Analysis of Performance of Packed Columns

There are two packed column experiments in the Unit Operations lab: Liquid-Liquid Extraction (LLE) and Gas Absorption (GA). In both of these experiments, a solute is removed from a carrier fluid and is absorbed by the solvent. The solvent is water in both experiments. The carrier fluid is a liquid (Isopar M) in the LLE experiment and air in the GA experiment. It can be assumed that the carrier fluid is immiscible with the solvent in both experiments. The information regarding the solute, solvent, and the carrier fluid is summarized in Table 1.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Solute</th>
<th>Carrier Fluid</th>
<th>Solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas absorption</td>
<td>CO₂ or ammonia</td>
<td>Air</td>
<td>Water</td>
</tr>
<tr>
<td>Liquid-liquid extraction</td>
<td>Methyl Ethyl Ketone</td>
<td>Isopar M</td>
<td>Water</td>
</tr>
</tbody>
</table>

In both experiments the carrier fluid has a lower density than water. Therefore, the carrier fluid and water are introduced at the bottom and top of the column, respectively, as illustrated in Figure 1.

$L'$ = molar flow rate of solvent  
$L$ = molar flow rate of solvent phase  
$V'$ = molar flow rate of carrier fluid  
$V$ = molar flow rate of carrier fluid phase  
$x$ = molar fraction of solute in solvent  
$y$ = molar fraction of solute in carrier fluid

Figure 1. Schematics of the packed column experiments.
Material Balance

The solute material balance around the dashed-line box in Figure 1 is

\[ L_{in}x_{in} + V(z)y(z) = L(z)x(z) + V_{out}y_{out} \]  (1)

Here, we use the notation introduced in Figure 1. In general, the flow rates \( L \) and \( V \) of the solvent and carrier fluid phases change along the column due to the solute mass transfer from one phase to another. On the other hand, the flowrates \( L' \) and \( V' \) of the inert solvent and the carrier fluid remain constant. The flowrates \( L' \) and \( V' \) are related to the flowrates \( L \) and \( V \) by the following relationships:

\[ L' = L(1 - x); \quad V' = V(1 - y) \]  (2)

Substituting (2) into (1), we obtain:

\[ L' \frac{x_{in}}{1 - x_{in}} + V' \frac{y(z)}{1 - y(z)} = L' \frac{x(z)}{1 - x(z)} + V' \frac{y_{out}}{1 - y_{out}} \]  (3)

This equation simplifies if the solute concentration is sufficiently low, so that \( L \approx L' \) and \( V \approx V' \):

\[ L'x_{in} + V'y(z) = L'x(z) + V'y_{out} \]  (4)

We will use the dilute solute approximation throughout this document. If necessary, this theory can be extended to the non-dilute solute case. The material balance (4) yields the following operating line equation:

\[ y = \frac{L'}{V'}x + \left( y_{out} - \frac{L'}{V'}x_{in} \right) \]  (5)

McCabe-Thiele Analysis

Let us approximate a packed column by a sequence of \( N \) equilibrium stages, as illustrated in Figure 2. Let \( x_m \) and \( y_m \) denote the solute molar fractions in the solvent and the carrier fluid at the \( m \)-th stage.

The operating line is the material balance for the dashed box in Figure 2. It now relates the molar fraction \( y_{m+1} \) of the solute in the carrier fluid stream entering the \( m \)-th stage with the molar fraction \( x_m \) of the solute in the solvent stream leaving the \( m \)-th stage,

\[ y_{m+1} = \frac{L'}{V'}x_m + \left( y_{out} - \frac{L'}{V'}x_{in} \right) \]  (6)

