Study of the change in the mass-transfer coefficients in differential bed of a sorbent during its saturation with adsorbate*

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Two methods chosen with respect to the experimental course of adsorption isotherm were used for the calculation of the mass-transfer coefficient during the saturation of sorbent. Using the experimental relationships between the concentration of adsorbate in adsorbent and time measured for different systems by those two methods the curves representing the mass-transfer coefficient as a function of time and sorbent saturation were calculated and drawn. It was proved that the value of the mass-transfer coefficient changed during saturation for all systems investigated. This value decreased with an increasing saturation of the sorbent due to the increasing resistance to the mass transfer in the solid phase.

Были использованы два подхода для расчета коэффициента массопередачи во время адсорбции, которые были выбраны в связи с экспериментально установленной формой изотермы адсорбции. Из экспериментальным путем измеренных зависимостей количества адсорбированного вещества от времени для разных систем, были вычислены и нарисованы кривые зависимости коэффициента массопередачи от времени и от адсорбированного количества. Было показано, что для всех исследуемых систем значение коэффициента массопередачи во время адсорбции изменяется, причем оно понижается с повышением адсорбированного количества вследствие повышения сопротивления массопередачи в гранулах сорбента.

This paper deals with the problems concerning the variability of the mass-transfer coefficient during the saturation of sorbent. The study is based on the reasonable physical assumption that the value of the partial mass-transfer coefficient in a solid phase changes during the saturation of sorbent. For the mass transfer in gaseous phase the frequently used idea of a constant coefficient was adopted [1, 2]. With respect to the character of adsorption isotherm in a system investigated experimentally and the possibility of using one of the equations of adsorption isotherm for the description, two methods were applied for the calculation of the mass-transfer coefficient during saturation.

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The first method is based on the assumption of a linear course of the sections of adsorption isotherm for two subsequent experimental points of the kinetic curve. The expression of the equation of adsorption kinetics is based on the ideas of the film theory according to which the rate of adsorption in a differential bed is described by the equation

$$\frac{\mathrm{d}a}{\mathrm{d}t} = k_\mathrm{w}(C_0 - C^*). \tag{1}$$

The assumption of linearity of the sections enables us to write for the adsorption isotherm in a given interval

$$a_i - a_{i-1} = \Gamma_i(C_i^* - C_{i-1}^*). \tag{2}$$

By introducing dimensionless variables

$$q = \frac{a}{a_0} \quad \text{and} \quad Q^* = \frac{C^*}{C_0} \tag{3}$$

and substituting (2) and (3) into (1) the solution of the equation of the rate of adsorption is given by eqn (5) for the boundary conditions qualified by expressions (4)

$$q = q_{i-1}, \qquad Q^* = Q_{i-1}^*, \qquad t = t_{i-1},$$

$$q = q_i, \qquad Q^* = Q_i^*, \qquad t = t_i; \tag{4}$$

$$\frac{k_{\mathrm{w}_i} \Delta t_i}{\Gamma_i} = \ln\left(1 + \frac{\Delta Q_i^*}{1 - Q_i^*}\right). \tag{5}$$

For the quantities Δt_i and ΔQ_i^* it may be written

$$\Delta t_i = t_i - t_{i-1},$$

$$\Delta Q_i^* = Q_i^* - Q_{i-1}^*.$$

The equation has been solved providing that $\Gamma_i = \text{const}$ in each interval $\langle q_{i-1}, q_i \rangle$ and the kinetic curve goes through all experimental points. According to eqn (5), it is possible to determine the average values of the mass-transfer coefficient in every time interval Δt_i corresponding to the values ΔC_i^* or ΔQ_i^*.

The merit of this method consists in its simplicity and universality as regards the direct determination of the sections from the experimental equilibrium curve.

