Journal of Engineering Physics and Thermophysics, Vol. 74, No. 2, 2001

LINEAR DYNAMICS OF DESORPTION ON ADSORBENT LAYERS OF ARBITRARY LENGTH

A. V. Larin and K. E. Polunin

UDC 541.183:543.54

Based on the concept of an equilibrium adsorption layer in the theory of plates, an analytical solution of the problem of the linear dynamics of desorption is obtained. The regularities of the formation and motion of the output curves of desorption on adsorbent layers of small length are analyzed. The calculated and experimental data are found to be in fine agreement. A program is worked out to predict and to model the dynamics of adsorption and desorption on adsorbent layers of arbitrary length.

The theory of adsorption dynamics is comprehensively studied for the case of a linear adsorption isotherm with account for various smearing factors and for the variant of interaction of adsorbates [1–3]. In the frontal linear dynamics of adsoption and desorption, the inverse problem is completely solved by the method of moments [4, 5]. It is pertinent to note that solutions of the inverse problem similar to those in [4, 5] are applicable to adsorbent layers of arbitrary length.

It is also of interest to develop reliable algorithms for direct calculation of the output curves of desorption dynamics and at the same time to reveal the regularities of the dynamics of desorption depending on the length of an adsorbent layer. Previously [6], based on the concept of an equilibrium adsorption layer in the theory of plates proposed in [7], we obtained an analytical solution of the problem of the linear frontal dynamics of adsorption and analyzed its mechanism on the inlet portion of an adsorbent layer. In the present work, we employ the same approach. The aim of the work is to analyze the regularities of the linear dynamics of desorption on adsorbent layers of arbitrary length by solving analytically the primal problem within the framework of the new concept of the theory of plates.

Analytical Solution. In each of the variants of the theory of plates, in order to obtain analytical expressions, we solve the system consisting of n ordinary differential equations

$$da_n/dt + dc_n/dt = (v/H)\,[c_{n-1} - c\,(a_n)]\,, \tag{1}$$

where $n = L/H$; H is the height equivalent to a theoretical plate (HETP) or the layer of equilibrium adsorption in accordance with the model [7]. Unlike the generally accepted interpretation of the theory of plates, the functions $c_{n-1} = c_{n-1}(t)$ and $c_n = c_n(t)$ in the model [7] are determined as local, not mean, concentrations in a plate at the inlet and outlet of the nth plate.

For the linear isotherm of adsorption $a = \Gamma c$ with account for the initial and boundary conditions of desorption dynamics $c_n = c_0 = \text{const}$ and $a_n = a_0 = \Gamma c_0$ for $t = 0$ and $c_{n=0} = 0$ for $t > 0$, Eq. (1) for $n = 1$ is written as follows:

$$dc_1/dt = b\,(0 - c_1) = -\,bc_1\,, \tag{2}$$

where $b = v/H(1 + \Gamma)$ is the coefficient.

Institute of Physical Chemistry, Russian Academy of Sciences, Moscow, Russia: email: Roldugin@serv1.phyche.ac.ru. Translated from Inzhenerno-Fizicheskii Zhurnal, Vol. 74, No. 2, pp. 48–50, March–April, 2001. Original article submitted April 13, 2000; revision submitted August 16, 2000.

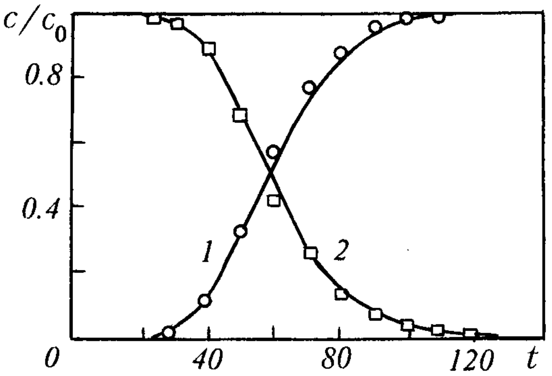

Fig. 1. Output curves of the dynamics of adsorption (1) and desorption (2) calculated from the experimental data [5] for b = 0.166, v = 0.96 cm/sec, and n = 10. The solid lines are the calculated data, the circles are the experimental data from [5].

Upon the integration of (2) between the limits from 0 to t and from c_0 to c_1, we arrive at

$$\ln (c_1/c_0) = -bt \quad \text{or} \quad c_1 = c_0 \exp (-bt) . \tag{3}$$

By analogy with [6] this equation can be solved further by the method of variation of constants. Finally, we have

$$c_n/c_0 = \exp (-bt) \sum_{n=1}^{n} [b^{n-1} t^{n-1}/(n-1)!] . \tag{4}$$

Results and Discussion. In [6], the following solution was obtained for the variant of the frontal dynamics of adsorption:

$$c_n/c_0 = 1 - \exp (-bt) \sum_{n=1}^{n} [b^{n-1} t^{n-1}/(n-1)!] . \tag{5}$$

A comparative analysis of (4) and (5) shows that the functions of the relative concentration c_n/c_0 of two independent variables, namely, the time t and the relative length of an adsorbent layer n, are the dependent quantities, which implies the following. The output curves measured in the dynamics of adsorption and desorption under the same conditions must be mutually symmetric relative to the coordinate c/c_0. The same symmetry must also be fulfilled for the concentration distribution functions along the n axis for t = const.

Correctness of the conclusion drawn and the solution (4) obtained can be verified by the results of a comparison of the numerical results obtained by Eq. (4) and the experimental data [5], where a study was made of the frontal dynamics of acetylene adsorption and desorption from helium at 25°C on activated carbon (Columbia 4LXC). Calculation by (4) and (5) was done for the experiment carried out for a linear flow velocity of v = 0.96 cm/sec on a 0.46-cm-diam. column and for an adsorbent layer length L equal to 10 cm.

