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Author
Miyauchi, Terukatsu.

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LONGITUDINAL DISPERSION IN SOLVENT-EXTRACTION COLUMNS: MATHEMATICAL THEORY

Terukatsu Miyauchi

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ABSTRACT

The influence of longitudinal dispersion of fluid in continuous counter-current solvent-extraction columns has been analyzed theoretically, by application of a simplified model which utilizes mean diffusivities and mean velocities for both continuous and dispersed phases. From the mathematical treatment of the model, it has been found that the influence of the longitudinal dispersion on the extent of extraction can be expressed as a function of four dimensionless parameters. These parameters include, as variables, the rates of longitudinal dispersion, the over-all mass-transfer coefficient, the equilibrium partition ratio, and the rates of fluid flow. Solutions for various special cases of mixing behavior have been presented, which apply directly to specific types of apparatus.

The longitudinal dispersion has an undesirable effect, especially when a high degree of extraction is desired. The theory developed shows that there will be a maximum attainable extent of extraction, under any given pattern of longitudinal dispersion. This means that the extent of extraction is limited by this phenomenon, even if the over-all coefficient of mass transfer is increased to infinity. It is necessary to define three kinds of over-all HTU: two of these, used previously, include the effect of the longitudinal dispersion.
INTRODUCTION

In continuous countercurrent solvent-extraction columns, it is widely recognized that the effective coefficient of mass-transfer is lowered by longitudinal dispersion in either phase. This effect should be particularly large, in such apparatus as the Mixco column reported by Oldshue and Rushton, the rotating-disc column reported by Reman and Olney, and pulsed columns. Attempts have already been made to obtain mass-transfer coefficients by measuring concentration distributions within an extractor. This approach should be more accurate than the alternative of using a logarithmic mean driving force computed only from the end concentrations of the incoming and outgoing streams. Recently, a theoretical approach that permits evaluation of local behavior of pulsed columns has been reported from this laboratory by Lane, Lehman, and Rubin, and experimental measurements of dispersion in packed columns are now being made by Jacques and Vermeulen.

In order to interpret the behavior of continuous solvent-extraction columns, it is desirable to analyze the interrelation between such variables as the true coefficient of mass transfer, the rate of longitudinal dispersion of fluid in each phase, the flow rate of each stream, the partition ratio of the transferring component, and the extent of extraction. This paper has been developed so as to combine these variables with over-all behavior of continuous extraction columns. A simplified model of flow behavior has been used, similar to one assumed previously in relation to one-dimensional homogeneous-phase flow systems.

For homogeneous systems with noticeable longitudinal dispersion, this model has already been found by Yagi and Miyauchi to give a better representation of the Mixco and related columns than the concept of "equivalent completely mixed stage" reported recently by Young.
BASIC EQUATIONS

Basic Differential Equations

For homogeneous continuous-flow systems Damköhler has given an equation of continuity,

$$\frac{\partial c_i}{\partial \theta} = - \text{div} (-E_i \text{grad } c_i) - \text{div} (u_i \frac{\partial c_i}{\partial z}) + \phi (c_i),$$

where $u_i$ is the linear velocity of the fluid and $c_i$ is the concentration of the $i$th component, at the point of interest.¹ For one-dimensional steady-state flow systems, in which a mean diffusivity and a mean velocity of the $i$th component are assumable, Damköhler's equation becomes

$$E_i \frac{d^2 c_i}{dz^2} - u_i \frac{dc_i}{dz} - \phi (c_i) = 0.$$

For one-dimensional countercurrent two-phase mass-transfer processes, this equation is modified as follows by introducing a void fraction $\epsilon$ for each phase, and substituting the mass-transfer term for $\phi (c_i)$:

$$\begin{align*}
\epsilon_x E_x \frac{d^2 c_x}{dz^2} - F_x \frac{dc_x}{dz} - K_x a (c_x - m c_y) &= 0, \\
\epsilon_y E_y \frac{d^2 c_y}{dz^2} + F_y \frac{dc_y}{dz} + K_x a (c_x - m c_y) &= 0,
\end{align*}$$

(1)

where the direction of mass transfer is taken from phase $X$ to phase $Y$, and a linear-distribution equilibrium (with $m$ as the partition coefficient) is assumed; $K_x$ represents the over-all mass-transfer coefficient relative to phase $X$, $a$ is the interfacial area per unit volume, and $F$ is the superficial velocity of the designated phase.

These equations are based on a simplified model which assumes that the two liquid phases flow in opposite directions, with each phase undergoing longitudinal dispersion, as shown in Fig. 1. Accordingly, the process of mass transfer is assumed to take place across the phase boundary, PQ. However, in an actual extractor, one phase is dispersed into the other as shown in Fig. 2.
Fig. 1. Proposed model
Fig. 2. Actual situation in an extractor
Fig. 3. Concentration distribution in an extractor. Curve ABDE, actual distribution of $c_x$; curve FGHK, same for $c_y$. Curve AD'E, apparent distribution of $c_x$ assuming piston flow; curve FH'K, same for $c_y$. 
If the droplets coalesce and break up so rapidly that there is no fluctuation in their concentration at any particular point, the two models become identical.

If not, the concentration variations between droplets at a section will reflect the gradient of average concentration under conditions of constant $E_x$ and $E_y$. This point is discussed in Appendix 1; it is concluded that the simplified model provides a sound and workable approach.

Rearranging the equations into dimensionless form, we have

\[
\begin{align*}
\frac{d^2 C_x}{dZ^2} - P_x B \frac{dC_x}{dZ} - N_{ox} P_x B (C_x - mC_y) &= 0 \\
\frac{d^2 C_y}{dZ^2} + P_y B \frac{dC_y}{dZ} + N_{oy} P_y B (C_x - mC_y) &= 0
\end{align*}
\]

where $C_x = c_x / c_x^0$, $C_y = c_y / c_y^0$, $P_x = u_x d / E_x$, $P_y = u_y d / E_y$, $N_{ox} = K_x aL / F_x$, $N_{oy} = K_x aL / F_y$, $B = L / d$, $u_x = F_x / \epsilon_x$, $u_y = F_y / \epsilon_y$, and $Z = z / L$.

**Boundary Conditions**

The rate of longitudinal dispersion in an extractor is assumed to be much higher than that in the incoming and outgoing streams away from the extractor. The suitable boundary conditions are given as follows. Integration of Eq. 1 for phase $X$, over an arbitrary length of column, $l$, gives

\[
\frac{\epsilon_x E_x}{l} \left[ \left( \frac{dc_x}{dz} \right)_l - \left( \frac{dc_x}{dz} \right)_0 \right] - F_x (c_x l - c_{x0}) - n = 0,
\]

where $c_{x0} = (c_x)_Z = 0$, $c_x l = (c_x)_Z = I$, and $n$ is the total amount of component (in moles) transferred from phase $X$ to phase $Y$ between the point of interest and the $X$ inlet.
At the X-inlet end of the column, the net flow is given in dimensionless terms by the sum

\[
\frac{1}{P_x B} \left( \frac{dC_x}{dZ} \right)_0 - C_x^0 = -1
\]

Outside the column, the net flow is \(-C_x^0\), or \(-1\), because \(P_x B \to 0\) and \((dC_x/dZ)_0 \to 0\) for the model assumed. Equating the net flows, at \(Z = 0\), gives

\[
- \left( \frac{dC_x}{dZ} \right)_0 = P_x B \left( 1 - C_x^0 \right).
\]

(3a)

At the X-outlet end, a comparison of the net flows inside and outside yields the relation

\[
\frac{1}{P_x B} \left( \frac{dC_x}{dZ} \right)_1 = C_x^1 - C_x^0,
\]

where \(C_x^1 = (C_x)_Z = 1\), and \(C_x^1\) is the concentration of outgoing phase X.

