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APPLICATION OF THE MODEL OF THE LAYER OF EQUILIBRIUM ADSORPTION TO NON-IDEAL NON-LINEAR CHROMATOGRAPHY

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SUMMARY

The model of the layer of equilibrium adsorption (LEA) allows reliable solutions in non-ideal chromatography with arbitrary isotherms. The layer of the equilibrium adsorption, L_e, serves as an effective kinetic constant. The exit concentration for this layer is equal at any moment of time to the concentration which is in equilibrium with the mean amount of adsorption on the whole layer. A simple first order differential equation is sufficient for the solution of direct and inverse chromatographic problems. The basic assumptions of the LEA model are confirmed by experimental data.

INTRODUCTION

This work deals with one of the significant branches of chromatographic theory which concerns the regularities of the mass exchange between the mobile and the stationary phases. The main problem is the search for a correlation between the distribution functions in the mobile phase, $c(l,t)$, and in the stationary phase, $a(l,t)$, along a chromatographic column of length l at any time t on the one hand, and the sorption isotherm, the kinetic constants and experimental conditions on the other hand.

It is customary to consider and solve a system of equations for the mass balance, sorption kinetics and sorption isotherm. The theory of ideal chromatography has been developed[1,2], but the theory of non-ideal chromatography has been applied only to the case of linear isotherms[3–5]. This can easily be accounted for by the lack of a direct solution of the system of equations for the arbitrary isotherm. Most authors have adopted an approach based on a representation of the sorption isotherm by a linear, rectangular or some other simple form. The variety of distribution functions $c(l,t)$ and $a(l,t)$ is defined by the quite complicated kinetic expressions or by the influence of different correlations in the mass-transfer stages.

As in ideal chromatography, it can be assumed that the $c(l,t)$ and $a(l,t)$ functions in real chromatography are mainly influenced by sorption isotherms, whereas the sorption kinetics itself including longitudinal diffusion has a less important rôle.

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The purpose of this study is to describe the possibilities of the layer of the equilibrium adsorption (LEA) model[6], which is based on real sorption isotherms and involves a simplified kinetic expression where only one effective constant, L_e, denoting the layer of the equilibrium adsorption, is used.

THEORETICAL

The LEA model utilizes the main idea of plate theory[3], in which the effective kinetic coefficient is characterized by the height equivalent to a theoretical plate (HETP).

For each HETP, the distribution between two phases (sorption and concentration) is linear *at any moment of time*. For example, this aspect was particularly emphasized in ref. 7.

Simultaneously with plate theory, the concept of the equilibrium achievement step was proposed. This concept[8,9] assumes that the equilibrium on the layer equivalent to a theoretical plate is achieved either during the discontinuous step of duration or during the corresponding push of the mobile phase. It was applied to the layer-by-layer method which extended plate theory to a description of real chromatography[10–12]. The chromatographic constants were taken as the experimental constants in the mass-balance equation. The physical meaning of the dimensionless chromatographic constants, defined as the ratio of the elementary volume of the mobile phase to the elementary volume of the stationary phase, was not determined.

Thus the method was suitable for numerical solutions of chromatographic problems with non-linear isotherms, including the sorption of mixtures[13]. Nevertheless, the introduction of the time scale greatly complicates the description of real chromatography and reduces the value of this approach.

In the LEA model the constants of the individual kinetic stages are expressed only in terms of a column length scale. By analogy with the height, H, equivalent to a theoretical plate, L_e represents the sum of separate terms that express the constants of the elementary kinetic stages, *i.e.*, the superposition principle of broadening factors is held to be valid for non-linear isotherms. For the equilibrium adsorption layer the exit concentration is numerically equal to the concentration, $c(\bar{a})$, which is in equilibrium with the mean value of the adsorption, $\bar{a}$, on the whole layer *at any moment of time*.

