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Detail study on Solvent Extraction

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Abstract

Along with fractional crystallisation and distillation, liquid-liquid extraction should be taken into consideration as a desirable strategy for product recovery and purification. One of the main benefits of extraction is the ability to separate materials according to chemical type rather than physical characteristics like freezing point or vapour pressure. Since just a small amount of a selective solvent must be employed, it is frequently possible to save energy when recovering valuable components from diluted broth solution, which facilitates recovery from the concentrated extract. Simple shake-outs over the necessary concentration range are frequently used to test the selectivity of potentially attractive solvents. These distributional data can be used to compute the amounts of solvent and theoretical stages in various combinations.

Keywords: Fractional crystallization; Liquid-liquid extraction; Solvent; Extraction

1.0 EXTRACTION CONCEPTS

Liquid-liquid extraction is a unit operation frequently employed in the ~~pharmaceutical industry,~~ as in many others, for recovery and purification of a desired ingredient from the solution in which it was prepared. Extraction may also be used to remove impurities from a feed stream.

Extraction is the removal of a soluble constituent from one liquid into another. By convention, the first liquid is the *feed* (*F*) which contains the solute at an initial concentration X_f. The second liquid is the *solvent* (*S*) which is at least partially immiscible with the feed. The solvent may also have some solute present at an initial concentration of Y_s, but usually Y_S is essentially zero.

The solvent does the extraction, so the solvent-rich liquid leaving the extractor is the *extract* (*E*). With the solute partially or completely removed from the feed, the feed has become *refined* so the feed-rich liquid leaving the extractor is the *raffinate* (*R*).

When the feed and solvent are brought together, the *solute* (*A*) will distribute itself between the two liquid phases. At equilibrium, the ratio of this distribution is called the *distribution coefficient* (*m*):

$$m \, 5 \, \frac{Y_A}{X_A} \, 5 \, \frac{\text{concentration of } A \text{ in extract phase}}{\text{concentration of } A \text{ in raffinate phase}}$$

The distribution coefficient, *m*, is a measure of the affinity of the solute (*A*) for one phase (*E, S*) over the other phase (*F, R*). The concentration of *A* may be expressed in various units, but for ease of subsequent calculations, it is preferable to express the concentration on a solute-free basis for both phases. For example, in the extraction of acetone from water with toluene:

$$X \, 5 \, \frac{\text{weight acetone}}{\text{weight acetone — free water}}$$

$$Y \, 5 \, \frac{\text{weight acetone}}{\text{weight acetone — free toluene}}$$

$$m \, 5 \, \frac{Y}{X}$$

Although the units of *m* appear to be dimensionless, they actually are (weight acetone-free water)/(weight acetone-free toluene).

If more than one solute is present, the preference, or *selectivity*, of the solvent for one (*A*) over the other (*B*) is the *separation factor* (a).

$$a_{AB} \, 5 \, \frac{m_A}{m_B}$$

The separation factor (a_{AB}) must be greater than unity in order to separate *A* from B by solvent extraction, just as the relative volatility must be greater than unity to separate *A* from B by distillation.

The analogy with distillation can be carried a step further. The extract phase is like the vapor distillate, a second phase wherein the equilibrium distribution of *A* with respect to B is higher than it is in the feed liquid (liquid bottoms).

Extraction requires that the solvent and feed liquor be at least partially immiscible (two liquid phases), just as distillation requires both a vapor and a liquid phase.

Extraction requires that the solvent and feed phases be of different densities.

Even though extraction may successfully remove the solute from the feed, a further separation is required in order to recover the solute from the solvent, and to make the solvent suitable for reuse in the extractor. This recovery may be by any other unit operation, such as distillation, evaporation, crystallization and filtration, or by further extraction.

Extraction is frequently chosen as the desired primary mode of separation or purification for one or more of the following reasons:

1. Where the heat of distillation is undesirable or the temperature would be damaging to the product (for example, in the recovery of penicillin from filtered broth).
2. Where the solute is present in low concentration and the bulk feed liquor would have to be taken overhead (most fermentation products).
3. Where extraction selectivity is favorable because of chemical differences, but where relative volatilities overlap.

4. Where extraction selectivity is favorable in ionic form, but not in the natural state (such as citric acid).
5. Where a lower form or less energy can be used. The latent heat of most organic solvents is less than 20% that of water, so recovery of solute from an organic extract may require far less energy than recovery from an aqueous feed.

1.1 Theoretical Stage

The combination of mixing both feed and solvent until the equilibrium distribution of the solute has occurred, and the subsequent complete separation of the two phases is defined as one theoretical stage (Fig. 11.1). The two functions may be carried out sequentially in the same vessel, simultaneously in two different zones of the same vessel, or in separate vessels (mixers and settlers).

Extraction may also be performed in a continuous differential fashion (Fig. 11.2), or in a sequential contact and separation where the solvent and feed phases flow countercurrently to each other between stages (Fig. 11.3).

2.0 DISTRIBUTION DATA

Although data for many systems are available in the literature [1], in many cases it will be necessary for the engineer to obtain the distribution information for his own specific application.

The simplest method is to mix solvent and feed liquors containing varying quantities of solute in a separatory funnel, and analyze each phase for solute after settling. Where feed and solvent are essentially immiscible, the binary plot, such as shown in Fig. 11.4, is useful. For later ease of calculation, it is desirable to express concentrations on a solute-free basis. If there is extensive miscibility, a ternary plot (Fig. 11.5) would be preferable. Tie lines represent the equilibrium between the coexisting phases.

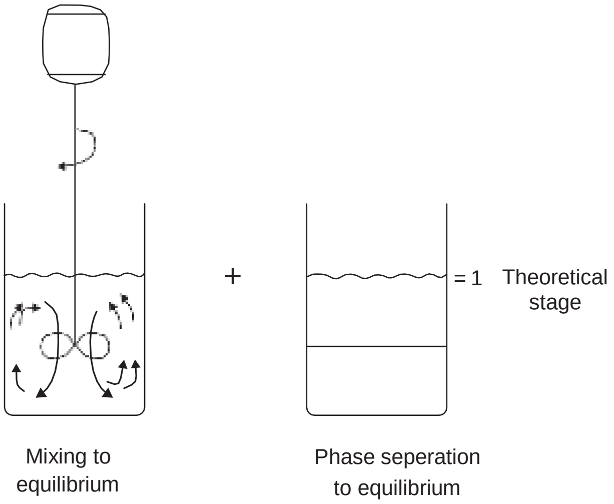

FIGURE 11.1 Theoretical stage.

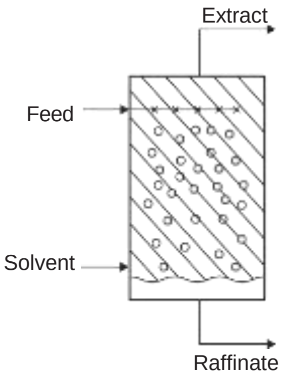

FIGURE 11.2 Differential extraction.

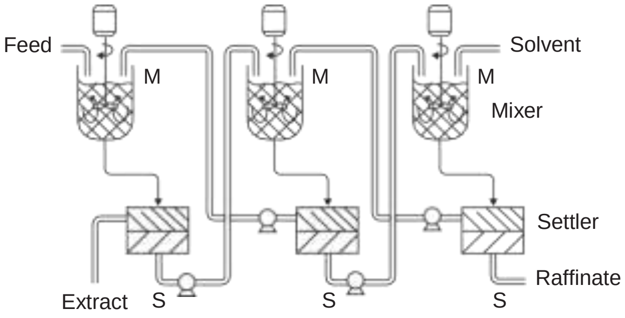

FIGURE 11.3 Sequential contact and separation.

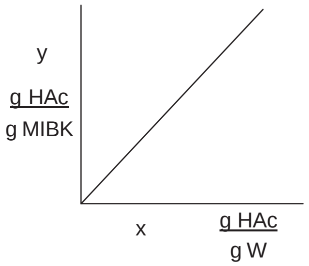

FIGURE 11.4 Binary plot of distribution data.

