

## Liquid-Liquid Extraction with Ternary Systems

In *liquid-liquid extraction*, a liquid feed of two or more components to be separated is contacted with a second liquid phase, called the *solvent*, which is immiscible or only partly miscible with one or more components of the liquid feed and completely or partially miscible with one or more of the other components of the liquid feed. Thus, the solvent, which is a single chemical species or a mixture, partially dissolves certain components of the liquid feed, effecting at least a partial separation of the feed. Liquid-liquid extraction is sometimes called *extraction*, *solvent extraction*, or *liquid extraction*. These, as well as the term *solid-liquid extraction*, are also applied to the recovery of substances from a solid by contact with a liquid solvent, such as the recovery of oil from seeds by an organic solvent. Solid-liquid extraction (leaching) is covered in Chapter 16.

According to Derry and Williams [1], liquid extraction has been practiced since at least the time of the Romans, who separated gold and silver from molten copper by extraction using molten lead as a solvent. This was followed by the discovery that sulfur could selectively dissolve silver from an alloy with gold. However, it was not until the early 1930s that the first large-scale liquid-liquid extraction

process began operation. In that industrial process, named after its inventor L. Edeleanu, aromatic and sulfur compounds were selectively removed from liquid kerosene by liquid-liquid extraction with liquid sulfur dioxide at 10 to 20°F. Removal of aromatic compounds resulted in a cleaner-burning kerosene. Liquid-liquid extraction has grown in importance in recent years because of the growing demand for temperature-sensitive products, higher-purity requirements, more efficient equipment, and availability of solvents with higher selectivity.

The simplest liquid-liquid extraction involves only a ternary system. The feed consists of two miscible components, the *carrier*, *C*, and the *solute*, *A*. Solvent, *S*, is a pure compound. Components *C* and *S* are at most only partially soluble in each other. Solute *A* is soluble in *C* and completely or partially soluble in *S*. During the extraction process, mass transfer of *A* from the feed to the solvent occurs, with less transfer of *C* to the solvent, or *S* to the feed. However, complete or nearly complete transfer of *A* to the solvent is seldom achieved in just one stage, as discussed in Chapter 4. In practice, a number of stages are used in one- or two-section, countercurrent cascades, as discussed in Chapter 5.

### 8.0 INSTRUCTIONAL OBJECTIVES

After completing this chapter, you should be able to:

- Explain differences among liquid-liquid extraction, stripping, and distillation.
- List situations where liquid-liquid extraction might be preferred to distillation.
- Explain why so many different types of equipment are used for liquid-liquid extraction.
- List major types of equipment used for liquid-liquid extraction and compare their advantages and disadvantages.
- List major factors involved in the selection of extraction equipment.
- List factors that influence liquid-liquid extraction.
- List characteristics of an ideal solvent.
- Define the distribution coefficient and show its relationship to activity coefficients and relative selectivity of a solute between carrier and solvent.
- Make a preliminary selection of a solvent using group-interaction rules.
- Distinguish, for ternary mixtures, between Type I and Type II systems.
- For a specified recovery of a solute, calculate with the Hunter and Nash method, using a triangular diagram, minimum solvent requirement and number of equilibrium stages for ternary liquid-liquid extraction in a countercurrent cascade.