The coefficient \(1/P_x B\) is always positive or zero. At the boundary, the concentration gradient calculated from the left-hand term is opposite in sign to the gradient given by the right-hand term. Thus the only condition allowed by this equation is

\[
C_x^1 = C_x^0, \quad (dC_x/dZ)_1 = 0.
\]

(3b)

Because the boundary region is small, mass transfer in this region is neglected, and the boundary condition becomes identical with the result given by Danckwerts.2

The boundary conditions for phase Y are derived from the similar consideration described above. Thus the boundary conditions for phase X and phase Y are

\[
\begin{align*}
Z = 0: & \quad - (dC_x/dZ) = P_x B (1 - C_x^0), \quad - (dC_y/dZ) = 0 \\
Z = 1: & \quad - (dC_x/dZ) = 0, \quad - (dC_y/dZ) = P_y B (C_y^1 - C_y^0)
\end{align*}
\]

(4)
Eliminating the term $C_y$ from Eq. (2) gives a single linear differential equation of fourth order,

$$d^4 C_x/dZ^4 - a d^3 C_x/dZ^3 - \beta d^2 C_x/dZ^2 - \gamma dC_x/dZ = 0,$$

where $a$, $\beta$, and $\gamma$ are constants independent of $Z$, as defined below.

**General Case**

By solving Eq. (5) so as to satisfy the boundary conditions, one obtains the following solutions:

$$C_x - mC_y = A_1 e^{\lambda_1 Z} + A_2 e^{\lambda_2 Z} + A_3 e^{\lambda_3 Z} + A_4 e^{\lambda_4 Z}$$

and

$$m(C_y - C_y^1) = a_1 A_1 e^{\lambda_1 Z} + a_2 A_2 e^{\lambda_2 Z} + a_3 A_3 e^{\lambda_3 Z} + a_4 A_4 e^{\lambda_4 Z}$$

where

$$A_1 = DA_1/DA, A_2 = DA_2/DA, A_3 = DA_3/DA, A_4 = DA_4/DA;$$
\[
\begin{align*}
D_A &= D_{A1} - \\
\begin{vmatrix}
1 - \frac{\lambda_2}{P_y B} & 1 - \frac{\lambda_3}{P_x B} & 1 - \frac{\lambda_4}{P_y B} \\
\lambda_2 a_2 & \lambda_3 a_3 & \lambda_4 a_4 \\
\lambda_2 e & \lambda_3 e & \lambda_4 e \\
\end{vmatrix} \\
D_{A1} &= \begin{vmatrix}
\lambda_2 a_2 & \lambda_3 a_3 & \lambda_4 a_4 \\
\lambda_2 e & \lambda_3 e & \lambda_4 e \\
(1 + \frac{\lambda_2}{P_y B}) a_2 e & (1 + \frac{\lambda_3}{P_y B}) a_3 e & (1 + \frac{\lambda_4}{P_y B}) a_4 e \\
\end{vmatrix} \\
D_{A2} &= \begin{vmatrix}
\lambda_3 a_3 & \lambda_4 a_4 \\
\lambda_3 e & \lambda_4 e \\
\end{vmatrix} \\
D_{A3} &= \begin{vmatrix}
\lambda_2 a_2 & \lambda_4 a_4 \\
\lambda_2 e & \lambda_4 e \\
\end{vmatrix} \\
D_{A4} &= \begin{vmatrix}
\lambda_2 a_2 & \lambda_3 a_3 \\
\lambda_2 e & \lambda_3 e \\
\end{vmatrix}
\end{align*}
\]

\[a_j = 1 + \frac{\lambda_j}{N_{ox}^2 - \frac{\lambda_j^2}{N_{ox}P_y B}}\]

(j = 1, 2, 3, and 4),

\[
\begin{align*}
\lambda_1 &= 0 \\
\lambda_2 &= a/3 + 2\sqrt{p}\cos\left(\frac{u}{3}\right) \\
\lambda_3 &= a/3 + 2\sqrt{p}\cos\left(\frac{u}{3} + 2\pi/3\right) \\
\lambda_4 &= a/3 + 2\sqrt{p}\cos\left(\frac{u}{3} + 4\pi/3\right)
\end{align*}
\]
where \( u \) is determined as an angle between 0 and \( \pi \), such that

\[
\cos u = q/p^{3/2} ;
\]

and

\[
\begin{align*}
p &= (a/3)^2 + \beta/3 \\
q &= (a/3)^3 + a\beta/6 + \gamma/2
\end{align*}
\]

with

\[
\begin{align*}
a &= \mathcal{P}_x B - \mathcal{P}_y B \\
\beta &= N_{ox} \mathcal{P}_x B + \mathcal{P}_x B \mathcal{P}_y B + N_{ox} \mathcal{P}_y B (1 - \Lambda) \\
\gamma &= N_{ox} \mathcal{P}_x B \mathcal{P}_y B (1 - \Lambda)
\end{align*}
\]

The solutions are obtained as Eq. (6) only for

\[
q^2 - p^3 = \frac{1}{27} \left( a^3_\gamma - a_2^2 \beta^2/4 + 9a\beta\gamma/2 - \beta^2 + 27\gamma^2/4 \right) < 0.
\]

This relation is satisfied for ordinary extraction operations, except when both phases are perfectly mixed. In this case, the relation becomes zero. The terminal values of \( C_x \) and \( mC_y \) are given as follows:

\[
\begin{align*}
\frac{C_x0 - mC^1_y}{1 - mC^1_y} &= A_1 + A_2 + A_3 + A_4 \\
\frac{C_x1 - mC^1_y}{1 - mC^1_y} &= A_1 e^{\lambda_1} + A_2 e^{\lambda_2} + A_3 e^{\lambda_3} + A_4 e^{\lambda_4} \\
\frac{m(C_y0 - C^1_y)}{1 - mC^1_y} &= a_1 A_1 + a_2 A_2 + a_3 A_3 + a_4 A_4 \\
\frac{m(C_y1 - C^1_y)}{1 - mC^1_y} &= a_1 A_1 e^{\lambda_1} + a_2 A_2 e^{\lambda_2} + a_3 A_3 e^{\lambda_3} + a_4 A_4 e^{\lambda_4}
\end{align*}
\]

\[(6a)\]
For \( \gamma = 0 \) or \( mF_x/F_y \neq 1 \), the solution of Eq. (5) takes a different form:

\[
\begin{align*}
C_x - mC_y^1 & = B_1 + B_2Z + B_3e^{\mu_3Z} + B_4e^{\mu_4Z} \\
\frac{m(C_y - C_y^1)}{1 - mC_y^1} & = B_1 + B_2/N_{ox} + B_3Z + b_3B_3e^{\mu_3Z} + b_4B_4e^{\mu_4Z},
\end{align*}
\]

where

\[
\begin{align*}
B_1 & = D_{B2}/D_B, \quad B_2 = D_{B2}/D_B, \quad B_3 = D_{B3}/D_B, \quad \text{and} \quad B_4 = D_{B4}/D_B, \\
b_3 & = 1 + \frac{\mu_3}{N_{ox}} - \frac{\mu^2_3}{N_{ox}P_B} \\
b_4 & = 1 + \frac{\mu_4}{N_{ox}} - \frac{\mu^2_4}{N_{ox}P_B}, \\
\mu_3 & = \frac{a}{2} + \sqrt{(a/2)^2 + \beta} \\
\mu_4 & = \frac{a}{2} - \sqrt{(a/2)^2 + \beta},
\end{align*}
\]

and

\[
\begin{align*}
D_B & = D_{B1} - \\
D_{B1} & = \begin{vmatrix}
1 & b_3\mu_3 & b_4\mu_4 \\
1 & \mu_3 & \mu_4 \\
1 & \mu_3e^{\mu_3} & \mu_4e^{\mu_4}
\end{vmatrix} \\
D_{B2} & = -\begin{vmatrix}
b_3\mu_3 & b_4\mu_4 \\
\mu_3e^{\mu_3} & \mu_4e^{\mu_4}
\end{vmatrix} \\
D_{B3} & = (e^{\mu_4} - b_4)\mu_4 \\
D_{B4} & = -(\mu_3 - b_3)\mu_3
\end{align*}
\]
RELATION BETWEEN APPARENT AND TRUE HTU AND NTU

Definition of HTU

There should be three kinds of HTU (height of transfer unit), depending on the definition of the concentration driving force.

