$$V_{j+1}y_{j+1,i}+L_{j-1}x_{j-1,i}-L_jx_{ji}-V_jy_{ji}=0 \qquad \text{(A-1)}$$

Overall material balances [N]:

$$V_{j+1}+L_{j-1}-L_j-V_j=0 \qquad \text{(A-2)}$$

Vapor-liquid equilibrium [NC]:

$$y_{ji}=K_{ji}x_{ji} \qquad \text{(A-3a)}$$

$$l_{ji}=A_{ji}v_{ji} \qquad \text{(A-3b)}$$

where

$$A_{ji}=(L_j/V_jK_{ji})$$

Stoichiometric equations [$2N+2$]:

$$\Sigma x_{ji}=1.0; \ \Sigma y_{ji}=1.0; \ \Sigma y_{N+1,i}=1.0; \ \Sigma x_{0i}=1.0$$

Heat balances [N]:

$$L_{j-1}h_{j-1}+V_{j+1}H_{j+1}-L_jh_j-V_jH_j+Q_j=0 \qquad \text{(A-4)}$$

Nomenclature

A	= absorption factor	[—]
C	= number of components	[—]
EPS	= convergence criteria, 0.0001	[—]
G	= enthalpy function	[—]
H	= vapor enthalpy	[BTU/mol]
h	= liquid enthalpy	[BTU/mol]
K	= equilibrium ratio	[—]
L	= liquid phase rate	[lb-mol/hr]
L_0	= lean oil flow rate	[lb-mol/hr]
l	= component liquid flow rate	[lb-mol/hr]
N	= total number of plates	[—]
P	= pressure	[psia]
Q	= heat input or output	[BTU/hr]
T	= temperature	[°F]
V	= vapor phase rate	[lb-mol/hr]
V_{N+1}	= rich gas rate	[lb-mol/hr]
v	= component vapor flow rate	[lb-mol/hr]
x	= liquid composition	[mole fraction]
y	= vapor composition	[mole fraction]

⟨Subscripts⟩

i	= refers to component number
j	= refers to stage number
n	= number of iteration

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ANALYTICAL SOLUTIONS FOR THE BREAKTHROUGH CURVES OF BICOMPONENT FIXED-BED ADSORPTION UNDER THE LANGMUIR ISOTHERMS

KOUICHI MIURA AND KENJI HASHIMOTO

Department of Chemical Engineering, Kyoto University, Kyoto 606

In a separate paper[2] the authors clarified that the so-called constant pattern (CP) behavior is established even for binary component systems in relatively long columns and under favorable adsorption isotherms, and that intraparticle diffusion is approximated by the linear-driving force (LDF) approximation with good accuracy for bicomponent systems. Cooney and Strusi[1] found that a linear relation holds between the fluid-phase concentrations of two interacting components when the ratio of the overall mass transfer coefficients is unity, and they have derived an analytical solution for calculating the breakthrough (BT) curves for a special case of the Langmuir isotherm system. However, they did not clarify the conditions under which the solution is applicable, nor verify the solution experimentally. Furthermore, they used overall mass transfer coefficients in the analysis.

The purposes of this paper are to derive analytical solutions for three special cases of the Langmuir isotherm systems by extending the treatment of Cooney and Strusi, and to clarify the conditions under which the analytical solutions are approximately applicable.

1. Development of the Analytical Solutions

1.1 Basic equations

The calculation of the BT curves for zone II is the object of the analysis. The dimensionless basic equations under the CP and LDF approximations are written as follows[2]:

Bed:
$$\bar{y}_1=\delta(\bar{x}_1-1)+1 \qquad (1)$$

$$\bar{y}_2=\bar{x}_2 \qquad (2)$$

Rate equations:

$$\frac{1}{1+\zeta_2}\frac{d\bar{y}_1}{d\theta_T}=\phi_f\delta(\bar{x}_1-x_{1i})=\frac{\phi_f\delta}{\zeta_1}(y_{1i}-\bar{y}_1) \qquad (3)$$

$$\frac{1}{1+\zeta_2}\frac{d\bar{y}_2}{d\theta_T}=\bar{x}_2-x_{2i}=\frac{1}{\zeta_2}(y_{2i}-\bar{y}_2) \qquad (4)$$

The definitions of the dimensionless parameters in the above equations are given in a separate paper[2].

The solid-phase concentrations at the particle surface, y_{1i} and y_{2i}, are related to x_{1i} and x_{2i} through the following dimensionless Langmuir isotherms:

$$y_{1i}=x_{1i}/\{(P_1+P_2-1)+(1-P_2)x_{1i}+(1-P_1)x_{2i}\} \qquad (5a)$$

$$y_{2i}=x_{2i}/\{(P_1+P_2-1)+(1-P_2)x_{1i}+(1-P_1)x_{2i}\} \qquad (5b)$$

In the separate paper Eqs. (1) to (5b) were solved numerically by use of the concentrations at the solid-fluid interface as the dependent variables. The analytical scheme was abbreviated as the CP–LDF method.

