A Method for Calculating Breakthrough Curves of Bicomponent Fixed-Bed Adsorption under Constant Pattern and Linear Driving Force

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A simplified method was developed for calculating the breakthrough curves in fixed-bed adsorption with two solutes under the constant pattern (CP) and the linear driving force (LDF) approximations, in which both external fluid film mass transfer and intraparticle diffusion resistances were taken into account. By comparing three design methods derived without the CP approximation, the LDF approximation was found to be valid in the case of surface diffusion kinetics and also to hold approximately in the case of pore diffusion kinetics. The minimum column length required to establish the constant pattern was estimated by two methods, one employing the CP approximation, the other not, and the minimum column length was found to be estimated only by the simplified method. Experimental breakthrough curves were obtained for an aqueous solution of dodecylbenzenesulfonate and p-nitrophenol and a gaseous mixture of benzene and toluene. They were compared with the breakthrough curves predicted by the simplified method.

Introduction

Fixed-bed adsorbers have been widely employed in processes for solvent recovery, gas separation, wastewater treatment and so on. Several design methods for fixed-bed adsorbers have been presented, but most are concerned with the single-component system.

Recently, several investigators have presented methods for calculating the breakthrough (BT) curves of binary-component systems. Carter and Husain solved basic equations numerically by assuming pore diffusion kinetics for intraparticle diffusion. This method is mathematically rigid, but the programming procedure is rather complicated and the computation time required is inconveniently long. To reduce these difficulties the so-called linear driving force (LDF) approximation, the validity of which is recognized for the single-component system, was introduced by Gariepy and Zwiebel and Hsieh et al. Simpler solutions have been obtained by employing the constant pattern (CP) approximation by Cooney and Lightfoot and Thomas and Lombardi, though they took into account only the intraparticle diffusion resistance. Cooney and Strusi also demonstrated that an analytical solution can be obtained for a special case in which the adsorption isotherm is expressed by the Langmuir equations and the ratio of the overall mass transfer coefficients of the two components is unity. Takeuchi et al. presented a simplified method for calculating the break time and the length of adsorption zone, and showed experimentally that the constant pattern holds in relatively long columns.

Although several methods have been presented, the accuracies and the interrelations of these methods have not been clarified. Moreover, the validity of the LDF approximation has not been examined for binary component systems, and the conditions under which the CP approximation holds have not been examined.

In this paper a simplified method is presented for calculating the BT curves by taking into account both intraparticle and external fluid film mass transfer resistances under the CP and the LDF approximations. The Langmuir and the Freundlich type of adsorption isotherms are assumed in the development of the simplified method. The validity of the CP and the LDF approximations is examined by comparing the simplified method with the numerical solutions obtained without the CP and the LDF approximations. BT curves were measured for an aqueous solution of dodecylbenzenesulfonate (DBS) and p-nitrophenol (PNP) and a gaseous mixture of benzene and toluene.
under several experimental conditions. The BT curves corresponding to these experimental conditions were predicted by the simplified method by use of adsorption isotherms and intraparticle diffusivities determined beforehand. Then the usefulness of the simplified method is discussed by comparing the experimental and the predicted BT curves.

1. Adsorption Isotherms

In this work the adsorption isotherm was assumed to be represented by the Langmuir or Freundlich type of equation:

(a) Langmuir isotherm:

\[ q_i = \frac{a_i C_i}{(1 + b_i C_i)} \quad (i = 1, 2) \]  

(b) Freundlich isotherm:

\[ q_i = \frac{C_i}{(1 + a_i C_i)^{1/n}} \quad (i = 1, 2) \]

where \( C_i (i = 1, 2) \) is the fluid-phase concentration, \( q_i \) is the solid-phase concentration, and the others are constants. The Langmuir isotherm has been widely employed by many investigators, and the isotherm of Freundlich type is an empirical equation which satisfactorily correlates experimental data, as was shown by Fritz et al. Equations (1) and (2) are rewritten by introducing dimensionless concentrations, \( x_i \) and \( y_i \), which are normalized by the values at the column inlet, \( C_{i0} \) and \( q_{i0} \).

