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NOTE

FAST DETERMINATION OF LANGMUIR ISOTHERM PARAMETERS IN LARGE CONCENTRATION OF ONE SOLUTE

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Abstract—A simple method is presented to obtain the Langmuir isotherm parameters. Although this method is limited to the case of large concentration, a few injections enable the determination of the parameters. For a sample of thymine, with the injection volumes of 1.0 and 1.5 ml, the parameters of a and b are determined as 15.83 ml/ml and 0.12 ml/mg, respectively.

INTRODUCTION

There is considerable industrial interest in both scale-up and optimization of chromatographic operation [1]. Scaling-up or optimizing a chromatographic system requires the characterization of the fundamental mechanism to construct the suitable mathematical model, which can be used to predict the chromatographic performance without a number of experiments [2]. A general model of the migration of large concentration bands in chromatography is obtained by the mass balances of each of the chemical species.

Guiochon and his fellows of Oak Ridge National Lab. extensively researched the theory of nonlinear liquid preparative chromatography, where the volume of sample or the concentration is increased in order to achieve a large throughput [3,4]. A adsorption isotherm is the major factor affecting the liquid-solid preparative chromatographic process. The purpose of this work is to suggest the simple method of the determination of the Langmuir isotherm parameters in large concentration of one solute.

METHODOLOGY

The adsorption coefficient is the ratio of the amount of solute per unit volume of stationary phase (q) to that of solute per unit volume of mobile phase (c) and it is expressed as

$$K=(V_R-V_0)/V_{sp} \tag{1}$$

, where V_R = retention volume of solute (= Ft_R)
V_0 = retention volume of unretained solute (= Ft_0)
V_{sp} = volume of stationary phase
F = flow rate of mobile phase
t_R, t_0 = retention time of solute and unretained solute, respectively.

As the sample amount is increased, the peak shape is deviated from the Gaussian curve. In case of extremely large concentration, the front edge of a peak is very steep. If the mass transfer from stationary to mobile phase is very fast and the axial dispersion is negligible, the peak has little tailing as shown in Figure 1. We can divide the peak in Figure 1 into n sections, and from the definition of Eq. (1),

$$q(c_1)=(c_1-0)(t_{R1}-t_0)F/V_{sp}. \tag{2}$$

Similarly,

$$q(c_2)=q(c_1)+(c_2-c_1)(t_{R2}-t_0)F/V_{sp} \tag{3}$$

$$q(c_3)=q(c_2)+(c_3-c_2)(t_{R3}-t_0)F/V_{sp} \tag{4}$$

$$\vdots$$

$$q(c_n)=q(_{n-1})+(c_n-c_{n-1})(t_{Rn}-t_0)F/V_{sp}. \tag{5}$$

In liquid chromatography, a solute has adsorption isotherm that can be described well to a first approximation by Langmuir adsorption isotherm of the form

$$q(c)=ac/(1+bc) \tag{6}$$

, where a, b = Langmuir isotherm parameters.
Rearranging Eq. (6) gives

$$c/q=1/a+(b/a)c. \tag{7}$$

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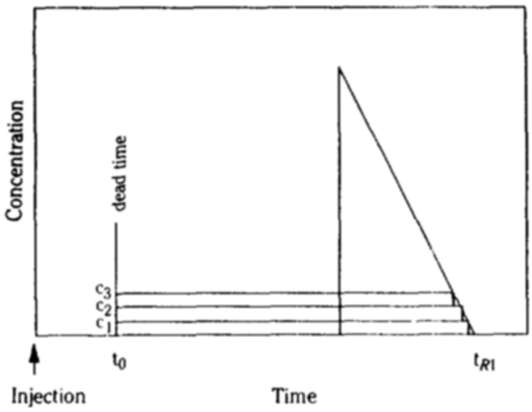
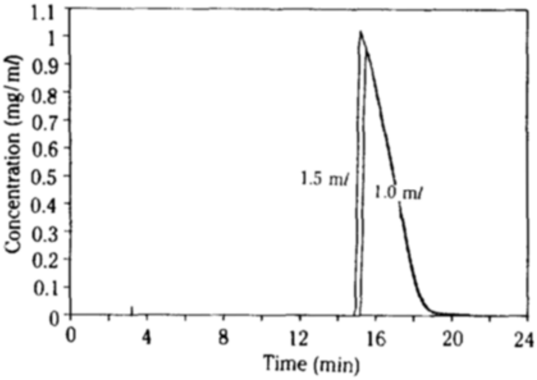


