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Translated by V. Brezová

Diffusion Coefficients of n-Hexane in Particles of Molecular Sieve NaY Determined by means of Chromatographic Measurements

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Received 12 December 1990

Accepted for publication 8 June 1992

The values of effective diffusion coefficients of n-hexane in the presence of nitrogen (1.48—5.60) × 10^{-9} m^2 s^{-1} were determined at 160—240 °C under the assumption that the particle of molecular sieve NaY can be described by a quasi-homogeneous model. Considering a biporous structure in this particle, the determined values of diffusion coefficients D_a/r_0^2 of n-hexane in a molecular sieve crystal in the presence of nitrogen are ranging from 32.4 to 41.4 s^{-1}.

Values of diffusion coefficients in a single particle of adsorbent as well as equilibrium data are a necessary prerequisite for mathematical modelling of the adsorption separation units. With regard to the complexity of the adsorbent structure, a dependence of the diffusion coefficient on the properties of adsorbent, adsorptive, and carrier gas has not been formulated up to now. In characterizing the transport of adsorptive in a single adsorbent particle, experimental values of diffusion coefficients are used in models describing both adsorption and desorption.

In describing the transport of adsorptive in a complicated porous structure of adsorbent, mostly two approaches are applied. In the first one, the porous substance is supposed to be a quasi-homogeneous isotropic medium from the standpoint of mass transport [1, 2]. The second one proposes that the porous structure of the adsorbent particle can be approximated by two kinds of pores, *i.e.* by the so-called biporous structure [3, 4]. Particles of molecular sieve NaY employed in this study consist of zeolite crystals with dimensions in μm, entrance openings of nm irregularly distributed in a particle of adsorbent and joined by the secondary pores having a most frequent radius of about 120 nm [5]. Therefore, the assumption to describe the mass transfer in a particle of adsorbent also by diffusion in a biporous particle of adsorbent is justified.

The relationships used for the determination of diffusion coefficients are presented in [5].

EXPERIMENTAL

n-Hexane (Lachema, Brno) had the following composition (*x*/mole %): n-hexane 98.47; 3-methylpentane 1.13; 2-methylpentane 0.40.

Elution chromatographic curves for n-hexane from a molecular sieve bed NaY at temperatures of 160, 200, and 240 °C and flow-rates of carrier gas from 115 to 378 cm^3 min^{-1} were estimated on an apparatus described previously [5]. The characteristics of columns and working conditions are given in Table 1.

Table 1. Characteristics of Columns and Working Conditions

Quantities	Column		
	U_1	U_2	U_3
Length of bed /cm	3.70	3.80	3.60
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 /(cm^3 min^{-1}) (25 °C, 101.3 kPa)	115—378	135—371	130—345

In the treatment of results, times for injecting samples into the column were neglected. The value $\tau_0^2/12$ was smaller than 5 % of the lowest value of the second statistical moment. Furthermore, correction with regard to dead volumes was omitted.

Statistical moments of n-hexane determined from measurements in columns filled with glass spheres having an equivalent radius of 0.433 mm did not reach 3 % of the values of statistical moments determined from measurements on particles of molecular sieve NaY.

RESULTS AND DISCUSSION

The values of μ_1' found for individual screened fractions of the particles of molecular sieve NaY and given temperatures are plotted as a function of L/v in Fig. 1. 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 were calculated according to the Student distribution t on a chosen level of significance. The determined values of equilibrium constant K and values of intervals of reliability κ_K are listed in Table 2.

According to the van't Hoff equation, the relationship between log K and $1/T$ represented in Fig. 2 enabled to determine the change in adsorption enthalpy ($-\Delta H$) = 39.3 kJ mol^{-1}.

The values of diffusion coefficients D' determined according to eqns (*13*) and (*14*) in Ref. [5] on the assumption that a particle of adsorbent represents a quasi-homogeneous medium and using dependences illustrated in Figs. 3 and 4 are given in Table 3. The values of effective diffusion coefficients D_e calculated by eqn (*24*) in Ref. [5] are also given in Table 3.