(a) Langmuir isotherm:

\[ x_i = \frac{x_i}{C_{i0}} \quad (i = 1, 2) \]

(b) Freundlich isotherm:

\[ \log y_i = \frac{1}{n} \log x_i + \log K_i \]

The parameters involved in the above equations are defined as follows:

\[ P_i = (1 + b_i C_{i0})/(1 + b_i C_{i0} + b_i C_{i0}) \]

\[ K_i = 1 + T_i C_i^{1/2}/C_{i0} \]

2. Design Methods without Use of the Constant Pattern Concept (NCP Methods)

For adsorption onto adsorbent particles in an isothermal fixed bed where radial concentration gradients and the effects of axial dispersion are assumed to be negligible, the mass balance equation for each component in the bed can be written as follows:

\[ \frac{d(C_i)}{dz} + e_0 (C_i) + \rho_i (\partial q_i/\partial t) = 0 \quad (i = 1, 2) \]

where \( C_i \) is the concentration in the bulk phase of the bed, \( q_i \) the average amount adsorbed over a particle, \( e_0 \) the void fraction of the bed, \( \rho_i \) the bed density, \( z \) the column length, and \( t \) the time.

The following three models were employed to represent the rate of intraparticle diffusion.

Model I: pore diffusion kinetics (abbreviated as P)

Model II: surface diffusion kinetics (S)

Model III: linear driving force approximation (LDF)

Equation (7) was solved numerically with the above three models for intraparticle diffusion. To identify the system the following dimensionless parameters were defined.

\[ \phi_j = k_{fj}/k_{f1} \]

\[ \phi_s = k_{sj}/k_{s1} \]

\[ \zeta_j = k_{fj} a_j/(k_f a_j (q_{j0}/C_{j0})) \quad (j = 1, 2) \]

\[ \delta = (q_{j0}/C_{j0})/(q_{j0}/C_{j0}) \]

where \( k_{fj} (j = 1, 2) \) is the fluid film mass transfer coefficient, \( a_j \) the specific particle surface area, and \( k_{sj} \) is related to surface diffusivity \( D_{sj} \) or pore diffusivity \( D_{pj} \), as follows:

\[ k_{sj} a_j = 15D_{sj}/(1 - \varepsilon_0) \]

or

\[ k_{sj} a_j = 15D_{pj}/(1 - \varepsilon_0) \]

In this paper the parameter \( \delta \) is always selected to be greater than unity. Therefore the component having the larger adsorption coefficient always corresponds to component 2. For the Langmuir isotherm system, \( \delta \) is equal to \( a_2/a_1 \). If the adsorption parameters, the parameter \( \delta \) and three of the four parameters \( \zeta_j, \zeta_s, \phi_j \), and \( \phi_s \) are given, the basic equations can be solved against the following dimensionless time and column length.

\[ \theta = k_{fj} a_j (1 - \varepsilon_0)C_{j0}/(q_{j0}/C_{j0}) \]

\[ X = k_{sj} a_j \varepsilon_0 \]

The three design methods developed in this section are abbreviated as NCP-P, NCP-S and NCP-LDF. The abbreviation NCP means that the approximation of the constant pattern was not employed; P, S, and LDF refer to the models of intraparticle diffusion.

The basic equations for the NCP-P and NCP-S methods were solved by a procedure similar to that developed by Carter and Husain, and those for the NCP-LDF method were solved by using an ordinary finite difference scheme with the boundary conditions given by Hsieh et al.

3. Simplified Design Method under the Constant Pattern and the Linear Driving Force Approximations (CP-LDF)

3.1 Relation of fluid-phase concentration and solid-phase concentration

Figure 1 shows schematic dimensionless BT curves
for the case in which the constant pattern (CP) is completely established. A distinct feature of the binary adsorption is that the concentration of component 1, which has the smaller adsorption coefficient, exceeds the value at the column inlet because of the displacement effect of component 2, and reaches a constant value, \(x_{1m}\). The concentration distribution is divided into five zones according to Cooney and Strusi. Since the concentration change in zone IV may be computed by single-component theories, the analysis is mainly concerned with the calculation of concentration change in zone II.

In zone II the following equations hold from the fact that the travelling velocity of the adsorption zone of component 1 is equal to that of component 2 and is constant:

\[
y_1 = \delta(x_1 - 1) + 1 \quad \text{(16)}
\]
\[
y_2 = x_2 \quad \text{(17)}
\]

Similarly, the following equation holds for component 1 in zone IV.

\[
y_1 = \left(\frac{q_{1m}}{C_{1m}}\right) x_{1m} x_2 \quad \text{(18)}
\]

where \(q_{1m}\) is the amount adsorbed in equilibrium with \(C_{1m}\).