This definition can be explained by reference to Fig. 1. The distribution of the arbitrary substance in the stationary phase along the column (adsorption), curve 1, corresponds to its distribution in the mobile phase (curve 2) in the case of ideal chromatography. In the real process where broadening of chromatographic zones takes place, the real concentration (curve 3) will correspond to the real adsorption curve 1. For any sorption system it is always possible to evaluate the thickness of the layer, L_e, for which the mean adsorption, $\bar{a}$, will be in equilibrium with the concentration, $c(\bar{a})$, leaving this layer.

The value of L_e is determined by all factors which broaden the chromatographic zone and may be taken as an effective kinetic constant without serious error. Such a simplification permits one to combine in a simple first order differential equation the features of the mass balance, of the sorption kinetics and of the sorption isotherm.

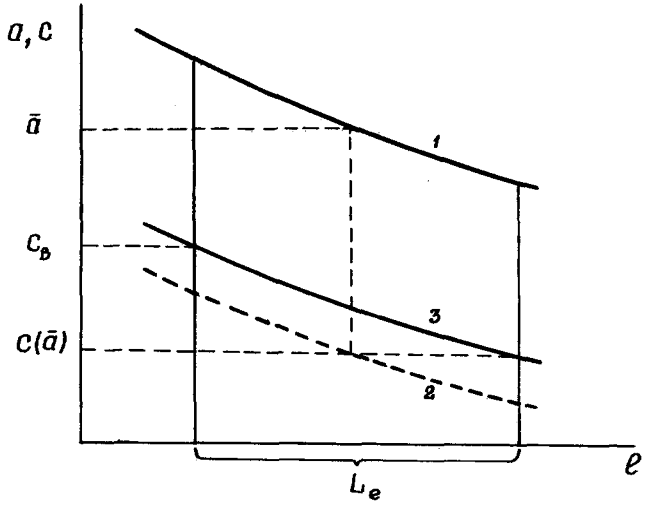

Fig. 1. Diagram of the layer of the equilibrium adsorption. Curves: 1, adsorption; 2, concentration in ideal chromatography; 3, real concentration.

The equation originally suggested[6] may be written in the form

$$\frac{d\bar{c}}{dt} + \frac{d\bar{a}}{dt} = \frac{v}{L_e}[c_B - c(\bar{a})] \tag{1}$$

where $\bar{a}$ and $\bar{c}$ are the mean adsorption and concentration in the column volume of thickness L_e, v is the superficial velocity of the mobile phase, c_B is the concentration entering the layer L_e; $c(\bar{a})$ is the exit concentration and at the same time the analytical or numerical expression for a sorption isotherm and t is the time. Eqn. 1 is valid for any location of the equilibrium adsorption layer relative to the length of the chromatographic column. It permits solutions of direct and inverse problems in real chromatography and some applications will now be described.

APPLICATIONS TO CHROMATOGRAPHIC PROBLEMS

Both elution and frontal chromatography can be described by mass-exchange theory. However, the different evolution of the time and column-length distribution functions determined by the different initial conditions means that the solutions for the direct and inverse problems have their own characteristic properties.

The assumption $d\bar{c}/dt \ll d\bar{a}/dt$ makes the solution of eqn. 1 rather simple and is valid for all convex isotherms. It is also valid for linear isotherms having Henry constants of less than 50–100. Some deviations in the final results may indicate concave isotherms but in a region corresponding to very low concentrations, which themselves do not determine the whole form of either the breakthrough or the elution curve.

Usually breakthrough and elution curves are measured experimentally for various column lengths. These experimental data also permit evaluation of the form of the distribution functions along the column length. Therefore the examination of the common mass-exchange problem must be carried out relative to the concentration curves which are introduced in the model considered as the $c(\bar{a})$ and c_B functions.

The direct problem

In the case of direct problems, for determination of either the elution curve or the breakthrough curve from a chromatographic column of length l, n differential equations must be solved where $n = l/L_e$. The solution for a linear isotherm in plate theory was analysed previously[14].

