

## KINETICS OF ADSORPTION OF HEPTANE ON ACTIVE CARBON SUPERSORBON

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Kinetics of the adsorption of heptane under different pressures and at different temperatures has been studied. Correlation of data according to a second-order equation was used to calculate half-time of adsorbate transport in pores. The correlation equation involves the effect of the pressure in pores for one component adsorption. The half-time was calculated from the whole course of kinetic isotherm. The empirical two-constant dependence of the half-time on pressure can be used to determine the possible mechanism of adsorbate transport in pores. In the adsorbent-adsorbate system studied the activation energy of heptane transport is 80 per cent of the value of isosteric heat. By using the end points of individual kinetic isotherms, the equilibrium isotherms at temperatures 0, 30, and 70°C were constructed and these were correlated by Dubinin equation for the first structure type. Isochronous isotherms in coordinates of Langmuir and Dubinin equation were also constructed.

When diffusion coefficients in porous adsorbents are determined under nonstationary conditions, the adsorbed amount is followed experimentally, as a function of time. The measurement is carried out under constant pressure (concentration) of gas at particle surface or under varying pressure at a constant volume of the apparatus. In both cases, differential equations of diffusion are applied, the solution of which gives dependence of the relative adsorption  $\phi$  on the dimensionless Fourier criterion  $Fo = D_e \tau / R^2$ .

### THEORETICAL

For isotropic environment in porous adsorbents when determining diffusion coefficients under nonstationary conditions, differential equations applied has the form  $\partial(a' + c) / \partial \tau = D \nabla^2 c$ , in which  $\nabla^2$  is Laplace operator,  $a'$  and  $c$  are concentrations of the adsorbate in the adsorbed and gaseous phase, respectively, recalculated to volume unit of particle. Providing that in each point of the considered element there exists equilibrium between gaseous and adsorbed phase, the adsorbed amount  $a'$  can be replaced by the adsorption isotherm  $a' = f(c)$  and Eq. (1) can be then

written:

$$\partial c / \partial \tau = D_e \nabla^2 c, \quad (1)$$

where  $D_e$  is the effective diffusion coefficient which for the linear isotherm is constant but for another type of the isotherm is not.  $D_e = D/(1 + \Gamma)$ , where  $\Gamma$  is Henry coefficient and for the linear isotherm  $a' = \Gamma c$ . For nonlinear isotherm  $\Gamma = \partial a' / \partial c \approx \Delta a' / \Delta c$ . From the above it follows that the effective diffusion coefficient changes with change of Henry coefficient. In case of Langmuir type isotherm, the effective diffusion coefficient increases since  $\Gamma$  decreases with increasing concentration  $c$ . For particles of regular geometric shapes, solution of Eq. (1) was presented in the preceding work<sup>1</sup>. The work reported also simple relations for calculating diffusion coefficients by means of half-time for individual geometric shapes of particles under constant pressure, the survey of which is given in Table I.

If the effective diffusion coefficient increases with increasing concentration (pressure), then at the same time the half-time has to decrease. This fact can be expressed by the empirical two-constant equation

$$\tau_{0.5} = k P_e^{-n}. \quad (2)$$

Isosteric heat is defined by the relation  $(\partial \ln P_e / \partial T)_{a_e} = Q_{\text{iso}} / RT^2$ ; temperature dependence of the effective diffusion coefficient can be expressed by the equation  $\partial \ln D_e / \partial T = E / RT^2 = -\partial \ln \tau_{0.5} / \partial T$ . By introducing logarithms and by deriving Eq. (2) according to temperature at a constant adsorbed amount, one obtains the following expression

$$E = n Q_{\text{iso}}, \quad (3)$$

TABLE I

Effective diffusion coefficients for different geometric shapes of particles expressed by half-times

| Geometric shape of particle | Effective diffusion coefficient, $D_e$ | Accuracy of diffusion coefficient calculations, % |
|-----------------------------|--|---|
| Cylinder <sup>a</sup>       | $1.96L^2 / (\pi^2 \tau_{0.5})$         | 0.1   |
| Cylinder <sup>b</sup>       | $k'' R^2 / (\pi^2 \tau_{0.5})$         | 1   |
| Sphere                      | $0.308 R^2 / (\pi^2 \tau_{0.5})$       | —   |

