

LINEAR FRONT DYNAMICS OF SORPTION IN THE INLET SECTION OF A LAYER OF SORBENT

A. V. Larin and K. E. Polunin

UDC 541.183:543.54

On the basis of the concept of equilibrium adsorption in the theory of plates, an analytical solution of the direct problem of the linear front dynamics of sorption is found. Relations of motion of C-diagrams are analyzed in the inlet section of the sorbent, and the results obtained are compared with experimental data

The theory of the dynamics of sorption is comprehensively developed for the case of a linear sorption isotherm with account for known washing-out factors [1, 2], including the case of interaction of sorbates [3]. Nevertheless, development of this theory continues in some form. Proceeding from various models of washing-out of the sorption front and representation of the corresponding kinetic coefficients, particular authors obtain their own solutions, different from existing ones, for description of C-diagrams in the linear dynamics of sorption. For example, in [4], a solution for C-diagrams is written in the form of a Hermite polynomial, and the kinetic model corresponds to the general case in which internal and external diffusion and longitudinal transfer are simultaneously taken into consideration.

The solutions in [1-4] are obtained mainly for long lengths of the layer of sorbent. For example, in [2] relations of the dynamics of sorption are analyzed for lengths of layers of sorbent with $L/H > 20$. At the same time, the author of [5] paid attention to the special features of the process of the developed dynamics of sorption in the inlet section of a layer of sorbent, and corresponding relations were studied for the particular case of ion chromatography. In [6], on the basis of a model of a layer of equilibrium adsorption [7] that develops a new concept of the theory of plates, relations occurring in the inlet section of a sorbent layer are also analyzed and an analytical description of asymmetric chromatographic peaks is obtained for columns with L/H varying from units to tens.

In what follows we analyze relations of the linear front dynamics of sorption in the inlet section of a layer of sorbent by solving the direct problem on the basis of a new concept of the theory of plates.

Analytical Solution. In any version of the theory of plates, to obtain analytical expressions it is necessary to solve a system of n ordinary differential equations:

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

where $n = L/H$; H is the height that is equivalent to the theoretical plate (HETP) or the layer of equilibrium adsorption in accordance with the model of [7]; $a_n = a_n(t)$; $c(a_n) = c_n$.

The solution based on Eq. (1) is widely known in linear chromatography (the developed dynamics of sorption) and is ordinarily used with the assumption $n \rightarrow \infty$. In general form, the approach in [7] assumes use of nonsimplified solutions based on Eq. (1).

With account for the linearity of the sorption isotherm ($a = \Gamma c$), Eq. (1) can be expressed in the form

$$dc_n/dt = b(c_{n-1} - c_n), \quad (2)$$

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

For the front dynamics of sorption, the initial and boundary conditions have the form $c_n = 0$ at $t = 0$ and $c_0 = \text{const}$ at $t > 0$.

Institute of Physical Chemistry of the Russian Academy of Sciences, Moscow, Russia; Technical University, Berlin, Germany. Translated from *Inzhenerno-Fizicheskii Zhurnal*, Vol. 71, No. 5, pp. 784-787, September-October, 1998. Original article submitted April 4, 1997.

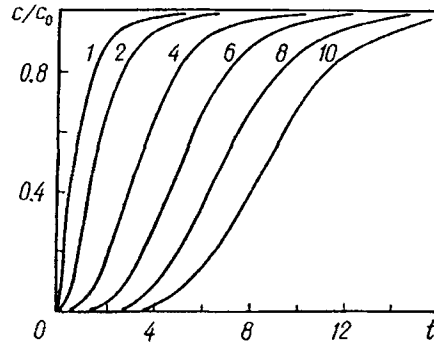


Fig. 1. C-diagrams of the dynamics of sorption calculated on the basis of (10) for $b = 1.11$ (c/c_0 is the relative concentration, the figures at the curves are $n = L/H$, $H = 2.55$ cm). t , min.

In order to obtain an analytical solution for $n = 1$, Eq. (2) is written as follows:

$$dc_1/dt = b(c_0 - c_1). \quad (3)$$

The method of variation of constants is used to seek a solution in the form of the function $c_n(t) = C_n(t) \exp(-bt)$. Then,

$$c_1(t) = C_1(t) \exp(-bt) \quad \text{or} \quad c_1 = C_1 \exp(-bt) \quad (4)$$

and

$$dc_1/dt = (dC_1/dt) \exp(-bt) - bC_1 \exp(-bt). \quad (5)$$

Here and below, $c_n(t) = c_n$ and $C_n(t) = C_n$.

Substitution of (4) and (5) into (3) gives

$$(dC_1/dt) \exp(-bt) - bC_1 \exp(-bt) = bc_0 - bC_1 \exp(-bt),$$

whence, after collecting like terms, $(dC_1/dt) \exp(-bt) = bc_0$, and after multiplying each side of the equation by $\exp(bt)$, we have

$$dC_1 = bc_0 \exp(bt) dt. \quad (6)$$

The integral of the left-hand side of (6) from 0 to t is equal to

$$\int_0^t dC_1 = c_1 \exp(bt) \quad (7)$$

and that of the right-hand side, to

$$\int_0^t bc_0 \exp(bt) dt = [\exp(bt) - 1] bc_0/b. \quad (8)$$

Then, $c_1 \exp(bt) = c_0 [\exp(bt) - 1]$, and having multiplied both sides of this equation by $\exp(-bt)$, we obtain

$$c_1 = c_0 [1 - \exp(-bt)]. \quad (9)$$

Repeating the solution for $n = 2$ etc. in this way, we finally obtain

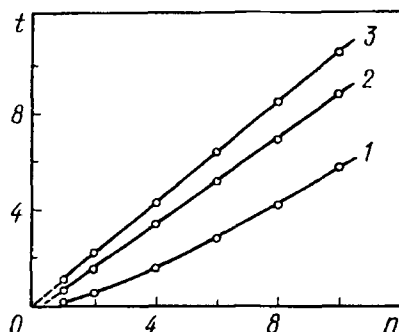


Fig. 2. Isopycs of sorption plotted from the calculation shown in Fig. 1: 1) $c/c_0 = 0.1$; 2) 0.5; 3) 0.7.

