

Adsorption kinetics in microporous adsorbents*

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A method of the investigation of adsorption kinetics by means of statistical moments as well as the statement of the most important relations derived by the authors for the testing of transport mechanisms is presented. The testing of deviations from the Damköhler model is illustrated on the system benzene—activated carbon Supersorbon. The deviations found are interpreted as a diffusion process into the regions which represent the space between the transport pores. From the pressure dependence of the first statistical moment of kinetic curves conclusions are drawn on the pressure dependence of diffusion coefficient in the regions between the transport pores.

Описывается способ исследования кинетики адсорбции с помощью метода статистических моментов и приводится обзор наиболее важных соотношений, которые авторы вывели для контроля механизмов переноса. Определение отклонений от модели Дамкелера демонстрируется на системе бензол—активированный уголь Суперсорбон. Полученные отклонения объясняются диффузионными процессами в области, которые образованы пространством между транспортными порами. На основе зависимости первого статистического момента кинетических кривых от давления делаются выводы о зависимости диффузионного коэффициента от давления в областях между транспортными порами.

The concept of adsorption kinetics comprises the complex of the rate processes which take place during the establishment of adsorption equilibrium. The intricacy of these problems consists mainly in the fact that the rate processes take place in the field of adsorption forces. The investigation of adsorption kinetics provides data for the prediction of the efficiency of adsorption beds and on the other hand it gives information important for the preparation of new adsorbents as well as the optimization of their structure from the kinetic point of view.

The topic of this study is the investigation of the internal kinetics of the adsorption of gases and vapours which includes the transport phenomena taking place in the space between the surface of adsorption granule and adsorption site. The

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transport of the adsorbate molecules in the space between granules is beyond the scope of the present study because these problems are connected mainly with the hydrodynamics of the system. It is the phenomenological approach that has been used to describe the systems investigated. This approach is in conformity with the prevailing experimental technique which provides results by the measurements of macroscopic quantities such as pressure, mass flow, *etc.*

Theoretical

It was shown previously by one of the authors [1] that in some cases the process of the uptake to adsorption equilibrium cannot be described by a simple diffusion scheme proposed by Damköhler [2]. In this model it is postulated that the overall rate of the process is determined merely by a diffusion transport of the adsorbate molecules within a uniform system of transport pores of adsorbent. It is evident that the adequacy of this model depends on a number of factors, especially on the structure of the adsorbent itself. However, for some adsorbents, *e.g.* zeolites and ion-exchange resins a bidisperse structure of the porous system plays a role in the kinetics of adsorption. The first attempts to interpret the kinetic data by means of the models involving more than one diffusion rate step were made [3] with the systems mentioned above. Though the solutions are relatively simple for the Damköhler diffusion model, more complicated rate schemes lead to intricate expressions the use of which is problematic. Since we had found that the Damköhler model is not a good representation of the experimental data even for such a system as activated carbon—benzene we used a new method to analyse the mechanisms of adsorption kinetics. In this method the statistical moments of kinetic curves [4—7] are used for the characterization of the overall kinetics. It has been shown that this method provides very simple relationships for the Damköhler model. They express the connection between the statistical moments of kinetic curves and diffusion coefficients as well as the other basic variables of the experiment, *e.g.* the characteristic dimensions of the adsorbent granules, their shape factor, the value of the constant characterizing a linear adsorption isotherm or the curvature of a nonlinear adsorption isotherm, *etc.* The merit of this method consists in its ability to analyze rate mechanisms involving several rate steps [8—10]. A more detailed description of the method is presented below and the most important results are surveyed in the following paragraphs.

We obtain experimentally (*e.g.* gravimetrically) a kinetic curve, *i.e.* the time dependence of the relative saturation $\gamma(t)$ of adsorbent granule by adsorbate. This quantity is defined by eqn (1)

$$\gamma(t) = \frac{\Delta g(t)}{\Delta g(\infty)}, \quad (1)$$

where $\Delta g(t)$ and $\Delta g(\infty)$ is the change in weight of the adsorbent granule corresponding to time $t = t$ and $t \rightarrow \infty$, respectively.

