Adsorption Kinetics for the Case of Step and S-Shape Isotherms

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The kinetics of diffusion in a spherical pellet saturated by a sorbate in the presence of an inert component are considered for the case of a step isotherm. A new convective flux inside the pores due to sorption effect has been taken into consideration, and an analytical expression for sorption kinetics is obtained. The convective flux may result in considerable increase in the sorption rate. It is also found that the formula obtained also gives a satisfactory description of sorption kinetics for the case of an S-shaped isotherm.

Introduction

The knowledge of an analytical expression for sorption kinetics in a pellet is very valuable in calculating adsorption separation processes. The reason is that the numerical computation of mass and heat balances equations for each granule, in addition to the balances for the bed, greatly complicates the task. In the present work adsorption kinetics of a spherical pellet saturated by sorbate in the presence of an inert component for the case of a step isotherm has been investigated. Such a type of isotherm can be considered as an extreme variant of S-shaped isotherm (Figure 1) and was classified as type V (Brunauer et al., 1940). Such isotherms describe the behavior of adsorptive systems with large intermolecular attraction effects, such as sorption of water vapors on activated carbon (Stoeckli et al., 1983), or sorption of phosphorous vapors on zeolite NaX (Barrer and Whiteman, 1967). In many cases of practical importance S-shaped isotherms could be more or less successfully approximated by a step isotherm (Figure 1):

$$a = f(c) = \begin{cases} 0 & \text{when } c < c^* \\ a_0 & \text{when } c \geq c^* \end{cases} \tag{1}$$

Most notably, however, the step isotherm describes the behavior of the systems: hydrogen and a hydride-forming metal (intermetallic compound) which have recently been increasingly used in the hydrogen energy technologies because of their ability to absorb hydrogen and its isotopes quickly, reversibly, selectively and copiously (Alefeld and Völkl, 1978). These systems possess a characteristic hydride-forming pressure at which almost a complete saturation of the sorbent takes place and which is an exponential function of inverse temperature.

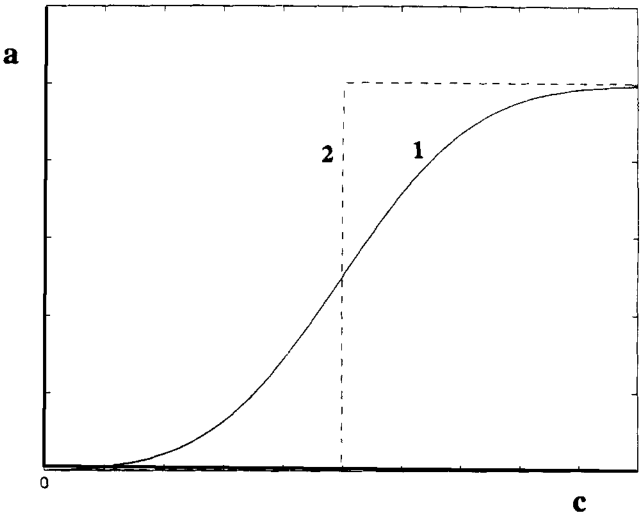

Figure 1. S-shaped sorption isotherm (1); its approximation by a step isotherm (2).

The total flux in a porous sorbent may be given to a high degree of approximation by the sum of the individual fluxes:

$$j = j_g + j_s + j_v \tag{2}$$

where j_g and j_s are fluxes due to gaseous and surface diffusion, respectively; and j_v is a viscous flow due to a gradient of total pressure. Furthermore, we assume that the gas molecules are a continuum, transport by surface diffusion is negligibly small, and there is a constant pressure inside a pellet. Even though pressure is assumed to be constant, in solving the problem we shall introduce the convective flux and accordingly, the expression for the total flux of sorbate inside the pore of a pellet may be rewritten as a sum of diffusive and convective flux terms:

$$j = -D\cdot\frac{\partial c}{\partial r} + \upsilon\cdot c \tag{3}$$

The convective flux should be taken into account in heterogeneous processes occurring when the number of moles of substance in gaseous phase changes. Thus, Crank (1975) considered a diffusive transport in the two regions separated by a plane surface. The process of diffusion may cause changes which bring about the disappearance or appearance of matter at the interface, and hence a resulting bodily movement of the matter in one or both regions relative to the interface. To avoid introducing a convective term in the treatment, the coordinate systems in both regions were specified so that the positions of the interface remained stationary with respect to each medium, correspondingly.

