

Design of Liquid-Liquid Extraction Columns

All rights reserved, Armando B. Corripio, Ph.D., P.E., 2014
Cain Department of Chemical Engineering Corripio@LSU.edu
Louisiana State University, Baton Rouge, LA

Contents

Design of Liquid-Liquid Extraction Columns.....	1
Introduction	2
1 Liquid-Liquid Extraction	2
2 Balances on Liquid-Liquid Extraction	3
Case A. The Raffinate Product Composition is Specified	7
Case B. The Solute Recovery is specified	8
3 Determining the Number of Required Equilibrium Stages	9
Example 1. Extraction of Acetone from Methyl-Isobutene-Ketone (MIK) (Taken from McCabe, Smith and Harriott, <i>Unit Operations of Chemical Engineering</i> , 7 th ed., Example 23.3, page 784.) A countercurrent extraction plant is used to extract acetone from its mixture with water by means of methyl-isobutene-ketone (MIK) at a temperature of 25°C. The feed consists of 40 weight% acetone and the balance water. Pure solvent is to be used and the column operates at 25°C and the feed flow is 8,000 kg/hr. How many ideal stages are required to extract 99% of the acetone fed using a reasonable solvent rate? What is the extract composition after removal of the solvent? ..	11
4 Determining the Diameter of a Liquid-Liquid Extraction Column	17
4.1 Column Diameter	17
Example 2. Sizing the Acetone-Water-MIK Extraction Column .	19

4.2 Column Height	21
5 Insoluble Diluent and Solvent	21
6 Extraction of Dilute Solutions	22
7 Parallel Extraction	22
Example 3. Batch Parallel Extraction of a Dilute Solution.	22
Summary	26
Review Questions	26
Problems	28

Introduction

Liquid-liquid extraction is an important unit operation used to separate liquid components when distillation is difficult and/or expensive. Many textbook extraction problems are difficult to solve when the solvent inlet flow is specified, sometimes as a multiple of the minimum solvent flow; however, engineers in industry are usually free to choose the solvent flow as a design variable. The difficulty of solving the liquid-liquid extraction problem is reduced when the extract product composition is selected for the design variable instead of the solvent inlet flow, as will be demonstrated here.

1 Liquid-Liquid Extraction

Liquid-liquid extraction consists of extracting a solute from a liquid solution using a liquid solvent which is at least partially immiscible with the solution. This means that the

extract, consisting of the solute and the solvent, forms a separate liquid phase from the raffinate, consisting of the solute and the diluent. The diluent is the liquid in the original solution other than the solute.

The equipment from extraction can be a series of countercurrent stages, each consisting of a mixer and a decanter or settler, arranged in a countercurrent cascade, or in a tray or packed tower, as Figure 1 shows.

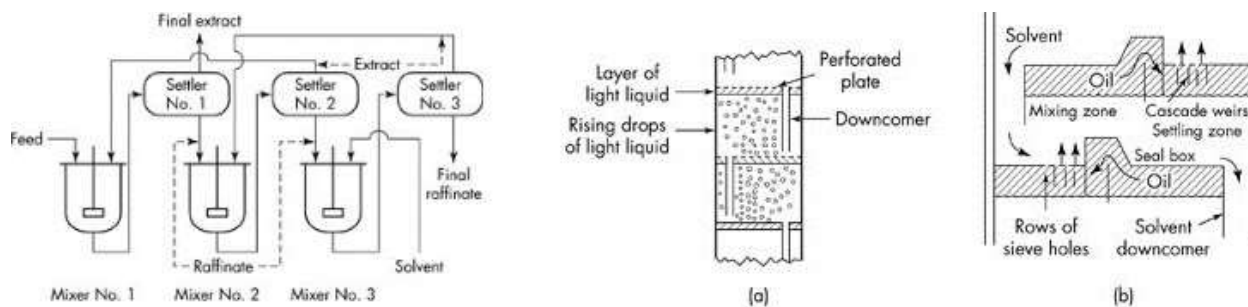


Figure 1. Extraction Cascade of Mixers and Settlers, and Extraction Tray Tower

When a tower is used one of the phases, called the dispersed phase, bubbles through the other, called the continuous phase. The less dense or light phase flows up the tower while the denser or heavy phase flows down the tower. The trays or dispersers can be designed so that either phase can be the disperse phase.

2 Balances on Liquid-Liquid Extraction

In general, in liquid-liquid extraction all three components are present in both phases, that is, the diluent is partially soluble in the extract phase and the solvent is partially

soluble in the raffinate phase. This means that two weight fractions are needed to define each phase (the third fraction is obtained from the sum of the three weight fractions being equal to 1.0). In this notes we will use the following notation:

x = weight fraction of a component in the raffinate phase

y = weight fraction of a component in the extract phase

Subscripts: A for the solute

 B for the diluent

 S for the solvent

Notice that these are capital letters. The lower case letters are used for the following subscripts: a for the flows and compositions at the end of the cascade or tower where the feed enters and the extract leaves, and b for the other end. So, for example, x_{Aa} is the weight fraction of the solute in the feed, y_{Ba} is the weight fraction of the diluent in the extract. Figure 2 shows a schematic of a cascade:

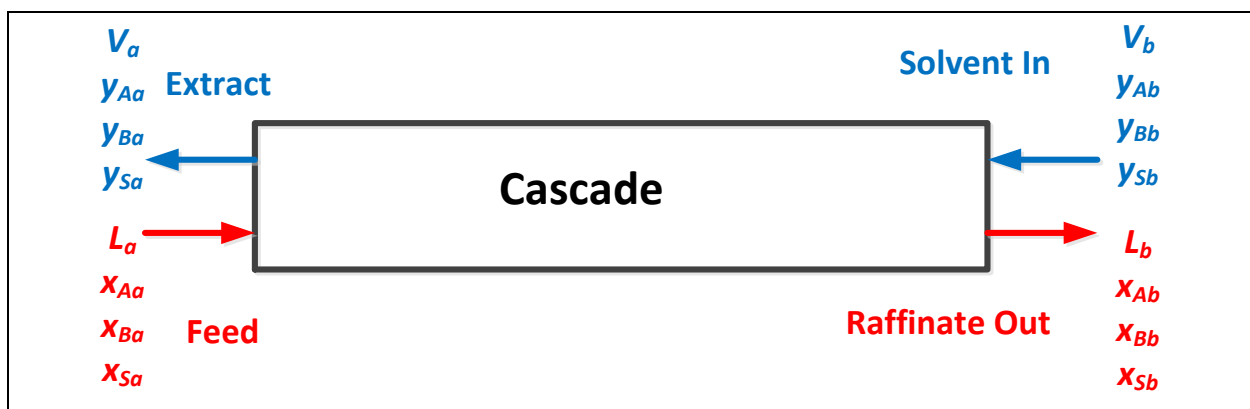


Figure 2. Schematic of a Liquid-Liquid Extraction Cascade

An extraction tower will be vertical with the same notation as Figure 2. If the raffinate phase is denser than the extract phase, the feed will enter at the top of the tower and flow down, and the solvent at the bottom and flow up. Otherwise the direction of flow will be reversed. The schematic of Figure 2 represents the complete battery of N stages used in the separation.

Figure 2 shows that there are twelve variables associated with the inlet and outlet streams to the cascade, the flow and two weight fractions of each of the four streams (the third weight fraction of each stream is determined by difference from 1.0). With three components, solute, diluent and solvent, we can write three independent mass balances:

$$\text{Total mass:} \quad L_a + V_b = L_b + V_a \quad (1)$$

$$\text{Solute mass:} \quad L_a x_{Aa} + V_b y_{Ab} = L_b x_{Ab} + V_a y_{Aa} \quad (2)$$

$$\text{Diluent mass:} \quad L_a x_{Ba} + V_b y_{Bb} = L_b x_{Bb} + V_a y_{Ba} \quad (3)$$

The solvent balance is not independent of these three. From experimental data we can obtain

- the solubility of the diluent in the extract, y_{Ba} , and
- the solubility of the diluent in the raffinate, x_{Bb} .

With these five relationships, we need seven specifications to define the problem.

In any design problem the feed flow L_a and two feed weight fractions, x_{Aa} and x_{Ba} , are known, as well as two solvent weight fractions, y_{Ab} and y_{Bb} , giving us five specifications. (If the

feed flow is not known, a *basis* is used, e.g., 100 kg, as the number of stages is not dependent on the total feed flow.) The last two specifications needed are

- either the solute recovery or the solute weight fraction in the raffinate product x_{Ab} , and
- either the solvent rate V_b or the solute weight fraction in the extract product y_{Aa} .

