Liquid-Liquid Extraction

5.1 Introduction.

The separation of the components of a liquid mixture by treatment with a solvent in which one or more of the desired components is preferentially soluble is known as liquid–liquid extraction—an operation which is used, for example, the separation of hydrocarbons in the petroleum industry and in chemical industries, such as separation of aromatics from kerosene-based fuel oils to improve their burning qualities and the separation of aromatics from paraffin and naphthenic compounds to improve the temperature-viscosity characteristics of lubricating oils. It may also be used to obtain relatively pure compounds such as benzene, toluene, and xylene from catalytically produced reformats in the oil industry and in the metallurgical and biotechnology industries.

In this operation, it is essential that the liquid-mixture feed and solvent are at least partially if not completely immiscible and, in essence, three stages are involved:

(a) Bringing the feed mixture and the solvent into intimate contact.

(b) Separation of the resulting two phases.

(c) Removal and recovery of the solvent from each phase.

It is possible to combine stages (a) and (b) into a single piece of equipment such as a column which is then operated continuously. Such an operation is known as differential contacting. Liquid–liquid extraction is also carried out in stagewise equipment, the prime example being a mixer-settler unit in which the main features are the mixing of the two liquid phases by agitation, followed by settling in a separate vessel by gravity. The extraction operation may be either a physical operation, or a chemical operation.

Extraction is in many ways complementary to distillation and is preferable in the following cases:

(a) Where distillation would require excessive amounts of heat, such as, for example, when the relative volatility is near unity.

(b) When the formation of azeotropes limits the degree of separation obtainable in distillation.

(c) When heating must be avoided.

(d) When the components to be separated are quite different in nature.

(e) When one of the components is present at such low concentration that distillation becomes not possible and economic.

*For high – molecular weight fatty acids can be separated from vegetable oils by extraction with liquid propane or by high vacuum distillation, which is more expensive.

5.2 Choice of Solvent.

1. Selectivity: the effectiveness of solvent B for separating a solution of A and C (desired components) is measured by comparing the ratio of C to A in the B-rich phase to that in A-rich phase at equilibrium. For all useful extraction operation, the selectivity must exceed unity, the more so that the better. If the selectivity is unity , no separation is possible.

2. Recoverability.

3. Density: the larger difference in densities of the saturated liquid phases I necessary.

4. Interfacial tension: should be high, due to more readily coalescence of emulsions will occur but the more difficult the dispersion of one liquid in the other will be.

5. Chemical reactivity: should be stable chemically and inert toward the other components of system and material of construction.

6. Viscosity, Vapor Pressure, Freezing Point: should be low for ease in handling and storage.

7. The solvent should be antitoxic, nonflammable and low cost.

5.3 Extraction Processes.

The three steps outlined in Section above 5.1, necessary in all liquid–liquid extraction operations, may be carried out either as a batch or as a continuous process. In the single-stage batch process illustrated in Figure 5.1, the solvent (B) and solution (A and C) are mixed together and two liquid layers formed which insoluble, then allowed to separate into the two phases-the extract E containing the required solute in the added solvent(rich-B) and the raffinate R, the weaker solution with some associated solvent(rich-A). With this simple arrangement mixing and separation occur in the same vessel. A continuous multistage such as two-stage operation is shown in Figure 5.2,

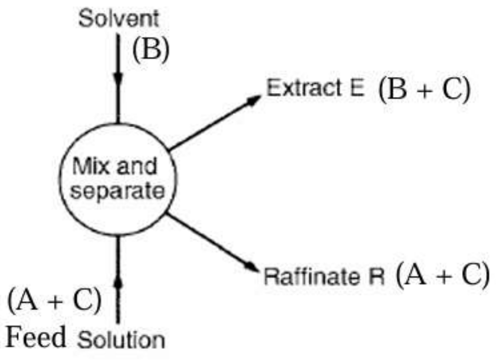


Figure 5.1. Single-stage batch extraction.

where the mixers and separators are shown as separate vessels. There are three main forms of equipment. First there is the mixer-settler as shown in Figure 5.1, secondly, there is the column type of design with trays or packing as in distillation and, thirdly, there are a variety of units incorporating rotating devices. In all cases, the extraction units are followed by distillation or a similar operation in order to recover the solvent and the solute. Some indication of the form of these alternative arrangements may be seen by considering two of the processes referred to in Section 5.1.

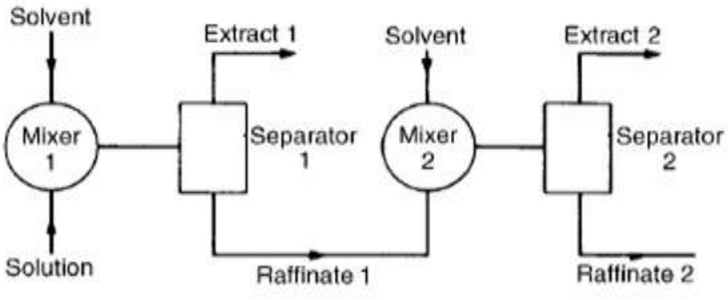


Figure 5.2. Multiple-contact system with fresh solvent.

