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FRONTAL ISOTHERMAL SORPTION DYNAMICS FOR ISOTHERM OF NONSIMPLE FORM IN THE PRESENCE OF COMPLEX FORMATION IN THE MOVING PHASE

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Approximate analytic solutions of the equations of nonequilibrium sorption dynamics are obtained for convex–concave and concave–convex isotherms, taking into account the formation of nonsorbent complexes of the material in the mobile phase.

The isothermal sorption dynamics of a material in a porous undeformed medium with the formation of a nonsorbent complex of the material with concentration c_C, is described by the material balance equation [1]

$$\frac{\partial a}{\partial t}+\frac{\partial c}{\partial t}+\frac{\partial c_C}{\partial t}+u\,\frac{\partial (c+c_C)}{\partial x}=D\,\frac{\partial^2 (c+c_C)}{\partial x^2} \tag{1}$$

and equations expressing the relation between the concentrations a–c and c_C–c. In the case of nonequilibrium dynamics, the concentration relation a–c is specified by the kinetic equation, taken here in the form of the equation of intradiffusional kinetics, where the nonequilibrium nature of the sorption process is expressed in terms of τ [2]

$$a=f(c)-\tau\,\frac{df}{dc}\,\frac{\partial c}{\partial t}. \tag{2}$$

An equation of this form is used to solve a number of nonlinear problems of sorption dynamics [3-5].

If the rate of complex formation is large, then $c_C=\varphi(c)$, where the function $\varphi(c)$ may be determined as the complex-formation isotherm. The initial and boundary conditions of the equations of frontal sorption dynamics for a semiinfinite column ($0 \leqslant x < \infty$) take the form

$$c(0,\,t)=1;\quad c_C(0,\,t)=\varphi(1);\quad c(x,\,0)=c_C(x,\,0)=c(\infty,\,t)=c_C(\infty,\,t)=0. \tag{3}$$

For concave and convex isotherms f(c), $\varphi(c)$, use of the integral-relation method leads to an approximate solution [6] describing the sorption front, and conditions of sharpening and hollowing out of the front as a function of the ratio of curvature parameters of the isotherm are introduced. In the case of equilibrium dynamics, i.e., a = f(c), using the characteristic equation corresponding to Eq. (1) with D = 0

$$\left(\frac{dx}{dt}\right)_C=\frac{u}{1+df/dC},\quad \frac{df}{dC}=\frac{f'(c)}{1+\varphi'(c)},\quad C=c+\varphi(c),$$
$$f(C)=f(c(C)), \tag{4}$$

it is simple to show that when $d^2f/dC^2 < 0$ (i.e., f(C) is convex) the front is stationary,

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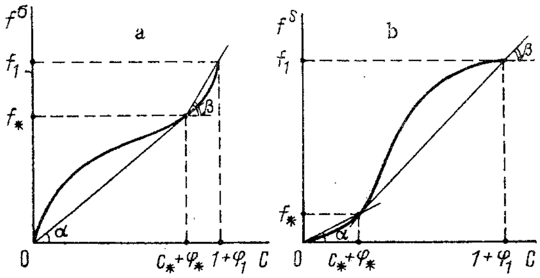

Fig. 1. Convex–concave (a) and concave–convex (b) isotherms as a function of total concentration of material C; tan α = k_*; tan β = k_{1*}.

and when $d^2f/dC^2 > 0$ (i.e., f(C) is concave) the front is being eroded.