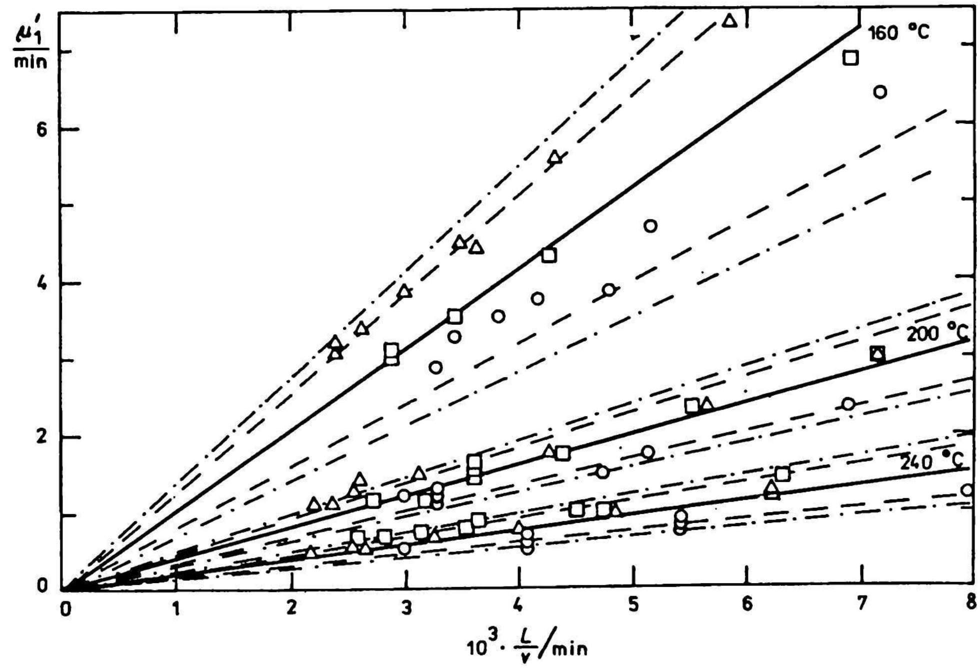

Fig. 1. Relationship $\mu_1' = f(L/v)$. Screened fraction of particles of molecular sieve NaY with diameter of 0.80—1.00 mm (○), 0.63—0.71 mm (□), 0.40—0.63 mm (Δ); - - - - 95 % confidence interval, -·-·-·- 99 % confidence interval, —— obtained by the least squares method.

Table 2. Values of Equilibrium Constants of n-Hexane on Molecular Sieve NaY and Intervals of Reliability

Quantities	Temperature		
	160 °C	200 °C	240 °C
Number of measurements	21	23	25
$K/(m^3\ kg^{-1})$	0.768	0.296	0.141
$\kappa_K/(m^3\ kg^{-1})$ 95 % interval	0.179	0.045	0.030
99 % interval	0.243	0.061	0.041

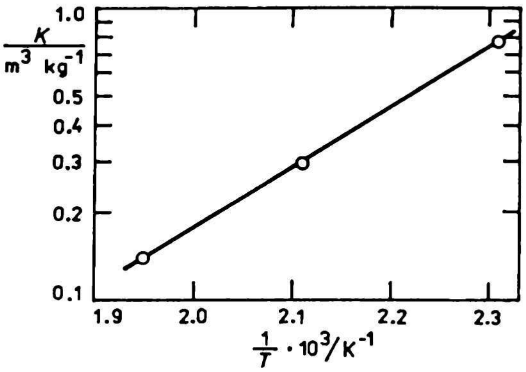

Fig. 2. Relationship $K = f(1/T)$.

The validity of relationship (*24*) for D_e is based on the presumption of an infinite rate of trapping the adsorptive in the solid surface from immediate proximity or an infinite rapid transformation of adsorptive into adsorbate at the adsorption surface.

