A CHROMATOGRAPHIC THEORY BASED ON THE CONCEPT OF A LAYER OF EQUILIBRIUM ADSORPTION

Kyung Ho Row† and Alexander V. Larin*

Department of Chemical Engineering, Inha University, 253 Yonghyun-dong, Nam-ku, Inchon 402-751, Korea
*Institute of Physical Chemistry, Russian Academy of Sciences, Leninskii pr. 31, Moscow 117915, Russian Federation

Abstract—The LEA model has been analyzed by comparing to other chromatographic theoretical approaches. In the LEA model a layer of equilibrium adsorption, L_e, serves as an effective kinetic constant. For the layer L_e the concentration issuing from this layer is in equilibrium with the average value of adsorption on the whole layer at any moment of time. The value of L_e is determined from all factors which broaden the chromatographic zone. Such an approach permits us to combine the features of the mass balance (solute continuity in a chromatographic column), of the mass transfer phenomenon, and of the adsorption isotherm into a single first order differential equation. Apart from other layer-by-layer models, the LEA model supposes that over the whole column a continuous (real) distribution of adsorption a (L, t) and concentration c (L, t) is observed. The usefulness of the LEA model in developing a chromatographic theory has been discussed.

Key words: Plate Theory of Chromatography, Non-Ideal Condition, Arbitrary Adsorption Isotherms, LEA Model

INTRODUCTION

A development of the phenomenological theory for chromatography (solute movement in a chromatographic column) is necessary for optimization, control and prediction of regularities of preparative chromatography, and for physicochemical application of chromatography to estimate properties of solutes, characteristics of solids (adsorbents and catalysts), and etc. The theory of chromatography deals with one of the significant branches of total mass- and heat transfer theory which concerns the solute exchange between the mobile and the stationary phases. The chromatographic theory is mainly formulated as the determination for a correlation between the distribution functions of the concentration $c = c$ (L, t) in the mobile phase and the adsorption $a = a$ (L, t) on the stationary phase along the chromatographic column of length L at any time t and the adsorption isotherm with the kinetic constants and experimental conditions.

The theory of non-ideal, non-linear (or real) chromatography has been inadequately developed [Giddings, 1965]. This can easily be accounted for by the lack of a direct solution of the system of equations for the arbitrary adsorption isotherms. In estimating the problem of single-component chromatography for arbitrary adsorption isotherms as a whole, one can agree with the view that the particular analytical or numerical solutions exists or have been developed so far. The present work examines the utility of the layer of equilibrium adsorption (LEA) model [Larin, 1983a], which is based on nonlinear adsorption isotherms and a simplified kinetic expression which has only an effective constant.

APPROACHES DEVELOPING THE CHROMATOGRAPHIC PLATE THEORY

The plate theory uses the ordinary differential equation and

as an example we demonstrated the equation from [Ha et al., 1987] with small changes:

$$V_s(da_i/dt) + V_m(dc_i/dt) = v(c_{i-1} - c_i) \tag{1}$$

where i notes the number of theoretical plate, v is the mobile phase flow rate, V_s and V_m are the volumes of the stationary and mobile phases of column that length equals to theoretical plate, respectively.

To obtain the solution for any initial conditions it is necessary to solve a set of N Eqs. (1) when the adsorption isotherm is linear. This way is identical to obtain both numerical and analytical solutions [Larin, 1983b]. It must be noted that for the solution of non-ideal chromatographic problem in the case of non-linear adsorption isotherms the ordinary differential equation like Eq. (1) was used very rarely [Sakodynsky, 1973].

Simultaneously with the plate theory, the concept of the equilibrium achievement step was proposed. This concept [Gluekauf, 1955; Vink, 1964] assumes that the equilibrium 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 so-called layer-by-layer method which extended plate theory to a description of non-linear chromatography [Gapon and Gapon, 1948; Rachinskii, 1953; Smit, 1980]. The chromatographic constants were taken as the experimental constants in the partial differential 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. Using another scales it may be noted that the two scales ΔL and Δt have been used for characterization of adsorption kinetics in the layer-by-layer method. In general the same approach using the partial differential solute material balance equation and two scales ΔL and Δt for characterization of adsorption kinetics were proposed in [Rouchon et al., 1985] for numerical simulation of peak

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†To whom all correspondence should be addressed.

profiles in non-linear adsorption chromatography.