In a regular design problem the solvent flow V_b is a design variable the engineer can select. Higher solvent flow results in fewer required stages but a more dilute extract that is more costly to separate, while lower solvent flow results in a higher number of stages but a more concentrated extract. The problem is easier to solve if, instead of selecting the solvent flow, the extract product composition y_{Aa} is selected for the design variable. This is so because then the diluent composition, y_{Ba} , can be immediately determined from the solubility relationship or chart. The procedure for selecting the extract product composition is to look up the extract composition in equilibrium with the feed composition x_{Aa} and select a composition that is less than it, but not too much less. If the extract composition is selected as the value in equilibrium with the feed, the solvent rate will be the *minimum solvent rate* and the design will require an *infinite* number of stages.

There are then two possible versions of the design problem, one in which the composition of the raffinate product is specified, and the other in which the solute recovery is specified. Let us look at each of these in turn.

Case A. The Raffinate Product Composition is Specified

Let us first consider the problem where the raffinate product composition, x_{Ab} , is specified. This is also easier to solve than when the recovery of the solute is specified because the mass fraction of diluent in the raffinate, x_{Bb} , can be immediately determined from the solubility relationship or chart.

Solution. For the specifications assumed and the solubility relationships, all of the mass fractions in Equations (1) to (3), in addition to the feed flow L_a , are known. The equations form then a set of linear equations on the three unknown flows:

$$\begin{bmatrix} 1 & 1 & -1 \\ x_{Ab} & y_{Aa} & -y_{Ab} \\ x_{Bb} & y_{Ba} & -y_{Bb} \end{bmatrix} \begin{bmatrix} L_b \\ V_a \\ V_b \end{bmatrix} = \begin{bmatrix} L_a \\ L_a x_{Aa} \\ L_a x_{Ba} \end{bmatrix} \quad (4)$$

The solution of this system of equations is:

$$L_b = \frac{(y_{Ab}y_{Ba}-y_{Aa}y_{Bb})-(y_{Ab}x_{Ba}-x_{Aa}y_{Bb})+(y_{Aa}x_{Ba}-x_{Aa}y_{Ba})}{(y_{Ab}y_{Ba}-y_{Aa}y_{Bb})-(y_{Ab}x_{Bb}-x_{Ab}y_{Bb})+(y_{Aa}x_{Bb}-x_{Ab}y_{Ba})} L_a$$

$$V_a = \frac{(y_{Ab}x_{Ba}-x_{Aa}y_{Bb})-(y_{Ab}x_{Bb}-x_{Ab}y_{Bb})+(x_{Aa}x_{Bb}-x_{Ab}x_{Ba})}{(y_{Ab}y_{Ba}-y_{Aa}y_{Bb})-(y_{Ab}x_{Bb}-x_{Ab}y_{Bb})+(y_{Aa}x_{Bb}-x_{Ab}y_{Ba})} L_a$$

$$V_b = \frac{(y_{Aa}x_{Ba}-x_{Aa}y_{Ba})-(x_{Ab}x_{Ba}-x_{Aa}x_{Bb})+(x_{Ab}y_{Ba}-y_{Aa}x_{Bb})}{(y_{Ab}y_{Ba}-y_{Aa}y_{Bb})-(y_{Ab}x_{Bb}-x_{Ab}y_{Bb})+(y_{Aa}x_{Bb}-x_{Ab}y_{Ba})} L_a$$

Many modern calculators, MathCad, MATLAB, and other programs are capable of solving the system of linear equations (Equation 4). Given the complexity of the solution formulas given above it is probably better to use the features of the calculators and programs to avoid making a mistake in the calculations.

Case B. The Solute Recovery is specified

When the recovery of solute is specified instead of the raffinate product composition, the solubility relationship for the solvent in the raffinate must be solved along with the three balance equations. Given that the solute mass fraction in the raffinate product is also unknown, the equations to be solved are no longer linear. The solution must then be carried out by iteration as follows.

First assume the mass fraction of solvent in the raffinate product, x_{sb} . This is usually a small number near zero and zero is commonly assumed for the first iteration.

Next, calculate the mass flow of solute in the raffinate product as the amount not recovered:

$$L_b x_{Ab} = (1 - R) L_a x_{Aa} \quad (5)$$

Where R is the fraction of the solute recovered. The solute balance can be solved for the extract product flow when the solvent inlet stream does not contain solute, that is, when $y_{Ab} = 0$ or negligible:

$$V_a = \frac{L_a x_{Aa} + V_b(0) - L_b x_{Ab}}{y_{Aa}} \quad (6)$$

Then the remaining two balances can be solved simultaneously for the flows of the raffinate product, L_b , and inlet solvent, V_b , as follows:

$$\text{Total:} \quad V_b = L_b + V_a - L_a \quad (7)$$

$$\text{Diluent:} \quad L_a x_{Ba} - V_a y_{Ba} = L_b x_{Bb} - V_b y_{Bb} \quad (8)$$

Finally the raffinate product composition can be calculated:

$$x_{Ab} = \frac{L_b x_{Ab}}{L_b} \quad (9)$$

For the next iteration the composition of solvent in the raffinate, x_{sb} , is obtained at the calculated value of x_{Ab} from the solubility relationship or chart, and the calculations are repeated. As the solvent concentration in the raffinate is small, convergence is usually reached on the second iteration.

In summary, the difficulty of solving the balance equations for a liquid-liquid extraction problem is reduced when the extract product composition is selected for the design variable instead of the solvent inlet flow.

3 Determining the Number of Required Equilibrium Stages

As with other countercurrent stage operations the number of equilibrium stages can be determined by either stage-to-stage calculations or the McCabe-Thiele graphical procedure. Both of these methods require the equilibrium and operating relationships or lines. The equilibrium data is obtained experimentally and presented in either a correlation or in graphical form. The operating relationship is obtained from mass balances around stages 1 to n of the cascade:

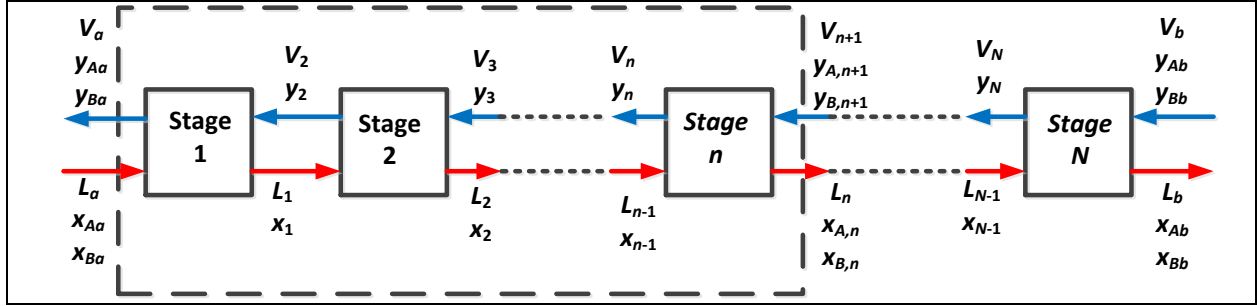


Figure 3. Balances Around Stages 1 to n

$$\text{Total mass:} \quad L_a + V_{n+1} = L_n + V_a \quad (10)$$

$$\text{Solute balance:} \quad L_a x_{Aa} + V_{n+1} y_{A,n+1} = L_n x_{A,n} + V_a y_{Aa} \quad (11)$$

$$\text{Diluent balance:} \quad L_a x_{Ba} + V_{n+1} y_{B,n+1} = L_n x_{B,n} + V_a y_{Ba} \quad (12)$$

These equations require an iterative solution; starting with a value of $x_{A,n}$, look up the solubility of the diluent in the raffinate $x_{B,n}$ and assume a value for $y_{B,n+1}$. Then solve Equations (10) and (12) simultaneously for L_n and V_{n+1} and calculate $y_{A,n+1}$ (from Equation 10):

$$y_{A,n+1} = \frac{L_n}{V_{n+1}} x_{A,n} + \frac{V_a y_{Aa} - L_a x_{Aa}}{V_{n+1}} \quad (13)$$

Then look up the solubility $y_{B,n+1}$ and repeat the calculation until it converges.

If the equilibrium and operating lines are approximately straight the number of required equilibrium stages can be estimated from the Kremser equation:

$$N = \frac{\ln\left(\frac{x_{Aa} - x_{Aa}^*}{x_{Ab} - x_{Ab}^*}\right)}{\ln\left(\frac{x_{Aa} - x_{Ab}}{x_{Aa}^* - x_{Ab}^*}\right)} \quad (14)$$

Where x_{Aa}^* and x_{Ab}^* are, respectively, the weight fractions of the raffinate in equilibrium with y_{Aa} and y_{Ab} .