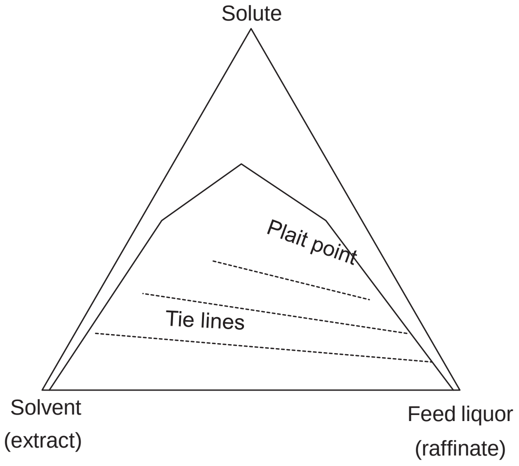

FIGURE 11.5 Ternary plot of distribution data.

Plotting the data on log-log graphs may be helpful in understanding some of the underlying phenomena and interpolating or extrapolating meager data. An example is shown in Fig. 11.6 for the distribution of phenol between water and various chlorinated methanes. In the dilute region, the limiting slope is generally always unity. However, as the solute becomes more concentrated, there may be a tendency for solute molecules to associate with each other in one of the phases. Thus, the equilibrium data in Fig. 11.6 suggest that the phenol molecules form a dimer in the organic phase, probably by hydrogen bonding, leading to a slope of 2 in the distribution plot.

The possibility of complex formation in one of the phases illustrates the concern that many industrial extraction processes involve not only the physical transfer of molecules across an interface, but also that there may be a sequence of chemical steps (which may be rate limiting) that have to occur before the physical transfer can take place.

Whenever the distribution coefficient is greatly different than unity, there is an implication that there exists an *affinity* of the solute for that specific solvent, and this affinity may involve some loose chemical bonding.

Examples of computer programs for predicting and correlating equilibrium data are described by Lo, Baird, and Hanson [2].

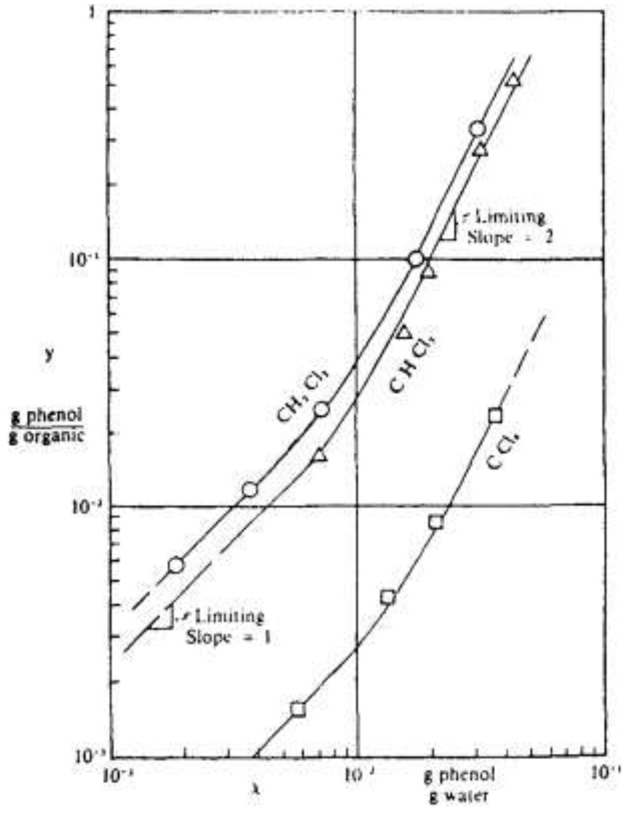

FIGURE 11.6 Distribution of phenol between water and chlorinated methanes.

3.0 SOLVENT SELECTION

The molecular formula of the solute may suggest the type of solvent which may be selective for its extraction, based on probable affinities between related functional groups. Thus, to extract organic acids or alcohols from water, an ester, ether, or ketone (of sufficient molecular weight to have very limited solubility in the aqueous phase) might be chosen as the solvent. The pH of aqueous phase feeds may also be very important. The sodium or potassium salts of an organic acid may well prefer the aqueous media at pH ▪ 10, but in the acidulated form may readily extract into the organic phase if the pH is low.

Specific factors taken into consideration in the selection of a solvent include:

1. *Selectivity*—the ability to remove and concentrate the solute from the other components likely present in the feed liquor.
2. *Availability*—the inventory of solvent in the extraction system can represent a significant capital investment.
3. *Immiscibility with the feed*—otherwise there will need to be recovery of the solvent from the raffinate, or a continual and costly replacement of solvent as make up.
4. *Density differential*—too low a density difference between the phases will result in separation problems, lower capacity, and larger equipment. Too large a density difference may make it difficult to obtain the drop sizes desired for best extraction.
5. *Reasonable physical properties*—too viscous a solvent will impede both mass transfer and capacity. Too low an interfacial tension may lead to emulsion problems. The boiling point should be sufficiently different from that of the solute if recovery of the latter is to be by distillation.
6. *Toxicity*—must be considered for health considerations of the plant employees and for purity of the product.
7. *Corrosiveness*—may require use of more expensive materials of construction for the extraction process equipment.
8. *Ease of recovery*—as transfer of the solute from the feed still entails the further separation of solute from the solvent, solvent recovery will need to be as complete and pure as possible to permit recycle to the extractor as well as minimizing losses and potential pollution problems.

CALCULATION PROCEDURES

Sizing the equipment required for a given separation will depend upon both the flow rates involved and the number of stages that will be required.

With a binary equilibrium plot, Fig. 11.7, the distribution of extract and raffinate following one stage of contact is readily determined. Representing a mass balance of the solute transferred:

$$(Y_S - Y_E)S = (X_F - X_R)F$$

$$\frac{(Y_S - Y_E)}{(X_F - X_R)} = \frac{F}{S}$$

Thus, a line can be drawn from X_F, with a slope of F/S to the intersection with the equilibrium line, thus establishing Y_E and X_R.

For multiple contact, Fig. 11.8, the operating line can be written around some point in the column between stage "n" and (n + 1):

$$S(Y_{n+1} - Y_S) = F(X_n - X_R)$$

$$(Y_{n+1} - Y_S) = \frac{F}{S}(X_n) - \frac{F}{S}(X_R)$$

Since liquid-liquid extraction frequently involves only a few stages, the above equation can be used for an analytical solution.

The desired concentration of extract Y_E is set equal to Y_1, and the raffinate in equilibrium with the first stage, X_1, is determined from the equilibrium curve. With this value of X_1, Y_2 is calculated from the above operating equation; then X_2 is determined from the equilibrium line and the calculation procedure is continued until $X_n \# X_r$.

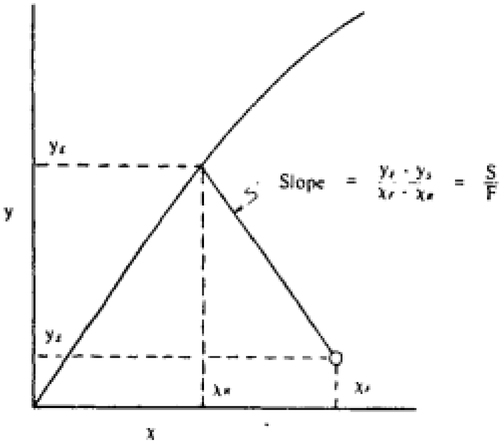

FIGURE 11.7 Graphical solution for single contact.

