SOLVENT EXTRATION N°1

English Translation by

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I. Background

Solvent extraction (or liquid-liquid extraction) is an isothermal unit operation involving two immiscible or partially miscible liquid phases in direct contact. The goal is to transfer one or more solutes from one liquid phase to another, thereby achieving a separation.

A single liquid extraction stage involves three steps, illustrated in Figure 1 for the case of one transferring solute:

- Mixing of the liquids, one of which (the feed mixture) contains the solute. The other (the solvent) has a higher affinity for the solute.

- Solute transfer from the feed mixture to the solvent. The direction of transfer is such that the phases approach an equilibrium condition. In an ideal equilibrium stage, the phases achieve equilibrium.

- Phase separation or disengagement, usually driven by a density difference.

The solvent phase leaves as the extract, which is now richer in solute. Ideally, the extract would contain all of the feed solute, but phase equilibrium conditions are almost never that favorable. Thus, some solute remains in the raffinate product, but the raffinate is leaner in solute than the feed.

Figure 1: Schematic of a solvent extraction stage.

In order to achieve a high degree of solute removal from the feed mixture, multiple stages are used (as in absorption and other separations driven by phase equilibrium effects). Such stages can be individual physical units, or they can be combined in a column.

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1 Perry’s Handbook, 7th Ed., Ch. 15 covers liquid-liquid extraction in more detail than is possible here.
configuration. In either case, the phases flow from stage to stage counter-currently as in absorption.

The solute transfer rate depends strongly on the interfacial area available for mass transfer. To encourage a high transfer rate, liquid extraction devices are designed to mix the phases intimately, leading to a high interfacial area.

II. Ternary liquid-liquid phase equilibria

1 – Partition Coefficient

Assume that a solute $B$ has equilibrated between two partially miscible liquid phases, one of which is mainly chemical $A$, and the other mainly chemical $C$. Let the $B$ concentration in the equilibrated phases be $x$ and $y$. The partition coefficient is the ratio of these concentrations, for example: $m = y/x$. The definition is somewhat arbitrary: various concentration units are used (e.g., mass fraction, mol fraction) and the ratio could be inverted, so be careful and consistent.

2 – Ternary LLE Diagram

It is convenient to display ternary liquid-liquid equilibria (LLE, at constant temperature and pressure) on an equilateral-triangle ternary diagram, an example of which appears below. Each triangle vertex represents a pure chemical (species $A$, $B$, and $C$ in this example). The composition of a mixture, such as the point $M$ in Fig. 2, is obtained by drawing projections parallel to each base through the mixture point, as shown. For example, to read the % B for point $M$, calculate the ratio $CM_B / CB$, where $CM_B$ represents the distance between points $C$ and $M_B$, etc. Thus, point $M$ is about 40% B, 40% A, and 20% C.
Point £N represents a mixture of roughly 50% A and B, with no C. Notice that a line drawn through £N and the pure £C vertex also passes through £M, i.e., the three points are colinear. This implies that we could obtain mixture £M by mixing the appropriate amounts of mixture £N and pure £C. The inverse lever-arm rule gives the required proportions:

\[
\frac{\text{amount of } \ N}{\text{amount of } \ S} = \frac{\text{length } \ PM}{\text{length } \ PN}
\]

### 3 – Phase Boundaries

Figure 3: Ternary LLE diagram showing phase boundaries and equilibrium tie lines
Figure 3 shows a ternary system in which two of the chemicals (A and S) are partially miscible, and the other two pairs (A and B, and B and S) are totally miscible. Zone (1) is a single-phase region. Points inside the curve \( f' - f - f'' \), i.e., zone (2), are mixtures that separate spontaneously into two equilibrium liquid phases. One phase will have a composition somewhere along the phase boundary \( f' - f \), and the other will be somewhere along the other phase boundary, \( f - f'' \). The line joining such a pair of phases in equilibrium is a tie line.

For example, point \( M \) is within zone (2), so it will separate into two equilibrium phases. Suppose the line going through \( M \) is a tie line, and that it crosses the phase boundaries at points \( R \) and \( E \), i.e., \( R, E, \) and \( M \) are colinear and on a tie line. Thus, \( R \) and \( E \) are the equilibrium phases obtained when \( M \) separates spontaneously. Also, the inverse lever rule gives the phase proportions, as follows:

\[
\frac{\text{amount E}}{\text{amount R}} = \frac{RM}{ME}
\]

Points along the line \( f'f'' \) represent mixtures of \( A \) and \( S \) (and zero \( B \)) that will split into equilibrium phases having compositions \( f' \) and \( f'' \). In other words, \( f' \) and \( f'' \) give the mutual solubilities of \( A \) and \( S \). As one adds \( B \), the tie lines change slope and become shorter, eventually disappearing at the critical point, \( f \).

