MASS TRANSFER COEFFICIENTS IN MIXER-SETTLER EXTRACTION COLUMN

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The volumetric over-all mass transfer coefficient $K_{oa}$ and the volumetric dispersed phase mass transfer coefficient $k_{d,a}$ in a mixer-settler extraction column were measured. In the measurement of $K_{oa}$, iodine was extracted from $I_2$-KI aqueous solution into heptane, while iodine was back-extracted from a heptane solution of iodine into sodium thiosulfate aqueous solution to obtain $k_{d,a}$. By using specific interfacial area determined from the estimated Sauter mean diameter of the dispersed drops and the estimated holdup of the dispersed phase, the mass transfer coefficients for the dispersed and the continuous phases were determined from the volumetric coefficients $K_{oa}$ and $k_{d,a}$. The coefficient $k_{d}$ for the dispersed phase coincided with the theoretical value based on diffusion within a rigid sphere using the residence time distribution of dispersed drops. On the other hand, the coefficient $K_{oa}$ for the continuous phase agreed well with the correlation of mass transfer around a rigid sphere by assuming that the relative velocity of the dispersed drop to the continuous phase was given by the terminal settling velocity of a rigid sphere having the same diameter and density as the drop.

Introduction

A countercurrent multistage extraction column is useful to separate liquid mixtures. A high stage efficiency and a large throughput are desirable for the extraction column. Agitation produces a large interfacial area to realize high stage efficiency, but throughput decreases with the decrease in drop diameter by agitation. In the mixer-settler type extraction column, however, the effect of agitation on the throughput is small, since the dispersed phase coalesces completely. Treybal (1964) proposed a rectangular tower in which each stage consisted of a mixer and a settler in horizontal arrangement, and showed that throughput increased with agitation speed. Rincón-Rubio et al. (1993) investigated the flooding behavior of the Wirz extraction column (one of the mixer-settler types) and showed that throughput varied little with agitation speed when drops coalesced completely. We proposed a mixer-settler extraction column (MS column) in which a mixer and a settler were in vertical arrangement in each stage, and showed that both the throughput (Takahashi et al., 1993a) and the stage efficiency (Takahashi et al., 1993b) increased with agitation speed. Nii et al. (1997) showed that a large maximum throughput could be realized with the MS column, and the throughput could be determined from the pressure balance among the pressure drop of the liquid flow, the suction pressure induced by the impeller, and the buoyant force of dispersed phase.

To design the extraction column, the mass transfer characteristics must also be known. In the usual extraction column, the diameter of dispersed drops and the dispersed phase holdup depend on the vertical position of the column (Kumar et al., 1986; Sarkar and Phillips, 1985; Kirou et al., 1988), and accurate estimation of these variations is difficult (Tsouris et al., 1994). This makes it difficult to determine the mass transfer coefficients in the extraction column. On the other hand, the partition between stages in the MS column is more complete than those in other extraction columns, and the hydrodynamic behavior in one stage may not be affected by those in other stages, i.e., the behavior is independent for each stage. The Sauter mean drop diameter in the Wirz column does not change with the stage number (Rincón-Rubio et al., 1994) and flooding in the MS column occurs simultaneously in every stage (Nii et al., 1997). This independency of each stage makes the analysis of mass transfer behavior simple.

In the present work the volumetric mass transfer coefficients of the MS column were measured with a single stage column, and the mass transfer coefficients of both dispersed and continuous phases are determined by use of the interfacial area estimated from the Sauter mean drop diameter (Takahashi and Takeuchi, 1992) and the dispersed phase holdup (Takahashi and Takeuchi, 1990). These coefficients are compared with theoretical values and with mass transfer coefficients obtained from a rigid sphere correlation.

1. Experimental

Experimental apparatus used in this work was the same as in the previous paper (Takahashi and Takeuchi,
Fig. 1  Schematic diagram of experimental apparatus

1990) and is shown schematically in Fig. 1. This corresponded to one stage of the MS column (Nii et al., 1997), and inner column diameter and column height were 100 mm. The column was divided into a mixer of 59 mm height and a settler of 38 mm height by a stator ring of 3 mm thickness having a 50 mm opening. A drop coalescer, which was a three dimensional lattice of 12 mm height and 2.5×2.3 mm rectangular pitch made of glass fiber meshes coated with PTFE, was set on the stator ring. Agitation in the mixer was carried out by a lifter-turbine impeller which had six-blades of 10 mm height and 14 mm width under a disk of 50 mm diameter. The impeller position was 51 mm from the bottom of the column to the upper surface of impeller disk.