3.2 Determination of the maximum concentration of component 1

The dimensionless maximum concentration of component 1 in zones II to IV, \(x_{1m}\), can be calculated by use of Eq. (16) and the adsorption isotherms. The concentration of component 2 is zero when \(x_1 = x_{1m}\) in zones II to IV. In zone II, \(x_1\) satisfies Eq. (16). Therefore \(x_{1m}\) is obtained as the point of intersection of Eq. (16) and the isotherm of component 1 corresponding to \(x_2 = 0\), which means that the following equations hold.

\[
\delta(x_{1m} - 1) + 1 = x_{1m}/(P_1 + P_2 - 1 + (1 - P_2)x_{1m}) \quad \text{(Langmuir)} (19a)
\]
\[
\delta(x_{1m} - 1) + 1 = K_2(x_{1m})^{1 - P_2} \quad \text{(Freundlich)} (19b)
\]

For the Langmuir isotherm, \(x_{1m}\) is obtained as the positive root of Eq. (19a). However, Eq. (19b) must be solved iteratively or graphically.

3.3 Solution of the CP-LDF method

(Zone II)

The rate equations for this method can be written in dimensionless form as follows:

\[
\frac{d\tilde{y}_1}{d\theta} = \phi_1 \frac{\delta(x_1 - x_{1s})}{\zeta_1} (y_{1s} - \tilde{y}_1) \quad \text{(20)}
\]
\[
\frac{d\tilde{y}_2}{d\theta} = \tilde{x}_2 - x_{2s} = \frac{1}{\zeta_2} (y_{2s} - \tilde{y}_2) \quad \text{(21)}
\]

In the single-component system, the parameter \(\eta\) was introduced to improve the LDF approximation. However, \(\eta\) is omitted here, because it was difficult to determine \(\eta\) for the binary-component system.

The solid-phase concentrations, \(\tilde{x}_1\) and \(\tilde{x}_2\), in Eqs. (20) and (21) can be replaced by \(\tilde{x}_1\) and \(\tilde{x}_2\) with the aid of Eqs. (16) and (17). The resulting equations were solved to obtain \(\tilde{x}_1\) and \(\tilde{x}_2\) as

\[
\tilde{x}_1 = (\zeta_1 x_{1s} + y_{1s} + \delta - 1)/(\zeta_1 + \delta) \quad \text{(22)}
\]
\[
\tilde{x}_2 = (\zeta_2 x_{2s} + y_{2s})/(\zeta_2 + 1) \quad \text{(23)}
\]

Differentiating Eqs. (22) and (23) with regard to \(\theta\), and eliminating \(\tilde{x}_1\) and \(\tilde{x}_2\) from the rate equations gives the following equations:

\[
\left(\zeta_1 + \frac{\partial y_{1s}}{\partial x_{1s}}\right) \frac{dx_{1s}}{d\theta} + \frac{\partial y_{1s}}{\partial x_{1s}} \frac{dx_{1s}}{d\theta} = \phi_1 (y_{1s} - \delta x_{1s} + \delta - 1) \quad \text{(24)}
\]
\[
\frac{\partial y_{2s}}{\partial x_{1s}} \frac{dx_{1s}}{d\theta} + \left(\zeta_2 + \frac{\partial y_{2s}}{\partial x_{1s}}\right) \frac{dx_{1s}}{d\theta} = y_{2s} - x_{2s} \quad \text{(25)}
\]

As \(y_{1s}\) and \(y_{2s}\) are written as functions of \(x_{1s}\) and \(x_{2s}\) through equilibrium relationships, the dependent variables in Eqs. (24) and (25) are \(x_{1s}\) and \(x_{2s}\). Therefore Eqs. (24) and (25) could be integrated with appropriate initial conditions by the Runge-Kutta-Gill method to obtain the relations between \(x_{1s}\) and \(x_{2s}\). The concentrations \(x_{1s}\) and \(x_{2s}\) can be converted easily to \(x_1\) and \(x_2\) by use of Eqs. (22) and (23). The detailed integration scheme of Eqs. (24) and (25) is presented in the Appendix.