Most literature data give a few tie-line composition pairs. You must either interpolate as best you can to obtain other tie lines, or fit the data to a thermodynamic model, then use the model to interpolate. The former approach is better unless you expect to re-use the model for another purpose.

### 4 – Staged separation

![Figure 4](image)

Figure 4: Three representations of a ternary system with limited miscibility.
Imagine a point $F$ along the line $AB$ in Fig. 4. Such a point cannot separate spontaneously into two liquid phases ($A$ & $B$ are completely miscible). Suppose that points $F$, $M$, and $S$ are colinear. Then mixing the appropriate proportions (inverse lever rule) of pure $S$ and mixture $F$ will yield mixture $M$. Finally suppose $R$, $M$ and $E$ are colinear and on a tie line. Then $M$ will separate into mixtures $R$ (the raffinate) and $E$ (the extract) the latter being more rich in $B$. In general, the location of $M$ governs the compositions of $R$ and $E$.

Figure 4 shows two other common ways to represent ternary LLE. The right triangle diagram in the middle shows the same data on an A-free basis. The vertices $B$ and $S$ represent 100% $B$ and 100% $S$ respectively. The other vertex is 0% $B$, 0% $S$. You read any point on this diagram as a certain %$B$ and %$S$, with the balance, % $A = 100 - %B - %S$. In effect, we have reduced the ternary system to a binary representation. $R$ and $E$ represent a raffinate and extract in equilibrium, as before. Let $x$ be the % of $B$ in the raffinate, and $y$ the % of $B$ in the extract. Then the locus of all possible extract/raffinate combinations generates an $x$-$y$ diagram like the one on the right-hand side of Fig. 4. This can be used to step off equilibrium stages, just as in absorption or other equilibrium-stage unit operations.

### III. Liquid Extraction Processes

#### 1 – Single Stage

Given a quantity of solution $F$ containing solute $B$, one adds a quantity of solvent $S$ (not necessarily pure). Assume that $M$ is the resulting mixture point colinear with $F$ and $S$, and that it is inside zone (2). Mixture $M$ separates to form extract $E_1$ and raffinate $R_1$ (see Fig. 5).

![Figure 5: Single-stage extraction.](image)

#### 2 – Multi-stage, cross-flow

If a single extraction stage doesn’t recover enough of the solute, raffinate $R_1$ can be contacted with additional solvent, forming another extract $E_2$ and raffinate $R_2$. This can be
repeated for \( n \) stages, as shown in Fig. 6. The \( n \) extracts, \( E_1 \) to \( E_n \), can be combined to form a single product.

\[ E_1 \quad E_2 \quad E_3 \quad \ldots \quad E_n \]

**Figure 6**: Multi-stage extraction, cross-flow of solvent.

**IV. Multi-stage, counter-current extraction**

The process shown in Fig. 6 can achieve a high recovery of B from mixture F, but at the cost of a high solvent consumption and a combined extract product that is dilute in B. Although the solvent, S, is chosen to make a subsequent S/B separation easy (e.g., by distillation), it is economically advantageous to minimize solvent use. A counter-current arrangement does this. See Figure 7. If these are equilibrium stages, the streams exiting stage \( i \), \( E_i \) and \( R_i \), are in equilibrium, and must correspond to a tie-line pair on the LLE diagram.
Mass Balance (steady state)

For a system boundary around the entire column, the steady-state conservation of total mass and solute gives:

Total mass: \( m_F + m_S = m_E + m_R = m_M \)

Solute B: \( x_F m_F + x_S m_S = y_1 m_E + x_n m_R = x_M m_M \)

where \( m_i \) is the mass flow rate of stream \( i \), and \( x_i \) or \( y_i \) is the solute mass fraction in stream \( i \). These equations have 8 unknowns. They can be solved for 2 unknowns if the other 6 are specified. In the experiment, the mass rates and compositions of the feed and solvent will be specified. Setting two other variables, e.g., \( x_n \) and \( m_R \), allows the equations to be solved.
The mass balance can also be solved graphically. Let a point M on the ternary diagram represent a hypothetical homogeneous mixture obtained by combining the two process feed streams. At steady-state, it must also represent the mixture one would obtain by combining the two product streams. Point M must be colinear with points F and S, and with points E and R. Thus, once F and S have been located, the solvent-to-feed ratio, \( m_S / m_F \) (and the inverse lever-arm rule) determines the location of M (see also its determination using the two mass balance equations above). Then if point R is chosen (it must be somewhere on a phase boundary), point E is determined by the point where a line through R and M crosses the other phase boundary. Alternatively, choosing point E determines point R.

