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ASYMPTOTIC PROPERTIES OF ONE-COMPONENT MODEL IN THE THEORY OF SORPTION DYNAMICS

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Asymptotic properties of integro-differential equations defining a one-component one-dimensional model of multistage dynamics of sorption is considered in the limit case when one of the kinetic stages is a limiting one.

1. The input system. The process of extraction of dissolved or suspended component from a fluid (gaseous) phase filtering through a sorbent layer is considered. In the one-dimensional approximation in the case of uniform motion of the fluid the equations of conservation of the component are of the form [1, 2]

$$v\partial c / \partial x + \varepsilon \partial c / \partial t + \partial a / \partial t = D_l \partial^2 c / \partial x^2 \tag{1.1}$$

$$a = \frac{3}{R^3} \int_0^R a_s(r; t, x)\, r^2\, dr \tag{1.2}$$

$$\partial a / \partial t = \beta (c - c^*), \quad a_s^* = f(c^*), \quad \partial (a_s r) / \partial t = D_i \partial^2 (a_s r) / \partial r^2 \tag{1.3}$$

where $c(x, t)$ is the concentration in the fluid phase per unit volume of the fluid phase; $a(x, t)$ is the macroconcentration of the component in the sorbent per unit of filter volume; $a_s(r; t, x)$ is the local concentration in the sorbent consisting of spheres of radius R; c^* and a^* are the equilibrium concentrations at the phase interface; x is a coordinate in the direction of filtration flow (at entry to the sorbent layer $x = 0$); v is the filtration rate, t is the time, r is the varying radius inside the sorbent spherical elements, ε is the macroporosity of the sorbent layer, D_l is the coefficient of lengthwise diffusion, D_i is the coefficient of diffusion inside sorbent grains, and β is the coefficient of mass transfer from the stream to the surface of sorbent elements.

Equation (1.1) defines the conservation of the sorbate, (1.2) defines the relation of local concentration in the sorbent to the macroconcentration, and Eqs. (1.3) represent the equations of external diffusion kinetics, of thermodynamic equilibrium (isotherms)(unless otherwise stated, we assume below that $f(c^*) = \Gamma c^*$, where Γ is the Henry constant), and the equation of diffusion within, the grains of sorbent, respectively.

We assume the sorbent layer to be semi-infinite, and consider the following boundary value problem:

$$c(0, t) = c_0, \quad a(x, 0) = a_s(r; 0, x) = 0 \tag{1.4}$$

The remaining conditions for various specific problems are defined in Sects. 2 and 3, below.

The model (1.1) — (1.4) is a multistage one, since three kinetic stages are taken into account, viz. the external, internal, and the lengthwise diffusion; it is also heterophase, since two phases of substance are considered. In a certain sense it is one of the simplest, since the multicomponent and multiphase stages such as, for instance, dissociation, and the formation of complexes are not taken into account.

To determine the characteristic dimensionless parameters of the problem we shall use the characteristic scales of time τ and length ξ of respective single-stage models. To external diffusion for $D_i = \infty$, $D_l = 0$ the characteristic time and length are, respectively, $\tau_e = \Gamma / \beta$ and $\xi_e = v / \beta$; for internal diffusion for $\beta = \infty$, $D_l = 0$ we have, respectively, $\tau_i = R^2 / D_i$, and $\xi_i = vR^2 / \Gamma D_i$; and for the lengthwise diffusion for $\beta = D_i = \infty$ we have, respectively, $\tau_l = D_l \Gamma / v^2$, and $\xi_l = D_l / v$. System (1.1) — (1.3) in dimensionless variables (any pair of τ and ξ) contains the dimensionless quantities

$$H = \tau_i / \tau_e = \beta R^2 / D_i \Gamma, \quad \Delta = \tau_l / \tau_e = D_l \beta / v^2 \qquad (1.5)$$
$$I = \tau_i / \tau_l = R^2 v^2 / \Gamma D_i D_l$$

The slowest kinetic stage of a multistage process will be called below the limiting stage. The rate of sorbtion depends on the consecutive effects of the external and internal mass transfer and is determined by the stage whose diffusion resitance is the higher. The effect of lengthwise diffusion is, on the other hand, the greater the more intense the diffusion stream. Hence the ratio of time scales, as defined by the dimensionless parameters in (1.5) determine the limiting stage.

