Dynamics of binary adsorption in a continuous stirred tank reactor

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In this paper two dynamical models of binary adsorption process in an isothermal CSTR reactor are developed. The first model assumes negligible resistance to mass transfer in the sorbent particle, in the second one the second Fick's law with constant diffusion coefficient is used as the model of the internal diffusion. A description of the algorithm for solution of the system of governing equations is given and numerical results are compared with experimental ones.

В работе разработаны две динамические модели процесса бинарной адсорпции в изотермическом реакторе непрерывного действия полного смешения. Первая модель предполагает пренебрежимо малое сопротивление переносу материи в частицах сорбента, во второй модели используется второй закон Фика с постоянным коэффициентом диффузии для описания внутренней диффузии. Приводится описание алгорифма решения системы уравнений управления и численные результаты сравниваются с экспериментальными данными.

In our previous papers [1, 2] models of the sorption of one component in a CSTR reactor have been developed. Three dynamical models have been used. In the first model we have assumed negligible resistance to mass transfer in the sorbent particle (*i.e.* equilibrium sorption), in the second and third models the second Fick's law with constant diffusion coefficient has been used as the model for internal diffusion in the sorbent particle. In Model 2 we have assumed the diffusion coefficient to be constant while in Model 3 we allowed the diffusion coefficient to be concentration-dependent.

In this paper we generalize the first and second models, *i.e.* the equilibrium model and the model with the constant diffusion coefficient, to the case of binary adsorption.

Equations of the models and methods of their solution

Consider a CSTR reactor containing sorbent particles placed in the stirrer blades. Assume that the reactor satisfies the following assumptions:

i) The reactor works under isothermal conditions (the temperature in the gaseous as well as solid phase is equal and constant).

ii) The mixing of the gaseous phase is perfect.

iii) The particles are approximately of the same shape and size and, consequently, the distribution of concentration of both components at a given time is the same on each of the particles.

iv) The resistance to the mass transfer from the gaseous phase to the particle is negligible.

Under these assumptions the material balance for each component can be expressed by the following equations

$$\frac{\mathrm{d}\varphi_i(t)}{\mathrm{d}t} = \frac{1}{V}\left[\dot{V}\,\varphi_{i0} - N\frac{\mathrm{d}M_i(t)}{\mathrm{d}t} - \dot{V}\,\varphi_i(t)\right], \quad i = 1, 2 \tag{1}$$

where φ_{i0} is the concentration of the i-th component in the inlet flow, $\varphi_i(t)$ is the concentration in the gaseous phase in the reactor (and due to assumption (ii) also in the outlet flow) at the time t, $M_i(t)$ is the adsorbed amount of the i-th component in one sorbent particle, N is the number of sorbent particles in the reactor, V is the volume of the gaseous phase in the reactor, and $\dot{V}$ is the volumetric flow rate.

The adsorbed amount of the i-th component in one particle is given by

$$M_i(t) = 4\pi \int_0^a r^2 c_i(t, r)\,\mathrm{d}r, \; i = 1, 2 \tag{2}$$

where a is the radius of the particle, r is the radial coordinate, and $c_i(t, r)$ is the concentration of the i-th component in the particle at the time t at the points of radius r.

The initial and boundary conditions follow from the organization of the experiment

$$\begin{gathered} \varphi_i(t) = \varphi_{i0} = 0 \quad c_i(t, r) = 0 \quad t < 0 \\ \varphi_{i0} = \text{const} \quad c_i(t, a) = C_i(\varphi_1, \varphi_2) \quad t \geqq 0 \end{gathered} \tag{3}$$

The solution of the system of eqns (*1*) and (*2*) with initial and boundary conditions (*3*) depends on the model of the internal diffusion in the sorbent particle and on the equation of the adsorption isotherm. If we assume equilibrium adsorption (*i.e.* Model 1), the concentration of the i-th component in the particle is

$$c_i(t, r) = C_i(\varphi_1, \varphi_2), \quad r \in (0, a) \tag{4}$$

and the adsorbed amounts are

$$M_i(t) = 4\pi \int_0^a r^2 C_i(\varphi_1, \varphi_2)\, \mathrm{d}r = \frac{4}{3}\pi a^3 C_i(\varphi_1, \varphi_2) \tag{5}$$