$$c_n/c_0 = 1 - \exp(-bt) \sum_{n=1}^n [b^{n-1} t^{n-1} / (n-1)!]. \quad (10)$$

Results and Discussion. The correctness of the solution obtained for C -diagrams of the linear dynamics of sorption was checked by comparing numerical calculations on the basis of (10) for medium and large n with results published in [1, 2], and they are found to agree completely. It should be noted again that unlike existing solutions, the expression for C -diagrams in the form of series (10) can be easily programmed and does not require tabulated functions.

We analyze relations of the linear dynamics of sorption in the inlet section of a layer of sorbent, i.e., in the case of small n . Numerical simulation is carried out for experimental conditions of the dynamics of sorption of argon from helium on active carbon according to results of [8]. Calculation on the basis of (10) is carried out for the experiment in [8] at 313 K, in which $\Gamma = 6.2$ and $v = 0.341$ cm/sec (20.46 cm/min). It is assumed that $H = 2.55$ cm. This can be the actual value of the HETP for the given grain size of the active carbon and linear flow velocity of the elutriator. Then, for the assumed constants, $b = 1.11$.

Analyzing the obtained data, we note that for small n C -diagrams of the dynamics of sorption obtained in this way on the basis of (10) (see Fig. 1) do not have the property of parallel transfer that is characteristic of the dynamics of sorption in the case of convex isotherms. Moreover, in the coordinates $c/c_0 - t$ the position of the C -diagrams does not depend on c_0 , which follows from solution (10). A graphical comparison shows satisfactory agreement of the experimental diagram from [8] and the present C -diagram for $n = 10$. This allows us to estimate the HETP defined in terms of H/d , where d is the diameter of a sorbent grain and is approximately equal to 20–25 for the conditions analyzed. Such values of the relative HETP indicate that the flow velocity v is not the optimum one that is characterized by minimum H and allow the suggestion that the analyzed coordinate of the flow velocity most likely corresponds to the part of the van Dimter curve to the left of its minimum.

On the basis of the C -diagrams obtained, so-called isopycs of sorption or isolines of equal concentration were plotted (Fig. 2). It follows from these curves, for example, that the isopyc of the relative concentration $c/c_0 = 0.1$ is not linear. Just as in the case of a convex isotherm of sorption, the isopyc of sorption corresponding to half the initial concentration is characterized by linearity, but it is not extrapolated to the origin of coordinates. At the same time, for the concentration $c/c_0 = 0.7$ the isopyc of sorption is satisfactorily approximated by a linear function and is extrapolated to the origin of coordinates. The special features of the linear front dynamics of sorption just mentioned can be useful in predicting and designing sorption filters.

Thus, an analytical expression is obtained for C -diagrams that can be used for calculations in the linear dynamics of sorption, including that in the inlet section of the layer of sorbent, in terms of the Henry constant and the effective kinetic constant expressed on a scale of length. These quantities can be calculated experimentally from a single experiment carried out under conditions of the front or developed dynamics of sorption. Experimental material systematized recently, for example, in [6], can probably be used to precalculate effective kinetic constants in the form of the HETP and to predict the behavior of C -diagrams in some cases in the linear dynamics of sorption and chromatography.

NOTATION

L , length of the layer of sorbent; H , height that is equivalent to the theoretical plate (HETP); n , number of theoretical plates (layers of equilibrium sorption) or relative length of the layer of sorbent; $a_n(t)$, averaged sorption in the n -th plate; t , time; $c(a_n)$, equation of the isotherm of sorption; $c_{n-1}(t)$ and $c_n(t) = c(a_n)$, concentrations at the inlet and outlet of the n -th plate, respectively; v , linear flow velocity; a , sorption; Γ , Henry constant; c , concentration; b , coefficient; c_0 , initial concentration; d , diameter of a sorbent grain.

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, *Ion Exchange and Chromatography* (ed. G. V. Samsonov) [in Russian], Leningrad (1984), pp. 104-112.
4. K.-H. Radeke, K. Wiedemann, and D. Gelbin, *Chem. Techn.*, **28**, 476-480 (1976).
5. N. S. Safonov, *Teor. Osnovy Khim. Tekhnol.*, **6**, No. 1, 127-129 (1972).
6. A. V. Larin, *Zh. Fiz. Khim.*, **67**, No. 3, 810-814 (1993).
7. A. V. Larin, *Inzh.-Fiz. Zh.*, **58**, No. 1, 148-149 (1990).
8. A. Bhairi, D. Rothstein, R. Madey, J.-Ch. Huang, and K. B. Lee, *J. Chromatogr.*, **361**, 3-11 (1986).