Example 1. Extraction of Acetone from Methyl-Isobutene-Ketone (MIK)(Taken from McCabe, Smith and Harriott, *Unit Operations of Chemical Engineering*, 7th ed., Example 23.3, page 784.) A countercurrent extraction plant is used to extract acetone from its mixture with water by means of methyl-isobutene-ketone (MIK) at a temperature of 25°C. The feed consists of 40 weight% acetone and the balance water. Pure solvent is to be used and the column operates at 25°C and the feed flow is 8,000 kg/hr. How many ideal stages are required to extract 99% of the acetone fed using a reasonable solvent rate? What is the extract composition after removal of the solvent?

The solubility chart is shown in Figure 4 below:

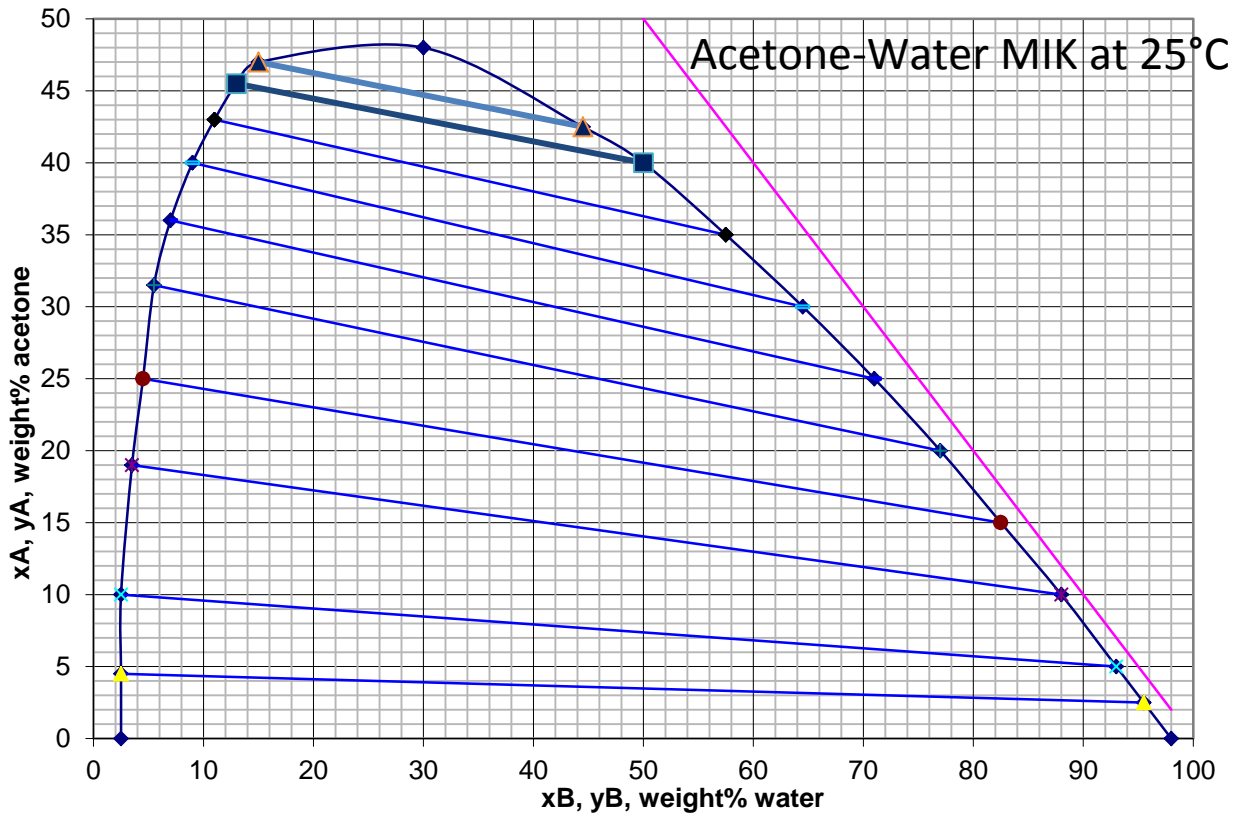


Figure 4. Solubility chart for acetone-water-MIK system at 25°C

In this diagram, typical of *Type I* systems, the area underneath the dome contains compositions that form two separate liquid phases. The point at the top of the dome is called the *plait point*; at this point the two phases in equilibrium have the same weight fractions, $x_B = y_B = 30$ weight% water and $x_A = y_A = 48$ weight% acetone.

- The curve to the left of the plait point shows the solubility of the water in the **extract phase** as a function of the weight fraction of the acetone in that phase. For example, at $y_A = 40$ weight% acetone, $y_B = 9$ weight% water.

- The curve to the right of the plait point shows the solubility of the water in the **raffinate phase** as a function of the weight fraction of acetone in that phase. For example, at $x_A = 30$ weight% acetone, $x_B = 64$ weight% water.
- The *tie lines* connecting points from the extract phase to the raffinate phase show the concentrations of the phases in equilibrium with each other. For example, the fourth line from the top shows that at $y_A = 40$ weight% acetone in the extract phase, the concentration of the raffinate phase in equilibrium with it is $x_A^* = 30$ weight% acetone.

You are strongly encouraged to carefully study the chart and make sure you can locate the points given above as examples. Your objective must be to be able to read any point in the chart by yourself.

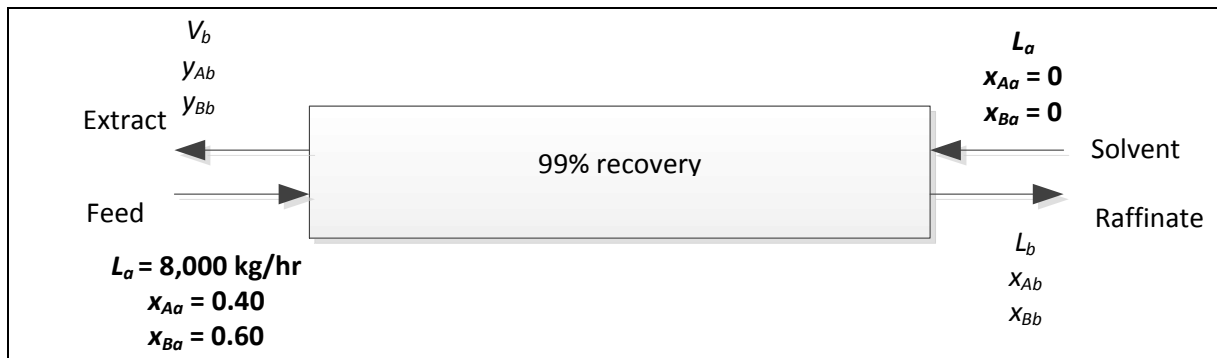


Figure 5. Schematic of Extraction Cascade for Example 1.

The unrecovered acetone goes to the raffinate:

$$L_b x_{Ab} = (1 - 0.99) (8,000 \text{ kg/hr}) (0.4) = 32 \text{ kg/hr}$$

From Figure 4 we see that the composition of the extract in equilibrium with the feed ($x_{Aa} = 0.40$) is $y_{Aa} = 0.46$. For our design variable we must select a value less than this, say

$$y_{Aa} = 0.30$$

From Figure 4 we find: $y_{Ba} = 0.05$.

When the solvent is pure the calculations are simpler because it does not contain solute, $y_{Ab} = 0$, or diluent, $y_{Bb} = 0$. So, from the solute balance:

$$V_a y_{Aa} = L_a x_{Aa} + V_b y_{Ab} - L_b x_{Ab} = 8,000(0.40) + V_b(0) - 32 = 3,168 \text{ kg/hr}$$

Thus, $V_a = 3,168/0.30 = 10,560 \text{ kg/hr}$

For the first iteration we must assume a solubility of the diluent in the raffinate product. From the chart (Figure 4) around the area of x_{Ab} near zero, we estimate $x_{Bb} = 0.96$. From Equation (8), the diluent balance:

$$L_a x_{Ba} - V_a y_{Ba} = L_b x_{Bb} - V_b y_{Bb}$$

$$8,000(0.60) - 10,560(0.05) = L_b(0.96) - V_b(0)$$

$$L_b = (4,800 - 528 + 0)/0.96 = 4,450 \text{ kg/hr}$$

The composition of the raffinate product is then:

$$x_{Ab} = 32/4,450 = 0.0072$$

From Figure 4, at $x_{Ab} = 0.0072$ we read: $x_{Bb} = 0.97$

Second iteration: $L_b = (4,800 - 528 + 0)/0.97 = 4,400 \text{ kg/hr}$

$$x_{Ab} = 32/4,400 = 0.0073$$

From Figure 4, at $x_{Ab} = 0.0073$, $x_{Bb} = 0.97$. We have converged.