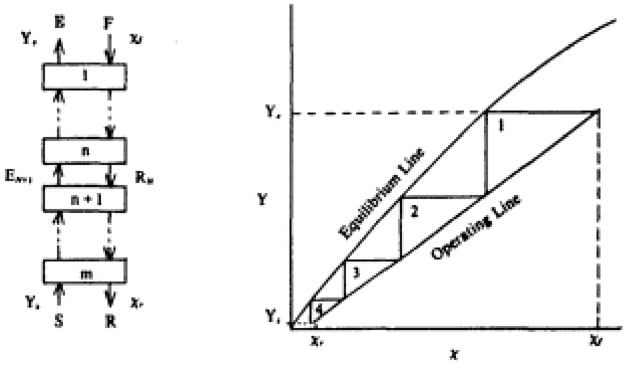

FIGURE 11.8 Graphical solution for multiple contact.

A graphical solution is also readily obtainable. The operating line, with slope F/S, is drawn from the inlet and outlet concentrations. The number of stages is then stepped off in the same fashion as with a McCabe Thiele diagram in distillation, as shown in Fig. 11.8.

With a ternary equilibrium diagram, such as Fig. 11.5, the process result can be determined graphically. In Fig. 11.9, the addition of solvent to a feed containing X_F solute will be along the straight line connecting S with X_F. From an overall mass balance, the composition M of the mixture of feed and solvent is determined. With M in the two-phase zone, the overall mixture M separates along a tie line to end points Y_E and X_R on the equilibrium curve. The relative quantities of each phase can be calculated using the inverse lever-arm rule.

With more than one contact, an operating point Q is located outside the ternary diagram, as shown in Fig. 11.10. With a specified solvent/feed ratio and a desired raffinate purity, X_1, with the given feed, X_F the composition of the final extract, Y_n, is fixed by material balance. Point Q is formed by the intersection of the line drawn from Y_n through X_F, with the line drawn from the fresh solvent Y_S through X_1.

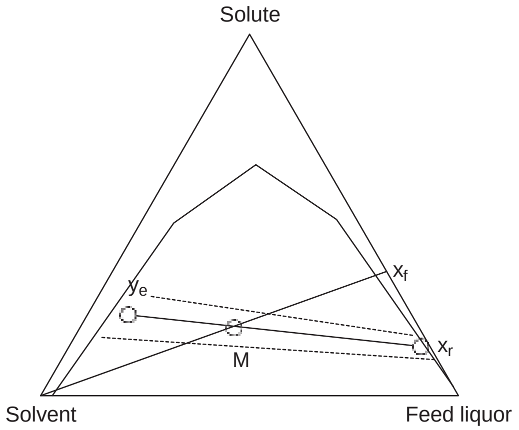

FIGURE 11.9 Graphical solution for single contact with ternary equilibrium data.

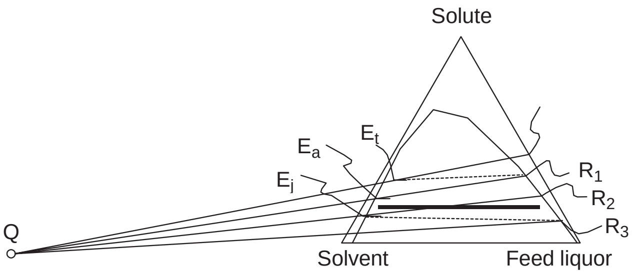

FIGURE 11.10 Graphical solution for multiple contact.

Point *M* in Fig. 11.9 represented the material balance:

$$F 1 S 5 E 1 R 5 M$$

Point *Q* in Fig. 11.10 represents a hypothetical quantity obtained by rearrangement of the above equation:

$$F 2 E 5 R 2 S 5 Q$$

The material balance for each stage is:

$$F 2 E_I 5 R_n 2 E_{n11} 5 Q$$

Thus, a line through *Q* represents the operating line between stages. The number of stages is obtained by sequentially stepping off first the equilibrium distribution along a tie line, and then to the next stage by a line drawn from point *Q* through the raffinate to locate the next extract.

Simplified Solution

If the *distribution coefficient* is constant, and if there is essentially no mutual solubility, the fraction not extracted, Ψ, can be calculated directly as a function of the extraction factor, *E*, and the number of stages, *n*.

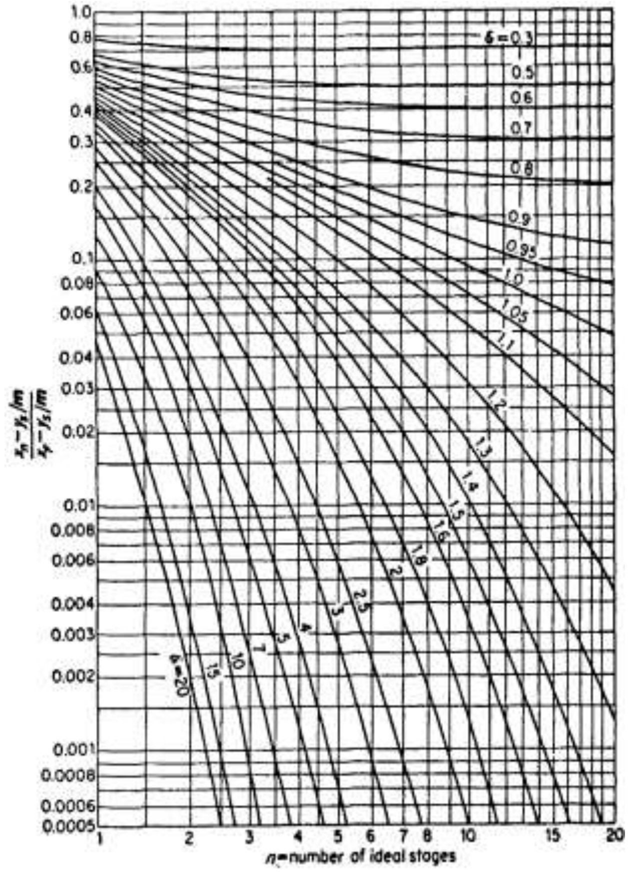

FIGURE 11.11 Countercurrent multistage extraction with immiscible solvents and constant distribution coefficient. *(From:* Liquid Extraction *by R.E. Treybal. Copyright© 1963, McGraw-Hill. Used with the permission.)*

$$\psi 5 \frac{X_1 2 Y_S=m}{X_F 2 Y_S=m}; \quad E 5 \frac{mS}{F}$$

$$\psi 5 \frac{E 2 1}{E^{n11} 2 1}; \quad E 6¼ 1$$

Treybal [3] discusses the derivation of these equations and presents a graphical solution reproduced here as Fig. 11.11.

Even when the two limitations of immiscibility and constant distribution coefficient do not quite hold, Fig. 11.11 does allow a quick estimate of the trade-offs between solvent/feed ratio and number of stages required to obtain a desired degree of extraction (raffinate purity).

The above solutions are all based on *ideal* or *theoretical* stages. Even in discrete stage systems, like mixer-settlers, equilibrium may not be attained because of insufficient time for diffusion of solute across the phase boundary or insufficient time for complete clarification of each stage.

In continuous differential extractors (columns) it has been convenient to think in terms of a height equivalent to a theoretical stage (HETS), and to correlate HETS as a function of system and equipment variables. Alternately, correlations may be obtained on the basis of the height of a transfer unit (HTU), which is more amenable to calculations which separately include the effects of backmixing [2,4].

Sample Stage Calculation

An aqueous waste stream containing 3.25% by weight phenol is to be extracted with one-third its volume of methylene chloride to produce a raffinate without more than 0.2% phenol. How many stages are required?

Graphical Solution. Figure 11.12 is constructed using the equilibrium data for the distribution of phenol between methylene chloride and water from Fig. 11.6.

