EXPERIMENTAL STUDY OF INFLUENCE OF SLIGHT DEVIATION FROM ADSORPTION ISOTHERM LINEARITY ON ELUTION PEAK PROFILES

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Introduction

An adsorption isotherm is the major factor affecting the peak profiles under conditions of high-performance chromatography[1]. It was repeatedly emphasized that peak profiles in high-performance chromatography depend on the concentration region measured which is defined by the value of sample size[2-4]. For example, it has been both experimentally and theoretically demonstrated that peak profiles in the small concentration region are corresponded to linear chromatography mechanisms, and when the sample size is increased, the non-linear model of chromatography permits accurate prediction of peak profiles in the region of big concentrations[5-6].

But when we consider the same concentration region the change of adsorption isotherm parameters leads only to the quantitative changes of the peak profile characteristics. The particular case is connected with minor deviations of the adsorption isotherm from the linear behavior . It was theoretically shown that a small deviation from the precision expression of adsorption isotherm (the small deviation from adsorption isotherm linearity) can lead to simulation of the peak profiles which differ significantly each from other in the same concentration region[7-9]. The purpose of this article is the experimental confirmation of this effect.

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

$$da / dt + dc / dt = (v / L_e) [c_B - f^{-1}(a)] \qquad (1)$$

where a and c are respectively the average solute concentrations in the stationary and mobile phases of the column bulk of length L_e, v is the mobile phase flow velocity, the layer of equilibrium adsorption L_e is an effective kinetic constant, c_B is the concentration entering to the layer L_e, $f^{-1}(a)$ 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 characterize 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[10] and has been repeatedly demonstrated on the linear chromatography experiments. So, in the LEA model the constant of the individual kinetic stages are expressed only in terms of a column length scale. By analogy with a definition given for HETP in [10], 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.

1. Experimental Results and Numerical Simulation

To study this phenomenon, the influence of deviation from adsorption isotherm linearity on peak profiles the experimental data of article[11] was used. In the reference of (11), it was studied the preparative high-performance liquid chromatography of thymine from water as mobile phase on Alltech C18 HS column. **Table 1** shows the experimental conditions[11]. The adsorption isotherm of thymine was measured by method of ideal chromatography and was approximated by Langmuir adsorption isotherm equation $q = ac/(1+bc)$, where q is adsorption on the stationary phase, mg of solute/ml of stationary phase, c is concentration in the mobile, mg of solute/ml of mobile phase, a and b are Langmuir adsorption isotherm parameters[11].

This adsorption isotherm (**Fig. 1**) has a slightly convexity form and is characterized by the next Langmuir adsorption isotherm parameters: $a = 15.83$ ml/ml and $b = 0.12$ ml/mg. The experimental elution peak profile with the injection volume of 1.0 ml (2 mg/ml thymine concentration) is shown in **Fig. 2** in comparing with the peak profiles calculated.
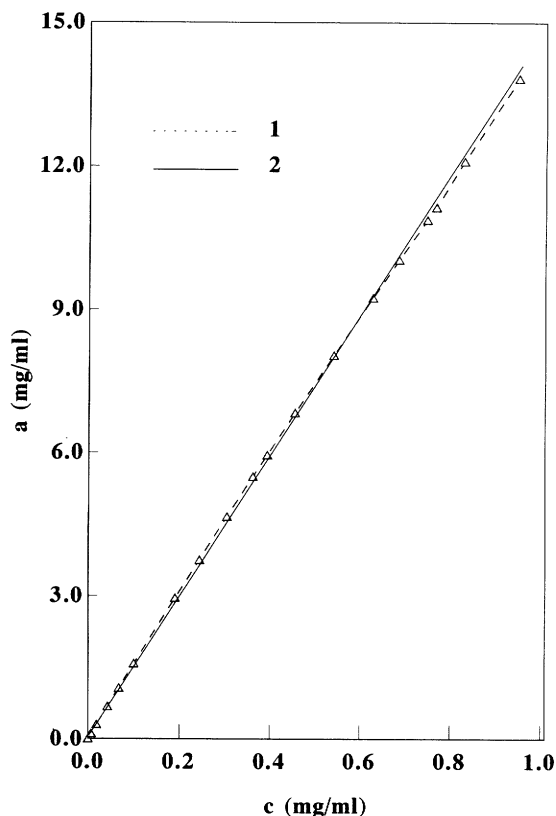
In our study the model of a layer of equilibrium adsorption (LEA model)[12] was used to simulate peak profiles both in non-ideal linear, and non-ideal non-linear chromatography. This model is quite suitable for design

