Lecture 7

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.

According to Derry and Williams, 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 carriel; 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. In practice, a number of stages are used in one- or two-section, countercurrent cascades.

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 (nor-ma1 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 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 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 ethyl-acetate solvent (normal b.p. = 77.1°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 ethylacetate-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°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 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 g/cm^3, and the interfacial tension between the two phases is appreciable, at more than 30 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 1, with diameters ranging up to at least 25 ft, have been built.

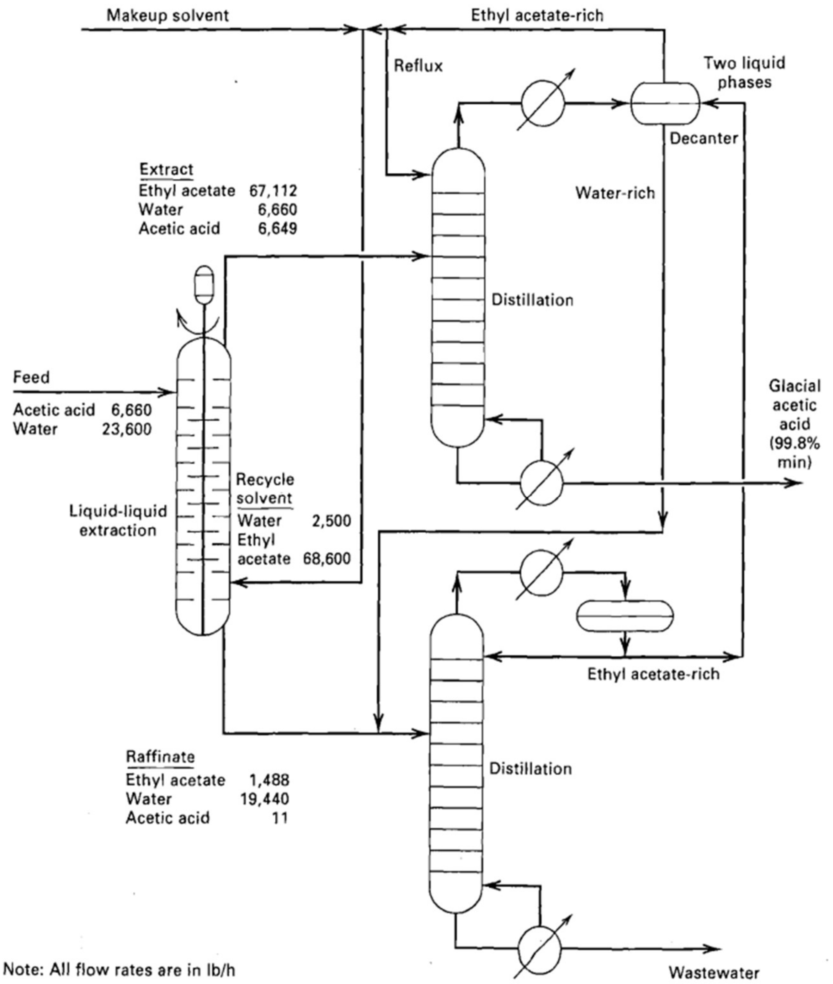

Figure 1 - Typical liquid-liquid extraction process