5.4 Equilibrium Data.

Extraction involves the use of systems composed of at least three substances and although for the most part the insoluble phase are chemically very differently, generally all three components appear at least to some extent in both phases. The following notation scheme will be used to describe the concentrations and amounts of this ternary mixture, for purposes of discussing both material balance and equilibrium.

- A and B are pure, substantially insoluble liquids, and C is the distributed solute. Mixtures to be separated by extraction are composed of A and C, and B is the extracting solvent.

- Quantities are measured by mass foe batch operations, mass/time for continuous operation.

E = mass/ time , extract.
R = mass/ time , raffinate.
B = mass/ time , solvent.
E´ = mass B-free/ time .
x = weight fraction C in the solvent-lean(rich-A).
y = weight fraction C in the solvent-rich(rich-B).

$$x' = \frac{x}{1-x} = \frac{mass\ C}{mass\ non-C-in\ raffinate}$$

$$y' = \frac{y}{1-y} = \frac{mass\ C}{mass\ non-C-in\ extract}$$

$$X = \text{weight fraction C in raffinate on a B-free basis} = \frac{mass\ C}{mass\ A + mass\ C}$$

$$Y = \text{weight fraction C in extract on a B-free basis} = \frac{mass\ C}{mass\ A + mass\ C}$$

$$N = \text{weight fraction B on a B-free basis} = \frac{mass\ B}{mass\ A + mass\ C}$$

The addition of a new solvent to a binary mixture of a solute in a solvent may lead to the formation of several types of mixture:

(a) A homogeneous solution may be formed and the selected solvent is then unsuitable.

(b) The solvent may be completely immiscible with the initial solvent.

(c) The solvent may be partially miscible with the original solvent resulting in the formation of one pair of partially miscible liquids.

(d) The new solvent may lead to the formation of two or three partially miscible liquids.

With conditions of type (b), the equilibrium relation is conveniently shown by a plot of the concentration of solute in one phase against the concentration in the second phase. Conditions given by (c) and (d) are usually represented by triangular diagrams.

Equilibrium Data on Triangular Coordinate.

One pair of partially miscible liquids.

The system, acetone (C) - Water (A) - methyl isobutyl ketone (B), as shown in Figure 5.3a, is of type (c).

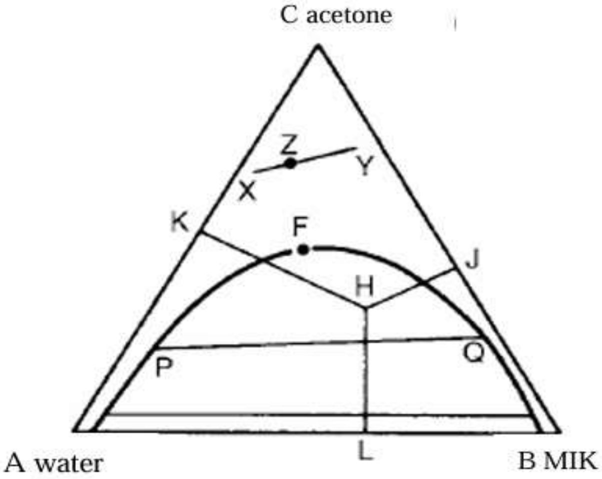


Figure 5.3a

Here the solute **C** is completely miscible with the two solvents **A** and **B**, although the two solvents are only partially miscible with each other. Each point inside the triangle represents the composition of a possible three-component mixture, a mixture indicated by point H consists of the three components A, B and C in the ratio of the perpendiculars HL, HJ, HK. A point at one of the three corners represents a pure component, while the normal distance between an interior point and the side opposite the corner for pure A represents the mole fraction or mass fraction of component A in the mixture. The distance HL represents the mass fraction Xc of C in the mixture at H, HJ represents X_B, HK represents X_A. Where $X_C + X_B + X_A = 1$

The area under the curved line NPFQM, the binodal solubility curve, represents a two-phase region which will split up into two layers in equilibrium with each other. These layers have compositions represented by points P and Q, and PQ is known as a “tie line”. Such lines, two of which are shown in the diagram, connect the compositions of two phases in equilibrium with each other, and these compositions must be found by practical measurement. There is one point on the binodal curve at F which represents a single phase that does not split into two phases. F is known as a ***plait point***, and this must also be found by experimental measurement. The plait point is fixed if either the temperature or the pressure is fixed.