Each of the steps of the McCabe-Thiele diagram corresponds to a theoretical equilibrium stage.
Several examples of the McCabe-Thiele diagram are shown in Figure 3, where it is assumed that $x_{in} = 0$, which is the case in our systems. Typically, the inlet concentrations of the solute are known and a desired concentration of the solute in the extract and/or raffinate is specified. Figure 3a and b compare two systems with the same $x_{in}$, $y_{in}$, and $x_{out}$, but different $y_{out}$. It is clear that the number of theoretical stages can be reduced by decreasing the slope $L'/V'$ of the operating line. However, this results in the larger raffinate concentration $y_{out}$, which may be undesirable. On the other hand, increasing the slope of the operating line will reduce $y_{out}$ while increasing the number of theoretical stages. In extreme cases, such as that shown in Figure 3c, the required number of stages is infinite. A further increase of $L'/V'$ results in a pinch point, i.e. the operating and equilibrium lines intersect between $x_{in}$ and $x_{out}$ and the desired outlet compositions cannot be achieved.

Another example is shown in Figure 3d. Here, we attempt to maximize the extract concentration $x_{out}$ for given $x_{in}$, $y_{in}$, and $y_{out}$. The largest $x_{out}$ can be achieved by decreasing the slope of the operating line until it intersects with the equilibrium line at $y = y_{in}$. Further decrease of $L'/V'$ will result in a pinch point on the diagram. Of course, in practice, one should choose an operating line corresponding to a finite number of theoretical stages.

McCabe-Thiele diagrams are useful for determining a reasonable range of flowrates $L'$ and $V'$ and qualitative analysis of a packed column. However, to make a quantitative prediction of the product compositions, one needs to know the number of theoretical stages in a packed column. This requires analysis of mass transfer across the solvent/carrier fluid interface, reviewed in the next section.
Mass Transfer Coefficients

Let subscript \( I \) denote the interface between the solvent and the carrier fluid, i.e. \( x_I \) and \( y_I \) are the solute concentrations on the opposite sides of the interface (see Figure 4). The solute transport from the carrier fluid to the solvent consists of the following steps:

1. Diffusion from the bulk carrier fluid to the interface between the carrier fluid and the solute. The driving force for this diffusion is the concentration difference \((y - y_I)\)
2. Transport across the interface.
3. Solute diffusion from the interface to the bulk solvent; the driving force for this diffusion is the concentration difference \((x_I - x)\).
The molar rate $\dot{N}$ (mol/s·m²) of solute transfer per unit area of the interface is

$$\dot{N} = k_y (y - y_I) = k_x (x_I - x). \quad (7)$$

Here, $k_x, k_y$ are the film mass transfer coefficients and subscript $I$ denotes the interface between the carrier fluid and the solvent. Eq. (7) states that the rate of the solute transport is proportional to the difference between the solute concentrations in the bulk fluid and at the interface. Since it is difficult to measure the interfacial area, one usually measures $k_xa$ or $k_ya$, where $a$ is the interfacial area per unit volume of packing. Then Eq. (7) becomes

$$\frac{Rate}{Volume} = \dot{N}a = k_y a(y - y_I) = k_x a(x_I - x). \quad (8)$$

The solute concentration at the interface $(x_I, y_I)$ is also difficult to measure. Therefore, it is more convenient to use overall mass transfer coefficients,

$$\dot{N}a = K_y a(y - y^{*}) = K_x a(x^{*} - x), \quad (9)$$

where $y^{*} = y^{*}(x)$ is the equilibrium molar fraction of the solute in the carrier fluid corresponding to the solute concentration $x$ in the solvent; $x^{*} = x^{*}(y)$ is similarly defined. Eq. (9) states that the rate of the solute transport is proportional to the difference between the actual and equilibrium solute concentrations.

There is a simple connection between the overall and film mass transfer coefficients when the equilibrium solvent concentration satisfies Henry’s law,

$$y^{*}(x) = mx \quad (10)$$

This law is valid at sufficiently small solute concentrations.

