of a particle of adsorbent	$m^3\,m^{-3}$
δ_a, δ_e, δ_i, δ_i^B	moment contributions given by eqns (14), (17), (18)	s
δ_0	moment contribution given by eqn (16)	
ε	porosity of a bed of adsorbent	$m^3\,m^{-3}$
ε_a	primary porosity (ratio of the volume of the primary pores to the volume of the microporous zone)	$m^3\,m^{-3}$
ε_i	secondary porosity (ratio of the volume of the secondary pores to the volume of a particle)	$m^3\,m^{-3}$
$\varkappa_k$	value determining the confidence interval given by eqn (21)	$m^3\,kg^{-1}$
μ_1'	the first simple statistical moment of elution curve	s
μ_2	the second central statistical moment of elution curve	s^2
ϱ_p	particle density	$kg\,m^{-3}$
τ	time	s
τ_0	time at the injection of sample into the column	s
τ_m	tortuosity factor	

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