The values of diffusion coefficients D' of n-hexane in the pores of particles of molecular sieve NaY decrease with increasing temperature, which is in discrepancy with theoretical knowledge concerning the dependence of the diffusion coefficient on temperature. This discrepancy will be studied in more detail in further works. The above-mentioned anomaly can be explained in the following way:

The values D' include the simultaneous course of adsorption and diffusion of adsorptive. Thus, these values depend not only on the transport properties of the system, but also on the rate of trapping adsorptive in the active surface. If one accepts the conditions of validity of the relation for D_e, then the adsorption rate is directly proportional to the equilibrium adsorption constant K. Table 2 reveals that over the investigated range of temperature 160—240 °C, this constant decreases from 0.768 to 0.141 $m^3\ kg^{-1}$, while the coefficient of molecular diffusion increases only about 1.3-times. Thus, it may happen that the temperature dependence of D' is given by the dependence of the equilibrium adsorption constant on temperature. From the relation for D_e the influence of the rate of adsorption on D' and D_e is evident. Relatively great changes of the value of the equilibrium constant with temperature caused that in contradistinction to D', the values of D_e increase with increasing temperature.

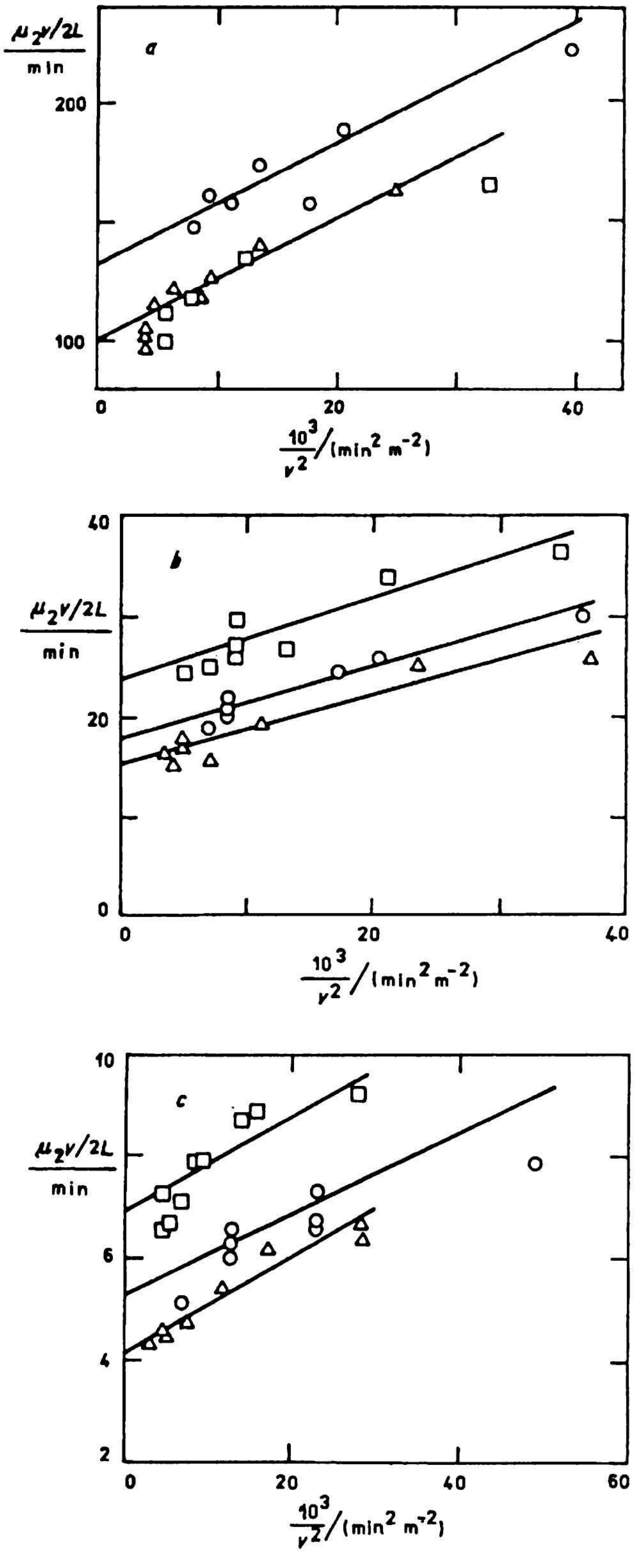

Fig. 3. Relationship $\mu_2 v/2L = f(1/v^2)$. *a)* 160 °C; *b)* 200 °C; *c)* 240 °C. Screened fractions of particles of molecular sieve NaY with diameter in mm: Δ 0.40—0.63, □ 0.63—0.71, ○ 0.80—1.00.

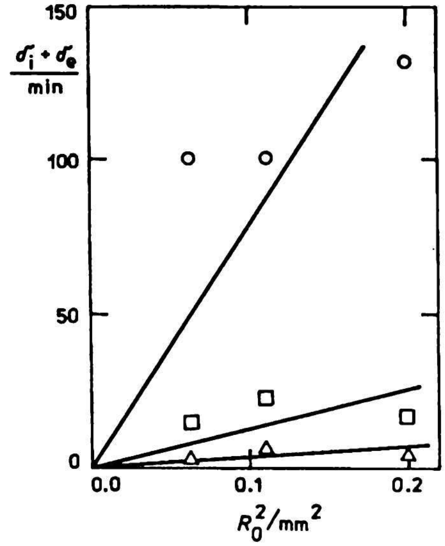

Fig. 4. Relationship $\delta_i + \delta_e = f(R_0^2)$. ○ 160 °C, □ 200 °C, Δ 240 °C.