However, in the case of polymolecular sorption [7] and ion-exchange complex-forming chromatography [8], nonmonotonic change in df/dC is possible: The isotherm may be convex–concave f^σ (Fig. 1a) or concave–convex f^s (Fig. 1b). (Below, quantities referring to f^σ and f^s are denoted by the superscripts σ and s, respectively.) The front as a whole, $0 \leqslant c \leqslant 1$, is eroded in both cases, but in a different manner: it follows from Eq. (4) that for the concave–convex isotherm f^s the part of the front with concentrations $0 \leqslant c_2 \leqslant c_*$ is eroded with time, while the part with concentrations $c_* \leqslant c_1 \leqslant 1$ is steady; for a convex–concave front f^σ, conversely, the part of the front c_2 is steady and the part c_1 is eroded. The point c_* is determined from the condition (Fig. 1)

$$\text{for } f^s: \frac{f'}{1+\varphi'}\bigg|_{c_*} = \frac{f_1 - f_*}{1 - c_* + \varphi_1 - \varphi_*} \equiv k_{1*}; \text{ for } f^\sigma: \frac{f'}{1+\varphi'}\bigg|_{c^*} = \frac{f_*}{1+\varphi_*} \equiv k_*, \tag{5}$$

where $\varphi_* \equiv \varphi(c_*)$; $f_* \equiv f(c_*)$; $\varphi_1 \equiv \varphi(1)$; $f_1 \equiv f(1)$

In the present work, an approximate solution of Eqs. (1)-(3) with D = 0 is proposed for nonlinear isotherms $f^{s,\sigma}(C)$. This solution is found by the integral-relation method, using two moving boundaries $T_1(X)$ and $T_*(X)$ for the concentrations c = 1 and c_*, respectively (Fig. 2) [9,10]. Substituting Eq. (2) into Eq. (1) and passing to the dimensionless time T and distance X, the following equations are obtained when D = 0 [6]

$$\frac{\partial c}{\partial T} + \frac{\partial \varphi(c)}{\partial T} + \frac{\partial f(c)}{\partial T} + \frac{\partial c}{\partial X} + \frac{\partial \varphi(c)}{\partial X} = \frac{\partial^2 f(c)}{\partial T^2}; \quad T = \frac{t}{\tau}, \quad X = \frac{x}{u\tau}. \tag{6}$$

The concentration distribution c(X, T) will be sought in the form (Fig. 2)

$$c_2(X, T) = c_* \exp\{-b^2(X)[T - T_*(X)]^2\}, \quad T_* > T > 0, \tag{7}$$

$$c_1(X, T) = 1 - 3(1 - c_*)\left(\frac{T_1 - T}{T_1 - T_*}\right)^2 + 2(1 - c_*)\left(\frac{T_1 - T}{T_1 - T_*}\right)^3,$$
$$T_1 > T > T_*. \tag{8}$$

To determine the as yet unknown dependences b(X), $T_*(X)$, and $T_1(X)$, the distributions in Eqs. (7) and (8) are required to satisfy integral relations of zero and first order (i = 0, 1), obtained from Eq. (6) by multiplying both sides by T^i and subsequently integrating with respect to T over the limits $(-\infty, T_*)$ or (T_*, T_1)

$$\frac{d}{dX}\int_{-\infty}^{T_*} T^i (c + \varphi(c))\, dT - (c_* + \varphi_*) T_*^i \frac{dT_*}{dX} + T_*^i (c_* + \varphi_* + f_*) -$$
$$- i \int_{-\infty}^{T_*} T^{i-1} (c + \varphi(c) + f(c))\, dT = -iT_*^{i-1} f_* + i(i-1)\int_{-\infty}^{T_*} T^{i-2} f(c)\, dT, \tag{9}$$

$$\frac{d}{dX}\int_{T_*}^{T_1} T^i (c + \varphi(c))\, dT - (1 + \varphi_1) T_1^i \frac{dT_1}{dX} + (c_* + \varphi_*) T_*^i \frac{dT_*}{dX} + T_1^i (1 + \varphi_1 + f_1)$$
$$- T_*^i (c_* + \varphi_* + f_*) - i \int_{T_*}^{T_1} T^{i-1} (c + \varphi(c) + f(c))\, dT = -i(f_1 T_1^{i-1} - f_* T_*^{i-1}) + i(i-1)\int_{T_*}^{T_1} f(c)\, T^{i-2}\, dT.$$

