

Figure 8.8 Scheme for selecting extractors.

[From K.-H. Reissinger and J. Schroeter, *I. Chem. E. Symp. Ser. No. 54*, 33–48 (1978).]

8.2 GENERAL DESIGN CONSIDERATIONS

The design and analysis of a liquid–liquid extractor involves more factors than for vapor–liquid operations because of complications introduced by the two liquid phases. One of the three different cascade arrangements in Figure 8.9, or a more complex arrangement, must be selected. The single-section cascade of Figure 8.9a is similar to that used for absorption and stripping. It is designed to transfer to the solvent a certain percentage of the solute in the feed. The two-section cascade of Figure 8.9b is similar to distillation. Solvent enters at one end and reflux, derived from the extract, enters at the other end. The feed enters between the two sections. With two sections, depending on solubility considerations, it is sometimes possible to achieve a reasonably sharp separation between components of the feed; if not, a dual-solvent arrangement with two sections, as in Figure 8.9c, with or without reflux at the two ends, may be advantageous.

For the latter configuration, which involves a minimum of four components (two in the feed and two solvents), computer-aided calculations are preferred, as discussed in Chapter 10. Although the configurations in Figure 8.9 are shown with packed sections, any of the extractors discussed in Section 8.1 may be considered. The factors influencing extraction include:

1. Entering feed flow rate, composition, temperature, and pressure
2. Type of stage configuration (one-section or two-section)
3. Desired degree of recovery of one or more solutes for one-section cascades
4. Degree of separation of the feed for two-section cascades
5. Choice of liquid solvent(s)

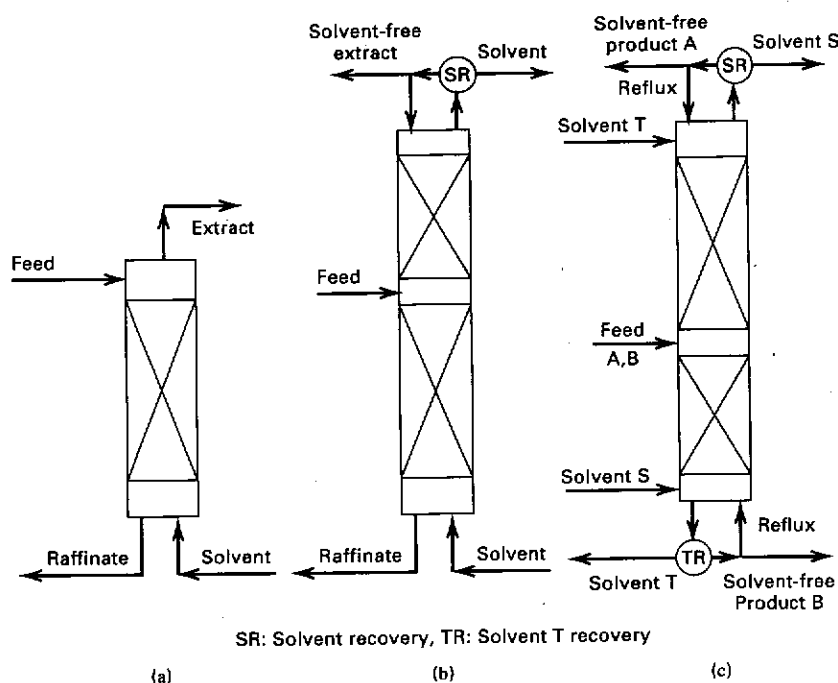


Figure 8.9 Common liquid-liquid extraction cascade configurations: (a) single-section cascade; (b) two-section cascade; (c) dual solvent with two-section cascade.