Substituting (10) into (9), we obtain

$$K_x = mK_y \quad (11)$$

Let us now connect the overall mass transfer coefficients $K_x$ and $K_y$ with the film mass transfer coefficients $k_x$ and $k_y$. Assume equilibrium at interface, i.e. $y_I = y^{*}(x_I) = mx_I$. Then
\[ y - y^* = (y - y_i) + (y_i - y^*) = (y - y_i) + m(x_i - x) = \dot{N}a \left[ \frac{1}{k_y a} + \frac{m}{k_x a} \right] \] (12)

The last equality in Eq. (12) follows from Eq. (8). Note also that from Eq. (9) it follows that

\[ y - y^* = \frac{\dot{N}a}{K_y a} \] (13)

Combining Eq. (12) and (13), we obtain

\[ \frac{1}{K_y a} = \frac{1}{k_y a} + \frac{m}{k_x a} \] (14)

Each term in Eq. (14) corresponds to the resistance to solute transport. Therefore, the overall resistance is a sum of resistances of different phases. If \( m \) is very large, the transfer is solvent-phase controlled and if \( m \) is small, the transfer is carrier fluid-controlled. For example, for CO\(_2\) absorption in water, \( m \) is large which indicates that CO\(_2\) poorly dissolves in water, which implies that the CO\(_2\) absorption is liquid-phase controlled. On the other hand, ammonia is very soluble in water and, hence, ammonia absorption is gas-phased controlled.

**Transfer Unit Analysis**

Consider the mass transfer of solute in a segment of the column of height \( dz \). The volume of this segment is \( A_c dz \), where \( A_c \) is the area of the column cross-section.

Rate of mass transfer in a segment of the column of height \( dz \) is

\[ \dot{N}aA_c dz = K_y a[y(z) - y^*(z)]A_c dz = K_x a[x^*(z) - x(z)]A_c dz \] (15)

On the other hand, the number of moles leaving the carrier phase and entering the solvent is

\[ -d(V'y) = d(L'x) = \dot{N}aA_c dz \] (16)

Combining equations (15) and (16), we obtain:

\[ dz = -\frac{d(V'y)}{K_y aA_c[y(z) - y^*(z)]} \] (17)

Assuming that \( K_y a \) is constant, we can integrate (17) from \( z = 0 \) to \( z = h \), where \( h \) is the total height of the packing. This gives us

\[ h = \frac{V'}{K_y aA_c} \int_{y_{in}}^{y_{out}} \frac{dy}{y^* - y} = H_{OG}N_{OG} \] (18)

Here,

\[ H_{OG} = \frac{V'}{K_y aA_c} \] (19)

is the **height of the transfer unit** and
\[ N_{OG} = \int_{y_{in}}^{y_{out}} \frac{dy}{y^* - y} \]  

is the number of transfer units in the column.

Similarly, we can integrate over the liquid composition,

\[ dz = \frac{d(L'x)}{K_x a A_c (x^* - x)} \]

Assuming that \( K_x a \) is constant throughout the column, we obtain

\[ h = \frac{L'}{K_x a A_c} \int_{x_{out}}^{x_{in}} \frac{dx}{x^* - x} = H_{OL} N_{OL}, \]

where

\[ H_{OL} = \frac{L'}{K_x a A_c} \]

is the height of the transfer unit and

\[ N_{OL} = \int_{x_{in}}^{x_{out}} \frac{dx}{x - x^*} \]

is the number of transfer units in the column.

It is recommended to use \( K_y \) (and \( H_{OG}, N_{OG} \)) to characterize the mass transfer when major resistance to transfer is in the carrier fluid phase. Similarly, if the major resistance is due to the solvent phase, use \( K_x, H_{OL}, N_{OL} \).

Let us now discuss calculation of the integrals in Eqs. (20) and (24). Since these integrals are very similar, here we only discuss the calculation of Eq. (20) in detail.

