Solvent extraction

Solvent extraction is generally known as liquid-liquid extraction. This is one of the early methods of separation. It finds extensive use as a routine separation method for both organic and inorganic compounds present in aqueous solution mixtures.

The method had become very popular because of its speed, ease and Convenience for handling mixtures containing the components in trace to macro amounts.

Many organic and biochemical compounds can be Separated without decomposition from their aqueous mixtures.

Principle and Process

Principle: Solvent extraction is based on the principle of Nernst Distribution Law it states that transfer of solutes from one solvent (usually water) to another solvent which are immiscible with each other.

they are brought into contact with each other in a device called separating funnel. During the period of intimate contact brought out through vigorous shaking of the two solutions, the solutes in the aqueous solution are distributed between water and the immiscible solvent to different degrees. This distribution of solutes is an equilibrium process.

The distribution law for a solute can be mathematically expressed as

$$D = \frac{[A]_{org}}{[A]_{aq}}$$

$D = K_D$ if the chemical species of the solute is the same in both the solvents (water and the organic solvent).

$[A]_{org}$ = Concentration of the solute in the immiscible solvent (or organic solvent) at equilibrium.

$[A]_{aq}$ = Concentration of the solute in the aqueous layer at equilibrium.

Thus the success of solvent extraction depends on the value of K_D. Greater the value of K_D, greater is the efficiency of the extraction process.

Extraction Process

Generally the solvent extraction technique is used in separating the soluble components or solutes present in an aqueous solution. This is done by shaking a known volume of the aqueous solution taken in a separating funnel with a known volume of the organic liquid (solvent) which is completely immiscible with water. The shaking is done thoroughly for sufficient time to ensure complete equilibration of the distribution of the solutes between water and the immiscible organic liquid. The separating funnel is shown in the figure 1.1.

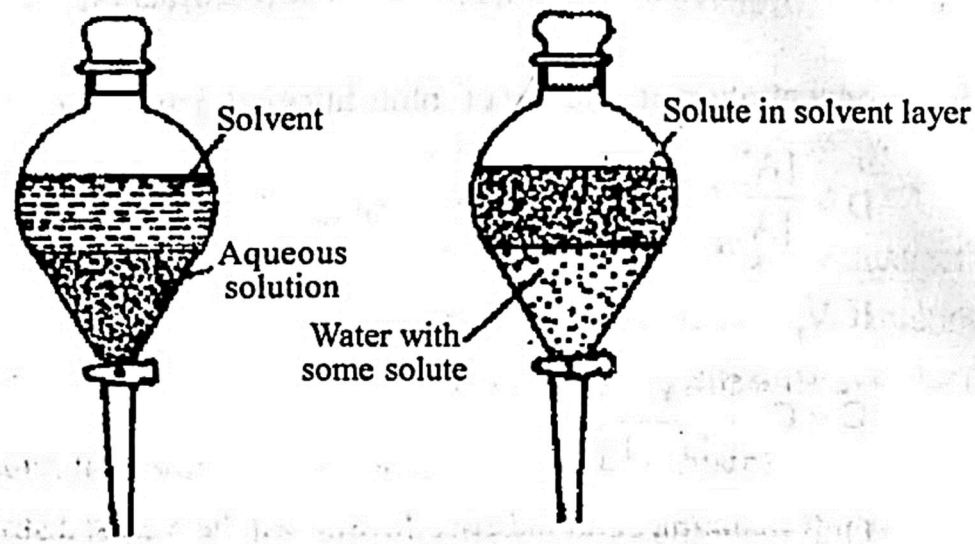


Fig. 1.1 : Separating funnel

The separating funnel is then kept aside in a stand for sufficient time for the clear separation of the aqueous and non-aqueous layers. If the separation is not perfect, generally anhydrous sodium sulphate salt is added to the content of the flask, and the mixture is shaken vigorously. This helps in the clear separation of the two layers (aqueous and organic layers)

Types of Solvent Extraction

1. **Batch Extraction Process**

In a batch extraction the aqueous solution containing the dissolved solute is shaken with an immiscible organic solvent in a closed vessel (separating funnel until equilibrium is attained as described in the earlier paragraph. The extraction can also be carried out in an open vessel (beaker) using a mechanical or magnetic stirrer.