6. Operating temperature
7. Operating pressure (greater than the bubble point of the system)
8. Minimum-solvent flow rate and actual solvent flow rate as a multiple of the minimum rate for one-section cascades or reflux rate and minimum reflux ratio for two-section cascades
9. Number of equilibrium stages
10. Emulsification and scum-formation tendency
11. Interfacial tension
12. Phase-density difference
13. Type of extractor
14. Extractor size and horsepower requirement

The ideal solvent has:

1. A high selectivity for the solute relative to the carrier, so as to minimize the need to recover carrier from the solvent
2. A high capacity for dissolving the solute, so as to minimize the solvent-to-feed ratio
3. A minimal solubility in the carrier
4. A volatility sufficiently different from the solute that recovery of the solvent can be achieved by distillation, but the vapor pressure should not be so high that a high extractor pressure is needed or so low that a high temperature is needed if the solvent is recovered by distillation
5. Stability to maximize the solvent life and minimize the solvent make-up requirement
6. Inertness to permit use of common materials of construction

7. A low viscosity to promote phase separation, minimize pressure drop, and provide a high solute mass-transfer rate
8. Nontoxic and nonflammable characteristics to facilitate its safe use
9. Availability at a relatively low cost
10. A moderate interfacial tension to balance the ease of dispersion and the promotion of phase separation
11. A large difference in density relative to the carrier to achieve a high capacity in the extractor
12. Compatibility with the solute and carrier to avoid contamination
13. A lack of tendency to form a stable rag or scum layer at the phase interface
14. Desirable wetting characteristics with respect to extractor internals

Solvent selection is frequently a compromise among all the properties listed above. However, initial consideration is usually given first to selectivity and environmental concerns, and second to capacity. From (2-20) in Chapter 2, the distribution coefficient for solute A between solvent S and carrier C is given by:

$$(K_A)_D = (x_A)^{II}/(x_A)^I = (\gamma_A)^I/(\gamma_A)^{II} \quad (8-1)$$

where II is the extract phase, rich in S, and I is the raffinate phase, rich in C. Similarly, for the carrier and the solvent, respectively,

$$(K_C)_D = (x_C)^{II}/(x_C)^I = (\gamma_C)^I/(\gamma_C)^{II} \quad (8-2)$$

$$(K_S)_D = (x_S)^{II}/(x_S)^I = (\gamma_S)^I/(\gamma_S)^{II} \quad (8-3)$$

From (2-22), the relative selectivity of the solute with respect to the carrier is obtained by taking the ratio of (8-1)

Table 8.4 Group Interactions for Solvent Selection

Group	Solute	Solvent								
		1	2	3	4	5	6	7	8	9
1	Acid, aromatic OH (phenol)	0	—	—	—	—	0	+	+	+
2	Paraffinic OH (alcohol), water, imide or amide with active H	—	0	+	+	+	+	+	+	+
3	Ketone, aromatic nitrate, tertiary amine, pyridine, sulfone, trialkyl phosphate, or phosphine oxide	—	+	0	+	+	—	0	+	+
4	Ester, aldehyde, carbonate, phosphate, nitrite or nitrate, amide without active H; intramolecular bonding, e.g., <i>o</i> -nitrophenol	—	+	+	0	+	—	+	+	+
5	Ether, oxide, sulfide, sulfoxide, primary and secondary amine or imine	—	+	+	+	0	—	0	+	+
6	Multihaloparaffin with active H	0	+	—	—	—	0	0	+	0
7	Aromatic, halogenated aromatic, olefin	+	+	0	+	0	0	0	0	0
8	Paraffin	+	+	+	+	+	+	0	0	0
9	Monohaloparaffin or olefin	+	+	+	+	+	0	0	+	0

(+) Plus sign means that compounds in the column group tend to raise activity coefficients of compounds in the row group.

(—) Minus sign means a lowering of activity coefficients.

(0) Zero means no effect.

Choose a solvent that lowers the activity coefficient.

Source: Cusack, R.W., P. Fremaux, and D. Glatte, *Chem Eng.*, 98(2), 66–76 (1991).

to (8-2), giving

$$\beta_{AC} = (K_A)_D / (K_C)_D = \frac{(x_A)^{\text{II}} / (x_A)^{\text{I}}}{(x_C)^{\text{II}} / (x_C)^{\text{I}}} = \frac{(\gamma_A)^{\text{I}} / (\gamma_A)^{\text{II}}}{(\gamma_C)^{\text{I}} / (\gamma_C)^{\text{II}}} \quad (8-4)$$

For high selectivity, the value of β_{AC} should be high, that is, at equilibrium there should be a high concentration of A and a low concentration of C in the solvent. A first estimate of β_{AC} is made from available values or predictions of the activity coefficients $(\gamma_A)^{\text{I}}$, $(\gamma_A)^{\text{II}}$, and $(\gamma_C)^{\text{II}}$, at infinite dilution where $(\gamma_C)^{\text{I}} = 1$, or by using liquid–liquid equilibrium data for the lowest tie line on a triangular diagram of the type discussed in Chapter 4. If A and C form a nearly ideal solution, the value of $(\gamma_A)^{\text{I}}$ in (8-4) can also be taken as 1.

