PARAMETER ESTIMATION IN ADSORPTION CHROMATOGRAPHY BY REAL-TIME ANALYSIS

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The objective of this note is to examine what rate parameters may be determined from a single measurement of the response curve in adsorption chromatography. The rate parameters involved in the usual model for reversible adsorption of a tracer in a fixed bed of adsorbent particles are the axial fluid dispersion coefficient $D_{ax}$, particle-to-fluid mass transfer coefficient $k_f$, intraparticle effective diffusivity $D_e$, adsorption equilibrium constant $K_A$, and adsorption rate constant $k_a$. The adsorption rate is supposed to be linear and reversible.

Kubin and Kucera showed that all five parameters were determinate, in theory, from five moments generated from a single measurement. However, their moment method has the disadvantage that small errors involved in the tailing portion of the curve are seriously magnified in the calculated values of higher moments. The technique modified by Smith et al. is to determine the parameter values from the first and second moments alone. In their analysis the parameters are determined from a series of measurements with varied flow rates and particle sizes, not from a single measurement.

In parameter estimation, in general, Clements, Anderssen and White, and Boëkses and Hofmann showed that the real-time method of analysis was superior to any of the methods in which a weighting function was involved.

In this note, an experimental response curve is tested for parameter estimation in the time domain. The curve is a delta response of $n$-butane imposed on a helium carrier flowing in a column packed with silica gel particles. The experimental conditions for one measurement are as follows:

- Bed void fraction = 0.395, particle void fraction = 0.486, particle diameter = 0.718 mm, particle density = 1.13 g/cm$^3$, column bed length = 13.0 cm, interstitial fluid velocity = 3.02 cm/sec, temperature = 348°K.

The conservation and rate equations for the system, and the formula for computing the response curve in the time domain in terms of the five parameters are described elsewhere. The predicted curve is then compared with the experimental response curve. If the difference $\varepsilon$, given by Eq. (1), is small, the parameter values used for the prediction may be regarded as correct.

$$\varepsilon = \left[ \frac{1}{t_b - t_a} \int_{t_a}^{t_b} \left( c_{exp}(t) - c_{calc}(t) \right)^2 dt \right]^{1/2} \tag{1}$$

Note that the comparison can be made over any arbitrary time interval, $t_a$ to $t_b$. For testing the butane-silica gel data, a central interval from $t_a=9$ min to $t_a=23$ min was chosen. The entire region ($t=0$ to $30$ min) of the experimental curve is not chosen because the response curve usually has relatively large errors at both short and long times.

From a series of measurements, at various velocities and for different particle sizes, in the same system, Schneider and Smith found $k_a=1,500$ cm$^3$/g·sec. For the external film mass transfer step they assumed a Sherwood number of 2.0. Under the same assumption the mass transfer coefficient for the present system becomes 13.7 cm/sec. The intraparticle effective diffusivity is considered to be in the range of $D_e=0.0006$ to 0.003 cm$^2$/sec.

For the first test, response curves were predicted with $k_a=1,500$ cm$^3$/g·sec, $k_f=13.7$ cm/sec and $D_e=0.0006$ to 0.003 cm$^2$/sec. The deviations of the predicted curves from the experimental curve are shown on the error surfaces in the plot of $K_A$ vs. $D_{ax}$, Fig. 1. The contour for a small $\varepsilon$, say $\varepsilon=0.0002$, indicates that curves predicted with any $K_A$ and $D_{ax}$ values inside the contour agree well with the experimental response curve. The valley, the contour with small $\varepsilon$, extends horizontally on the error map, indicating that $K_A$ is much more sensitive to $\varepsilon$ than $D_{ax}$. From Fig. 1 it is clear that $K_A=110$ cm$^3$/g. Figure 2 is the error map plotted as $K_A$ vs. $D_{ax}$ at fixed $D_{ax}$ values. It is again shown that $K_A$ is much more sensitive to $\varepsilon$ than $D_{ax}$ and that $K_A$ is 110 cm$^3$/g.

The next question is: can $D_e$ and/or $D_{ax}$ be determined. The sensitivity test is a plot of $D_e$ vs. $D_{ax}$
with $K_A = 110 \text{ cm}^3/\text{g}$. Such a plot is shown in Fig. 3. The range of these two parameters with $\varepsilon = 0.0002$ is very large, and it expands with increase in $D_{ax}$. The graph indicates that simultaneous determination of the two parameters, $D_x$ and $D_{ax}$, is not feasible. Even if we know one of them, the value of the other can cover a wide range and still maintain $\varepsilon = 0.0002$. If $D_{ax} = 0.4 \text{ cm}^2/\text{sec}$, for instance, $D_x$ can vary from 0.001 to 0.0028 cm$^2$/sec; if $D_{ax} = 0.0015 \text{ cm}^2/\text{sec}$, $D_{ax}$ can range from 0.25 to 0.56 cm$^2$/sec.