Frank-Kamenetskii (1969) also emphasized that if a heterogeneous reaction is accompanied by a change in volume, there will, inevitably, be a general flow of the reacting mixture in the direction normal to the surface at which the reaction is taking place. He evaluated the diffusion rate change by adding this convective current term to the diffusion flux. He also considered the condensation of vapors in the presence of noncondensing gases and showed that the convective flow may considerably alter the rate of condensation.

In case of adsorption in porous medium, the presence of a convective term in Eq. 3 means that because sorbate leaves gas phase, there is a general movement of the gas through the pores. For the sake of clarity, it should be noticed here that sometimes a term, called also a convective flux, is added in the right part of Eq. 1 (Yang, 1987). This term is due to diffusion and allows for the net diffusive flux in the pores. It, however, is negligibly small and may be omitted for equal countercurrent diffusion in large pores (Mason and Malinauskas, 1983).

Analytical Pseudo-Steady-State Solution

Let us consider the sorption kinetics in the presence of an inert component. As defined above, the problem will be treated for adsorbent with large pores so that there is no hydrodynamic resistance to convective flow.

Under the assumptions mentioned above, the sorbate diffusion equation in a spherical pellet is:

$$\frac{\partial c}{\partial \tau} + \frac{\partial a}{\partial \tau} = \frac{1}{r^2}\frac{\partial}{\partial r}(-r^2\cdot j) \tag{4}$$

where the flow j is determined by both diffusion and convection inside the pores of a pellet in accordance with Eq. 3. After substituting Eqs. 1 and 3 into 4 one may obtain:

$$[1+f'(c)]\frac{\partial c}{\partial \tau} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\left(D\frac{\partial c}{\partial r} - \upsilon\cdot c\right)\right] \tag{5}$$

Similarly, the diffusion equation for an inert component is:

$$\frac{\partial(c_o - c)}{\partial \tau} = \frac{1}{r^2}\frac{\partial}{\partial r}\left[r^2\left(D\frac{\partial(c_0 - c)}{\partial r} - \upsilon\cdot(c_o - c)\right)\right] \tag{6}$$

where (c_o) is the overall molar concentration of gas. At constant temperature and pressure $c_o = \text{const}$, and the addition of Eqs. 5 and 6 results in:

$$f'(c)\frac{\partial c}{\partial \tau} = \frac{c_o}{r^2}\cdot\frac{\partial}{\partial r}(\upsilon\cdot r^2) \tag{7}$$

The set of Eqs. 5 and 7 may be solved for c and υ, having determined appropriate initial and boundary conditions.

In the case of a step isotherm, a core saturation of the pellet takes place, that is, there exists a sharp boundary between saturated area and area free of sorbate in granule. The solution of such a moving boundary problem may often be obtained by using a pseudo-steady-state approximation scheme (Levenspiel, 1962). Let us assume that the rate of movement of the sorption interface is very much lower than the rate of gas-phase diffusion. In this case, the boundary between saturated and the region free of sorbate can be taken to be stationary at any time and a steady-state diffusion problem solved in a corresponding region determines gas-phase concentration profile of the sorbate.