An aqueous solution of I₂-KI was fed to the mixer, rose into the settler through the coalescer, and was channeled to the leveler from the bottom of the settler. Feeding of a dispersed phase of heptane to the mixer was started after filling the column with the aqueous solution. It rose through the coalescer with the aqueous phase and went out from the top of the column. Iodine in the aqueous phase was extracted into the organic phase in the column, and the concentrations in the outlet aqueous and organic phases decreased with time and became constant. Since steady state was achieved after flowing ca. 0.0018 m³ of solution (about four times the volume of the mixer), aqueous and organic samples were taken from the outlet levelers after flowing ca. 0.005 m³ of solution. Iodine concentrations in the organic phase were determined by a spectrophotometer and those in the aqueous phase by titration with a solution of sodium thiosulfate. The distribution ratio of iodine, \( m \), between aqueous solution and heptane was determined for each experimental run by measuring the iodine concentrations in both phases after equilibrating the outlet organic phase with the outlet aqueous phase. The distribution ratios, which varied with the concentration of iodide ion (Takahashi et al., 1987), were between 5 and 8 in the present experiments. For these values of \( m \), the mass transfer resistance in aqueous phase is dominant.

In the measurement of mass transfer coefficient within the dispersed phase, a heptane solution of iodine was fed as a dispersed phase and an aqueous solution of sodium thiosulfate as a continuous phase, and the iodine concentrations in the outlet organic phase and the feed solution were measured.

2. Results and Discussion

2.1 Volumetric over-all mass transfer coefficient

It is assumed that the extraction of iodine proceeded only within the mixer and both the concentrations of continuous and dispersed phases leaving the mixer were equal to those within the mixer (i.e., complete mixing). The volumetric over-all mass transfer coefficient, \( K_{ca} \), based on the continuous phase concentration is obtained by the following equation.

\[
K_{ca}(C_{con} - C_{con})V_M = Q_e(C_{in} - C_{con})
\]

(1)

where \( C_e \) is the iodine concentration in aqueous phase, \( V_M \) the volume of the mixer, and \( Q_e \) the flow rate of aqueous phase. The suffixes, out and in, express outlet and inlet, respectively. \( C_{con} \) is the aqueous concentration in equilibrium with the outlet organic phase and given by \( C_{con \text{, out}} = C_{d \text{, out}}/m \), where \( C_{d \text{, out}} \) is the average concentration of outlet organic droplets. The assumption of complete mixing does not mean a uniform concentration of the dispersed phase, but the average concentration of dispersed drops leaving the mixer is equal to that within the mixer. Dispersed drops have various concentrations corresponding to the residence time of the drop in the mixer.

The values of \( K_{ca} \) are shown in Figs. 2 and 3 for a
constant flow rate of continuous phase and that of dispersed phase, respectively. \( K_a a \) increases with agitation speed, \( n \), and the value for \( n = 12.1 \text{ s}^{-1} \) is about ten times that for \( n = 5.7 \text{ s}^{-1} \). The effect of dispersed phase flow rate, \( Q_d \), on \( K_a a \) in Fig.2 was larger than that of continuous phase flow rate in Fig.3. \( K_a a \) increases with an increase in \( Q_c \), while it decreases with an increase in \( Q_d \).