In the second method of calculation the kinetic equation of vapour adsorption on porous sorbents with the adsorption equilibrium described by the Brunauer, Emmett, and Teller equation [3] is employed

$$\frac{\mathrm{d}Q}{\mathrm{d}t} = \frac{k_\mathrm{w}}{\Gamma} \frac{(1-Q)(1-p_\mathrm{r}Q)^2[1+(c-1)p_\mathrm{r}Q]^2}{(1-p_\mathrm{r})[1+(c-1)p_\mathrm{r}][1+(c-1)p_\mathrm{r}^2Q^2]}. \tag{6}$$

The analytical solution of eqn (6) for the boundary conditions

$$t = 0, \qquad Q = 0;$$

$$t = t_i, \qquad Q = Q_i; \tag{7}$$

gives the following equation for the calculation of the coefficient k_{w_i}

$$k_{w_i} = \frac{\Gamma_i}{t_i} \frac{k_1 k_2}{c} \left[\frac{1}{1 + k_1 p_r Q_i} - \frac{1}{k_3} \ln (1 + k_1 p_r Q_i) \right] -$$

$$- \frac{k_3}{c} \left[\frac{1}{1 - p_r Q_i} + \frac{1}{k_2} \ln (1 + p_r Q_i) \right] + \frac{1 + k_1 p_r^2}{k_2 k_3} \ln (1 - Q_i) + 1, \qquad (8)$$

where $k_1 = c - 1$, $k_2 = p_r - 1$, and $k_3 = 1 + k_1 p_r$. This equation enables us to calculate the average value of k_{w_i} in the i-th experimental point of the kinetic curve.

The assumption of the variability of the mass-transfer coefficient and the calculation of the average coefficients by means of both methods were verified by an abundant experimental material. The kinetic curves were measured for the systems benzene—active carbon HS-43, CS_2—active carbon HS-43, benzene—molecular sieve Nalsit 13X, and benzene—synthetic faujasit NaY in a wide range of concentrations and flow rates.

Experimental and results

The measurements were performed at 20°C using active carbon HS-43 with the structure and physical properties as described before [4]. The active carbon was in the form of small balls with 4 mm diameter. The adsorption isotherm of CS_2 and benzene on this sorbent was determined by the dynamic method and the results were expressed in terms of the B.E.T. equation. The values of the constants a'_m and c for the systems investigated as well as the corresponding concentration intervals of validity are given in Table 1.

The adsorption isotherms on molecular sieves of the type Nalsit 13X and synthetic faujasit NaY were determined at 20°C. The diameter of the sieve meshes of a spherical shape was 3 mm.

Because of the character of adsorption isotherms of these systems it is not possible to describe them in terms of the B.E.T. equation and the values obtained from experimental isotherms are more suited for the calculation of the mass-transfer coefficient. These isotherms are shown in Fig. 1.

The adsorption kinetics was measured by the dynamic method on a bed of one grain thickness in such a way that the effect of adsorption dynamics in the bed on the rate of the process was eliminated. The working conditions were chosen within the range important for practical application. The concentration of gas varied from 8 to 50 g m^{-3} while the flowing rate outside the bed was between 40.0 and 80.0 cm s^{-1}. The procedure described previously [4, 5] was modified and used for experiments [5, 6]. The measure-

Table 1

Values of the constants a'_m and c

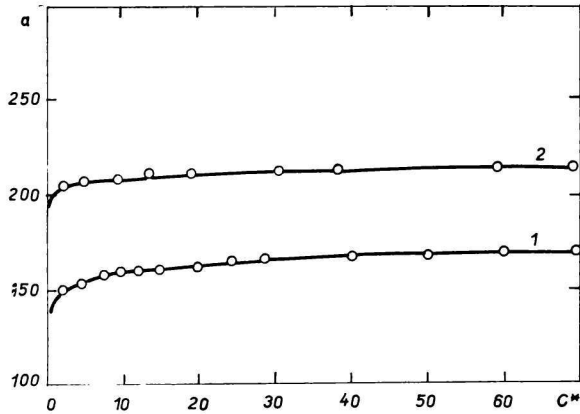| System	a'_m mM g^{-1}		Interval of validity g m^{-3}
HS-43 — C_6H_6	4.638	130.81	2.0 — 60.0
HS-43 — CS_2	4.299	327.36	7.1 — 21.1
	5.594	110.21	21.1 — 51.1

Fig. 1. Adsorption equilibria of benzene on a molecular sieve of the type Nalsit 13X and faujasit NaY at 20°C.
1. Nalsit 13X; *2.* faujasit NaY.