Using the above approach and letting ξ be the radius of the sorption front, integration of the diffusion Eq. 4 over the front $[\xi - 0;\ \xi + 0]$ gives:

$$\left(-D\cdot\frac{\partial c}{\partial r} + \upsilon\cdot c\right)\Bigg|_{\xi+0} - \left(-D\cdot\frac{\partial c}{\partial r} + \upsilon\cdot c\right)\Bigg|_{\xi-0} = a_o\cdot\frac{\partial \xi}{\partial \tau} \tag{8}$$

Since in the region $\xi < r \leq R_o$ sources of mass are absent, we have:

$$\upsilon(r) = \begin{cases} \upsilon_o\cdot\ R_o^2/r^2 & \text{when}\ \xi < r < R_o \\ 0 & \text{when}\ r < \xi \end{cases} \tag{9}$$

Taking into account $\upsilon|_{\xi+0} = \upsilon_o\cdot\ R_o^2/\xi^2$ and $c|_{\xi+0} = c^*$, the equation for the sorbate flux balance at the point ξ may be written as

$$-D\cdot\frac{\partial c}{\partial r}\Big|_{\xi+0} + \frac{\upsilon_o\cdot R_o^2}{\xi^2}c^* = a_o\cdot\frac{\partial \xi}{\partial \tau} \tag{10}$$

As may be seen from Eq. 10, the total mass flux of sorbate towards the sorption boundary is equated to the rate of disappearance of the unsaturated solid phase. The diffusive flux in the region $r < \xi$ is clearly zero. Functions $c(r)$ and $(\upsilon\cdot r^2)$ are sketched in Figure 2 as solid and dashed curves, respectively.

The diffusive flux of sorbate at $r = \xi + 0$ may be determined by solving a stationary equation of diffusion in the area $\xi < r < R_o$ with corresponding boundary conditions:

$$\frac{1}{r^2}\cdot\frac{\partial}{\partial r}\left[\left(-D\cdot\frac{\partial c}{\partial r} + \upsilon\cdot c\right)\cdot r^2\right] = 0 \tag{11}$$

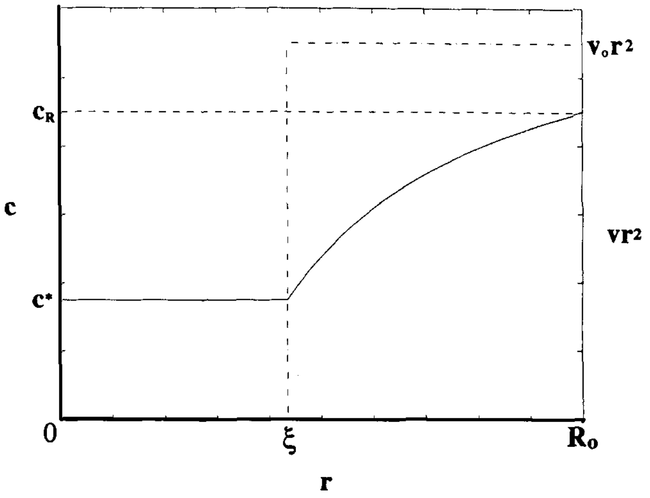

Figure 2. Sorbate concentration profile in gaseous phase c (solid curve) and convective flux velocity (as $v\cdot r^2$ function, dotted curve) vs. radial granule coordinate for a case of a step isotherm.

$$c|_{r=R_o}=c_R;c|_{r=\xi}=c^* \tag{12}$$

Using the relation 9, Eq. 11 may be rewritten as

$$\frac{\partial}{\partial r}\left(-D\cdot r^2\cdot\frac{\partial c}{\partial r}+R_o^2\cdot v_o\cdot c\right)=0 \tag{13}$$

An analytical solution of Eq. 13 with boundary conditions 12 is:

$$c=\frac{c^*-c_R\cdot\exp[\gamma(1-1/\eta)]+(c_R-c^*)\cdot\exp[\gamma(1-1/R)]}{1-\exp[\gamma(1-1/\eta)]} \tag{14}$$

where $R=r/R_o$, $\gamma=v_o\cdot R_o/D$, and $\eta=\xi/R_o$ is the dimensionless radial coordinate of sorption front. After substituting Eq. 14 into Eq. 10 one may obtain:

$$-\frac{v_o}{\eta^2}\cdot\frac{(c_R-c^*)}{1-\exp[\gamma(1-1/\eta)]}\cdot\exp[\gamma(1-1/\eta)]+\frac{v_o\cdot c^*}{\eta^2}$$
$$=a_o\cdot\frac{d\xi}{d\tau}=\frac{R_oa_od\eta}{d\tau} \tag{15}$$