(Zone IV)

The analytical solutions for the single-component system developed by the authors are applicable simply by changing the integral constants, though several parameters must be redefined. To determine the integral constants, the areas designated \(S_1\) and \(S_2\) in Fig. 1 must be estimated by integrating the breakthrough curves of zone II. The final resulting equations are given in Table 1 for both Langmuir and Freundlich isotherms. They are represented by use of a general dimensionless time, \(\theta_T\), and a general dimensionless column length, \(X_T\), which are defined by

\[
\theta_T = \theta/(1 + \zeta_T) \quad \text{(28)}
\]
\[
X_T = X/(1 + \zeta_T) \quad \text{(29)}
\]

4. Calculated Results

4.1 The validity of the LDF approximation

Figure 2 illustrates the differences between the con-
Table 1 Analytical solutions for zone IV

(a) Langmuir

Analytical solutions

\[ \frac{\partial X_{in}}{\partial x_{in}} = -k_T \frac{1}{1-K} \ln (1-X_{in}) \]

(b) Freundlich

\[ \frac{\partial Y_{in}}{\partial x_{in}} = -k_T \frac{1}{1-K} \ln (1-Y_{in}) \]

Conversion of \( X_{in} \) to \( x_{1i} \)

\[ x_{1i} = x_{1in}(1+\zeta) \]

Definition of parameters

\[ X_{in} = \frac{C_{in}K_{m}}{K + (1-K)C_{in}}, \quad Z_{in} = \frac{K_{in}a_{in}/K_{in}}{C_{in}}, \quad K = 1/(1+b_{in}), \quad \beta = \alpha_{in} - \beta \]

Fig. 2 Comparison of concentration distributions in the bed calculated by three methods without constant pattern approximation

Fig. 3 Comparison of breakthrough curves calculated by NCP-LDF and CP-LDF methods

Concentration distributions calculated by three methods, NCP-P, NCP-S and NCP-LDF for a Langmuir isotherm system. As time elapses the concentration distributions develop and the five zones shown schematically in Fig. 1 are clearly formed. This fact indicates that the constant pattern is established in a relatively long bed.

The results calculated by the NCP-S and the NCP-LDF methods are almost coincident, and only a slight difference appears between the results obtained by the NCP-P and NCP-LDF methods. By changing the combination of parameters, several concentration distributions were calculated by the three methods, and similar results to those shown in Fig. 2 were obtained in each case. Thus the LDF approximation was found to be valid for the system in which surface diffusion is controlling, and the approximation may be also applicable to pore diffusion controlling systems.

4.2 Minimum column length required to establish the constant pattern

To clarify the conditions under which the simplified CP-LDF method is applicable, the minimum column length required to establish the constant pattern was estimated. Here the dimensionless minimum column length, \( X_T \) \(_{\text{min}} \), is defined as the column length at which the dimensionless maximum concentration of component 1 reaches 0.99x\(_{in}\) for the first time. First, \( X_T \) \(_{\text{min}} \) was estimated by the NCP-LDF method. The solid lines in Fig. 3 show the BT curves calculated by the NCP-LDF method at different column lengths for the same system as in Fig. 2. It is seen that the constant pattern is virtually established at \( X_T = 15 \); \( X_T \) \(_{\text{min}} \) is about 15 for this case. However, the NCP-LDF method is not so simple for practical applications. Therefore it is desirable to estimate \( X_T \) \(_{\text{min}} \) by the CP-LDF method alone.

When the BT curves are calculated by the CP-LDF method at shorter column lengths at which the constant pattern is not completely established, the BT curves of zone II and zone IV intersect. The BT curves for \( X_T = 5 \) and 15 in Fig. 3 show such intersections. As column length increases the \( x_{1i} \) value at the points of intersection increases and reaches 0.99x\(_{in}\) at

\[ I_a = \frac{1}{1-\beta} \left[ 1 + \sum_{k=1}^{\infty} (-1)^k \frac{(2\beta-1)(3\beta-2) \cdots (k(\beta-1)+\beta)}{k!(k+1)!} \right] \]

\[ I_p = \frac{1}{1-\beta} \left[ 1 + \sum_{k=1}^{\infty} (-1)^k \frac{(2\beta-1)(3\beta-2) \cdots (k(\beta-1)+1)}{k!(k+1)!} \right] \]

\[ I_a \] and \( I_p \) are shown graphically against \( \beta \) in the previous paper.
Table 2: Experimental conditions and results