"True" values

By the original definition of HTU, "true" HTU is the ratio of volumetric flow rate across a unit cross section to the true over-all coefficient of mass transfer:

$$H_{ox} = \frac{F_x}{K_x a}$$

Likewise, the true number of over-all transfer units (NTU) is

$$N_{ox} = K_x a \frac{L}{F_x}$$

"Measured" values

When an extractor behaves in the same manner as the proposed model, the actual concentration distribution for the X phase in the extractor is given by curve ABDE of Fig. 3 and for the Y phase by curve FGHK. These two curves can be known by measuring the concentration distribution in the extractor. The number of transfer units defined from these measured values is

$$N_{oxM} = \int_{C_{x0}}^{C_{x1}} \frac{dC_x}{C_x - mC_y}$$

From this definition of NTU, an apparent HTU is derived at

$$H_{oxM} = \frac{L}{N_{oxM}}$$

"Piston-flow" values

Another apparent NTU is defined in terms of the logarithmic-mean driving force computed from the exterior incoming and outgoing concentrations at both ends of the extractor:
Integration of the right-hand side of this equation gives Eqs. (15) and (17). The corresponding apparent HTU is defined as

\[ H_{oxP} = \frac{L}{N_{oxP}}. \]  

(10.a)

\[ H_{oiM} \] and \[ H_{oiP} \] should include the effect of longitudinal dispersion of the transferring material. In general, one will find \[ H_{oiP} > H_{oiM} > H_{oi} \].

**Relations Between \( H_{ox} \), \( H_{oxM} \), and \( H_{oxP} \)**

From Eq. (6.a), the outlet concentration \( C_{x1} \) is given as

\[ \frac{C_{x1} - mC^1_y}{1 - mC^1_y} = \sum_{j=1}^{4} A_j b_j, \quad (j = 1, 2, 3, \text{ and } 4), \]  

(11)

where \( A_i \) and \( \lambda_i \) are the functions of \( N_{ox} \) for given values of \( mF_x/F_y \), \( P_xB \), and \( P_yB \) and independent of \( C^1_y \). On the other hand, \( C_{x1} \) is given as follows from Eq. (15), *for the case in which the X- and Y-phases are assumed to follow piston flow:

\[ \frac{C_{x1} - mC^1_y}{1 - mC^1_y} = \frac{(1 - \Lambda)e^{\lambda}}{1 - \Lambda e^{\lambda}}, \]  

(11.a)

where \( \lambda = -\frac{N_{oxP}}{1 - \Lambda} \).

Comparison of Eqs. (11) and (11.a) gives an explicit relation between \( N_{ox} \) and \( N_{oxP} \),

\*For \( \Lambda = 1 \), use Eq. (17) instead of Eq. (15).
This equation shows that the relation between $N_{ox}$ and $N_{oxP}$ is independent of $C_y^1$. Accordingly, the ratio $H_{oxP}/H_{ox}$ is determined only by $P_xB$ and $P_yB$, and is not influenced by $C_y^1$.

** $H_{ox}$ and $H_{oxM}$

Equation 6 gives

$$C_x = mC_y = (1 - mC_y) \sum_{j=1}^{4} (1 - a_j) A_j e^{\lambda_j Z}.$$  

$$dC_x = (1 - mC_y) \sum_{j=1}^{4} A_j \lambda_j e^{\lambda_j Z} dZ.$$  

Accordingly one has

$$N_{oxM} = \int_0^1 \left[ \sum_{j=1}^{4} A_j \lambda_j e^{\lambda_j Z} / \sum_{j=1}^{4} (1-a_j)A_j e^{\lambda_j Z} \right] dZ. \quad (12)$$

This equation gives us the value of $H_{oxM}$. The ratio $H_{oxM}/H_{ox}$ is equal to $N_{ox}/N_{oxM}$ and is larger than 1. These ratios are also independent of $C_y^1$, because $A_j$, $\lambda_j$, and $a_j$ do not include $C_y^1$.

** For $\Lambda = 1$, use Eq. (7) instead of Eq. (6).
Numerical Example

The following parameters can be considered for illustration: \( \Lambda = 1, \) \( P_x B = P_y B = 4, \) \( N_{ox} = 5, \) \( C_y^1 = 0. \) The concentration distribution is given by

\[
C_x = 0.8110 - 0.5176 Z + 0.3862 \times 10^{-4} e^{7.49Z} + 0.0209 e^{-7.49Z} \\
mC_y = 0.7080 - 0.5176 Z - 1.168 \times 10^{-5} e^{7.49Z} - 0.0691 e^{-7.49Z}.
\]

The resulting numerical values are shown in Table I.

<table>
<thead>
<tr>
<th></th>
<th>Calculated concentration distributions</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( Z )</td>
<td>0</td>
<td>0.1</td>
</tr>
<tr>
<td>( C_x )</td>
<td>0.832</td>
<td>0.769</td>
</tr>
<tr>
<td>( mC_y )</td>
<td>0.638</td>
<td>0.624</td>
</tr>
<tr>
<td>( C_x - mC_y )</td>
<td>0.194</td>
<td>0.145</td>
</tr>
<tr>
<td>( 1/(C_x - mC_y) )</td>
<td>5.15</td>
<td>6.90</td>
</tr>
</tbody>
</table>

Graphical integration gives

\[
N_{oxM} = \int_{0.362}^{0.832} \frac{dC_x}{(C_x - mC_y)} = 3.87.
\]
Calculation from Eq. (17), below, gives

\[ C_{xl} = \left(1 + N_{oxP}\right)^{-1} = 0.362, \text{ or } N_{oxP} = 1.76. \]

Accordingly one finds

\[
H_{ox} : H_{oxM} : H_{oxP} = \frac{N_{ox}^{-1}}{N_{oxM}^{-1}} : \frac{N_{ox}^{-1}}{N_{oxP}}
\]

\[ = 1.0 : 1.29 : 2.84. \]

This result shows that \( H_{oxM} \) and \( H_{oxP} \) express apparent HTU values that include the effect of fluid mixing, while \( H_{ox} \) gives the true coefficient of mass transfer. As \( N_{ox} \) increases, the ratio of \( H_{oxP}/H_{ox} \) increases always more rapidly than the ratio of \( H_{oxM}/H_{ox} \).
SOLUTIONS FOR SPECIAL CASES

Solutions for various special cases are obtained by simplification of the basic equations. Table II summarizes these cases and indicates the physical situations to which they correspond.

Table II

<table>
<thead>
<tr>
<th>$P_{xB}$</th>
<th>$P_{yB}$</th>
<th>$\Lambda$</th>
<th>Case</th>
<th>Equation</th>
<th>Type of application</th>
</tr>
</thead>
<tbody>
<tr>
<td>finite</td>
<td>finite</td>
<td>$\neq 1$</td>
<td>$G_1$</td>
<td>(6), (6a)</td>
<td>Mixco., pulsed, rotating-disc, and packed* columns. Gas bubbles through a long column with mechanical agitation.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$= 1$</td>
<td>$G_2$</td>
<td>(7)</td>
<td></td>
</tr>
<tr>
<td>$\infty$</td>
<td>$\infty$</td>
<td>$\neq 1$</td>
<td>1</td>
<td>(14), (15)</td>
<td>Perfect countercurrent piston-flow operation</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$= 1$</td>
<td>2</td>
<td>(16), (17)</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>all</td>
<td>3</td>
<td>(18)</td>
<td>Perfect mixing</td>
</tr>
<tr>
<td>0</td>
<td>$\infty$</td>
<td>all</td>
<td>4</td>
<td>(19)</td>
<td>Large gas bubbles through a mixing tank*</td>
</tr>
<tr>
<td>$\infty$</td>
<td>0</td>
<td>all</td>
<td>5</td>
<td>(20)</td>
<td></td>
</tr>
<tr>
<td>finite</td>
<td>$\infty$</td>
<td>$\neq 1$</td>
<td>6</td>
<td>(21)</td>
<td>Dispersed phase in non-coalescing free flow through a long column, without mechanical agitation*</td>
</tr>
<tr>
<td></td>
<td>finite</td>
<td>$= 1$</td>
<td>7</td>
<td>(22)</td>
<td></td>
</tr>
<tr>
<td>$\infty$</td>
<td>finite</td>
<td>$\neq 1$</td>
<td>8</td>
<td>(24)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$= 1$</td>
<td>9</td>
<td>(25)</td>
<td></td>
</tr>
<tr>
<td>0</td>
<td>finite</td>
<td>all</td>
<td>10</td>
<td>(26)</td>
<td>Small gas bubbles through a mixing tank</td>
</tr>
<tr>
<td>finite</td>
<td>0</td>
<td>all</td>
<td>11</td>
<td>(27)</td>
<td></td>
</tr>
</tbody>
</table>

