ESTIMATION OF ADSORPTION PARAMETERS OF A BINARY SYSTEM BY APPLYING THE LEWIS RULE

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Introduction

Reversed-phase liquid chromatography has been gaining popularity as one of the most reliable and versatile tools for analytical separation and quantification of mixtures⁸. In the course of development of this chromatographic technique, considerable attention has been given to its preparative use on a large scale as well as for analytical purposes^{1, 2, 4, 5, 10, 11}. It is important to develop not only superior preparative equipment that achieves high chromatographic efficiency but also a standard strategy for the scale-up approach to preparative separations.

Preparative chromatography is often operated under mass overload conditions, unlike an analytical procedure³. The development of preparative separations is accompanied by additional problems such as non-linearity of an adsorption isotherm and the concentration dependence of diffusivity. Because the properties of preparative separations differ considerably from those of analytical ones, conventional theory for analytical liquid chromatography cannot be applied directly to preparative separations. Simulation of chromatographic processes is useful in establishing a strategy for optimization of preparative operations⁵. First, exact representation of adsorption equilibria is required to simulate chromatographic separations accurately.

A number of methods based on the combination of single-component isotherms have been proposed for estimation of adsorption isotherms for multicomponent systems⁹. In the previous paper, the authors reported a simple method for estimation of an adsorption isotherm by analyzing a desorption curve⁶. This paper is concerned with adsorption equilibria of binary systems in reversed-phase liquid chromatography.

1. Experimental

A high-performance liquid chromatograph equipment unit was employed. A small volume of sample

solutions was introduced into a fluid flow by use of a sample injector. A column was kept at 298 ± 0.1 K in a thermostated water bath. The concentration of the sample in effluent was monitored by an ultraviolet detector.

The column was 6 mm in inside diameter and 150 mm in length. The average diameter of ODS particles was $45 \mu\text{m}$. The carrier solvent was a mixture of methanol and pure water (50/50, vol.). As sample materials, *p*-ethylphenol (PEP), 1-naphthol (1-NAPH), *p*-sec-butylphenol (PSBP), and *p*-tert-butylphenol (PTBP) were used, with uracil as an inert substance.

Adsorption isotherms of the adsorbates were determined by breakthrough and desorption experiments. The concentration of the adsorbates was changed stepwise from 1×10^{-3} to 1×10^{-2} g/cm³. For binary systems, measurements of adsorption isotherms were carried out in the same manner at various concentrations of each component in the concentration range.

2. Results and Discussion

2.1 Adsorption isotherms of each adsorbate

Single-component isotherms of the adsorbates could be expressed by the Langmuir equation, as was shown in the previous paper^{6, 7}. Langmuir parameters used are listed in Table 1. The figures of saturated amount adsorbed were of the same order of magnitude.

2.2 Adsorption equilibria of binary systems

An attempt was made to represent the adsorption isotherms of the binary systems by the Markham-Benton equation⁹.

$$q_i = q_{mi} K_i c_i / (1 + \sum K_i c_i) \quad (1)$$

Adsorbed amounts were calculated by using the Langmuir parameters listed in Table 1 without modification. Examples of the binary system of *p*-ethylphenol and 1-naphthol are shown in Figs. 1 and 2. Adsorption equilibria of the binary system could be represented by Eq. (1). Similar results could be obtained for the binary

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Table 1. Langmuir parameters

Adsorbate	q_m [mmol/g]	K [cm ³ /mmol]
p-Ethylphenol	0.94	8.66
1-Naphthol	0.75	13.6
p-sec-Buthylphenol	0.70	13.8
p-tert-Buthylphenol	0.70	11.4

Fig. 1 Adsorption from binary-solute system: p-ethylphenol (1) - 1-naphthol (2) at 298 K

system of *p-sec*-butylphenol and *p-tert*-butylphenol.

2.3 Estimation of langmuir parameters

Adsorption equilibria of binary systems in the reversed-phase mode can be expressed by the Markham-Benton equation with Langmuir parameters of single-component isotherms. In many cases, the isotherm of an objective component can be determined by using purified substance. An adsorption isotherm of a contaminant, however, cannot be measured directly because its standard material cannot be obtained. It is necessary to develop an estimation method of Langmuir parameters from adsorption data in binary systems by using a small amount of samples since objective components purified by reversed-phase liquid chromatography are usually expensive.

