Kinetics and Dynamics of Gas and Vapour Adsorption on Solid Sorbents. II.
Adsorption Dynamics in Fixed Bed at Constant Value of the Overall Mass-Transfer Coefficient and at Negligible Influence of Longitudinal Diffusion

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This paper presents the equations of adsorption dynamics in fixed bed which are valid on condition that the overall mass-transfer coefficient is constant and the influence of longitudinal diffusion negligible. In this connection, some analytical expressions describing the limiting shape of adsorption isoplanes have been deduced for the validity region of the Freundlich as well as of the Langmuir equation of adsorption isotherm.

In the preceding paper [1], the equations of material balances valid for isothermal processes in fixed as well as continuous column have been expressed in dimensionless form

$$\frac{\varepsilon_v}{\Gamma_{0v}} \cdot \frac{\partial Q}{\partial \tau} + \frac{\partial Q}{\partial H} + \frac{\partial q}{\partial \tau} - \frac{1}{K_m} \cdot \frac{\partial q}{\partial H} = \Omega_0 \frac{\partial^2 Q}{\partial H^2} \cdot \tag{1}$$

$$\frac{\partial q}{\partial \tau} - \frac{1}{K_m} \cdot \frac{\partial q}{\partial H} = \Phi(Q - Q^*) \cdot \tag{2}$$

The boundary conditions are

$$Q(0,\tau) = 1, \tag{3}$$

$$q(H_k,\tau) = q_1 = \text{const}$$

for $\tau \geqslant 0$.

The initial conditions are

$$Q(H,0) = 0,$$

$$q(H,0) = 0 \tag{4}$$

for $0 \leqslant H \leqslant H_k$.

Also the equations of equilibrium curves in dimensionless coordinates $q-Q$ have been deduced for some types of adsorption isotherms. On the basis of these relationships, the equations of adsorption dynamics in fixed column are expressed on condition that the overall mass-transfer coefficient during saturation is constant and the influence of longitudinal diffusion is negligible.

In fixed bed is $v = 0$ and thus $1/K_m = 0$. The assumption of negligible influence of the longitudinal diffusion is bound to the condition $\Omega_0 = 0$. Since it is supposed that $k_v = $ const, it is suited to define the characteristic value of the mass-transfer coefficient k_{0v} by the relationship

$$k_{0v} = k_v, \tag{5}$$

that means $\Phi \equiv 1$ and the equations (1) and (2) turn into a simplified form

$$\frac{\varepsilon_v}{\Gamma_{0v}} \cdot \frac{\partial Q}{\partial \tau} + \frac{\partial Q}{\partial H} + \frac{\partial q}{\partial \tau} = 0, \tag{6}$$

$$\frac{\partial q}{\partial \tau} = Q - Q^* . \tag{7}$$

The initial conditions (4) remain unchanged but instead of two boundary conditions (3) a single condition will do

$$Q(0,\tau) = 1 \quad \text{for } \tau \geqslant 0. \tag{8}$$

In general, the equation system (6, 7) with the initial condition (4) and the boundary condition (8) is to be solved by numerical methods. A general analytical solution is possible only in the case of a linear shape of adsorption isotherm, *i.e.* if $Q^* = q$; this solution has been published by several authors [2—10]. *Rosen* [11, 12] used an integral-differential equation ensuing from the description of adsorbate transport inside sorbent particles by means of the II. Fick's law to express the transfer rate for a linear course of adsorption isotherm. He published a general solution in the form of improper integral of a rather complicated function as well as numerical and graphical data allowing the calculation of relative concentration in a wide range of values of relevant dimensionless parameters.

Most technological applications of adsorption processes involve the systems in which the shape of adsorption isotherm differs considerably from a linear one. That is why these general solutions have only a limited range of applicability.

Zabežinskij, Žuchovickij, and co-workers [13—16] published the results of numerical solution of the equation system (6, 7) under the conditions (4, 8), based on the assumption that the adsorption equilibria might be expressed by the Langmuir isotherm. They also formulated the assymptotic expressions describing the course of adsorption at $t \to \infty$.