For high solvent capacity, the value of $(K_A)_D$ should be high. From (8-2) it is seen that this is difficult to achieve if A and C form nearly ideal solutions, such that $(\gamma_A)^{\text{I}} = 1.0$, unless A and S have a great affinity for each other, which would result in a negative deviation from Raoult's law to give $(\gamma_A)^{\text{II}} < 1$. Unfortunately, such systems are rare.

For ease in solvent recovery, $(K_S)_D$ should be as large as possible and $(K_C)_D$ as small as possible to minimize the presence of solvent in the raffinate and carrier in the extract. This will generally be the case if activity coefficients $(\gamma_S)^{\text{I}}$ and $(\gamma_C)^{\text{II}}$ at infinite dilution are large.

If a water-rich feed is to be separated, it is common to select an organic solvent; for an organic-rich feed, an aqueous solvent is often selected. In either case, it is desirable

to select a solvent that lowers the activity coefficient of the solute. Consideration of molecule group interactions can help narrow the search for such a solvent before activity coefficients are estimated or liquid–liquid equilibrium data are sought. A table of interactions for solvent-screening purposes, as given by Cusack et al. [21], based on a modification of the work of Robbins [22], is shown as Table 8.4, where the solute and solvent each belong to any of nine different chemical groups. In this table, a minus (—) sign for a given solute–solvent pair means that the solvent will desirably lower the value of the activity coefficient of the solute relative to its value in the feed solution. For example, suppose it is desired to extract acetone from water. Acetone, the solute, is a ketone. Thus, in Table 8.4, group 3 applies for the solute, and desirable solvents are of the type given in groups 1 and 6. In particular, trichloroethane, a group 6 compound, is known to be a highly selective solvent with high capacity for acetone over a wide range of feed compositions. However, if the compound is environmentally objectionable, it must be rejected. A more sophisticated solvent-selection method, based on the UNIFAC group-contribution method for estimating activity coefficients and utilizing a computer-aided constrained optimization approach, has been developed by Naser and Fournier [23].

In Chapter 4, ternary diagrams were introduced for representing liquid–liquid equilibrium data for three-component systems at constant temperature. Such diagrams are available for a large number of systems, as discussed by

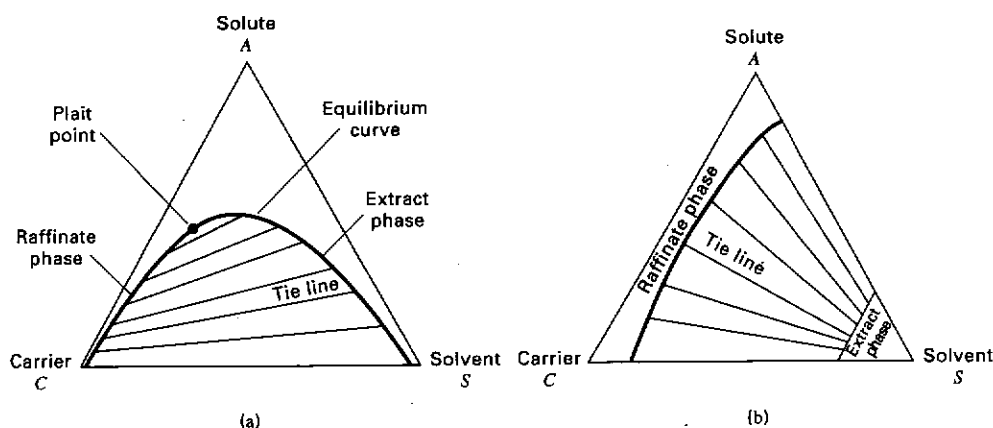


Figure 8.10 Most common classes of ternary systems: (a) type I, one immiscible pair; (b) type II, two immiscible pairs.

