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Simulation of adsorption dynamics in adsorbent layers of short length. Estimation of the concentration region of validity of Zeldovich′s equality

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The frontal adsorption dynamics with the convex adsorption isotherm at a stage of parallel transfer, was numerically simulated. The change with time in the mean adsorption values a_c in the adsorbent layers of short length ΔL and corresponding concentrations $c_{\Delta L}$ at the outlet from ΔL was calculated. Zeldovich′s equality, which suggests that the ratio of $c_{\Delta L}$ to a_c is equal to the ratio of the inlet fluid phase concentration to the amount adsorbed at equilibrium, is fulfilled at $\Delta L \to 0$ over the interval of relative concentrations from 10^{-4} to 1. This indicates that Zeldovich′s equality is fulfilled as local at any limiting stage of mass transfer. The nonequilibrium dynamics of adsorption always has the finite ΔL value at which the calculated $c_{\Delta L}$ and a_c values approximately coincide with the a and c values of the equilibrium adsorption isotherm.

Key words: simulation, adsorption dynamics, convex adsorption isotherm, adsorbent layers of short length, Zeldovich′s equality.

The solution of the direct problem of adsorption dynamics usually includes the description of breakthrough curves obtained at the length of the adsorbent layer L = const or concentration fronts when time t = const. The phenomenological description of regularities of the formation of adsorption fronts is of certain interest, being important, for example, in studies of the catalyst poisoning with the physically adsorbed gas. To solve this problem, one can use Zeldovich′s equality, which allows the calculation of the amount adsorbed from the effluent concentration.

This equality, which has been theoretically shown initially by Zeldovich,[1] is written in the form

$$c/c_0 = a/a_0, \qquad (1)$$

where c and a are the local values of the effluent concentration and adsorption value, c_0 is the inlet concentration, and a_0 is the adsorption value at equilibrium with c_0.

Equality (1) was proposed for the description of the frontal nonequilibrium adsorption dynamics with the convex adsorption isotherm at the stage of parallel transfer of the stationary adsorption front. Then different approaches to the interpretation and derivation of equality (1) were developed.[2—4] Earlier the limits of validity of (1) for different adsorptive concentrations were estimated neither experimentally nor theoretically.

The purpose of this work is to determine the limit of validity of (1) by the simulation of the adsorption dynamics in adsorbent layers of short length.

Numerical simulation

The processes of adsorption dynamics (AD) in adsorbent layers with different ΔL lengths were simulated. The mean adsorption value a_c on this adsorption layer and concentration $c_{\Delta L}$ or concentration $c_1(t)$ at the outlet of this layer were simultaneously calculated using the approach based on the model of equilibrium adsorption layer and developed to solve the inverse problem for the frontal and breakthrough dynamics of adsorption.[5]

In this approach, the mean adsorption value a_c on the adsorbent layer with the length $\Delta L = L_1 - L_2$ is determined. With this purpose, summation of the functions of the concentration *vs.* time (breakthrough curves measured on the adsorbent layers L_1 and L_2 long) is effected by the following equation:

$$a = (v/\Delta L)\int_0^t [c_2(t) - c_1(t)]\mathrm{d}t\,, \qquad (2)$$

in which $c_1(t)$ and $c_2(t)$ are the breakthrough curves measured for the adsorbents layers with lengths L_1 and L_2 ($L_1 > L_2$) and simultaneously $c_1(t)$ is the concentra-

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tion $c_{\Delta L}$ at the outlet of the layer ΔL, and v is the linear velocity of the vapor-air flow, mobile phase. The functions $c_1(t)$ and $c_2(t)$ can be determined experimentally or theoretically. For commonly used dimensionalities, the constant factor in Eq. (2) is presented in the form $w/\Delta m$, where w is the flow rate of the mobile phase, and Δm is the adsorbent weight in a ΔL long column.

For convex adsorption isotherms, integration in Eq. (2) becomes possible on the basis of one experimental (theoretical) breakthrough curve $c_1(t)$ measured at the stage of parallel transfer of the adsorption front. This possibility is due to the fact that for stationary conditions the value of the $c_2(t)$ function for arbitrary L_2 necessary for calculations using Eq. (2) can easily be obtained by the transference of the breakthrough curve $c_1(t)$ measured for the adsorbent layer L_1. The mean adsorption value a_c in the adsorbent layer with $\Delta L = L_1 - L_2$ is calculated as follows (Fig. 1).

The curve $c_2(t)$ is plotted in parallel to the measured (calculated) breakthrough curve $c_1(t)$, and the value $\Delta L = L_1 - L_2$ is determined from the equality

$$\Delta L = L_1 - L_2 = L_1(t_1 - t_2)/t_1, \quad (3)$$

where t_1 and t_2 are the breakthrough times of the halved concentration for the breakthrough curves, measured for the adsorbent layer L_1 and plotted for the adsorbent layer L_2, respectively.

The adsorption values a_i for the corresponding concentrations c_{1i} are calculated according to Eq. (2). The integral in the right part of Eq. (2) is determined from the surface area S_i confined by the curves $c_1(t)$ and $c_2(t)$ and the vertical to time t_i of the appearance of concentration c_{1i}. The successive calculation of the adsorption values for the whole interval of measured or calculated concentrations is carried out in the same way.

