ISOTHERMAL DYNAMICS OF SORPTION IN POROUS MEDIA FOR A NONLINEAR ISOTHERM

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The invariant solutions of the equations of sorption dynamics are obtained in the externally diffusive kinetic range for an s-type isotherm.

The isothermal dynamic characteristics of sorption in porous, nondeformable media may be described in the externally diffusive kinetic range by the material-balance equation (allowing for longitudinal mixing), the equation of externally diffusive sorption kinetics in porous grains, and the initial and boundary conditions:

$$\frac{\partial c}{\partial z}+\frac{\partial q}{\partial t}=\alpha\frac{\partial^2 c}{\partial z^2},\quad \gamma\frac{\partial q}{\partial t}=c-\varphi(q),\quad \varphi=f^{-1},\ \alpha+\gamma=1, \tag{1}$$

$$c|_{t=0}=c_0\exp\left(\frac{z}{2\alpha}\right)\frac{\operatorname{sh}\lambda(b_0-z)}{\operatorname{sh}\lambda b_0},\quad \lambda=\frac{1}{2\alpha}\sqrt{1+4\frac{\alpha}{\gamma}},\quad q|_{t=0}=0,$$

$$c|_{z=0}=c_0,\quad q|_{z=0}=H(t),\quad 0\leqslant z\leqslant b_0. \tag{2}$$

The numerical method of solving system (1) was considered in [1]. The same paper gave an implicit iterative difference scheme of the second order of accuracy, and also the necessary and sufficient conditions for the absolute stability and convergence of the implicit iterative difference scheme for an arbitrary nonlinear sorption isotherm. The system of quasilinear equations (1) for a convex isotherm allows an invariant solution [2], corresponding to the traveling-wave condition (stationary leading edge). From physical considerations regarding the monotonic fall in the function c, q we may find the following condition for the convexity of the sorption isotherm under traveling-wave conditions:

$$w(q-q^0)+c^0>c>\varphi(q),\quad w=(c_0-c^0)(q_0-q^0)^{-1}. \tag{3}$$

It was shown in [1] that an isotherm lying above the straight line joining the origin of the curve $(f(c^0), c^0)$ (c^0 is the initial equilibrium concentration) to the end of the curve $(f(c_0), c_0)$, (c_0 is the final maximum equilibrium concentration) satisfies Eq. (3) and is thus a convex isotherm. In the particular case of $c^0=0$, $f(c^0)=0$, $c_0=1$, $f(c_0)=1$ the convex isotherm lies above the straight line connecting the beginning and end of the curve (0, 0) and (1, 1). In Fig. 1 the convex isotherms lie in a region bounded by a triangle with coordinates 0, q = 1, 1. At first glance it might seem that we should have to regard functions lying below the straight line connecting the initial and final points of the curve $(f(c^0), c^0)$ and $(f(c_0), c_0)$ as concave isotherms f. The isotherm 1 in Fig. 1, in particular, may be regarded as concave and isotherm 2 as convexo-concave. However, detailed analysis shows that the concept of a concave isotherm for externally diffusive sorption kinetics has to be determined in a different way from the concept of a convex isotherm. A concave isotherm is, in fact, one for which $d^2f(c)/dc^2>0$ in the range $c^0\leq c\leq c_0$. According to this definition, the isotherms 1 and 2 in Fig. 1 will be convexo-concave. The convex region of the isotherms occurs for

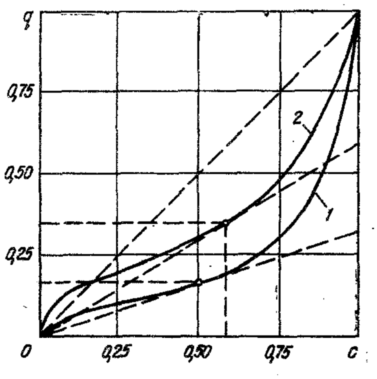

Fig. 1. Sorption isotherms.