The operating line is determined on a solute free basis as follows:

$$X_F 5 \frac{3:25ð100Þ}{96:75} 5 \frac{3:36\ \text{g phenol}}{100\ \text{g water}}$$

$$X_R 5 \frac{0:2ð100Þ}{99:8} 5 \frac{0:20\ \text{g phenol}}{100\ \text{g water}}$$

Thus, per 100 g of water feed, the amount of phenol removed is:

$$3:36 2 0:20 5 3:16\ \text{g}$$

At a volumetric feed rate of solvent equal to one-third the feed, and a specific gravity of 1.31 for methylene chloride, the weight ratio of solvent to feed is:

$$\frac{W_S}{W_F} 5 \frac{1}{3}\frac{ð1:31Þ}{ð1:0Þð0:9675Þ} 5 0:451$$

The phenol removed from the 100 g of water (3.16 g) must be in the extract, which contains 45.1 g of methylene chloride:

$$Y_E \; 5 \; \frac{3{:}16}{45{:}1} ð100Þ \; 5 \; 7{:}01 \; \frac{\text{g phenol}}{100 \text{ g MeCl}_2}$$

The operating line is drawn from (3.36, 7.01) to (0.20, 0.00) in Fig. 11.12 and the stages stepped off. The stages are counted at the intersections with the equilibrium line. It is seen that the fourth stage produces a raffinate with a value less than required. Thus, the number of theoretical stages is interpolated to be 3.8.

Analytical Solution. The equation for the operating line is determined from the inlet and outlet concentrations. The operating line equation relates the extract concentration of one stage to the raffinate concentrate from the previous stage.

$$Y_{n11} \; 5 \; \frac{W_F}{W_S} X_n \; 2 \; \frac{W_F}{W_S} X_R$$

$$Y_{n11} \; 5 \; 2{:}22X_n \; 2 \; 0{:}444$$

Starting with Y_E, which is Y_1 for the first extraction stage, the raffinate X_1 in equilibrium is determined from the distribution curve Fig. 11.6:

at

Y_1 5 7.01, X_1 5 1.43
Y_2 5 2.22(1.43) 2 0.444 5 2.73
X_2 5 0.784 from Fig. 11.6
Y_3 5 2.22(0.784) 2 0.444 5 1.30
X_3 5 0.42 from Fig. 11.6
Y_4 5 2.22(0.42) 2 0.444 5 0.488
X_4 5 0.150 from Fig. 11.6

Since X_4 is less than the observed X_r 5 0.20, the fractional stage is estimated as follows:

$$\frac{X_3 \; 2 \; X_r}{X_3 \; 2 \; X_4} \; 5 \; \frac{0{:}42 \; 2 \; 0{:}20}{0{:}41 \; 2 \; 0{:}15} \; 5 \; \frac{0{:}22}{0{:}26} \; 5 \; 0{:}85$$

So the total number of stages is calculated to be 3.85.

Short-Cut Solution. The curved equilibrium relationship means that the Treybal plot, Fig. 11.11, perhaps cannot be used. The required stages can be bracketed by calculating the extraction factor at each end of the extraction. At the dilute end:

$$D \; 5 \; \frac{0{:}63}{0{:}20} \; 5 \; 3{:}15$$

$$E \; 5 \; \frac{W_S}{W_F} D \; 5 \; ð0{:}451Þð3{:}15Þ \; 5 \; 1{:}42$$

$$\psi \; 5 \; \frac{0{:}2}{3{:}36} \; 5 \; 0{:}060$$

n 5 4.9 from Fig. 11.11

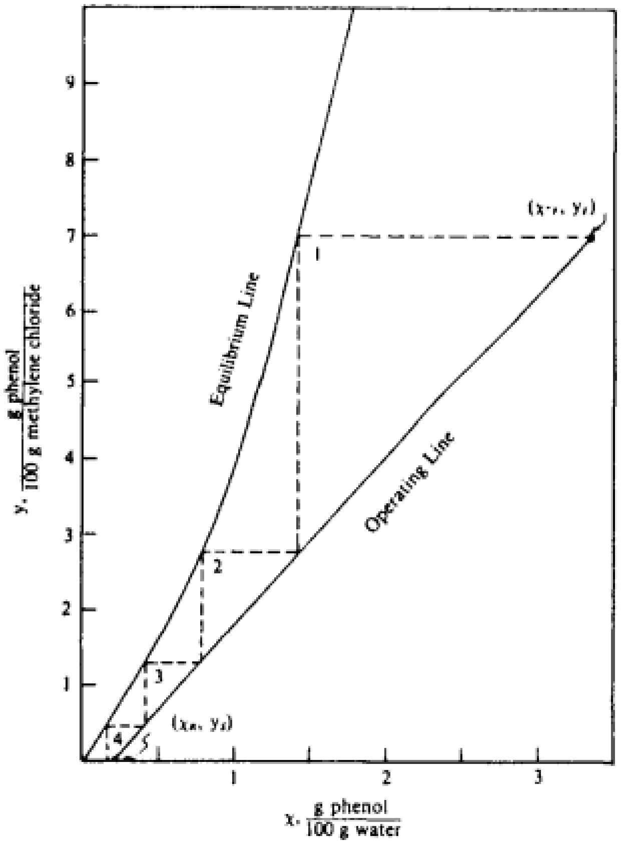

FIGURE 11.12 Stages for sample calculation.

At the concentrated end:

$$D \; 5 \; \frac{7{:}01}{1{:}43} \; 5 \; 4{:}90$$

$$E \; 5 \; ð0{:}451Þð4{:}90Þ \; 5 \; 2{:}21$$

n 5 3.5 from Fig. 11.11

Using an average extraction factor of E 5 1.81, the number of stages from the Treybal plot is 4.1.

The Treybal plot can be used to provide estimates for other requirements as well. For example, if it were desired to increase the amount of phenol extracted from 94 to 99%, what increase in solvent flow or number of stages would be required?

$$\text{At } E \; 5 \; 1{:}81; \quad \Psi \; 5 \; 0{:}01; \quad n \; 5 \; 6{:}3 \text{ stages}$$

$$\text{At } n \; 5 \; 4{:}1; \quad \Psi \; 5 \; 0{:}01; \quad E \; 5 \; 2{:}8 \text{ required}$$

Thus, the solvent flow would have to be increased by a factor of:

$$\frac{2{:}8}{1{:}81} \; 5 \; 1{:}55$$

Thus, to increase extraction from 94 to 99% would require 57% more stages or 55% more solvent, or some lesser combination of both.

5.0 DROP MECHANICS

An understanding of the performance of extraction equipment is furthered by an understanding of what may be going on inside individual drops. With the assumption of transfer of a solute *A* from a dispersed feed phase into a continuous solvent, as shown in Fig. 11.13, a concentration profile across the interface would appear to have a discontinuity (Fig. 11.14). The discontinuity is a consequence of the distribution coefficient, and reflects the general practice of choosing a solvent which has a greater preference for the solute than the feed phase has. If activities instead of concentrations were used, there would be no discontinuity at the interface.

Transfer of solute across the interface can be assumed to be controlled by what happens through the immobilized films on both sides of the interface. Handlos and Baron [5] have presented generalized correlations for the calculation of the individual inside and outside coefficients for mass transfer across these films.

Small drops lead to more transfer area and better extraction, but to slower settling and less capacity. Thus, selection of extraction equipment frequently involves a compromise choice balancing efficiency against capacity.

The terminal velocity of liquid drops is the same as solid spheres when the diameter is small. The drag coefficient versus Reynold's number can be recalculated to provide a diameter-free ordinate versus a velocity-free abscissa to facilitate direct solution, as shown in Fig. 11.15. With drops, a maximum velocity is attained, and this maximum has been correlated with a parameter based on physical properties of the system.

The practical sequence of this phenomenon in column extraction is illustrated in Fig. 11.16. Drops larger than *d** won't travel any faster, so there is no capacity gain, and they have less specific area, so there will be an efficiency loss. Drops smaller than *d** will result in more extraction by providing more transfer area and a longer contact time, but at the potential expense of lower capacity.