The material balance equations are then as follows

$$\frac{\mathrm{d}\varphi_i(t)}{\mathrm{d}t} = \frac{\dot{V}}{V}\left[\varphi_{i0} - \varphi_i(t)\right] - \frac{4\pi N a^3}{3V}\,\frac{\mathrm{d}C_i(\varphi_1, \varphi_2)}{\mathrm{d}t} \tag{6}$$

As the equation of the adsorption isotherm we choose the Langmuir equation in the form

$$C_i(\varphi_1, \varphi_2) = \frac{b_i k_i \varphi_i}{1 + k_1\varphi_1 + k_2\varphi_2} \tag{7}$$

After substituting for $C_i(\varphi_1, \varphi_2)$ into eqn (*6*) the following system of two differential equations is obtained

$$\frac{\mathrm{d}\varphi_1(t)}{\mathrm{d}t}\,\gamma_1(\varphi_1, \varphi_2) = \delta_1(\varphi_1, \varphi_2) + \omega_1(\varphi_1)\,\frac{\mathrm{d}\varphi_2(t)}{\mathrm{d}t} \tag{8}$$

$$\frac{\mathrm{d}\varphi_2(t)}{\mathrm{d}t}\,\gamma_2(\varphi_1, \varphi_2) = \delta_2(\varphi_1, \varphi_2) + \omega_2(\varphi_2)\,\frac{\mathrm{d}\varphi_1(t)}{\mathrm{d}t} \tag{9}$$

where

$$\omega_1(\varphi_1) = 4\pi a^3 N b_1 k_1 k_2 \varphi_1$$

$$\omega_2(\varphi_2) = 4\pi a^3 N b_2 k_1 k_2 \varphi_2$$

$$\gamma_1(\varphi_1, \varphi_2) = 3V(1 + k_1\varphi_1 + k_2\varphi_2)^2 + 4\pi N a^3 b_1 k_1 (1 + k_2\varphi_2)$$

$$\gamma_2(\varphi_1, \varphi_2) = 3V(1 + k_1\varphi_1 + k_2\varphi_2)^2 + 4\pi N a^3 b_2 k_2 (1 + k_1\varphi_1)$$

$$\delta_1(\varphi_1, \varphi_2) = 3\dot{V}(1 + k_1\varphi_1 + k_2\varphi_2)^2\,(\varphi_{10} - \varphi_1)$$

$$\delta_2(\varphi_1, \varphi_2) = 3\dot{V}(1 + k_1\varphi_1 + k_2\varphi_2)^2\,(\varphi_{20} - \varphi_2)$$

Eqns (*8*) and (*9*) we solved numerically by the Runge—Kutta method of the 4th order.

For Model 2 we assume that the particles are homogeneous and isotropic and we use the second Fick's law with constant diffusion coefficient as a model of the internal diffusion

$$\frac{\partial c_i(t, r)}{\partial t} = D_i\left[\frac{\partial^2 c_i(t, r)}{\partial r^2} + \frac{2}{r}\,\frac{\partial c_i(t, r)}{\partial r}\right], \quad i = 1, 2 \tag{10}$$

Because of spherical symmetry of the concentration in the particle ($\partial c_i(t, 0)/\partial r = 0$), under the initial and boundary conditions (*3*), the solution of this equation

can be expressed by the infinite series form given in [3]. Substituting this series into eqn (*2*) we obtain for the adsorbed amounts

$$M_i(t)=\frac{8a^3}{\pi}\left[\beta_i(t)-\int_0^t \alpha_i(t-\lambda)\frac{\mathrm{d}C_i(\varphi_1(\lambda),\,\varphi_2(\lambda))}{\mathrm{d}t}\mathrm{d}\lambda\right],\quad i=1,2 \qquad (11)$$