1. 2 Relation between the concentrations of component 1 and component 2 in zone II

Cooney and Strusi[1] showed that the following linear relation holds between $\bar{x}_1$ and $\bar{x}_2$ in zone II when the ratio of the overall mass transfer coefficients is unity.

$$\bar{x}_1=(1-x_{1m})\bar{x}_2+x_{1m} \qquad (6)$$

The case pointed out by them corresponds mathematically to the case of $\zeta_1\to\infty$, $\zeta_2\to\infty$ and $\phi_s=1$; in other words, intraparticle diffusion controls and the solid-phase mass transfer coefficients are identical. This case is called case 3 in this paper. The parameter ϕ_s is the ratio of k_{s1} to k_{s2}.

It was found in the more detailed study that the same relation as that shown by Eq. (6) holds in two cases other than the case 3 first found by Cooney and Strusi. The two cases are that in which ratios of both the fluid- and the solid-phase mass transfer coefficients are unity, namely $\phi_f=1$ and $\phi_s=1$ (case 1), and that in which external fluid-film mass transfer is controlling and the ratio of the mass transfer coefficients is unity, that is $\zeta_1=0$, $\zeta_2=0$ and $\phi_f=1$ (case 2). In these three cases, a linear relation was also found to hold between the dimensionless concentrations at the solid-fluid interface, x_{1i} and x_{2i}.

$$x_{1i}=(1-x_{1m})x_{2i}+x_{1m} \qquad (7)$$

Using the relations of Eqs. (6) and (7), analytical solutions can be obtained*.

1. 3 Solutions of the basic equations

Case 1: both resistances are significant and both ϕ_f and ϕ_s are unity

On eliminating x_{1i} from Eq. (5b) by use of Eq. (7) the following isotherm is obtained for component 2.

$$y_{2i}=x_{2i}/\{\alpha+(1-\alpha)x_{2i}\} \qquad (8)$$

where α is defined as

$$\alpha=P_1+P_2-1+(1-P_2)x_{1m} \qquad (9a)$$

or

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* The proof that Eqs. (6) and (7) satisfy the basic equations in the three cases is available.

$$\alpha=(q_{10}/C_{10})/(q_{1m}/C_{1m}) \qquad (9b)$$

Equations (2), (4) and (8) coincide with the basic equations for the single-component system if α is regarded as the separation factor and the subscript 2 is eliminated. Therefore, the following analytical solution[3] for the single-component system can be applied.

$$\theta_T-X_T=\frac{1}{1+\zeta_2}\left[\frac{1}{1-\alpha}\ln x_{2i}-\frac{\alpha}{1-\alpha}\ln(1-x_{2i})\right.$$
$$\left.-\ln\{\alpha+(1-\alpha)x_{2i}\}-\frac{\alpha}{1-\alpha}\ln\alpha+1\right]$$
$$+\frac{\zeta_2}{1+\zeta_2}\left\{\frac{\alpha}{1-\alpha}\ln x_{2i}-\frac{1}{1-\alpha}\ln(1-x_{2i})-1\right\} \qquad (10)$$

Conversion from x_{2i} to $\bar{x}_2$ is performed by

$$\bar{x}_2=\left\{\zeta_2 x_{2i}+\frac{x_{2i}}{\alpha+(1-\alpha)x_{2i}}\right\}/(\zeta_2+1) \qquad (11)$$

Case 2: Fluid-film mass transfer controlling ($\zeta_1=0$, $\zeta_2=0$) and $\phi_f=1$

In this case the solution is reduced from Eq. (10) if ζ_2 is set equal to 0. The concentration x_{2i} is converted to $\bar{x}_2$ by use of Eq. (11).

$$\theta_f-X_f=\frac{1}{1-\alpha}\ln\bar{x}_2-\frac{\alpha}{1-\alpha}\ln(1-\bar{x}_2)+1 \qquad (12)$$

where

$$\theta_f=k_f a_v\left(t-\frac{\varepsilon_b}{u}z\right)/(\rho_b q_{20}/C_{20}) \text{ and } X_f=k_{f2}a_v(z/u)$$

Case 3: Intraparticle diffusion controlling ($\zeta_1\to\infty$, $\zeta_2\to\infty$) and $\phi_s=1$

The solution for this case can be also obtained by letting ζ_2 tend to infinity in Eq. (10).

$$\theta_s-X_s=\frac{\alpha}{1-\alpha}\ln\bar{x}_2-\frac{1}{1-\alpha}\ln(1-\bar{x}_2)-1 \qquad (13)$$

where

$$\theta_s=k_{s2}a_v\left(t-\frac{\varepsilon_b}{u}z\right)/\rho_b \text{ and } X_s=k_{s2}a_v(q_{20}/C_{20})(z/u)$$

Equation (13) coincides with the equation derived by Cooney and Strusi if their parameter β is replaced by $\alpha/(1-\alpha)$.

In the above three cases the concentrations of component 1 are calculated by the aid of Eq. (6).