The constants H and Γ were determined by the method of moments directly from the output curve of adsorption dynamics presented graphically in [5]. The value of the coefficient b equal to 0.166 min^{-1} and calculated for v = 0.96 cm/sec or 57.6 cm/min was then used in all subsequent calculations. Here, it should be noted that the value of the initial concentration c_0 is not taken into account in the calculations since from Eqs. (4) and (5) it follows that the position of the output curves in the coordinates $c_n/c_0 - t$ does not depend on c_0.

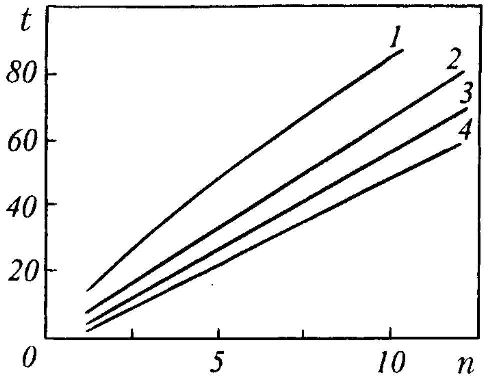

Fig. 2. Isolines of the relative concentrations of the dynamics of desorption calculated for $b = 0.166$: 1) $c/c_0 = 0.1$; 2) 0.3; 3) 0.5; 4) 0.7. t, min.

A graphical comparison of dependences (4) and (5) (see Fig. 1) shows fair agreement of the experimental curves obtained in [5] and the output curves of the dynamics of adsorption and desorption calculated for the case $n = 10$ or for an HETP equal to 1 cm. The value of the relative HETP determined as the ratio H/d, where d is the diameter of an adsorbent grain for the conditions analyzed when $d = 0.92$ cm [5], is approximately equal to 11. The comparatively high value of the relative HETP is indicative of the fact that the flow velocity v is not optimal, for which it is characteristic to have a minimum H. This allows us to suppose, similarly to an analysis of the experimental results [4] carried out by Eq. (5) in [6], that the analyzed coordinate of the flow velocity corresponds to that part of the Van Dimter curve which is to the left of the minimum in the region of low velocities of the mobile phase.

This conclusion is also confirmed by the fact that in the region of linear velocities equal to 1.9 and 3.79 cm/sec the output curves of the dynamics of adsorption and desorption in [5] are most satisfactorily approximated for $n = 20$–25 when the HETPs are equal to 0.5–0.4 cm, respectively.

Based on the output curves of desorption dynamics calculated for different n and for a constant HETP ($H = 1$ cm), we constructed isolines of the equal concentrations (Fig. 2). As is seen from the figure, the isolines of the relative concentrations equal to 0.1 and 0.7 are not linear. The isoline for $c/c_0 = 0.5$ is linear but is not extrapolated to the origin of coordinates, which fully agrees with the behavior of the isoline for $c/c_0 = 0.5$ in the dynamics of adsorption [6]. Moreover, the isoline for $c/c_0 = 0.3$ is approximated well by a linear function and is extrapolated to the origin of coordinates. The noted features of the linear frontal dynamics of adsorption and desorption, which are determined by the fact that functions (4) and (5) are dependent quantities, can be of help in modeling and optimization of adsorption processes. Thus, based on the new concept suggested in [7] in the theory of plates an analytical solution of the primal problem of the linear nonequilibrium dynamics of desorption is obtained that fits the experimental data well for small n. This confirms the correctness of using unsimplified expressions in the theory of adsorption dynamics, especially for columns of small finite length, that are obtained in solving the system of n equations (1). The equations for the output curves in the form of series (4) and (5) are easily programmed and do not require the use of tabulated functions. Modeling of the processes according to (4) and (5) is carried out based on the values of the Henry constant and of the effective kinetic constant expressed in the scale of length. These quantities can easily be calculated on the basis of a single experiment performed under the conditions of the frontal or developing dynamics of adsorption.

NOTATION

L, length of the adsorbent layer, cm; H, height equivalent to a theoretical plate; n, number of theoretical plates (of equilibrium-adsorption layers) or relative length of the adsorbent layer; $a_n(t)$, averaged value of the adsorption on the nth plate; t, time, min; $c(a_n)$, equation of the adsorption isotherm; $c_{n-1}(t)$ and $c_n(t) = c(a_n)$, concentrations at the inlet and outlet of the nth plate; v, linear flow velocity, cm/sec; a_0, adsorption that is equilibrium to the initial concentration c_0 , for which the adsorbent layer was saturated prior to desorption; a, adsorption; Γ, Henry constant; c, concentration; b, coefficient.

REFERENCES

1. A. A. Zhukhovitskii, Ya. L. Zabezhinskii, and A. N. Tikhonov, *Zh. Fiz. Khim.*, **19**, No. 6, 253–261 (1945).
2. E. Gluekauf, *Trans. Faraday Soc.*, **51**, 34–44 (1955).
3. G. É. El’kin, in: G. V. Samsonov (ed.), *Ion Exchange and Chromatography* [in Russian], Leningrad (1984), pp. 104–112.
4. A. Bhairi, D. Rothstein, R. Madey, J.-Ch. Huang, and K. B. Lee, *J. Chromatogr.*, **361**, 3–11 (1986).
5. R. Forsythe, R. Madey, P. J. Photinos, and D. Rothstein, *Sep. Sci. Tech.*, **23**, Nos. 14–15, 2319–2328 (1988).
6. A. V. Larin and K. E. Polunin, *Inzh.-Fiz. Zh.*, **71**, No. 5, 784–787 (1998).
7. A. V. Larin, *Izv. Akad. Nauk SSSR, Ser. Khim.*, No. 1, 236–237 (1983).