Figures 4-6 show the effects of the separate parameters on the shapes of the predicted curves. The parameter values used for the computation are listed in Table 1.

Figure 4 shows that $K_A$ is the most sensitive parameter. A change of about 20% in $K_A$ results in a considerable change in the shape and location of the peak of the curve. Figures 5 and 6 show that the shapes of the curves are also affected by $D_{ax}$ and $D_x$, but are not sensitive to $k_a$ and $k_f$. Variation of two orders of magnitude in these parameters results in but

![Fig. 1 Error map in plot of $K_A$ vs. $D_{ax}$ at fixed $D_x$ values](image1)

![Fig. 2 Error map in plot of $K_A$ vs. $D_x$ at fixed $D_{ax}$ values](image2)

![Fig. 3 Error map in plot of $D_x$ vs. $D_{ax}$ at $K_A = 110 \text{ cm}^3/\text{g}$](image3)

![Fig. 4 Effect of $K_A$ on shape of predicted response curve](image4)

![Fig. 5 Effect of $D_{ax}$](image5)

![Fig. 6 Effects of $D_x$, $k_a$ and $k_f$](image6)
slight differences in the shape of the response curve. The major conclusion from this study is that sensitivity tests should be made when evaluating equilibrium and rate parameters from response measurements in adsorption chromatography. Such tests will indicate which parameters may be evaluated accurately. As far as the present example of physical adsorption is concerned, the most sensitive among the five parameters is the adsorption equilibrium constant, and it is accurately determined from a single measurement. The axial fluid dispersion coefficient and the intraparticle effective diffusivity could not be determined simultaneously. If one is known the other may be estimated, but the result is of uncertain accuracy.

The particle-to-fluid mass transfer coefficient and the adsorption rate constant, which have little effect upon the shape of the response curve, could not be determined.

**Nomenclature**

- \( c_{\text{exp}}(t) \) = measured concentration (normalized) of adsorbate tracer in the response curve to a shot input
- \( c_{\text{calc}}(t) \) = calculated concentration (normalized) of tracer in the response curve to a shot input
- \( D_{\alpha} \) = axial dispersion coefficient in the bed of adsorbent particles
- \( D_e \) = effective intraparticle diffusivity of tracer
- \( K_A \) = adsorption equilibrium constant
- \( k_a \) = first-order adsorption rate constant

**Table 1** Parameter values used for computing response curves

<table>
<thead>
<tr>
<th>Curve No.</th>
<th>( K_A ) [cm³/g]</th>
<th>( D_{\alpha} ) [cm²/sec]</th>
<th>( k_a ) [cm³/g·sec]</th>
<th>( k_f ) [cm/sec]</th>
<th>( D_e ) [cm²/sec]</th>
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<tr>
<td>1</td>
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<td>1,500</td>
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<tr>
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<td>13.7</td>
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<tr>
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</tr>
<tr>
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<tr>
<td>7</td>
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</tr>
<tr>
<td>8</td>
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<td>1,500</td>
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</tr>
<tr>
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<tr>
<td>11</td>
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<td>0.3</td>
<td>1,500</td>
<td>137</td>
<td>0.001</td>
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</tbody>
</table>

- \( k_f \) = particle-to-fluid mass transfer coefficient
- \( t \) = time
- \( \varepsilon \) = error function representing the difference between the experimental and calculated response curves, as defined by Eq. (1)

**Literature Cited**


**SIMULTANEOUS MEASUREMENTS OF THICKNESS AND LOCAL MASS TRANSFER RATE ON FALLING LIQUID FILMS**

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Falling liquid films can be seen in many kinds of equipment, and the rate of mass transfer through films in particular is essential for equipment design. Wave motions, which appear downstream of the location of wave inception on films, significantly enhance mass transfer rates. Many studies of mass transfer through both gas-liquid and solid-liquid interfaces of wavy liquid flow under various conditions have been made experimentally and theoretically. However, these investigations dealt with only the time-averaged values of mass transfer rates. Instantaneous measurements of local liquid-solid