### 2.2 Interfacial area

To obtain the mass transfer coefficient, specific interfacial area, \( a \), in the mixer must be known, which is given by

\[ a = \frac{6\phi}{d_{32}} \tag{2} \]

where \( \phi \) is dispersed phase holdup in the mixer and \( d_{32} \) the Sauter mean diameter of dispersed drops. In the present mixer the value of \( \phi \) below the impeller differed from that above the impeller, these holdups were given as follows by Takahashi and Takeuchi (1990). Since agitation above the lifter-turbine impeller is mild, the dispersed phase holdup, \( \phi^U \), above the impeller can be related with the slip velocity, \( v_s \), between two phases rising around the impeller.

\[ v_s = \frac{1}{(1/A)}\left\{ Q_u / \phi^U - Q_d / (1 - \phi^U) \right\} \tag{3} \]

where \( A \) is a cross sectional area of flow path around the impeller. The slip velocity is correlated by the following equation.

\[ v_s = 0.00029(3.3\Delta \rho \gamma)^b, \quad b = 0.2 + 13n^{-1.65} \tag{4} \]

where \( \Delta \rho \) is density difference between phases and \( \gamma \) is interfacial tension. The value of \( \phi^U \) can be calculated with Eqs.(3) and (4) for given flow rates, agitation speed and physical properties. Equation (4) is derived from experiments of heptane-water and TBP-heptane-water systems. The physical properties used in the present study are shown in Table 1, which are almost same as the heptane-water system.

### Table 1 Physical properties of phases

<table>
<thead>
<tr>
<th></th>
<th>dispersed phase</th>
<th>continuous phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>density [kg/m³]</td>
<td>682</td>
<td>997</td>
</tr>
<tr>
<td>viscosity [Pa·s]</td>
<td>8.94×10^{-4}</td>
<td>1.33×10^{-9}</td>
</tr>
<tr>
<td>diffusivity [m²/s]</td>
<td>3.86×10^{-9}</td>
<td>5.06×10^{-2}</td>
</tr>
</tbody>
</table>

There is a core of circulation flow below the impeller, and the holdup of dispersed phase in the core is uniform, which is expressed as \( \phi^L \). The dispersed phase leaves in proportion to \( \phi^L - \phi^U \) from the core toward the upper part of the impeller by mixing. The dispersed phase is also accompanied by the total flow, \( Q_d + Q_c \), and the leaving flow rate of dispersed phase from the core is given by

\[ Q_d = K_s A (\phi^L - \phi^U) + (Q_d + Q_c) \phi^L \tag{5} \]

where \( K_s \) is the dispersion coefficient of dispersed drops and is correlated by

\[ K_s = 0.0043 + 260n^{-7} \tag{6} \]

There was an error in the expression of Eq.(6) in the previous paper (Takahashi and Takeuchi, 1990). The coefficients are independent of \( Q_d, Q_c, \Delta \rho \), and \( \gamma \), and are constant for large agitation speed \( n > 7 \text{ s}^{-1} \). At low agitation speed, large drops may leave the circulation core under the influence of buoyancy, and the value of \( K_s \) will increase with a decrease in \( n \). The value of \( \phi^L \) is determined from Eqs. (5) and (6) by use of \( \phi^U \) obtained above. The value of \( \phi \) can be obtained by averaging \( \phi^U \) and \( \phi^L \) as

\[ \phi = (\phi^U V^U + \phi^L V^L) / V_M \tag{7} \]

where \( V^L \) and \( V^U \) are volumes below and above the impeller, respectively.

On the other hand, \( d_{32} \) is correlated as follows (Takahashi and Takeuchi, 1992)

\[ d_{32} / D_i = 0.86W e^{0.72 \theta_8^{0.36}} \tag{8} \]

where \( D_i \) is impeller diameter, \( W \) is the Weber number (\( = n^2 D_i^3 \rho / \eta \)) and \( \theta_8 \) is the average residence time of dispersed drops in the circulating core (\( = V^H \phi^U / Q_d \)). The specific interfacial area can be calculated from Eqs.(2), (7) and (8) with the assumption that the values of \( d_{32} \) above and below the impeller are same. An example of calculated value of \( a \) for the present experimental condition is shown in Fig.4 with \( \phi^U, \phi^L \) and \( d_{32} \). As \( n \) increases, the values of \( \phi^U \) and \( \phi^L \) increase and \( d_{32} \) decrease, i.e., the interfacial area increases substantially with an increase in \( n \). The calculated value of \( a \) for each experiment is shown in Figs.2 and 3. It increases with \( n \) or \( Q_d \) and decreases with \( Q_c \). The changes in \( K_a a \) are similar to
those in \( a \), i.e., the volumetric over-all mass transfer coefficient varies according to the change in interfacial area. The over-all mass transfer coefficient \( K_c \) does not change with \( n \), \( Q_m \) or \( Q_c \).