To integrate Eq. 15 it is necessary to determine the value of convective flux velocity v_o on the external surface of the pellet. Integrating Eq. 7 over the granule radius gives:

$$\frac{\partial}{\partial\tau}\int_0^{R_o}4\cdot\pi\cdot r_o^2\cdot a\cdot dr=-4\cdot\pi\cdot c_o\cdot[v_o\cdot R_0^2-(v\cdot r^2)|_{r=0}] \tag{16}$$

The left side of Eq. 16 represents the value of sorption rate per pellet which in the case of core saturation is $4\,\pi a_0 d\xi/d\tau$. Using this we come to an expression for the value of v_o:

$$v_o=\frac{a_o}{c_o}\cdot\frac{\xi^2}{R_o^2}\cdot\frac{d\xi}{d\tau} \tag{17}$$

Solving Eqs. 15, 17 about v_o and ξ, we obtain the equation for determination of the location of the dimensionless sorption interface coordinate η as a function of time:

$$\frac{d\eta}{d\tau}=\frac{a_o}{c_o}\cdot\frac{D}{\eta(\eta-1)}\cdot\ln\frac{c_o-c_R}{c_o-c^*}$$

Dividing variables and integrating this equation over time from 0 to τ and over radius from ξ to R_o, we obtain an expression reflecting the dependence of an adsorption front coordinate on time when one or both of the external sorbate concentration c_R or the temperature-dependent value of c^* is changing:

$$2\eta^3-3\eta^2+1=6\cdot\frac{c_o}{a_0}\cdot\frac{D}{R_o^2}\cdot\int_0^r\ln\frac{c_o-c^*}{c_o-c_R}d\tau \tag{18}$$

It is interesting to note that Frank-Kamenetskii (1969) obtained a similar logarithmic quantity which accounts for the process rate change due to convective flux for the cases of heterogeneous reaction with the participation of condensed phase and for condensation of vapors in the presence of noncondensing gases.

Let us now estimate the contribution of the convective flux to the total flux of sorbate inside a pellet. Assuming that c_R and c^* are constant values, the time corresponding to a complete saturation of a pellet T (at $\eta=0$) can be readily determined from integrating Eq. 18:

$$T=\frac{a_0\cdot R_o^2}{6\cdot c_o\cdot D}\cdot\frac{1}{\ln[(c_o-c^*)/(c_o-c_R)]}$$

For the case of a rectangular (irreversible) isotherm when convective flux effect is not taken into consideration, there is a well-known formula for saturation of a pellet (Dedrick and Beckman, 1967):

$$2\eta^3-3\eta^2+1=6\cdot\frac{c_R\cdot D}{a_o\cdot R_o^2}\cdot\tau$$

It may be shown that when replacing a rectangular isotherm by a step one, the above formula transforms into

$$2\eta^3-3\eta^2+1=6\cdot\frac{(c_R-c^*)\cdot D}{a_o\cdot R_0^2}\cdot\tau \tag{19}$$

with the time of a complete pellet saturation T'

$$T'=\frac{a_0\cdot R_o^2}{6\cdot D}\cdot\frac{1}{(c_R-c^*)}$$

The contribution of the convective flux to the total flux of sorbate inside granule pores may be represented by the value of T/T', which is the ratio of times of a full pellet saturation when convective flow effect is involved and when it is not:

$$T/T' = \frac{\Gamma^* - \Gamma_R}{\ln(\Gamma^*/\Gamma_R)} \tag{20}$$

where $\Gamma^* = 1 - c^*/c_o$, $\Gamma_R = 1 - c_R/c_o$. The convective flux as it is seen from Eq. 20 and Figure 3 may result in a considerable sorption rate increase. Its contribution to the total flow increases with increasing c^*, corresponding to the breakpoint of the isotherm, as well as with an increase of the initial sorbate concentration c_R. Thus, for example, at $c^* = 0$ and $c_R/c_o = 0.6$ a complete saturation of a pellet is achieved 1.5 times faster than when the convective flux is absent ($T/T' = 0.66$), whereas at $c^* = 0.9$ and $c_R/c_o = 0.8$ the above value is equal to about 7 times ($T/T' = 0.14$). If the adsorptive component is highly diluted with an inert gas (c^*, $c_R \ll c_o$) both Γ^* and Γ_R are far less than unity. Calculations with Eqs. 18 and 19 coincide, and the influence of convective flow on the adsorption rate is negligibly small.