Below we consider the asymptotic properties of unsteady sorbtion processes when one of the stages is the limiting one. Under unsteady conditions the use of single-stage models as a whole is incorrect, since on certain stages of the process the effect of nonlimiting stages may be the determining one. In fact, the quantities H, Δ, and I define the ratio of streams of substance only when the respective phase concentration gradients are of the same order in dimensionless variables. For instance, under the boundary conditions (1.4) the gradients in the fluid and solid phases attain their maxima at the beginning of the process, hence the effects of external and lengthwise diffusion can be considerable, in spite the magnitude of the dimensionless parameters (1.5).

Let us consider the process stages in which it is necessary to take into account the multistage structure properties and show the asymptotic boundaries of such stages.

2. The external diffusion as the limiting stage ($\tau_e \gg \tau_i$, $\tau_e \gg \tau_l$). At the beginning of a dynamic sorbtion process that satisfies conditions (1.4) it is necessary to take into account the external and the lengthwise diffusions, hence we set $H = 0$, $\Delta \ll 1$, and represent system (1.1) — (1.4) and the boundary conditions for a semi-infinite layer $x \geqslant 0$ in the form

$$\partial u / \partial X + \varepsilon \Gamma^{-1} \partial u / \partial T + \partial q / \partial T = \Delta \partial^2 u / \partial X^2 \qquad (2.1)$$
$$\partial q / \partial T = u - q \quad (X \geqslant 0,\ T \geqslant 0)$$
$$u(0, T) = 1, \quad q(X, 0) = 0, \quad (\partial u / \partial X)_{X \to \infty} = 0$$
$$u = c / c_0, \quad q = a / \Gamma c_0, \quad X = x / \xi_e, \quad T = t / \tau_e$$

Since at the beginning of sorbtion the concentration q is low, we consider, instead of system (2.1) the equation

$$\partial u / \partial X + \varepsilon\Gamma^{-1}\partial u / \partial T + u = \Delta\partial^2 u / \partial X^2$$

with the same boundary conditions. Its solution is of the form [3]

$$\begin{gathered} u(X, T) = {}^1/_2 (\exp Y_- \operatorname{erfc} Z_- + \exp Y_+ \operatorname{erfc} Z_+) \\ Y_\pm = X / 2\Delta \pm X [\Delta^{-1} + (2\Delta)^{-2}]^{1/2} \\ Z_\pm = \varepsilon^{1/2}\Gamma^{-1/2}T^{-1/2}X / 2 \pm \varepsilon^{-1/2}\Gamma^{1/2}T^{1/2} [1 + 1 / (4\Delta)]^{1/2} \end{gathered} \tag{2.2}$$

Analysis of solution (2.2) enables us to establish temporary boundaries of the lengthwise diffusion effects. We shall call that stage the Δ-zone.

By setting in system (2.1) $\Delta = 0$ we obtain a solution which under conditions (1.4) has at instant $T^\circ = \varepsilon X / \Gamma$ the discontinuity

$$T < T^\circ, \quad u = 0; \quad T = T^\circ, \quad u = \exp(-X) \tag{2.3}$$

The allowance for lengthwise diffusion for any X and Δ as small as desired leads to a continuous increase of concentration from zero. For $T \leqslant \varepsilon X^2 / (4\Delta\Gamma)$ we represent solution (2.2) in the form

$$u = u_0 = \operatorname{erfc}\left(\frac{\varepsilon^{1/2} X}{2\sqrt{\Delta\Gamma T}}\right) + O\left[\sqrt{\frac{\Delta\Gamma T}{\varepsilon X^2}} \exp\left(-\frac{\varepsilon X^2}{4\Delta\Gamma T}\right)\right]$$

which within the second term is the solution of problem

$$\varepsilon\Gamma^{-1}\partial u_0 / \partial T = \Delta\partial^2 u_0 / \partial X^2, \quad u_0(X, 0) = 0, \quad u_0(0, T) = 1$$

Consequently, for fairly small times T the lengthwise diffusion predominates not only over the external diffusion mass transfer but, also, the convection one. Thus the "left-hand" boundary T_{el}^* of the Δ-zone for any $X \neq 0$ is determined by the equality $T_{el}^* = 0$.