When the applicability of the Markham-Benton equation is established, the Lewis relation is expected to hold⁹⁾.

$$q_i / q_i^0 + q_j / q_j^0 = 1 \quad (2)$$

Adsorption data of the binary systems in this study are plotted according to Eq. (2). The value of q_i^0 was calculated with the Langmuir equation of *i*-th component by assuming that c_i was equal to c^0 . Similarly for the other component *j*, q_j^0 was calculated by using the Langmuir equation of *j*-th component under the condition that c_j was equal to c^0 . As shown in **Fig. 3**, a linear relation was observed. It is confirmed that the Lewis equation holds in a reversed-phase liquid chromatographic system.

The following procedure can be proposed for esti-

Fig. 2 Adsorption from binary-solute system: p-ethylphenol (1) - 1-naphthol (2) at 298 K

Fig. 3 Lewis plot of amounts adsorbed on ODS

mation of Langmuir parameters from adsorption data of binary systems by applying the Lewis equation. Adsorbability and physical properties of contaminants are assumed to be similar to those of objective components because the contaminants are usually by-products of synthesis or fermentation steps in practice.

(1) Henry constants, $q_{mi}K_i$ and $q_{mj}K_j$, for an objective component (*i*) and a contaminant (*j*) are determined from pulse response experiments.

(2) According to the simple methods proposed in the previous paper⁶⁾, the saturated amount adsorbed q_{mi} and the adsorption equilibrium constant K_i are determined.

(3) The value of q_i^0 in Eq. (2) can be calculated from the total concentration of the components in a binary system because Langmuir parameters q_{mi} and K_i of *i*-th component are already known. As the amounts of the components adsorbed in the binary system, q_i and q_j ,

Table 2. Estimation of Langmuir parameters for the binary-solute system of p-Ethylphenol and 1-Naphthol by the Lewis equation

Solute	Exptl.		Calcd.		Calcd.	
	q_m [mmol/g]	K [cm ³ /mmol]	q_m [mmol/g]	K [cm ³ /mmol]	q_m [mmol/g]	K [cm ³ /mmol]
PEP	0.94	8.66	Objective component		0.98	8.47
1-NAPH	0.75	13.6	0.78	13.3	Objective component	

are experimentally measured, q_j^0 can be obtained from Eq. (2). When a single-component isotherm can be represented by the Langmuir equation, q_j^0 can be expressed as follows.

$$q_j^0 = q_{mj} K_j c^0 / (1 + K_j c^0) \quad (3)$$

Because the values of q_j^0 , $q_{mj}K_j$, and c^0 in Eq. (3) are already known, firstly K_j can be calculated. Then q_{mj} can be obtained by dividing the Henry constant of j -th component, $q_{mj}K_j$, by the value of K_j calculated previously.

As shown in Table 2, good agreement was observed between Langmuir parameters experimentally determined and the values estimated by the proposed method. In Table 2, Langmuir parameters were calculated for each case, in which p -ethylphenol or 1-naphthol was assumed to be an objective component. To obtain accurate results by the proposed method, as many adsorption experiments as possible must be carried out. Changes in composition of components, however, are not required. Changes in the degree of dilution of a sample suffice for the change in adsorption conditions.

Estimation of adsorption isotherms in multicomponent systems has been carried out on the basis of the combination of single-component isotherms⁹⁾. In this work the characteristics of binary adsorption equilibria in reversed-phase liquid chromatography were studied. It was experimentally confirmed that a binary adsorption isotherm could be expressed by the Markham-Benton equation, using Langmuir parameters for single adsorp-

tion isotherms, and that the Lewis relation held for the reversed-phase liquid chromatographic mode. On the basis of the results, a simple method was proposed for the estimation of Langmuir parameters from the adsorption data of a binary system. The method requires in practice only three preliminary experimentally measured data, namely one pulse response curve and one breakthrough curve of a mixture and one desorption curve of an objective component.

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Nomenclature

c	=	concentration in mobile phase	[mmol/cm ³]
c^0	=	total concentration of a binary system,	
		$c_i + c_j$	[mmol/cm ³]
K	=	adsorption equilibrium constant	[cm ³ /g]
q	=	amount adsorbed	[mmol/g]
q_m	=	saturated amount adsorbed	[mmol/g]
q^0	=	amount adsorbed in equilibrium with c^0	[mmol/g]

<Subscripts>

i	=	i -th component (objective component)
j	=	j -th component (contaminant)

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