

# Extraction

One area in food processing that is receiving increasing attention is extraction. This separation process involves two phases. The solvent is the material added to form a phase different from that where the material to be separated originally was present. Separation is achieved when the compound to be separated dissolves in the solvent while the rest of the components remain where they were originally. The two phases may be solid and liquid, immiscible liquid phases, or solid and gas. Solid-liquid extraction is also called leaching. In supercritical fluid extraction, gas at supercritical conditions contacts a solid or a liquid solution containing the solute. Extraction has been practiced in the vegetable oil industry for a long time. Oil from soybean, corn, and rice bran cannot be separated by mechanical pressing, therefore, solvent extraction is used for their recovery. In the production of olive oil, the product from the first pressing operation is the extra virgin olive oil, the residue after first press may be re-pressed to obtain the virgin olive oil, and further recovery of oil from the cake is done by solvent extraction. Oil from peanuts is recovered by mechanical pressing and extraction of the pressed cake to completely remove the oil. One characteristic of solvent extracted oilseed meal is the high quality of the residual protein, suitable for further processing into food-grade powders. They may also be texturized for use as food protein extenders.

Extraction of spice oils and natural flavor extracts has also been practiced in the flavor industry. Interest in functional food additives used to fortify formulated food products has led to the development of extraction systems to separate useful ingredients from food processing waste and medicinal plants.

Extraction is also used in the beet sugar industry to separate sugar from sugar beets. Sugar from sugar cane is separated by multistage mechanical expression with water added between stages. This process may also be considered a form of extraction. Roller mills used for mechanical expression of sugar cane juice is capital intensive and when breakdowns occur, the down time is usually very lengthy. It is also an energy intensive process, therefore, modern cane sugar processing plants are installing diffusers, a water extraction process, instead of the multiple roller mills previously used.

In other areas of the food industry, water extraction is used to remove caffeine from coffee beans, and water extraction is used to prepare coffee and tea solubles for freeze or spray drying. Supercritical fluid extraction has been found to be effective for decaffeinating coffee and tea and for preparing unique flavor extracts from fruit and leaves of plants.

### 14.1 TYPES OF EXTRACTION PROCESSES

Extraction processes may be classified as follows.

### 14.1.1 Single-Stage Batch Processing

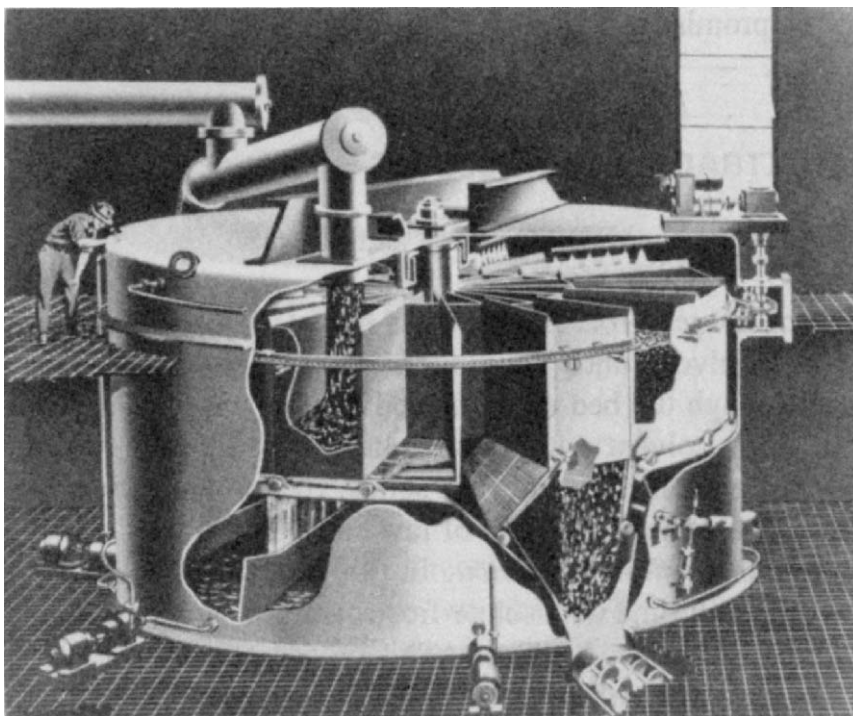
In this process, the solid is contacted with solute-free solvent until equilibrium is reached. The solvent may be pumped through the bed of solids and recirculated, or the solids may be soaked in the solvent with or without agitation. After equilibrium, the solvent phase is drained out of the solids. Examples are brewing coffee or tea, and water decaffeination of raw coffee beans.

### 14.1.2 Multistage Cross-Flow Extraction

In this process, the solid is contacted repeatedly, each time with solute free solvent. A good example is soxhlet extraction of fat in food analysis. This procedure requires a lot of solvent, or in the case of a soxhlet, a lot of energy is used in vaporizing and condensing the solvent for recycling, therefore, it is not used as in industrial separation process.

### 14.1.3 Multistage Countercurrent Extraction

This process utilizes a battery of extractors. Solute-free solvent enters the system at the opposite end from the point of entry of the unextracted solids. The solute-free solvent contacts the solids in the last extraction stage, resulting in the least concentration of solute in the solvent phase at equilibrium at this last extraction stage. Thus, the solute carried over by the solids after separation from the solvent phase at this stage is minimal. Solute-rich solvent, called the extract, emerges from the system at the first extraction stage after contacting the solids that had just entered the system. Stage to stage flow of solvent moves in a direction countercurrent to that of the solids. The same solvent is used from stage to stage, therefore solute concentration in the solvent phase increases as the solvent moves from one stage to the next, while the solute concentration in the solids decreases as the solids move in the opposite direction. A good example of a multistage countercurrent extraction process is oil extraction from soybeans using a carousel extractor. This system called the “rotocell” is now in the public domain and can be obtained from a number of foreign equipment manufacturers. A similar system produced by Extractionstechnik GmbH of Germany was described by Berk in a FAO publication. In this system (Fig. 14.1), two cylindrical tanks are positioned over each other. The top tank rotates while the lower tank is stationary. Both top and bottom tanks are separated into wedges, such that the content of each wedge are not allowed to mix. Each wedge of the top tank is fitted with a swinging false bottom to retain the solids, while a pump is installed to draw out solvent from each of the wedges except one, in the lower tank. A screw conveyor is installed in one of the wedges in the lower tank to remove the spent solids and convey them to a desolventization system. The false bottom swings out after the last extraction stage to drop the solids out of the top tank into the bottom wedge filled with the screw conveyor. The movement of the wedges on the top tank is indexed such that with each index, each wedge will be positioned directly over a corresponding wedge in the lower tank. Thus, solvent draining through the bed of solids in a wedge in the top tank will all go into one wedge in the lower tank. Solvent taken from the wedge forward of the current wedge is pumped over the bed of solids, drains through the bed, and enters the receiving tank, from which another pump transfers this solvent to the top of the bed of solids in the preceding wedge. After the last extraction stage, the swinging false bottom drops down releasing the solids, the swinging false bottom is lifted in place, and the empty wedge receives fresh solids to start the process over again. A similar system although of a different design, is employed in the beet sugar industry.