For elution chromatography it can be assumed that the sample is introduced into the column by a short impulse. It is suggested here that the whole quantity of the introduced substance, q, is distributed in the first equilibrium adsorption layer, L_e, situated at the column start under $t = 0$. Then, proceeding from eqn. 1, the solution of the direct problem reduces to an uncomplicated integration

$$\int_{\bar{a}_0}^{\bar{a}} \frac{d\bar{a}}{c(\bar{a})} = -\frac{v}{L_e} \cdot t \tag{2}$$

where $\bar{a}_0 = q/L_eS$, and S denotes the cross-section of the chromatographic column.

The solutions obtained in the form of elution curves from the column $l = L_e$ for concave, $a = kc^2$, and convex, $a = w - p \log (c_s/c)$, sorption isotherms are

$$c = c_m^1 - \frac{v}{L_e} \cdot \frac{t}{2k} \tag{3}$$

and

$$c = \frac{c_m^1 pL_e}{pL_e + 2.3C_m^1 t} \tag{4}$$

where c_m^1 is the peak maximum corresponding to the quantity of introduced substance, q, and k, w, p and c_s are empirical coefficients.

The expressions obtained for the elution curves from the function c_B by use of equations of types 3 or 4 are extremely cumbersome for the second and subsequent layers. Therefore numerical methods are preferred for solution of the system of n equations in the case of long columns. This involves successive integration of eqn. 1 by the finite difference method and is carried out to an order suggested in ref. 15.

First we determine the amount of material sorbed on all the sequential equilibrium adsorption layers, $\Delta\bar{a} = c_B v \cdot \Delta t/L_e$, for the first given time step, Δt. In the case considered (elution chromatography), the decrease in the amount of material sorbed in the first layer, L_e, is calculated at $c_B = 0$ and for subsequent layers c_B is determined by the concentration that is in equilibrium with the value of $\bar{a}$ for the previous layer using the given adsorption isotherms. The adsorption increment is then estimated from eqn. 1 without taking account of $d\bar{c}/dt$, and the total value of $\bar{a}$ is calculated by a corresponding summation of $\Delta\bar{a}$ in each layer. Thus in the second and subsequent layers a successive accumulation of the sorbed material occurs. In the case of frontal chromatography, $c_B = c_0$ for the first equilibrium adsorption layer.

The machine time required with modern computers is only a few seconds both for elution and frontal chromatography. The optimum interval for numerical integration, Δt, is fixed by calculations with various Δt. This interval is chosen such that the computed distribution functions coincide with each other within a given accuracy. It should be stressed that the integration interval, Δt, in the LEA model is just the step in numerical integration. In the case of convex isotherms, Δt must not exceed 30–60 s, whereas for linear isotherms, $\Delta t < 0.5$–1 s.

The results of the numerical calculations are presented in Figs. 2–5. A concave isotherm was expressed by the function $a = kc^2$, where $k = 1.41 \cdot 10^6$ cm^3/mg. A convex isotherm was expressed by the Dubinin–Radushkevich equation[16] in the form:

$$a = 285 \cdot \exp\left[-0.159\left(\log\frac{3529}{c}\right)^2\right]$$

The superficial velocity of the mobile phase, $v = 500$ cm/min, and the thickness of the equilibrium adsorption layer, $L_e = 0.5$ cm. The latter value and other conditions are taken from ref. 15. This order of magnitude L_e is characteristic of the case of sorption on porous sorbents. It should be noted that for other conditions and constants the quality of the profiles of the curves shown in Figs. 2–5 is not changed.