*See Appendix 1
Case 1. \( P_x B \to \infty, P_y B \to \infty; \wedge \neq 1. \)

From Eq. (2), we have:

\[
\begin{align*}
\frac{dC_x}{dZ} + N_{ox}(C_x - mC_y) &= 0 \\
\frac{dC_y}{dZ} + N_{oy}(C_x - mC_y) &= 0
\end{align*}
\]

and

\[C_{x0} = 1, \quad C_{y1} = C_y^1.\]

The solutions are

\[
\begin{align*}
\frac{C_x - mC_y^1}{1 - mC_y^1} &= \frac{e^{\lambda Z} - \lambda \cdot e^{\lambda}}{1 - \lambda \cdot e^{\lambda}} \\
\frac{m(C_y - C_y^1)}{1 - mC_y^1} &= \frac{(e^{\lambda Z} - e^{\lambda}) \cdot \lambda}{1 - \lambda \cdot e^{\lambda}}
\end{align*}
\]

where

\[\lambda = - N_{ox} (1 - (\wedge)).\]

The terminal (product) values of \(C_x\) and \(C_y\) are given by

\[
\begin{align*}
\frac{C_{x1} - mC_y^1}{1 - mC_y^1} &= \frac{(1 - \lambda) \cdot e^{\lambda}}{1 - \lambda \cdot e^{\lambda}} \\
\frac{m(C_y0 - C_y^1)}{1 - mC_y^1} &= \frac{(1 - e^{\lambda}) \cdot \lambda}{1 - \lambda \cdot e^{\lambda}}
\end{align*}
\]
Case 2. $P_B \rightarrow \infty, P_C \rightarrow \infty; \Lambda = 1$.

From Eq. (13) we have

$$\frac{d^2 C}{dZ^2} = 0.$$ 

Solution of the equation so as to satisfy the boundary conditions yields

$$\begin{align*}
\frac{C_x - mC_y^1}{1 - mC_y^1} &= \frac{1 + N_{ox} (1 - Z)}{1 + N_{ox}} \\
\frac{m (C_y^1 - C_y^0)}{1 - mC_y^1} &= \frac{N_{ox} (1 - Z)}{1 + N_{ox}}
\end{align*}$$

(Eq. 16)

$$\begin{align*}
\frac{C_{x1} - mC_y^1}{1 - mC_y^1} &= \frac{1}{1 + N_{ox}} \\
\frac{m (C_y^0 - C_y^1)}{1 - mC_y^1} &= \frac{N_{ox}}{1 + N_{ox}}
\end{align*}$$

(Eq. 17)

Equations (14) through (17) correspond to the well-known Kremser or Underwood equations for counter-current continuous operations.

Case 3. $P_x \rightarrow 0; P_C \rightarrow 0$.

In this case, both phases undergo perfect mixing. Equations (1) reduce to

$$u_x \epsilon_x (c_x^0 - c_{x1}) = u_y \epsilon_y (c_y^0 - c_y^1) = \zeta_{aL} (c_{x1} - mc_y^0),$$

or
\begin{align*}
1 - C_{x1} &= N_{ox}(C_{x1} - mC_{y0}) \\
C_{y0} - C_{y}^1 &= N_{oy}(C_{x1} - mC_{y0}) \\
\begin{cases}
\frac{C_{x1} - mC_{y}^1}{1 - mC_{y}^1} &= \frac{1 + N_{ox}(\Lambda)}{1 + N_{ox}(1 + \Lambda)} \\
\frac{m(C_{y0} - C_{y}^1)}{1 - mC_{y}^1} &= \frac{N_{ox}}{1 + N_{ox}(1 + \Lambda)}
\end{cases}
\end{align*}

These equations give, for \(C_{x1}\) and \(C_{y0}^1\):

Case 4. \(P_{xB} \rightarrow 0; P_{yB} \rightarrow \infty\).

The basic equations are:

\begin{align*}
\begin{cases}
dC_{y}/dZ + N_{oy}(C_{x1} - mC_{y}) &= 0 \\
C_{x1} &= 1 - (F_{y}/F_{x})(C_{y0} - C_{y1}) \\
C_{y1} &= C_{y}^1
\end{cases}
\end{align*}

The solutions is:

\begin{align*}
\begin{cases}
\frac{C_{x1} - mC_{y}^1}{1 - mC_{y}^1} &= \frac{\Lambda}{(1-e^{-N_{ox} \Lambda}) + \Lambda} \\
\frac{m(C_{y0} - C_{y}^1)}{1 - mC_{y}^1} &= \frac{\Lambda N_{ox}}{(1-e^{-N_{ox} \Lambda}) + \Lambda}
\end{cases}
\end{align*}
Case 5. \( P_xB \to \infty; \ P_yB \to 0 \).

The basic equations are

\[
\begin{aligned}
dC_x/dZ + N_{ox}(C_x - mC_y0) &= 0 \\
C_y0 &= C_y^1 + (F_x/F_y)(1 - C_x1) \\
C_x0 &= 1
\end{aligned}
\]

The solutions is

\[
\begin{aligned}
\frac{C_x1 - mC_y^1}{1 - mC_y} &= \frac{e^{-N_{ox}} + (1 - e^{-N_{ox}}) \Lambda}{1 + (1 - e^{-N_{ox}}) \Lambda} \\
\frac{m(C_y0 - C_y^1)}{1 - mC_y} &= \frac{(1 - e^{-N_{ox}}) \Lambda}{1 + (1 - e^{-N_{ox}}) \Lambda}
\end{aligned}
\]

(20)

Case 6. \( P_xB \) finite; \( P_yB \to \infty; \Lambda \neq 1 \)

The basic equations are

\[
\begin{aligned}
d^2C_x/dZ^2 - P_x B dC_x/dZ - N_{ox} P_x B (C_x - mC_y) &= 0 \\
dC_y/dZ + N_{oy} (C_x - mC_y) &= 0
\end{aligned}
\]

(21)

The boundary conditions are

\[
\begin{aligned}
-(dC_x/dZ)_Z = 0 &= P_x B (1 - C_x0) \\
-(dC_x/dZ)_Z = 1 = 0 \quad \text{and} \quad C_y1 = C_y^1
\end{aligned}
\]
The solution is

\[
\begin{align*}
\frac{C_x - mC_y^1}{1 - mC_y^1} &= F_1 e^{\lambda_1 Z} + F_2 e^{\lambda_2 Z} + F_3 e^{\lambda_3 Z} \\
\frac{m(C_y - C_y^1)}{1 - mC_y^1} &= f_1 F_1 e^{\lambda_1 Z} + f_2 F_2 e^{\lambda_2 Z} + f_3 F_3 e^{\lambda_3 Z}
\end{align*}
\]

(21a)

with

\[
F_1 = D_{F1}/D_F, \quad F_2 = D_{F2}/D_F, \quad \text{and} \quad F_3 = D_{F3}/D_F
\]

\[
D_F = D_{F1} + \left| \begin{array}{ccc}
1 - \lambda_2/P_{xB} & 1 - \lambda_3/P_{xB} \\
\lambda_2 & \lambda_3
\end{array} \right|
\]

\[
D_{F1} = \left| \begin{array}{ccc}
\lambda_2 & \lambda_3 \\
f_2 & f_3
\end{array} \right|, \quad D_{F2} = \lambda_3, \quad D_{F3} = -\lambda_2 e^{\lambda_2} (i = 1, 2, \text{and } 3)
\]

\[
f_i = 1 + \lambda_i/N_{ox} - \lambda_i^2/N_{ox} P_{xB}
\]

(\(i = 1, 2, \text{and } 3\))

\[
\lambda_1 = 0
\]

\[
\lambda_2 = (a/2) + \sqrt{(a/2)^2 + b}
\]

\[
\lambda_3 = (a/2) - \sqrt{(a/2)^2 + b}
\]

\[
a = P_{xB} + (\land)N_{ox}
\]

\[
b = (1 - \land)N_{ox} P_{xB}
\]
Case 7. $P_x B$ finite; $P_y B \rightarrow \infty$; $\Lambda^{1} = 1$