The other limit is when the concentration of adsorptive c_R is approaching the total concentration in the gas phase c_o. We see from Eq. 18 that if one switches to pure adsorptive component at time zero ($c_R/c_o = 1$), the adsorption becomes instantaneous. This is because of the steady-state approximation used, which takes a steady-state gas-phase concentration profile to obtain solution. This approach is not valid when the concentration of sorbate c_R is approaching the total concentration in the gas phase c_o. In fact, when $c_R = c_o$ (pure adsorptive component on the external surface of the pellet) the steady-state solution predicts no mass transfer in the gas phase that causes an instantaneous advancement of the adsorption interface in the pellet. To illustrate the limited applicability of the steady-state approximation, Figure 3 also shows the results obtained from a direct numerical integration of the nonsteady-state problem (see next section for details). The value T in this case corresponds to the time of 99.5% pellet saturation. One can see that there is a good agreement between a numerical solution and analytical correlation 18 except for the region of high relative adsorptive concentrations ($c_R/c_o > 0.95$).

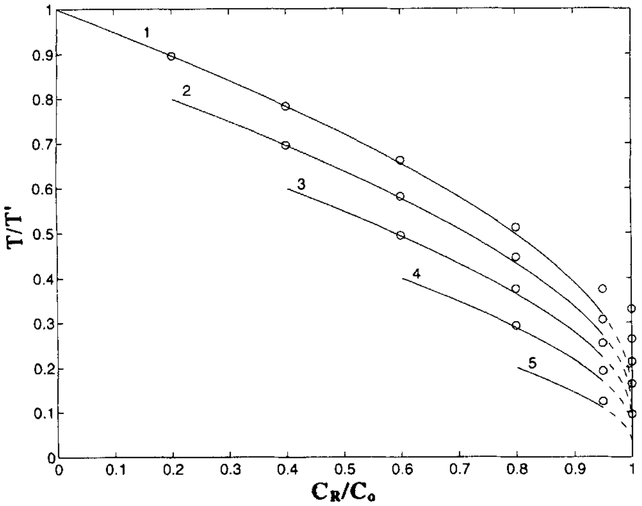

Figure 3. Dependence of T/T' value on concentration c_R (solid curves) at various values of c^*: 1 – $c^* = 0$; 2 – $c^* = 0.2 \cdot c_o$; 3 – $c^* = 0.4 \cdot c_o$; 4 – $c^* = 0.6 \cdot c_o$; 5 – $c^* = 0.8 \cdot c_o$.

Circles represent the data obtained from numerical calculations for values of T corresponding to time of 99.5% pellet saturation.

Numerical Calculations

In order to verify Eq. 18, a set of Eqs. 5 and 7 was solved using numerical methods. For this, the equation of diffusion 5 was rewritten as:

$$\frac{\partial c}{\partial \tau} = \frac{1}{1 + da/dc} \cdot \frac{1}{r^2}\left[r^2\left(D\frac{\partial c}{\partial r} - v \cdot c\right)\right] \tag{21}$$

In the case of a step isotherm 1:

$$da/dc = a_o \cdot \delta(c - c^*), \tag{22}$$

where δ is Dirac function, moreover,

$$\int_0^1 \delta(c - c^*)\,dc = 1 \tag{23}$$

To obtain a numerical solution, the delta function in Eq. 21 was smoothed and the derivative in Eq. 21 was replaced by the approximating function:

$$\frac{da}{dc} = \frac{1}{\sqrt{2}\,\pi\sigma_x} \cdot \exp\left[-\frac{(c - c^*)^2}{2\pi \cdot \sigma_x^2}\right] \tag{24}$$

for which condition 23 is true. This provided a conservative solution (Samarsky, 1971), while allowing use of numerical grid methods.

