Diffusion of *n*-pentane vapour in a crystal of molecular sieve 5A

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The diffusion of *n*-pentane in the particles of the molecular sieve 5A prepared by pressing pure zeolite and in those prepared with a binding agent was investigated. It was found that it is possible to compare the values of the effective diffusion coefficient obtained for both types of the molecular sieve particles using the characteristic dimension of zeolite crystals.

The up to now published calculation methods of adsorbers based on the corresponding physical description of sorption assume that the overall mass transfer resistance can be divided, at least, into two partial resistances: the fluid-phase and the solid particle--phase resistances. A large number of papers concerning the fluid-phase mass transfer, so that its value can be calculated from the known dimensionless correlations are available [1]. The description of the adsorbate transport in the pores of the solid phase raised difficulties in the determination of the solid-phase partial resistance. The published data on transport of a substance in molecular sieves refer to different types of adsorbents, such as pure crystals, particles from pressed crystals and particles of molecular sieves with a binding agent. The majority of these data deal with adsorption of substances without an inert component. The analysis of experimental kinetic data for sorption of substances in particles of pressed zeolite crystals or in those of molecular sieve with a binding agent proves that the primary pores of the particles rather than the secondary pores are decisive for the mass transfer-resistance [2—4].

Experimental results obtained by us and other investigators by means of known equations generally used to characterize the diffusion transport of the substance in the adsorbent particle, demonstrate the inconsistency of the effective diffusivity value as a measure of the mass-transfer rate. It is supposed that this discrepancy follows from difficulties in the determination of the existing relation between the effective diffusivity, characterizing the diffusion rate inside the crystal of the synthetic zeolite, and its value during the transport of the substance in the pure zeolitic granules prepared by pressing or in the particles pelletized with a binding agent.

In our opinion this problem can be simplified by ascribing an appropriate value to the dimension of length occurring in the diffusion equations. We conclude that this dimension is related only to the geometric characteristics of the zeolite crystals.

Mathematical analysis

The transport mechanism is described by the commonly used model resulting from II Fick law.

The transport of an adsorbate in the heterogeneous isotropic medium at infinite sorp-

tion rate of the adsorbate on the adsorbent surface, and assuming a linear equilibrium relationship

$$q = RC$$

or

$$q = RC + e \tag{1}$$

can be expressed by the following diffusion equation [4]

$$\frac{\partial C}{\partial \tau} = D_e \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right). \tag{2}$$

Actual physical definition of the effective diffusivity D_e depends on the transport mechanism of the substance in the adsorbent pores.

On condition that a uniform initial adsorbate concentration in the pores of the particle exists and a constant adsorbate concentration is kept on the particle surface, the solution of eqn (2) for radial diffusion inside a sphere having a radius r is given by eqn [5, 6]

$$\frac{M_\tau}{M_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left[- \frac{D_e \, n^2 \, \pi^2 \, \tau}{r^2} \right] \tag{3}$$

and for diffusion inside a cylinder with a radius r and length l is given by eqn [7]

$$\frac{M_\tau}{M_\infty} = 1 - \frac{32}{\pi^2} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{1}{\mu_n^2 \, (2m-1)^2} \exp \left[- \left(\frac{\mu_n^2}{r^2} + \frac{(2m-1)^2 \, \pi^2}{l^2} \right) D_e \, \tau \right]. \tag{4}$$

In the same way the equations for desorption under the corresponding boundary conditions can be derived. The desorption equation for a spheric adsorbent particle is

$$\frac{M_\tau}{M_\infty} = \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp \left[- \frac{D_e \, n^2 \, \pi^2 \, \tau}{r^2} \right] \tag{5}$$

and for the cylindric particle

$$\frac{M_\tau}{M_\infty} = \frac{32}{\pi^2} \sum_{n=1}^{\infty} \sum_{m=1}^{\infty} \frac{1}{\mu_n^2 \, (2m-1)^2} \exp \left[- \left(\frac{\mu_n^2}{r^2} + \frac{(2m-1)^2 \, \pi^2}{l^2} \right) D_e \tau \right]. \tag{6}$$

The concentration independence of diffusivity D_e is another assumption for the derivation of eqns (2—6). For our experimentally obtained data this inevitable condition for their evaluation by these equations is fulfilled by the step-by-step proportioning of small adsorbate quantities, which results in small changes of the adsorbate concentrations of the adsorbent. This procedure permits also to represent the equilibrium function for the narrow concentration interval by the equation of a straight line.