The statistical moments of the n -th order of a kinetic curve are then given by eqn (2)

$$\lambda_n = \int_0^{\infty} \frac{d\gamma}{dt} t^n dt. \quad (2)$$

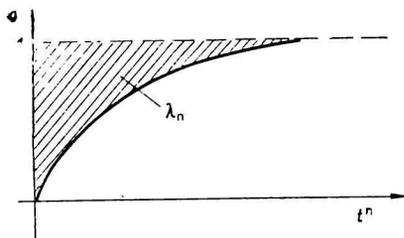


Fig. 1. Kinetic curve in coordinates γ vs. t^n .

The shaded area represents the value of λ_n .

The values of statistical moments may be easily evaluated from the kinetic experiments when a step-change in concentration is brought to the surface of adsorption granule at the time $t = 0$. As obvious from Fig. 1, the corresponding values of moments equal the area bounded by the kinetic curve plotted in coordinates γ vs. t^n , the axis of ordinates, and the straight line $\gamma = 1$. In the investigation of adsorption kinetics we have been able for the time being to manage with the first statistical moment which may be determined with a sufficient accuracy by numerical integration or by weighing the corresponding areas.

First, we solved a few kinetic problems by the moment method assuming that the rate of process was controlled by diffusion in the transport pores. The pore structure is supposed to be homogeneous and isotropic. We used the simplified model according to which the driving force of the process is the concentration gradient in the volume of these pores. Then the adsorption kinetics is described by the equation

$$\frac{\partial c}{\partial t} + \frac{\partial a}{\partial t} = \frac{\partial c}{\partial t} f'(c) = \text{div}(D \text{grad } c), \quad (3)$$

where c stands for the concentration of sorbate in the volume of transport pores, a is the corresponding concentration of the adsorbate bound to the solid skeleton of adsorbent, $f'(c)$ is the slope of adsorption isotherm, and D is the diffusion coefficient of a given component in transport pores.

The values of statistical moments found theoretically for a few shapes of particles assuming that the adsorption isotherm is linear and the diffusion coefficient inde-

Table 1

Values of dimensionless statistical moments for linear and extremely convex adsorption isotherm

Geometry of granule	Sphere	Cylinder			Infinite plate
		$L/R = 2$	$L/R = 4$	$L/R = \infty$	
$(A_1)_0 = \frac{1}{K} \frac{D}{R^2} \lambda_1$	$1/15 = 0.0667$	0.0751	0.0995	$1/8 = 0.1250$	$1/3 = \bar{0.3}$
$(A_1)_\infty = \frac{c_0}{a_0} \frac{D}{R^2} \lambda_1$	$1/30 = 0.0\bar{3}$			$1/16 = 0.0625$	$1/6 = \bar{0.16}$

pendent of concentration are given in Table 1. The symbol λ_1 denotes the first statistical moment of kinetic curve, $(\lambda_1)_0$ is the corresponding dimensionless quantity, K is the slope of adsorption isotherm, R is the radius of a spherical or cylindrical particle or the half-thickness of a particle in the form of an infinite plate, and L is the length of a particle in the form of a finite cylinder.

Furthermore, we investigated the effect of nonlinearity of adsorption isotherm. For a rectangular isotherm described by the relations

$$\begin{aligned} a &= 0 \quad \text{for } c = 0, \\ a &= a_0 \quad \text{for } c > 0 \end{aligned} \tag{4}$$

we found for three shape factors ($\nu = 1$, infinite plate; $\nu = 2$, infinite cylinder; $\nu = 3$, sphere) the relationship [6]

$$(\lambda_1)_\infty = \frac{1}{2} (\lambda_1)_0, \tag{5}$$

where $(\lambda_1)_0$ is the value of the dimensionless moment for linear adsorption isotherm and $(\lambda_1)_\infty$ is the corresponding value for the isotherm defined by relations (4).