2.3 Over-all mass transfer coefficient

The over-all mass transfer coefficient \( K_c \) is obtained by dividing the volumetric coefficient by the interfacial area and shown in Fig. 5 as \( Sh_{OC} = (K_c \cdot d_{32}/D_c) \) to compare with the data for various extraction columns given by Kumar and Hartland (1988). The diffusion coefficient of iodine in water was given by Durrall and Oldham (1968) as in Table 1. Reynolds number, Re, in the abscissa are obtained with the slip velocity calculated by Eq.(3) with the column cross sectional area and \( \phi^2 \) instead of \( A \) and \( \phi^2 \) in Eq.(3), respectively.

According to Kumar and Hartland, correlations for several extraction columns, i.e., a Kühni column, a rotating disc column (RD), an enhanced coalescing column (EC) and a pulsed sieve extraction column (PSE), are almost the same, while the correlation deviates from the present experimental points. The Reynolds number in the present experiments is small due to the small slip velocity because of the small drop diameter. Drop diameters were in the range of 0.15-0.67 mm as shown in Fig. 4. With such a small drop diameter, the extraction columns given by lines 1-5 in Fig. 5 can not be operated. Since a relatively large number of drops circulates within the mixer in the present experiments, the dispersed phase holdup is larger than that in the Kühni column (line 1), and \( v_0 \) calculated by Eq.(3) is 0.0007-0.003 m/s. Because the distribution ratio in the present experiments is large, mass transfer resistance in the continuous phase is dominant and \( Sh_{OC} \) is larger than the value of \( Sh_{OC} = 2 \) for the quiescent continuous phase.

2.4 Dispersed phase mass transfer coefficient

The volumetric dispersed phase mass transfer coefficient, \( k_{dt} \), is determined by the following equation from the back extraction of iodine in the iodine-heptane solution by the aqueous solution of sodium thiosulfate.

\[
k_{dt}C_{d,\text{out}}V_M = Q_d(C_{d,\text{in}} - C_{d,\text{out}})
\]

where \( C_{d,\text{in}} \) is the inlet iodine concentration in heptane. The iodine concentration at the interface is assumed to be zero because of the instantaneous reaction between iodine from the organic phase and sodium thiosulfate in the aqueous phase. The effects of flow rates of dispersed and continuous phases on \( k_{dt} \) are shown in Figs. 6 and 7, respectively. The value of \( k_{dt} \) increases with the increase in \( Q_d \), while it varies little with the change in \( Q_c \).

By use of the calculated interfacial area, the dispersed phase mass transfer coefficients is obtained from the volumetric mass transfer coefficients in Figs. 6 and 7 and shown in Fig. 8. The coefficient increases with agitation speed, but it varies little with the change in \( Q_d \) or \( Q_c \).

2.5 Dispersed phase mass transfer coefficient based on rigid sphere model

For the present back-extraction, the average concentration, \( C_{d,\text{av}} \), of iodine in a drop of residence time \( t \) is given by the diffusion model within a rigid sphere as follows (Crank, 1975)
\[
\frac{C_{\text{d, in}} - C_{\text{d, out}}}{C_{\text{d, in}}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{4Dn^2\pi^2t}{d^2}\right)
\]

(10)

The value of \( C_{\text{d, out}} \) is calculated by use of the average residence time \( \theta_0 = V_m/\varphi Q_0 \) as \( t \) in Eq. (10), and \( k_d \) is determined from Eq. (9). The calculated values of \( k_d \) are larger by several orders than the observed ones as shown in Fig. 9. The calculated concentration of outlet drop having the residence time \( \theta_0 \) is very small. There are drops of various residence time, and the drop concentration increases with the decrease in the residence time. Therefore, the average concentration of outlet drops may differ from the value calculated by the average residence time.