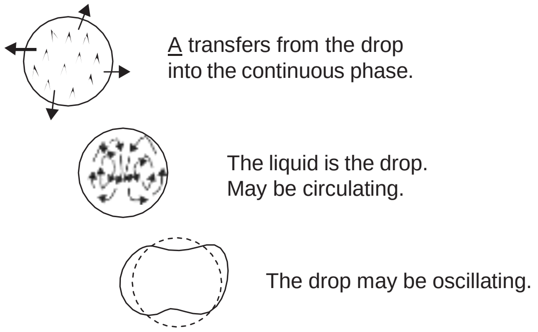

FIGURE 11.13 Drop mechanics.

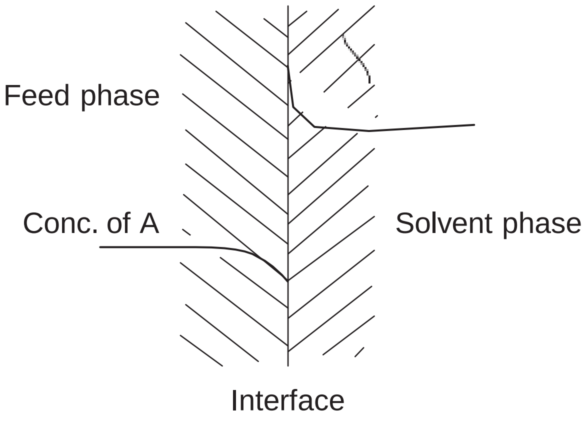

FIGURE 11.14 Solute concentration at the interface.

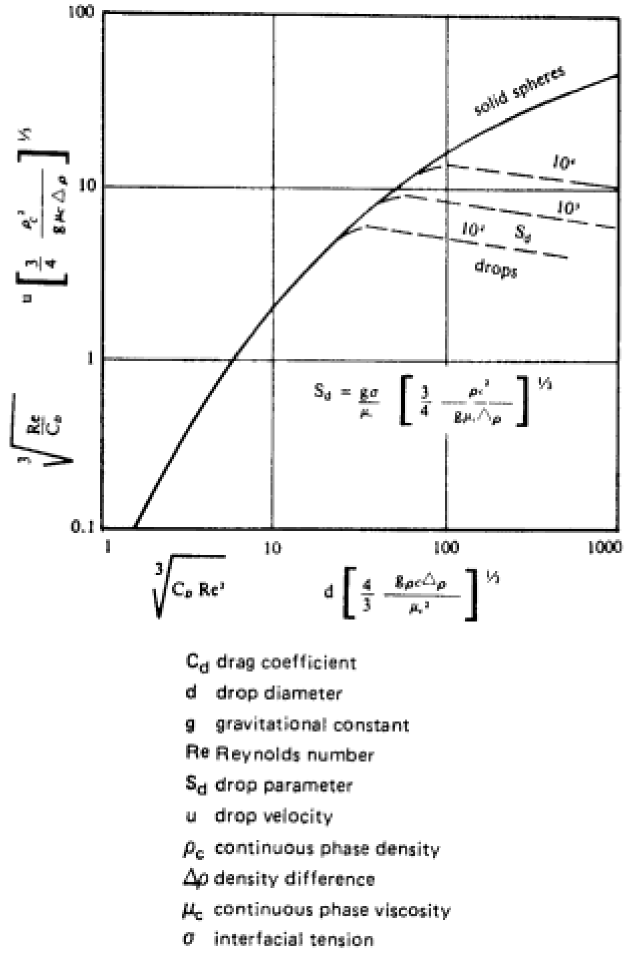

FIGURE 11.15 Dimensionless drop velocity vs. dimensionless drop diameter.

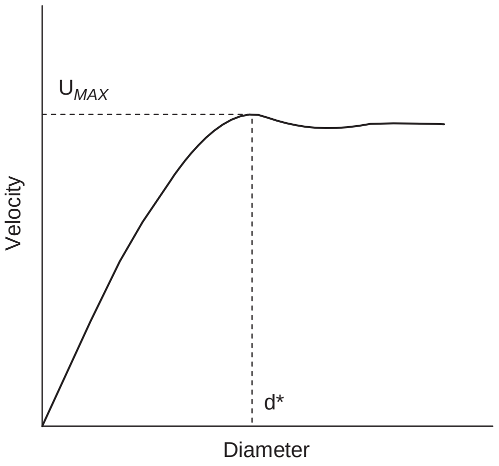

FIGURE 11.16 Drop velocity vs. drop diameter.

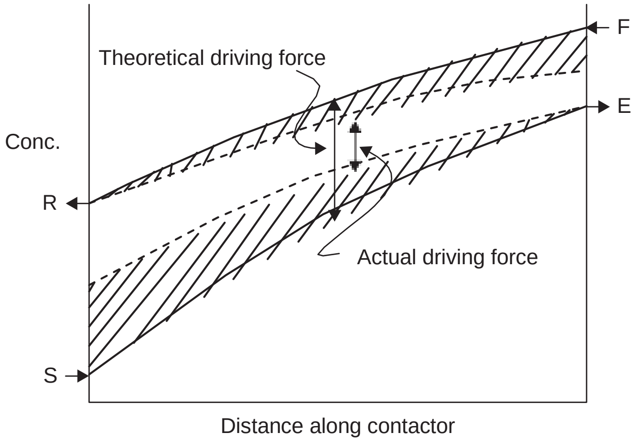

FIGURE 11.17 Effect of backmixing on extraction driving force.

It is generally desirable to provide as uniform a drop size as possible. A wide range in drop sizes may allow the smaller drops to attain equilibrium, but they are en route longer, while the larger drops zip through, not attaining equilibrium.

It is also considered desirable to allow drops to coalesce and be redispersed, as mass transfer from a forming drop is always higher than it is from a stagnant drop.

Backmixing caused by flow patterns induced in the equipment can also deleteriously affect performance by reducing the driving force gradient, as illustrated in Fig. 11.17. Sleicher [6] presents procedures for calculating the consequences of backmixing on overall extraction results.

TYPES OF EXTRACTION EQUIPMENT

Extraction equipment can be classified by function as providing discrete stages or continuous differential contact. Separation may be by gravity alone or by centrifugal force. Additional energy may be applied to control drop size, either by mechanical agitation or pulsation. This classification is shown in Table 11.1, along with major examples of available equipment.

TABLE 11.1 Classification of Industrial Extraction Equipment

Flow by	Drop Size Control by	Stagewise	Continuous Differential
Gravity alone	Gravity alone	Perforated Place Column	Spray Column Packed Column
	Mechanical rotation	Mixer-Settler	RDC Oldshue-Rushton Column ARD Column Kühni Column Raining Bucket Contactor
	Mechanical reciprocation		Karr Column Pulsed Packed Column Pulsed Perforated Plate Column
Centrifugal Force	Flow through baffles	Westfalia Extractor Robatel Extractor	Podbielniak Extractor Alfa Laval Extractor

Non-Agitated Gravity Flow Extractors

Spray Column. The simplest differential extractor is the spray column (Fig. 11.18a), which depends upon the initial dispersion of the dispersed phase to create favorably sized droplets. There is no means provided to redisperse this phase if any coalescence occurs. Although the equipment is simple and inexpensive, it is difficult to obtain more than one stage extraction. The passage of the dispersed phase induces considerable backmixing of the continuous phase, particularly in larger diameter columns.

Packed Column. (Fig. 11.18b) Interphase contact can be improved in the spray column by providing extensive surface for coalescence and redispersion. This surface is provided with packing which provides surface while maintaining a large open area for flow, such as Raschig rings, Berl saddles, and variants thereof. There is some loss in capacity because of the cross section occupied by the packing, but this is more than offset by the gain in improved mass transfer and lessening of continuous phase backmixing.