So, the methods [Gluekauf, 1955; Vink, 1964; Gapon and Gapon, 1948; Rachinskii, 1953; Smit et al., 1980; Rouchon et al., 1985] are suitable for numerical solutions of direct chromatographic problem with non-linear adsorption isotherms, including the chromatography of mixtures [Streltzov et al., 1974]. Nevertheless, an additional introduction of the time scale Δt greatly complicate the description of real chromatography and reduces a value of this approach. In our opinion, the combined use of both scales ΔL and Δt for an expression of kinetic constants does not allow a solution based on the layer-by-layer method to be regarded as reliable. Therefore this does not permit one to pass on to the prediction of the peak profiles and to solve the inverse problem of chromatography.

A new variant of the layer-by-layer method based on an equilibrium adsorption layer had been proposed by in [Larin, 1983a]. The use of the LEA model for solving direct and inverse chromatographic problems has led to a good agreement between the calculated and experimental results obtained in different modes of non-linear, non-ideal chromatography. The LEA model utilizes the main idea of plate theory, in which the effective kinetic coefficient is characterized by the height equivalent to a theoretical plate (HETP). For each HETP, the solute distribution between two phases (adsorption and concentration) is linear at any moment of time [Keulemans, 1957]. It means that time t serves only as the independent variable.

The original equation of the LEA model is an ordinary first order differential equation which may be written as

$$d\bar{a}/dt + d\bar{c}/dt = (v/L_e) \ [c_B - f^{-1}(\bar{a})] \tag{2}$$

where $\bar{a}$ and $\bar{c}$ are the average solute concentrations in the stationary and mobile phases of the column bulk of length L_e respectively, v is the mobile phase flow rate, the layer of equilibrium adsorption L_e is an effective kinetic constant, c_B is the concentration entering to the layer L_e, $f^{-1}(\bar{a})$ is the concentration issuing from this layer and also the analytical expression of the adsorption isotherm, and t is the time.

In the LEA model it is proposed that the constant which characterizes the solute mass transfer kinetics and the longitudinal mass transfer should only be expressed in terms of the adsorbent layer length. This method of depicting the kinetic constant, which employs the principle of the superposition of broadening factors, arises from the theory of van Deemter [van Deemter et al., 1956] and has been repeatedly demonstrated on the linear chromatography experiments. So, in the LEA model the constant of the individual kinetic stages is expressed only in terms of a column length scale. By analogy with a definition given for HETP in [van Deemter et al., 1956], an effective kinetic constant L_e represents the sum of separate terms that express the constants of the elementary kinetic (mass-transfer) stages, including the longitudinal (axial) dispersion.

LAYER OF EQUILIBRIUM ADSORPTION

The layer of equilibrium adsorption L_e, for which the outlet concentration at any instant is equal to the concentration $f^{-1}(\bar{a})$ appertaining by equilibrium to the average adsorption value, $\bar{a}$, for the whole layer, is determined as an effective kinetic constant in the LEA model. Let us consider a geometrical illustration of L_e, taking an actual calculation of the frontal variant of chromatography as an example from [Larin, 1990]. Fig. 1 shows the distri-
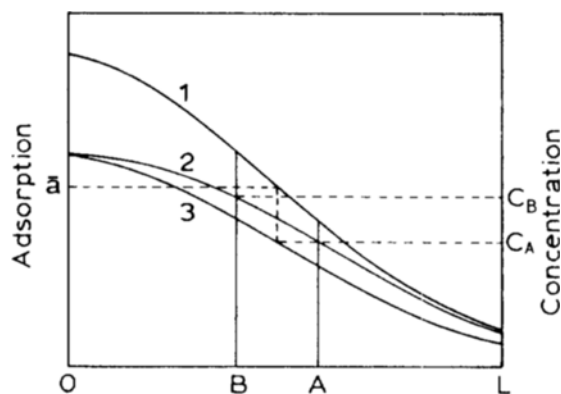