From Eq. (21a), the equation to be solved is

$$\frac{d^3 C_x}{dZ^3} - a \frac{d^2 C_x}{dZ^2} = 0.$$  

The boundary conditions are the same as in Case (6). The suitable solutions are

$$\begin{align*}
C_x - mC^1_y 
\frac{1}{1 - mC^1_y} &= G_1 + G_2 Z + G_3 e^{aZ}, \\
\frac{m(C_y - C^1_y)}{1 - mC^1_y} &= G_1 + \frac{G_2}{N_{ox}} + G_2 Z - (N_{ox}/P_x B)G_3 e^{aZ},
\end{align*}$$

(22)

where

$$a = P_x B + \Lambda^{1} N_{ox} = P_x B + N_{ox},$$

and

$$\begin{align*}
G_1 &= D_{G1}/D_G, & G_2 &= D_{G2}/D_G, & G_3 &= D_{G3}/D_G, \\
D_G &= D_{G1} + \begin{vmatrix}
-1/P_x B - (N_{ox}/P_x B) \\
1 & a e^a
\end{vmatrix}, \\
D_{G1} &= \begin{vmatrix}
a e^a \\
1 + 1/N_{ox} - (N_{ox}/P_x B)e^a
\end{vmatrix}, \\
D_{G2} &= a e^a), \text{ and } D_{G3} = -1.
\end{align*}$$
Case 8. $P_x \rightarrow \infty; P_y$ finite; $\wedge \neq 1$.

The basic equations are

\[
\begin{align*}
\frac{dC_x}{dZ} + N_{ox} (C_x - mC_y) &= 0 \\
\frac{d^2C_y}{dZ^2} + P_y R \frac{dC_y}{dZ} + N_{oy} P_y (C_x - mC_y) &= 0
\end{align*}
\]

Dimensionless boundary conditions are

\[
\begin{align*}
C_x(0) &= 1, \quad (dC_y/dZ)_Z = 0 = 0 \\
-d(C_y/dZ)_Z &= 1 = P_y B (C_y - C_y^1)
\end{align*}
\]

By a procedure similar to Case 7, the basic equations can be combined to give

\[
\frac{d^3C_x}{dZ^3} + h \frac{d^2C_x}{dZ^2} + k \frac{dC_x}{dZ} = 0,
\]

where

\[
\begin{align*}
h &= N_{ox} + P_y B \\
k &= N_{ox} P_y B (1 - \wedge)
\end{align*}
\]

The solutions depend upon whether $k \neq 0$ or $k = 0$. For $k \neq 0$ or $\wedge \neq 1$, the solution is

\[
\begin{align*}
\frac{C_x - mC_y^1}{1 - mC_y^1} &= H_1 e^{\lambda_1 Z} + H_2 e^{\lambda_2 Z} + H_3 e^{\lambda_3 Z} \\
\frac{m(C_y - mC_y^1)}{1 - mC_y^1} &= h_1 H_1 e^{\lambda_1 Z} + h_2 H_2 e^{\lambda_2 Z} + h_3 H_3 e^{\lambda_3 Z}
\end{align*}
\]
where

\[ H_1 = \frac{D_{H1}}{D_H}, \quad H_2 = \frac{D_{H2}}{D_H}, \quad \text{and} \quad H_3 = \frac{D_{H3}}{D_H}, \]

and

\[ D_H = \begin{pmatrix} h_2 & h_3 \\ 1 + \frac{\lambda_2}{P_B} e^{h_2} & (1 + \frac{\lambda_3}{P_B}) e^{h_3} \end{pmatrix} \]

\[ D_{H1} = \begin{pmatrix} h_2^2 & h_3^2 \\ (1 + \frac{\lambda_2}{P_B}) e^{h_2} & (1 + \frac{\lambda_3}{P_B}) e^{h_3} \end{pmatrix} \]

\[ D_{H2} = h_3 \lambda_3 \quad ; \quad D_{H3} = -h_2 \lambda_2 \]

\[ h_i = 1 + \frac{\lambda_i}{N_{ox}} \quad (i = 1, 2, \text{and} 3), \]

\[ \begin{cases} \lambda_1 = 0 \\ \lambda_2 = -\frac{h}{2} + \sqrt{\left(\frac{h}{2}\right)^2 - k} \\ \lambda_3 = -\frac{h}{2} - \sqrt{\left(\frac{h}{2}\right)^2 - k} \end{cases} \]

\[ h = N_{ox} + P_B y \]

\[ k = N_{ox} P_B \left(1 - \frac{1}{N_{ox}}\right) \]

Case 9. \( P_x B \to \infty; \quad P_y B \text{ finite; } \frac{1}{N_{ox}} = 1. \)

Eq. (23) becomes

\[ \frac{d^3 C_x}{dZ^3} + h \frac{d^2 C_x}{dZ^2} = 0. \]

The final solution is

\[ \begin{cases} C_x - mC_y^1 \\ 1 - mC_y^1 \end{cases} = J_1 + J_2 Z + J_3 e^{-hZ} \]

\[ m(C_y - C_y^1) \\ 1 - mC_y^1 \]

\[ = J_1 + J_2/N_{ox} + J_2 Z + \left(1 - \frac{h}{N_{ox}}\right) J_3 e^{-hZ}, \quad (25) \]
where

\[ J_1 = \frac{D_{J1}}{D_J}, \quad J_2 = \frac{D_{J2}}{D_J}, \quad \text{and} \quad J_3 = \frac{D_{J3}}{D_J}, \]

and

\[ D_J = 1 + D_{J1} \]

\[ D_{J1} = \begin{vmatrix} 1 - \frac{1}{D_J} & (1 - \frac{h}{N_{ox}}) e^{-h} \\ \frac{1}{1 + 1/N_{ox} + 1/P_B} & e^{-h} \end{vmatrix} \]

\[ D_{J2} = (1 - \frac{h}{N_{ox}}) e^{-h}, \quad \text{and} \quad D_{J3} = 1. \]

Case 10. \( P_B = 0; \) \( P_B \) finite.

The basic equations are

\[
\begin{align*}
\frac{d^2 C_y}{dZ^2} + P_B \frac{dC_y}{dZ} + N_{ox} P_B (C_{x1} - mC_y) &= 0 \\
C_{x1} \text{ is constant throughout the column.}
\end{align*}
\]

The boundary conditions are

\[
\begin{align*}
- \left( \frac{dC_y}{dZ} \right)_{Z=0} &= 0 \\
-(dC_y/dZ)_{Z=1} &= P_B (C_{y1} - C_y)
\end{align*}
\]

The solutions are:

\[
\begin{align*}
\frac{C_{x1} - mC_y^1}{1 - mC_y^1} &= \left( 1 + \frac{\lambda_2 - \lambda_1}{\lambda} \right) \\
m(C_y0 - C_y^1) &= \left( 1 + \frac{\lambda_2 - \lambda_1}{\lambda} \right) \\
m(C_y - C_y^1) &= \left( 1 + \frac{\lambda_2 e^{\lambda_1 Z} - \lambda_1 e^{\lambda_2 Z}}{\lambda} \right)
\end{align*}
\]
where

\[
\begin{align*}
D &= (\lambda_1 e^{\lambda_2} - \lambda_2 e^{\lambda_1}) + \left(\lambda_1 + \lambda_2\right) (e^{\lambda_1} - e^{\lambda_2}) \\
\lambda_1 &= \left(\frac{P_y B}{2}\right)^{-\frac{1}{2}} \left[\sqrt{\frac{P_y B}{2}} + N_{ox} P_y B' \Lambda\right] \\
\lambda_2 &= -\left(\frac{P_y B}{2}\right)^{-\frac{1}{2}} \left[\sqrt{\frac{P_y B}{2}} + N_{ox} P_y B' \Lambda\right]
\end{align*}
\]

Case 11. \( P_x B \) finite; \( P_y B = 0 \).