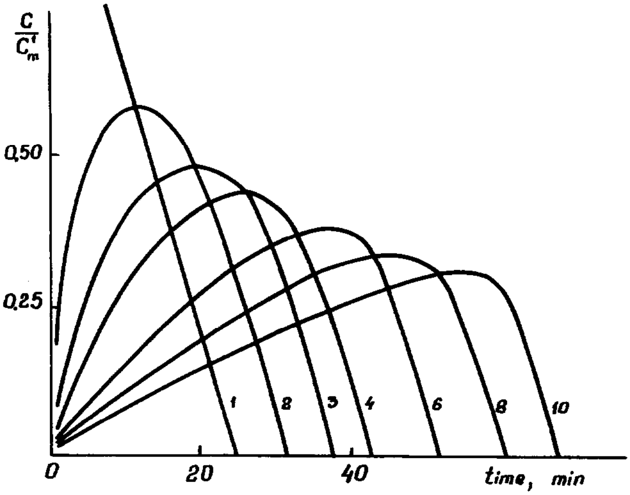

Fig. 2. Elution curves for a concave sorption isotherm ($\bar{a}_0 = 100$ mg/cm^3). Numbers on the curves denote the relative column length, l/L_e.

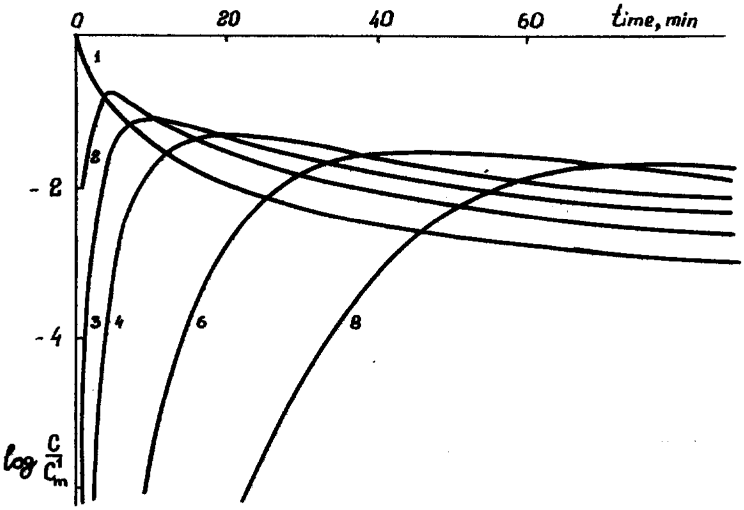

Fig. 3. Elution curves for a convex sorption isotherm ($\bar{a}_0$ = 100 mg/cm^3). Details as in Fig. 2.

Elution curves for a chromatographic column of length $l = L_e$ (Figs. 2 and 3) are characterized by an improvement in the maximum with the velocity of the mobile phase and then by a decreasing function. The elution band profile is gradually transformed upon increasing the column length. The peculiarities of elution chromatography have been examined previously[17].

Experimental data for frontal chromatography (sorption dynamics) with nonlinear isotherms are extensively reported in the literature. The data from systematic precision measurements[18,19] of breakthrough curves on microporous sorbents over a broad range of concentration and column length are of particular importance. A comparison of data obtained from calculations according to the LEA model with the

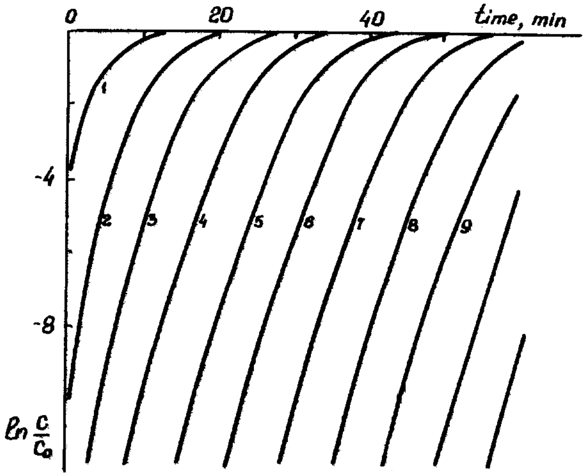

Fig. 4. Breakthrough curves for a convex isotherm.

