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Short Communication

Modification of the *h*-root method for the determination of multicomponent Langmuir coefficients in liquid chromatography

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Abstract

A refined version of the *h*-root method is presented for the measurement of Langmuir equilibrium coefficients in liquid chromatography. As in the original method, the measurement is based on the column behavior in the frontal mode. However, in the present case only frontal capacity factors are required, as opposed to the original requirement of a complete effluent composition history. It has been shown that this refinement significantly reduces the experimental effort required for the measurement of the equilibrium coefficients.

1. Introduction

The equilibrium adsorption of the solutes from liquids onto solids is of fundamental importance in liquid chromatography. Adsorption behavior is conventionally described in terms of adsorption isotherms. For linear chromatography, solute concentrations in the liquid are low, and interferences between species both in the liquid and on the solid surface are negligible. Thus, adsorption is restricted to the linear region, and a limited amount of adsorption data are necessary for system design and optimization; typically, the Henry's law constant, expressed as the elution capacity factor, obtained from single-component data, is sufficient. In contrast, for non-linear (overload) chromatography, solute concentrations are high and interferences between species can be significant. Thus, characterization of adsorption behavior over a much wider range of the composition space is essential.

The conventional approach to measuring adsorption isotherms in liquid–solid systems is batch equilibrations. Unfortunately, this approach is tedious and time consuming, especially for multicomponent systems. In an attempt to develop quick and accurate methods for measuring isotherms, particularly multicomponent isotherms, a number of chromatographic techniques have been proposed [1–4]. Among these is the *h*-root method (HRM) [4]. HRM is based on the coherence theory of chromatography [5], and is applicable to systems obeying the multicomponent Langmuir isotherm. In its present form the method requires isocratic elution to establish behavior in the dilute solution region, and a single multicomponent frontal experiment to characterize competitive interferences. A practical difficulty concerns the latter experiment. HRM requires the determination of a complete

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effluent composition history; that is, the column effluent concentration trace for each component must be experimentally obtained. For example, for a four component system, a detailed composition history similar to Fig. 1 has to be generated. This is an exacting analytical requirement. Furthermore, though ideally only one frontal experiment is necessary, the possibility of experimental error necessitates at least one other confirming frontal experiment, further increasing the required experimental effort.

In this communication, a refined form of HRM is presented. This version eliminates the need for a complete frontal composition history, and uses instead the feed composition and frontal capacity factors to determine competitive interactions. The practical implication of this refinement is important. Where HRM originally required a detailed frontal chromatogram such as Fig. 1, for the current approach only the frontal capacity factor for each of the fronts, that is, the detector response of the effluent (Fig. 2), is necessary. Thus, no additional analytical work is necessary. The refined HRM method has also been presented in terms of conventional chromatographic parameters (capacity factors), facilitating its use.

Because this contribution is a refinement of a published method, the basis and assumptions of HRM will not be repeated, and the unfamiliar reader is referred to the original publication [4] for details.

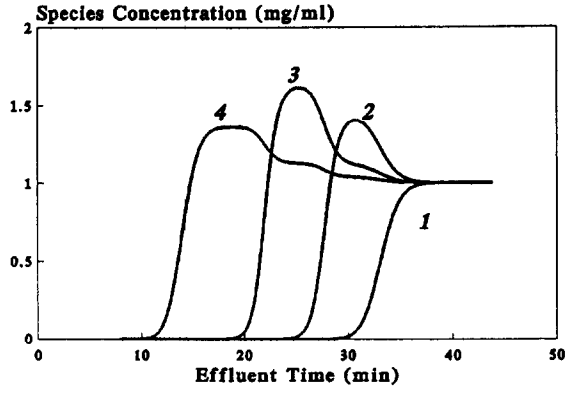

Fig. 1. Typical frontal effluent composition history for a four-component mixture.