ments were performed in a stream of nitrogen serving as a carrier gas at 20°C and the concentration of adsorbate in the carrier gas was determined by means of an interfero-meter. The losses in pressure in individual parts of apparatus were taken into account
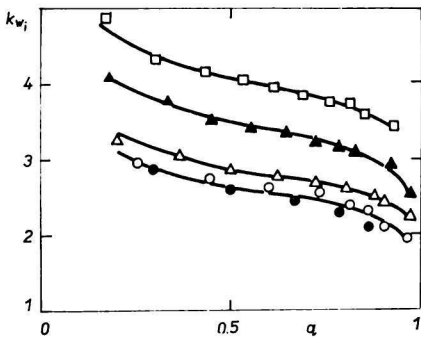

Fig. 2. Mass-transfer coefficient k_{w_t} as a function of the relative concentration of adsorbate in adsorbent for the system carbon dioxide—active carbon HS-43.

k_{w_t} is expressed in l g^{-1} min^{-1}.

□ $C_0 = 8.0$ g m^{-3}, $\Theta = 0.649$; ▲ $C_0 =$ $= 10.0$ g m^{-3}, $\Theta = 0.664$; △ $C_0 =$ $= 15.0$ g m^{-3}, $\Theta = 0.740$; ○ $C_0 =$ $= 25.0$ g m^{-3}, $\Theta = 0.860$; ● $C_0 =$ $= 30.0$ g m^{-3}, $\Theta = 0.939$:
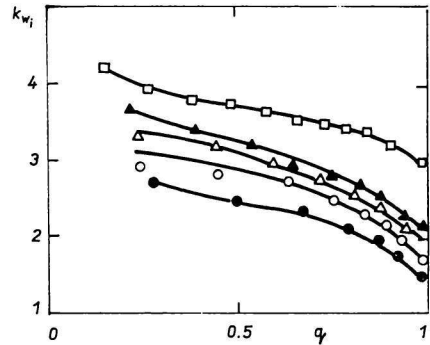
$w = 80.0 \pm 0.1$ cm s^{-1}.

Fig. 3. Mass-transfer coefficient k_{w_t} as a function of the relative concentration of adsorbate in adsorbent for the system benzene—active carbon HS-43.

□ $C_0 = 10.0$ g m^{-3}, $\Theta = 0.796$; ▲ $C_0 =$ $= 20.0$ g m^{-3}, $\Theta = 0.935$; △ $C_0 =$ $= 25.0$ g m^{-3}, $\Theta = 0.978$; ○ $C_0 =$ $= 30.0$ g m^{-3}, $\Theta = 1.009$; ● $C_0 =$ $= 40.0$ g m^{-3}, $\Theta = 1.073$.

$w = 80.0 \pm 0.1$ cm s^{-1}.

for the calculation of the real volumetric rate. This quantity was calculated for the pressure and temperature in the column with sorbent.

The evaluation of the results has shown that eqn (8) is applicable to the systems benzene—active carbon HS-43, CS_2—active carbon HS-43 in the concentration ranges chosen, where the B.E.T. equation of adsorption isotherm satisfactorily describes the course of experimental isotherm. The Figs. 2 and 3 show the change in the mass-transfer
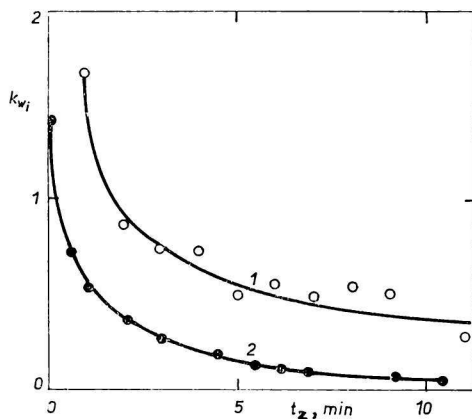

Fig. 4. Mass-transfer coefficient k_{w_i} as a function of time $t_z = k\ t$. Initial concentration of adsorbate $C_0 = 20.0$ g m^{-3}, the flowing rate outside bed $w = 40.0 \pm 0.1$ cm s^{-1}. 1. Benzene—molecular sieve Nalsit 13X; 2. benzene—molecular sieve faujasit NaY.

coefficient during saturation (curves expressing k_{w_i} as a function of q) for five arbitrarily chosen initial concentrations C_0 in gaseous mixture. The plots demonstrate the decrease in k_{w_i} with increasing value of q and the degree of covering of the surface Θ.