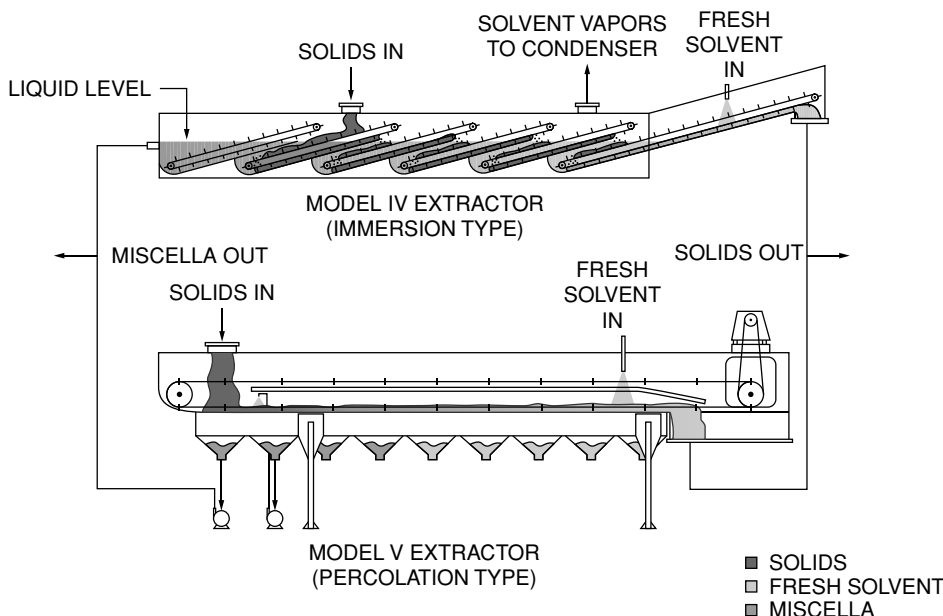


**Figure 14.1** The rotating basket extractor. (Source: Berk, Z. 1992. Technology for the production of edible flours and protein products from soybeans. FAO Agricultural Services Bulletin 97. Food and Agriculture Organization of the United Nations, Rome.)

#### 14.1.4 Continuous Countercurrent Extractors

In this system, the physical appearance of an extraction stage is not well defined. In its most simple form, an inclined screw conveyor may be pictured. The conveyor is initially filled with the solvent to the overflow level at the lower end, and solids are introduced at the lower end. The screw moves the solids upward through the solvent. Fresh solvent introduced at the highest end, will move countercurrent to the flow of solids picking up solute from the solids as the solvent moves down. Eventually, the solute-rich solvent collects at the lowermost end of the conveyor and is withdrawn through the overflow. In this type of extraction system, term “height of a transfer unit” (HTU) is used to represent the length of the conveyor where the solute transfer from the solids to the solvent is equivalent to one equilibrium stage in a multistage system.

Continuous conveyor type extractors are now commonly used in the oilseed industry. One type of extractor is a sliding cell basket extractor (Fig. 14.2A). The baskets affixed to a conveyor chain have false bottoms, which permits solvent sprayed at the top to percolate through and collect at a reservoir at the bottom of the unit. Pumps take the solvent from the reservoirs and takes them to nozzles at the top of the baskets. The discharge point of the solvent at the top of the baskets is advanced such that the solvent weak in solute is fed to the baskets forward of the baskets from where the solvent had



**Figure 14.2** Continuous belt-type extractor. (A) An immersion-type multistage countercurrent extractor. (B) A percolation-type extractor.

previously percolated. These units have been described in Berk's article and are produced by a German firm, Lurgi, GmbH. Another extractor suitable for not only oilseed extraction but also for extraction of health-functional food ingredients from plant material, is a perforated belt extractor. Figure 14.2B shows a perforated belt extractor produced in the United States by Crown Iron Works of Minneapolis, Minnesota. This unit is made to handle as small as 5 kg of solvent/h. A single continuous belt moves the solids forward while solvent is sprayed over the solids. A series of solvent collection reservoirs underneath the conveyor evenly spaced along the length of the unit, separates the solvent forming the different extraction stages. Each collection reservoir has a pump which takes out solvent from one stage and this liquid is applied over the solids on the conveyor in such a manner that the liquid will drain through the bed of solids and collect in another collection reservoir of the preceding stage.

Most extractions in the food industry involve solid-liquid extraction, therefore, the discussion in this chapter will be limited to solid-liquid extraction.

## 14.2 GENERAL PRINCIPLES

The following are the physical phenomena involved in extraction processes.

### 14.2.1 Diffusion

Diffusion is the transport of molecules of a compound through a continuum in one phase, or through an interface between phases. In solid liquid extraction (also known as leaching), the solvent must diffuse

into the solid in order for the solute to dissolve in the solvent, and the solute must diffuse out of the solvent saturated solid into the solvent phase. The rate of diffusion determines the length of time needed to achieve equilibrium between phases. In Chapter 12, section “Mass Diffusion,” the solution to the differential equation for diffusion through a slab is presented in Equation (12.41) in terms of the average concentration of solute within a solid as a function of time. This equation may be used to calculate the time needed for equilibrium to be achieved when the quantity of solid is small relative to the solvent such that concentration of solute in the solvent phase remains practically constant. Qualitatively, it may be seen that the time required for diffusion to occur in order to reach equilibrium, is inversely proportional to the square of the diffusion path. Thus, in solvent extraction, the smaller the particle size, the shorter the residence time for the solids to remain within an extraction stage.

Particle size, however, must be balanced by the need for the solvent to percolate through the bed of solids. Very small particle size will result in very slow movement of the solvent through the bed of solids, and increases the probability that fines will go with the solvent phase interfering with subsequent solute and solvent recovery.

In soybean oil extraction, the soy is tempered to a certain moisture content in order that they can be passed through flaking rolls to produce thin flakes without disintegration into fine particles. The thin flakes have very short diffusion path for the oil, resulting in short equilibrium time in each extraction stage, and solvent introduced at the top of the bed of flakes percolates unhindered through the bed. The presence of small particle solids is not desirable in this system because the fine solids are not easily removed from the solvent going to the solvent/oil recovery system. The high temperature needed to drive off the solvent will result in a dark colored oil if there is a large concentration of fine particles.

In cottonseed and peanut oil extraction, a pre-press is used to remove as much oil as can be mechanically expressed. The residue comes out of the expeller as small pellets which then goes into the extractor.

Some raw materials may contain lipoxygenase, which catalyzes the oxidation of the oil. Extraction of oil from rice bran involves the use of an extruder to heat the bran prior to extraction to inactivate lipoxygenase. The extruder produces small pellets which facilitates the extraction process by minimizing the amount of fines that goes with the solvent phase.