where

$$\alpha_i(t)=\sum_{n=1}^{\infty}\frac{1}{n^2}\,e^{-D_i n^2\pi^2 t/a^2}$$

$$\beta_i(t)=C_i(\varphi_1(t),\,\varphi_2(t))\sum_{n=1}^{\infty}\frac{1}{n^2}$$

Substituting eqn (*11*) into the material balance equations (*1*) we obtain

$$\frac{\mathrm{d}\varphi_i(t)}{\mathrm{d}t}=\frac{\dot{V}}{V}[\varphi_{i0}-\varphi_i(t)]-\frac{8Na^3}{V\pi}\frac{d}{\mathrm{d}t}\left[\beta_i(t)-\right.$$

$$\left.-\int_0^t \alpha_i(t-\lambda)\frac{\mathrm{d}C_i(\varphi_1(\lambda),\,\varphi_2(\lambda))}{\mathrm{d}t}\mathrm{d}\lambda\right],\quad i=1,2 \qquad (12)$$

Integrating eqn (*12*) we obtain the resulting equations for concentrations $\varphi_i(t)$

$$\varphi_i(t)=\frac{\dot{V}}{V}\varphi_{i0}t-\frac{8Na^3}{V\pi}\left[\beta_i(t)-\int_0^t \alpha_i(t-\lambda)\frac{\mathrm{d}C_i(\varphi_1(\lambda),\,\varphi_2(\lambda))}{\mathrm{d}t}\mathrm{d}\lambda\right]-$$

$$-\frac{\dot{V}}{V}\int_0^t \varphi_i(t)\,\mathrm{d}t,\quad i=1,2 \qquad (13)$$

Model 2 consists of the system of eqns (*7*), (*11*), and (*13*), which we solve by the following iterative method: Having computed the values φ_i, M_i, C_i for some t, choose a value of φ_i^0 for $(t+\Delta t)$, compute C_i from eqn (*7*), M_i from eqn (*11*), and φ_i from eqn (*13*). If the difference between φ_i^0 and φ_i is greater than the predetermined tolerance, adjust the choice of φ_i^0, otherwise continue the computation for the next time step.

Experimental

The dynamics of binary adsorption has been measured in a laboratory isothermal continuous stirred tank reactor with spherical sorbent particles of approximately equal diameter placed in the stirrer blades. The reactor, together with the set of equipment for the preparation of the sorption gas, analyzer of the gaseous stream, and the set of the equipment for measuring and controlling important operational variables is described in [4].

The measurements used in this paper have been performed on the molecular sieve Calsit 5A at temperature 80°C with n-heptane (component 1) and n-octane (component 2) as adsorbates. The volume of the gaseous phase in the reactor and the volumetric flow rate have been 101.4 cm^3 and 23.5 cm^3 min^{-1}, respectively. The revolution of the stirrer has been kept sufficiently high (750 min^{-1}) in order to enable us to assume perfect mixing and, consequently, uniform concentration of both the components in the gaseous phase throughout the reactor and to neglect the resistance to the mass transfer from the gaseous phase to the particle (assumptions (ii)—(iv)). The concentrations in the flow of inert gas (nitrogen) at the inlet into the reactor were $\varphi_{10} = 0.991 \times 10^{-5}$ g cm^{-3}, $\varphi_{20} = 1.160 \times 10^{-5}$ g cm^{-3} (the ratio of partial pressures was 1 : 1). The concentrations in the outflowing stream have been measured during the experiment by a gas chromatograph. The adsorbed amounts have been obtained from the material balance. The total weight of pure sorbent has been 1.2624 g (90 particles of mean diameter 0.145 cm).

In the case of Model 2 we have approximated the values of the diffusion coefficients by $D_{1,2} = 0.2 \times 10^{-5}$ cm^2 s^{-1} [1].