From the mathematical point of view, the problem is considerably simplified if the equilibrium curve is convex with respect to the axis q, *i.e.* if holds

$$\frac{d^2Q^*}{dq^2} > 0 . \tag{9}$$

As known [17], a state, in which the adsorption wave moves along the bed with constant velocity and does not change its shape, is established after a sufficiently long period of time in this case. It follows from the material balance of the process that this velocity is equal to the forward velocity of sorption front at equilibrium sorption and can be expressed by the following equation [17]

$$u = \frac{w}{\Gamma_{0v} + \varepsilon_v} . \tag{10}$$

To express the shape of adsorption wave, it is convenient to transform the variables in such a way that the origin of coordinate system corresponds to the instantaneous position of equilibrium adsorption front. The system of partial differential equations then turns in the limit $t \to \infty$ into a system of ordinary differential equations which are much easier to be solved. It is possible to use two variants of this transformation.

Zeldovič [18] and *Todes* [19] used the transformation of the longitudinal coordinate

$$\xi = h - u t, \tag{11}$$

which is suited to express the shape of adsorption isochrones. Since it is experimentally simpler to investigate the course of adsorption isoplanes, it is convenient to apply the second modification of the above transformation and to transform the time coordinate [20]

$$z = t - \frac{h}{u} \tag{12}$$

or in dimensionless expression

$$Z = \frac{k_{0v}}{\Gamma_{0v}} \cdot z = \tau - \left(1 + \frac{\varepsilon_v}{\Gamma_{0v}}\right) H. \tag{13}$$

By using the transformation (*13*) and the relationship

$$\lim_{\tau \to \infty} \left(\frac{\partial Q}{\partial H}\right)_Z = \lim_{\tau \to \infty} \left(\frac{\partial q}{\partial H}\right)_Z = 0, \tag{14}$$

the partial differential equations (*6, 7*) can be converted into the ordinary differential equations

$$-\frac{dQ}{dZ} + \frac{dq}{dZ} = 0, \tag{15}$$

$$\frac{dq}{dZ} = Q - Q^*. \tag{16}$$

The boundary and initial conditions (*4, 8*) with respect to

$$\lim_{\tau \to \infty} q(0,\tau) = 1 \tag{17}$$

yield the conditions

$$\lim_{Z \to -\infty} Q = \lim_{Z \to -\infty} q = 0, \tag{18}$$

$$\lim_{Z \to +\infty} Q = \lim_{Z \to +\infty} q = 1. \tag{19}$$

The solution of the equations (*15, 16*) with the boundary conditions (*18, 19*) has the form

$$q = Q, \tag{20}$$

$$Z = \int \frac{dQ}{Q - Q^*} + K. \tag{21}$$

The integration constant K in the relationship (21) may be expressed on the basis of the material balance of column

$$(a_{0v}^{\bullet} + \varepsilon_v \, C_0) \, u \, t = \int_0^{\infty} (a_v + \varepsilon_v \, C) \, \mathrm{d}h, \tag{22}$$

from which owing to the relationships (10, 12, 13, 20) the following condition may be deduced according to the procedure of Račinskij [21]

$$\int_0^1 Z \, \mathrm{d}Q = 0. \tag{23}$$

The combination of the expressions (21) and (23) affords the final expression for Z:

$$Z = \int \frac{\mathrm{d}Q}{Q - Q^*} - \int_0^1 \mathrm{d}Q \int \frac{\mathrm{d}Q}{Q - Q^*}. \tag{24}$$

The expression (24) enables us to calculate the break-through time according to the equation

$$t(Q, h) = \frac{\Gamma_{0v} + \varepsilon_v}{w} \, h + \frac{\Gamma_{0v}}{k_{0v}} \, Z(Q), \tag{25}$$

which is identical with the Šilov equation

$$t(Q, h) = K_D \, h - t_1, \tag{26}$$

where the dynamical constant reads

$$K_D = \frac{\Gamma_{0v} + \varepsilon_v}{w} = u^{-1} \tag{27}$$

and the loss time equals

$$t_1 = - z = - \frac{\Gamma_{0v}}{k_{0v}} Z(Q). \tag{28}$$

Provided that the adsorption equilibria obey the Freundlich adsorption isotherm, the equation of equilibrium curve is given by the relationship [1]

$$Q^* = q^{\frac{1}{n}}. \tag{29}$$

The condition (9) is fulfilled for every $n \in \langle 0,1)$.