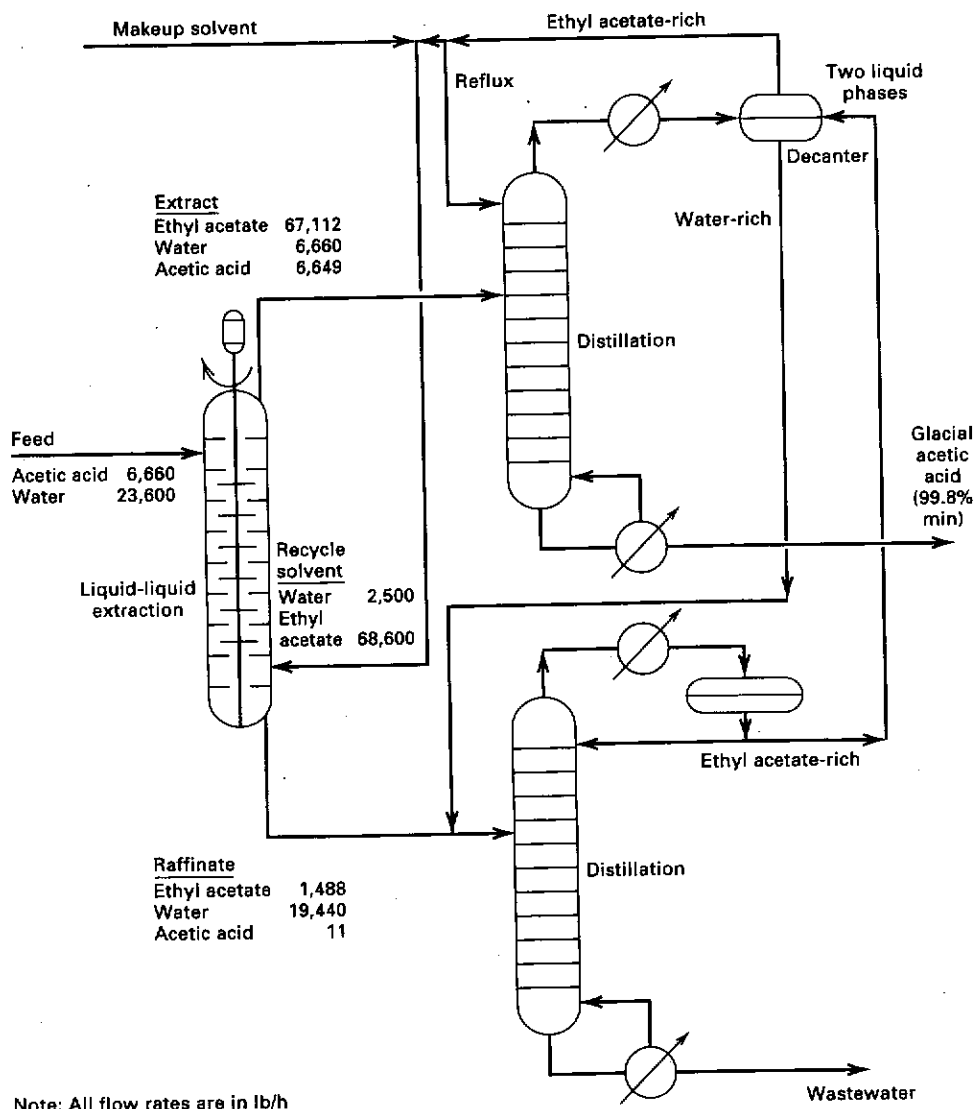
- Determine usefulness of extract reflux and carry out calculations with the Maloney and Schubert graphical method for a two-section extraction cascade that uses extract reflux.
- Design a cascade of mixer-settler units based on mass-transfer considerations.
- Determine the size of multicompartiment extraction columns, including consideration of the effect of axial dispersion.

### Industrial Example

Acetic acid is produced by methanol carbonylation or oxidation of acetaldehyde, or as a by-product of cellulose-acetate manufacture. In all three cases, a mixture of acetic acid (normal b.p. = 118.1°C) and water (normal b.p. = 100°C) must be separated to give glacial acetic acid (99.8 wt% min). When the mixture contains less than 50% acetic acid, separation by distillation is expensive because of the need to vaporize large amounts of the more volatile water, with its very high heat of vaporization. Accordingly, an alternative

liquid-liquid extraction process is often considered. A typical implementation is shown in Figure 8.1. In this process, it is important to note that two additional distillation separation steps are required to recover the solvent for recycle to the extractor. These additional separation steps are common to almost all extraction processes.

In the process of Figure 8.1, a feed of 30,260 lb/h, of 22 wt% acetic acid in water, is sent to a single-section extraction column, operating at near-ambient conditions, where the feed is countercurrently contacted with 71,100 lb/h of



Note: All flow rates are in lb/h

Figure 8.1 Typical liquid-liquid extraction process.

ethyl-acetate solvent (normal b.p. =  $77.1^{\circ}\text{C}$ ), saturated with water. The extract (solvent-rich product), being the low-density liquid phase, exits from the top of the extractor with 99.8% of the acetic acid originally contained in the feed. The raffinate (carrier-rich product), being the high-density liquid phase, exits from the bottom of the extractor and contains only 0.05 wt% acetic acid. The extract is sent to a distillation column, where glacial acetic acid is the bottoms product. The overhead vapor, which is rich in ethyl acetate but which also contains appreciable water vapor, splits into two liquid phases upon condensation. The two phases are separated by gravity in the decanter. The lighter ethyl-acetate-rich phase is divided into two streams. One is used for reflux for the distillation operation and the other is used for solvent recycle to the extractor.