Once point E is known (= \( E_1 \)), if we assume ideal equilibrium stages, the equilibrium tie line through \( E_1 \) determines the location of \( R_1 \). Next we would like to determine \( E_2 \) (the passing stream for \( R_1 \)). To do so, define a mass balance envelope that goes around one end of the column (say the end where \( E_1 \) exits) and cuts through the passing streams of interest (\( R_1 \) and \( E_2 \) in this case). In general, for the passing streams between stages \( i \) and \( i+1 \), we get

\[
\begin{align*}
\text{Total mass:} & \quad m_{R_i} - m_{E_{i+1}} = m_F - m_E = m_D \\
\text{Solute B:} & \quad x_{R_i} m_{R_i} - y_{E_{i+1}} m_{E_{i+1}} = x_F m_F - y_E m_E = x_D m_D
\end{align*}
\]

where \( D \) is a hypothetical mixture composition representing the difference between the upward and downward flowing phases. There is no introduction or removal of material at an intermediate stage in the column, so this same \( D \) point must apply for each set of passing streams. To locate it graphically, note that F, E and D must be colinear, and S, R and D must be colinear. Thus, point D is the intersection of a line through F and E with a line through R and S. NOTE: D is hypothetical and usually lies outside the ternary diagram, as in the example in Fig. 8. If so, at least one of the compositions defining D is negative.

Once D has been established it is possible to step off stages as follows:

1. To determine \( E_{i+1} \), the unknown passing stream between stages \( i \) and \( i+1 \), Draw a line through the known point \( R_i \) and D. \( E_{i+1} \) must be on this line, and it must also be on the phase boundary opposite \( R_i \). Thus, \( E_{i+1} \) is determined.

2. Use a tie line from \( E_{i+1} \) to locate point \( R_{i+1} \).

3. If stage \( i+1 \) is not the last, i.e., if \( x_{i+1} > x_R \), repeat steps 1 and 2.
In general, unless you have been very fortunate in your choice of E and R, you won’t hit \( x_R \) perfectly with an integer number of equilibrium stages. You can determine how much you would overshoot the assumed \( x_R \) in one more stage, then use linear interpolation to determine the hypothetical fractional needed to achieve \( x_R \).

\[
\begin{align*}
B & \quad E = E_1 \\
F & \quad E = E_2 \\
R_1 & \quad E = E_3 \\
D & \quad R_n = R
\end{align*}
\]

\( S \)

**Figure 8**: Graphical determination of the number of equilibrium stages.

The *minimum solvent-to-feed ratio* needed to achieve a particular separation corresponds to a choice of R and E such that one of the lines through point D coincides with a tie line. This represents a *pinch condition* for which compositions no longer change from stage to stage. In other words, an infinite number of stages would be needed to achieve the separation. The pinch can occur at one end of the column or somewhere in the middle. If the solvent is a pure material, as in Fig. 8, the pinch can’t occur at the end where the solvent enters (there will always be a mass transfer driving force at that end).

To determine whether the pinch occurs at the other end, locate (by interpolation) a tie line that, when extended, would go through point F. The E defined by this tie line is a potential condition of \( \left( \frac{m_S}{m_F} \right)_{\text{min}} \) because the line through E and F also defines point D. It is the true pinch location if you are able to step stages from the other end of the column until you reach the pinch.

Another check is to plot the equilibrium and operating lines in the format of the right-most graph in Fig. 4. The operating line is the locus of all passing stream compositions, which can be obtained by radiating lines from the D point, as in Fig. 8. If the operating line touches but does not cross the equilibrium line, you have determined the true pinch condition. If you have assumed a pinch at the end but this causes the operating line to cross the
equilibrium line, the pinch must be in the middle, and you will have to find it by graphical trial and error.

In practice, one chooses \( m_S / m_F \) such that

1. \( m_S / m_F > (m_S / m_F)_{\text{min}} \), and

2. The extraction factor is between about 1.5 and 2. The extraction factor is

\[
\varepsilon = m \frac{m_E}{m_R}
\]

where \( m \) is the partition coefficient.