The basic equations are

\[
\begin{align*}
d^2C_x/dZ^2 - P_x B dC_x/dZ - N_{ox} P_x B (C_x - mC_y) &= 0 \\
mC_y &= \text{constant throughout the column.}
\end{align*}
\]

The boundary conditions are

\[
\begin{align*}
-(dC_x/dZ)_Z = 0 &= P_x B (1 - C_{x0}) \\
-(dC_x/dZ)_{Z=1} = 0
\end{align*}
\]

The solutions are

\[
\begin{align*}
\frac{C_x - mC_y^1}{1 - mC_y^1} &= 1 - \frac{1 - (\lambda_2 e^{(\lambda_2 + \lambda_1)Z} - \lambda_1 e^{(\lambda_1 + \lambda_2)Z})/D}{1 + \left\{ 1 + \frac{(\lambda_1 - \lambda_2)}{D} e^{(\lambda_1 + \lambda_2)} \right\} \Lambda} \\
\frac{C_{x1} - mC_y^1}{1 - mC_y^1} &= 1 - \frac{1 + (\lambda_1 - \lambda_2) e^{(\lambda_1 + \lambda_2)}/D}{1 + \left\{ 1 + \frac{(\lambda_1 - \lambda_2)}{D} e^{(\lambda_1 + \lambda_2)} \right\} \Lambda} \\
\frac{m(C_y0 - C_y^1)}{1 - mC_y^1} &= 1 - \frac{1}{1 + \left\{ 1 + \frac{(\lambda_1 - \lambda_2)}{D} e^{(\lambda_1 + \lambda_2)} \right\} \Lambda}
\end{align*}
\]
where

\[ D = (\lambda_2 e^{\lambda_2} - \lambda_1 e^{\lambda_1}) - \frac{\lambda_1 \lambda_2}{\lambda_1 + \lambda_2} (e^{\lambda_2} - e^{\lambda_1}) \]

\[ \lambda_1 = \left( \frac{P_x B}{2} \right) + \sqrt{\left( \frac{P_x B}{2} \right)^2 + N_{ox} P_x B} \]

\[ \lambda_2 = \left( \frac{P_x B}{2} \right) - \sqrt{\left( \frac{P_x B}{2} \right)^2 + N_{ox} P_x B} \]
CHARACTERISTICS OF THE PROPOSED MODEL

Figures 4, 5, and 6 show the concentration distributions calculated for three particular sets of parameters. Comparison of Fig. 5 with Fig. 4 shows the effect of increasing $N_{ox}$. Comparison of Fig. 6 with Fig. 4 shows the effect of decreasing the extraction coefficient $x F_x/F_y$.

From these figures, some particular characteristics are seen as follows:

1. The concentration driving force between two phases is obviously lowered by back-mixing of fluid, but not so much as was expected. At both ends of an extractor, the concentration driving force becomes higher than that in piston flow for the same $N_{ox}$.

2. The concentration of incoming streams increases or decreases abruptly at the time the streams enter the extractor. In contrast, the concentration curve for outgoing streams becomes flat as they approach the outlet, and no discontinuity in concentration occurs at the exit.

3. When extraction is accompanied by back-mixing of fluid, the extent of extraction is lowered in comparison with the case of piston flow, especially at high values of $N_{ox}$ and low values of $P_x B$ or $P_y B$. This lowering of the yield is attributable partly to the decrease of concentration driving force, and partly to back-mixing of the transferring component.

These characteristics are shown further in Figs. 7 through 10. Figure 7 shows the effects of $P_x B$ and $N_{ox}$ on $C_{x0}$, the dimensionless concentration of phase X just inside the inlet.

As $N_{ox}$ increases, $C_{x0}$ gradually becomes insensitive to $N_{ox}$ and is controlled by the Péclet group, $P_x B$ (or $P_y B$).

Figure 8 shows the effect of $N_{ox}$ and $P_x$ on $C_{x1}$, the concentration of outgoing X phase. $C_{x1}$ also becomes insensitive to $N_{ox}$. From these facts, an approximate value of $P_x B$ may be estimated by measuring $C_{x1}$ and $C_{x0}$ experimentally, if the effect of mass transfer at the phase boundary between heavier and lighter phases at settling sections is properly corrected for.

Figure 9 shows the influence of $P_x B$ and $N_{ox}$ on the ratio of $H_{top}/H_{tOX}$. These numerical values are computed from Eq. (11.b) at $m F_x/F_y = 1$ and $P_x B = P_y B$. The ratio increases with decreasing Péclet group, and increasing $N_{ox}$. 
Fig. 4. Concentration distribution:
$P_x B = P_y B = 4, \ N_{ox} = 5, \ \Lambda = 1$
Fig. 5. Concentration distribution:
$P_x B = P_y B = 4, N_{ox} = 100, \Lambda = 1$
Fig. 6. Concentration distribution:
\[ P_x B = P_y B = 4, \; N_{ox} = 5, \; \Lambda = 2/3 \]
Fig. 7. Variation of $c_{x0}$ inside column at inlet end ($\Lambda = 1$, $P_x B = P_y B$).
Figure 10 illustrates local accumulation or depression of a transferring component in the X phase due to longitudinal dispersion, fluid flow, and mass transfer.

More complete numerical computations are in progress and will be presented in a later paper.

EXTENT OF EXTRACTION AT AN INFINITE MASS-TRANSFER COEFFICIENT

As is evident from Figs. 5 and 8, the extent of extraction approaches a certain value as $N_{ox}$ or $K$ increases, at given values of $P_x B$ and $P_y B$. It is interesting to examine how the extent of extraction is limited by the longitudinal dispersion of each phase, under the limiting condition of an infinite value of the true over-all coefficient of mass transfer.

If the $N_{ox}$ included in Eqs. (6) and (7) is increased to infinity, the following solutions are finally derived.

Case 12. $\Lambda \neq 1; N_{ox} \to \infty$

For the solution given by Eq. (6), the ratio $q/p^{3/2}$ decreases to zero, and $u$ approaches $\pi/2$. If $q$ is positive, $q/p^{3/2}$ is also positive and $u$ approaches $\pi/2$ in the first quadrant. (If $q$ is negative, a similar end result is obtained.) The difference, $(\pi/2) - u$, is positive and approaches zero. That is,

$$\cos u = \sin (\pi/2 - u) = q/p^{3/2} \to 0^+.$$  

On the other hand, one obtains

$$\sin (\pi/2 - u) = (\pi/2 - u), \text{ if } (\pi/2 - u) < 1.$$  

Accordingly, one obtains

$$\pi/2 - u = q/p^{3/2}$$

or

$$u/3 = (\pi/6 - q/3p^{3/2})$$
Fig. 8. Variation of $c_x$ at column outlet ($\wedge = 1, P_x B = P_y B$).
Fig. 9. Ratio of apparent "piston-flow" HTU to "true" HTU as a function of $P_x B = P_y B$.
Fig. 10. Local accumulation and depletion of transferring material in X stream ($P_x B = P_y B = 4$, $N_{ox} = 5$, $\gamma = 1$).
From this value of \( u \),

\[
\lambda_2 = a/3 + 2\sqrt{p} \cos (\pi/6 - q/3^2/2),
\]

with

\[
\cos (\pi/6 - q/3^2/2) = \cos (\pi/6) \cos (q/3^2/2) + \sin (\pi/6) \sin (q/3^2/2) = \sqrt{3/2 + (q/3^2/2)/2},
\]

\[
\therefore \lambda_2 = a/3 + q/3p + \sqrt{3p}.
\]

Similarly,

\[
\lambda_3 = a/3 + q/3p - \sqrt{3p},
\]

\[
\lambda_4 = a/3 - 2(q/3p).
\]

Substitution for \( a \) in these equations yields

\[
\lambda_1 = 0,
\]

\[
\lambda_2 = \frac{1}{2} \left[ \frac{(P_x B)^2 - \Lambda (P_y B)^2}{P_x B + \Lambda (P_y B)} \right] + \sqrt{3p},
\]

\[
\lambda_3 = \frac{1}{2} \left[ \frac{(P_x B)^2 - \Lambda (P_y B)^2}{P_x B + \Lambda (P_y B)} \right] - \sqrt{3p},
\]

\[
\lambda_4 = \frac{(\Lambda - 1) P_x B P_y B}{P_x B + \Lambda P_y B}.
\]

Substituting these roots into Eq. (6), and setting \( N_{ox} \to \infty \), gives

\[
a_1 = a_4 = 1,
\]

\[
a_2 = a_3 = - \Lambda (P_x B/P_y B).
\]
Introducing these values in Eq. (6), and eliminating negligible terms, we obtain finally

\[
\frac{C_x - mC_y}{1 - mC_y^1} = \frac{\left(1 - \sum \right) \frac{P_x B_1 P_y}{P_x B + \sum P_y}}{\sum P_B^2} - \exp \left[\frac{(1 - \sum) P_x B_1 P_y}{P_x B + \sum P_y} - (1 - Z)\right] \}
\]