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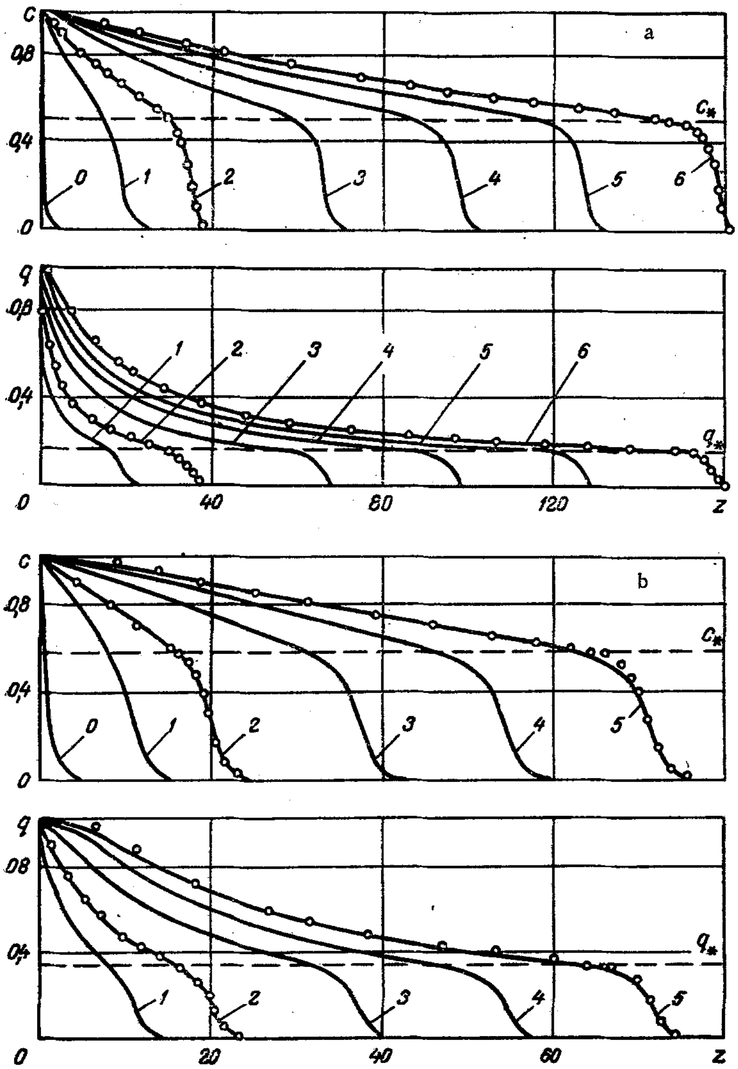

Fig. 2. Frontal dynamic curves for an s-shaped isotherm (p=9, b=0.9) (a) and for an s-shaped isotherm (p=10.3, b=0.8) (b).

$0 \leq c \leq c_*$ (c_* is the point of intersection of the isotherm with the tangent arising from the origin of coordinates). For $c^* \leq c \leq 1$ the condition $d^2f/dc^2 > 0$ is satisfied, and in this region the isotherm will be concave. In the appendices of [3] such convexo-concave isotherms are called s-type, and are often described by the BET equation

$$q = \frac{(1-b)(1+p)c}{(1-bc)(1+pc)}, \quad 0 \leqslant q \leqslant 1, \ 0 \leqslant c \leqslant 1. \tag{4}$$

For the convex part of the isotherm we have a traveling-wave mode described by the invariant solution $y = z - wt(w = (c_* - c^0)(q_* - q^0)^{-1}, \ q_* = f(c_*))$. In the region of the convex part of the isotherm $0 \leq c \leq c_*$ we may write the system (1) in the following way:

$$c - wq = \alpha \frac{dc}{dy}, \quad -\gamma w \frac{dq}{dy} = c - \varphi(q), \ w = c_*/q_*, \ c^0 = 0. \tag{5}$$

In order to integrate the system (5), we divide the second equation of (5) by the first,

$$\frac{dc}{dq} = \gamma w (c - wq) \alpha^{-1} [\varphi(q) - c]^{-1}, \ 0 \leqslant q \leqslant q_*. \tag{6}$$

The resultant Eq. (6) may be integrated numerically by the Runge–Kutta method, from which we obtain the relationship $c = F_0(q)$. Allowing for this relationship, the second equation of (5) has the form

$$-\gamma w \frac{dq}{dy} = F_0(q) - \varphi(q). \tag{7}$$

Integrating Eq. (7) we obtain

$$q(y) = H^{-1}(y - y_0),\ H(q) = \int \frac{1}{\gamma w} [\varphi(q) - F_0(q)]^{-1} \alpha q. \tag{8}$$