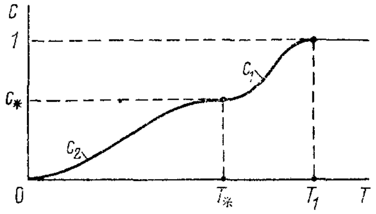

Fig. 2. Yield curve of the concentration c for isotherms of type $f^{\sigma,s}$ at a definite distance X: $T_*(X)$ and $T_1(X)$ are the moving concentration boundaries $c = c_*$ and $c = 1$, respectively (all quantities are dimensionless).

The dependences $b(X), T_*(X)$, and $T_1(X)$ are determined from the two zero-order relations in Eqs. (9) and (10) and one first-order relation: for a convex–concave isotherm (f^{σ}), Eq. (9), $i = 1$; and for a concave–convex isotherm (f^{s}), Eq. (10), $i = 1$. The solution of Eqs. (9) and (10) is performed for isotherms $f(c)$, $\varphi(c)$ of polynomial form with integer indices

$$f(c) = \gamma c + \varepsilon c^{m_1} + \zeta c^{m_2}, \quad \varphi(c) = kc + hc^{n_1} + rc^{n_2}, \tag{11}$$

where ε, ζ, and h, r are nonlinearity parameters of the isotherms f, φ. This form of isotherm allows both cases of isotherm (f^{σ}, f^{s}) to be covered when $m_1 = n_1 = 2$, $m_2 = n_2 = 3$

$$\left.\frac{d^2f^s}{dC^2}\right|_{c=1} = A + 3B + 3F < 0, \quad \left.\frac{d^2f^s}{dC^2}\right|_0 = A > 0,$$

$$\left.\frac{d^2f^{\sigma}}{dC^2}\right|_{c=c_*} = A + 3Bc_* + 3Fc_*^2 > 0, \quad \left.\frac{d^2f^{\sigma}}{dC^2}\right|_0 = A < 0, \tag{12}$$

where

$$F = h\zeta - r\varepsilon; \quad B = \zeta(1 + k) - r\gamma; \quad A = \varepsilon(1 + k) - h\gamma.$$

When $m_1 = n_1 = 2$, $m_2 = n_2 = 3$, Eq. (5), from which the value of c_* for the isotherm in Eq. (11) is determined, is smoothed as follows

$$\text{for} \quad f^{\sigma}: Fc_*^2 + 2Bc_* + A = 0; \quad \text{for} \quad f^{s}: Fc_*^2 + 2(F + B)c_* + B + A = 0. \tag{13}$$

For example, if:

a) $\varepsilon, \zeta < 0$ (isotherm f(c) is convex) and $h, r > 0$ (isotherm $\varphi(c)$ is concave) then F, B, $A < 0$;

b) $\varepsilon, \zeta > 0$ (isotherm f(c) is concave) and $h, r < 0$ (isotherm $\varphi(c)$ is convex) then F, B, $A > 0$;

c) $\zeta = r = 0$ (isotherms f(c) and $\varphi(c)$ are square), then $F = B = 0$, and no solution to Eq. (13) exists, i.e., isotherms of the type of $f^{\sigma,s}(c)$ are impossible in these cases. For $k = h = r = 0$, the solution obtained describes the sorption dynamics in the absence of complex formation for sorption isotherms of type $f^{\sigma,s}(c)$ (if ε and ζ are of opposite sign).