The water-rich phase from the decanter is sent, together with the raffinate from the extractor, to a second distillation column, where wastewater is removed from the bottom and the ethyl-acetate-rich overhead distillate is recycled to the decanter. Makeup ethyl-acetate solvent is provided for solvent losses to the glacial acetic acid and wastewater products.

At an average extraction temperature of  $100^{\circ}\text{F}$ , six equilibrium stages are required to transfer 99.8% of the acetic acid from the feed to the extract using a solvent-to-feed ratio of 2.35 on a weight basis, where the recycled solvent is saturated with water. For six theoretical stages, a mechanically assisted extractor is preferred and a rotating-disk contactor (RDC), in a column configuration, is shown in Figure 8.1. The organic-rich phase is dispersed into droplets by rotating disks, while the water-rich phase is a continuous phase throughout the column. Dispersion and subsequent coalescence and settling takes place easily because at extractor operating conditions, liquid-phase viscosities are less than 1 cP, the phase-density difference is more than  $0.08\text{ g/cm}^3$ , and the interfacial tension between the two phases is appreciable, at more than  $30\text{ dyne/cm}$ .

The column has an inside diameter of 5.5 ft and a total height from the tangent of the top head to the tangent of the bottom head of 28 ft. The column is divided into 40 compartments, each 7.5 in. high and each containing a 40-in.-diameter rotor disk located between a pair of stator (donut) rings of 46-in. inside diameter. Above the top stator ring and below the bottom stator ring are settling zones. Because the light liquid phase is dispersed, the liquid-liquid interface is maintained near the top of the column. The rotors are mounted on a centrally located single shaft driven at a nominal 60 rpm by a 5-hp motor, equipped with a speed changer, the optimal disk speed being determined during plant operation. The HETP for the extractor is 50 in., equivalent to 6.67 compartments per theoretical stage. The HETP would be only 33 in. if axial (longitudinal) mixing did not occur.

Because of the corrosive nature of aqueous acetic acid solutions, the extractor is constructed of stainless steel. Since 1948, hundreds of extraction columns similar to that of Figure 8.1, with diameters ranging up to at least 25 ft, have been built. As discussed in Section 8.1, a number of other extraction devices are suitable for the process in Figure 8.1.

Liquid-liquid extraction is a reasonably mature separation operation, although not as mature or as widely applied as distillation, absorption, and stripping. Since the 1930s, more than 1,000 laboratory, pilot-plant, and industrial extractors have been installed. Procedures for determining the number of theoretical stages to achieve a desired solute recovery are well established. However, in the thermodynamics of liquid-liquid extraction, no simple limiting theory, such as that of ideal solutions for vapor-liquid equilibrium, exists. In many cases, experimental equilibrium data are preferred over predictions based on activity-coefficient correlations. However, such data can often be correlated well by semi-theoretical activity-coefficient equations such as the NRTL or UNIQUAC equations discussed in Chapter 2. Also, considerable laboratory effort may be required just to find an acceptable and efficient solvent. Furthermore, as will be discussed in the next section, a wide variety of industrial extraction equipment is available, making it necessary to consider many alternatives before making a final selection. Unfortunately, no generalized capacity and efficiency correlations are available for all equipment types. Often, equipment vendors must be relied upon to determine equipment size, or pilot-plant tests must be performed, followed by application of scale-up procedures recommended by the vendor or taken from sources such as this textbook.

Since the introduction of industrial liquid-liquid extraction processes, a large number of applications have been proposed and developed. The petroleum industry represents the largest-volume application for liquid-liquid extraction. By the late 1960s, more than  $100,000\text{ m}^3/\text{day}$  of liquid feedstocks were being processed with physically selective solvents [2]. Extraction processes are well suited to the petroleum industry because of the need to separate heat-sensitive liquid feeds according to chemical type (e.g., aliphatic, aromatic, naphthenic) rather than by molecular weight or vapor pressure. Table 8.1 shows some representative, industrial extraction processes. Other major applications exist in the biochemical industry, where emphasis is on the separation of antibiotics and protein recovery from natural substrates; in the recovery of metals, such as copper from ammoniacal leach liquors, and in separations involving rare metals and radioactive isotopes from spent-fuel elements; and in the inorganic chemical industry, where high-boiling constituents