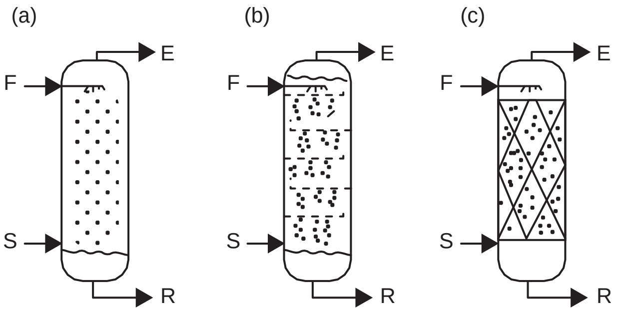

FIGURE 11.18 Non-agitated gravity flow extractors. *(a)* Spray, (b) packed, and *(c)* perforated plate.

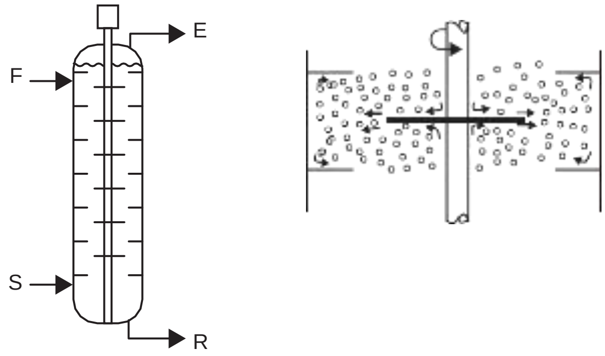

FIGURE 11.19 Rotating disc contactor (RDC).

Packing should be chosen that preferentially is wetted by the continuous phase to discourage formation of rivulets of the dispersed phase bypassing through the column. In large diameter columns, redistribution trays should be installed to overcome potential channeling. Smaller packing size is generally more efficient, but restricts flow more, and is more prone to fouling by trapping solids. Eckert [7] summarizes design criteria for the selection of packing for packed columns.

Perforated Plate Column. (Fig. 11.18c) Sieve trays can be placed in the spray column to cause coalescence and redispersion of the dispersed phase. The trays can be designed to permit flow of both phases through the same perforations, but such trays generally have a quite narrow operating range. Generally, some sort of *downcomer* (or *upcomer*) is provided to allow a separate path for the continuous phase and one-way flow of the dispersed phase through the perforations. The density difference between the two phases and the height of coalesced phase provide the driving force for redispersion through the orifices.

In contrast with vapor-liquid columns, tray efficiencies are very low (5 to 30%) in liquid-liquid systems. The trays do limit continuous phase backmixing as well as provide drop redispersion, but at the expense of reduced capacity.

Stirred Gravity Flow Extractors

Provision of a shaft through the extraction column allows for repeated redispersion of the drops via various impellers located along the shaft. A variety of industrial equipment is available, with the differences being in the design of the impellers on the shaft for dispersion, and stators in the column for baffling and coalescence. Stirred columns offer the operator increased flexibility in operation by independent control over the dispersion process.

RDC Column. The *rotating disc contactor* (Fig. 11.19) provides for redispersion by a series of discs along the shaft, combined with a series of fixed stators. Vortices are formed in each *compartment*, and the shear of the fluid against the rotor or stator causes the drop breakup. In many instances, performance can be predicted from first principles, relating drop size to the energy input, and calculating slip velocity and mass transfer coefficients based on that diameter and the physical properties of the system (see Strand, Olney & Ackerman [8]).

With increasing rotational speed, efficiency improves as drops become smaller, but maximum capacity is lessened. Increased rotational speed also increases continuous phase backmixing, and causes some segregation of the phases as the lighter phase accumulates around the shaft while the denser phase hugs the wall. At the same energy input, dispersing the light phase leads to smaller drops because all of the light phase must pass over the tips of the spinning discs; whereas dispersion of a denser phase is brought about primarily by fluid motion over the stationary ring baffles.

Oldshue-Rushton Column. This column is similar to the RDC, except that the flat rotor discs have been replaced with turbine type agitators (Fig. 11.20). As with the RDC, the diameter of the agitators can be varied along the shaft to compensate for the progressive change in the physical properties of the system as extraction occurs.

Other variations of stirred columns which are available include the *asymmetric rotating disc* (ARD) contactor, the *Kühni column*, and two types of *Scheibel columns*. The rotor of the ARD is located off center, which permits more elaborate baffling for the necessary transport of flows with less backmixing.

The Kühni column employs radial flow impellers located between perforated plates for compartmentalization. The first Scheibel column used wire mesh zones to promote coalescence and limit backmixing between turbine-agitated mixing zones. A later Scheibel column used a shrouded radial impeller and multiple ring baffles to direct most of the rotor's energy towards dispersion and away from axial mixing.

Raining Bucket Contactor. This contactor consists of a series of scoops located on a slowly rotating, baffled rotor within a horizontal cylindrical vessel (Fig. 11.21).

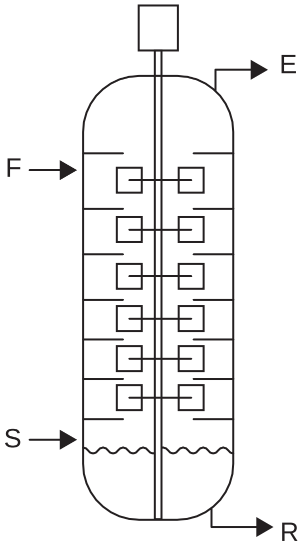

FIGURE 11.20 Oldshue-Rushton column.

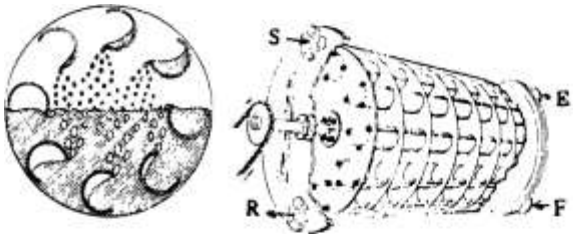

FIGURE 11.21 Raining bucket contactor.

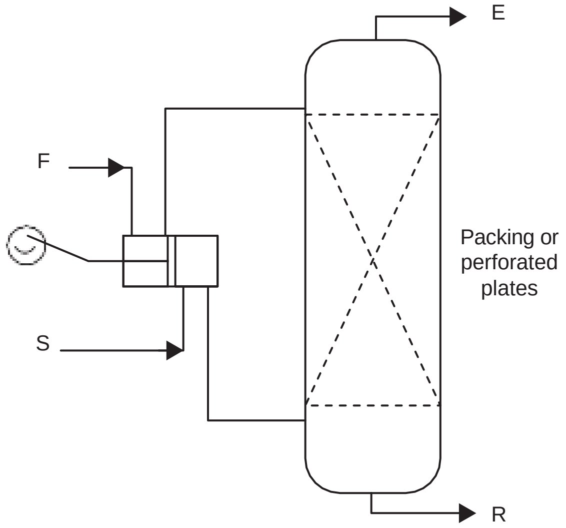

FIGURE 11.22 Liquid pulsed columns.

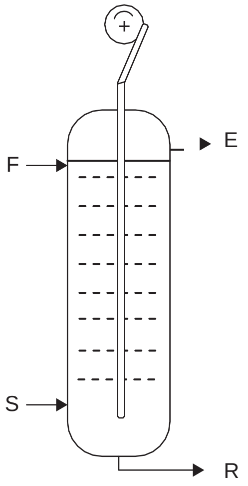

FIGURE 11.23 Karr reciprocating plate column.

An interface is maintained near the middle, and the scoops capture and then allow one phase to rain through the other, and vice versa, once each revolution.

There is little, if any, control of droplet size, but the raining bucket contactor is the only one that disperses each phase in the other. If the flow ratio differs greatly from unity, backmixing of the low flow phase can be serious, and line out with changed operating conditions can take a long time.

Pulsed Gravity Flow Extractors

Liquid Pulsed Columns. The liquid in a packed or perforated plate column may be pulsed to promote better mass transfer (Fig. 11.22). If a sieve plate column is pulsed, downcomers are no longer required. Pulsing can be caused by a piston pump or by air pulsing external to the column. Frequencies are generally 1 to 3 Hz and amplitude up to 20 mm. Drop size is dependent upon the product of amplitude times frequency. As this product is increased, the smaller diameter drops so produced lead to more holdup and better mass transfer, but to a fall off in capacity. Eventually, at a high enough amplitude x frequency product, backmixing increases to the extent that efficiency also begins to diminish.