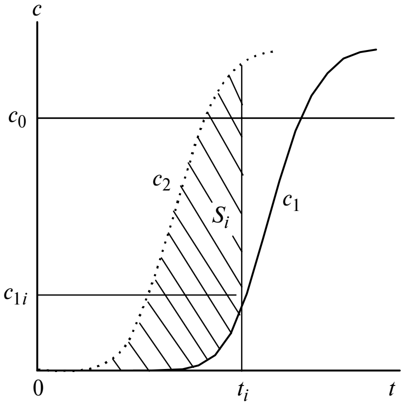

Fig. 1. Scheme of calculation of mean adsorption values on adsorbent layers of short length at the stage of parallel transfer: c_0, initial concentration; c_1, breakthrough curve measured on the adsorbent layer with L_1; c_2, breakthrough curve on the adsorbent layer with L_2 obtained by parallel transfer of curve c_1; and S_i, surface area confined by curves c_1 and c_2 and the vertical to time t_i of the appearance of concentration c_{1i}.

The previously published data[6] on the adsorption dynamics of ethyl chloride on active carbon were used for numerical simulation. The initial concentration was 5 mg L^{-1}, flow rate of the vapor-air flow was 500 cm min^{-1}, and size of adsorbent granules was $\approx$ 0.1 cm. The adsorption isotherm is presented by the following equation of the theory of volume filling of micropores[7]: $a = 285\exp[-0.159\log^2(3529/c)]$. For calculations, the initial length of the adsorbent layer L_1 was taken to be 8 cm, which corresponds to the established regime of parallel transfer.[6] The section of the adsorbent layer length ΔL was varied from 0.715 to 0.018 cm. The model of equilibrium adsorption layer[8] was used for the calculation of breakthrough curves $c_1(t)$ and $c_2(t)$. The curves $c_2(t)$ can be obtained from any appropriate model or by simple graphical transfer of the corresponding values of curve $c_1(t)$.

Results and Discussion

The plots $a_c/a_0 = f(c_{\Delta L}/c_0)$ calculated for different intervals of the relative adsorptive concentration and the equilibrium adsorption isotherm related to a_0 and c_0 are presented in Fig. 2. It is seen that with decreasing ΔL these plots gradually approach linear Eq. (1). Thus, for the nonequilibrium frontal dynamics of adsorption at the stage of parallel transfer of the adsorption front in a wide interval of changing relative concentrations c/c_0 from 10^{-4} (and lower) to 1, the differences $Z = (a_c/a_0 - c_{\Delta L}/c_0)$ tend to zero at $\Delta L \to 0$. This implies that Eq. (1) is the equality of the local values c/c_0 and a/a_0 at $\Delta L = 0$.

The dependence of the Z difference on relative concentrations is more pronounced in Fig. 3. It is seen that for different $c_{\Delta L}/c_0$ values, the plots of Z *vs.* ΔL can be convex, linear, and concave. We will not discuss in this work reasons for different functional relations between Z and ΔL at different $c_{\Delta L}/c_0$ values but note that for any $c_{\Delta L}/c_0$, including very low values, Z approaches zero at $\Delta L \to 0$.

For other variants of the frontal adsorption dynamics, for example, at a concave isotherm, the scheme presented above cannot be used for calculations because, in this case, the stage of parallel transfer is not observed. For the linear frontal adsorption dynamics our predictions are as follows. At the asymptotic stage where L are sufficiently high, the equality $a_c/a_0 = \Gamma(c_{\Delta L}/c_0)$, where Γ is Henry's constant, should be obeyed between the relative mean adsorption on the adsorbent layer ΔL and outlet concentration behind the ΔL layer. Since a_c is measured on the adsorbent layer with the final length for local a and c values Z is negative, whereas for the linear desorption dynamics it is positive.

In addition, for the final ΔL value, which is equal to 0.5 cm in the given case (see Fig. 2, *a* and *b*), the calculated a_c/a_0 and $c_{\Delta L}/c_0$ values coincide completely