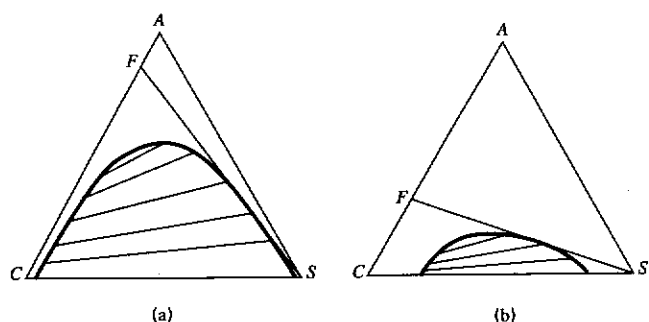


Figure 8.11 Effect of solubility on range of feed composition that can be extracted.

Humphrey et al. [6]. For liquid-liquid extraction with ternary systems, the most common diagram is Type I, shown in Figure 8.10a; much less common is Type II, shown in Figure 8.10b. Examples of Type II systems are (1) *n*-heptane/aniline/methyl cyclohexane, (2) styrene/ethylbenzene/diethylene glycol, and (3) chlorobenzene/water/methylethyl ketone. For Type I, the solute and solvent are miscible in all proportions, while in Type II they are not. For Type I systems, the greater the two-phase region on line CS, the greater will be the immiscibility of carrier and solvent. The closer the top of the two-phase region is to apex A, the greater will be the range of feed composition, along line AC, that can be separated with solvent S. In Figure 8.11, it is possible to separate feed solutions only in the composition range from C to F because, regardless of the amount of solvent added, two liquid phases are not formed in the feed composition range of FA (i.e., FS does not pass through the two-phase region).

The system in Figure 8.11a has a wider range of feed composition than the system in Figure 8.11b. For Type II systems, a high degree of insolubility of S in C and C in S will produce a desirable high relative selectivity, but at the expense of solvent capacity. Thus, solvents that result in Type I systems are more desirable.

Whether a ternary system is of Type I or Type II often depends on the temperature. For example, data of Darwent and Winkler [24] for the ternary system *n*-hexane (H)/methylcyclopentane (M)/aniline (A) for temperatures of 25, 34.5, and 45°C are shown in Figure 8.12. At the lowest temperature, 25°C, we have a Type II system because both H and M are only partially miscible in the aniline solvent. As the temperature increases, the solubility of M in aniline increases more rapidly than the solubility of H in aniline until at 34.5°C, the critical solution temperature for M in aniline is reached. At this temperature, the system is at the border of Type II and Type I. At 45°C, the system is clearly of type I, with aniline more selective for M than H. Type I systems have a plait point (P in Figure 8.10a); type II systems do not.

Except in the near-critical region, pressure has little if any effect on liquid-phase activity coefficients and, therefore, on liquid-liquid equilibrium. It is only necessary to select an operating pressure of at least ambient, and greater than the bubble-point pressure of the two-liquid-phase mixture at any location in the extractor. Most extractors operate at near-ambient temperature. If feed and solvent enter the extractor at the same temperature, the operation will be nearly isothermal because the only thermal effect is the heat of mixing, which is usually small.

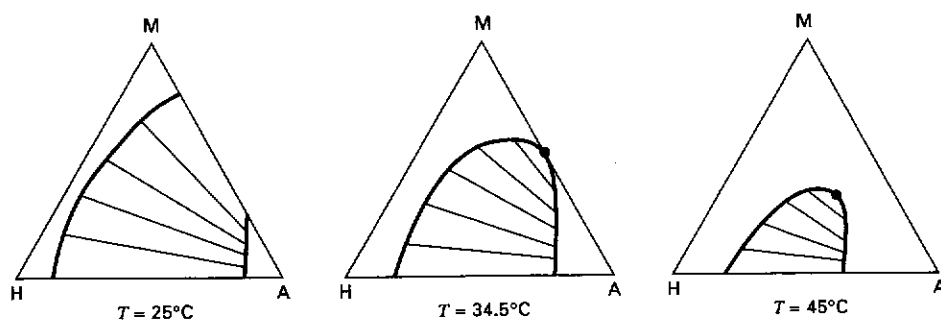


Figure 8.12 Effect of temperature on solubility for the system *n*-hexane (H)/methylcyclopentane (M)/aniline (A).