From the total balance we obtain the solvent rate:

$$V_b = V_a + L_b - L_a = 10,560 + 4,400 - 8,000 = 6,960 \text{ kg/hr}$$

The extract product composition after the solvent is removed is

$$y_{Aa}/(y_{Aa} + y_{Ba}) = 0.30/(0.30 + 0.05) = 0.857$$

To determine the required number of equilibrium stages we use the McCabe-Thiele graphical procedure on the x_A - y_A diagram. This requires plotting the equilibrium line, given by the end points of the tie lines in the solubility chart (Figure 4), as follows:

y_A	4.5	10	19	25	33	36	40	42	45.5	47
x_A^*	2.5	5	10	15	20	25	30	35	40	42.5

These are for each of the tie lines in Figure 4 from the bottom up.

The operating line goes through the two end points (x_{Aa}, y_{Aa}) and (x_{Ab}, y_{Ab}) . To check if the operating line is approximately straight and an intermediate point is necessary, we calculate the slope of the operating line L/V at both ends of the extraction cascade:

$$L_a/V_a = 8,000/10,560 = 0.76 \quad L_b/V_b = 4,400/6,960 = 0.63$$

So the operating line is not straight. To calculate the intermediate point we pick a liquid stream composition near the middle of the range, say $x_A = 0.20$, and obtain the diluent composition corresponding to this value from the solubility chart (Figure 4), as $x_B = 0.77$. For the first trial we guess a

diluent composition in the extract of $y_B = 0.03$ and write the balances around the left portion of the battery:

$$\text{Total balance: } 8,000 + V = L + 10,560$$

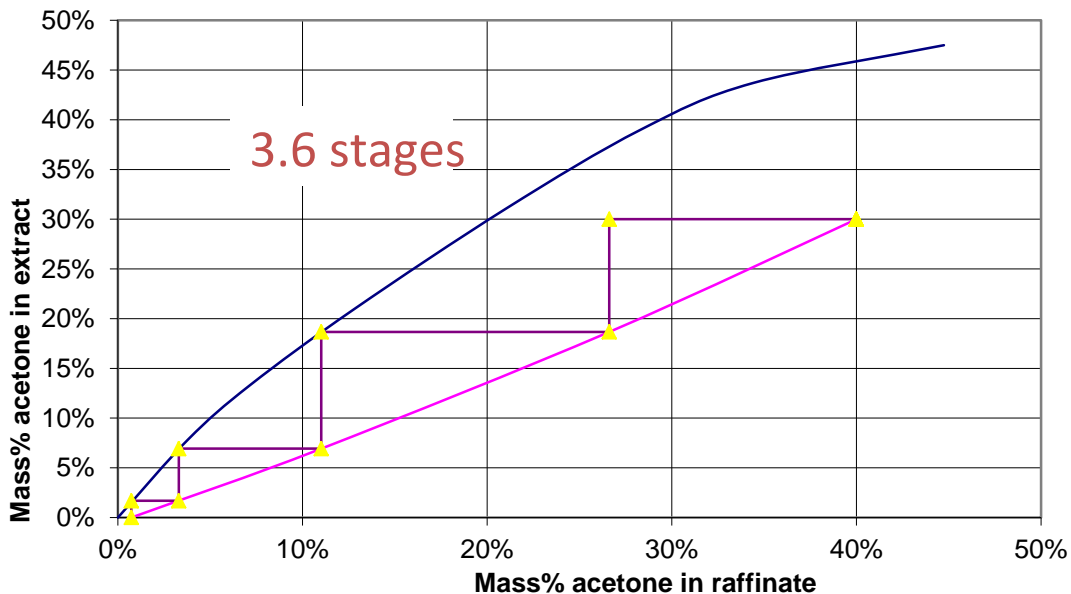
$$\text{Diluent balance: } 100(0.60) + V(0.03) = L(0.77) + 132(0.05)$$

Solve simultaneously to obtain: $V = 8,440 \text{ kg/hr}$, $L = 5,880 \text{ kg/hr}$

The solute balance gives the solute mass fraction in the extract stream:

$$y_A = [5,880(0.20) + 10,560(0.30) - 8,000(0.40)]/8,440 = 0.136$$

A check on Figure 4 shows that at $y_A = 0.136$, $y_B = 0.03$, as guessed. The operating line is drawn through the two end points and the intermediate point to complete the McCabe-Thiele diagram, as shown below:



In this solution we used a slightly lower solvent rate than the solution by McCabe, Smith and Harriott, requiring 3.6 stages as compared to 3.4 stages in the original problem.

We have seen that when the designer is free to select the solvent rate in a liquid-liquid extraction problem, the problem is simplified by selecting the extract composition instead. As most courses on unit operations are design-type courses, the problems given to the students should leave them the freedom to select the design variable that makes it easier to solve the problem. When the Ponchon-Savarit graphical solution procedure was eliminated from our textbooks, liquid-liquid extraction became one of the hardest problems for the students to solve. The method suggested here reduces some of this difficulty.

4 Determining the Diameter of a Liquid-Liquid Extraction Column

Ref: Seader, Henley and Roper, *Separation Process Principles*, 3rd ed., 2011, pp. 334-335.

4.1 Column Diameter

In a liquid-liquid extraction column there are two liquid phases flowing past each other. The less dense phase flows upward and the denser phase flows down. One of the phases is *dispersed* and the other is *continuous*. Droplets of the disperse phase move through the continuous phase.

The sizing procedures consists of determining the sum of the velocities of the two phases at flooding and then use a fraction, usually 50% of the flooding value, to size the column. The velocities are superficial, that is, based on the total cross-sectional area of the column.

The chart of Figure 6 gives the sum of the superficial velocities at flooding versus the ratio of the velocities of the two phases:

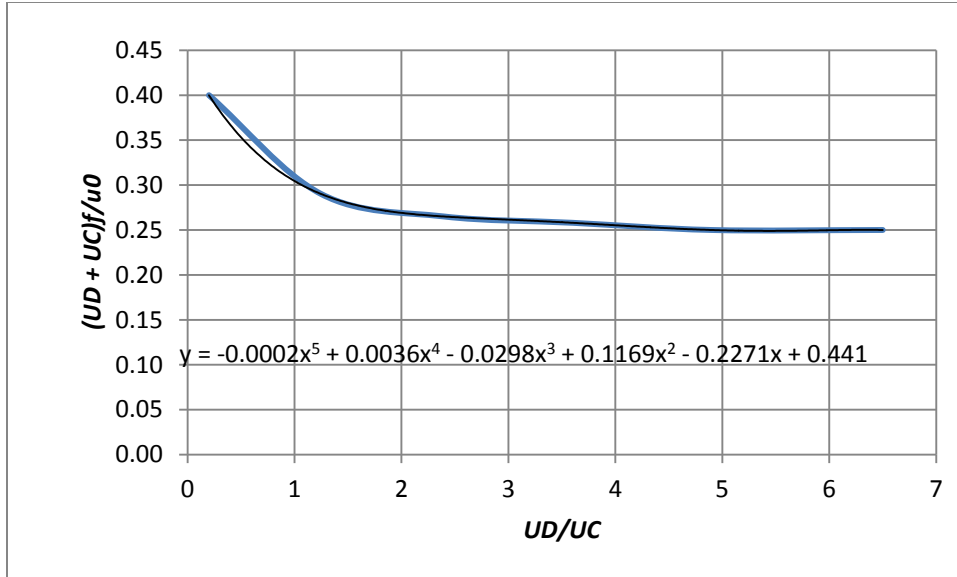


Figure 6. Superficial flooding velocity in a liquid-liquid extraction column.

U_D and U_C are the superficial velocities of the dispersed and continuous phases, respectively. u_0 is the characteristic rise velocity for a single droplet. For systems in which one of the phases is water, the following dimensionless number has been determined experimentally:

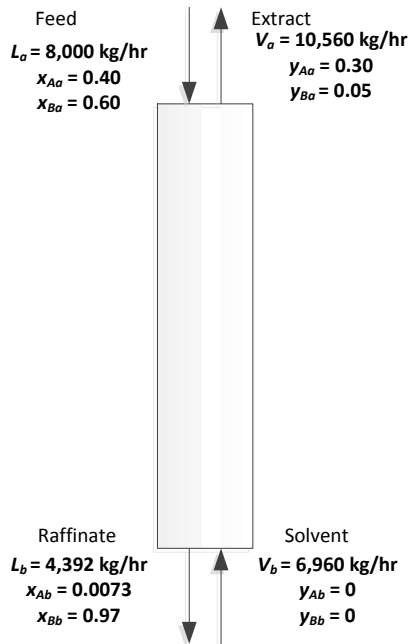
$$\frac{u_0 \mu_C \rho_C}{\sigma \Delta \rho} = 0.01 \quad (11)$$

Where μ_C is the viscosity of the continuous phase, ρ_C is the density of the continuous phase, σ is the surface tension, and $\Delta \rho$ is the difference in density of the two phases.