Let us determine the "right-hand" boundary of the Δ-zone. We shall consider the solution of problem (2.1) at the beginning of the steady mode. It follows from (2.2) that as $T \to \infty$ we have $u^\circ = Y_-$, which for $\Delta \leqslant 1$ is the same as the expression (2.3) for the single-stage external-diffusion model. We shall call the right-hand boundary of the Δ-zone the instant $T_{el}^{**}(X)$ at which solution (2.2) reaches with the specified accuracy δ the value u°, i.e., $[u^\circ - u(X, T_{el}^{**})] / u^\circ = \delta$. For $X \gg \Delta$ the boundary of the Δ-zone is determined with an accuracy within terms of order E / X^2 by formula

$$T_{el}^{**} = T^\circ + \Delta\varepsilon\varphi^2 / (2\Gamma) \tag{2.4}$$

where φ is determined by the equation $\delta = \operatorname{erfc}(\varphi/2)$.

The width of the Δ-zone thus depends on the sorbtion properties of the system and increases with increasing, X ; the lower the coefficient Γ, as for example, in the regeneration of sorbents, the more pronounced is the effect of the lengthwise diffusion.

The use of solution (2.2) within the limits of the Δ-zone is admissible. Let us determine the time interval $0 \leqslant T \leqslant T_0$ within which the simplified equation valid, i.e. the quantity $q < \delta_1$, where δ_1 is the admissible error of the determination of q. Solution of the problem of external diffusion kinetics implies that

$$\delta_1 = \exp(-T_0)\int_0^{T_0} (\exp\tau)\, u(X,\tau)\, d\tau < \exp(-X)\,[1 - \exp(-T_0)]$$

from which we obtain the expression for the estimate $T_0 > -\ln(1 - \delta_1 \exp X)$.

The above estimate is too low, since within the limits of the Δ-zone $u < u^\circ$. Hence solution (2.2) is valid within the limits of the Δ-zone under condition $T < T_0$.

Let us now determine the zone of the internal diffusion kinetics influence in the last stages of sorbtion under the condition that the external diffusion is still the limiting stage. We call that stage the i-zone. Since in the final stages the gradients in the solution are at their minimum values, we can set $\Delta = 0,\ H \ll 1$.

Let us consider system (1.1) – (1.3) supplemented by the condition of absence of sinks at the centers of grains $\lim_{r\to 0} (r\partial a_s) / \partial r = 0$, when $D_l = 0$. Using the Laplace transform with respect to time, and analyzing the expansion in the neighborhood of $t = \infty$, we obtain

$$u_i(X_i, T_i) = 1 - X_i / T_i + {}^1/_2 T_i^{-2}(X_i / 15 + X_i^2 / 2) + O(T_i^{-3}) \tag{2.5}$$

$$u_{ie}(X_i, T_i) = 1 - X_i / T_i + {}^1/_2 T_i^{-2}(X_i / 15 + X_i^2 / 2 + X_i / H) + O(T_i^{-3})$$

where u_{ie} is the solution when $H \neq 0$, u_i corresponds to $H = \infty$ (single stage internal diffusion process), and $X_i = x / \xi_i$, $T_i = t / \tau_i$.

The boundary of the zone of internal diffusion kinetics influence, i.e. of the i-zone, is determined by the condition $|u_{ie} - u_i| = \delta_{ie}$, where δ_{ie} is the accuracy of boundary determination. For the left-hand boundary of the i-zone we obtain from expansion (2.5) the formula

$$T_{ei}^* = \sqrt{X_i / (2H\delta_{ie})} \tag{2.6}$$

The right-hand boundary is defined by formula $T_{ei}^{**} = \infty$, since solution (2.5) asymptotically approaches unity as $T_i \to \infty$. It follows from (2.6) that with decreasing H, i.e. with decreasing internal diffusion input, parameter T_{ei}^* increases in proportion to $H^{1/2}$ and the i-zone correspondingly narrows. Note also the i-zone decrease as X increases.