Fig. 1. Schematic description of a layer of equilibrium adsorption.
[Curves: $1-a(L, t^*)$, $2-c(L, t^*)$, $3-c_{id}(L, t^*)$]

bution of the solute between the mobile and the stationary phase at time $t^* = 20$ minutes as can be calculated according to any models of linear chromatography [Streltzov et al., 1974; Gubkina et al., 1985; Forsythe et al., 1988; Row, 1988; Larin, 1984; Dubinin et al., 1980]. The conditions were as follows: Henry's adsorption isotherm coefficient equal to 15.7 l/g; initial concentration, $c_0 = 5$ mg/l; $L_e = 0.5$ cm (or $m_e = 0.706$ g, where m_e is a mass of adsorbent situated in a fixed bed of length equal to L_e); mobile phase (air) flow rate $= 1.57$ l/min; internal cross-section of fixed-bed holder, $S = 3.14$ cm^2.

Additionally a hypothetical function of solute concentration in the mobile phase-a concentration $c_{id}(L, t)$ is introduced. For this function we shall assume that the local equilibrium $c_{id}(L, t^*) = f^{-1}[a(L, t^*)]$ is observed. Then we can choose an arbitrary abscissa, i.e. a coordinate A to which, for a given moment of time t^*, the concentration c_A on the $c(L, t^*)$ curve corresponds. From an axiomatic standpoint, it will always be possible to find a single coordinate on L axis (in our case the coordinate B) and, correspondingly, a single adsorbent layer length $L_e = BA$, for which the average adsorption value $\bar{a}$ determined as:

$$\bar{a} = [\int_A^B a(L, t^*)dL]/AB = [\int_0^{L_e} a(L, t^*)dL]/L_e \tag{3}$$

will be in equilibrium with the concentration c_A issuing from the layer L_e.

Hence, it follows that for real convective mass exchange in the adsorbing medium one can always define an element of the layer, called the layer of equilibrium adsorption L_e [Larin, 1983a], for which the following equality applies:

$$c_B = f^{-1}(\bar{a}) = f^{-1}\{[\int_0^{L_e} a(L, t^*)dL]/L_e\} \tag{4}$$

From Eqs. (3) and (4) it follows that the material balance equation (equation of solute continuity in chromatographic column) for an element of the adsorbent layer length L_e can be presented in the form of an ordinary differential equation. Eq. (2) is correct for any position of the layer L_e along the column length L. If there is considered the total case, Eq. (2) can be presented as the following form

$$da_i/dt + dc_i/dt = (v/L_e)[c_{i-1} - f^{-1}(a_i)] \tag{5}$$

where i denotes the i-th equilibrium adsorption layer.

Eqs. (4) and (5) combine the material balance and the adsorption mass transfer kinetics in the form of the effective kinetic
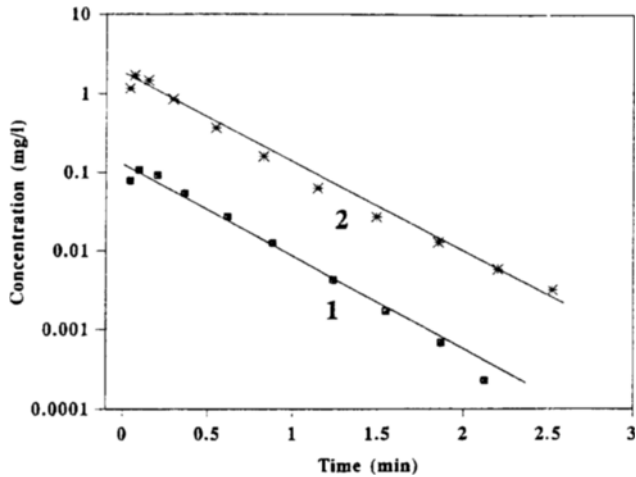
Fig. 2. Ethyl chloride elution curves (peak profiles) measured on activated carbon in air at 423 K.
[The length of adsorbent column is 0.7 cm. Sample size: (1) 0.1 and (2) 1.0 mg. The points are experimental data, the solids are theoretical data.]

constant L_r and the adsorption isotherm equation $f^{-1}(a)$.