In cane sugar diffusers, hammer mills are used to disintegrate the cane such that the thickness of each particle is not more than twice the size of the juice cells. Thus, equilibrium is almost instantaneous upon contact of the particles with water. The cane may be pre-pressed through a roller mill to crush the cane and produce very finely shredded solids for the extraction battery.

### 14.2.2 Solubility

The highest possible solute concentration in the final extract leaving an extraction system is the saturation concentration. Thus, solvent to solids ratio must be high enough such that, when fresh solvent contacts fresh solids, the resulting solution on equilibrium, will be below the saturation concentration of solute.

In systems where the solids are repeatedly extracted with recycled solvent (e.g., supercritical fluid extraction), a high solute solubility will reduce the number of solvent recycles needed to obtain the desired degree of solute removal.

### 14.2.3 Equilibrium

When the solvent to solid ratio is adequate to satisfy the solubility of the solute, equilibrium is a condition where the solute concentration in both the solid and the solvent phases are equal. Thus,

the solution adhering to the solids will have the same solute concentration as the liquid or solvent phase. When the amount of solvent is inadequate to dissolve all the solute present, equilibrium is considered as a condition where no further changes in solute concentration in either phase will occur with prolonged contact time. In order for equilibrium to occur, enough contact time must be allowed for the solid and solvent phases.

The extent to which the equilibrium concentration of solute in the solvent phase is reached in an extraction stage is expressed as a stage efficiency. If equilibrium is reached in an extraction stage, the stage is 100% efficient and is designated an “ideal stage.”

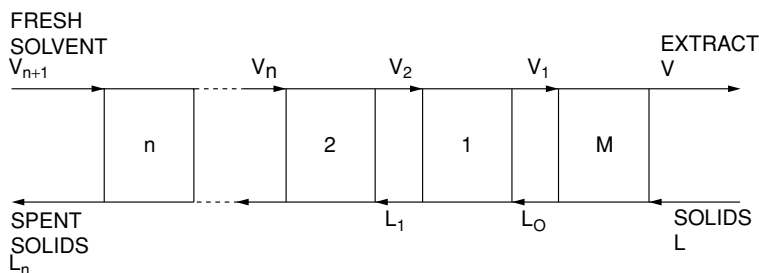
### 14.3 SOLID-LIQUID EXTRACTION: LEACHING

#### 14.3.1 The Extraction Battery: Number of Extraction Stages

Figure 14.3 shows a schematic diagram of an extraction battery with  $n$  stages. The liquid phase is designated the overflow, the quantity of which is represented by  $V$ . The solid phase is designated the underflow, the quantity of which is represented by  $L$ . The extraction stages is numbered 1 after the mixing stage where the fresh solids first contacts the solute laden extract from the other stages, and  $n$  as the last stage where fresh solvent first entered the system and where the spent solids leave the system. The stage where extract from the first extraction stage contacts the fresh solids, is called the mixing stage. It is different from the other stages in the extraction battery because at this stage the solids have to absorb a much larger amount of solvent than in the other stages.

Each of the stages is considered an ideal stage. Solute concentration in the underflow leaving stage  $n$ , must be at the designated level considered for completeness of the extraction process. Residual solute in the solids fraction must be maintained at a low level. If it is a valuable solute, the efficiency of solute recovery is limited only by the cost of adding more extraction stages. On the other hand, if the spent solids is also valuable and the presence of solute in the spent solids affects its value, then the number of extraction stages must be adequate to reduce the solute level to a minimum desirable value. For example, in oilseed extraction, the residual oil in the meal must be very low, otherwise the meal will rapidly become rancid.

Determination of the number of extraction stages may be done using a stage by stage material balance. Because the only conditions known are those at the entrance and outlet from the



**Figure 14.3** Schematic diagram of an extraction battery for multistage countercurrent extraction.

extraction system, the stage by stage material balance will involve setting up a system of equations that are solved simultaneously to determine the conditions of solute concentration in the underflow and overflow leaving each stage. The procedure will involve assumption of a number of ideal stages, solving the equations, and comparing if the calculated level of solute in the underflow from stage  $n$ , matches the specified value. The process is very tedious. A graphical method is generally used.

### 14.3.2 Determination of the Number of Extraction Stages Using the Ponchon-Savarit Diagram

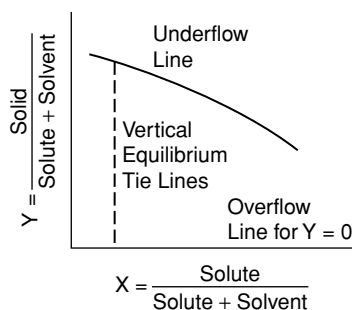
This graphical method for determining the number of extraction stages in a multi-stage extraction process, involves the use of an X-Y diagram. The coordinates of this diagram are defined as follows:

$$Y = \frac{\text{solid}}{\text{solute} + \text{solvent}}$$

$$X = \frac{\text{solute}}{\text{solute} + \text{solvent}}$$

where solid = concentration of insoluble solids; solute = concentration of solute, and solvent = concentration of solvent. Thus, the composition of any stream entering and leaving an extraction stage can be expressed in terms of the coordinates X,Y.

Figure 14.4 shows the X-Y diagram for a solid-liquid extraction process. The overflow line represents the composition of the solvent phase leaving each stage. If no solids entrainment occurs, the overflow line should be represented by  $Y = 0$ . The underflow line is dependent on how much of the solvent phase is retained by the solids in moving from one stage to the next. The underflow line will be linear if the solvent retained is constant, and curved when the solvent retained by the solids varies with the concentration of solute. Variable solvent retention in the underflow occurs when the presence of solute increases significantly the viscosity of the solvent phase.



**Figure 14.4** The underflow and overflow curves and equilibrium tie lines on a Ponchon-Savarit diagram.

### 14.3.3 The Lever Rule in Plotting Position of a Mixture of Two Streams in an X-Y Diagram

Let two streams with mass,  $R$  and  $S$ , and with coordinates  $X_r$  and  $Y_r$ , and  $X_s$  and  $Y_s$ , respectively, be mixed together to form  $T$  with coordinates  $X_t$  and  $Y_t$ . The diagram for the material balance is shown in Fig. 14.5(I). If  $R$  and  $S$  consist of only solute and solvent, solute balance results in:

$$RX_r + SX_s = (R + S)X_t \quad (14.1)$$

A solids balance gives:

$$RY_r + SY_s = (R + S)Y_t \quad (14.2)$$

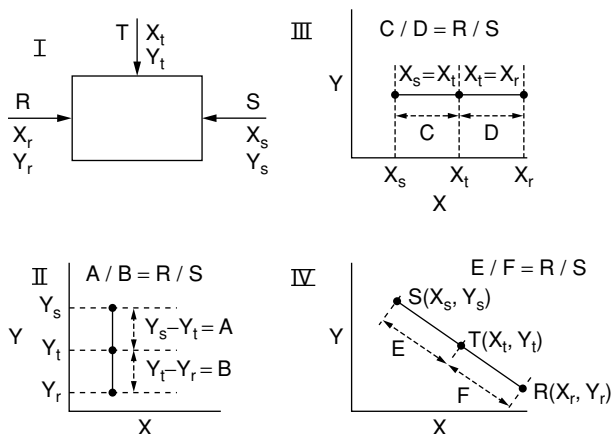
Solving for  $R$  in Equation (14.1) and  $S$  in Equation (14.2) and dividing:

$$\frac{R}{S} = \frac{X_s - X_t}{X_t - X_r} = \frac{Y_s - Y_t}{Y_t - Y_r} \quad (14.3)$$

Figure 14.5(II) represents the term involving  $Y$  in Equation (14.3). The coordinate for the mixture should always be between those of its components. The ratio of the distance between the line  $Y = Y_s$  and the line  $Y = Y_t$ , represented on the diagram by  $A$ , and the distance between the line,  $Y = Y_t$  and the line  $Y = Y_r$ , represented on the diagram by  $B$ , will equal the ratio of the mass of  $R$  and  $S$ .