Substituting Eqs. (8) and (11) into Eq. (10) when $i = 0$ gives the following result after integration

$$T_* = WT_1 + (1 + k_{1*})(1 - W)X, \quad T_1 - T_* = (1 - W)[T_1 - (1 + k_{1*})X], \tag{14}$$

where

$$W = 1 - \frac{1 - c_* + \varphi_1 - \varphi_*}{gK_1 + pK_2 + vK_3}; \quad g = (1 - c_*)[1 + k + 2hc_* + 3rc_*^2];$$

$$p = (1 - c_*)^2 (h + 3rc_*); \quad v = (1 - c_*)^3 r; \quad K_j = \int\limits_0^1 (1 - 3x^2 + 2x^3)^j \, dx,$$

$$j = 1, 2, 3.$$

Solving the two remaining integral relations by means of Eqs. (7), (11), and (14) gives

$$\frac{\sqrt{\pi}}{2b}=\frac{1}{R}\,[T_*-(1+k_*)\,X],\quad R=1-\left(1-\frac{1}{\sqrt{2}}\right)h_*-\left(1-\frac{1}{\sqrt{3}}\right)r_*,$$

$$h_*=\frac{hc_*^2}{c_*+\varphi_*},\quad r_*=\frac{rc_*^3}{c_*+\varphi_*},\tag{15}$$

$$y_1^s-\ln|1+y_1^s|=SX,\quad y_1^s=\frac{G}{f_1-f_*}\,[T_1-(1+k_{1*})\,X],\tag{16}$$

$$y_2^\sigma-\ln|1+y_2^\sigma|=\sigma X,\quad y_2^\sigma=\frac{H}{f_*}\,[T_*-(1+k_*)\,X],\tag{17}$$

where

$$G=\frac{(K_2-K_3)\,(1-c_*)^4}{gK_1+pK_2+vK_3}\,[B+F\,(1+c_*)];\quad S=\frac{G^2}{(f_*-f_1)\,d}>0;$$

$$d=(1-c_*+\varphi_1-\varphi_*)\left[1-2\,\frac{(1-c_*+\varphi_1-\varphi_*)\,(gK_4+pK_5+vK_6)}{(gK_1+pK_2+vK_3)^2}\right];$$

$$H=\left(1+\frac{1}{\sqrt{3}}-\sqrt{2}\right)\frac{c_*^3\,(A+Bc_*)}{(c_*+\varphi_*)\,R};\quad \sigma=\frac{H^2}{k_*}\left\{\frac{4}{\pi R}\left(1-\frac{1}{2}\,h_*-\frac{2}{3}\,r_*\right)-1\right\}^{-1}>0;$$

$$K_j\doteq\int_0^1 x\,(1-3x^2+2x^3)^{j-3}\,dx,\quad j=4,\ 5,\ 6.$$

If approximating the real isotherms by Eq. (11) is not sufficiently accurate, the number of terms in Eq. (11) may be increased and the order of the polynomials m, n changed. In this case the form of the solutions in Eqs. (14)-(17) remains as before; all that is changed is the value of the constants K_1-K_6, p, g, and v, and, of course, the constants G, H, S, and σ.

The basic integral parameters of the sorption front at a distance X from the origin of the column are the mean outlet time (or center of gravity $\overline{T}_i$) and width (or dispersion Δ_i) of the corresponding concentration curves $\partial C_i/\partial T$

$$\overline{T}_i=\int_{p_i}^{q_i}T\,\frac{\partial C_i}{\partial T}\,dT\Big/\int_{p_i}^{q_i}\frac{\partial C_i}{\partial T}\,dT,\quad C_i=c_i+\varphi\,(c_i),\tag{18}$$

$$\Delta_i^2=\int_{p_i}^{q_i}(T-\overline{T}_i)^2\,\frac{\partial C_i}{\partial T}\,dT\Big/\int_{p_i}^{q_i}\frac{\partial C_i}{\partial T}\,dT,\quad \{p_1q_1\}=\{-\infty,\ T_*\},\ \{p_2q_2\}=\{T_*T_1\}.\tag{19}$$

