EFFECT OF INTERACTIONS BETWEEN DIFFUSION FLUXES IN TERNARY DISTILLATION OF METHANOL-2-PROPanOL-WATER SYSTEM BY A VERTICAL FLAT PLATE WETTED-WALL COLUMN

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Experimental studies to the effect of interactions between diffusion fluxes in ternary distillation of the methanol-2-propanol-water system are made by a vertical flat plate wetted-wall column under total reflux conditions for wide ranges of vapor flow rates and liquid concentrations.

Observed vapor-phase diffusion fluxes are compared with the results of numerical analysis for ternary mass transfer in the laminar boundary layer with surface mass injection or suction. The effects of partial condensation of mixed vapors and interactions of diffusion fluxes are examined with reference to the laminar boundary layer theory for ternary mass systems. A correlation for the vapor-phase diffusion fluxes in ternary distillation is proposed by considering the effect of interactions between diffusion fluxes under high mass flux conditions.

Introduction

Mass transfer in multicomponent distillation is a very complicated phenomenon, where interactions between mass and heat fluxes through the boundary conditions at the vapor-liquid interface and interactions between diffusion fluxes of different species through concentration driving forces take place. Although some theoretical and experimental approaches\(^3\) have been made to mass transfer in ternary distillations with due consideration to multicomponent diffusion, few are known that take account of the effect of interactions between diffusion fluxes in the flow field.

In our previous papers, some numerical examinations were made of ternary mass transfer in a laminar boundary layer by considering the effect of interactions between diffusion fluxes with surface mass injection or suction. The purpose of the present work is to make an experimental study of heat and mass transfer in ternary distillation under total reflux conditions for wide ranges of vapor flow rates and liquid concentrations, and to compare the experimental results with the numerical ones by the laminar boundary layer theory for ternary systems\(^7\). Table 1 summarizes the numerical results for flux equations.*

Table 1. Flux equations by laminar boundary layer theory

<table>
<thead>
<tr>
<th>Flux equation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Nu}_x = \frac{q_x}{k(T_x - T_0)} = 0.332 \cdot R_e^{1/2} \cdot P_r^{1/3} \cdot g(F(0), P_r) )</td>
<td>Vapor-phase sensible heat flux</td>
</tr>
<tr>
<td>( \text{Sh}<em>{Ax} \left( \frac{J</em>{Ax}}{N_{Ax}} \right) = \frac{J_{Ax}}{\rho D_{dAx}} = Sh_{Ax} (J_{Ax}^0, N_{Ax}^0) \cdot P_A \cdot G_A )</td>
<td>Vapor-phase diffusion flux</td>
</tr>
</tbody>
</table>

where

\[ g(F(0), P_r) = \begin{cases} 1 + 1.20 P_r^{0.68} F(0)^{0.04} & (F(0) > 0) \\ 1 - 0.96 P_r^{0.43} |F(0)|^{0.91} & (F(0) < 0) \end{cases} \]

\[ P_r = 1 + 0.64 \frac{Sc_{ij}^{0.18}}{Sc_{ij}^{0.19}} \frac{\Lambda_{ij}}{\Delta_{ij}} \]

\[ G_i = J_{ix}(N_{ix}, F(0)) = 0 \]

\[ Sc_{ij} = \sqrt{D_{ij}} \]

* The effect of thermal diffusion is not considered in the present study because the temperature differences between the vapor-free stream and the interface are less than 4 K.

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1. Experimental Apparatus and Procedures

1.1 Experimental apparatus

Figure 1 shows a schematic diagram of the experimental apparatus. The test section is a vertical flat plate wetted-wall column with a vapor-liquid contacting.
area 18 mm wide and 196 mm long, details of which were shown elsewhere.\(^5,9\) On the opposite side of the wetted-wall, two 0.25 mm-outer diameter sheathed Chromel-Alumel thermocouples at respective heights of 16 and 156 mm from the lower edge of the wetted-wall are mounted on separate traversing mechanisms for measurements of vapor-phase temperature profiles.

1.2 Measurements
1) Reflux flow rates and concentrations The bottom and top reflux flow rates are measured by two precision rotameters within 1\% error. The bottom and top concentrations of each component, \(c_{d,1}, c_{d,2}\), are measured by a gas chromatograph within an error of less than 0.1 mol%.