The second method involving the calculation of the values of the coefficients by means of eqn (5), too, proved to be suited for the evaluation of the measurements carried out with all systems investigated. The values of the coefficients obtained by both methods were found to be in good agreement. The $k_{w_i}-t$ plots showed analogous course of the change in the coefficient and the slope of the curves was comparable.

The mass-transfer coefficients in the systems benzene—Nalsit 13X and benzene—synthetic faujasit NaY could be evaluated only by means of eqn (5) because the B.E.T. equation of adsorption isotherm was not suited for the description of adsorption equilibria in these systems. The mass-transfer coefficients are plotted against time for these systems in Fig. 4. The k_{w_i} values represent the average values for the interval q_i, q_{i-1} or t_i, t_{i-1} and are, therefore, plotted in graphical representations as functions of the mean value of the corresponding time interval. If the relationships between k_{w_i} and t_z obtained from the kinetic measurements on a differential bed of sorbent with the initial concentration of adsorbate in gas $C_0 = 20$ g m^{-3} are compared for both systems, it appears that, on the average, the numerical values obtained for the molecular sieve NaY are lower than those obtained for the sieve 13X. The resistance to the mass transfer starts to rise rapidly at the very beginning of sorption process. This phenomenon is related with the character of sorption on active surface which is confirmed by the course of adsorption isotherm. For the system benzene—Nalsit 13X k_{w_i} decreases (or the resistance to mass transfer increases slower) and consequently the rate of adsorption is higher than it is on the sieve NaY. This is also confirmed by data given in Table 2 where the values of q and t obtained under equal conditions for both the systems are confronted.

Table 2

Values of q and t for the systems benzene—Nalsit 13X and benzene—faujasit NaY

C$_6$H$_6$—Nalsit 13X				C$_6$H$_6$—faujasit NaY			
q	t/min	q	t/min	q	t/min	q	t/min
0.220	1	0.732	7	0.139	1	0.731	17
0.333	2	0.805	8	0.277	3	0.794	21
0.431	3	0.870	9	0.424	6	0.819	23
0.528	4	0.935	10	0.529	9	0.882	29
0.593	5	0.951	11	0.601	11	0.916	34
0.667	6	—	—	0.685	15	0.950	39

$C_0 = 20$ g m^{-3}, $w = 40$ cm s^{-1}.

The values of k_{w_i} calculated according to eqn (8) for a differential bed of active carbon HS-43 and two kinds of vapour, *i.e.* carbon disulfide and benzene, are represented in Fig. 5. The data calculated from the kinetic curves for the initial concentration of adsorbate $C_0 = 50$ g m^{-3} and equal working conditions were compared. It is obvious from the relationship between k_{w_i} and q that, in general, higher values of the mass-transfer coefficient are attained in the system CS$_2$—active carbon HS-43 while the decrease in these values is more moderate with increasing q. This indicates the dependence of k_{w_i} on the effective diameter of molecule.

The film model [7] describing the rate of sorption on the basis of eqn (1) was used for expressing the rate of the process which takes place on one grain of sorbent. The undoubted
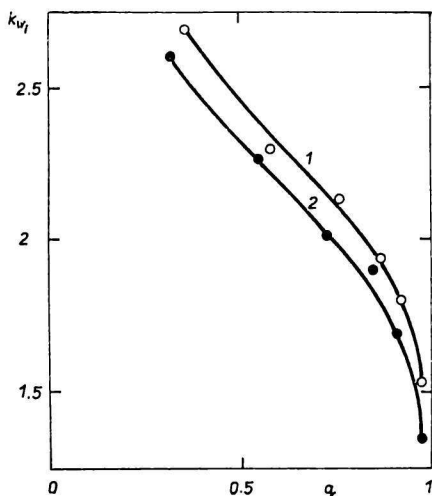