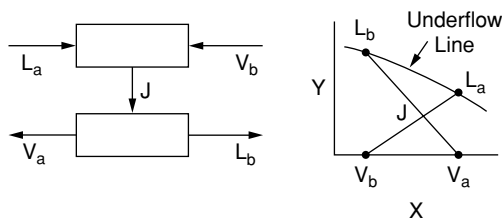
Figure 14.5(III) represents the term involving  $X$  in Equation (14.3). Again, the ratio of the masses of  $R$  and  $X$  equals the ratio of the distance  $C$ /distance  $D$  in the  $X$ - $Y$  diagram. The composite of the material balance is drawn in Fig. 14.5(IV). The coordinates of points  $S$  and  $R$  when plotted in the  $X$ - $Y$  diagram and joined together by a straight line, will result in the point representing  $T$  to be in the line between  $S$  and  $R$ . The ratio of the distance on the line, between  $S$  and  $T$ , represented by  $E$ , and that between  $R$  and  $T$ , represented by  $F$  is the ratio of the mass of  $R$  to  $S$ .

These principles show that a material balance can be represented in the  $X$ - $Y$  diagram with each process stream represented as a point on the diagram and any mixture of streams can be represented



**Figure 14.5** Representation of a material balance on the  $X$ - $Y$  diagram, and the lever rule for plotting mass ratio of process streams as ratio of distances between points on the  $X$ - $Y$  diagram.





**Figure 14.6** Representation of the point J as the intersection of lines connecting four process streams entering and leaving a system.

by a point on the line drawn between the coordinates of the components of the mixture. The exact positioning of the location of the point representing the mixture can be made using the lever rule on distances between the points as represented in Fig. 14.5(IV).

#### 14.3.4 Mathematical and Graphical Representation of the Point J in the Ponchon-Savarit Diagram

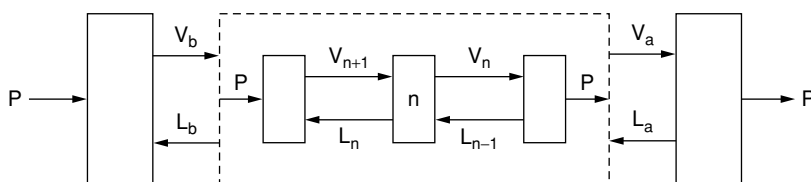
Consider underflow,  $L_b$  mixing with overflow,  $V_a$ , and the solid and solvent phases later separated to form the overflow stream  $V_b$  and the underflow stream  $L_a$ . A total mass balance gives:

$$L_b + V_a = V_b + L_a = J \quad (14.4)$$

The mixture of  $L_b$  and  $V_a$  forms the point J, shown in Fig. 14.6. A line drawn between the coordinates of  $L_b$  and  $V_a$  and another line drawn between the point  $V_b$  and  $L_a$  will intersect at point J. The point J may be used to help in plotting points representing the incoming and exiting streams in an extraction battery from the solvent to solids ratio.

#### 14.3.5 Mathematical and Graphical Representation of the Point P

The point P is a mixture that results when the underflow leaving a stage mixes with the overflow entering that stage. It is also the mixture of overflow leaving a stage and underflow entering that stage. The mixture representing point P is shown schematically in Fig. 14.7. A total mass balance around



**Figure 14.7** Representation of the point P for the common point through which all lines connecting the underflow leaving and the overflow entering an extraction stage must pass.

the system represented by the dotted line in Fig. 14.6 gives:

$$-V_b + L_b = -V_a + L_a = -V_{n+1} + L_n = P \quad (14.5)$$

Thus, the point P will be an extrapolation of the line that joins  $V_b$  and  $L_b$ ; the line that joins  $V_a$  and  $L_a$ ; and the line that joins  $V_{n+1}$  and  $L_n$ . All lines which join the underflow stream leaving a stage and the overflow stream which enters that stage, will all meet at a common point P. This is a basic principle used to draw the successive stages in a Ponchon-Savarit diagram for stage by stage analysis of an extraction process.

### 14.3.6 Equation of the Operating Line and Representation on the X-Y Diagram

Figure 14.8 represents an extraction battery with  $n$  cells. Each stage in the extractor may also be called an extraction cell. Cell  $n + 1$  is the cell after cell  $n$ . The subscripts on the overflow stream,  $V$ , and the underflow stream,  $L$ , represent the cell from which the stream is leaving. Thus, the solvent phase entering cell  $n$  comes from cell  $n + 1$  and is designated  $V_{n+1}$  and the solid phase leaving cell  $n$  is designated  $L_n$ . Let  $V$  represent the mass of solute and solvent in an overflow stream, and  $L$  represent the mass of solute and solvent in an underflow stream. A material balance around the battery of  $n$  cells is as follows:

Total mass balance:

$$V_{n+1} + L_a = L_n + V_a; \quad V_{n+1} = L_n + V_a - L_a \quad (14.6)$$

Solute balance:

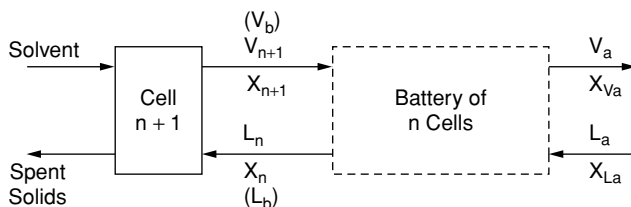
$$V_{n+1}X_{n+1} = V_aX_{Va} - L_aX_{La} + L_nX_n \quad (14.7)$$

Substituting Equation (14.6) in Equation (14.7) and solving for  $X_{n+1}$ :

$$X_{n+1} = \frac{L_n}{L_n + V_a - L_a} X_n + \frac{V_a X_{Va} + L_a X_{La}}{L_n + V_a - L_a} \quad (14.8)$$

Equation (14.8) is the equation of an operating line. It shows that the point representing stage  $n + 1$ , which has the coordinate  $X_{n+1}$ , is on the same line drawn through the point representing stage  $n$ , which has the coordinate  $X_n$ .