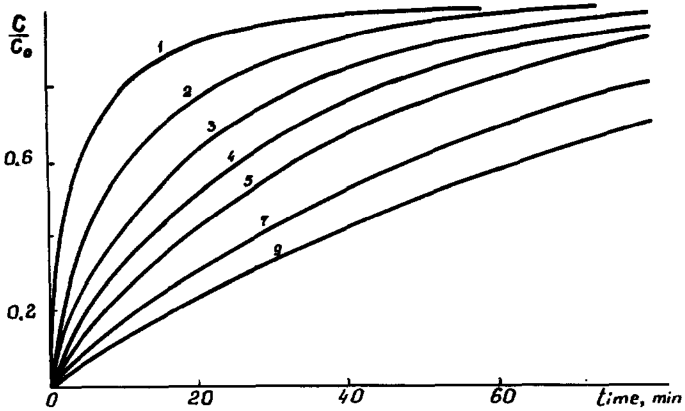

Fig. 5. Breakthrough curves for a concave isotherm.

experiment data reveals a good agreement and supports the assumptions made about the practical independence of the effective kinetic constant of the degree of filling (coverage) in different sorption systems and about the use of the superposition principle for the separate terms which express the constants of the elementary kinetic stages.

Breakthrough curves for the convex isotherm (Fig. 4) agree closely with experimental data[19] and show the characteristic properties observed experimentally. A feature of the proposed LEA model is the absence of an instantaneous breakthrough stage in accordance with eqn. 1, where $c(\bar{a}) = 0$ when $t = 0$.

The breakthrough curves for the concave isotherm (Fig. 5) are characterized by the absence of a low-concentration region and have a "kinetic" shape, confirmed indirectly by the similar trend in the experimental data for the adsorption dynamics of water vapour on carbonaceous adsorbents.

The inverse problem

The solution of the inverse problem in the LEA model, when $\mathrm{d}\bar{c}/\mathrm{d}t \ll \mathrm{d}\bar{a}/\mathrm{d}t$, is concluded by the integration:

$$\int_0^{\bar{a}} \mathrm{d}\bar{a} = \bar{a} = \frac{v}{L_e} \int_0^t [c_B - c(\bar{a})]\,\mathrm{d}t \qquad (5)$$

The functions $c(\bar{a})$ and c_B simultaneously represent the breakthrough or elution curves obtained from chromatographic columns of various lengths l_1 and l_2 under the same conditions.

A common method of solution of the inverse problem involves successive integration according to eqn. 5 and the evaluation of the dependence of $\bar{a}_i$ on $c(\bar{a}_i)$, *i.e.*, the sorption isotherms for certain l_1 and l_2. The effective kinetic constant, L_e, is equal to the difference $(l_1 - l_2)$ when the calculated sorption isotherm more completely approximates the sorption isotherm or some of its fragments measured experimentally. So in some cases the solution of the inverse problem is possible with the help of only one elution or breakthrough curve.

In elution chromatography when the layer L_e is situated at the beginning of a column the following expressions may be integrated:

$$\bar{a} = \bar{a}_0 - \frac{v}{L_e} \cdot \int_0^t c(\bar{a})\, \mathrm{d}t \tag{6}$$

$$\bar{c} = \frac{v}{L_e} \cdot \int_t^\infty c(\bar{a})\, \mathrm{d}t \tag{7}$$

Fig. 6 illustrates the calculation according to eqn. 7. For each time t_i corresponding to the concentration $c(\bar{a}_i)$ the amount of sorption, $\bar{a}_i$, is determined. The integral in eqn. 7 is obtained graphically as the area S_i.

The time, t, is the independent variable and the concentration, $c(\bar{a})$, is the integrated function. It is obvious that the solution of the inverse problem in real chromatography when $l = L_e$ is quite opposite to the one in ideal chromatography, where the concentration is the independent variable and the integration function represents the appearance time of the sample or the mobile phase volume which passed before its appearance.