Under an assumption of complete mixing within the mixer, the residence time distribution is expressed as

\[
f(t) = (1/\theta_0) \exp(-t/\theta_0)
\]

(11)

Then, the fraction, \( X \), of iodine back extracted within the mixer is given as

\[
X = \frac{C_{\text{d, in}} - C_{\text{d, out}}}{C_{\text{d, in}}} = \int_0^{\infty} \left( \frac{C_{\text{d, in}} - C_{\text{d, out}}}{C_{\text{d, in}}} \right) f(t) dt
\]

(12)

On the other hand, the dispersed phase mass transfer coefficient is derived from Eq.(9) as follows.

\[
k_d = \frac{Q_d}{uV_m} \frac{(C_{\text{d, in}} - C_{\text{d, out}})/C_{\text{d, in}}}{(d_{32}/6)(Q_d/\varphi V_m)X/(C_{\text{d, out}}/C_{\text{d, in}})}
\]

\[
= (d_{32}/6\theta_0)(X/(1-X))
\]

(13)

The value of \( k_d \) calculated by Eq.(13) is shown in Fig. 10. In the calculation, Sauter mean diameter \( d_{32} \) is used as the drop diameter \( d \) in Eq.(10), and the diffusion coefficient of iodine in heptane is estimated with the Wilke-Chang correlation by use of the observed value for CO2 in heptane (Sherwood et al., 1975) as shown in Table 1. Although \( k_d \) decreases with \( \theta_0 \), the change is very small for \( \theta_0 > 10 \) s. In the present experiments \( \theta_0 \) varies between 15 s and 51 s, and the effect of \( \theta_0 \) on \( k_d \) may be negligible.
The theoretical values of $k_d$ calculated for the experimental conditions are shown in Fig. 8 with two lines as largest and smallest values for various flow rates of the dispersed and the continuous phase. The variation of calculated $k_d$ with the flow rates is small and it mainly depends on the change in drop diameter which varies with the average residence time, i.e., the dispersed phase holdup. Though all experimental values are larger than the theoretical ones, the difference between them is small. It can be concluded that the dispersed phase mass transfer coefficient can be calculated based on the diffusion model within the droplet by taking into account the residence time of the drops.

2.6 Continuous phase mass transfer coefficient

According to the addition rule of mass transfer resistance expressed by the volumetric mass transfer coefficients

$$1 / K_c a = (1 / k_d a) + (1 / mk_c a)$$

(14)

the volumetric mass transfer coefficients, $k_c a$, in the continuous phase are determined from $K_{c a}$ in Figs. 2 and 3 and $k_{d a}$ in Figs. 6 and 7. As shown in Fig. 11, $k_c a$ is proportional to the specific interfacial area, that is, $k_c$ varies little with the agitation speed or the flow rates of dispersed and continuous phases.

The dispersed drops are circulated with the continuous phase below the impeller in the mixer. When the drop diameter is small as in the present experiment, the relative velocity between the drop and the continuous phase may be small, which depends on the gravitational force. Here, we assumed that the relative velocity is expressed by the terminal settling velocity of a rigid sphere having the same diameter and density as the dispersed drop. The terminal velocity, $v_t$, is given as follows (Kagakukogaku Benran, 1988).

$$v_t = d^2 \Delta \rho g / 18 \eta$$ for $Re < 1$

(15)

where $A_1 = 4.8 (\rho / \rho_d) d^{1/2}$, $A_2 = 2.54 (\Delta \rho g / \rho_d)^{1/2}$

The mass transfer coefficient around a rigid sphere is correlated by Ranz and Marshall (1952) as follows.

$$Sh_c = 2.0 + 0.60 Re^{1/2} Sc^{1/3}$$

(17)

The continuous phase mass transfer coefficients, $k_c$, for the present experiments is determined from values of $k_d a$ and $a$ obtained above, and $Sh_c$ is plotted against $Re^{1/2} Sc^{1/3}$ in Fig. 12, where $Re$ is calculated with the terminal velocities of drops as mentioned above. In the figure, Eq. (17) is also drawn with a solid line. The present experimental results coincide very well with the correlation of the solid line, that is, the continuous phase mass transfer coefficient can be given by the mass transfer coefficient around a rigid sphere calculated with the terminal settling velocity as the relative velocity between phases. The over-all volumetric mass transfer coefficients $K_{c a}$ for the conditions as in Figs. 2 and 3 are calculated from Eqs. (2), (7), (8), (13), (14) and (17). The calculated values are shown in Figs. 2 and 3 by broken lines, which agree very well with the observed values.