It can be shown that the coordinates of point P represented by Equation (14.5) can also satisfy Equation (14.8), thus, a line drawn from a point representing stage  $n$  to point P will allow the determination of a point representing the coordinate of stage  $n + 1$ .



**Figure 14.8** Diagram representing the system used to make a material balance for deriving the equation of the operating line in a Ponchon-Savarit diagram.

### 14.3.7 Construction of the Ponchon-Savarit Diagram for the Determination of the Number of Ideal Extraction Stages

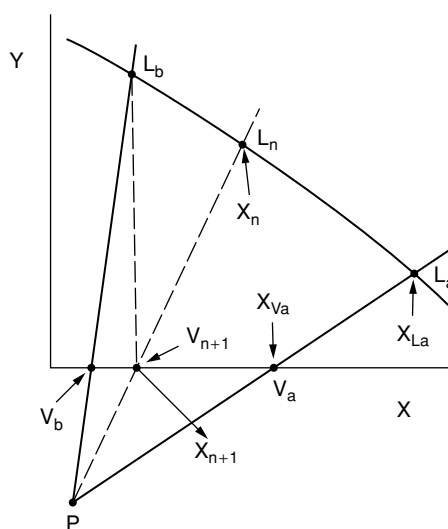
Figure 14.9 shows the X-Y diagram for determination of the number of ideal stages. Known points representing the coordinates of solvent saturated solids from the mixing stage,  $L_a$ , the extract,  $V_a$ , the spent solids,  $L_b$ , and the fresh solvent entering the system,  $V_b$ , are plotted first on the X-Y diagram. A total material balance must first be made to determine the coordinates of  $L_b$  and  $V_a$  from the solvent to solids ratio.

Point P is established from the intersection of lines going through  $L_b$  and  $V_b$  and  $L_a$  and  $V_a$ .

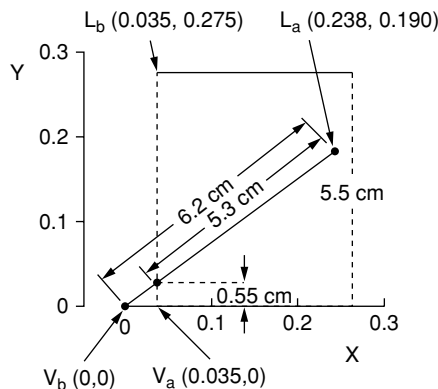
The condition of equilibrium is represented by a vertical line. Equilibrium means that  $X_{L_n}$  and  $X_{V_n}$  are equal. The equilibrium line is also known as a “tie line” and may not be vertical if equilibrium is not achieved. However, it is easier to assume equilibrium to occur, determine the number of ideal extraction stages, and incorporate the fact that equilibrium does not occur in terms of a stage efficiency.

The succeeding stages are established by drawing a line from the point representing stage n on the underflow line to point P. The intersection of this line with the overflow curve will determine  $X_{n+1}$ .

**Example 14.1.** Draw a diagram for a single stage extraction process involving beef (64% water, 20% fat, 16% nonextractable solids) and isopropyl alcohol in a 1 to 5 ratio. Isopropyl alcohol and water are totally miscible, and the mixture is considered to be the total solvent. Assume all fat dissolves in this solvent. Following equilibrium, the solids fraction separated by filtration retained 10% by weight of the total solution of fat and solvent. Determine graphically the concentration of the fat in the extract and calculate the fat content in the solvent free solids.



**Figure 14.9** Plotting of point P, the operating line, and the equilibrium tie-line on a Ponchon-Savarit diagram.



**Figure 14.10** X-Y diagram for a single-stage extraction process.

**Solution:**

Basis: 100 kg beef. Because the X-Y diagram uses as a denominator for the X and Y coordinates only the mass of the solution phase rather than total mass, the distances on the diagram should be scaled on the basis of the mass of solute and solvent present in each stream. Let  $L_a$  represent the beef.

$$X_{L_a} = 20/(20 + 64) = 0.238$$

$$Y_{L_a} = 16/(20 + 64) = 0.190$$

The solvent,  $V_b$ , will have the coordinates (0,0) because it contains no solute nor solids.  $L_a$  and  $V_b$  are plotted in Fig. 14.10.

Point J, the point representing the mixture before filtration is determined using the lever rule as follows: The ratio of the length of line segment  $L_aJ$ /length of line segment  $V_bL_a$  equals the ratio of the mass of solvent and solute in  $V_b$  to the total mass of solvent and solute in  $V_b$  and  $L_a$ .

$$\text{Let: } V_bL_a = 100 \text{ units}$$

The ratio  $V_b/(L_a + V_b) = 500/(20 + 64 + 500) = 0.856$ . Therefore, the distance  $V_bJ$  should be 85.6 units. For example, when plotting on a scale of 1 cm = 0.5 units for X and Y, length of  $V_bL_a = 6.2$  cm. Thus,  $L_aJ$  should be  $6.2(0.856) = 5.31$  cm long. These distances, when plotted, establish point J, which has coordinates (0.035, 1.1275). The vertical line  $X = 0.035$  is the equilibrium line. Assuming no insoluble solids in the extract,  $V_a$  has coordinates (0.035, 0). Point  $L_b$  is determined by plotting the distance  $V_aL_b$  (5.5 cm), which is 10 times  $V_aJ$  (0.55 cm) because 10% of the solution is retained in the underflow. The ratio  $X_{L_b}/Y_{L_b} = \text{solute/solids in } L_b = \text{mass fraction solute in the solvent free solids} = 0.127$ .

**Example 14.2.** Table 14.1 represents the amount of solution retained in soybean meal as a function of the oil concentration.

- Draw the underflow curve.
- If a solvent to soy ratio of 0.5 to 1 is used for extraction, and the original seed contains 18% oil, determine the number of extraction stages needed such that the meal after final desolventization will have no more than 0.01 kg oil/kg oil free meal.

**Table 14.1** Data for Overflow Composition During Extraction of Oil from Soybeans.

$X = \frac{\text{kg oil}}{\text{kg soln.}}$	$\text{Soln. retained}$ $\text{kg/kg solids}$	$Y = \frac{\text{Solids}}{\text{kg soln.}}$
0	0.5	2.0
0.1	0.505	1.980
0.2	0.515	1.942
0.3	0.530	1.887
0.4	0.550	1.818
0.5	0.571	1.751
0.6	0.595	1.680
0.7	0.620	1.613

Solution represents the solvent phase, mass of solvent plus mass of dissolved solute.

**Solution:**

- (a) The coordinates of points representing the underflow curve are given in Table 14.1. The parameter  $Y$  is the reciprocal of the solution retained/kg solids. The underflow curve is linear except for the last three points at high oil concentrations where there was a slight deviation from linearity. A regression analysis results in the equation of the best fit line as:

$$Y = -0.5775 X + 2.036$$

Figure 14.11 shows the Ponchon-Savarit diagram for this problem. The underflow curve is plotted in Fig. 14.12.