**Numerical Integration**

In our Liquid-Liquid Extraction system, the equilibrium relationship \( y = y^*(x) \) is nonlinear. In this case, the integral in Eq. (20) should be computed numerically, e.g., using the trapezoidal rule:

\[ \int_{y_{in}}^{y_{out}} f(y)dy = \sum_{k=1}^{M-1} \left[ \frac{f(y_k) + f(y_{k+1})}{2} \right] \Delta y, \]

where \( f(y) \) is the function to be integrated,

\[ f(y) = \frac{1}{y^*(y) - y} \]
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\[ y_k = y_{in} + (k - 1)\Delta y, k = 1, ..., M \]  \hspace{1cm} (27)

are the grid points used in the numerical integration (note that they are not the same as \( y_k \)'s in the McCabe-Thiele analysis shown in Figure 3), \( M \) is the total number of grid points, and

\[ \Delta y = \frac{y_{out} - y_{in}}{M - 1} \]  \hspace{1cm} (28)

is the grid size. Note that, according to Eqs. (27) and (28),

\[ y_1 = y_{in} \text{ and } y_M = y_{out}. \]  \hspace{1cm} (29)

To perform the integration, we need to obtain the relationship between \( y(z) \) and \( y^*(z) \). To do this, we use the material balance (5) relating \( y(z) \) and \( x(z) \). Once \( x(z) \) is known, we can obtain the corresponding equilibrium concentration \( y^*(z) \) from the equilibrium curve. This will allow us to generate a table similar to the one below:

<table>
<thead>
<tr>
<th>( y(z) )</th>
<th>( x(z) )</th>
<th>( y^*(z) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( y_1 = y_{in} )</td>
<td>( x_1 = x_{out} )</td>
<td>( y_1^* = y^*(x_1) )</td>
</tr>
<tr>
<td>( y_2 = y_{in} + \Delta y )</td>
<td>( x_2 )</td>
<td>( y_2^* = y^*(x_2) )</td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>( y_M = y_{out} )</td>
<td>( x_{in} )</td>
<td>( y_M^* = y^*(x_M) )</td>
</tr>
</tbody>
</table>

This table provides the relationship between \( y \) and \( y^* \), which can be used to obtain \( f(y) \) and perform the summation (25).

**Analysis of Experimental Data**

For each of the experimental runs, you should:

- Verify material balance for the solute.
- Compute \( K_a \) or \( K_y \) using the approach outlined above.

It is recommended to record the data in a table similar to the one below:

<table>
<thead>
<tr>
<th>Run 1</th>
<th>( V ) (mol/s)</th>
<th>( L ) (mol/s)</th>
<th>( A ) (-)</th>
<th>( y_{in} ) (-)</th>
<th>( y_{out} ) (-)</th>
<th>( K_a ) or ( K_y ) (mol/s•m⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Run 2</td>
<td>( V_1 )</td>
<td>( L_1 )</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>...</td>
<td>( V_2 )</td>
<td>( L_2 )</td>
<td>...</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

**Empirical Correlations for Mass Transfer Coefficient**
Using the experimentally obtained dependence of $Ka$ (here, $K = K_x$ or $K_y$) on the flow rates, obtain the parameters $C_1$, $C_2$ and $C_3$ in the following empirical correlation:

$$Ka = C_1 V^{C_2} L^{C_3}. \quad (30)$$

Take natural logarithm,

$$\ln(Ka) = \ln C_1 + C_2 \ln V + C_3 \ln L \quad (31)$$

and plot data from the runs corresponding to the same $V$ but different $L$ on a log-log plot and obtain constant $C_3$ from the slope of this regression line, as illustrated in Figure 5. Similarly, plot $\ln(Ka)$ versus $\ln V$ and obtain $C_2$ from the slope of the corresponding regression line. $C_1$ can be obtained from the average intercept of these two lines.

![Figure 5. Example of log-log plot of $K_a$ versus $L$ at constant $V$](image)

**References**

1. Perry’s Chemical Engineers Handbook.