KINETIC ISOTHERMS OF CYCLOHEXANE ON ACTIVE CARBON "SUPERSORBON"*

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Dedicated to Professor E. Hála on the occasion of his 60th birthday.

The kinetic isotherm makes it possible to compute the value of diffusion coefficient and, from its temperature dependence, to calculate the activation energy of the adsorbate transfer in the adsorbent pores. The data of kinetic isotherms have been taken over from our previous paper. On the basis of comparison of the activation energy with the isosteric heats and with enthalpy of vaporization we can judge of a probable mechanism of transfer.

From the results given in this paper, it is possible to draw conclusion that the adsorbate transfer in pores of the active carbon "Supersorbon" is controlled by a surface diffusion and by a viscous flow, too.

The rate of adsorption is limited by the rate of transfer of gas molecules from the bulk phase to the adsorption centres. The mechanism of the transfer of adsorbate depends on the adsorbent structure and on the conditions under which the adsorption process takes place. There exists a pressure gradient in the adsorbent pores when adsorbing individual substances. If the pore radius r is many times greater than the mean free path of molecules, $\lambda/r \ll 1$, then the adsorbate transfer in pores is characterized by a viscous flow. In micropores, $\lambda/r \gg 1$ and then the particle flow is molecular. In this case the collisions of molecules with the pore walls are significant and the molecules are adsorbed for a certain time period. Owing to thermal motion the molecules are desorbed, no direction of motion of the desorbed molecule being preferred. The adsorbate transfer in pores can be also influenced by a surface diffusion, *i.e.* by the migration of adsorbed molecules along the surface to energetically more advantageous places or by the transfer of liquified adsorbate owing to capillary forces.

In all the above-mentioned cases, the rate of transfer depends on the pressure gradient. In different ways of the adsorbate transfer, the rate is formally described by the same equation of diffusion with the effective diffusion coefficient D_e which is established on the basis of experimental data. The temperature and pressure dependence of the diffusion coefficient enables us to determine the mechanism of the adsorbate transfer.

Diffusion is described by the Fick equation

$$\partial(a' + c)/\partial\tau = D\,\nabla^2 c\,, \qquad (1)$$

where a' is the value of adsorption at the given conditions of temperature and pressure,

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T, P, related to a unit volume of adsorbent, c the concentration of gas, τ time and D the diffusion coefficient.

The adsorption itself takes place as a rule immediately, *i.e.* the equilibrium between the bulk and adsorbed phases is established practically at once so that we can write $a' = \mathrm{f}(c)$. This expression describes the equilibrium adsorption isotherms and on inserting into Eq. (*1*) we get

$$\partial c/\partial \tau = D\,\nabla^2 c/(1 + \mathrm{f}'(c))\,, \qquad (2)$$

where $\mathrm{f}'(c) = \partial \mathrm{f}(c)/\partial c$.

Eq. (*2*) can be also written in the form $\partial c/\partial \tau = D_e\,\nabla^2 c$, where $D_e = D/(1 + \Gamma)$, where Γ is the Henry constant.

Timofeev[1] reports the solution of Eq. (*2*) for different geometric shapes of the adsorbent grains. The simple relation makes it possible to calculate the effective diffusion coefficient

$$D_e = kR^2/(\pi^2 \tau_{0\cdot5})\,, \qquad (3)$$

where k is the ratio of the radius and length of the grain, R/L.

The temperature dependence of diffusion coefficient can be expressed by the equation

$$D_e = D_0 \exp\left(-E/RT\right), \qquad (4)$$

where E is the coefficient which, for the sake of simplicity, will be called the activation energy.

In our foregoing work[2], the dependence of the half-time on pressure was expressed by the relation

$$\tau_{0\cdot5} = kP^{-n}\,, \qquad (5)$$

where k, n are constants. From the definition of isosteric heat and Eqs (*4*) and (*5*) it follows $E = nQ_{\mathrm{iso}}$.

The half-times are to be determined either on the basis of the equation derived previously[3] or by reading the time for $a/a_e = 0{\cdot}5$ from the kinetic isotherm, where a_e is the equilibrium amount at a given temperature and pressure.