Inspection of Figure 6 shows that if the larger of the two flows is used as the dispersed phase the resulting flooding velocity u_0 is higher and thus the column diameter is smaller.

Example 2. Sizing the Acetone-Water-MIK Extraction Column

Estimate the height and diameter of a column to carry out the extraction of Example 1. Use an over-all column efficiency of 20% and a tray height of 12 inches.



Solution: We size the column at the top where the feed enters, because there the flows of the extract and raffinate phases are highest. The flows from Example 1 are:

Feed: $L_a = 8,000 \text{ kg/hr}$

Extract: $V_a = 10,560 \text{ kg/hr}$

The specific gravities of acetone, MIK and water are 0.79, 0.80 and 1.0, respectively (Perry's *Chemical Engineers' Handbook*, 8th ed., Tables

2-1 and 2-2). Estimate the specific gravity of the feed and extract assuming additive volumes of acetone, MIK and water:

Feed:
$$G_{xa} = \frac{1}{\frac{0.40}{0.79} + \frac{0.60}{1.0}} = 0.90$$

Extract:
$$G_{ya} = \frac{1}{\frac{0.30}{0.79} + \frac{0.05}{1.0} + \frac{0.65}{0.80}} = 0.80$$

Selecting the larger flow, the extract, as the dispersed phase, the ratio of the velocities is:

$$\frac{U_D}{U_C} = \frac{V_a}{G_{ya}} \frac{G_{xa}}{L_a} = \frac{10,560}{0.80} \frac{0.90}{8,000} = 1.49$$

From the chart of Figure 6 we get, for the sum of the velocities at flooding,

$$\frac{(U_D + U_C)_f}{u_0} = 0.28$$

To get u_0 , we use the viscosity of feed close to that of water at 25°C, 1 cP (0.001 Pa-s, Perry's, 8th ed., p. 2-448), feed density of 900 kg/m³ and extract density of 800 kg/m³ (sp.gr. of 0.90 and 0.80, respectively, determined above); the difference in density is (900 - 800) = 100 kg/m³, and the surface tension between the phases is 32 dyne/cm (0.032 N/m, typical of water interfaced with organics). From Equation (11):

$$u_0 = \frac{0.01\sigma\Delta\rho}{\mu_c\rho_c} = \frac{(0.01)(0.032)(100)}{(0.001)(900)} = 0.036 \frac{m}{s}$$

The sum of the superficial velocities of the phases at 50% of flooding, using the value from Figure 3 (0.28):

$$(U_C + U_D)_{50\%} = 0.5(0.28)u_0 = (0.5)(0.28)\left(0.036 \frac{m}{s}\right) = 0.0052 \frac{m}{s}$$

The total volumetric flow of the two phases:

$$\left(\frac{10,560 \text{ kg/hr}}{800 \text{ kg/m}^3} + \frac{8,000 \text{ kg/hr}}{900 \text{ kg/m}^3}\right) \frac{\text{hr}}{3,600\text{s}} = 0.0061 \frac{\text{m}^3}{\text{s}}$$

Required column area:

$$A_c = \frac{0.0061 \text{ m}^3/\text{s}}{0.0052 \text{ m/s}} = 1.18 \text{ m}^2$$

Required column diameter:

$$D_c = \sqrt{\frac{4(1.18 \text{ m}^2)}{\pi}} = 1.2 \text{ m (4.0 ft)}$$

As the velocity is the superficial velocity, it is not necessary to account for the area taken by the downcomers.

4.2 Column Height

In Example 1 we determined the number of required equilibrium stages is 3.6. With 20% over-all column efficiency and 12-in tray spacing:

Number of trays: $3.6/0.20 = 18$

Column height: $18(12 \text{ inch})(1 \text{ ft}/12 \text{ inch}) = 18 \text{ ft} (5.5 \text{ m})$

5 Insoluble Diluent and Solvent

When the diluent solubility in the extract phase and that of the solvent in the raffinate phase are negligible, that is $y_B \cong 0$ and $x_S \cong 0$, then the extraction problem is simplified because it is no longer necessary to carry two weight fractions for each stream. Also, the diluent and solvent balances become:

$$L(1 - x_A) = L_a(1 - x_{Aa}) = L_b(1 - x_{Ab})$$

$$V(1 - y_A) = V_a(1 - y_{Aa}) = V_b(1 - y_{Ab})$$

This greatly simplifies the balance calculations. Where have you seen these equations before?

6 Extraction of Dilute Solutions

When the feed and extract solutions are dilute ($x \ll 1, y \ll 1$) the calculations are further simplified because then the flows of the raffinate and extract phases are constant from stage to stage:

$$L = L_a = L_b$$

$$V = V_a = V_b$$

7 Parallel Extraction

Countercurrent extraction is efficient in terms of obtaining the most solute recovery with the least amount of solvent thus producing the most concentrated extract. Under certain conditions parallel extraction is used. In parallel extraction the raffinate flows from stage to stage but fresh solvent is used in each stage. Such operation requires more solvent and produces a more dilute extract, but requires fewer stages, particularly when the feed is dilute to start with.

Another situation where parallel extraction is used is when the amounts to be processed are small, as in pharmaceutical applications. Then the extraction must be carried out in batch mode and parallel extraction is required, as in the following example.

Example 3. Batch Parallel Extraction of a Dilute Solution.

A pharmaceutical product must be extracted from a solution containing 5 gm/L of the product with a solvent having a

distribution coefficient of 15. (The distribution coefficient is the ratio y/x of the concentration of the extract to that of the raffinate in equilibrium with it.) For 10 L of feed, determine,

- a) The amount of solvent required to recover 99% of the product in one extraction.
- b) The amount of solvent required to re recover 99% of the product in two equal extractions using the same amount of fresh solvent each time.
- c) How many extractions are required to recover 99% of the product using a 1.0 L of fresh solvent each time?

Solution. Assume the densities of the raffinate and extract are not functions of composition as the solutions are so dilute. Assume further that the solvent is not soluble in the raffinate and the diluent is not soluble in the extract.

Schematic of each extraction:

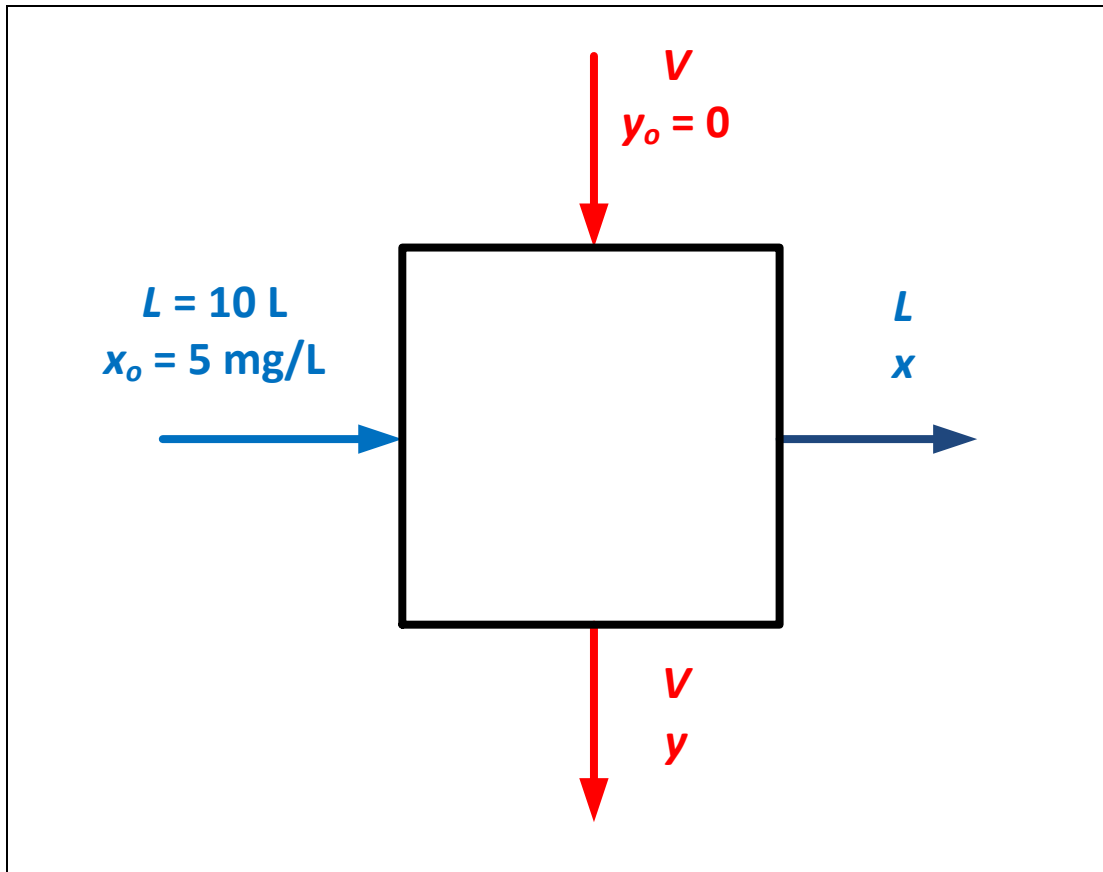


Figure 7. Schematic of Extraction for Example 3

1. One extraction:

Solute balance for one extraction: $Lx_0 + V(0) = Lx + Vy$

Distribution coefficient: $y = 15x$

Combine and solve for V: $V = \frac{L(x_0 - x)}{15x} = \frac{L}{15} \left(\frac{x_0}{x} - 1 \right)$