Experimental

Materials

n-Pentane, rectified on a column with 50 theoretical stages, density at 20°C 0.6263 g cm^{-3}; n_D^{20} 1.3577, b.p. 36.2°C/760 torr. Composition (mole %): *n*-pentane 99.4, *i*-pentane 0.3, 2,2-dimethylbutane 0.1, 2-methylpentane 0.2.

Adsorbents

The spheric particles of molecular sieve 5A with a binding agent: diameter 2.70−2.95 mm; amount of binding agent 20 wt %; secondary pores volume 0.271 cm^3 g^{-1}.
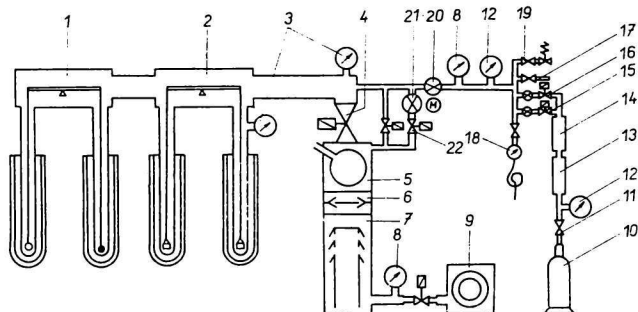

Fig. 1. The diagram of the Gravimat.

1. Buoyancy manometer; *2.* sorption balance; *3.* ionization vacuum gauge; *4.* main valve; *5.* nitrogen cold trap; *6.* thermoelectric baffle; *7.* oil diffusion pump; *8.* heat conductivity vacuum gauge; *9.* vacuum pump; *10.* nitrogen tank; *11.* reduction valve; *12.* spring manometer; *13.* adsorption column; *14.* drying column; *15.* inlet valve 1; *16.* inlet valve 2; *17.* inlet valve 3; *18.* vapour pressure manometer; *19.* safety valve; *20.* connecting valve; *21.* vario valve; *22.* outflow valve 1 and 2.
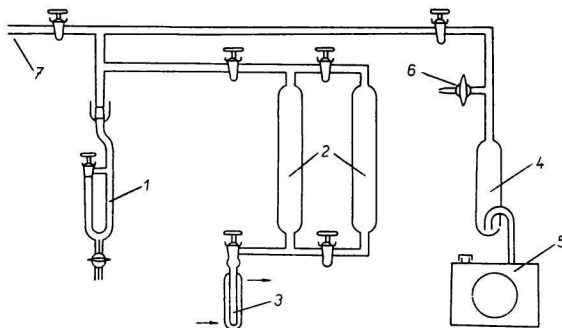

Fig. 2. The diagram of the dosing device.

1. manometer; *2.* adsorbate vapours reservoir; *3.* liquid adsorbate reservoir; *4.* oil separator; *5.* rotary oil pump; *6.* tap; *7.* pipe to the Gravimat.

Cylinders from pressed crystals of molecular sieve 5A: diameter 10.098 mm, length 2.968; secondary pores volume 0.273 cm^3 g^{-1}. The crystals of molecular sieve 5A were prepared in the Research Institute of Petroleum and Hydrocarbon Gases, Bratislava in 1966. Composition of the zeolite (wt %): Na$_2$O 4.36, Al$_2$O$_3$ 36.84, CaO 15.76, SiO$_2$ 43.04. The equivalent diameter of the crystal particles determined as weighted diameter of a set of 3126 particles from photographies of the zeolite 2.98 × 10^{-4} cm.