From Eqs. (18) and (19), using the distributions in Eqs. (7) and (8), Eqs. (14) and (15), and the isotherm in Eq. (11), the following expressions are obtained for these integral characteristics

$$\overline{T}_1=(1+k_{1*})\,X,\tag{20}$$

$$(\Delta_1)^2=[T_1-(1+k_{1*})\,X]\,|d|,\tag{21}$$

$$\overline{T}_2=T_*-\frac{\sqrt{\pi}}{2b}\,R=(1+k_*)\,X,\tag{22}$$

$$\Delta_2=\frac{1}{b}\sqrt{1-\frac{1}{2}\,h_*-\frac{2}{3}\,r_*-\frac{\pi}{4}\,R^2}\,.\tag{23}$$

The velocity of motion of the centers of gravity $\overline{T}_i$ in Eqs. (20) and (22) of the fronts C_i are determined by the "slopes" k_{1*} and k_* (Fig. 1) of the sections of the isotherm corresponding to sections c_1 and c_2 of the front, respectively.

The solution in Eqs. (7), (8), and (14)-(17) gives the quantitative characteristics of the motion and erosion of the sorption front. Thus, from this solution it is easy to obtain estimates of the distance X_{st} travelled by the front, after which steady conditions of motion of the front c_1 for f^s (c_2 for f^σ) set in. Using Eqs. (12) and (13) it is simple to prove that H, G < 0 and, of course, that the solution of the transcendental Eqs. (16) and (17), $y_{1,2}\to-1$ as $X\to\infty$. With an accuracy of up to 1% ($y_{1,2}^{st}=-0.99$), the front widths $\Delta_{1,2}\sim|y_{1,2}|$ [see Eqs. (21), (23), (16), and (17)] become constant Δ_{ist} when $X>X_{st}$, where

$$X_{\mathrm{st}}^{s}=\frac{3.6}{S}, \quad X_{\mathrm{st}}^{\sigma}=\frac{3.6}{\sigma}, \tag{24}$$

$$\Delta_{1\,\mathrm{st}}^{s}=\frac{f_1-f_*}{|G|}\sqrt{|d|},$$

$$\Delta_{2\,\mathrm{st}}^{\sigma}=\frac{f_*(c_*+\varphi_*)}{\left(1+\frac{1}{\sqrt{3}}-\sqrt{2}\right)c_*^3\,|A+Bc_*|}\sqrt{\frac{4}{\pi}\left(1-\frac{1}{2}h_*-\frac{2}{3}r_*\right)-R^2}\,. \tag{25}$$

Since the coefficients σ and S are determined by the parameters A, B, and F, the quantity X_{st} in Eq. (24) is determined by a combination of the nonlinearity parameters h, ε, and r, ζ. As the difference between ε(1 + k) and hγ, and that between ζ(1 + k) and rγ, increase, so A, B, and F become larger.

The motion of the mobile boundary is described by relations obtained from Eqs. (14)-(17)

$$T_1^s=(1+k_{1*})X+\frac{f_1-f_*}{G}y_1^s, \quad T_*^s=T_1^s-(1-W)\frac{f_1-f_*}{|G|}, \tag{26}$$

$$T_*^{\sigma}=(1+k_{1*})X+\frac{f_*(c_*+\varphi_*)Ry_2^{\sigma}}{\left(1+\frac{1}{\sqrt{3}}-\sqrt{2}\right)c_*^3(A+Bc_*)},$$

$$T_1^{\sigma}=\frac{1}{W}\left[T_*^{\sigma}-(1-W)(1+k_{1*})X\right]. \tag{27}$$

As is evident from Eqs. (26) and (27), taking into account that $y_{1,2}\to -1$, the velocity of the boundaries T_1, T_* becomes constant when $X > X_{st}$, and equal to the velocity of the centers of gravity $\overline{T}_i$.