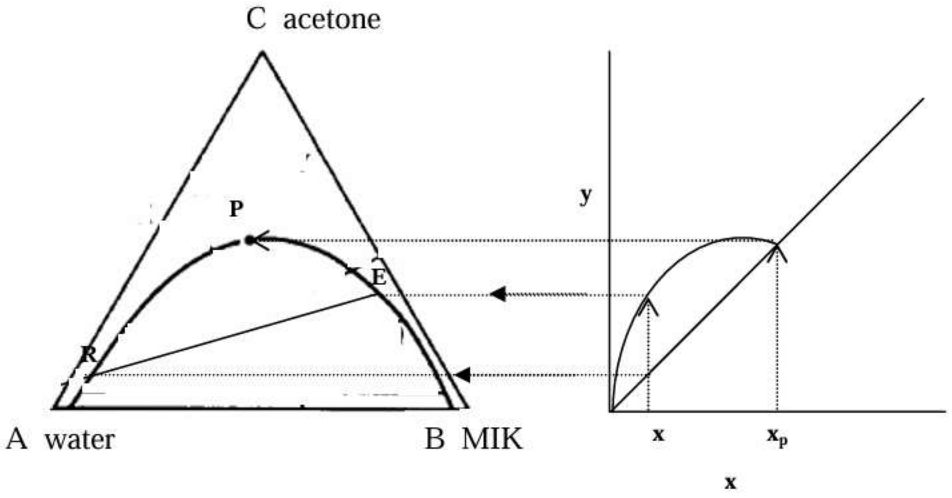


Figure 5.3b

Two or three partially miscible liquids.

In Figure 5.4 the two-phase regions merge on varying the temperature. Aniline (**A**), water (**B**), and phenol (**C**) represent a system of the latter type. Under the conditions shown in Figures 5.4, **B** and **C** are miscible in all proportions, although **B** and **A**, and **A** and **C** are only partially miscible. Figure 5.4 show equilibrium relationship for the aniline–water–phenol at high temperature.

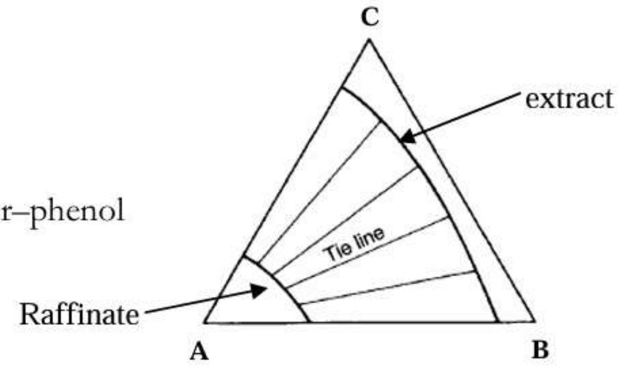


Figure 5.4
relationship for the aniline–water–phenol

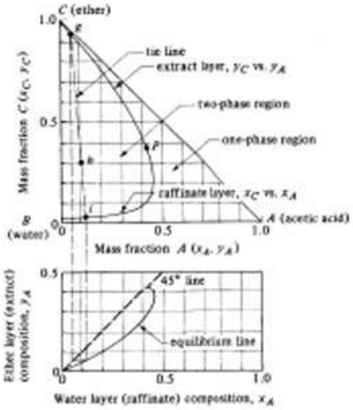
Equilibrium Data on Rectangular Coordinate.

In some system equilateral triangular coordinates have some disadvantage, therefore special cases a more useful method for plotting the three component data using rectangular coordinate as in acetic acid(A)-water(B)-isopropyl ether(C) as shown in Figure 5.5.

The solvent pair B and C partially miscible.
The concentration of component C is plotted in a vertical axis and A in a horizontal axis, while the concentration of B can be obtained as:-

$$X_B = 1 - X_A - X_C$$
$$Y_B = 1 - Y_A - Y_C$$

The line gi is called the tie line, I represent the water Rich layer(raffinate)and j is the solvent rich layer (isopropyl ether).The te line also drawn by distribution Diagram y vs. x plotted below the phase diagram.



- The system another rectangular system can be plotted on a B-free basis using x , y diagram .The equilibrium data (solubility data) in extraction ,these coordinate are plotted on a B-free basis (solvent free basis).These coordinate are represented by , x , y, N, where x is A rich , y is B rich and N is the B concentration on a B-free basis as shown on Figure 5.5.

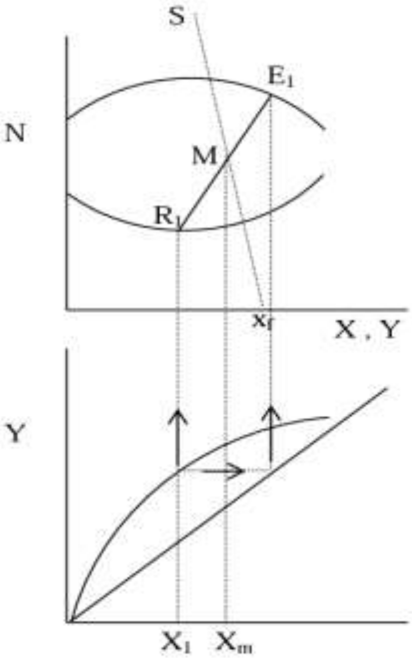


Figure 5.5

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