2) Mass and diffusion fluxes The vapor-phase average mass fluxes of each component, \(N_i\), are obtained from the top and the bottom reflux flow rates and concentrations, from which the average values for the normal components of the surface velocities, \(v_s\), and the vapor-phase average diffusion fluxes, \(J_{is}\), are calculated by the following equations:\(^1,6,8,9\)

\[
v_s = \frac{(N_A + N_B + N_C)}{\rho_{Gs}} \tag{7}**
\]

\[
J_{is} = N_i - (N_A + N_B + N_C)\omega_{is} \quad (i = A, B, C) \tag{8}
\]

The vapor-phase average diffusion fluxes are made dimensionless by: \(^7\)

\[
Sh_{GAA}(J_{is}/N_i) = J_{is}/\rho_{Gs}D_{GAA}\omega_{is} \tag{9a}
\]

\[
Sh_{GBB}(J_{is}/N_i) = J_{is}/\rho_{Gs}D_{GBB}\omega_{is} \tag{9b}
\]

** Because the differences between the top and the bottom liquid concentrations of each component are less than 3%, the surface concentrations of the vapor and the liquid are taken to be uniform in the data processing.

Table 2. Ranges of experimental variables

<table>
<thead>
<tr>
<th>(c_{d})</th>
<th>(0.18-0.87)</th>
<th>(0.10-0.66)</th>
<th>(0.54-0.60)</th>
<th>(0.66-1.16)</th>
<th>(0.61-2.70)</th>
<th>(0.70-7.43)</th>
<th>(0.82-0.86)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Re)</td>
<td>(10,000-22,100)</td>
<td>(11,000-22,100)</td>
<td>(1,15-2.70)</td>
<td>(4.70-7.43)</td>
<td>(P_{Gi})</td>
<td>(0.13-0.07)</td>
<td>(0.13-0.07)</td>
</tr>
</tbody>
</table>

where \(D_{GAA}\) and \(D_{GBB}\) are multicomponent diffusion coefficients defined by: \(^12\)

\[
D_{Gii} = D_{Gji}(1 - \gamma_i)D_{Gij}/S \tag{10a}
\]

\[
D_{Gij} = D_{Gij}(1 - \gamma_i)D_{Gji}/S \quad (i, j = A, B) \tag{10b}
\]

\[
S = y_AD_{GBC} + y_BD_{GAC} + y_CD_{GAB} \tag{10c}
\]

3) Surface temperatures and sensible heat fluxes The surface temperatures of the liquid film are determined by extrapolation of the observed vapor-phase temperature profiles to the vapor–liquid interface. The vapor-phase local sensible heat fluxes, \(q_{Gx}\), are calculated from the observed temperature gradients, \((\partial T/\partial y)_s\), by:

\[
q_{Gx} = -k_{Gx}(\partial T/\partial y)_s \tag{11}
\]

The vapor-phase local sensible heat fluxes are made dimensionless by: \(^5,9\)

\[
Nu_{Gx} = q_{Gx}/\kappa_{Gx}(T_s - T_{Gx}) \tag{12}
\]

4) Temperatures of inlet reflux liquid Temperature differences between the bubble points of the inlet reflux and the actual temperatures were kept within 5 K throughout this work.

1.3 Vapor-liquid equilibria and physical properties
Vapor-liquid equilibria of the methanol–2-propanol–water system were estimated from the vapor pressures of pure components by Antoine’s equation and the liquid-phase activity coefficients by Wilson’s equation, where Antoine’s constants and Wilson’s parameters by Gmehling et al.\(^4\) were used. The binary diffusion coefficients and the viscosities of pure vapors were estimated by Hirscher’s method\(^14\) and the thermal conductivities of pure vapors by Eucken’s method.\(^14\) The viscosities and the thermal conductivities of mixed vapors were estimated by Wilke’s method.\(^14\)

1.4 Ranges of variables
Distillation runs were made for the methanol–2-propanol–water system under total reflux conditions for various vapor-phase Reynolds numbers and liquid concentrations. Table 2 shows the ranges of experimental variables in the present study.

2. Experimental Results
2.1 Vapor-phase temperature profiles and sensible heat fluxes
Figure 2 shows an example of observed vapor-
phase temperature profiles at 76 mm from the lower edge of the wetted wall. The solid line in the figure represents the theoretical temperature profile for the same operating conditions and the dotted line the theoretical one for low mass flux conditions \( F(0) = 0 \) by a laminar boundary layer theory.\(^5\) The observed temperature profile shows good agreement with the theoretical one. The observed surface temperature, \( T_{sob} \), also agrees well with the bubble point of the liquid at the interface, \( T_{b} \), concentrations of which are calculated from the bulk liquid concentrations by Higbie's penetration theory.\(^6 \) Similar comparisons for the other data were made to show that the observed temperature profiles were in good agreement with the theoretical ones and that the observed surface temperatures were the bubble points of the liquid at the interface.