Fig. 5. Mass-transfer coefficient k_{w_i} as a function of the relative concentration of adsorbate in adsorbent for the systems benzene—active carbon HS-43 and carbon disulfide—active carbon HS-43.
1. Carbon disulfide—active carbon HS-43;
2. benzene—active carbon HS-43.
$C_0 = 50.0$ g m^{-3}, $w = 80.0 \pm 0.1$ cm s^{-1}.

virtue of this model consists in a more simple expression and solution of the equation. When applied to a given system, it becomes, under simplifying assumptions generally used, comparable with the models regarded as more exact. The results obtained by measuring the rate curves and the relationship between q and t_z for a differential bed and one grain in the system CS_2—HS-43 at equal initial concentration of the adsorbate in gas $C_0 = 20$ g m^{-3} are shown in Fig. 6. The character of the relationships appears to be
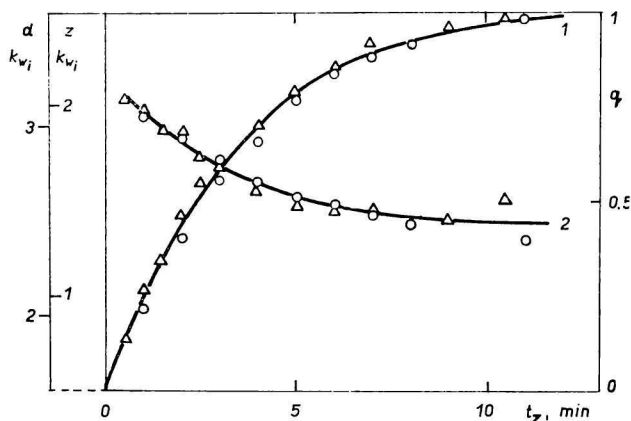

Fig. 6. Kinetic curve for the adsorption of carbon disulfide on active carbon HS-43 and variation of the mass-transfer coefficient with time t_z for a differential bed ($k_{w_i}^d$) and one grain of sorbent ($k_{w_i}^z$).
○ Differential bed; △ one grain.
1. $f(q, t_z)$; *2.* $f(k_{w_i}, t_z)$.
$C_0 = 20.0$ g m^{-3}, $w = 80.0 \pm 0.1$ cm s^{-1}.

equal and on transforming the time coordinate, all experimental points fit approximately in one curve. The values of k_{w_i} calculated from eqn (8) were plotted in the same graph. The character of these relationships is approximately equal for both the systems investigated. It is evident that the values of k_{w_i} decrease with increasing relative saturation of the sorbent q. The numerical values of k_{w_i} obtained for one grain of sorbent are lower in the whole range which may be due to the effect of the hydrodynamic conditions under which the measurements were performed.

Symbols

a concentration of adsorbate in adsorbent referred to a volume unit of bed
a_0 equilibrium concentration of adsorbate in adsorbent corresponding to C_0 referred to a volume unit of bed
a_i concentration of adsorbate in adsorbent in the i-th experimental point
C^* equilibrium concentration of adsorbate in gas corresponding to the concentration of adsorbate in adsorbent
C_0 concentration of adsorbate

c constant in the B.E.T. equation of adsorption isotherm

k_w overall mass-transfer coefficient

p partial vapour pressure of adsorbate

p_r p/p_s

p_s pressure of saturated vapour of adsorbate

Q relative concentration of adsorbate in gas

Q^* relative equilibrium concentration of adsorbate in gas

Q_i relative concentration of adsorbate in gas corresponding to the value of a_i

q relative concentration of adsorbate in adsorbent

q_i relative concentration of adsorbate in adsorbent attained in the i-th experimental point

t time

t_i time necessary for the saturation of adsorbent to the value of q_i

t_z time defined by the relation $t_z = k\,t$ where k is a constant

w flowing rate of gaseous mixture outside the bed

Γ ratio a_0/C_0

Γ_i ratio $(a_i - a_{i-1})/(C_i^{\cdot} - C_{i-1}^{\cdot})$

Θ degree of covering of surface

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