Conclusion

The volumetric mass transfer coefficients $k_d a$ of the continuous phase could be calculated from $K_{c a}$ and $k_{d a}$ by use of the addition rule of mass transfer resistance. By using the specific interfacial area $a$ estimated from the Sauter mean diameter $d_{50}$ of dispersed drops and the dispersed phase holdup $\phi$, the mass transfer coefficients $K_c$, $k_d$ and $k_c$ can be determined from $K_{c a}$, $k_{d a}$ and $k_d a$, respectively. The correlation for $K_c$ in the literature, which can be applied for a Kühni column, a RDC, an EC column and a PSE, can not be applied for the present MS column where the diameter of dispersed drops is smaller by about
one order of magnitude than those in above columns. The dispersed phase mass transfer coefficient $k_d$ depends on agitation speed but not on the flow rates of both phases. The value of $k_d$ coincides with the theoretical value based on the diffusion within a rigid sphere using the residence time distribution of dispersed drops. The continuous phase mass transfer coefficient $k_c$ does not vary with the agitation speed as well as the flow rates of both phases. The continuous phase mass transfer coefficient can be given by the correlation of mass transfer around a rigid sphere by use of the terminal settling velocity of a rigid sphere with the same diameter and density as the dispersed drop as the relative velocity between the dispersed drop and the continuous phase.

**Nomenclature**

- $A$ = cross sectional area of flow path around impeller [m$^2$]
- $a$ = specific interfacial area of dispersed phase [m$^2$/mol]
- $C$ = iodine concentration in continuous or dispersed phase [mol/m$^3$]
- $C_{C,out}$ = aqueous concentration in equilibrium with outlet organic phase; $C_{C,out}/m$ [mol/m$^3$]
- $D_i$ = diffusion coefficient of iodine in aqueous phase [m$^2$/s]
- $D_{k}$ = diffusion coefficient of iodine in organic phase [m$^2$/s]
- $d_i$ = impeller diameter [m]
- $d_d$ = drop diameter [m]
- $d_{s,2}$ = Sauter mean diameter of dispersed drops [m]
- $g$ = gravitational acceleration [m/s$^2$]
- $K_c$ = over-all mass transfer coefficient based on continuous phase concentration [m/s]
- $K_d$ = dispersion coefficient of dispersed drops [m/s]
- $k_c$ = continuous phase mass transfer coefficient [m/s]
- $k_d$ = dispersed phase mass transfer coefficient [m/s]
- $m$ = distribution ratio of iodine between aqueous and organic phases (—)
- $n$ = agitation speed [s$^{-1}$]
- $Q$ = flow rate of the continuous or dispersed phase [m$^3$/s]
- $Re$ = Reynolds number, $ ho_d u_d/\eta_d$ or $ \rho u_d/\eta$ (—)
- $Sc$ = Schmidt number, $ \nu/\alpha$ (—)
- $Sh_{OC}$ = Sherwood number with continuous phase over-all mass transfer coefficient, $k_{d,OC} D_{oc}$ (—)
- $Sh_c$ = Sherwood number with continuous phase mass transfer coefficient, $k_{d,oc} D_c$ (—)
- $t$ = time [s]
- $V_m$ = volume of mixer part [m$^3$]
- $V_d$ = volume below impeller [m$^3$]
- $V_i$ = volume above impeller [m$^3$]
- $v_d$ = slip velocity of dispersed drops to continuous phase [m/s]
- $v_i$ = terminal settling velocity [m/s]
- $We$ = Weber number, $n^2 D_i^3 p_d/\gamma$ (—)
- $\gamma$ = interfacial tension [N/m]
- $\phi$ = holdup of dispersed phase (—)
- $\phi_d$ = holdup of dispersed phase below the impeller (—)
- $\phi_i$ = holdup of dispersed phase above the impeller (—)
- $\eta$ = viscosity of continuous phase [Pa s]
- $\theta$ = average residence time of dispersed drops [s]
- $\rho$ = density [kg/m$^3$]

$\Delta p$ = density difference between dispersed and continuous phases (kg/m$^3$)

<Subscript>
- $c$ = continuous phase
- $d$ = dispersed phase
- $in$ = inlet
- $out$ = outlet
- $t$ = residence time

**Literature cited**