Evaluations of individual mass transfer resistances in vapor and liquid phases showed that the order of magnitude of the liquid-phase resistances was less than 20\%, which indicates that heat and mass transfer processes in ternary distillation of the methanol–2–propanol–water system are vapor-phase controlled, as was the case for the acetone–methanol–ethanol system.\(^9\) For this reason, vapor-phase sensible heat and diffusion fluxes will be examined in later studies.

Figure 3 shows a correlation of the local Nusselt numbers in terms of vapor-phase local Reynolds numbers, \( Re_{Gv} \), where \( g(F(0), Pr_{Gv}) \) in the ordinate represents the effect of partial condensation of mixed vapors on the local Nusselt numbers estimated by Eq. (3). The solid line in the figure represents the theoretical values by Eq. (1). As was the case for ternary distillation of the acetone–methanol–ethanol system,\(^9\) the data showed good agreement with the theory.

### 2.2 Effects of Reynolds numbers and partial condensation of mixed vapors on the diffusion fluxes

Figure 4 shows the effect of vapor-phase average Reynolds numbers, \( Re_{G} \), on the average diffusion fluxes of methanol, \( J_{As} \). The solid line in the figure represents the theoretical values by the laminar boundary layer theory.\(^7\) The observed diffusion fluxes are in good agreement with the theoretical ones with a slope of 1/2. Similar results were obtained for the diffusion fluxes of 2-propanol.

Figure 5 shows the effect of partial condensation of mixed vapors on the average diffusion fluxes of methanol. The ordinate is the ratio of the observed diffusion fluxes to the theoretical ones under low mass flux conditions, \( J_{As}/J_{As,F(0)=0} \), and the abscissa is the average stream function at the interface, \( F(0) \), which is a measure of the effect of partial condensation of mixed vapors on the average diffusion fluxes given by:

\[
F(0) = \frac{1}{Z} \int_0^Z F(0)dx = -\frac{4}{3}(v/U)Re_0^{1/2}
\] \(^{(13)}\)
The solid line in the figure represents the theoretical values calculated by the method proposed in our previous paper. Good agreement is observed between the data and the theory. Similar results were obtained for the diffusion fluxes of 2-propanol.

### 2.3 Effect of driving forces on the diffusion fluxes

Figure 6 shows the effect of driving forces of methanol, $\Delta \omega_{GA}$, on the diffusion fluxes of methanol with the driving forces of 2-propanol, $\Delta \omega_{GB}$, as parameter. The ordinate is the diffusion fluxes corrected for the effect of partial condensation of the mixed vapors, $J_{Gd}/Ga$. The solid lines in the figure represent the theoretical values for the same operating conditions by the laminar boundary layer theory. Although a linear relation between the diffusion fluxes of methanol and their driving forces holds for this system, the diffusion fluxes are also affected by the driving forces of 2-propanol.

Figure 7 shows the effect of driving forces of 2-propanol on the diffusion fluxes of methanol. The solid lines in the figure represent the theoretical values. Although some scattering of the data is observed for a high value of $\Delta \omega_{GB}$, fairly good agreement between the data and the theory is observed. This may suggest a possibility of the effect of interactions between diffusion fluxes for this system.

To confirm this in more detail, the diffusion fluxes of methanol corrected for the effect of high mass flux ($F(0) < 0$***), $J_{A}(GdA\omega_{GA})$, are plotted against $(1/Sc_{GB})(\Delta \omega_{GB}/\Delta \omega_{GA})$, a parameter which represented the effect of interaction between diffusion fluxes in ternary mass transfer (Eq. (4)). Figure 8 shows the results. The solid line in the figure represents the theoretical values for low mass flux conditions ($F(0) = 0$***). Good agreement is observed between the data and the theory. Similar comparisons for the observed diffusion fluxes of 2-propanol were also made to show good agreement. These facts may indicate that the effect of interactions between the diffusion fluxes cannot be neglected for the methanol–2-propanol–water system in contrast with the acetone–methanol–ethanol system.

### 3. Correlation of Vapor-Phase Diffusion Fluxes in Ternary Distillation

Figure 9 shows the effect of interactions between diffusion fluxes on the diffusion fluxes of methanol and 2-propanol in ternary distillation. The ordinate represents ratios of the observed diffusion fluxes corrected for the effect of high mass flux to the theoretical ones for binary mass transfer under low mass flux conditions, $Sh_{GA}(J_{0}^{0} / \sqrt{N})$:

$$Sh_{GA}(J_{0}^{0} / \sqrt{N}) = 0.664 \cdot Re_{G}^{1/2} \cdot Sc_{GB}^{1/3}$$ (14)³

The abscissa is a measure of the effect of interaction between diffusion fluxes proposed in our previous paper.³ The solid line in the figure represents the correlation of numerical data for low mass flux conditions (Eq. (4)). Good agreement is observed between the data and the correlation. This may indicate that the low mass flux correlation for the
effect of interactions between diffusion fluxes is applicable to ternary mass transfer under high mass flux conditions, if due consideration to the effect of partial condensation is given.