- (b) The composition of the final extract and spent solids stream is calculated by performing a material balance around the whole system. Basis: 1 kg soybean; solvent = 0.5 kg. From the specified level of oil in the extracted meal:

$$\text{kg oil in spent solids} = \frac{0.01 \text{ kg oil}}{\text{kg solids}} \times 0.82 \text{ kg solids} = 0.0082$$

From the data in Table 14.1, at very low oil contents, the amount of solution retained by the solids is 0.5 kg/kg solids.

$$\text{kg soln. in spent solids} = \frac{0.5 \text{ kg soln.}}{\text{kg solids}} \times 0.82 \text{ kg solids} = 0.41$$

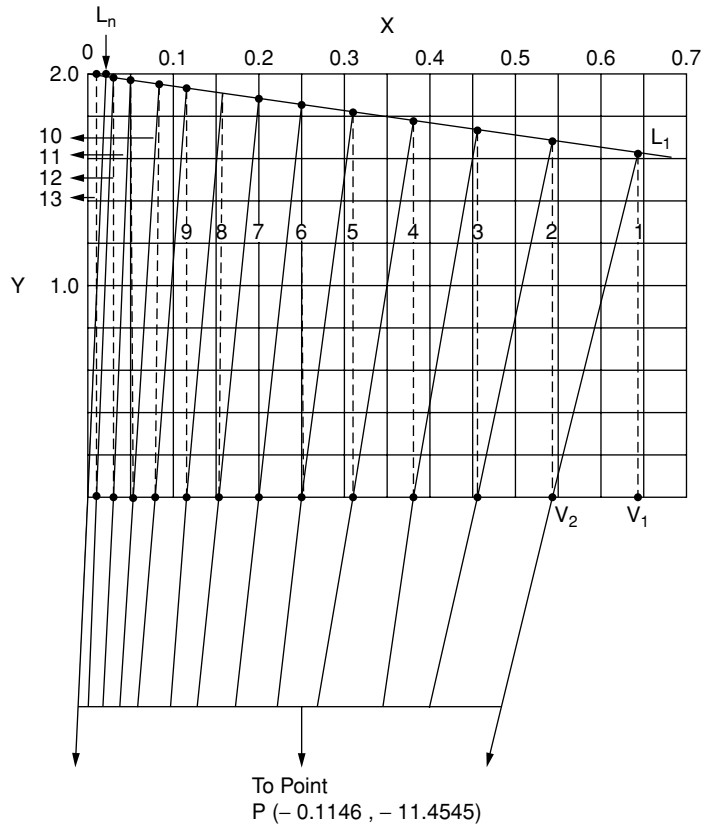
$$\text{kg solvent} = \frac{1 \text{ kg solvent}}{1.0082 \text{ kg soln.}} \times 0.41 \text{ kg soln.} = 0.4018 \text{ kg solvent in spent solids}$$

$$\text{Mass of } L_n, \text{ the spent solids} = 0.82 + 0.0082 + 0.4018 = 1.23 \text{ kg}$$

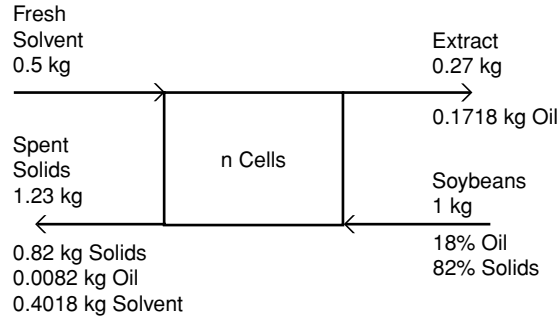
Coordinates of spent solids,  $L_n$ :

$$X = 0.0082 / 0.41 = 0.02 \text{ kg solute/soln.}$$

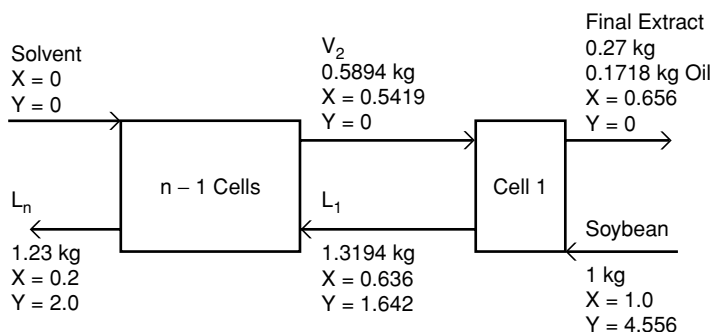
$$Y = 1 \text{ kg solids} / 0.5 \text{ kg soln.} = 2.0 \text{ kg solids/kg soln.}$$



**Figure 14.11** The underflow curve and operating lines establishing the number of equilibrium stages needed to solve the example problem on continuous countercurrent oil extraction from soybeans.



**Figure 14.12** Overall material balance to determine the extract mass and composition and spent solids mass and composition for the example problem on soybean extraction.



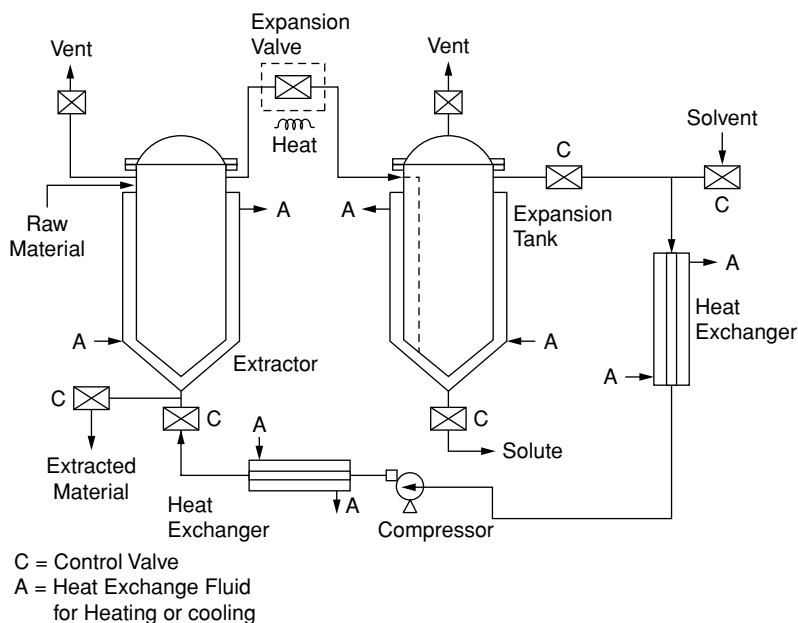
**Figure 14.13** Diagram showing material balance around the mixing stage, Cell 1, to establish the composition of overflow stream leaving and underflow stream entering the extraction battery after the mixing stage.