Mechanically Pulsed Column. The *Karr column* (Fig. 11.23) consists of perforated plates ganged on a common shaft which is oscillated by an external drive. The perforated area and hole size are much larger than in typical sieve plate operation. At high amplitude x frequency product in larger columns, the tendency for excessive backmixing can be curtailed by installation of some fixed baffles.

Mixer-Settlers. The extraction function of bringing feed and solvent intimately together, and then allowing them to separate is frequently done in mixer-settlers. The functions may be done in separate vessels, or in different portions of the same vessels, or sequentially in the same vessel on a batch basis. As noted earlier in Fig. 11.3, the flows of feed and solvent can be countercurrent to each other through a series of mixer-settlers.

Sizing of the mixer is based upon providing sufficient agitation and sufficient residence time to allow equilibrium to be approached, and thus will depend upon the flows to be processed as well as the physical properties of the two liquids. Since some extractions actually involve a chemical reaction, the time of contact can be very important. If, for reasons of improved mass transfer, it is desired to disperse the high flow phase, it may be necessary to recycle some of the low flow phase to keep an appropriate phase ratio in the mixer different than the feed flow ratio.

The settler must provide a long enough quiescent residence time for the emulsion which is produced in the mixer to break, and a low enough lineal velocity for the two phases to become essentially free of entrainment. In some instances, coalescing material, such as wire mesh, may be installed to lessen entrainment, however, such material should be used with some caution because of the tendency for fouling by accumulation of foreign material.

It is frequently possible to introduce one of the phases into the eye of the impeller, and thus be able to pump one entering fluid while the other flows by gravity from the next upstream and downstream stages, without the need for separate interstage pumps.

Centrifugal Extractors

Many of the commercial extraction processes encountered in the pharmaceutical industry involve systems which emulsify readily and are exceedingly difficult to separate cleanly. Stability of the solute may also be a factor, and rapid separation may be required to prevent degradation and loss of the product. Centrifugal extractors fill an important niche for just such problems.

The most common centrifugal extractor is the Podbielniak® Contactor, as shown in cutaway view in Fig. 11.24. Essentially it is a sieve plate column that has been wrapped around a shaft and spun to create a multigravitational force to do both the redispersion and the separation. All fluids enter and leave through shaft passageways and mechanical seals.

The performance of centrifugal extractors has been described by Todd and Davies in general detail [9] and specifically for pharmaceutical use [10]. The primary benefits of centrifugal extractors accrue from their compactness and superior clarifying capabilities. Solvent inventory can be held to a minimum. Centrifugal extractors are also particularly appropriate handling high phase ratios, as the low flow phase can be kept continuous without much backmixing, thereby allowing the large flow fluid to be dispersed to provide more mass transfer area.

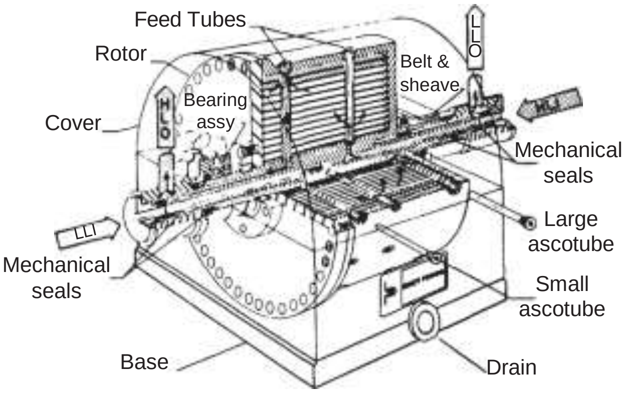

FIGURE 11.24 Podbielniak® centrifugal extractor.

The Podbielniak and Alfa Laval centrifugal extractors are essentially continuous differential contactors. The Westfalia and Robatel centrifugal extractors contain discrete mechanical stages, and flow from one to another is effected by spill over discs and skimmers according to usual centrifugal clarifier practice. As the number of discrete stages is increased, the allowable flow rates are proportionately decreased.

Equipment Size Calculation

Agitated Columns. The size of an extraction column frequently can be estimated from a knowledge of the flow rates and physical properties, combined with some empirical generalizations.

1. The maximum capacity (at zero stirrer speed or pulsation) is directly related to the terminal velocity of the dispersed phase through the minimum physical constriction in the column.
2. The terminal velocity of the dispersed phase droplets is related to the physical properties of the system by the correlation shown in Fig. 11.15.
3. For many systems, the effect of hindered settling can be approximated by:

$$V_t = \frac{1}{1-h}\,\frac{V_d}{h} + \frac{V_c}{1-h}$$

   where V_t, V_d, V_c are the superficial lineal velocities of the drop, dispersed phase, and continuous phase, and h is the holdup.
4. Agitated columns are frequently operated so that the capacity is half what it would be at no agitation (zero rpm or pulsation). Agitation is used to reduce droplet diameter to this equivalent point to increase mass transfer rate and mass transfer area.
5. For sizing purposes, the diameter of the column will be chosen so that the column is operating at 75% of the flood point.

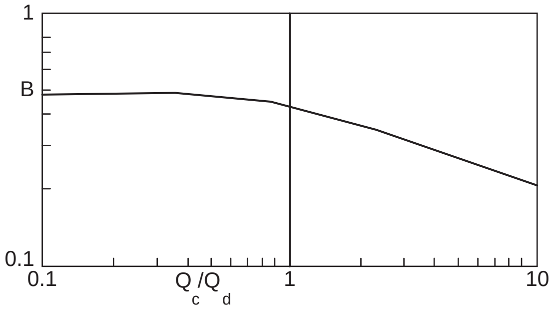

FIGURE 11.25 Empirical constant *B* for determining agitated column diameter.

6. The holdup at flooding can be determined by differentiating the equation in criterion #3. Combining this relationship with all the constants leads to the following equation:

$$D\,5\,\frac{0{:}09}{B}Q_d^{0{:}5}\ \frac{\mu_c}{\sigma}^{0{:}88}\ 1\frac{\rho_e^2}{\mu_c\Delta\rho}^{0{:}138}$$

(with D in meters, Q_d in m^3/h, μ_c in poise, σ in dynes/cm, and ρ in g/cc). The factor B is related to holdup and dependent upon phase ratio, as shown in Fig. 11.25.

The countercurrent contact zone height will depend primarily upon the number of stages required (n) and the column characteristics. The effect of backmixing also increases the column diameter. A reasonable first approximation of extraction height (L) required for agitated columns is:

$$L\,5\,0{:}94n\sqrt{D}\quad \text{ð}L \text{ and } D \text{ in metersÞ}$$

Most columns also require clarifying zones at each end to provide for coalescence and to minimize entrainment. These zones also are dependent upon column diameter. The combined height required (Z) for the clarifying zones can be approximated by:

$$Z\,5\,3\sqrt{D}\quad \text{ð}Z \text{ and } D \text{ in metersÞ}$$

Estimates of column size required for three different cases are tabulated in Table 11.2. Case A involves the removal of dioxane from a benzene stream with water as the extracting solvent. Case B involves the recovery of methyl ethyl ketone from a heptane stream with water. Case C is for the removal of phenol from an aqueous stream with methylene chloride.

In addition to the calculated heights and diameters, the total traffic flow (the sum of both flows divided by the column cross-section) is listed. Typical traffic flows for agitated columns are in the 25 to 100 m^3/m^2 hr range.

The manufacturer of the extraction column will likely select the next larger diameter size for which he has standardized components. He may also insist upon some pilot plant test to confirm the capacity and efficiency requirements.