We find the integration constant y_0 from the integrated form of the material-balance equation (1). After certain transformations we obtain

$$y_0 = -\int_0^{q_*} \frac{1}{q_*} H(q)\, dq + \alpha [1 - c(0)/c_*]. \tag{9}$$

In the region of the concave isotherm $c_* \le c \le c_0$, system (1) may only be integrated numerically with the aid of an electronic computer if $\alpha \ne \gamma \ne 0$. However, for large values of the time $t \ge t_*$ ($z \ge z_*$) the shape of the spreading frontal dynamic curve in the region of the concave isotherm is largely determined by the curvature of the isotherm, since its spreading attributable to the curvature will be greater than its spreading attributable to the finite velocity of the externally diffusive mass transfer ($\gamma \ne 0$) and the finite velocity of effective longitudinal mixing ($\alpha \ne 0$). The value of t_* (and, correspondingly, z_*) depends on the shape of the concave region of the sorption isotherm. Allowing for the foregoing discussion, when $t \ge t_*$ ($z \ge z_*$) the system of equations (1) transforms into the following form for the concave part of the isotherm:

$$\frac{\partial c}{\partial z} + \frac{\partial q}{\partial t} = 0,\ c|_{t=0} = c^0,\ q = f(c). \tag{10}$$

For the concave part of the isotherm ($d^2f/dc^2 > 0$) the hyperbolic system (10) allows an invariant solution $y = z/t$, which after certain transformations may be written in the form

$$q = f(c),\ c(z, t) = \begin{cases} c_0,\ z < z_1,\ z_1 = t\left[\dfrac{df(c_0)}{dc}\right]^{-1}, \\ c_0 F\left(\dfrac{1}{y}\right),\ z_1 \leqslant z \leqslant z_2,\ z_2 = t\left[\dfrac{df(c_*)}{dc}\right]^{-1}, \\ c_*,\ z > z_2,\ F^{-1}(c) = \dfrac{df}{dc}. \end{cases} \tag{11}$$

It is interesting to compare the analytical invariant solutions (11) with the exact numerical solutions of the system (1). By way of example we applied a BÉSM-6 computer to the isotherms 1 and 2 (Fig. 1) and numerically integrated the system of equations (1)-(2) for the following values of the parameters: $c^0 = 0$, $c_0 = 1$, $b_0 = 180$, $\alpha = \gamma = 0.5$, $h = 0.06$, $\tau = 0.03$. The results of the integration are indicated by the continuous lines for the isotherm 1 in Fig. 2a, and for the isotherm 2 in Fig. 2b (0) t=0, 1) t=5, 2) 10, 3) 20, 4) 30, 5) 40, 6) 50). The invariant solutions are shown as circles in the figure. Figure 1 illustrates the s-shaped isotherms (4): isotherm 1 for the parameters $p = 9$, $b = 0.9$, $c_* = 0.5$, $q_* = 0.165$, isotherm 2 for the parameters $p = 10.3$, $b = 0.8$, $c_* = 0.575$, $q_* = 0.348$. For the convex part of the isotherm in the region $0 \le c \le c_*$ the invariant solutions are found by integrating Eqs. (6), (8), and (9). In the region $c_* \le c \le 1$ the invariant solutions for the concave part of the isotherm are found from Eqs. (11). It follows from an analysis of the results presented in Fig. 2a and b that the frontal dynamic curves for the s-shaped isotherm may be described to a satisfactory accuracy by invariant solutions $y = z - wt$ in the region of the convex part of the isotherm, in accordance with Eqs. (6), (8), and (9), and invariant solutions $y = z/t$ in the concave part of the isotherm, in accordance with Eqs. (11).

In the absence of longitudinal mixing ($\alpha = 0$) and for an infinitely high rate of mass transfer ($\gamma = 0$) the system of equations (1) transforms into the limiting equation (10) or the limiting equation

$$\frac{\partial q}{\partial t} + \frac{\partial \varphi(q)}{\partial z} = 0,\ R(q) = \frac{d^2\varphi}{dq^2}. \tag{12}$$

The system of equations (1) has a continuous solution, while the limiting equations (10) and (12) for the convex function f (concave φ) have a discontinuous solution. The existence and uniqueness of the generalized discontinuous solutions of the hyperbolic equation (12) were proved in [4] for $R > 0$. The construction of generalized discontinuous solutions for an arbitrary function R was considered in [5]. However, the generalized discontinuous solutions have to be considered as a limiting case of the continuous solutions of (8) for $\alpha = \gamma = 0$.

NOTATION

c, concentration of the sorbed gas (liquid) in the filtration flow; q, concentration of the absorbed substance; α, relative coefficient of longitudinal mixing; γ, relative kinetic coefficient; f, φ, functions describing the forward and reverse sorption isotherms; h, τ, coordinate and time steps, respectively.

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