APPLICATIONS TO A DEVELOPMENT OF CHROMATOGRAPHIC THEORY

The assumption $dc/dt \ll da/dt$ makes the solution of a set of Eq. (2) rather simple and is valid for all convex adsorption isotherms. Some deviations in the final results may be occurred in the concave adsorption isotherms but in a region corresponding to very low concentrations, which themselves do not determine totally a form of either the breakthrough or the elution curves. The application of the LEA model involves the solution of a set of N equations, Eq. (2) or Eq. (5), where $N = L/L_r$ is the relative column length or the number of theoretical plates, and L is the actual column length.

The analytical solution for a linear adsorption isotherm under the plate theory approach was analyzed previously [Ha et al., 1987; van Deemter et al., 1956; Gubkina et al., 1985; Forsythe et al., 1988; Row, 1988; Larin, 1984; Dubinin et al., 1980]. For elution mode of chromatography this solution can be presented in the next form

$$c_i = (a_0/\Gamma)(\alpha t)^{i-1} \exp(-\alpha t)/(i-1)! \qquad (6)$$

where $\alpha = v/(1+\Gamma)L_r$, and Γ is Henry's constant, $a_0 = q/L_r S$, S is the cross-section of chromatographic column, and q is the solute size introduced.

From the Eq. (6) it follows the next expression for a peak profile at the end of the first layer, L_r:

$$c_1 = (a_0/\Gamma)\exp(-\alpha t), \text{ or } Ln(c) = Ln(a_0/\Gamma) - vt/[(1+\Gamma)L_r] \qquad (7)$$

To examine such an unusual expression for peak profiles in non-ideal linear chromatography, the experimental study was performed on the column of relative short length [Larin et al., 1994], where the elution chromatography of ethyl chloride on active carbon have been studied under different temperature conditions, when the adsorption isotherm is linear. Fig. 2 shows the calculated peak profiles, which are in a good agreement with the experimental data for columns of length L-L_r. The peak profiles for this
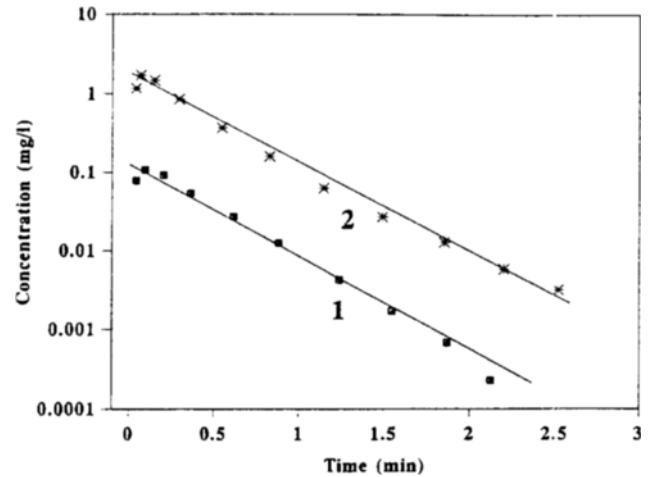

Fig. 3. Breakthrough curves corresponding to the frontal adsorption chromatography of ethyl chloride on active carbon at 293 K. (The curves refer to the time of half-concentration emergence, $t_{0.5}$. The corresponding values of L_r were: 1-0.2; 2-0.5; 3-0.7; and 4-0.9 cm, respectively. The curves which were calculated from the LEA model are depicted by the solid lines, while the points denote experimental data of [Dubinin et al., 1980].)

case correspond to Eq. (7).

To obtain an analytical solution in non-ideal chromatography the general approach will be the next. For elution chromatography it can be assumed that a short impulse sample is introduced into the column. It is suggested here that the whole quantity of the introduced substance, q, is distributed in the first equilibrium adsorption layer, L_r, situated at the column inlet under $t = 0$. Then proceeding from Eq. (2), the solution reduces to a simple integration

$$\int_{a_0}^{\bar{a}} [d\bar{a}/f^{-1}(\bar{a})] = -vt/L_r \qquad (8)$$

where $\bar{a}_0 = q/L_r S$ [see explanations in Eq. (6)].