**Table 8.1** Representative Industrial Liquid-Liquid Extraction Processes

Solute	Carrier	Solvent
Acetic acid	Water	Ethyl acetate
Acetic acid	Water	Isopropyl acetate
Aconitic acid	Molasses	Methyl ethyl ketone
Ammonia	Butenes	Water
Aromatics	Paraffins	Diethylene glycol
Aromatics	Paraffins	Furfural
Aromatics	Kerosene	Sulfur dioxide
Aromatics	Paraffins	Sulfur dioxide
Asphaltenes	Hydrocarbon oil	Furfural
Benzoic acid	Water	Benzene
Butadiene	1-Butene	aq. Cuprammonium acetate
Ethylene cyanohydrin	Methyl ethyl ketone	Brine liquor
Fatty acids	Oil	Propane
Formaldehyde	Water	Isopropyl ether
Formic acid	Water	Tetrahydrofuran
Glycerol	Water	High alcohols
Hydrogen peroxide	Anthrahydroquinone	Water
Methyl ethyl ketone	Water	Trichloroethane
Methyl borate	Methanol	Hydrocarbons
Naphthenes	Distillate oil	Nitrobenzene
Naphthenes/aromatics	Distillate oil	Phenol
Phenol	Water	Benzene
Phenol	Water	Chlorobenzene
Penicillin	Broth	Butyl acetate
Sodium chloride	aq. Sodium hydroxide	Ammonia
Vanilla	Oxidized liquors	Toluene
Vitamin A	Fish-liver oil	Propane
Vitamin E	Vegetable oil	Propane
Water	Methyl ethyl ketone	aq. Calcium chloride

such as phosphoric acid, boric acid, and sodium hydroxide need to be recovered from aqueous solutions.

In general, extraction is preferred to distillation for the following applications:

1. In the case of dissolved or complexed inorganic substances in organic or aqueous solutions.

## 8.1 EQUIPMENT

Given the wide diversity of applications, one might expect a correspondingly large variety of liquid-liquid extraction devices. Indeed, such is the case. Equipment similar to that used for absorption, stripping, and distillation is sometimes used, but such devices are inefficient unless liquid viscosities are low and the difference in phase density is high. For that reason, centrifugal and mechanically agitated devices are often preferred. Regardless of the type of equipment, the

2. The removal of a component present in small concentrations, such as a color former in tallow or hormones in animal oil.
3. When a high-boiling component is present in relatively small quantities in an aqueous waste stream, as in the recovery of acetic acid from cellulose acetate. Extraction becomes competitive with distillation because of the expense of evaporating large quantities of water with its very high heat of vaporization.
4. The recovery of heat-sensitive materials, where extraction may be less expensive than vacuum distillation.
5. The separation of a mixture according to chemical type rather than relative volatility.
6. The separation of close-melting or close-boiling liquids, where solubility differences can be exploited.
7. Mixtures that form azeotropes.

The key to an effective extraction process is the discovery of a suitable solvent. In addition to being stable, nontoxic, inexpensive, and easily recoverable, a good solvent should be relatively immiscible with feed components(s) other than the solute and have a different density from the feed to facilitate phase separation. Also, it must have a very high affinity for the solute, from which it should be easily separated by distillation, crystallization, or other means. Ideally, the distribution coefficient for the solute between the two liquid phases should be greater than 1; otherwise a large solvent-to-feed ratio is required. When the degree of solute extraction is not particularly high and/or when a large extraction factor can be achieved, an extractor will not require many stages. This is fortunate because mass-transfer resistance in liquid-liquid systems is often high and stage efficiency is low in commercial contacting devices, unless mechanical agitation is provided.

In this chapter, equipment for conducting liquid-liquid extraction operations is discussed and fundamental equilibrium-based and rate-based calculation procedures are presented mainly for extraction in ternary systems. The use of graphical methods is emphasized. Except for systems dilute in solute(s), calculations for higher-order multicomponent systems are best conducted with computer-aided methods discussed in Chapter 10.

necessary number of theoretical stages is computed. Then the size of the device for a continuous, countercurrent process is obtained from experimental HETP or mass-transfer-performance-data characteristic of the particular piece of equipment. In extraction, some authors use the acronym HETS, height equivalent to a theoretical stage, rather than HETP. Also, the dispersed phase is sometimes referred to as the *discontinuous phase*, the other phase being the *continuous phase*.