<sup>a</sup> Adsorbate enters the particle only via one base of the cylinder, the other external cylinder surface is close-packed. <sup>b</sup> Values of the constants  $k''$  for different particle length,  $L$ , to particle radius,  $(R)$ , ratios:  $L/R = 1$  ( $k'' = 0.168$ ), 2 (0.318), 4 (450),  $\infty$  (0.599).

since from temperature dependence of the effective diffusion coefficient, the activation energy of adsorbate transport can be determined. The half-time is indirectly proportional to the diffusion coefficient and thus the activation energy is  $n$ -multiple of the isosteric heat.

The half-time was calculated by using Eq. (4)

$$d\varphi/d\tau = (d\varphi/d\tau)_0 (1 - \varphi)^2, (T, P_e) \quad (4)$$

which describes change of the relative adsorption with time, and for  $\varphi = 0$ , the right side of the equation then gives the initial rate for given temperature and pressure. On writing Eq. (4) the following assumptions can be adopted<sup>2</sup>:

a) Eq. (5) is valid

$$da/d\tau = K \Delta a \Delta P, (T, P_e) \quad (5)$$

b) the rate  $da/d\tau$  is proportional to changes in adsorption and pressure at the constant temperature and pressure outside the particle,

c) the relative quantity of adsorption is defined by the relation  $\varphi = a/a_e$ ,

d) Henry coefficient is expressed by the expression  $\Delta a = \Gamma \Delta P$ , where  $\Delta a = a_e - a$ ,  $\Delta P = P_e - P$ ; for  $\tau = 0$ ,  $P = 0$ ,  $a = 0$  is  $\Gamma = a_e/P_e$ ,

e) by introducing the above conditions into Eq. (5), one obtains Eq. (4). For the initial conditions given, the equation expresses after integration in the linear form  $Y = k'X + q$ , where  $Y = \tau/a$ ,  $X = \tau$ ,  $q = \tau_{0.5}/a_e$ ,  $k' = 1/a_e$ , the ratio  $q/k'$  gives  $\tau_{0.5}$ ;

f) the half-time is expressed by reciprocal value of the initial rate  $\tau_{0.5} = 1/(d\varphi/d\tau)_0$ ;

g) relative value of adsorption in dependence on time is expressed by the relation  $\varphi = \tau/(\tau_{0.5} + \tau)$ ;

h) if pressure change is not considered, Eqs (4) and (5) are transformed into the first-order equation.

## EXPERIMENTAL

The adsorbent used was the active carbon Supersorbon. The sample had the form of an equilateral cylinder of 6 mm diameter and was connected to a quartz spiral by a platinum wire. The spiral had 50 threads of 25 mm diameter with the sensitivity of 0.7 mg per mm. The measurements were carried out in a greaseless adsorption apparatus<sup>1</sup> under constant pressure with the use of patents<sup>3-5</sup>. The adsorbent was activated before each measurement for 5 to 6 h at temperatures 340–360°C and the pressure  $1.3 \cdot 10^{-4}$  Pa. After steady given temperature and required pressure had been established, the space in which the spiral was placed was connected with the 33 l-reservoir of heptane vapours by means of a valve<sup>6</sup> of the 6 mm diameter. The reservoirs ensured constant pressure of the adsorbate during the measurement. On opening the valve, stop-watches were set off and the elongation of the spiral was read at fixed time intervals. At the end of the measurement,

the pressure was measured and the equilibrium value of adsorption was read; hence one point of the equilibrium isotherm, isobar or isostere was thus determined. Sealing of the valve connecting the space in which the spiral was placed with the reservoirs containing adsorbate was checked before each measurement, the nodal position of the spiral in vacuo and after establishment of the given pressure being controlled. The time needed to establish the equilibrium changed from 30 to 120 min, depending on temperature and pressure. Measurements were carried out at temperatures 0, 30, and 70°C in the pressure range from 92 to 3 026 Pa.