Figure 14.13 shows the overall material balance with the mass and components of each stream entering and leaving the extraction battery.

$$\text{Mass of extract } V_a = 1.5 - 1.23 = 0.27 \text{ kg}$$

$$\text{Mass of oil } V_a = 0.82 - 0.0082 = 0.1718 \text{ kg}$$

The Ponchon-Savarit diagram can be constructed only for the cells following the mixing stage. Figure 14.14 shows the material balance for the mixing stage which is considered as cell 1 in this case,



**Figure 14.14** Schematic diagram of a supercritical fluid extraction system.

and the stream entering and leaving stage 2. Material balance around cell 1:

Final extract,  $V_a$ :  $X = 0.1718/0.27 = 0.636 \text{ kg oil/kg soln.}$

Because the last three data points deviated slightly from linearity, the amount of solution retained by the solids in stream  $L_1$  will be calculated by interpolation from the tabulated data instead of the regression equation. Because final extract  $V_a$  is in equilibrium with the solids in stream  $L_1$ , the  $X$  coordinate of stream  $L_1$  must be the same as for the final extract. Thus,  $X$  for stream  $L_1 = 0.636 \text{ kg oil/kg soln.}$  From Table 14.1 by interpolation, the solution retained by the solids if the solute concentration is  $0.636 \text{ kg oil/kg soln.}$  is

$$= 0.595 + (0.620 - 0.595)(0.656 - 0.6)/(0.7 - 0.6) = 0.609 \text{ kg soln/kg solids.}$$

Total mass of  $L_1 = 0.82 \text{ kg solids} + 0.609(0.82) = 1.3194 \text{ kg}$

$Y$  for stream  $L_1 = 1/0.609 = 1.642 \text{ kg solids/kg soln.}$  The mass and composition of stream  $V_2$  can now be calculated.

$$\text{Mass of } V_2 = L_1 + V_a - 1 = 1.3194 + 0.27 - 1 = 0.5894 \text{ kg}$$

$$\text{Mass oil in } L_1 = \left[ \frac{0.609 \text{ kg soln.}}{\text{kg solids}} (0.82 \text{ kg solids}) \right] \left( \frac{0.656 \text{ kg oil}}{\text{kg soln.}} \right) = 0.3276 \text{ kg}$$

Oil balance around cell 1:

$$\text{Oil in } V_2 = 0.1718 + 0.3276 - 0.18 = 0.3194 \text{ kg}$$

$X$  coordinate for  $V_2$ :

$$X = 0.3194/0.5894 = 0.5419$$

The streams to be considered to start plotting of the Ponchon-Savarit diagram are streams  $V_2$  and  $L_1$ , and the solute-free solvent stream and the spent solids stream,  $L_n$ .

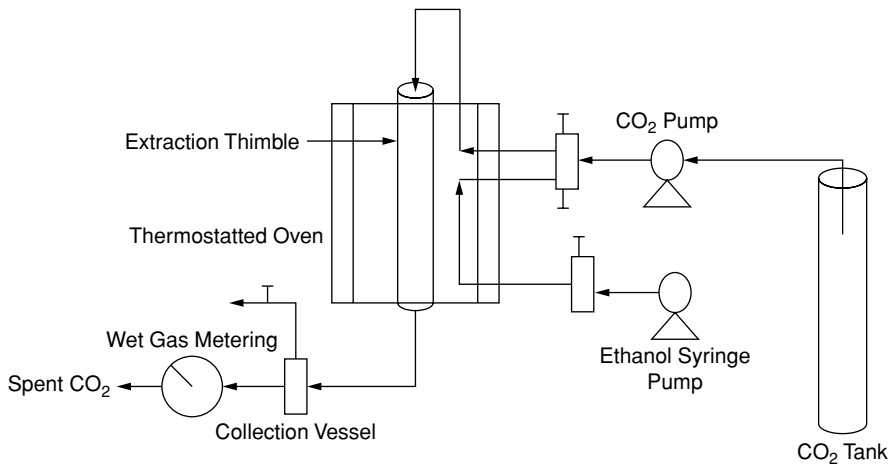
$V_2$  and  $L_1$  are first plotted in Fig. 14.11. A line is drawn through the two points and extended beyond the graph. The equation of the line that connects the two points may also be determined. Points representing the solute-free solvent and the spent solids stream,  $L_n$ , are plotted next. The solute free solvent is represented by the origin. A line is drawn through the two points and extended until it intersects the previous line drawn between  $L_1$  and  $V_2$ . The equation for the line may also be determined and the point of intersection, representing the point,  $P$ , can be calculated by solving the two equations simultaneously. The coordinate of point  $P$  is  $-0.1146, -11.4545$ .

An equilibrium line drawn from  $V_2$  to the underflow curve will locate a point that represents  $L_3$ . Drawing a line from this point to connect with point  $P$  will locate an intersection on the overflow curve, for the point representing  $V_3$ . The process is repeated, until the last line drawn from the underflow curve to point  $P$  will intersect the overflow curve at a point that is equal to or less than the specified  $X$  for the spent solids,  $L_n$ . The number of extraction stages is the number of equilibrium tie-lines drawn in the diagram in Fig. 14.11. In this problem, 13 equilibrium stages are required.

#### 14.4 SUPERCRITICAL FLUID EXTRACTION

Supercritical fluid extraction may be done on solids or liquids. The solvent is a dense gas at conditions of temperature and pressure where further increase in pressure or a reduction in temperature will not result in a phase change from gas to liquid. The density of a supercritical fluid, however, is almost that





**Figure 14.15** Schematic diagram of a supercritical fluid extraction system using entrained ethanol in supercritical carbon dioxide.

of a liquid, but it is not a liquid. In addition, the solubility of solutes in a supercritical fluid approaches the solubility in a liquid. Thus, the principle of solute extraction from solids using a supercritical fluid is very similar to that for solid-liquid extractions.

#### 14.4.1 Extraction Principles

Supercritical fluid extraction is done in a single-stage extractor with or without recycling of the solvent. When recycling is used, the process involves a reduction of pressure to allow the supercritical fluid to lose its ability to dissolve the solute, after which the solid is allowed to separate by gravity, and the gas at low pressure is compressed back to the supercritical conditions and recycled. Temperature reduction may also be used to drop the solute and the solvent is reheated for recycling without the need for recompression.

Figure 14.14 shows a schematic diagram of a supercritical fluid extraction system. The basic components are an extractor tank and an expansion tank. Supercritical fluid conditions are maintained in the extractor. Temperature is usually maintained under controlled conditions in both tanks. Charging and emptying the extractor is a batch operation. The pressure of the supercritical fluid is reduced by throttling through a needle valve or orifice after which it enters an expansion tank where the supercritical fluid becomes a gas. Because solute solubility in the gas is much less than in the supercritical fluid, solute separates from the gas in the expansion tank. The spent gas is then recompressed and recycled. Heat exchanges are needed to maintain temperatures and prevent excessive cooling at the throttling valve due to the Joule-Kelvin effect.