2. Examination of Applicability of the Analytical Solutions to Practical Problems

The three cases presented above will probably be seldom encountered in practice, and strictly speaking the usefulness of the analytical solutions is restricted. However, in cases where the linear relation holds approximately between $\bar{x}_1$ and $\bar{x}_2$, the analytical solutions can be considered applicable.

Figures 1(a) to 1(c) show the relations between $\bar{x}_1$ and $\bar{x}_2$ calculated by the CP-LDF method for a combina-

tion of the parameters ($P_1=0.5$, $P_2=0.6$ and $\delta=3.0$). It was found from these figures that the linear relation holds approximately between $\bar{x}_1$ and $\bar{x}_2$ if ϕ_f and ϕ_s do not deviate greatly from unity. Takeuchi et al.[4] assumed that the linear relation holds approximately in their analysis without any proof. Their assumption seems to be reasonable judging from the results of this work, at least for the Langmuir isotherm system.

To estimate more precisely the permissible deviation of ϕ_f and ϕ_s from unity for application of the analytical solutions to practical cases, the relations shown in Figs. 1(a) to 1(c) were replotted in the form of BT curves. **Figure 2** shows the BT curves corresponding to Fig. 1(c), that is, the case where both resistances are significant. In this figure k_{f2} and k_{s2} are fixed to investigate the effect of ϕ_f and ϕ_s. It is shown that the BT curves calculated by the CP-LDF method almost coincide with those calculated by the analytical solution (Eq. (10)) if ϕ_f and ϕ_s do not deviate greatly from unity. On the other hand, two sets of BT curves were in poor agreement when k_{f1} and k_{s1} were fixed even if an almost linear relation held between $\bar{x}_1$ and $\bar{x}_2$.

Similar investigations were performed for six combinations of the adsorption parameters, P_1 and P_2. In every case examined the BT curves calculated by the CP-LDF method almost coincided with those calculated by the analytical solutions when k_{f2} and k_{2s} were fixed and the following conditions were satisfied.

$$0.5<\phi_f<2.0 \text{ and } 0.5<\phi_s<10.0 \qquad (14)$$

Thus it was found that the analytical solutions were approximately applicable when the conditions of Eq. (14) are satisfied. The conditions are considered to be satisfied in most cases, because k_{f1} and k_{f2} seldom differ by a factor of two and k_{s1} and k_{s2} seldom differ by an order of one. Therefore the analytical solutions may be approximately applicable in most cases. Experimental verification of the analytical solutions was reported in the separate paper[2].
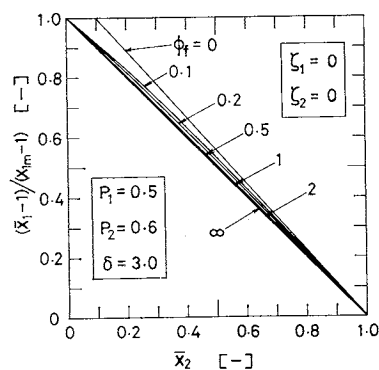
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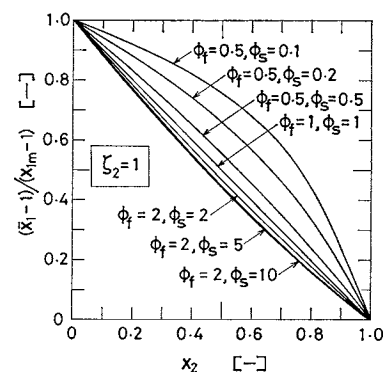
(Presented at 43rd Annual Meeting, SCEJ, Nagoya, April, 1978.)

(a) external fluid-film mass transfer controlling
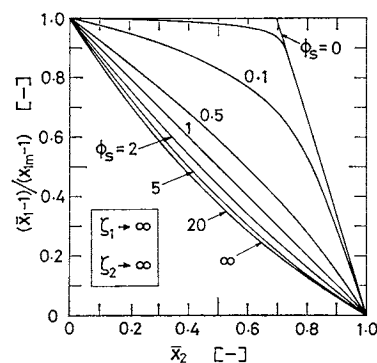
(b) intraparticle diffusion controlling

(c) both resistances are significant

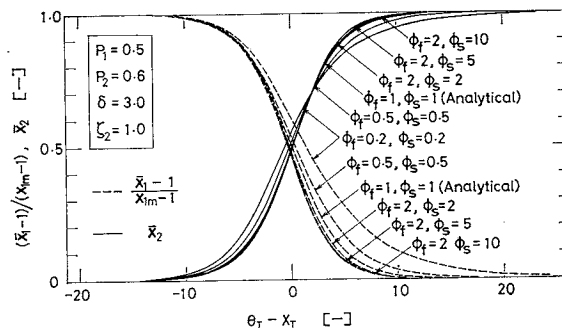Fig. 1 $\bar{x}_1$-$\bar{x}_2$ relationship

Fig. 2 Effect of ϕ_f and ϕ_s on breakthrough curves for the cases where both resistances are significant (k_{f2} and k_{s2} are fixed)