## RESULTS AND DISCUSSION

Timofeev<sup>7</sup> reports that at adsorption in wide pores, the activation energy required for removal of the molecule from the surface and for its transfer to the infinite equals to the differential adsorption heat. On the other hand, in micropores in which the action of opposite walls interfere with each other, adsorption forces are much increased. On transport of molecules in such pores, the activation energy is higher than the adsorption heat. In case of surface diffusion, temperature dependence of diffusion coefficients is analogous to the equation given on page 3118. The activation energy is here lower than the heat of adsorption.

In previous work<sup>8</sup> we used also Eq. (2) to characterize transport of adsorbate in pores of adsorbent. Kinetics of adsorption of pentane and hexane were measured and from this isotherm the isochrones were correlated by Dubinin equation. The so obtained values of the adsorbed amount agreed well with experimental values. Deviations did not exceed 1 per cent.

In the present work 17 isothermal dependences were measured at temperatures 0, 30 and 70°C, individual pressures outside particle being within the pressure range 92–3 026 Pa. Under initial conditions of the experiments ( $a = 0$ ,  $P = 0$ ,  $\tau = 0$ ), the sample of the adsorbent was in vacuum. For a constant temperature and equilibrium pressure outside particle  $P_e$ , Eq. (4) was integrated and from the linear dependence  $\tau/a$  vs  $\tau$ , the half-time was calculated. The slope of this dependence yielded the value of equilibrium amount and this value was then compared with experimental value. Eq. (4) was derived in our previous work<sup>2</sup> and since then its applicability has been confirmed for both fast and slow processes.

The values of half-times in dependence on pressure for temperatures 0, 30, and 70°C are presented in Fig. 1 in linear coordinates obtained by rewriting Eq. (2) to logarithmic form. The least squares method gave the following parameters of Eq. (2):  $\log k = 3.8385$ ,  $n = 0.779$  and correlation coefficient  $r = 0.984$ , which in an ideal case is equal to 1. To verify the applicability of Eq. (2), we used reported<sup>9</sup> experimental half-time at 50°C  $\tau_{0.5} = 67.7$  s and calculated the value of half-time according to Eq. (2), using calculated constants  $k$  and  $n$ . The so obtained value of half-time equals to 68.9 s which represents 1.8 per cent deviation from the experimental value. Similarly also other experimental data were in good accordance with calculated half-times.

The values of structure characteristics confirmed that the active carbon Supersorbon – according to Dubinin classification – belongs to the first structure type<sup>8,10</sup>. The values of constants  $W_0 = 0.4447 \text{ cm}^3/\text{g}$  for  $70^\circ\text{C}$ ,  $0.4432$  for  $30^\circ\text{C}$ , and  $0.4493$  for  $0^\circ\text{C}$ , determined from the abscissa of the linearized Dubinin equation demonstrate good agreement, which indicates that the evacuation of the adsorbent for individual kinetic measurements was performed carefully. The error in measurements of the limit adsorption space is smaller than 1 per cent. The equilibrium isotherm and isothermal isochrones in linearized coordinates of Langmuir equation are given in Fig. 2. Its relation to the half-time is described in another work<sup>11</sup>. From the isochrones, kinetic isotherms at another pressure can be then calculated.

In contradistinction to previous works<sup>8,11-13</sup> which for correlating experimental data made use empirically of Trapnell equation derived for chemisorption, in the present work data were correlated by an analogous equation derived<sup>2</sup> earlier starting from the physical concept of the existence of pressure difference outside and inside the particle, which does not assume chemisorption and is physically substantiated.