Table 1 Experimental conditions

bed length	25.0cm
inside diameter	0.46cm
particle diameter	0.007cm
flow rate	1.0ml/min
concentration	2.0mg/ml

Fig. 1 Adsorption isotherm of thymine from water on reversed-phase material. (Points are experimental data, 1 is approximation by Langmuir adsorption isotherm equation, 2 is approxiwation by linear equation)

calculations employing arbitrary initial conditions and adsorption isotherms. The basic assumptions of the LEA model are confirmed by experimental data. The application of the LEA model involves the solution of a set of N (N is a relative column length) ordinary first order differential equations of solute continuity in chromatographic column. The optimum interval of numerical integration, Δt, is fixed by calculation 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 intergration interval, Δt, in the LEA model is just the step in numerical integration.

To calculate peak profiles for the experimental conditions of the reference (11) it was used the integration interval $\Delta t = 0.05$ sec. For this value of Δt and more smallest values of Δt the solutions are stable and peak profiles calculated are coincided each with other closely. Final results simulated was corrected on the value of dead volume.
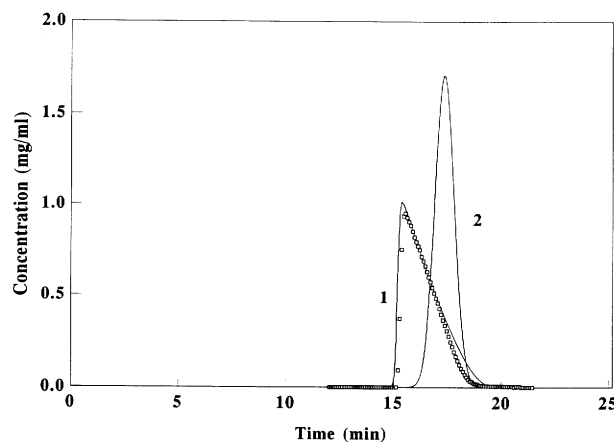
Fig. 2 Comparison of experimental thymine peak profiles and peak profiles calculated for $L/Le = N = 1000$. Mobile phase flow rate equal 1 ml/min, dead volume equal to 3.2 ml.
(Points are experimental data. Curve 1 was simulated using the Langmuir adsorption isotherm parameters, curve 2 was simulated using the linear adsorption isotherm.)

2. Discussion

Experimental adsorption isotherm was approximated by linear equation which has the next numerical form: $q = 14.71c + 0.041$ (correlation coefficient equals to 0.9996). The same experimental data was approximated by Henry's law equation when the line is arising from the origin: $q = 14.79c$ (correlation coefficient equals to 0.9995). The slope of this equations are not differed strongly from the constant $a = 15.83$ of Langmuir adsorption isotherm. The both linear adsorption isotherms are coincided and they are presented on Fig. 1 by one line 2. The peak profiles calculated using the both linear equations are coincided each with other closely too, and on Fig. 2 these peak profiles are presented by one curve number 2.

It follows from the result of these calculations (Fig. 2), that the peak profile calculated using the Langmuir adsorption isotherm equation, which more precisely approximates the experimental adsorption isotherm, corresponds to the experimental peak. The same shapes of peak profiles like a triangle was obtained in the case of Langmuir adsorption isotherm using another values of N. This peak profiles calculated ($N = 500$ and 2000) approximate satisfactorily the experimental peak profile and show a good coincidence for a tailing part of the experimental peak profile.

The results of numerical calculations using the linear adsorption isotherm (see Fig. 2) do not agree with experimental data show the characteristic properties of linear chromatographic behavior of peak profiles, when they correspond to Gaussian function. The position of peak maximum calculated using the linear adsorption isotherm differs greatly from the position of peak maximam obtained experimentally and numerically using the Langmuir adsorption isotherm. The same differences are retained when simulation for linear adsorption isotherm is performed for other values of N, where $N > 500$.

So, it was experimentally demonstrated that a slight

(negligible) deviation from the linearity of the adsorption isotherm leads in a great degree change of peak profiles and its characteristics for the same concentration region.

Conclusion

The experimental adsorption isotherm of thymine from water on reversed-phase material that has a slightly convex form and differs negligibly from linear dependence was approximated by linear and Langmuir adsorption isotherms. The numerical simulation of peak profiles in high-performance chromatography using both linear and Langmuir adsorption isotherms was performed. It had been demonstrated that in the case of precise expression of adsorption isotherm by Langmuir equation the peak profiles calculated are coincided with the experimental ones. The peak profiles calculated using the linear adsorption isotherm are not corresponded to experimental data. It confirms that a slight (negligible) deviation from the linearity of the adsorption isotherm leads in a great degree change of peak profiles.

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