If \( Z = 1 \), Eq. (28) (below) results. From Eq. (28), Eq. (29) or (30) can be derived easily by setting \( P_x B \) or \( P_y B \) equal to infinity.

a. \( P_x B \) finite, \( P_y B \) finite:

\[
\frac{C_x - mC_y}{1 - mC_y^1} = \frac{\left(1 - \sum \right) \frac{P_x B_1 P_y}{P_x B + \sum P_y}}{\sum P_B^2} - \exp \left[\frac{(1 - \sum) P_x B_1 P_y}{P_x B + \sum P_y} - (1 - Z)\right] \}
\]

b. \( P_x B \) finite, \( P_y B \to \infty \):

\[
\frac{C_x - mC_y}{1 - mC_y^1} = \frac{\left(1 - \sum \right)}{\sum P_B^2} \frac{(1 - \sum)}{P_x B} - \exp \left[\frac{(1 - \sum) P_x B}{P_x B} - (1 - Z)\right] \}
\]

c. \( P_x B \to \infty \), \( P_y B \) finite:

\[
\frac{C_x - mC_y}{1 - mC_y^1} = \frac{\left(1 - \sum \right)}{\sum P_B^2} \frac{(1 - \sum)}{P_y B} - \exp \left[\frac{(1 - \sum) P_y B}{P_y B} - (1 - Z)\right] \}
\]
Case 13. $\lambda = 1, N_{ox} \to \infty$

For the solution given by Eq. (7), the final solutions can be derived from the following approximations:

$$\mu_3 = \frac{a}{2} + \sqrt{\frac{(a/2)^2}{2} + \beta} \to \sqrt{\beta} \text{ when } N_{ox} \to \infty,$$

$$\mu_4 = \frac{a}{2} - \sqrt{\frac{(a/2)^2}{2} + \beta} \to \sqrt{\beta} \text{ when } N_{ox} \to \infty,$$

$$\mu_3 + \mu_4 = a.$$

The solution is

$$\frac{C_x - m C_y^1}{1 - m C_y^1} = \frac{(P_x B + P_y B) + P_x B P_y (1 - Z)}{2P_x B + P_x B P_y + 2P_y B}.$$ 

from which we can derive the following equations, setting $Z = 1$.

a. $P_x B$ finite, $P_y B$ finite:

$$\frac{C_{x1} - m C_y^1}{1 - m C_y^1} = \frac{P_x B + P_y B}{2P_x B + P_x B P_y + 2P_y B}. \quad (31)$$

b. $P_x B$ finite, $P_y B \to \infty$:

$$\frac{C_{x1} - m C_y^1}{1 - m C_y^1} = \frac{1}{2 + P_x B}. \quad (32)$$

c. $P_x B \to \infty$, $P_y B$ finite:

$$\frac{C_{x1} - m C_y^1}{1 - m C_y^1} = \frac{1}{2 + P_y B}. \quad (33)$$
Equations (28) through (33) are shown graphically in Figs. 11 through 13. As \( \Lambda \) decreases, the extent of extraction approaches unity. This limiting case of \( \Lambda \to 0 \) corresponds to the behavior of continuous-flow homogeneous-phase reactors with first-order reaction.

The limiting cases described in this section (Eqs.(28) through (33)) are useful in estimating the suitability of a given extractor for a given separation requirement.
CONCLUSIONS

1. A general theoretical treatment based on the proposed model has been presented, so as to permit evaluation of the over-all behavior of counter-current solvent-extraction columns, taking into consideration the effect of longitudinal dispersion of both fluids. The behavior is expressed as a function of four dimensionless parameters. Solutions for various special cases of the pattern of longitudinal dispersion have been presented and their actual applications are indicated.

2. Three kinds of over-all height of transfer unit have been distinguished, and the interrelation between them is shown. It is indicated that two of them, used in previous work, reflect the influence of longitudinal dispersion.

3. Illustrative numerical examples are given, which indicate that longitudinal dispersion produces an extremely undesirable effect when a high degree of extraction is desired, and that the lowering of the extent of extraction is attributable partly to a lowering of the concentration driving force and partly to longitudinal dispersion of the transferring component.

4. Finally, it is made clear that there is a maximum attainable extent of extraction under a given pattern of longitudinal dispersion. Solutions for this maximum extent of extraction have been derived by use of an infinite value for the true over-all mass-transfer coefficient.
Fig. 11. Limiting extent of extraction for $N_{\infty} = \infty$ (with $P_yB = \infty$) as a function of $P_xB$ and $\Lambda$ (See Eqs. 29 and 32).
Fig. 12. Limiting extent of extraction for $N_x = \infty$ (with $P_x = \infty$) as a function of $P_y$ and $\Lambda$ (See Eqs. 30 and 33).
Fig. 13. Limiting extent of extraction for \( N_\infty = \infty \) as a function of \( P_xB \) (or \( P_yB \)), with \( \lambda = 1 \)(See Eqs. 28 and 31).
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NOMENCLATURE

a  Interfacial area between two phases, per unit column volume (cm^2/cm^3)
B  L/d (dimensionless)

\( c_i \) Concentration of a transferring component in \( i \) phase (mole/cm^3)
\( c_x^0 \) Initial concentration of the incoming \( x \) phase (mole/cm^3)
\( c_x^L \) \( (c_x^0)_{z \rightarrow 0} \) (mole/cm^3)
\( c_y \) Initial concentration of the incoming \( y \) phase (mole/cm^3)
\( c_y^L \) \( (c_y^0)_{z \rightarrow L} \) (mole/cm^3)

d  A representative length (cm)

m  Equilibrium distribution coefficient of a transferring component between \( x \) and \( y \) phase (dimensionless)

\( u_i \) \( F_i/\epsilon_i \); True mean linear velocity of the \( i \) phase (cm/sec)

\( z \) Distance along the mean flow (the \( x \)-phase inlet is taken as the original point) (cm)

\( C_i = c_i/c_x^0 \)
\( C_x^0 = c_x^0/c_x^0 = 1 \)
\( C_{x0} = c_{x0}/c_x^0 \)
\( C_y = c_y/c_x^0 \)
\( c_{y1} = c_{y1}/c_x^0 \)

\( E_i \) Diffusivity of a transferring component in the direction of mean flow (cm^2/sec)

\( F_i \) Superficial volumetric flow rate of \( i \) phase across a unit cross section = \( u_i \epsilon_i \) (cm^3/cm^2 · sec)

\( H_{oi} = L/N_{oi} = F_i/K_x = \tilde{u}_i \epsilon_i/K_x \); True HTU (cm)

\( H_{oIM} \) Apparent HTU based on the measured concentration distribution in an extractor = \( L/N_{oIM} \) (cm)

\( H_{oIP} \) Apparent HTU based on terminal concentration values, assuming piston flow for \( x \) and \( y \) phase (cm)
\( K_x \)  
Over-all coefficient of mass transfer (cm/sec)

\( L \)  
Effective length of an extractor in the direction of the mean flow (cm)

\( N_{oi} \)  
\( \frac{aL/F_i}{(H)}_{oi} \) (dimensionless)

\( N_{oiM} \)  
\( \frac{L}{H_{oiM}} = \frac{\int_{C_{x0}}^{C_{x1}} \frac{dC_x}{C_x - mC_y}}{(dimensionless)} \)

\( N_{oiP} \)  
\( \frac{L}{H_{oiP}} = \frac{\int_{1.0}^{C_{x1}} \frac{dC_{xP}}{C_{xP} - mC_{yP}}}{(dimensionless)} \)

\( P_i \)  
\( u_i d/E_i \) : Péclet Number (dimensionless)

\( Z \)  
\( z/L \) (dimensionless)

\( \epsilon_i \)  
Void fraction of i-phase (dimensionless)

\( \phi(\epsilon_i) \)  
Volumetric rate of reaction (mole/cm\(^3\) sec)

\( \Lambda \)  
Extraction factor, \( mF_x/F_y \) (dimensionless)

Subscripts \( x \) and \( y \) refer to \( x \) and \( y \) phase respectively and \( i \) to \( i \)th component or phase.
APPLICABILITY OF THE MODEL

The basic equations are derived from the simplified model shown in Fig. 1. In an actual extractor, however, one phase (Y) is dispersed into a second phase (X) as shown in Fig. 2.