The values of the constants of the adsorption isotherm (7) we have obtained from the experimental equilibrium data by least-square fit estimation [5]. For the described system at temperature 80°C the values are: $b_1 = 0.0563$ g cm^{-3}; $b_2 = 0.1294$ g cm^{-3}; $k_1 = 4.288 \times 10^6$ cm^3 g^{-1}; $k_2 = 5.616 \times 10^6$ cm^3 g^{-1}.

Numerical results and conclusions

The experimental and computed dependences of the gaseous phase $\varphi_i(t)$ and the adsorbed amounts $A_i(t)$ on time are compared in Figs. 1 and 2.

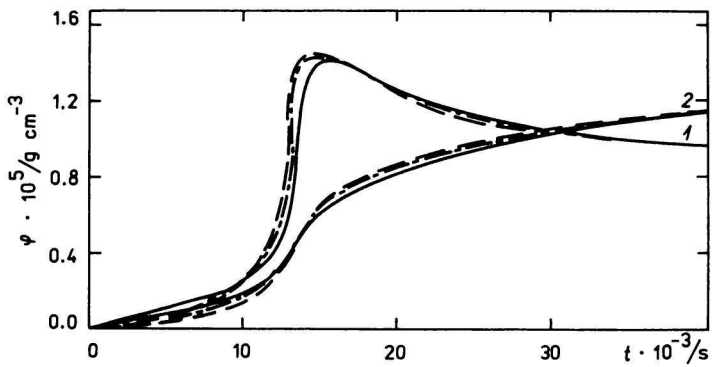

Fig. 1. Gaseous phase concentration $\varphi_i(t)$ *vs.* time.
1. n-Heptane; *2.* n-octane.
——— Experiment; – – – – Model 1; –·–·–·– Model 2.

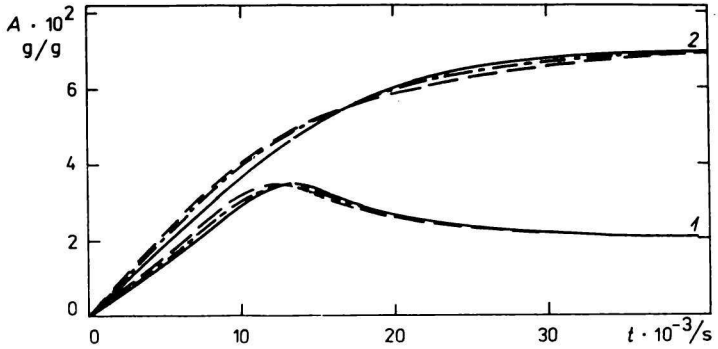

Fig. 2. Adsorbed amount $A_i(t)$ *vs.* time.
1. n-Heptane; *2.* n-octane.
——— Experiment; – – – – Model 1; –·–·–·– Model 2.

In the beginning n-heptane is adsorbed faster, later it is being replaced by n-octane. A consequence is the occurrence of maximum in the time dependences of $\varphi_1(t)$ and $A_1(t)$. This phenomenon is very well reflected by both the models. Figs. 1 and 2 exhibit very good coincidence of computed and experimental dependences. Model 2, in which mass transfer in the particle is modelled by the second Fick's law gives better coincidence than the equilibrium model. Model 1 is important as a limit case (it gives maximal adsorbed amounts and corresponding concentrations in the gaseous phase at a given time).

Symbols

$A_i(t)$ adsorbed amount of the i-th component at the time t [g/g]
a radius of the particle
b_i constants of the adsorption isotherm
$c_i(t, r)$ concentration of the i-th component in the particle at the time t at the points of radius r
C_i equilibrium concentration of the i-th component
D_i diffusion coefficient of the i-th component
k_i constants of the adsorption isotherm
$M_i(t)$ adsorbed amount of the i-th component in one particle at the time t
N number of sorbent particles
r radial coordinate
t time
V volume of the gaseous phase in the reactor
$\dot{V}$ volumetric flow rate
φ_{i0} concentration of the i-th component in gaseous phase in the inlet flow
$\varphi_i(t)$ concentration of the i-th component in gaseous phase in the reactor

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