We performed a more detailed investigation of the effect of the form of isotherm on the first moment for the particles showing the form of an infinite plate a for the Langmuir adsorption isotherm. On the basis of a numerical solution [7] we found the following relationship for the first statistical moment

$$\lambda_1 = (\lambda_1)_\infty (2 + b c_0) (1 + b c_0)^{-1}, \tag{6}$$

where c_0 is the increase in concentration on the outer surface of granule for a step-wise change in concentration and b is the constant of the Langmuir isotherm written in the form

$$a = a_\infty b c (1 + b c)^{-1}. \tag{7}$$

We found a different relationship for the identical system in the case of desorption. From numerical calculations [11] it follows that in the range $b c_0 \in \langle 0, 10 \rangle$ the variation of λ_1 may be approximately described by the linear relationship

$$\lambda_1 = 0.3 + 0.2 b c_0. \tag{8}$$

The moment method proved to be the most useful for the investigation of systems with polydisperse porous structure. In the following the resulting relationships derived for a typical bidisperse model of globular structure (Fig. 2) will be presented.

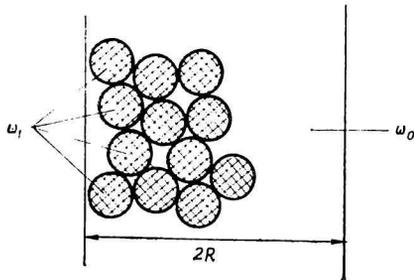


Fig. 2. Adsorbent particle ω_0 in the form of an infinite plate of the thickness $2R$ with bidisperse porous structure. The hatching of microregions represents the inside porous structure of the region ω_1 .

In this simplified case, a model of adsorbent represented by an agglomerate of the microregions of identical shape and size with its proper porous structure has been considered. In Fig. 2 the system of all microregions is denoted by the symbol ω_1 . The symbol ω_0 stands for the volume of the whole particle, the difference $\omega_0 - \omega_1$ thus corresponding to the macroporosity. To test the transport mechanism in bidisperse system the following formula was derived [9, 10]

$$\lambda_1^{\omega_0} = \frac{K \varphi}{r(\nu + 2) D \varphi} R^2 + \lambda_1^{\omega_1}, \quad (9)$$

where $\lambda_1^{\omega_0}$ is the first statistical moment related to the transport of adsorbate within the particle as a whole. The symbol $\lambda_1^{\omega_1}$ stands for the first statistical moment of a kinetic curve provided the transport in macroporosity is very rapid when compared with the transport into microregions. φ represents the volume of the region $\omega_0 - \omega_1$ per one gram of adsorbent. The meaning of other symbols is equal to that used previously.

From eqn (9) it is evident that the relationship between the first moment of kinetic curve and R^2 is represented by a straight line which cuts off a non-zero intercept on the axis of ordinates provided the mass transport takes place in both macro- and microporosity.

Results and discussion

We applied the equations given in the theoretical part of this paper to the investigation of the system benzene vapour—activated carbon Supersorbon. The kinetic curves were obtained by gravimetric measurement at constant pressure of the adsorbate vapour by using the successive pressure steps [5]. To test the transport mechanism and explain the deviations from the Damköhler model mentioned earlier [1, 12], we used relationship (9) which was correlated by the straight line

$$y = b_0 + b_1 x, \quad (10)$$

where b_0 and b_1 are the corresponding estimates of the intercept and slope of the dependence $\lambda_1^{\omega_0}$ on $K \varphi R^2$ (see eqn (9)). For these measurements the adsorbent

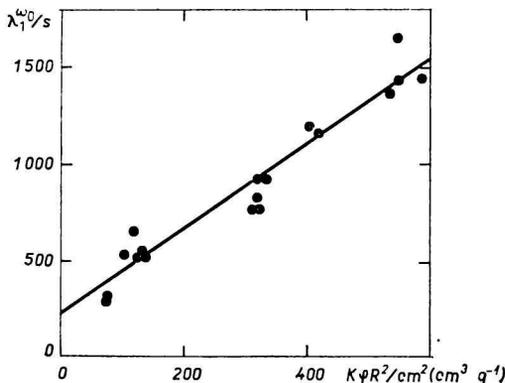


Fig. 3. $\lambda_1^{\omega_0}$ as a function of $K \varphi R^2$ for sample 1 and pressure step Δp_5 .