If the extraction factor is too small, a large number of stages will be needed to achieve the desired separation. A large value implies that the process is using a large solvent flow rate, which reduces capital costs but increases operating costs. The above guidelines are a rule-of-thumb that usually results in an economical operation.
V. Experiment

1 - Objective

The goal is to recover acetone from a cyclohexane/acetone mixture using water as the solvent. The available equipment is a plate-type extraction column with a Rushton-type mechanical mixer between plates to disperse one phase within the other (thereby increasing mass-transfer surface area). Flow is counter-current, by gravity (phase density differences).

2 - Materials

Figure 9 is a schematic. Numbered items there are as follows:

1 : Light-phase feed vessel (light = organic).
2 : Light-phase feed pump, positive displacement. *
3 : Heavy-phase feed vessel (heavy = aqueous).
4 : Heavy-phase feed pump, positive displacement. *
5 : Heavy-phase feed line.
6 : Upper glass decanter for disengaging the exiting light product from the incoming heavy feed.
7 : Rushton-type extraction column.
8 : Sampling points for light and heavy phases.
9 : Lower decanter for disengaging the exiting heavy product from the incoming light feed.
10 : Heavy phase product line arranged in a u-tube to keep the column from emptying.
11 : Heavy product storage vessel.
12 : Light product line.
13 : Light product storage vessel.
14 : Turbine agitation control **
15 : Heavy phase flow meter.
16 : Light phase flow meter.

* Regulate pumping rate by adjusting the frequency and amplitude of positive-displacement pulsations.

** The Rushton turbine RPM can be adjusted manually.
Figure 9: Schematic of the Liquid-Liquid Extraction System.
3 - **Conditions**

- Feed solution is cyclohexane with dissolved acetone as the solute.
- Solvent is water.
- Initial feed solution rate settings: pulsation 60, course 60.
- Initial solvent rate settings: pulsation 50, course 50.

![Diagram of experiment](image)

**Figure 10**: Overview of the Experiment.

4 - **Procedures**

- Verify that the two feed vessels contain enough solution to perform a run.
- Turn on the power at the control panel. Get help from the instructor the first time.
- Set the pumps to the desired rates (piston amplitude and pulsation frequency).
- Turn on the turbine and set/note the rotational speed.
- Verify that the product vessels are receiving liquid.
- Use the valve on the heavy product line to regulate the location of the phase disengagement interface. If the heavy phase is the dispersed phase, this interface will be at the bottom of the column, in decanter (9). If the light phase is dispersed, the interface will be in the other decanter (6). The goal is a *steady* interface location.
• Take a sample of the feed solution (from the feed tank, not the pump exit).
• About every 15 minutes, take an extract sample and analyze it (gas chromatography, GC). Wait for steady state.
• Use GC to determine the steady-state compositions of both feeds and both products.
• Measure feed and product rates. For the feeds, use the graduations on the feed tanks. For the products, use the rotameters and/or the amount collected in a small container over a measured time period.

6 – Variables

• Change the solvent rate to: course 30, pulsation 30. Hold other settings at their initial values (given in section 3).
• Use turbine position 2, with the feed and solvent rates at their Section 3 conditions.
• Change the feed solution rate to: course 40, pulsation 90. Hold other settings at the values given in section 3.

7 – Report requirements

• Draw the ternary diagram (see data below).
• Show points corresponding to the feed solution, raffinate, and extract.
• Determine graphically the number of equilibrium stages provided by the column and the HETP.
• Calculate the selectivity, \[ S = \frac{\left[ x_{\text{solute}} / x_{\text{inert}} \right]_{\text{extract}}}{\left[ x_{\text{solute}} / x_{\text{inert}} \right]_{\text{raffinate}}} \], where cyclohexanone is the inert in the extract phase, and water is the inert in the raffinate phase.
• Use the inverse lever rule and your diagram to calculate the solvent/feed ratio. Compare to the actual.
• Check the component mass balances.
• Calculate the extraction factor and % solute recovery from the feed.
• Determine and comment on the effects of the system variables.
VI – Data

The following data give % by mass for the ternary cyclohexane/acetone/water system at 20 C, 1 bar. Use the first table to plot the phase boundaries. Use the second table to locate tie-line pairs on the two phase boundaries.

1. Phase boundary points

<table>
<thead>
<tr>
<th>Cyclohexane (%)</th>
<th>Acétone (%)</th>
<th>Eau (%)</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
<td>S</td>
</tr>
<tr>
<td>67.53</td>
<td>31.98</td>
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<td>47.81</td>
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<td>38.88</td>
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<td>17.02</td>
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2. Tie line points

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<th>Organic Phase Acetone (mass %)</th>
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</thead>
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