For 99% recovery: $Lx = (1 - 0.99)Lx_0$ $x = 0.01x_0$

Calculate $V = (10/15) [(1/0.01) - 1] = 66 \text{ L}$

2. Two extractions:

Balance for each extraction: $Lx_i + V(0) = Lx_{i+1} + V(15)x_{i+1}$

So, $x_{i+1} = \frac{L}{L+15V}x_i$

First extraction: $x_1 = \frac{L}{L+15V}x_0$

Second extraction: $x_2 = \frac{L}{L+15V}x_1 = \left(\frac{L}{L+15V}\right)^2 x_0$

For 99% extraction: $Lx_2 = (1 - 0.99)Lx_0$ So, $x_2 = 0.01x_0$

$$\frac{L}{L+15V} = \sqrt{\frac{x_2}{x_0}} = \sqrt{0.01} = 0.10$$

Solve for V:

$$V = (L - 0.10L) / [(15)(0.10)] = 0.6L = 0.6(10 \text{ L}) = 6 \text{ L}$$

So, we must use 6 L for each extraction or 12 L total.

Concentration after first extraction: $x_1 = \frac{10}{10+6(15)}5 = 0.5 \frac{\text{mg}}{\text{L}}$

Concentration after second extraction: $x_2 = \frac{10}{10+6(15)}0.5 = 0.05 \frac{\text{mg}}{\text{L}}$

3. Number of extractions for $V = 1.0 \text{ L}$

From the formula for part (b): $x_n = \left(\frac{L}{L+15V}\right)^n x_0 = (1 - 0.99)x_0$

Solve for n: $n = \frac{\ln(0.01)}{\ln\left(\frac{10}{10+15(1)}\right)} = 5$

So it will take five times 1.0 L or 5 L.

Therefore the total volume of solvent required is 66 L for one extraction, 12 L for two extractions and 5 L for five extractions.

Summary

These notes have presented the design of liquid-liquid extraction operations. It has been shown that the over-all balance calculations are simplified when the engineer selects the extract composition as the design variable instead of the solvent rate. As with other countercurrent stage operations the number of required equilibrium stages can be determined by stage to stage calculations or by the McCabe-Thiele graphical procedure. When both the equilibrium and operating lines are approximately linear the Kremser equation provides a good estimate of the required number of stages.

The calculations are greatly simplified when the diluent is not soluble in the extract phase and the solvent is not soluble in the raffinate phase. Further simplification results when the solutions are dilute because then the rates of the extract and raffinate phases are approximately constant and the Kremser equation can be used to determine the number of equilibrium stages. The operation of parallel extraction was briefly introduced.

Review Questions

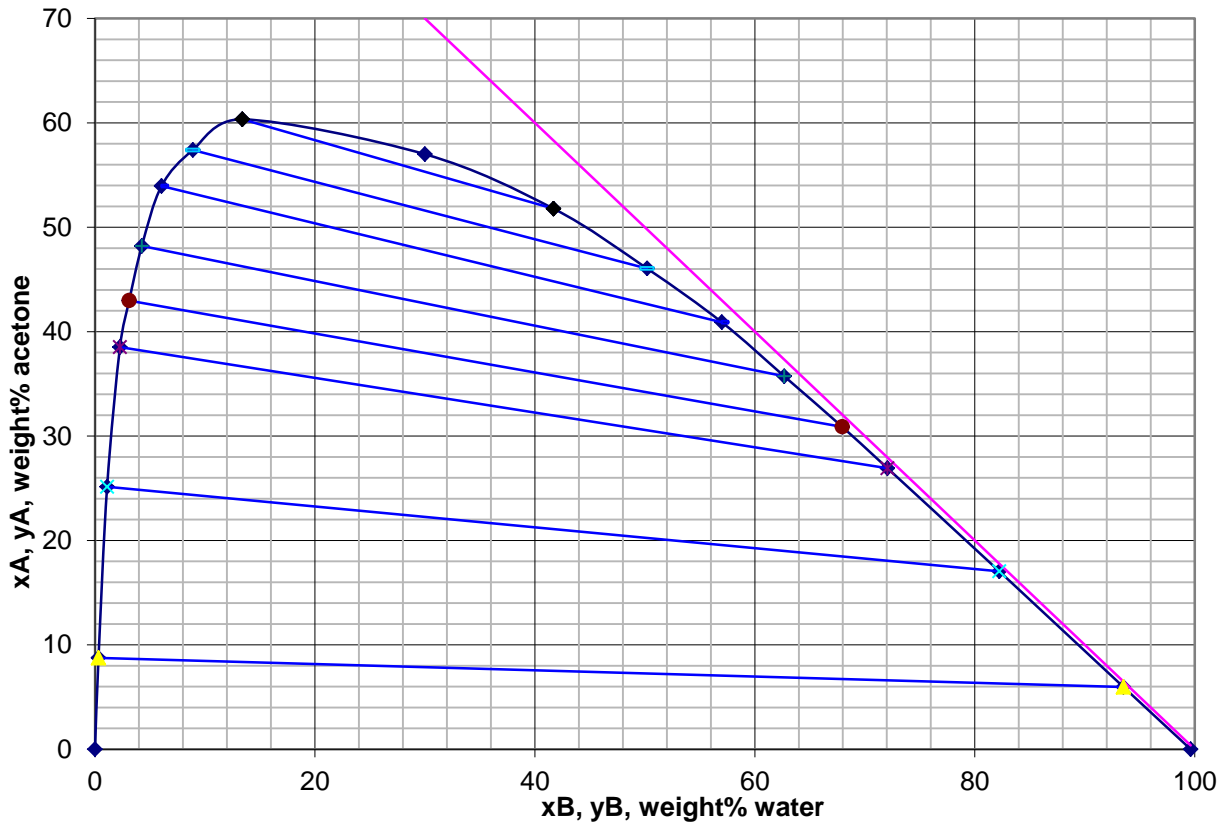
1. Briefly describe the operation of liquid-liquid extraction.
2. Which are the two phases involved in liquid-liquid extraction?

3. Which are the three components involved in liquid-liquid extraction?
4. What is the major requirement for the solvent in liquid-liquid extraction?
5. How many variables are required to define each stream in liquid-liquid extraction? What are they?
6. How many over-all independent balances can be written in liquid-liquid extraction?
7. What other two relationships are available in liquid-liquid extraction?
8. How many specifications are required to design a liquid-liquid extraction operation? What are they?
9. When left as a design variable, should the solvent rate or the extract product composition be selected? Why?
10. In the solubility chart of a Type I liquid-liquid extraction system, what is the *plait point*? What region represents the two-phase region? What are the *tie lines*?
11. How is the equilibrium relationship obtained from the solubility chart?
12. How is the operating line relationship obtained in liquid-liquid extraction?
13. What makes the extraction design problem simpler to solve?
14. What is *parallel extraction*? When is it used instead of countercurrent stage contact? What is its advantage? What is its disadvantage?
15. In batch parallel extraction, what is the advantage of carrying it out in successive contacts instead of a single contact?