In frontal chromatography the next equation is integrated for the first equilibrium adsorption layer (i=1)

$$\int_0^{\bar{a}} \{d\bar{a}/[c_0 - f^{-1}(\bar{a})]\} = -vt/L_r \qquad (9)$$

where c_0 is initial solute concentration.

The expressions obtained for the c_B (c_i) functions of by use of Eqs. (8) and (9) in the case of non-linear adsorption isotherms are extremely cumbersome for the second and subsequent layers. Therefore numerical methods are preferred for solution of the system of N equations, Eq. (2) or Eq. (5) in the case of long columns. This involves successive integration of Eq. (2) or Eq. (5) by the finite difference method and is carried out according to an order suggested in [Larin, 1983b; Larin, 1984].

Below the examples of the calculation of frontal and elutive chromatography of vapours on active carbons are presented using the Dubinin-Radushkevich adsorption isotherm equation in the following form:

$$a = k_1 \exp[-k_2 \log^2(k_3/c)] \qquad (10)$$

where a is the adsorption, mg/g; c is the concentration, mg/l; k_1, k_2 and k_3 are the coefficients.

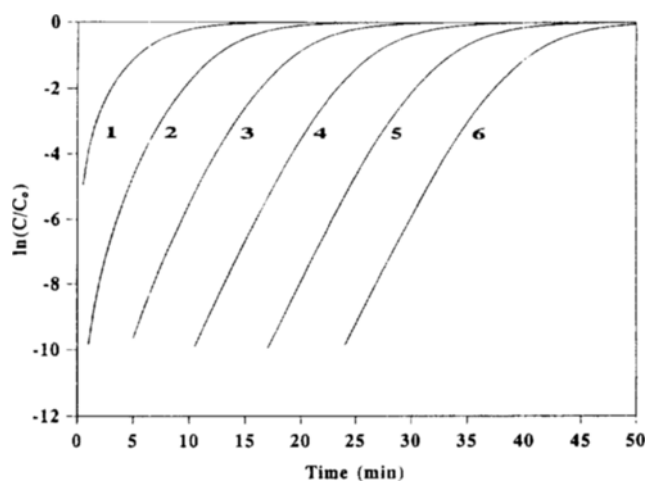Experimental data for frontal chromatography (adsorption dy-

Fig. 4. Breakthrough curves for a convex adsorption isotherm.
(All conditions are the same as on Fig. 3. Numbers on the right side of curves denote the relative column length, L/L_e, where $L_e = 0.5$ cm.)

Fig. 5. Peak profiles in elution chromatography for a convex adsorption isotherms.
(Details as in Fig. 4. Sample size = 157 mg, $c_0 = 50$ mg/l).

namics) with non-linear adsorption isotherms are extensively reported in the literature. The data from systematic precision measurements of break-through curves on microporous adsorbents over a broad range of concentration and column length are of particular importance. Fig. 3 illustrates the break-through curves calculated for different values of L_r at the parallel transfer stage for the conditions applying during the frontal adsorption chromatography of ethyl chloride on active carbon, using the data of [Dubinin et al., 1980]: $k_1 = 285$ mg/g; $k_2 = 0.159$; $k_3 = 3529$ mg/l; $c_0 = 5$ mg/l; and the mobile phase flow rate equals to 1.57 l/min. The temperature was 293 K.

Calculations with different values of L_r have been performed with the aim of determining the value of the effective kinetic constant (L_r) for a given adsorption system. It is seen (Fig. 3) that the most satisfactory approximation with experimental data (within experimental error) is observed for the break-through curve calculated for $L_r = 0.5$ cm, or the corresponding adsorbent mass $m_r = 0.706$ g.