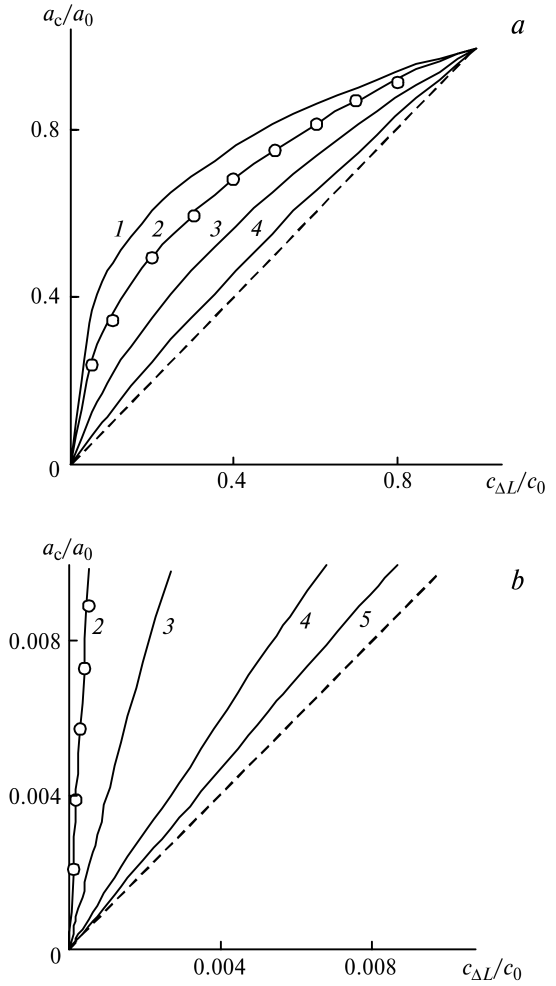

Fig. 2. Mean adsorption values a_c on the adsorbent layer ΔL at different adsorptive concentrations (*a* and *b*) behind the layer $c_{\Delta L}$ for ΔL: 0.715 (*1*), 0.5 (*2*), 0.25 (*3*), 0.072 (*4*) and 0.018 cm (*5*). Straight line $c/c_0 = a/a_0$ is dotted. Points are values of the equilibrium adsorption isotherm.

with the corresponding values of the equilibrium adsorption isotherm. This is also experimental evidence for the fact that an element of the adsorbent layer with the finite length ΔL, at the outlet of which the adsorptive concentration is equilibrium toward the mean adsorption value of this layer, can always be found in the nonequilibrium adsorption dynamics: $c_{\Delta L}/c_0 \approx \varphi(a_c/a_0)$, where φ is the inverse function of the adsorption isotherm. For the studied example of adsorption dynamics,[6] this equality is approximately fulfilled in the whole interval of measured concentrations, which indicates that the principle of superposition of broadening factors or additivity of coefficients of different stages of mass transfer is fulfilled in the case of the nonlinear adsorption isotherm.[1,2]

This approach to the estimation of the concentration limiting fulfilment of equality (1) reveals the equilibrium adsorption layer L_e in the nonequilibrium adsorption dynamics. The observed weak dependence of L_e on the degree of filling allows the substantiation of the new approach to the solutions of the direct and inverse problems of the nonequilibrium adsorption dynamics: development of a model of the equilibrium adsorption layer.[8]

Compare the observed regularities with concepts on local ratios between the adsorption and concentration values at the stage of parallel transfer. These concepts are formulated under the assumption that positions of curves similar to those in Fig. 2, *a* are determined by the limiting stage of mass transfer rather than the ΔL value.[1] According to this interpretation,[1] curve *2* in Fig. 2, *a* corresponds to the adsorption isotherm and variant of the ***equilibrium*** adsorption dynamics under the action of longitudinal effects. Then curves *3* and *4* positioned between the adsorption isotherm *2* and the straight line (Eq. (1)) describe the ***nonequilibrium*** adsorption dynamics under the action of longitudinal effects. The nonequilibrium adsorption dynamics in the absence of longitudinal effects is characterized by the fulfilment of Zeldovich's equality (1). At the same time, in all three cases,[1] whose solutions were obtained in the asymptotic regimes, the authors imply the nonequilibrium adsorption dynamics in which the parallel transfer of the stationary front of adsorption dynamics is observed.

The evident approach of $Z = (a_c/a_0 - c_{\Delta L}/c_0)$ to zero at $\Delta L \to 0$ obtained in this work should satisfy for all previously listed[1] variants of the nonequilibrium adsorption dynamics at the stage of parallel transfer. This allows us to believe that at any limiting stage of mass transfer with the convex adsorption isotherm equality (1) is fulfilled as local, *i.e.*, at $\Delta L = 0$.

Thus, the position of curves on the plots similar to those presented in Figs. 2 and 3 should be independent of variants of the adsorption dynamics but determined by the length of the adsorbent layer ΔL at which the

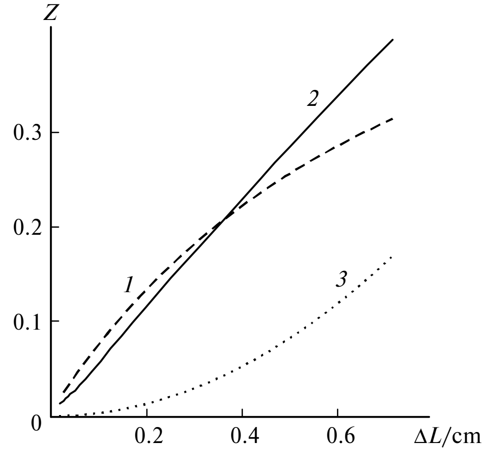

Fig. 3. Plot of the difference $Z = (a_c/a_0 - c_{\Delta L}/c_0)$ *vs.* length of adsorbent layer ΔL for relative concentrations c/c_0: 0.5 (*1*), 0.15 (*2*), and 0.01 (*3*).

mean adsorption value was measured. It can be expected that when the mass transfer coefficients are independent of the degree of filling one of these curves measured on the adsorbent layer ΔL coincides with the equilibrium adsorption isotherm.

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