<table>
<thead>
<tr>
<th>Component 1</th>
<th>Component 2</th>
<th>Run 1</th>
<th>Run 2</th>
<th>Run 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>p-nitrophenol</td>
<td>DBS</td>
<td>25.3, 50.5</td>
<td>50.5, 100.5</td>
<td>25.0, 50.3, 29.0</td>
</tr>
<tr>
<td>p-nitrophenol</td>
<td>benzene</td>
<td>25.0</td>
<td>100.9</td>
<td>75.5, 100.5</td>
</tr>
<tr>
<td>z [cm]</td>
<td></td>
<td>0.0364</td>
<td>0.0366</td>
<td>0.31</td>
</tr>
<tr>
<td>u [cm/sec]</td>
<td></td>
<td>0.39</td>
<td>0.40</td>
<td>0.41</td>
</tr>
<tr>
<td>$C_i$ [mg/l]</td>
<td></td>
<td>151</td>
<td>140</td>
<td>49.3</td>
</tr>
<tr>
<td>$C_j$ [mg/l]</td>
<td></td>
<td>48.9</td>
<td>50.9</td>
<td>35.8</td>
</tr>
<tr>
<td>$D_{ij}$ [cm$^2$/sec]</td>
<td></td>
<td>$2.2 \times 10^{-6}$</td>
<td>$2.4 \times 10^{-10}$</td>
<td>$2.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>$D_{k}$ [cm$^2$/sec]</td>
<td></td>
<td>$1.7 \times 10^{-10}$</td>
<td>$1.4 \times 10^{-9}$</td>
<td>$8.4 \times 10^{-6}$</td>
</tr>
<tr>
<td>$\xi$ [-]</td>
<td></td>
<td>0.27</td>
<td>16.4</td>
<td>1.39</td>
</tr>
<tr>
<td>$\xi_j$ [-]</td>
<td></td>
<td>1.11</td>
<td>0.20</td>
<td>1.02</td>
</tr>
<tr>
<td>$\xi_{in}$ [-]</td>
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<td>0.63</td>
<td>1.04</td>
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<tr>
<td>$\xi_{in} \times x_{in}$ [cm]</td>
<td></td>
<td>1.25</td>
<td>1.22</td>
<td>1.56</td>
</tr>
<tr>
<td>$\xi_{exp} \times x_{exp}$ [cm]</td>
<td></td>
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<td>1.18</td>
<td>1.47</td>
</tr>
<tr>
<td>$x_{min}$ [cm]</td>
<td></td>
<td>48.8</td>
<td>86.7</td>
<td>22.2</td>
</tr>
</tbody>
</table>

Figure 4 shows the experimental BT curves for run 2, measured at four different column lengths. The maximum concentration of DBS increases with increase of column length, and seems to reach a constant value at a column length of 100.5 cm. This indicates that the constant pattern held at this column length. In run 2, the influent concentration of each component was chosen so that DBS would correspond to component 1, which is displaced by component 2 in zone 2. On the other hand PNP corresponded to component 1 in run 1, as will be shown later. It is possible to choose component 1 arbitrarily for the Freundlich isotherm.

5. Examination of the Validity of the CP-LDF Method

5.1 Experimental

1) Liquid-phase adsorption (binary adsorption of DBS and PNP) Adsorption isotherms and breakthrough curves were obtained by the procedure described in a previous paper. The activated carbon used was the same, CAL, with a particle radius of 0.032 cm.

The adsorption isotherms estimated for this system were represented by the following Freundlich type equations:

$$q_p = 173C_P^{3.300}/(C_P^{0.185} + 0.333C_P^{0.386})$$
$$q_D = 178C_D^{4.185}/(C_D^{0.305} + 0.395C_D^{0.205})$$

where subscripts $D$ and $P$ denote DBS and PNP, respectively.

Breakthrough curves were obtained under two different sets of experimental conditions (runs 1 and 2). The experimental conditions for each run are given in Table 2. The intraparticle diffusivities, $D_{ij}$, were estimated in batch experiments by the procedure presented in the previous paper. The $D_{ij}$ values corresponding to the experimental conditions are also given in Table 2. The values $\xi_i$, $\xi_j$ and $\phi_i$ listed in Table 2 were calculated by use of the $D_{ij}$ values estimated and $k_{ij}$ obtained from the correlating equation of Carberry.

2) Gas-phase adsorption (binary adsorption of benzene and toluene) All the experiments for this system were performed by use of the adsorption columns packed with an activated carbon. The adsorption columns were made of glass tubing of 20.0 mm I.D. and ca. 25 cm length. The activated carbon used was B-GG (Fujisawa Pharmacy Co. Ltd.) with surface area (measured by the BET method using nitrogen at 77.5 K), particle density and particle radius of 844 m$^2$/g, 0.92 g/cm$^3$ and 0.183 cm, respectively. The air stream saturated with benzene and toluene was mixed with another air stream and introduced into the adsorption columns. The effluent gas was analyzed by gas chromatography to obtain the breakthrough curves. The influent concentrations of benzene and toluene were varied by adjusting the flow rates of the air streams. The air stream lines and the adsorption columns were immersed in a water bath regulated at 30.0±0.2°C.