Problems

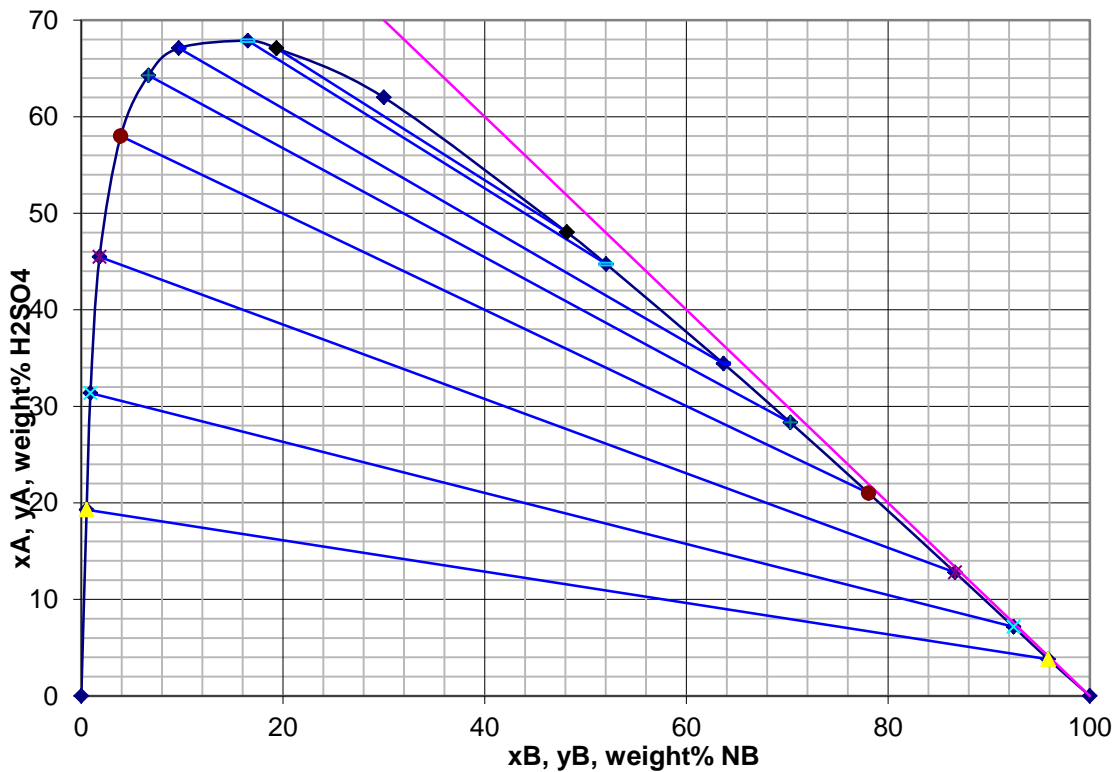
1. **Extraction of Acetone from Water using MIK.** You are to design a column to extract acetone from 3,500 kg/hr of a feed consisting of 38 weight% acetone and the balance water. Pure methyl isobutyl ketone (MIK) is to be used as the solvent and the column operates at 25°C. It is desired to extract 98% of the acetone in the feed. Draw a schematic of the column showing all the problem data and, using a reasonable solvent rate, determine the flow and composition of the extract and raffinate streams leaving the column, and the required number of equilibrium stages. Report also the composition of the extract on a solvent-free basis (this is the product composition after the solvent is removed for recycle). Solubility data at 25°C are given in Figure 4 of these notes.
2. **Sizing of Acetone-Water-MIK column.** For the conditions of Problem 1 determine the number of actual stages for an over-all column efficiency of 20%, the column height for 6-in spacing and 10% extra height, and the column diameter sized for 50% of the flooding velocity. The viscosity of MIK is 0.56 cP at 25°C.
3. **Design of a Liquid-Liquid Extraction Column.** You are to design a countercurrent extraction battery to extract acetone from 1,350 kg/hr of a feed consisting of 40 weight% acetone and 60 weight% water. Pure tri-chloro-ethane (TCE) is to be used as the solvent and the column operates at 25°C. It is desired to extract 97% of the acetone in the feed. Draw a schematic of the column showing all the problem data and, using a reasonable solvent rate, determine the flows and compositions of the extract and

raffinate products and the required number of equilibrium stages. Report also the composition of the extract product on a solvent-free basis (this is the composition of the product after the solvent is removed for recycling). Solubility and equilibrium data at 25°C are given in McCabe, Smith & Harriott, 7th ed., page 794. These data have been plotted below in the following solubility chart.



4. **Sizing of Acetone-Water-TCE column.** For the conditions of Problem 3 determine the number of actual stages for an over-all column efficiency of 20%, the column height for 12-in spacing and 10% extra height, and the column diameter sized for 50% of the flooding velocity. The viscosity of TCE is 0.55 cP at 25°C.

5. *Extraction of Sulfuric Acid from Nitrobenzene.* The reactor effluent from the nitration of benzene is to be treated with water solvent in a counter-current extraction column to recover the sulfuric acid catalyst. The effluent flows at the rate of 840 gallons per minute with a composition of 13.6 weight% H_2SO_4 and the balance nitrobenzene (NB). It is desired to remove 98% of the acid using a reasonable solvent rate. The specific gravity of the feed is 1.24 and the equilibrium chart is given below. Draw a schematic diagram of the column showing all the problem data and labeling all the flows and compositions. Using a reasonable solvent rate, determine the flows and compositions of the extract and raffinate products, and the required number of equilibrium stages.

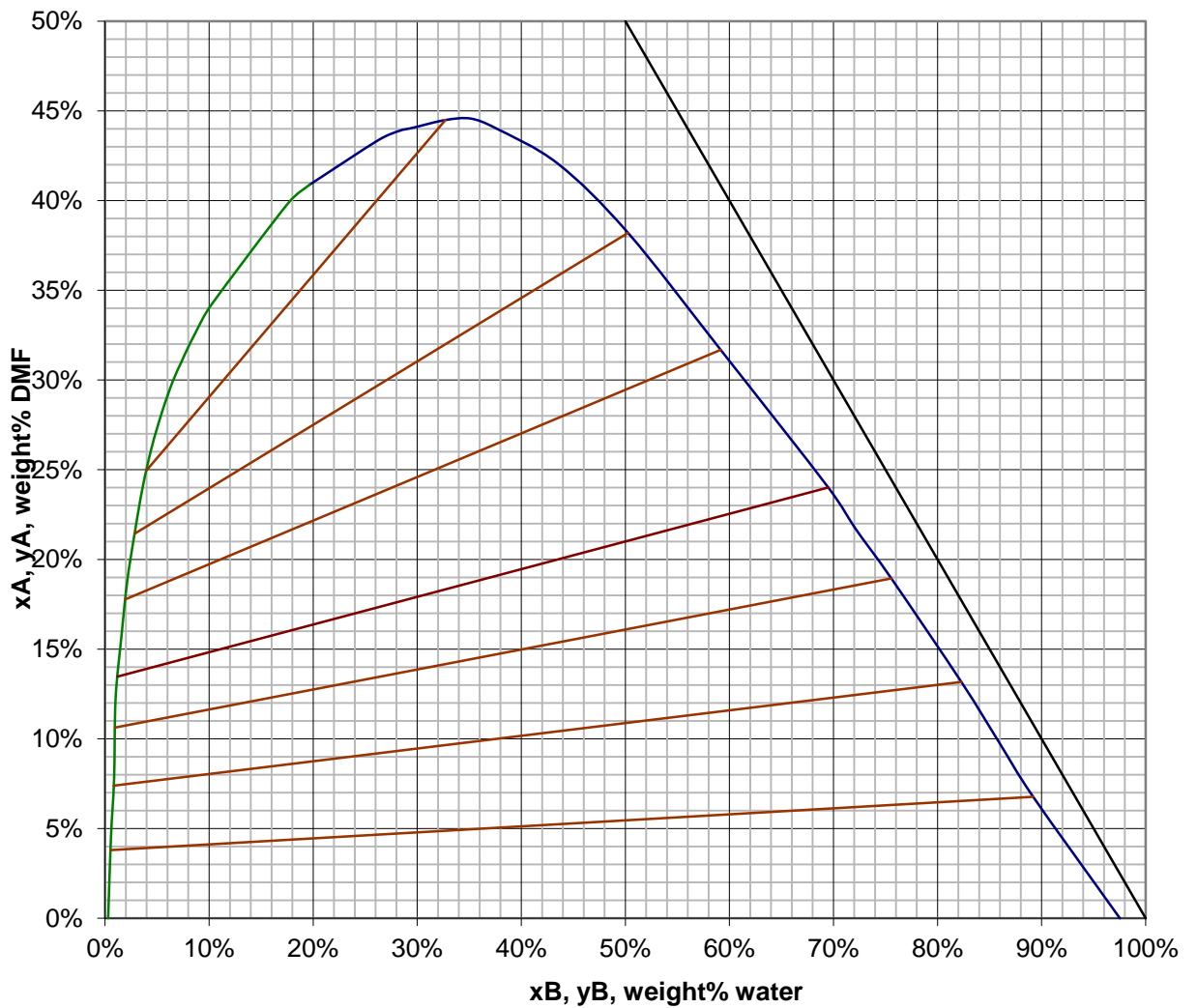


6. *Sizing of Sulfuric Acid Extraction Column.* For the conditions of Problem 5 determine the number of actual

stages for an over-all column efficiency of 20%, the column height for 12-in spacing and 10% extra height, and the column diameter sized for 50% of the flooding velocity.