TABLE 11.2 Examples of Column Sizing Calculations

Case			A	B	C
Remove solute from feed with solvent			Dioxane	MEK	Phenol
			Benzene (c)	Heptane (d)	Water (d)
			Water (d)	Water (c)	MeCl$_2$ (c)
Flow	Q_c	m^3/hr	20.6	30.9	7.6
	Q_d	m^3/hr	13.3	16.4	22.7
Ratio	Q_c/Q_d		1.54	1.88	0.33
Constant	B		0.356	0.344	0.447
Viscosity	μ_c	poise	0.0065	0.010	0.007
Int. tens.	σ	dyne/cm	30	45	45
Spec. grav.	ρ_c		0.884	1.00	1.31
	ρ_d		1.00	0.688	1.00
	Δ_ρ		0.116	0.312	0.31
	$Q_d^{0.5}$		3.65	4.06	2.75
	$\frac{\mu_c}{\sigma}\}^{0:088}$		0.476	0.477	0.462
	$n\ \frac{\rho_c^2}{\mu_c\Delta_\rho}\ o^{0:138}$		2.61	2.22	2.51
Diameter	D	m	1.146	1.122	0.642
Theo. stages,	n		4	6	4
Ht, contact	L	m	4.03	5.97	3.01
clarif.	Z	m	3.21	3.17	2.40
Total	H		7.24	9.14	5.41
Traffic flow		m/hr	32.9	47.9	93.6

Note: (c) 5 continuous phase; (d) 5 dispersed phase.

The manufacturers of other proprietary extraction devices, such as centrifugal extractors, will be able to provide estimates of the probable size equipment required, based on comparisons with similar systems and their own accumulated design experience.

Many pharmaceutical extractions do not lend themselves to simple straightforward analytical solutions. Rarely is there a case of simple extraction of a single solute from a clean feed with pure solvent. There may well be solids present which can stabilize emulsions and cause excessive entrainment. Usually, more than one solute is present, so selectivity as well as extent of extraction becomes important. Also, the solvent may contain residual solute from the solvent recovery section. Again, suppliers of extraction equipment should be contacted for their help in solving real industrial extraction problems.

Packed Columns. Capacity of packed columns is strongly dependent upon the packing being used. As the surface area of the packing is increased to improve efficiency, in general, both the hydraulic radius and the fraction void decrease, thereby increasing resistance to flow and lowering capacity. For a given extraction, the maximum capacity (flooding rate) generally follows the form:

$$V_d^{0:5}\ 1\ V_c^{0:5}\ 5\ K$$

where *K* is a function of packing characteristics and physical properties of the system.

Compared to agitated columns, both diameter and height will have to be larger. Flow redistributer are advisable at periodic intervals to offset the tendency for channeling and bypassing frequently encountered in packed columns. Characteristics of various packings and correlations for capacity and stage height are given by Treybal [3] and Eckert [7].

Mixer-Settlers. The mixing required for adequate dispersion can be determined and scaled-up by the methods outlined by Oldshue [11].

Sizing of settlers poses some uncertainty in that solvent recycle within the process may lead to accumulation of an interfacial *rag*, which tends to stabilize emulsions at the interface. For a first approximation, an arbitrary residence time, like 20 minutes, might be assumed unless bench shake-outs indicate an even longer time required for adequate clarification.

Proprietary Extractors. Manufacturers or proprietary design extraction equipment (such as the Podbielniak Centrifugal Extractor or the RTL (raining bucket) Contactor) provide catalogs listing the relative capacities of the various sizes of equipment which are offered. Pilot equipment is usually available for determining extraction performance, and the manufacturer utilizes both the pilot data and experience with similar systems to provide assured commercial designs.

7.0 SELECTION OF EQUIPMENT

The choice of extraction equipment should be based on the minimum annual cost for the complete package of extractor and accessory equipment, including operating and solvent loss costs.

In addition to the requirements of processing so much feed and solvent with a required number of theoretical stages, there are the practical considerations concerning contamination, entrainment, emulsification, floor space, height requirements, cleanability, and versatility to handle other than design rates. The suitability of various type extractors with respect to each of these considerations is listed in Table 11.3. Not all of the features compared in the table can be equated. The tabulation is provided to show comparisons to aid in the selection of suitable equipment.

TABLE 11.3 Extractor Selection Chart

	Low Cost		High Efficiency	Total Throughput	Flexibility	High Volumetric Efficiency	Lowest Space		Ability to Cope with Systems	
	Capital	Operating					Vertical	Floor	Which Emulsify	with Solids
Mixer settler	3	2	4	4	4	2	5	1	1	3
Spray	4	5	1	3	2	1	1	5	2	4
Perf. plate	4	5	2	2	2	2	1	4	3	2
Packed	4	4	2	2	2	2	1	4	3	1
Pulse	3	3	4	3	4	4	3	4	3	3
Agitated	3	4	4	3	4	4	3	4	3	3
Centrifugal	2	3	4	3	4	5	5	5	5	2
	5 is outstanding				2 is fair					
	4 is good				1 is poor					
	3 is adequate				0 is unsuitable					

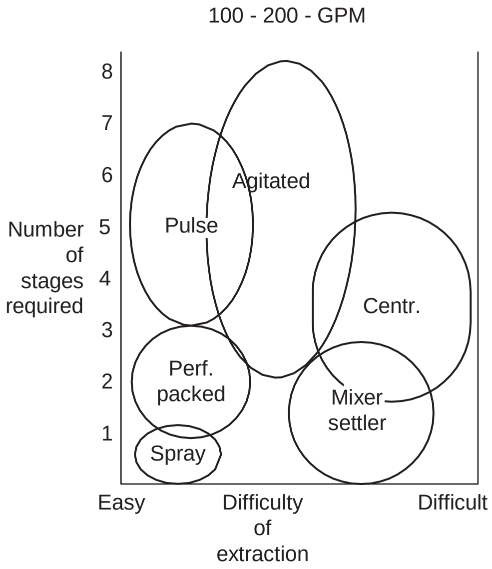

FIGURE 11.26 Extractor selection map.

Other criteria for the selection of an extractor are the ease of separation of the two phases and the difficulty of extraction. For example, if the two phases have a large density difference, or at least one is quite viscous, the energy required to get a good enough dispersion for good extraction may lead to excessive backmixing of the continuous phase.

The extractor selection map depicted in Fig. 11.26 reflects the above considerations plus the number of stages required. Where the degree of extraction exceeds the probable maximum staging achievable in one extractor, the extractors can be used in series.

8.0 PROCEDURE SUMMARY

Liquid-liquid extraction should be considered as a desirable route for product recovery and purification along with fractional crystallization and distillation. The ability to make separations according to chemical type, rather than according to physical properties such as freezing point or vapor pressure, is one of extraction's major attractions. Energy frequently can be saved in the recovery of valuable products from dilute broth solution since a small quantity of a selective solvent can be used, and recovery from the concentrated extract is then facilitated.

Selectivity of potentially attractive solvents can frequently be determined from simple shake-outs over the desired concentration range. From these distribution data, the combinations of amount of solvent and number of theoretical stages can be calculated.

Suppliers of extraction equipment will likely wish to participate in pilot testing to confirm the correlations for capacity and efficiency of the specific equipment being considered.

After installation, the equipment suppliers can also provide technical assistance in bringing the extraction equipment on line and solving problems which may arise from the commercial plant operation with its potential variation in feed and solvent quality and accumulation of impurities.

9.0 ADDITIONAL INFORMATION

With Treybal's book [3] essentially out of print, the *Handbook of Solvent Extraction* by Lo, Baird, and Hanson [2] provides a most comprehensive reference. In addition to the previously cited *Perry's Handbook* chapter on liquid extraction by Robbins [1], *The Essentials of Extraction* by Humphrey, Rocha, and Fair [12], and a three part *A Fresh Look at Liquid-Liquid Extraction* [13], provide briefer, but very useful guidelines. Details of extraction processes specifically involved in pharmaceutical production have been described by King et al. [14], and by Kroner, Hustedt, and Kula [15].

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