port of n-hexane in a particle of molecular sieve NaY in the presence of nitrogen, besides the molecular and Knudsen diffusion, also diffusion in the crystal of zeolite plays an important role.

The values of diffusion coefficients of n-hexane in transport pores and in the zeolite crystals determined by means of eqns (*15—18*) in Ref. [5] from the curves given in Fig. 5 are listed in Table 3. The values of diffusion coefficients in transport pores D_i, as well as the values of D' for the quasi-homogeneous model decrease with an increase in temperature. The cause of this apparent nonlogic consists in the fact that the experimental values D_i include also the influence of adsorption in crystals of zeolite, a so-called "sucking" of the adsorptive. This phenomenon is the higher, the higher is the equilibrium adsorbed amount, *i.e.* the equilibrium constant, under given conditions. A comparison of the values of D_i with calculated values of coefficients of molecular diffusion in a porous medium D_p and coefficients of Knudsen diffusion D_{kp} presented in Table 3 reveals that in the secondary pores of molecular sieve NaY the transport of n-hexane by molecular diffusion can be supposed.

Calculated values of D_a for $r_0 = 0.5 \times 10^{-6}$ m listed in Table 3 are in agreement with the value of 4.23×10^{-12} m^2 s^{-1} found by *Hsu* and *Haynes* [9]

Table 3. Diffusion Coefficients of n-Hexane in Particles of Molecular Sieve NaY

θ/°C	$\frac{D' \ 10^6}{\mathrm{m^2\ s^{-1}}}$	$\frac{D_e \cdot 10^9}{\mathrm{m^2\ s^{-1}}}$	$\frac{D_i \ 10^6}{\mathrm{m^2\ s^{-1}}}$	$\frac{D_a/r_0^2}{\mathrm{s^{-1}}}$	$\frac{D_a^* \ 10^{12}}{\mathrm{m^2\ s^{-1}}}$	$\frac{D_p \ 10^6}{\mathrm{m^2\ s^{-1}}}$	$\frac{D_{kp} \ 10^8}{\mathrm{m^2\ s^{-1}}}$
160	1.36	1.48	2.46	32.4	8.10	2.72	9.22
200	1.25	3.50	1.42	36.5	9.13	3.15	9.63
240	0.952	5.60	1.03	41.4	10.40	3.65	10.0

*Calculated for $r_0 = 0.5 \times 10^{-6}$ m.