Apparatus

The gravimetric sorption automat Gravimat [9] (Fig. 1) was used in the study of *n*-pentane adsorption on molecular sieve 5A. The proportioning device of the Gravimat which is suitable only for the determination of kinetic or equilibrium data of gas adsorption was disconnected behind the drying column *14* and the inlet of the apparatus was sealed. The vapours of *n*-pentane were fed into the adsorption section from the auxiliary glass equipment illustrated in Fig. 2. This was attached to the Gravimat by means of valve *17*. The temperature of the adsorbent during adsorption was measured with the suitable device [10]. For tempering and activation of adsorbent the electric heater of own design together with the temperature regulator made in the Research Institute of Petrochemistry were used.

Measuring procedure

After cooling, the reservoir *3* (Fig. 2) was made up to about 3/4 of the total volume with liquid *n*-pentane and the proportioning equipment was evacuated by means of a rotary oil pump. The air absorbed in *n*-pentane as well as the air from other parts of the reservoir *3* was removed through evaporation of *n*-pentane (1—2 cm^3). Independently of the proportioning equipment the adsorption section of the Gravimat was evaporated by means of the rotary oil pump *9*. After reaching the pressure lower than 0.2 torr in both the Gravimat and the glass equipment, these two parts of the apparatus were connected by opening the needle valve *17*. By means of a glass tap the vacuum pump was disconnected and the diffusion pump of the Gravimat *7* was put into operation. At the same time the heating was put into service. The molecular sieve was activated to a constant weight at 450°C and at 10^{-5}—10^{-6} torr (approx. 3 hrs). After tempering the molecular sieve to the desired temperature vapours of the adsorbed substance were introduced into the reservoir *2* (Fig. 2) and then, after shutting the valves on the pumping system of the Gravimat, into the section of the balance. The first amount of the adsorbed substance caused an increase of molecular sieve temperature from 10 to 20°C. Therefore the adsorption rate was not studied after the first introduction of the substance vapour. After reaching the equilibrium the second amount of vapours was introduced by the same procedure into the microbalance. During adsorption of the second dose of vapours the temperature of the sample and the pressure did not change significantly. The sample weight, the pressure of adsorbate, and the temperature of the sample were automatically recorded during adsorption. When equilibrium was reached, the third dose followed, *etc.*

The step-by-step decrease of pressure in the adsorption section by means of the rotary oil vacuum pump of the proportioning equipment was used in desorption.

Results and discussion

The equilibrium data obtained for adsorption of *n*-pentane on spheric molecular sieve particles prepared with a binding agent (experiments *1A, 1D, 2A, 2D*), and on cylindric particles prepared from pure zeolite by pressing (experiments *3A, 3D, 4A*) are shown in Fig. 3. This figure illustrates clearly that the shape and preparation procedure of the adsorbent have no effect upon the equilibrium function.
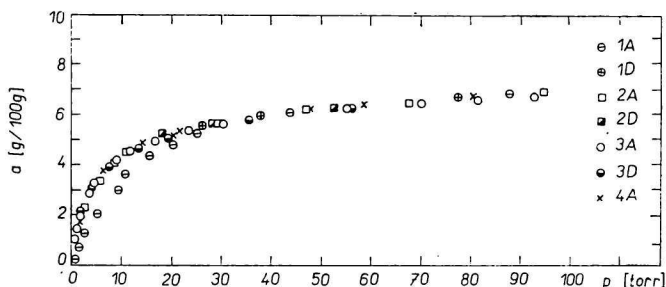

Fig. 3. Experimental equilibrium data of the system *n*-pentane—molecular sieve 5A: *1A* 152°C, adsorption; *1D* 152°C, desorption; *2A* 152°C, adsorption; *2D* 152°C, desorption; *3A* 150°C, adsorption; *3D* 150°C, desorption; *4A* 153°C, adsorption.