The set of Eqs. 7 and 21 with the use of Eq. 24 was solved by the finite difference method with the implicit scheme and adaptive grid generation (Thompson et al., 1985).

Initial and boundary conditions were chosen as following:

$$r = 0 \quad \partial c/\partial r = 0,\ v = 0;$$

$$r = R_o \quad c = c(\tau);$$

$$\tau = 0 \quad a(r,0) = c(r,0) = v(r,0) = 0$$

As an example, in Figure 4 the gas-phase sorbate concentration profiles as calculated vs. radial granula coordinate are shown at various instants of time. It was found that at $\sigma_x = 0.015$ (Figure 4a), the isotherm with Eq. 24 as its da/dc derivative approximates a step isotherm quite well, still providing a rather accurate numerical solution. The dashed lines in Figure 4 represent the adsorption front coordinate calculated on Eq. 18 at corresponding values of time τ/T. Numerical calculations were conducted both for constant concentration c_R on the external boundary of a pellet, and also with c_R varied according to several power functions. Calculations at time-dependent concentration c^* simulating nonisothermal

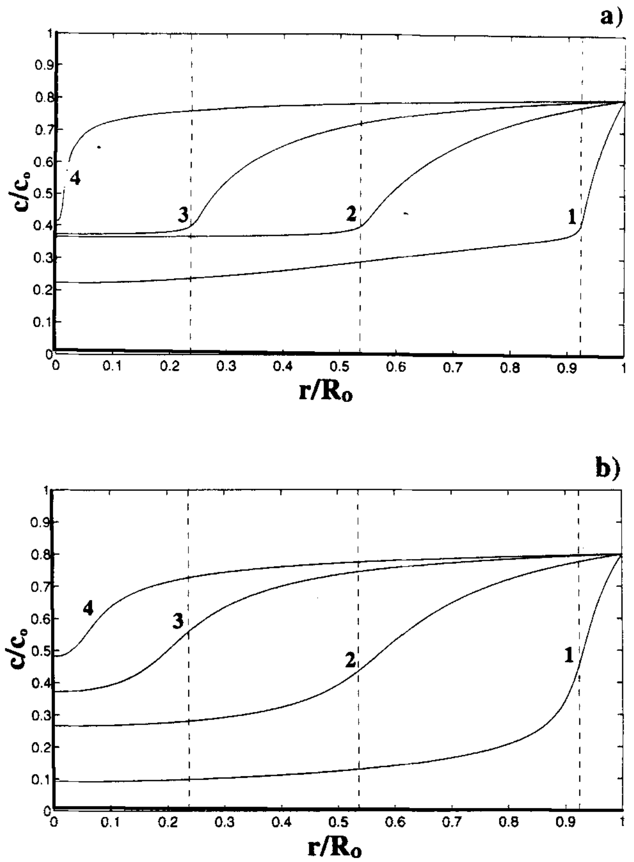

Figure 4. Gas-phase sorbate concentration profiles as calculated for two isotherms with (*a*) $\sigma_x = 0.015$; (*b*) $\sigma_x = 0.10$ at various instants of time.

1 − $\tau/T = 0.15$; 2 − $\tau/T = 1.15$; 3 − $\tau/T = 3.30$; 4 − $\tau/T = 6.65$. $c_R = 0.8\cdot c_o$; $c^* = 0.4\cdot c_o$; $a_o/c_o = 70$. Dashed lines show the adsorption front coordinate calculated on Eq. 18.

conditions were also carried out. It is found that the formula 18 describes the data of a numerical solution quite adequately (Figure 5) except for the region of high relative concentrations of adsorption for the reason discussed in the previous section.