granules shaped into the form of an infinite plate were used since this geometry made it possible to realize the dependence on the dimension of a particle. It is evident that the equations derived are applicable though activated carbon does not show globular structure; its structure is rather complementary to the globular one. Actually, it may be expected that the transport in ω_1 parallel with the transport in $\omega_0 - \omega_1$ is negligible with respect to the last one. Just in this case the influence of the term $\lambda_1^{\omega_1}$ is strongly expressed. The actual structure of active carbon is merely reflected in a different shape factor of the region ω_1 . The testing of the model was carried out for two particles of adsorbent denoted as sample 1 and sample 2. In Fig. 3, an example of the experimental dependence of $\lambda_1^{\omega_1}$ on $K \varphi R^2$ is shown.

Table 2

Approximation of the relationship between $\lambda_1^{\omega_1}$ and $K \varphi R^2$ by the straight line
 $y = b_0 + b_1 x$

Sample	Pressure step	b_1	s_{b_1}	b_0	s_{b_0}	Hypothesis
1	Δp_1	0.44	0.05	700	420	accepted
	Δp_2	0.87	0.04	440	90	rejected
	Δp_3	1.43	0.09	300	92	rejected
	Δp_4	1.96	0.08	280	50	rejected
	Δp_5	2.20	0.15	220	51	rejected
	Δp_1	0.44	0.09	800	810	accepted
	Δp_2	0.35	0.05	800	100	rejected
	Δp_3	0.70	0.10	380	110	rejected
	Δp_4	0.72	0.10	200	57	rejected
	Δp_5	0.92	0.17	140	28	rejected

s_{b_1} and s_{b_0} are the estimates of respective standard deviations.

$\Delta p_1 = 0.01 - 0.88$ torr, $\Delta p_2 = 0.96 - 1.90$ torr, $\Delta p_3 = 2.03 - 5.37$ torr, $\Delta p_4 = 5.65 - 10.94$ torr, $\Delta p_5 = 11.63 - 18.55$ torr.

The results of measurements as a function of pressure are summarized in Table 2. The correlation of experimental data was performed by the least-squares method and besides, the value of the intercept b_0 was tested in order to decide whether its existence was not due to an experimental error only. As obvious from the last column of Table 2, except the first pressure step a non-zero value of the intercept b_0 corresponding to the term $\lambda_1^{\omega_1}$ was proved on the significance level of 0.01. The fact that for the first pressure range the testing assigns a very low probability to the existence of the non-zero intercept does not mean that this intercept could not acquire higher values but it suggests that for the lowest pressures the contribution of the transport in microregions is negligible in comparison with the contribution of diffusion in macrostructure.

Besides, an important result appears to be the determination of the pressure dependence of the term $\lambda_1^{\omega_1}$ from which the pressure dependence of the effective diffusion coefficient within microregions may be obtained. On the basis of the assumption

of a diffusion transport within microregions we may write the following equation for $\lambda_1^{\omega_1}$

$$\lambda_1^{\omega_1} = \frac{A}{D_{\text{eff}}} \varrho^2, \quad (11)$$

where A is a constant related to the geometry of the region ω_1 , ϱ is the characteristic dimension of microregions, and D_{eff} is a diffusion coefficient characterizing the transport into microregions. We assume an inert adsorbent and therefore neither A nor ϱ depends on pressure. Thus, the dependence of $\lambda_1^{\omega_1}$ on pressure reveals that D_{eff} is a nondecreasing function of pressure in the range of pressures investigated. The problem of pressure dependence remains open for the time being. Recently, the workers in the department of M. M. Dubinin in Moscow started to tackle this problem. For a similar system (*n*-pentane—activated carbon in ground form) they obtained a dependence of diffusion coefficient on pressure with a character opposite to the one determined in our measurements [13]. For the present, we have not succeeded in our effort to calculate the absolute value of D_{eff} and interpret it because this problem is connected with the investigation of the topology and structure of the region ω_1 . The solution of this problem is the subject of our present research.

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