The effective diffusion coefficients obtained for adsorption of *n*-pentane on the same adsorbent samples as in the preceding illustration, are shown in Fig. 4 plotted against adsorbate concentrations on the adsorbent. The effective diffusion coefficient value
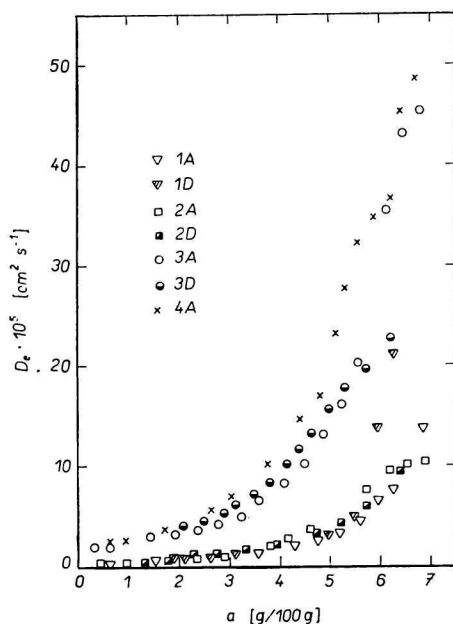

Fig. 4. Concentration dependence of the effective diffusion coefficient.

1A, 1D, 2A, 2D — the spheric molecular sieve particles prepared with a binding agent; *3A, 3D, 4A* — the cylindric particles prepared from pure zeolite by pressing.

is calculated from the kinetic measurements using eqns $(3—6)$ according to the method of *Crank* [8]. The difference in the diffusivity value for spheric and cylindric particles when the dimension of length of the particle is introduced into the rate equations of diffusion is thus evident from Fig. 4.

Assuming for both types of particles the equal volume of secondary pores and the distribution curve of their dimension of length as well as accepting that the mass transfer resistance is determined by the primary pores of the zeolite the differences in the diffusivity for spheric and cylindric particle can be related only to the fact that in correlating the measured kinetic data the dimension of length of the adsorbent is used. Interpreting the mass transfer inside the adsorbent as transport phenomenon in a spheric zeolite crystal permits to represent the obtained results for both series of measurement by a single function. This function is given in Fig. 5.
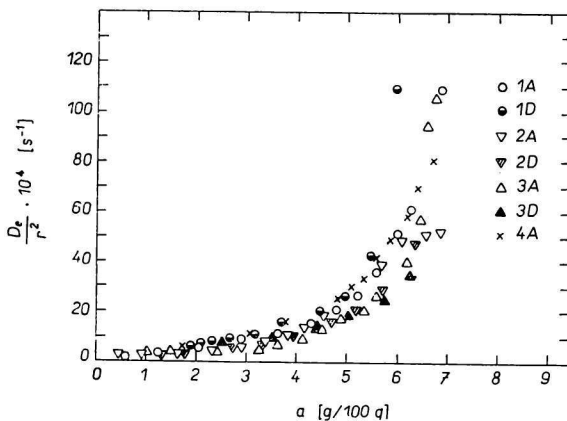

Fig. 5. Concentration dependence of the effective diffusivity.
D_e/r^2 were obtained for all experiments using eqns (3) or (5).

Although the actual value of the dimension of length for the zeolite crystal r is unknown, the dependence in Fig. 5 confirms the correctness of our assumption that the mass transfer resistance is determined by the primary pores of the zeolite crystal. The presented dependence is suitable for the calculation of the effective diffusivity for adsorbent particles of any arbitrary shape and size.

The geometric similarity of the zeolite crystal, the consistency of the distribution curve of the secondary pores volume are the conditions for the general validity of the derived correlation.

Symbols

a amount of the substance adsorbed on molecular sieve with 20 wt % binding agent

C adsorbate concentration in the fluid

D_e effective diffusivity

e constant in eqn (1)

l length of the cylinder

M_τ quantity of adsorbate sorbed in the particle at a time τ during the step change of adsorbate concentration on the adsorbent surface

M_∞ quantity of adsorbate sorbed in the particle at a time $\tau \to \infty$

q adsorbate concentration on the adsorbent

r radius

R constant in eqn (1)

μ_n roots of Bessel's function

τ time

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