Adsorption isotherms were measured by use of a shorter bed of activated carbon and a larger flow rate to shorten the time required. The experimental data were well correlated by the following Langmuir isotherms:

$$q_p = 13.8C_P/(1 + 0.032C_P + 0.098C_P)$$
$$q_D = 43.2C_D/(1 + 0.032C_D + 0.098C_D)$$
5.2 Results and discussion

The dimensionless maximum concentration of component 1, \( x_{\text{im}} \), was calculated by use of Eq. (19a) or (19b) for each run, and is given in Table 2 (denoted by \( x_{\text{im(exp)}} \)). The \( x_{\text{im}} \) value obtained experimentally is also given for each run in Table 2 (denoted by \( x_{\text{im(kp)}} \)). By comparing \( x_{\text{im(kp)}} \) with \( x_{\text{im(exp)}} \), the accuracy of the adsorption isotherms (Eqs. (30a) to (31b)) can be examined. The \( x_{\text{im(exp)}} \) value is a little smaller than the \( x_{\text{im(kp)}} \) value in every run. In general, it is very difficult to obtain reliable adsorption isotherms for binary component systems. In view of this difficulty, the difference found between \( x_{\text{im(kp)}} \) and \( x_{\text{im(exp)}} \) may not be so significant.

The minimum column lengths required to establish the constant pattern, \( z_{\text{min}} \), were estimated by the procedure presented in the previous section as 48.8, 86.7 and 22.2 cm for runs 1, 2 and 3, respectively. Therefore, the predicted BT curves and the experimental data were compared for the fourth column (length ca. 100 cm) in runs 1 and 2. The column length for run 3 (\( z=29.0 \text{ cm} \)) was greater than \( z_{\text{min}} \), and was sufficient to apply the CP-LDF method.

Figures 5(a), 5(b) and 5(c) show the comparisons for runs 1, 2 and 3, respectively. The solid lines show the BT curves predicted by the CP-LDF method by use of the adsorption isotherms and the intraparticle diffusivities estimated earlier.

In Fig. 5(a) the BT curve for DBS is well predicted by the CP-LDF method, but a discrepancy appears in the portion of higher PNP concentration. The predicted BT curve for PNP in zone IV deviates from the experimental BT curve, although their shapes are similar. The shape of the BT curves is affected mainly by the mass transfer coefficients, whereas the relative position of the BT curves is determined by the adsorption isotherms. Therefore, the deviation is considered to derive from the uncertainty of the adsorption isotherms. As stated above, it is very difficult to obtain reliable adsorption isotherms for binary component systems, especially when great difference exists between the intraparticle diffusivities of the two components, which is the case in this system.

In Fig. 5(b) the BT curve for DBS is also well predicted by the CP-LDF method, but a discrepancy appears in the portion of higher PNP concentration. The predicted BT curve for PNP in zone IV deviates from the experimental BT curve, although their shapes are similar. The shape of the BT curves is affected mainly by the mass transfer coefficients, whereas the relative position of the BT curves is determined by the adsorption isotherms. Therefore, the deviation is considered to derive from the uncertainty of the adsorption isotherms. As stated above, it is very difficult to obtain reliable adsorption isotherms for binary component systems, especially when great difference exists between the intraparticle diffusivities of the two components, which is the case in this system.

In Fig. 5(c) the BT curve for PNP in zone IV was similar to the experimental BT curve.
in shape to the experimental one, suggesting that the $D_s$ value estimated in the batch experiment is reasonable when only PNP is present, as in zone IV. Therefore it was inferred that the shape of the BT curve of PNP in zone II for run 2 was greatly affected by the presence of DBS, which has a much smaller $D_s$ value.