To confirm this, the same data are plotted against vapor-phase Reynolds number in Fig. 10. The ordinate represents the diffusion fluxes corrected for the effect of partial condensation of mixed vapors by $G_t$ and of interactions between diffusion fluxes by $P_l$, respectively. The solid line in the figure represents the low mass flux correlation for binary mass transfer in a laminar boundary layer by Eq. (14). The data show good agreement with the correlation. These results mean that the diffusion fluxes in ternary distillation of the methanol–2-propanol–water system can be correlated by the following equation:

$$Sh_{Gt}(J_{i}^\circ/N_i^\circ) = Sh_{Gi}(J_{i}^\circ/N_i^\circ) \cdot P_l \cdot G_i$$

For comparison, the diffusion fluxes without correction for the effect of high mass flux and of interaction between diffusion fluxes are shown in Fig. 11. A large scattering of the data and deviation from the binary correlation is observed.

Conclusions

Experimental studies to heat and mass transfer in ternary distillation of the methanol–2-propanol–water system by a vertical flat plate wetted-wall column were made, with the following results.

1) The effects on the diffusion fluxes of partial condensation of mixed vapors and of interactions between diffusion fluxes are in good agreement with the numerical results.

2) The observed diffusion fluxes corrected for the effect of partial condensation of the mixed vapors and of interaction between diffusion fluxes showed good agreement with the binary correlation.

Nomenclature

- $Sh_{ij}$ = binary diffusion coefficient for $i$-$j$ pair [m$^2$/s]
- $D_{ij}$ = multicomponent diffusion coefficient for $i$-$j$ pair defined by Eq. (10) [m$^2$/s]
- $F$ = dimensionless stream function ($=-\psi/(\nu x U_\infty)^{1/2}$) [-]
- $F(0)$ = dimensionless stream function at interface ($=-2(x/\nu)^{1/2} Re^{1/2}$) [-]
- $F(0)$ = average dimensionless stream function at interface defined by Eq. (13) [-]
- $G_t$ = function defined by Eq. (5) [-]
- $g$ = function defined by Eq. (3) [-]
- $J_i$ = diffusion flux for $i$-th component [kg/(m$^2$ s)]
- $N_i$ = mass flux for $i$-th component [kg/(m$^2$ s)]
- $Nu_x$ = local Nusselt number ($=-q_x/\kappa (T_s - T_w)$) [-]
- $P_l$ = a function defined by Eq. (4) [-]
- $Pr$ = Prandtl number ($=c_p/\alpha k$) [-]
- $q_{Gx}$ = vapor-phase sensible heat flux [W/m$^2$]
- $Re_G$ = average Reynolds number ($=\rho U_\infty x/\mu$) [-]
- $Re_x$ = local Reynolds number ($=\rho U_\infty x/\mu$) [-]
- $Sc_G$ = multicomponent Schmidt number for $i$-$j$ pair defined by Eq. (6) ($=\nu D_{ij}$) [-]
- $T$ = temperature [K]
- $U$ = free stream vapor velocity [m/s]
- $v$ = $j$-component of velocity [m/s]
- $x$ = distance from lower edge of wetted wall [m]
\( y \) = distance from liquid surface [m]
\( y_i \) = vapor-phase mole fraction for \( i \)-th component
\( Z \) = length of wetted wall [m]
\( \Delta \omega_i \) = concentration driving force for \( i \)-th component
\( \eta \) = dimensionless distance \( = y (U_m/vx)^{1/2} \) [—]
\( \theta_i \) = dimensionless concentration \( = (\omega_i - \omega_b)/(\omega_i - \omega_w) \) [—]
\( \kappa \) = thermal conductivity [W/(m·s·K)]
\( \mu \) = viscosity [Pa·s]
\( \nu \) = kinematic viscosity [m²/s]
\( \rho \) = density [kg/m³]
\( \psi \) = stream function [s⁻¹]
\( \omega_i \) = mass fraction of \( i \)-th component

(Subscript)
\( A \) = most volatile component
\( B \) = intermediate component
\( b \) = bubble point
\( C \) = least volatile component
\( d \) = dew point
\( G \) = vapor phase
\( ob \) = observed value
\( s \) = vapor-liquid interface
\( 1 \) = bottom
\( 2 \) = top
\( \infty \) = vapor-free stream or main liquid stream

Literature Cited