The results obtained demonstrate that the calculation of break-through curves in accordance with the LEA model, based on Eq. (10) for the adsorption isotherm and involving only one effective kinetic constant L_r, is in good agreement with experimental data. This illustrates both the reliability of the LEA model and the correctness of involving the principle of broadening factor superposition with non-linear adsorption isotherms. As the length of the adsorbent fixed-bed is increased (see Fig. 4), the break-through curves plotted using log(c/c_0) versus t coordinates demonstrate the characteristic properties observed experimentally [Dubinin et al., 1980], i.e. an initial unsteady-state stage in the frontal chromatography followed by parallel transport of the adsorption front, etc. A feature of the proposed model is the absence of an instantaneous break-through stage as suggested by Eq. (2) or Eq. (5), where $f^{-1}(\bar{a}) = 0$ when $t = 0$.

The peak profiles were calculated for the conditions of ethyl chloride adsorption on active carbon [Dubinin et al., 1980]. In this case the peak profile for a chromatographic column of length $L = L_r$ (Fig. 5) is characterized by improvement in the maximum with the velocity of the mobile phase and then by a decreasing
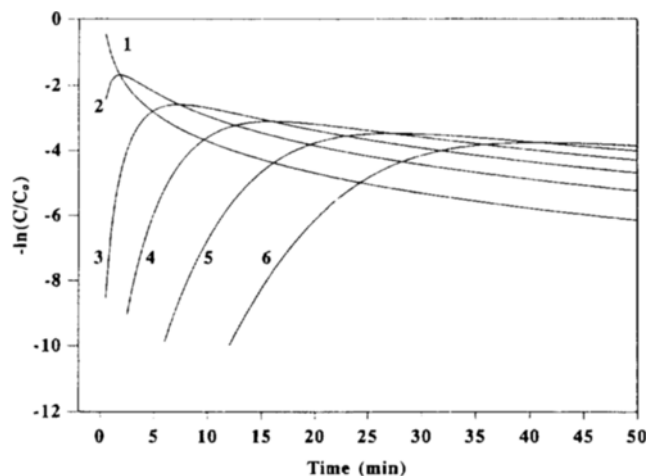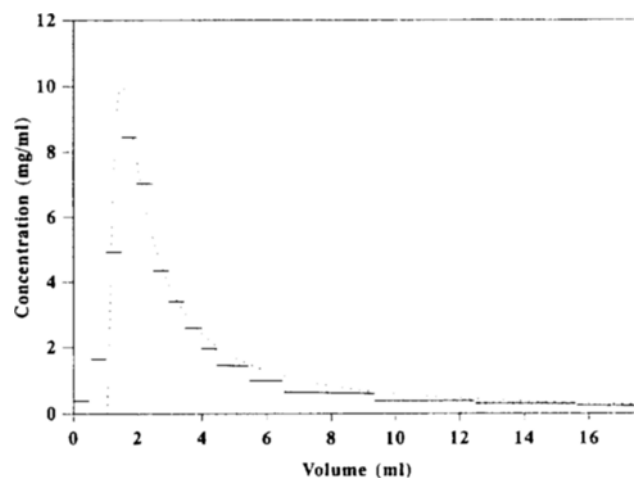

Fig. 6. Elution peak for the ethoxylated isononylphenol adsorption from n-decane on the silica layer with a mass of 0.218 g.
(The mobile phase flow rate is 1 ml/min. The solid lines are the experimental data, and the dotted line is the calculated curve. Sample size = 42 mg)

function. The elution band profiles is gradually transformed upon increasing the column length. The peculiarities of elution chromatography have been examined by Larin [Larin, 1984]. In all cases, the peak profiles calculated for column length of iL_r intersects the maximum of the peak profiles calculated for the column length of $(i+1)L_r$.