To examine whether the calculated and the experimental BT curves assume similar shape on decreasing the $D_s$ value of PNP, the BT curves in zone 2 were recalculated by changing the ratio of $D_{s,PNP}$ to $D_{s,DBS}$, designated by $\phi_2$, to 0.1, 0.5 and 1.0. The condition $\phi_2 = 1.0$ means that $D_{s,PNP}$ was equated to $D_{s,DBS}$ as a limiting situation. The recalculated results are shown by broken lines in Fig. 5(b). The slope of the recalculated BT curve decreases with increase of $\phi_2$, and becomes similar to that of the experimental BT curve for PNP when $\phi_2$ is between 0.5 and 1.0. This means that $D_{s,PNP}$ must be decreased to near the value of $D_{s,DBS}$ for the experimental and the calculated BT curves to assume similar shape, though $D_{s,PNP}$ estimated in the batch experiment was larger than $D_{s,DBS}$ by the order of two.

On the other hand, in Fig. 5 (c) (run 3) fairly good agreement was obtained between the experimental data and the predicted BT curves, though a slight discrepancy appears in the portion of higher benzene concentration. One of the possible reasons why the discrepancy appears is that the temperature in the adsorption column may rise on account of the large value of heat of adsorption for benzene. The slope of the predicted BT curve for toluene was a little steeper than that of the experimental BT curve, but no such significant difference was found as was found for PNP in Fig. 5 (b). The $D_s$ values of this system differed greatly when only PNP is present, as in zone IV. Therefore, it was inferred that the shape of the BT curve of PNP when $\phi_2$ is between 0.5 and 1.0.

Appendix: Integration of Eqs. (24) and (25)

Equations (24) and (25) are solved to obtain $dx_{1i}/d\theta$ and $dx_{2i}/d\theta$ as

$$
\begin{align}
\frac{dx_{1i}}{d\theta} &= (H_1G_1 - H_1H_3)(F_1G_3 - G_1F_3) \\
\frac{dx_{2i}}{d\theta} &= (F_1H_2 - H_1F_3)(F_3G_3 - G_1F_2)
\end{align}
$$

where

$$
\begin{align}
F_1 &= \psi_2 + \frac{\partial \psi_1}{\partial x_{1i}} \frac{\partial x_{1i}}{\partial \theta} \\
G_1 &= \frac{\partial \psi_1}{\partial x_{1i}} \\
H_1 &= \psi_1(x_{1i} - x_{1m} + \delta - 1), \quad H_2 = x_{2i} - x_{2m}
\end{align}
$$

The initial conditions for Eqs. (A-1) and (A-2) are $x_{1i}=x_{1m}$ and $x_{2i}=0$ at $\theta=0$ (see Fig. 1). However, the right-hand sides of Eqs. (A-1) and (A-2) tend to zero at the initial conditions, so that integration cannot be started from there. To overcome this difficulty the integration was started from a small $x_{1i}$ value ($10^{-4}$ was employed here) and the corresponding $x_{1i}$ value. To determine the $x_{1i}$ value Eq. (A-1) was divided by Eq. (A-2).

$$
\frac{dx_{1i}}{dx_{2i}} = \frac{(H_1G_1 - H_1H_3)(F_1G_3 - G_1F_3)}{(F_1H_2 - H_1F_3)}
$$

L'Hospital's rule was applied at the initial condition, $x_{1i}=x_{1m}$ and $x_{2i}=0$, to obtain the initial value of $dx_{1i}/dx_{2i}$. Then the $x_{1i}$ value corresponding to $x_{2i}=10^{-6}$ was obtained by the Runge-Kutta-Gill (R. K. G.) method. With the Freundlich isotherm, the terms $\partial \psi_1/\partial x_{1i}$ and $\partial \psi_1/\partial x_{2i}$ tend to $+\infty$ and $-\infty$ at $x_{2i}=0$, respectively. Therefore Eqs. (4a) and (4b) were approximated by the linear relations over the range $x_{2i}=0 - 10^{-6}$, then L'Hospital's rule was applied.

Equations (A-1) and (A-2) could be integrated with the modified initial conditions, $x_{2i}=10^{-6}$ and the corresponding $x_{1i}$ value, by the R. K. G. method, but the result gives only the relation of $x_{1i}$ and $x_{2i}$ vs. $\theta$ (see Fig. 1). This must be converted to the relation of $x_1$ and $x_2$ vs. $\theta$. The concentrations based on the constant pattern (CP) and the linear driving force (LDF) approximations by taking into account both external fluid film mass transfer and intraparticle diffusion resistances. It was found that the LDF approximation is valid in the case of surface diffusion kinetics and holds approximately in the case of pore diffusion kinetics. To clarify the conditions under which the simplified method is applicable, the minimum column length required to establish the constant pattern was estimated by two methods, one employing the CP approximation, the other not. It was clarified that the minimum column length may be estimated only by the method employing the CP approximation.