Part of the concentration front (c_2 for f^s and c_1 for f^{σ}) is progressively eroded. It follows from Eqs. (14), (15), (21), and (23) that when $X > X_{st}$ the width of the eroding part of the front increases in proportion to the distance covered X and

$$\Delta_1^{\sigma}=\frac{\sqrt{|d|}}{W}\left\{(k_{1*}-k_*)X+\frac{f_*(c_*+\varphi_*)R}{\left(1+\frac{1}{\sqrt{3}}-\sqrt{2}\right)c_*^3(A+Bc_*)}\right\},$$

$$\Delta_2^{s}=\left[(k_{1*}-k_*)X+\frac{W}{G}(f_1-f_*)\right]\sqrt{\frac{4}{\pi R^2}\left(1-\frac{1}{2}h_*-\frac{2}{3}r_*\right)-1}\,. \tag{28}$$

The coefficient for X in Eq. (28) is

$$k_{1*}-k_*=\begin{cases}\dfrac{c_*(1-c_*^2)(A+Bc_*)}{(c_*+\varphi_*)(1-c_*+\varphi_1-\varphi_*)(2+c_*)} & \text{for } f^s,\\[2ex] \dfrac{(1-c_*^2)(A+Bc_*)}{(c_*+\varphi_*)(1-c_*+\varphi_1-\varphi_*)} & \text{for } f^{\sigma},\end{cases} \tag{29}$$

i.e., this coefficient is also determined by the parameters A, B, and F.

It is difficult to estimate the accuracy of the approximate solutions obtained in Eqs. (14)-(17), because of the lack of any other solutions of Eqs. (1)-(3) for the isotherms $f^{\sigma,s}(C)$. However, as is shown by comparison with experiment [11] and with known theoretical solutions of a number of linear and nonlinear problems of sorption dynamics [12], the version of the integral-relation method here considered is of good accuracy (with an error of 3-5%).

NOTATION

c, c_C, dimensionless (expressed in terms of the inlet concentration) concentrations of the sorbed material and the complex, respectively, in the moving phase; *a*, dimensionless (expressed in units of inlet concentration) concentration of material in the sorbent, referred to unit volume of the moving phase; C, dimensionless total concentration of material in the moving phase; f(c), φ(c), equation of sorption isotherm and complex-formation isotherm, respectively; x, coordinate; X, dimensionless coordinate; t, time; T, dimensionless time; u, mean flow rate, m/sec; D, longitudinal diffusion coefficient, m^2/sec; τ, kinetic parameter (lag time); m_i, n_i, exponents; γ, k, Henry coefficient for isotherms f and φ, respectively.

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ENGINEERING METHOD OF DETERMINING AND DESCRIBING THE DIRECTIONAL REFLECTION CHARACTERISTICS OF OPAQUE STRUCTURAL MATERIALS

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and Yu. A. Shuba

UDC 669.018.29:535.312

A model for the reflective properties of opaque materials and a method for experimental determination of its parameters are proposed.

At this time, the mathematical modeling of radiant heat transfer processes of engineering systems for which it is impossible to conduct a direct experiment or is fraught with great difficulties plays an ever-increasing role. To assure the modeling, it is necessary to know not only the reflection and radiation coefficients of the materials, but also their directional characteristics which describe the spatial distribution of the reflected and intrinsic radiation. The investigations of a number of authors have shown that thermophysical computations which do not take account of the directional radiation characteristics of the structural materials can result in substantial errors [1,2].

One possible means of describing the bireflectional reflective properties of a surface, i.e., the properties characterized by two directions, illumination and observation, is the use of theoretical dependences relating the probabilistic characteristics of the reflected radiation field to the statistical characteristics of the surface roughness [3]. The optical properties of the material and the parameters adequately describing the roughness of its surface should be known. However, the use of a theoretical method is not always possible for structural materials because of the difficulties in determining their optical properties and roughness [4].

In the practice of illumination-engineering computations for materials with an isotropic surface and directionally scattered [5], or directionally diffuse nature, according to the new illumination-engineering terminology [6], of the reflection, the spatial reflection index for specific conditions of directional illumination is approximated by an ellipsoid of revolution whose major axis is oriented in the specular direction [7].

The purpose of this paper is to investigate the possibility of using the illumination-

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