The basic equation expressing the behavior of the continuous phase is reported \(^{16}\) to be suitable for Mixco and similar type columns. There is more question as to the conditions under which the model fits the dispersed phase, because the basic equation requires that all droplets at a given cross section have the same concentration.

There are two typical mechanisms that may cause longitudinal dispersion of the dispersed phase. One is longitudinal back-mixing of liquid droplets caused by local eddy motion of the mixed phases; the other is an apparent dispersion caused by a velocity distribution for the droplets, without any accompanying back-mixing of droplets. In the following description, the former is named "the eddy mechanism", and the latter "the velocity-distribution mechanism". The mathematical treatment expressed by Eq. (1) is called "the apparent-diffusivity method".

Two criteria exist for the applicability of the model assumed here. One is the residence-time distribution and the other the extraction behavior. The former can be measured by transient behavior - e.g., the outlet response to a delta (or pulse) function introduced at the extractor inlet - and is determined only by the longitudinal dispersion of the droplets.

On the other hand, the extraction behavior is influenced both by mass transfer between the droplets and the continuous phase and by the residence-time behavior of each phase.
I. Eddy Mechanism

A mechanically agitated column is the typical example. All droplets are presumed to have the same mean diameter, which will depend on the mixing geometry and power input.

Residence-Time Behavior

If local eddy motion of the mixed phases is superimposed upon a rising (or descending) motion of droplets, the apparent-diffusivity method provides a satisfactory approximation for the eddy mechanism, because reasonable mean diffusivities can be assumed in each phase. In addition, \( E_y \) may be of the same order of magnitude as \( E_x \) and may remain nearly unchanged throughout the column. In the approach to the ideal case, \( P_y B \) is proportional to the column height.

Under mixing conditions that favor rapid coalescence and redispersion of droplets, the physical situation becomes susceptible to the apparent-diffusivity method, because the behavior of the dispersed phase approaches that of a second continuous phase through the equalization of all the droplets at any one level in the extractor.

Extraction Behavior

In the case of negligible coalescence and redispersion of the droplets, they behave independently of one another. The concentration of different droplets at any given cross section is, therefore, not the same.

There are four parameters, \( P_x B \), \( P_y B \), \( N_{Ox} \), and \( \Lambda \), which determine the extraction behavior. The applicability of the apparent-diffusivity method can be discussed in terms of all these parameters, except \( P_x B \), for the following cases:

(A) \( P_y B \approx 0 \). Under this condition, the mean concentration of phase \( Y \) is constant throughout the column. Accordingly, the extraction behavior corresponds to that of the homogeneous-phase flow reactors with first-order reaction. The model is applicable for all values of \( P_x B \), \( N_{Ox} \), and \( \Lambda \).
In this case, there is negligible back-mixing of the dispersed phase. Therefore, the apparent-diffusivity method is applicable to all values of $P_B$, $N_{ox}$, and $\Lambda$.

(C) $P_B$ finite. Under this condition, the concentration driving force between a droplet and the continuous phase changes from time to time owing to eddy motion of the droplet. This change reflects the concentration distribution of phase $X$ and the magnitude of $N_{ox}$ (which is proportional to the mass-transfer rate).

There are three extreme cases under which the apparent-diffusivity method is applicable. The method probably remains valid under intermediate conditions, but this case needs further investigation.

1. $N_{ox}$ and $K_x$ very high. Owing to the high rate, the droplets are always nearly in equilibrium with the surrounding continuous phase. Hence there is little effect of back-mixing of droplets on the extraction behavior.

2. $N_{ox}$ and $K_x$ very low. Lengthwise gradient for the driving force is very small compared with the total driving force. So there is again little effect of back-mixing of the dispersed phase.

3. $P_B \approx 0$. Because the concentration distribution of phase $X$ is constant throughout the column, the extent of extraction of each droplet is determined by the length of residence time. This comes from the assumption that the rate of extraction is expressed by a rate equation of the first order.

The extent of extraction of the dispersed phase may be calculated by the apparent-diffusivity method for any values of $P_B$, $N_{ox}$, and $\Lambda$.

For moderate values of $N_{ox}$, there is a possibility that the calculations based on the apparent-diffusivity method deviate from the exact solution. When $\Lambda$ is around 1, this deviation may not be serious, because the concentration gradient in phase $X$ and phase $Y$ is fairly linear, and $d^2C_y/dZ^2$ is small. When coalescence and redispersion of droplets occur, the behavior of the dispersed phase becomes more favorable to the apparent-diffusivity method, for the reason described for residence-time behavior. There is a positive indication of coalescence and redispersion of liquid droplets for agitated liquid-liquid extractors.\textsuperscript{12, 13}

In conclusion, the apparent-diffusivity method is applicable to the eddy mechanism except perhaps in the range where $P_B$ and $N_{ox}$ are finite and $\Lambda$ is not around 1. Further experimental or theoretical study is needed for this range. Even here, however, it is entirely permissible to apply the apparent-diffusivity method, if enough coalescence and redispersion occur.
II. Velocity-Distribution Mechanism

A typical example is noncoalescing free flow of the dispersed phase through a long column without mechanical agitation. The residence-time distribution depends on the velocity distribution of droplets, which is nearly constant throughout the column height; hence the superficial Péclet group \((P_y B)_u\) determined from transient behavior remains unchanged with changing column height.

Under the following restrictions, the extent of extraction in the case of the velocity-distribution mechanism can be computed from the apparent-diffusion method.\(^7\)

For \((P_y B)_u > 50\), and \(\Delta\) around 1,

a. when \((N_{ox})_u\) is smaller than 20, the extent of extraction is given by Eq. (6), using \(P_B\) and \((P_y B)_u\),

b. when \((N_{ox})_u\) is greater than 20, the extent of extraction is given by the apparent diffusion method, using the measured \(P_x B\), and an infinite value for \(P_y B\) irrespective of the measured value of \((P_y B)_u\).

For \((P_y B)_u \leq 50\), the apparent-diffusion method is not generally applicable without serious error.

When the eddy mechanism is superimposed on the velocity-distribution mechanism, the following treatment is recommended.\(^7\)

Contribution of the velocity-distribution mechanism to the over-all longitudinal dispersion effective to extraction is apparently expressed by a superficial mean diffusivity \(D_{yu}\) for \((P_y B)_u \approx 50\). Assuming additivity of the superficial diffusivities that came from the different mechanisms, one obtains the over-all diffusivity or the diffusivity \(E_{ym}\) measured experimentally by the transient method from

\[
E_{ym} = E_y + D_{yu}
\]

or

\[
1/(P_y B)_{ym} = 1/P_y B + 1/(P_y B)_u
\]

where \(E_y\) and \(P_y B\) are the mean diffusivity and Péclet group of the eddy mechanism.
When \((P_yB)_m\) is measured as a function of column height, we may have such a relation as

\[
(P_yB)_m \propto B^n \quad \text{for} \quad 0 \leq n \leq 1,
\]

because \((P_yB)_u\) remains unchanged with \(B\), and \(P_yB\) is proportional to \(B\).

The possible values of \(n\), giving the lowest limit under which the apparent diffusion method cannot be applied without serious error, are as follows:

<table>
<thead>
<tr>
<th>((P_yB)_m)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n)</td>
<td>0.8</td>
<td>0.6</td>
<td>0.4</td>
<td>0.2</td>
<td>0.0</td>
</tr>
</tbody>
</table>

For example, when \((P_yB)_m\) is around 30 and \(n\) is greater than 0.4, the extent of extraction may safely be calculated by the apparent-diffusion method, using \((P_yB)_m\) as the effective Peclet group for phase Y in the range of \((N_{ox})_u < 20\).

Note:

The special notations used here are as follows:

\[
(N_{ox})_u = (K_a)_u L/F_y,
\]

\[
(K_a)_u = \text{overall coefficient of mass transfer, when all droplets have an equal velocity, and pass through a column in plug flow},
\]

\[
(P_yB)_u = (U_y d/D_{yu}) (L/d).
\]

To determine \((P_yB)_u\) from the transient behavior it is recommended that the width of the residence-time distribution curve be used (i.e., the outlet response to the delta function) at the mid-point of its maximum height.
LITERATURE CITED

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