Fig. 1. Method for calculating Langmuir isotherm parameters, a and b.



g. 2. Elution profiles of thymine in large concentration.
(flow rate 1.0 mℓ/min, thymine concentration 2.0 mg/mℓ)

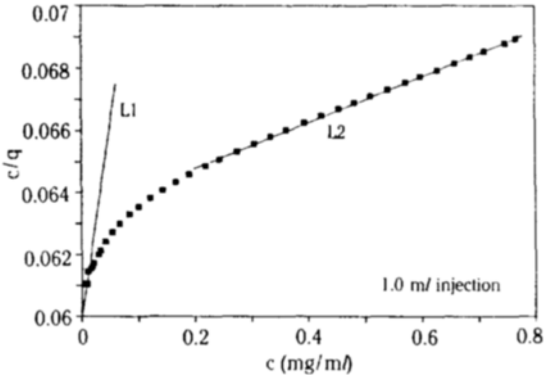


Fig. 3. Plot of c/q to c.
[L1 = linear equilibrium, L2 = range of data for calculation of Eq. (7)]

Therefore, the parameters of a and b can be calculated from the intercept and slope of the plot of c/q to c.

EXPERIMENTS

A liquid chromatograph of Waters was used with a Model 600E multisolvent delivery system, a Model U6K injector, and a Model 490 programmable multiwavelength detector. The column was an Alltech 250 mm (length) × 4.6 mm (I.D.) C18 HS column (0.07 mm packing dia.). UV absorbance was monitored at 254 nm.

Special grade HPLC water was obtained from American Burdick and Jackson (Muskegon, MI) and was used as a mobile phase without further purification. Thymine and uracil were purchased from Sigma (St. Louis, MO). Standards were prepared in aqueous solution and calibration charts were constructed from the peak areas at different concentrations.

Experimental data points were acquired by a Maxima 820 chromatography workstation (Dynamic Solutions, Millipore, Ventura, CA) at a acquisition rate of 10 points/min, and then the data was translated into DIF file for exporting to the Lotus 123^{tm}.

RESULTS AND DISCUSSION

The elution profiles with the injection volumes of 1.0 and 1.5 mℓ (2 mg/mℓ concentration of thymine) are shown in Figure 2. They are obtained at a flow rate of 1.0 mℓ/min and room temperature. The injection amount is about a thousand times larger than that used in the analytical liquid chromatography. The peak shapes are in close agreement with the peak in Figure 1 except for a slight tail at the end of the experimental elution profiles. Therefore, we can proceed to calculate the Langmuir isotherm parameters, a and b. The residence times of thymine are 15.6 and 15.3 min for the injection volume of 1.0 and 1.5 mℓ, respectively. The dead time, t_0, was measured from the retention time of uracil and it was 3.2 min.

The column is defined by its total porosity, which is set equal to 0.765, a value often encountered in this type of chromatographic column. The total porosity is comprised of the interparticle porosity (void fraction) and the intraparticle porosity. The void fraction is frequently designated as 0.41 (5), while the stagnant fluid occupies the remaining portion in the pores of chromatographic support. Hence, V_{sp} is determined by the substraction of the volume of mobile phase from the total column volume, and it is found to be 0.97 mℓ.

The Langmuir equilibrium isotherm provides the reasonable base for the liquid-solid chromatography. Figure 3 shows that the plot of c/q to c in the condition of the Langmuir isotherm. The relationship between c/q and c is not entirely in the linear range especially at the lower concentration than 0.2 mg/m*l*. Only above that concentration, the data were taken for calculation of the Langmuir isotherm parameters (see solid line L2 in the figure). From the intercept and slope in Eq. (7), with the injection volumes of 1.0 and 1.5 m*l*, the parameter of a and b are determined by a simple linear regression as 15.83 m*l*/m*l* and 0.12 m*l*/mg, respectively. Another solid line, L1, shows the linear equilibrium isotherm in the range close to the origin.

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