RESULTS

In Fig. 1, the kinetic isotherms are given, $a = \mathrm{f}(\tau)$, of cyclohexane on active coal "Supersorbon" at a temperature of 30°C and at various pressures P_e (P_e is the equilibrium pressure at the adsorbent grain) which have been taken over from foregoing paper[4]. On the assumption which is common and necessary for solving the differential equations of diffusion, *i.e.* that the adsorption itself takes place immediately, and using the constants reported in our previous paper[4], the pressures, corresponding to the adsorbed amounts which had been determined when measuring kinetic isotherm, have been calculated from equilibrium isotherms. Under the above-mentioned assumption it is possible to write

$$\partial a'/\partial\tau = (\partial a'/\partial P)(\partial P/\partial\tau)\,. \tag{6}$$

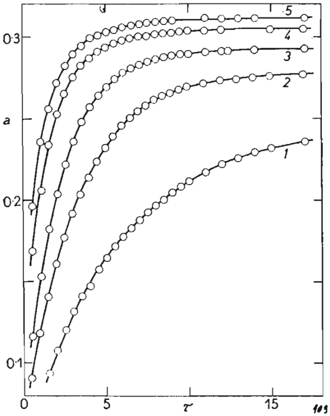

FIG. 1

Kinetic Isotherms of Cyclohexane[4] on Active Carbon "Supersorbon" at a Temperature of 30°C and Various Pressures P_e

a Adsorbed amount in grams per one gram of sorbent, τ time (min), *1* 179 Pa, *2* 611 Pa, *3* 1·27 kPa, *4* 3·29 kPa, *5* 5·85 kPa.

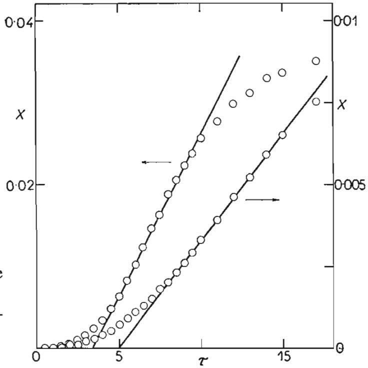

FIG. 2

Dependence of Relative Pressure *X* on Time (min)

Equilibrium pressure at the grain of adsorbent 179 Pa and 611 Pa.

From Figs 2–4 it is obvious that the relative pressure increases first in dependence on time, in the middle part is linear and in the end decreases. From the linear parts, the line slopes $dX/d\tau$ have been determined, where $X = P/P_0$ (P_0 is the saturated vapour pressure of adsorbate at a temperature of 30°C).

On the basis of the kinetic isotherms of cyclohexane on active carbon "Supersorbon" measured at the constant pressure $P_e = 3{\cdot}63$ kPa and in the temperature

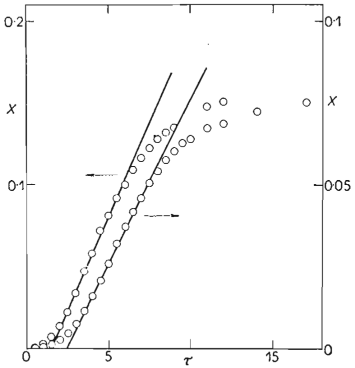

FIG. 3

Dependence of Relative Pressure X on Time (min)

Equilibrium pressure at the grain of adsorbent 1·27 kPa and 3·29 kPa.

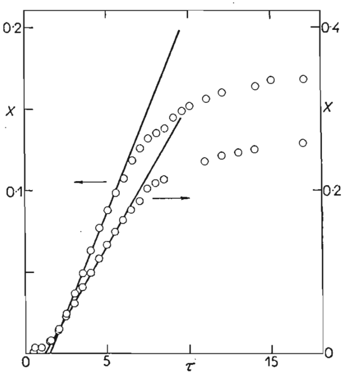

FIG. 4

Dependence of Relative Pressure X on Time (min)

Equilibrium pressure at the grain of adsorbent 3·63 kPa and 5·85 kPa.

TABLE I

Dependence of Adsorption on Isosteric Heat in Comparison with Activation Energy and Enthalpy of Vaporization

e_e, g/g	0·236	0·266	0·289	0·300	0·305
Q_{iso}, kJ/mol	52·5	51·1	55·1	55·1	56·9

range of 7 – 50°C, the slopes $dX/d\tau$ have been established and from the relation

$$\frac{d \ln (dX/d\tau_e)}{dT} = \frac{E}{RT^2} - \frac{\Delta H_v}{RT^2} \qquad (7)$$

the activation energy has been determined (ΔH_v is the enthalpy of vaporization of adsorbate, according to ref.[5] equal to 33·0 kJ/mol).

Fifteen kinetic isotherms had been measured within the range of temperatures of 7 – 50°C at a constant pressure and the mean value of the calculated half-times is 20·2 s. The values of Q_{iso} given in Table I and their comparison with the heat of vaporization and activation energy calculated in this work (17·8 kJ/mol) enable us to draw conclusion that the transfer of adsorbate in pores is accompanied both by the surface diffusion and by the viscous flow.

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