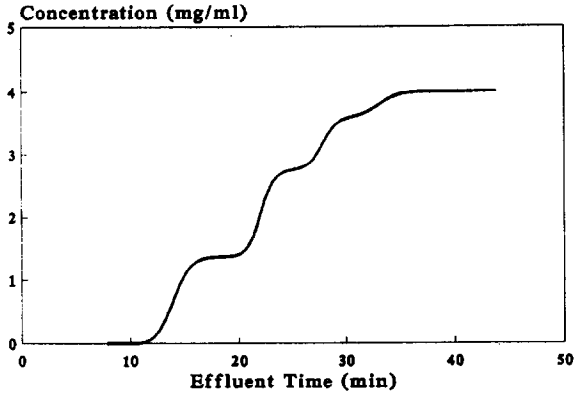

Fig. 2. Typical frontal detector response for a four-component mixture.

2. Theory

HRM is based on the multicomponent Langmuir isotherm, which for an n component system takes the form:

$$Q_i^* = \frac{k_i' c_i}{1 + \sum_{j=1}^{n} b_j c_j} \quad i = 1, \ldots, n \tag{1}$$

where Q_i^* is the adsorbed concentration based on the column volume. Within the framework of the coherence theory of chromatography [5], the composition space is orthogonalized into the h-space using the transformation:

$$\sum_{i=1}^{n} \frac{b_i c_i}{h \frac{k_i'}{k_1'} - 1} = 1 \tag{2}$$

In the h-space, the adjusted velocity of a composition front with the jth root as the variable root is given by:

$$U_j = h_j \prod_{i=1}^{n} h_i \prod_{i=1}^{n} \alpha_{i1} \tag{3}$$

The relation between true and adjusted velocities is:

$$\frac{L}{T_j} = u_j = \frac{u_0}{1 + \frac{k_{n+1}'}{U_j}} \tag{4}$$

where the $(n+1)$th component is considered a "dummy" species. This is a fictitious species present in both phases. The concentration of this species is defined as the difference between the total concentration of all real species present in each phase and some arbitrary constant [5]. The introduction of a dummy species enables the treatment of an n-component non-stoichiometric system as an equivalent $(n+1)$-component stoichiometric system.

2.1. Frontal chromatography

A schematic representation of the column profile for frontal development of an n-component mixture is shown in Fig. 3. The horizontal lines represent sharp waves, and the compositions of the plateau regions are expressed in terms of h roots. Notice that across each wave only one h root varies. This is an important advantage of the h transformation. Using this characteristic with the known presaturant composition (h'') and the wave velocities (v_i), Eq. 3 can be used to calculated the influence composition (h'). Initially, the column contains no adsorbates and (h'') can be calculated from [4]:

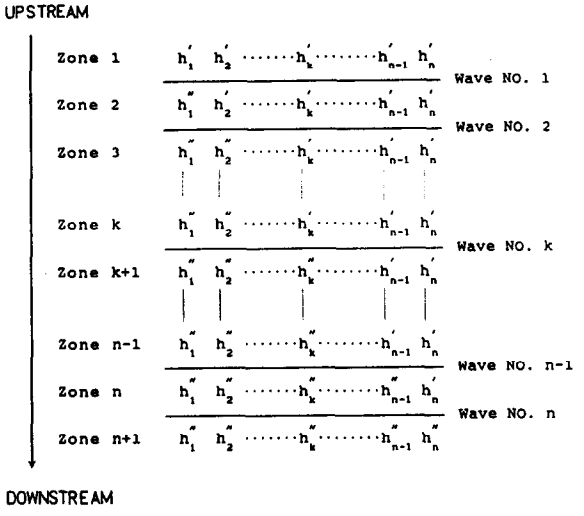

Fig. 3. Schematic representation of column behavior in h-space for frontal chromatography of an n-component mixture. Solid, horizontal lines represent migrating composition waves.

$$h''_j = \frac{k'_1}{k'_j} \quad j = 1, \ldots, n \tag{5}$$

Also, it has been shown [4] that

$$h'_n = \frac{k'_1}{k'_{n+1}} U_n \tag{6}$$

and

$$h'_j = \frac{k'_1}{k'_{j+1}} \frac{U_j}{U_{j+1}} \quad j = 1, \ldots, n-1 \tag{7}$$