We also applied formula 18 for describing sorption kinetics in the case of an S-shaped isotherm, because parameter σ_x in the approximation function 24 determines the "dispersion" of isotherm. Calculations carried out at various values of σ_x show that formula 18 adequately describes sorption kinetics not only for a step isotherm but also may be used for calculation of adsorption kinetics for systems having S-shaped isotherms. As an example, in Figures 4b and 5 sorption isotherm calculated from Eq. 24 for parameter $\sigma_x = 0.10$ was used to calculate concentration profiles dynamics and sorption kinetic curves. Those obtained by numerical calculation agree well with those from the formulae 18 and 19.

Thus, in this work the analytical expression for calculation of sorption kinetics in the case of a step isotherm has been obtained. Convective flux was found to result in a marked increase in the sorption kinetic rate. The formulae obtained also satisfactorily describe sorption kinetics for case of S-shaped isotherms.

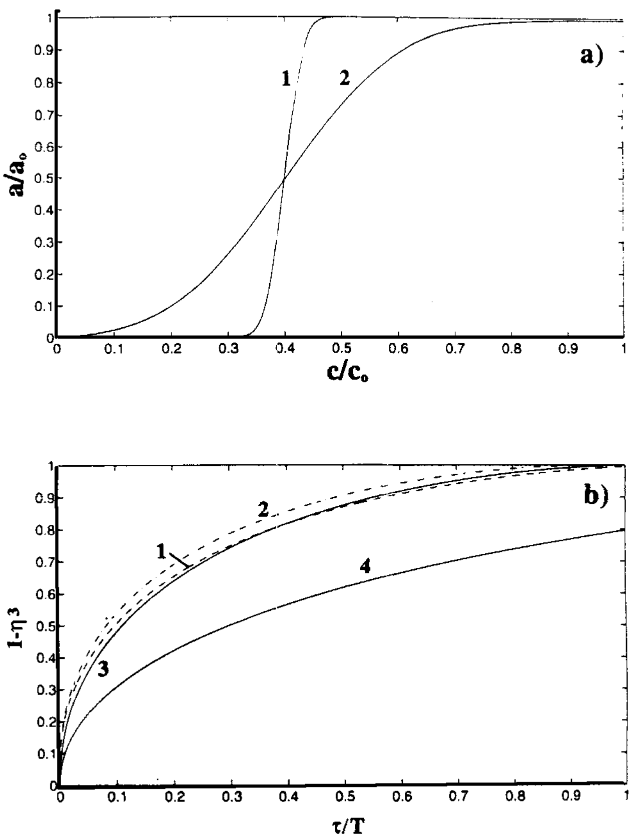

Figure 5. Calculated on Eq. 24 S-shaped isotherms (a); corresponding sorption kinetic curves (b).

1,2-numerical calculations; 3,4-calculations for the case of a step isotherm on Eq. 18 and 19, respectively. 1 − $\sigma_x = 0.015$; 2 − $\sigma_x = 0.10$. $c_R = 0.8\cdot c_o, c^* = 0.4\cdot c_o$; $a_o/c_o = 70$.

Notation

a = concentration of sorbate in solid phase
a_o = concentration of sorbate in solid phase corresponding to a complete saturation of solid phase
c = concentration of sorbate in gaseous phase
c^* = concentration of sorbate in gaseous phase at which a complete saturation of sorbent occurs in case of a step isotherm
c_o = total concentration in the gas phase, adsorptive component + inert
$c_R = c|_{r=R_o}$ = concentration of sorbate in gaseous phase on the external surface of the pellet
D = effective pore diffusivity
j = flow of sorbate inside the pores of a pellet
r = radial pellet coordinate
R_o = pellet radius
$R = r/R_o$ = dimensionless pellet radius
T/T' = ratio of the times of a complete pellet saturation when convective flux effect is involved and when it is not, respectively
v = convective flux velocity inside pellet pores
$v_o = v|_{r=R_o}$ = value of v at $r = R_o$

Greek letters

$\gamma = v_o\cdot R_o/D$
$\eta = \xi/R_o$ = dimensionless sorption front radial coordinate
ξ = sorption front radial coordinate
τ = time

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