The equation considering the above pressure change was tested and verified on different systems formed by organic vapours and sorbents of different chemical nature. The most interesting results were obtained for adsorption of industrial injurants, styrene<sup>14</sup> and ethylbenzene<sup>15</sup>, from outgases on active carbon. The results demonstrated that the use of the equation is fully justified since it yields essentially

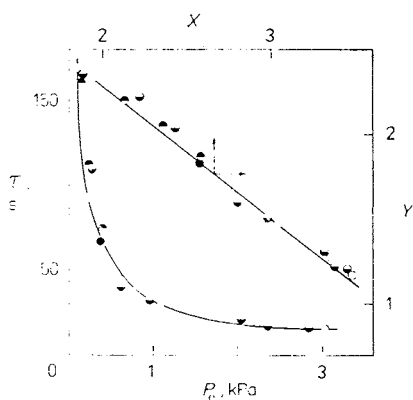


FIG. 1

Dependence of half-time of heptane adsorption on active carbon Supersorbon for different temperatures and pressures.  $\odot$   $0^\circ\text{C}$ ,  $\square$   $30^\circ\text{C}$ ,  $\triangle$   $50^\circ\text{C}$ ,  $\diamond$   $70^\circ\text{C}$ .  $X = \log P_e$  [ $P_e$ , Pa],  $Y = \log \tau_{0.5}$  [ $\tau_{0.5}$ , s]

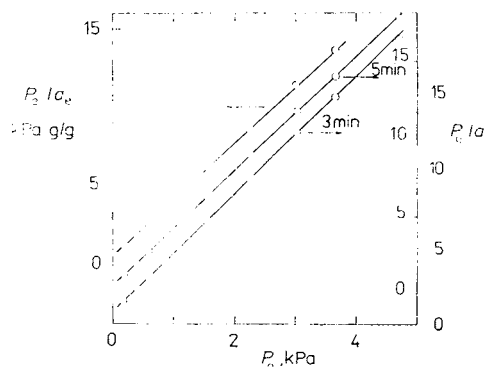


FIG. 2

Isothermal isochrones of heptane adsorption on active carbon Supersorbon in linear coordinates of Langmuir equation at  $70^\circ\text{C}$

equivalent results with experimental data, in contradistinction to the first-order equation which does not include pressure effect and gives the half-time by 100 per cent higher. Recently, the proposed equation has been tested for polymer membranes and the calculated half-times agreed well with experimental data<sup>16</sup>. The equation which takes into account pressure change can be used both for fast kinetic processes where half-time is ca 20 s as well as for slow processes where half-time ranges from minutes to hours.

The equilibrium adsorption isotherms can serve for calculating isosteric heat, eventually, based on potential theory the heat is calculated<sup>17</sup> and compared with the activation energy of adsorbate transport in pores. Judged from the value of activation energy, one can assume from works<sup>18-20</sup> that we deal here with surface diffusion, viscous flow of liquid adsorbate etc.

#### SYMBOLS

|              |  |
|--------------|--|
| $a$          | value of adsorption at a given time in unit mass of adsorbent, g/g |
| $a'$         | concentration of adsorbate in adsorption layer, mol/m <sup>3</sup> |
| $a_c$        | equilibrium value of adsorption in unit mass of adsorbent, g/g     |
| $D$          | diffusion coefficient, m <sup>2</sup> /s                           |
| $D_e$        | effective diffusion coefficient, m <sup>2</sup> /s                 |
| $E$          | activation energy, J/mol   |
| $Fo$         | Fourier dimensionless criterion                                    |
| $k$          | constant, s Pa <sup>n</sup>  |
| $k'$         | constant, g/g  |
| $k''$        | constant   |
| $K$          | constant, s/Pa   |
| $L$          | particle length, m   |
| $n$          | dimensionless constant   |
| $P$          | pressure in pores (bulk phase), Pa                                 |
| $P_e$        | equilibrium pressure outside particle, Pa                          |
| $q$          | constant, sg/g   |
| $Q_{iso}$    | isosteric heat, J/mol  |
| $r$          | correlation coefficient  |
| $R$          | particle radius, m   |
| $T$          | temperature, K   |
| $W_0$        | limit volume of adsorption space, cm <sup>3</sup> /g               |
| $\Gamma$     | dimensionless Henry coefficient                                    |
| $\pi$        | Ludolf number  |
| $\tau$       | time, s  |
| $\tau_{0.5}$ | half time, s   |
| $\varphi$    | relative adsorption  |
| $\nabla^2$   | Laplace operator   |

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