In the article [Larin et al., 1994], the adsorption isotherm and elution peak profiles for the ethoxylated isononylphenol (the average degree of ethoxylation is 4)-n-decane-silica (with a specific surface area of 120 m²/g and grain size of 0.20-0.36 mm) were measured. The investigations were performed using column liquid chromatography. The dried adsorbent of a given weight was placed in a glass column (inner diameter of 0.5 cm) with a porous glass bottom. The bulk density of the adsorbent layer was 0.53 g/ml. Then the n-decane, degassed in helium, was pumped through the silica layer to remove the air. Then, the introduced
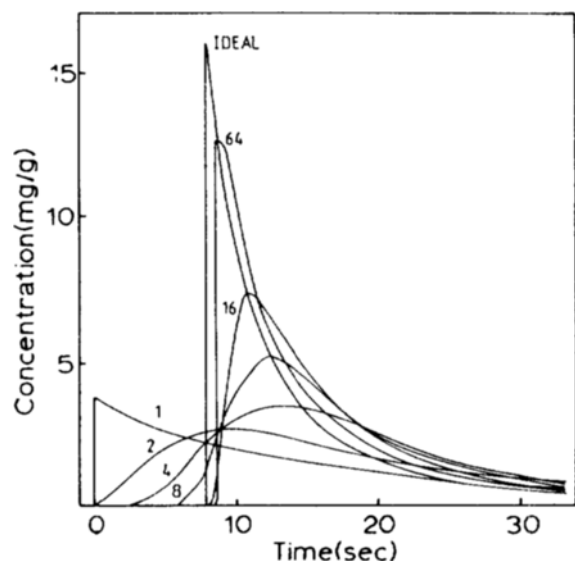
Fig. 7. Peak profiles calculated for a convex adsorption isotherm.
(Numbers on the curves denote the relative column length, L/L_e. IDEAL = the line from ideal chromatography. Column adsorbent mass = 0.96 g; Sample size = 1 mg; Mass flow rate of mobile phase = 0.68 g/min)

Fig. 8. Elution curves for a concave adsorption isotherm $a = kc^2$.
[Numbers on the curves denote the relative column length, L/L_e. ∞ = the line calculated from Eq. (12).]

solute was repeatedly treated by portions of fresh n-decane. At the column outlet, the solute content in solution fractions was measured by spectrophotometric technique at a wavelength of 277 nm.

The adsorption isotherm of n-decane on silica is satisfactorily approximated by the Freundlich equation:

$$a = 106c^{0.225} \tag{11}$$

where a is the adsorption, mg/g; c is the concentration, mg/ml.

The experimental elution peak profile in this case (Fig. 6) was approximated for different values of L_e under the same conditions (the adsorption isotherm, flow rate of mobile phase, and solute sample size). The simulation was performed out so that $L = L_e N$, where L is the absolute column length, and N is a natural number. The experimental curve was found to be satisfactorily approximated by the calculated curve when N = 2 and $L_e = 10.5$ mm. The calculated and experimental peak profiles are in a good agreement in a wide range of experimental conditions, including the dependences on sample size changes [Larin et al., 1994].

With regard to the average value of the adsorbent particle diameter the relative effective kinetic constant L_e/d_p, equal to -40 for ethoxylated isononylphenol-n-decane-silica system, is 2-3 times larger than the values of the relative HETP in HPLC. This fact may be explained both by low density of the column packing, and by the effect of micellization on the kinetics of the overall process.

The Freundlich adsorption isotherm had been used for numerical simulation of peak profiles according to the conditions and constant presented in [Larin, 1987; Chuduk and Eltekov, 1980], where was studied the adsorption chromatography of anisole from heptane using silica SCP as the stationary phase. Figure 7 depicts a series of peak profiles calculated for different values of the effective constant L_e compared with the peak profile observed in ideal chromatography. It follows from the results of these calculations (Fig. 7) that the peak maxima do not coincide with the
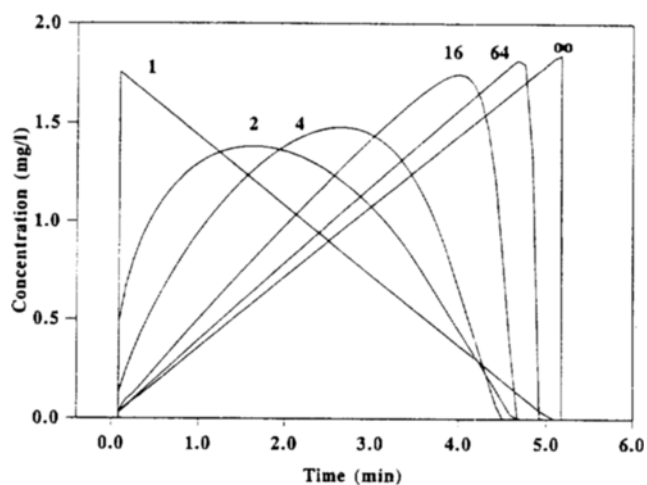
peak profile in ideal chromatography in the case of columns of short length (L/L_e = 1, 2 and 4). However, the peak maxima approximate to the ideal chromatography peak profile with increasing value of L/L_e. The line for the ideal chromatography was calculated from the following equation,