Defining the frontal capacity factor, K'_i, as:

$$K'_i = \frac{T_i - T_0}{T_0} \tag{8}$$

the adjusted velocities can be related to chromatographic retention. Substituting Eq. 8 in Eq. 4,

$$U_j = \frac{k'_{n+1}}{K'_j} \tag{9}$$

Substituting Eq. 9 in Eqs. 6 and 7,

$$h'_n = \frac{k'_1}{K'_n} \tag{10}$$

and

$$h'_j = \frac{\dfrac{k'_1}{K'_j}}{\dfrac{k'_{j+1}}{K'_{j+1}}} \quad j = 1, \ldots, n-1 \tag{11}$$

2.2. Methodology of modified h-root method

HRM divides the determination of Langmuir parameters into two parts. Intrinsic affinity coefficients, a_i ($a_i = k'_i/\phi$), are obtained from linear elution chromatography, and competitive interference coefficients, b_i, from non-linear frontal experiments. In the modified approach, the determination of a_i remains unchanged, and are calculated from linear retention data as follows:

$$k'_i = \frac{t_i - t_0}{t_0} = a_i \phi \tag{12}$$

a_i can also be calculated from the frontal capacity factor, since in the linear region $k'_i = K'_i$.

As in the original method, the modified approach also uses non-linear frontal chromatography for the determination of b_i. However, the calculation method, and, hence, the data required are different. For non-linear frontal chromatography, the feed compositions, expressed in the h space, are given by Eqs. 10 and 11. Substituting these in Eq. 2,

$$\sum_{i=1}^{n} \left(\frac{\frac{c_i^f}{k'_i} b_i}{\frac{K'_n}{K'_n} - 1} \right) = 0 \quad (13)$$

and

$$\sum_{i=1}^{n} \left(\frac{\frac{c_i^f}{K'_{j+1} k'_i} b_i}{\frac{K'_j k'_{j+1}}{K'_j k'_{j+1}} - 1} \right) = 0 \quad j = 1, \ldots, n-1 \quad (14)$$

All the terms in Eqs. 13 and 14, except b_i, can be experimentally obtained. The elution capacity factors, k'_i, can be obtained from linear elution data (Eq. 12). Feed concentrations will generally be known, or can be determined. The frontal capacity factors can be calculated from the non-linear frontal chromatogram, by applying Eq. 8 to each of the fronts. Thus, the n equations Eqs. 13 and 14 can be used to determine the n unknowns b_i. It should be noted that with this approach the composition history of the non-linear frontal chromatograms is not required, facilitating the experimental effort significantly.

3. Conclusions

A modified version of HRM has been presented for the calculation of multicomponent Langmuir coefficients. At a minimum, the modified method requires only an elution experiment and a detector trace of the frontal column response. This substantially reduces experimental effort, as compared to the original method, which was based on the availability of a complete frontal composition history.

4. Symbols

a_i	Langmuir affinity coefficient (ml/g)
b_i	Langmuir competitive interference coefficient (ml/mg)
c_i	mobile phase concentration based on fluid volume (mg/ml)
c_i^f	feed concentration based on fluid volume (mg/ml)
h_i	h-root (dimensionless)
k'_i	elution capacity factor at infinite dilution (dimensionless)
K'_i	frontal capacity (dimensionless)
L	column length (cm)
Q_i^*	equilibrium concentration (mg/ml)
t_i	retention time for linear, isocratic elution (min)
t_0	column hold-up time (min)
T_i	breakthrough time for frontal boundary (min)
T_0	column hold-up time (min)
u_i	velocity (cm/min)
u_0	interstitial velocity (cm/min)
U_i	adjusted velocity (dimensionless)

Greek symbols

α_{ij}	separation factor (dimensionless)
ϕ	column phase ratio (g/ml)

Superscripts

$'$	feed
$''$	presaturant

Subscripts

i	species i
j	species j

5. Acknowledgement

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