After substitution of (29) into (24) and after integration, we obtain

$$Z = \frac{n}{1 - n} \ln \frac{Q^{\frac{1}{n} - 1}}{1 - Q^{\frac{1}{n} - 1}} + 1 + \frac{n}{1 - n} \int_0^1 \ln(1 - Q^{\frac{1}{n} - 1}) \, \mathrm{d}Q. \tag{30}$$

The definite integral in this equation cannot generally be expressed by means of elementary functions. It is to be expressed by means of an infinite series. The definite integral in the equation (30) can be expressed as a limit

$$\int_0^1 \ln(1 - Q^{\frac{1}{n}} - 1) \, dQ = \lim_{Q \to 1} \int_0^Q \ln(1 - Q^{\frac{1}{n}} - 1) \, dQ. \tag{31}$$

The function to be integrated is developed into a series

$$\ln(1 - Q^{\frac{1}{n} - 1}) = - \sum_{i=1}^{\infty} \frac{Q^{\frac{1-n}{n} \cdot i}}{i}, \tag{32}$$

which is uniformly convergent for every $Q \in \langle 0,1)$ and can be integrated term by term. The integration and substitution into (30) with respect to (31) gives

$$Z = \frac{n}{1 - n} \ln \frac{Q^{\frac{1}{n}} - 1}{1 - Q^{\frac{1}{n}} - 1} + 1 - \left(\frac{n}{1 - n}\right)^2 \sum_{i=1}^{\infty} \frac{1}{i\left(i + \frac{1}{n}\right)}. \tag{33}$$

For some values of n, it is possible to express Z as a sum of finite number of terms. Then the following expression is valid for every n of the form $n = m(m + 1)^{-1}$; m being a positive integer

$$Z = \frac{n}{1 - n} \ln \frac{Q^{\frac{1}{n}} - 1}{1 - Q^{\frac{1}{n}} - 1} + 1 - \frac{n}{1 - n} \sum_{i=1}^{\frac{n}{1-n}} \frac{1}{i}. \tag{34}$$

In the paper [22], there are other two solutions for $n = \dfrac{1}{3}$

$$Z = \frac{1}{2} \ln \frac{Q^2}{1 - Q^2} + \ln 2, \tag{35}$$

for $n = \dfrac{1}{4}$

$$Z = \frac{1}{3} \ln \frac{Q^3}{1 - Q^3} + \ln \sqrt{3} + \frac{\pi \sqrt{3}}{18}. \tag{36}$$

Provided that the adsorption equilibria respond to the Langmuir adsorption isotherm, the equation of equilibrium curve is given by the expression [1]

$$Q* = \frac{(1 - \Theta_0) \, q}{1 - \Theta_0 \, q}. \tag{37}$$

The condition (9) is fulfilled for every $\Theta_0 \in (0,1\rangle$. After substituting (37) in (24) and after integrating, we obtain

$$Z = \frac{1}{\Theta_0} \ln \frac{Q}{1 - Q} + \ln(1 - Q) + 1. \tag{38}$$

The analysis of experimental results has shown that the supposition of a constant overall resistance against the mass transfer is not generally fulfilled. In subsequent paper we shall therefore express the equations of adsorption dynamics in fixed bed with respect to the variability of resistance in the solid phase.

Symbols

$a_{0v}^{\bullet}$ equilibrium concentration of adsorbate in adsorbent corresponding to the concentration C_0 and referred to a volume unit of bed

C_0 concentration of adsorbate in the gas entering the column

H dimensionless coordinate

H_k dimensionless height of column

h coordinate

K integration constant in the equation *(21)*

K_D dynamical constant

K_m the slope of the operating line for the process in $Q-q$ coordinates

k_v overall mass-transfer coefficient referred to a volume unit of bed

k_{0v} the characteristic value of the overall mass-transfer coefficient referred to a volume unit of bed

n exponent in the Freundlich equation of adsorption isotherm

Q relative concentration of adsorbate

$Q*$ relative equilibrium concentration of adsorbate

q relative concentration of adsorbate in adsorbent

q_1 relative concentration of adsorbate in adsorbent at the top of column

t time

t_1 loss time according to Šilov

u the rate of transfer of the equilibrium sorption front

w linear gas velocity based on empty column cross-section

Z dimensionless transformed time

z transformed time

Γ_{0v} ratio $a_{0v}^{\bullet}/C_0$

ε_v porosity of the adsorbent bed

Θ_0 equilibrium degree of covering of active surface at the concentration C_0

ξ transformed coordinate

τ dimensionless time

Ω_0 criterion characterizing the part of longitudinal diffusion in the material balance of a volume element of bed

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