The position of the i-zone for nonlinear isotherms is evaluated by formula (2.6) where $H = \beta R^2 / (D_i\gamma)$ and γ is the slope of the tangent to the isotherm at point $u = q = 1$.

3. Inner diffusion as the limiting stage $(\tau_i \gg \tau_e,\ \tau_i \gg \tau_l)$. In this case the effect of nonlimiting stages is significant at the initial stages of sorbtion. Let us consider the solution beyond the limits of the Δ-zone, where it is possible to set $\Delta = 0$.

As shown in [4], in the case of single-stage internal diffusion model the approximate solution for $T_i \ll 1$ is of the form

$$u_i = \exp(3X_i) \operatorname{erfc}[3X_i/(2T_i^{1/2})]$$

It follows from this that $u_i(X_i, 0) = 0$ for any $X_i > 0$. On the other hand, when the internal and external diffusions are taken into account, the solution for $T \leqslant T^\circ$ coincides with (2.3). Hence, for any as high as desired H, there exists a specific stage, which we shall call the e-zone, in which the progress of the operation is determined by the nonlimiting external diffusion stage.

For small times T_i the last of Eqs. (1.3) may be written in the form

$$\begin{gathered} \partial a_s / \partial t = D_i \partial^2 a_s / \partial y^2 \\ y = 0, D_i \partial a_s / \partial y = \beta\omega^{-1} [V - a_s(1-\varepsilon)/\Gamma], \quad t = 0 \\ a_s = 0 \end{gathered} \tag{3.1}$$

where y is a coordinate along the normal to the sorbent surface, $y = R - r$, ω is the specific surface of the sorbent charge, and V is the concentration of the fluid phase in which mass transfer takes place. For small times T_i we set $V = c_0 \exp(-\beta x/v)$.

The solution of problem (3.1) is of the form [3]

$$\begin{gathered} a_s = \Gamma V (1-\varepsilon)^{-1} \{\operatorname{erfc}[y/(2\sqrt{D_i t})] - \exp(hy + h^2 D_i t) \times \\ \operatorname{erfc}[y/(2\sqrt{D_i t}) + h\sqrt{D_i t}]\} \\ h = \beta(1-\varepsilon)/(\omega\Gamma D_i) \end{gathered}$$

from which follows the approximate expression for the surface concentration

$$a_s(0, t) = 2V\Gamma h\sqrt{D_i t} / [\sqrt{\pi}(1-\varepsilon)] + O(h^2 D_i t)$$

Passing to dimensionless variables X and T and using for u the external diffusion kinetics equation (1.3), and taking simultaneously into account the external and internal diffusion, we obtain a solution of the form

$$\begin{gathered} T < T^\circ, \quad u_{ei} = 0; \quad T \geqslant T^\circ, \quad u_{ei} = \\ \exp(-X)\{1 + {}^2/_3 \pi^{-1/2} X [H(T - T^\circ)]^{1/2}\} \end{gathered} \tag{3.2}$$

The comparison of (3.2) and (2.3) shows that the magnitude of the concentration jump is determined by external diffusion, while the increase of concentration is due to internal diffusion, i.e. to the limiting stage.

The right-hand boundary T_{ei}^{**} of the e-zone is determined by the condition $(u_{ei} - u_e)/u_e = \delta_{ei}$. In the same approximation as that in which solution (3.2) was obtained, the solution for u_e of the form $u_e = \exp(-X)[1 + X(T - T^\circ)]$ directly follows from Eqs. (1.3) and (2.3) of kinetics. Hence the right-hand boundary of the e-zone is determined by the equality

$$T_{ei}^{**} = T^\circ + 9\pi\delta_{ei}^2 / (4HX^2)$$

The e-zone width is inversely proportional to H, i.e. it becomes narrower as the effect of the limiting stage increases.

The considered here asymptotic properties of system (1.1) — (1.3) also indicate regions in which a particular (parabolic for the Δ- and i-zones, and hyperbolic for the e-zone) type of the input system predominates.

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