The inverse problem in frontal chromatography is solved by the integration in eqn. 5. For a convex isotherm, the solution is based on one experimental breakthrough curve measured at the stage of parallel transport of the adsorption front, as previously reported[20], and may be explained with the help of Fig. 7. The curve 2 is constructed relative to the experimental breakthrough curve 1 by transposing each concentration point by the same distance along the time axis. It determines the func-

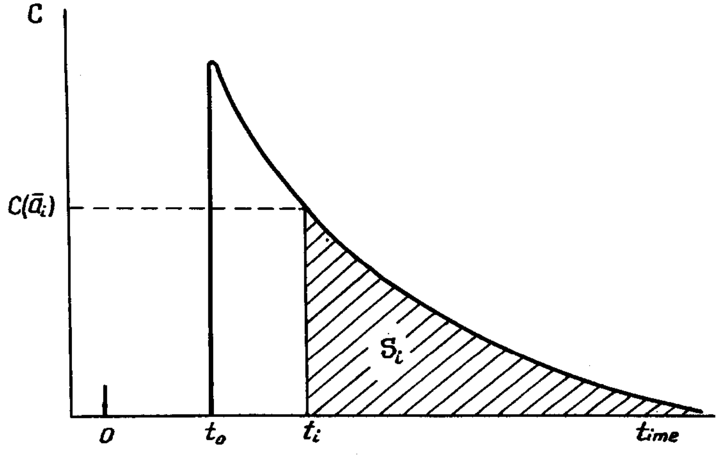

Fig. 6. Solution of the inverse problem in elution chromatography for $l = L_e$.

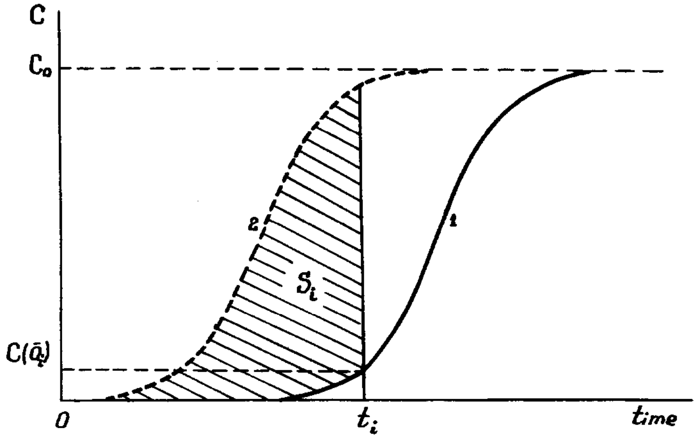

Fig. 7. Solution of the inverse problem in frontal chromatography (sorption dynamics) for convex isotherms at the stage of parallel transport.

tion c_B for the LEA layer given by

$$L_e = l \cdot \frac{t_1 - t_2}{t_1} \tag{8}$$

where l is the length of the layer at which the breakthrough curve was obtained and t_1 and t_2 denote the times for equal exit concentrations according to the measured (1) and calculated (2) curves.

The amounts of adsorption, $\bar{a}_i$, corresponding to the concentrations $c(\bar{a}_i)$ are calculated from eqn. 5. The integral at the right-hand side of eqn. 5 is defined as the area S_i, which is limited by curves 1 and 2 and the perpendicular to the time, t_i, corresponding to the appearance of concentration $c(\bar{a}_i)$. The values of $\bar{a}_i$ are calculated for the whole interval of measured concentrations. A solution of the inverse problem in sorption dynamics[20] also shows the absence of a dependence of the effective kinetic constant on the degree of filling (coverage).

CONCLUSIONS

The model of the layer of the equilibrium adsorption, unlike other well known theoretical models, permits discrete solutions relative to the chromatographic column length. This results in considerable simplification of the initial system of equations and reduces it to one first order differential equation. It also appears possible to describe chromatographic processes on the basis of real sorption isotherms and the one effective kinetic constant.

Numerical solutions of direct and inverse chromatographic problems according to the suggested model are straightforward. The LEA model may be used for description of the mass exchange in different aspects of real chromatography.

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