$$\partial a/\partial t + \partial c/\partial t - v(\partial c/\partial L) = 0 \tag{12}$$

and it connects the peak maxima for different sample sizes only at a certain length of column.

Elution mechanisms for concave adsorption isotherm $a = kc^2$ have been considered for the next conditions: $k = 1.41 \times 10^6$ ml /mg, v = 500 cm/min, $L_e = 0.5$ cm. Fig. 8 illustrates this result. In both cases (see Fig. 7 and Fig. 8) peak profiles calculated for different value of the relative column length L/L_e are compared with the corresponding peak profile calculated according to the ideal chromatography theory using Eq. (12).

The results presented in Figs. 7 and 8 indicate that an increase in the value L/L_e leads to the peak profiles in non-ideal chromatography approaching the peak profile in ideal chromatography. Thus, ideal conditions in chromatography are determined by increasing the relative length of the column L/L_e. For adsorption isotherms used in modelling peak profiles this means: at values of L/L_e > 250 the real processes in the chromatographic column can be described with sufficient accuracy on the basis of the theory of ideal chromatography.

Indeed, if the ratio L/L_e, the relative length of a column, is assumed to be sufficiently large, L_e may be regarded as dL. By the same token, the difference between the inlet and outlet concentrations also tends to a limiting value, i.e. using respectively Eqs. (6) and (9) and a scheme of Fig. 1, we have: $[c_B - f^{-1}(a)] = [c_{i-1} - f^{-1}(a)] = (c_B - c_A) \sim dc$.

If these approximations are taken into account, Eq. (2) or Eq. (5) of the LEA model changes to the mass balance equation relating to solute continuity in ideal chromatography. This analysis reveals a quantitative relationship between the ideal model and the LEA model depending on the relative length of the column. In other words, for columns of short relative length, Eq. (2) of the LEA model is suitable for describing real chromatographic processes when kinetic factors and axial dispersion are taken into account.

ACKNOWLEDGEMENTS

NOMENCLATURE

a   : adsorption on stationary phase, f(c) [mg/g]

ā   : average adsorption value on a layer L_e

A   : arbitrary coordinate on L axis

B   : coordinate on L axis

c   : concentration in mobile phase, $f^{-1}(a)$ [mg/l, mg/ml, mg/g]

c_0 : initial solute concentration in frontal chromatography [mg/l]

c̄   : average concentration value on a layer L_e

c_A : concentration corresponding to coordinate A

c_B : concentration corresponding to coordinate B

c_{id} : concentration corresponding to ideal conditions

d_p : adsorbent particle diameter [mm]

f(c) and $f^{-1}(a)$: functions representing adsorption isotherms

i   : number of layer L_e or theoretical plate

k   : coefficient of concave adsorption isotherm [ml/mg]

k_1, k_2 and k_3 : coefficients of Dubinin-Radushkevich's equation, Eq. (10)

L   : column length [cm]

L_e : effective kinetic constant, a layer of equilibrium adsorption [cm]

m_r : adsorbent mass corresponding to layer L_e [g]

N   : total numbers of layers L_e or theoretical plates

q   : sample size [mg]

S   : cross-section of chromatographic column [cm²]

t   : time [sec, min]

v   : mobile phase flow rate [cm³/min]

V_m, V_s : volumes of gas and liquid phases of one plate, respectively

Greek Letters

$\alpha = v/(1+\Gamma)L_e$: constant used in Eqs. (6) and (7)

Γ : coefficient of Henry's adsorption isotherm equation

ΔL, Δt : kinetic constants of layer-by-layer method

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