7. Di-methyl formamide (DMF) is used as a solvent for the production of Nylon. The DMF is to be extracted from waste water for recycle and to avoid the contamination of the environment by the water stream. The feed enters at 30,000 kg/hr containing 32 weight% DMF and the balance water. The solvent contains 1 weight% water and the balance methylene chloride CH_2Cl_2 . It is desired to produce a raffinate product with less 0.05 weight% DMF. Draw a schematic of the column showing all the problem data and, using a reasonable solvent rate, determine the flows and compositions of the extract and raffinate products and the required number of equilibrium stages. Report also the composition of the extract product on a solvent-free basis (this is the composition of the product after the solvent is removed for recycling). The solubility chart is given below.

8. **Sizing of DMF extraction column.** For the conditions of Problem 7 determine the number of actual stages for an over-all column efficiency of 20%, the column height for 12-in spacing and 10% extra height, and the column diameter sized for 50% of the flooding velocity. The viscosity of methylene chloride is 0.42 cP at 25°C.

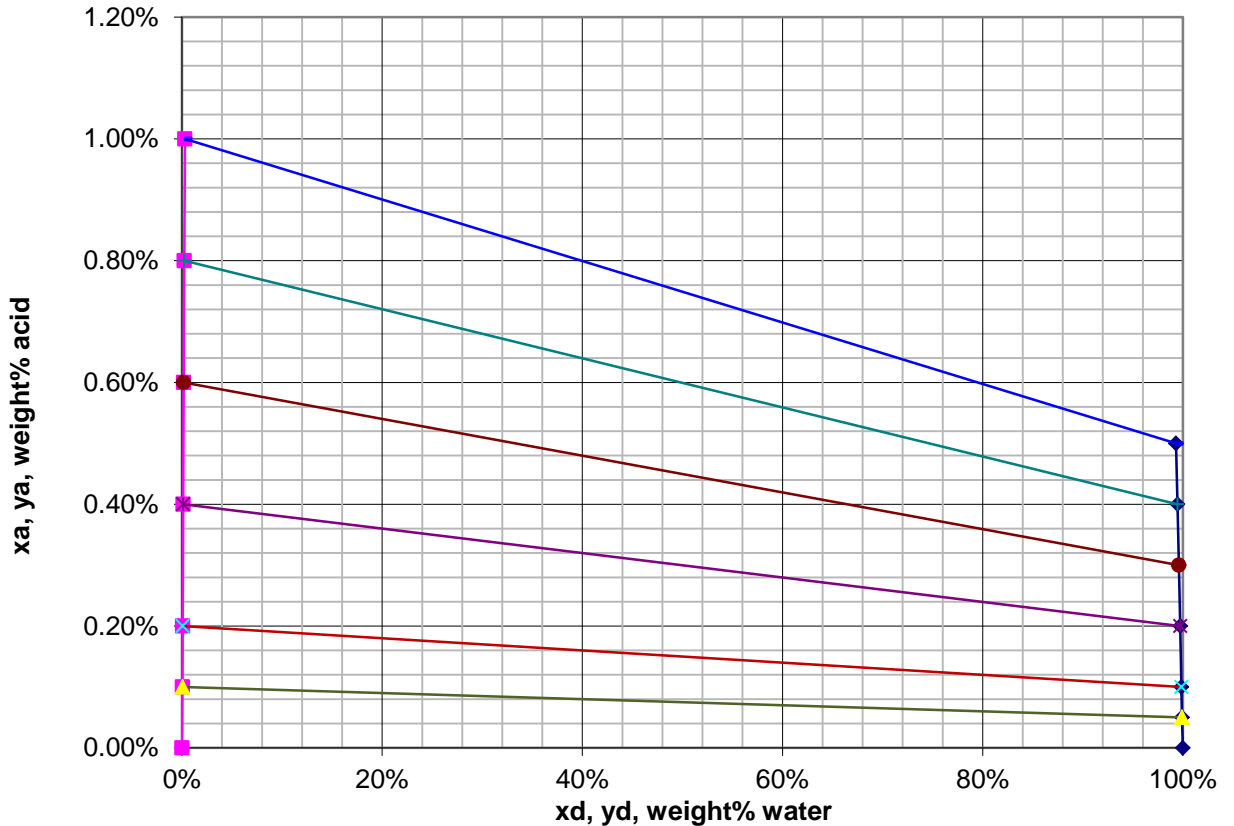


9. **Extraction of Acids from Waste Water.** (Adapted from SH&LP Problem 73.) The water used in a chemical processing plant contains a mixture of organic acids. The acids are not particularly toxic to the environment in small concentrations, but the concentration in the process water stream is 0.5% by weight leaving the process, and that concentration is too large for discharge. The acids cannot be used in the plant for any other purpose, and there is insufficient acid for their recovery, purification, and

sale. The acids are soluble in hydrocarbons, and it is decided to extract the acids from the water streams by countercurrent liquid-liquid extraction, and then use the hydrocarbon as a fuel for one of the plant process heaters. There is no chlorine, nitrogen, or sulfur in the acids, so when they are burned with the fuel, they will not contribute any additional pollution to the air. The hydrocarbon used for the extraction is the fuel oil for the process heaters. Equilibrium data for the acid-water-oil system are given in the table below. Determine how much oil will be required to reduce the concentration of acid from the 0.5 mass percent in the feed to 0.05 mass percent, which has been found to be acceptable for discharge. The oil rate used in the process will be 1.5 times the minimum, and the water to be treated will enter the extraction system at a rate of 3500 gallons per day. The oil has a specific gravity of 0.88. Assume the process is to be performed in a countercurrent liquid-liquid extractor having an overall efficiency of 20%. How many stages will be required for the extractor?

Mass percent in water layer			Mass percent in oil layer		
Acid	Water	Oil	Acid	Water	Oil
0.05	99.90	0.04	0.10	0.05	99.85
0.10	99.85	0.05	0.20	0.08	99.76
0.20	99.73	0.07	0.40	0.12	99.48
0.30	99.60	0.10	0.60	0.17	99.23
0.40	99.46	0.14	0.80	0.23	98.97
0.50	99.31	0.19	1.00	0.30	98.70

These data are plotted below.



10. **Sizing of acid extraction column.** For the conditions of Problem 9 determine the column height for 12-in spacing and 10% extra height, and the column diameter sized for 50% of the flooding velocity. The viscosity of the fuel oil is 0.37 cP at 25°C.

11. **Extraction of Dilute Solutions.** Pharmaceutical products are recovered from dilute aqueous fermentation broths by extraction with various solvents. It is desired to recover 80% of a drug from a dilute aqueous solution. The distribution coefficient K_D is 50.

- (a) For extraction on a single equilibrium stage, draw a schematic diagram and determine the required ratio of solvent to feed solution.
- (b) If two sequential equilibrium stages are used using half the fresh solvent from part (a) in each stage, what

fraction of the drug in the feed will be recovered? Draw a schematic of the operation.

(c) What fraction of the drug will be recovered if the two equilibrium stages from part (b) are arranged as a countercurrent continuous extraction battery using all the solvent from part (a)? Draw a schematic of the battery.

State all assumptions.

12. Extraction of Penicillin from Broth. (Based on data of McCabe, Smith & Harriett, 7th edition, Example 23.2, page 780.) Penicillin F is recovered from a dilute aqueous fermentation broth by extraction with amyl acetate using 6 volumes of solvent per 100 volumes of aqueous phase. At pH = 3.2 the distribution coefficient K_D is 80. For each part of the problem draw a schematic and show all the problem data on the sketch. (a) What fraction of the penicillin would be recovered by a single ideal stage? (b) What would be the recovery with two-stage extraction using half of the fresh solvent in each stage? (c) How many ideal stages would be required to give the same recovery as in part (b) in a counter-flow cascade using 6 volumes of solvent per 100 volumes of feed? What if only 3 volumes of solvent per 100 volumes of feed are used in the cascade? What would be the advantage of using less solvent? State all assumptions.

13. Parallel Extraction of a Dilute Solution. A pharmaceutical product is recovered from 100 ml of a dilute aqueous fermentation broth by extraction with amyl acetate. The distribution coefficient K_D is 45 and the broth initially contains 500 mg of the drug. (a) How much solvent is required to recover 90% of the drug in a single ideal stage? (b) How much total solvent is required to recover

90% of the drug in three extractions using the same amount of fresh solvent each time? Draw a schematic of the operation and state all assumptions.

14. Parallel Extraction of Dilute Solution. It is desired to recover a solute from a dilute aqueous solution by extraction with a solvent using a mass ratio of solvent to aqueous phase of 25:100. The feed concentration is 0.5 weight% and the distribution coefficient K_D for the solute is 30. (a) What fraction of the solute would be recovered by a single ideal stage? (b) What would be the recovery with a three-stage extraction using one third of the fresh solvent in each stage? Draw a schematic of the operation and state all assumptions.