For systems n-hexane—particles of molecular sieve NaY, we have not found values of diffusion coefficients measured in the presence of an indifferent component in available literature. *Eberly* [6] found out for the system n-hexane—particles of molecular sieve NaY at 93 °C by using the gravimetric method in the absence of an indifferent component that $D_e/R_0^2 = 0.137$ s^{-1}. This made possible to calculate $D_e = 1.44 \times 10^{-8}$ m^2 s^{-1} for the applied effective radius of particles of sieve 0.324 mm. Though, this value is consistent with the determined values of D_e, it shows a significant difference between the values of effective diffusion coefficients of compounds in particles of molecular sieve determined in the absence or presence of an indifferent component.

In Table 3 are also presented diffusion coefficients of the molecular D_p and Knudsen diffusion D_{kp} found for the mean radius of straight pores of a molecular sieve particle $r_e = 2.412 \times 10^{-7}$ cm, calculated on the porous medium according to eqn (*26*) in Ref. [5]. The value of the tortuosity factor was in accordance with [7, 8] chosen as $\tau_m = 4$. Calculated values of diffusion coefficients of the molecular and Knudsen diffusion in a porous medium are more than one decimal order higher than the determined values of effective diffusion coefficients. Thus, we can conclude that during the trans-

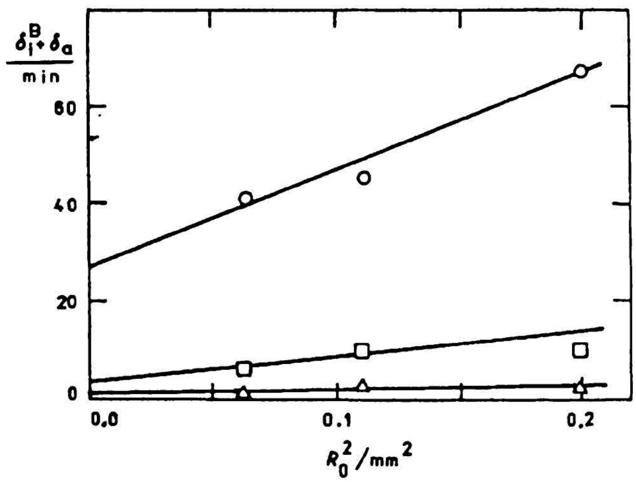

Fig. 5. Relationship $\delta_i^B + \delta_a = f(R_0^2)$. ○ 160 °C, □ 200 °C, Δ 240 °C.

for the system n-hexane—crystals of molecular sieve NaY at 202 °C.

SYMBOLS

D'	diffusion coefficient in pores of adsorbent	$m^2\ s^{-1}$
D_a	diffusion coefficient in the primary pores	$m^2\ s^{-1}$
D_e	effective diffusion coefficient	$m^2\ s^{-1}$
D_i	diffusion coefficient in the secondary pores	$m^2\ s^{-1}$
D_p, D_{kp}	coefficients of the molecular and Knudsen diffusion calculated for porous medium	$m^2\ s^{-1}$
K	equilibrium adsorption constant	$m^3\ kg^{-1}$
L	height of a bed of adsorbent	m
r_0	radius of zeolite crystals	m
R_0	radius of particles of adsorbent	m
v	interparticle velocity of carrier gas	$m\ s^{-1}$
δ_a, δ_e, δ_i, δ_i^B	moment contributions given by eqns (*13—18*) in [5]	s
μ_1'	the first simple statistical moment of elution curve	s
μ_2	the second central statistical moment of elution curve	s^2
τ_0	time at the injection of sample into the column	s
τ_m	tortuosity factor	–

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