Two of the major problems of supercritical fluid extraction are channeling of solvent flow through the bed of solids, and entrainment of the nonextractable component by the solvent. Time of solid-solvent contact is the quotient of extraction vessel volume divided by the solvent volumetric flow rate. The volume is calculated at the temperature and pressure inside the extraction vessel. Normally, volume of the solvent is measured at atmospheric pressure after the gas exited the expansion tank. From this measured volume, the number of moles of gas is calculated and the volume of the supercritical fluid in

the extraction vessel is then calculated using the equations of state for gases. The contact time should be adequate to permit solvent to penetrate solid particles and permit diffusion of solute from inside the solid particles into the solvent phase. To achieve equilibrium between the solution inside solid particles and the solvent phase, solvent flow must be adjusted to achieve the necessary contact time and to provide enough solvent such that concentration of dissolved solutes in the solvent phase will be below the solubility of solute in the solvent. A large quantity of solute to be extracted would require a larger rate of solvent flow to permit thorough solute extraction within a reasonable length of time. Supercritical fluid penetration into the interior of a solid is rapid, but solute diffusion from the solid into the supercritical fluid may be slow thus requiring prolonged contact time in the extraction vessel. Solvent flow rate, pressure, and temperature in the extraction vessel are the major supercritical fluid extraction process parameters.

#### 14.4.2 Critical Points of Supercritical Fluids Used in Foods

Carbon dioxide is the most widely used supercritical fluid. The compound is nontoxic, nonflammable, and is inexpensive and readily available. The critical point of carbon dioxide is 31.1°C and 7.39 MPa (74 Bars). At temperature and pressure above the critical point, the fluid is supercritical. Ethanol may also be added in small amounts to supercritical carbon dioxide to change its polarity in some extractions. The critical point of ethanol is 243°C and 6.38 MPa (64 Bars). Water may also be transferred from the solid to the solvent phase therefore the supercritical fluid in the extraction vessel may contain water. The critical point of water is 364°C and 22.1 MPa (221 Bars).

#### 14.4.3 Critical Point of Mixtures

The critical point of a mixture of compounds may be calculated as a mole fraction weighted average of the individual components.

$$T_c = 3(x_1 T_{c1} + x_2 T_{c2} \dots + x_n T_{cn})$$

$$P_c = 3(x_1 P_{c1} + x_2 P_{c2} \dots + x_n P_{cn})$$

#### 14.4.4 Properties of Supercritical Fluids Relative to Gases

The relative density of a supercritical fluid is in the range 0.1 to 1 compared with a density of 1 for liquids and 0.001 for gases. The relative viscosity is 0.1 to 1 compared with 1 for liquids and 0.01 for gases. The relative diffusivity is 10 to 100 compared with 1 for liquids and  $10^4$  for gases.

#### 14.4.5 Supercritical Fluid Extraction Parameters

Separation of multiple solutes from a solid may be the objective of a supercritical fluid extraction process. For example, components of a fat or oil high in polyunsaturated fatty acids may be removed from the mixture leaving triglycerides with saturated fatty acids with higher melting points and higher resistance to oxidation. Another example is the separation of phospholipids from the triglycerides in soybean oil to prevent gumming of the oil. Solubility of solutes in the supercritical solvent may be a function of pressure and/or temperature. Table 14.2 shows the solubility of some compounds in supercritical carbon dioxide. These data show that the right conditions may be selected to maximize

**Table 14.2** Solubility of various compounds in supercritical CO<sub>2</sub> (In mg/g).

Pressure(Bars)/ Temperature °C	80/40	90/40	100/40	200/40	80/50	90/50	100/50	200/50	162/45	146/45
Limonine	5.8	CM				17.1	CM			
Lauric acid			6.8	11.6						
Palmitic acid			0.8	4.4						
Trilaurin			0.1	26.8						
Tripalmitin				0.3						
Trimyristin			0.5	5.6						
β-carotene				0.0021				0.0028		
Stearic acid <sup>1</sup>									23.8	23.8
Water					1.6		1.9	2.8		

<sup>1</sup> Solvent is CO<sub>2</sub> with acetic acid at 0.03 mole fraction as entrainer.

CM = completely miscible

solute solubility. Another method for changing solubility is the use of entrainers. For example, in Table 14.2, tristearin solubility in carbon dioxide with an acetic acid entrainer is very high at relatively low pressure. Data in Table 14.2 also shows that a pressure of 200 Bars and 40°C should be good for extracting neutral lipids. Another example is the enhancement of the solubility of lecithin when ethyl alcohol is an entrainer in supercritical carbon dioxide. Other compounds with improved solubility in supercritical carbon dioxide-ethanol include limonoids from citrus seeds and phospholipids such as phosphatidyl ethanolamine and phosphatidyl choline from dried egg yolk.

Another technique used to separate solutes is by using a two-stage process. For example, one group of compounds may easily dissolve in the solvent under a given set of conditions while leaving the less soluble ones in the solid. A second extraction under conditions that favor the dissolution of the remaining solute in the solid in the solvent will result in the isolation of these group of compounds from the other group removed in the first extraction. The following examples are optimized extraction conditions reported in the literature:

1. Preparation of ginger flavor extract from dried ginger. CO<sub>2</sub> at 15 g/min. First-stage extraction at 79 Bars and 30°C; second stage at 246 Bars and 40°C. ( Yonei, Y, et al J. Sup. Fl. 8:156–161, 1995).
2. Flavor extracts from coriander seed: 250 Bars and 40°C. Celery powder and sage: 70 Bars and 20°C (Catchpoole, O.J. et al. J. Sup. Fl. 9:273–279, 1996).
3. Egg phospholipids from dried egg yolk. First stage: CO<sub>2</sub> at 414 Bars and 45°C. Second stage: CO<sub>2</sub> – 5% ethanol at 414 Bars and 45°C (Shah A. et al. J. Sup. Fl. 30:303–313, 2004).

## PROBLEMS

- 14.1. Ground roasted coffee contains 5% soluble solids, 3% water, and 92% inert insoluble solids. In order to obtain an extract with high soluble solids content without having to concentrate it for spray drying, a counter-current extraction process is to be used to prepare this extract.

It is desired that the final extract contain 0.1 kg solubles/kg water and that the spent coffee grounds should have solubles not to exceed 0.005 kg/kg dry inert solids.

- (a) Determine the water to coffee ratio to be used in the extraction.
  - (b) The coffee grounds carry 1 kg water/kg of solubles-free inert solids, and this quantity is constant with solute concentration in the extract. Calculate the number of extraction stages needed for this process.
- 14.2. A process for extracting sugar from sweet sorghum involves pressing the cane through a three-roll mill followed by shredding the fibrous residue (bagasse) and extracting the sugar out with water. The sorghum originally contained 20% fiber, 16% sugar, and 64% water. After milling, the moisture content of the bagasse is 55%. Because the fiber is used for fuel, after the extraction battery, the solids is squeezed to remove the absorbed solution and the squeezed solution is added to the last stage of the extractor. The following are the constraints: The sugar recovery must be a minimum of 99%, and the concentration of sugar in the final extract must be 10%. The bagasse carries a constant amount of solution, 1.22 kg solution/ kg fiber. Calculate:
- (a) The water to solids ratio needed.
  - (b) The number of ideal extraction stages.
  - (c) The final sugar content if the extract is mixed with the juice first pressed out of the cane.

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