The simplified method was applied to two binary adsorption systems of an aqueous solution of dodecylbenzenesulfonate (DBS) and p-nitrophenol (PNP) and a gaseous mixture of benzene and toluene. The predicted breakthrough curves showed good agreement with the experimental breakthrough curves for DBS and the gaseous mixture. However, the slope of the predicted breakthrough curves for PNP in zone II was much steeper than that of the experimental breakthrough curves. It was necessary to employ much smaller values of intraparticle diffusivities for PNP to fit the predicted breakthrough curves with the experimental ones.
can be easily converted to $x_1$ and $x_2$ through Eqs. (22) and (23), and the integral constant $\theta_0$ can be determined from the following overall mass balance of component 2.

$$\int_0^1 (1-x_2)dx_2 = \frac{X - \theta_0}{X - s_2} = \frac{\theta_0}{X - s_2}$$

(A-5)

that is,

$$\theta_0 = X - s_2$$

(A-6)

where $s_2$ is the area obtained by integrating the BT curve for component 2 as shown in Fig. 1.

The procedure presented above can be applied to other adsorption systems if the equations representing adsorption isotherms are differentiable. It can also be easily extended to systems of three or more components if the constant pattern approximation is valid in such systems.

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### Nomenclature

- $a$, $a_2$ = specific surface area in the bed [cm$^2$/cm$^3$]
- $a_1$, $a_2$ = constants in Langmuir isotherms [m/(g)], [l/g]
- $b_1$, $b_2$ = constants in Langmuir isotherms [m/(mg)], [l/(mg)]
- $C$ = fluid-phase concentration [mg/ml], [mg/l]
- $C_0$ = concentration in the void space of the bed [mg/ml], [mg/l]
- $C_{1,m}$ = maximum concentration of component 1 in zones II to IV (constant) [mg/ml], [mg/l]
- $D_p$ = effective pore diffusivity [cm$^2$/sec]
- $D_s$ = effective surface diffusivity [cm$^2$/sec]
- $K = \frac{1}{(1 + b_1 C_{1,m})}$
- $K_1$, $K_2$ = parameters in dimensionless Freundlich isotherms
- $k_f$ = fluid film mass transfer coefficient [cm/sec]
- $k_a$ = coefficient concerning the intraparticle diffusion [g/cm$^3$-sec]
- $P_1$, $P_2$ = parameters in dimensionless Langmuir isotherms
- $q$ = amount adsorbed within a particle [mg/g]
- $\bar{q}$ = average amount adsorbed in the bed [mg/g]
- $q_{1,m}$ = $q_1$ value in equilibrium with $C_{1,m}$ [mg/g]
- $R = \frac{1}{\theta/(1 + \xi)}$
- $R_1$, $R_2$ = parameters in Freundlich isotherms
- $s_1$, $s_2$ = surface area obtained by integrating the breakthrough curves of zone II
- $T_1$, $T_2$ = parameters in Freundlich isotherms
- $t$ = time [sec], [hr]
- $u$ = superficial fluid velocity [cm/sec]
- $X = \frac{q_1 q_0}{q_1 q_0}$
- $X_F = \frac{X(1 + \xi)}{\theta}$
- $X_{T_{min}} = \frac{X_T}{X}$
- $X_T$ = dimensionless minimum column length required to establish the constant pattern
- $x_1$, $x_2$ = powers of Freundlich isotherms
- $\beta$ = $a_1 - \beta_0$
- $\beta_1$, $\beta_2$ = powers of Freundlich isotherms
- $\gamma_1$, $\gamma_2$ = powers of Freundlich isotherms
- $\overline{q}_{20}$ = void fraction of the bed
- $\overline{q}_{21}$ = $k_{ad}/(k_{a1} q_0/C_{1,m})$
- $\overline{q}_{22}$ = $k_{a2}/(k_{a2} q_0/C_{2,m})$
- $\theta$ = $\theta_{2a}$
- $\theta_0$ = $\theta_{2a}$ value where numerical integration was started
- $\theta_{2a} = \theta_{2a}$ value measured from $\theta_0$
- $\theta_T = \theta/(1 + \xi)$
- $\rho_b$ = bed density [g/cm$^3$]
- $\rho_s$ = particle density [g/cm$^3$]
- $\phi_f = k_{1,1} k_{2,2}$
- $\phi_s = k_{1,1} k_{2,2}$

### Literature Cited