If the value of 'D' is large, say 10, and equal volumes of the two solvents are taken (water and non-aqueous liquid) batch extraction leads to a large percentage extraction of solute into the organic liquid. The concentration of the solute left in the aqueous phase after one equilibration with volume 'V of the aqueous phase and the volume V, of the organic phase is given by the equation.

$$C = C_o \left[\frac{V}{DV_o + V}\right] = C_o \left[\frac{1}{(D\,(V_o/V)+1)}\right]$$

C_o = Concentration of solution of solute before extraction

C = Concentration of solution of solute after extraction

$$D = \frac{[A]_{org}}{[A]_{aq}} \qquad A = \text{solute}$$

If $V_o = V$, Then, the above equation is converted to

$$C = C_o \left[\frac{1}{D+1}\right]$$

One generally expresses the result of the extraction process in terms of the percentages of extraction (%E) of the solute.

$$\%\,E = \frac{100\,D}{(D+1)}$$

In cases where volumes (V_o, V) are not equal,

$$\%\,E = \frac{V_o}{V}\left[\frac{100D}{D + V/V_o}\right]$$

When % E approaches 100, 'D' tends towards infinity. But meaningful values of 'D' be usually between $10^{-4} - 10^{4}$.

The quantity of solute remaining in the aqueous phase after a single extraction is dependent on the value of 'D' and on the value of (V/V_o). After 'n' extractions, the concentration of the solute remaining in the aqueous phase is given by the equation

$$C = C_o \left[\frac{V}{V + DV_o} \right]^n$$

It can be shown that for a given volume of the extracting liquid (organic solvent), **the extraction is more efficient if small portions of the extracting liquid is used (organic solvent) instead of using the entire volume of the extracting liquid (organic solvent) in a single extraction.**

Suppose that 50mL of water containing 0.1 g of iodine are shaken with 25 mL of carbon tetrachloride. The distribution coefficient of iodine between water and carbon tetrachloride at the ordinary laboratory temperature is 1/85, i.e., at equilibrium the iodine concentration in the aqueous layer is $1/85^{th}$ of that in the carbon tetrachloride layer. The weight of iodine remaining in the aqueous layer after one extraction with 25 mL, and also after three extractions with 8.33 mL of the solvent, can be calculated by application of the above formula. In the first case, if x, g of iodine remains in the 50 mL of water, its concentration is $x1/50$g mL^{-1}; the concentration in the carbon tetrachloride layer will be $(0.1 - x1)/25$ g mL^{-1}.

Hence:

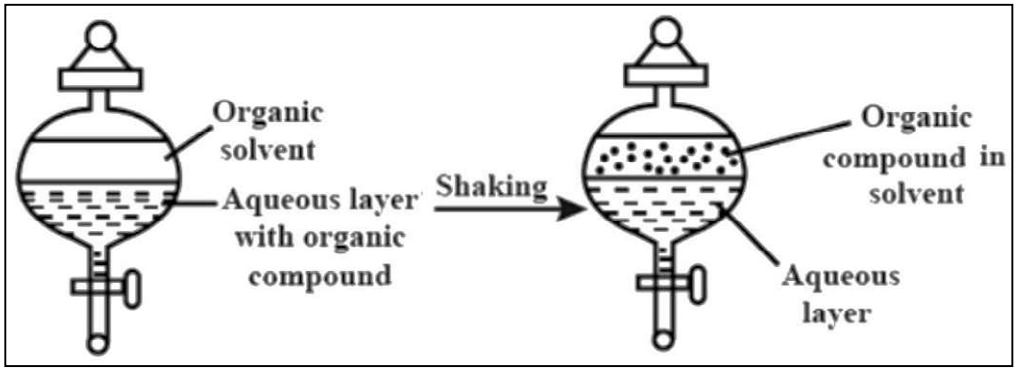
$$\frac{x_1/50}{(0.1 - x_1)/25} = \frac{1}{85}, \text{ or } x_1 = 0.00230 \text{ g}$$

The concentration in the aqueous layer after three extractions with 8.33 mL of carbon tetrachloride is given by:

$$x_3 = 0.1\left(\frac{(1/85) \times 50}{(50/85) + 8.33}\right)^3 = 0.000\,028\,7 \text{ g}$$

Prepared by Dr. D. Chenna Rao

Acid/Neutral Organic Compound Mixture Extraction/Separation:



Organic acids and organic neutral can be separated from neutral organic compounds via a base/acid extraction process.

This type of extraction takes advantage that most organic acids (or bases) and organic neutral compounds are soluble in organic solvents while their conjugate acid or conjugate base ions are soluble in water.

If you have a mixture of benzoic acid (organic acid) and naphthalene (neutral organic molecule), these compounds will be soluble in the solvent diethyl ether.

Adding an aqueous basic solution will cause an acid base reaction between the aqueous base and the organic acid. The organic neutral compound will not be affected. Because the conjugate base of benzoic acid is an ion, it is more soluble in water than ether and thus partitions into the water layer. (Figure)

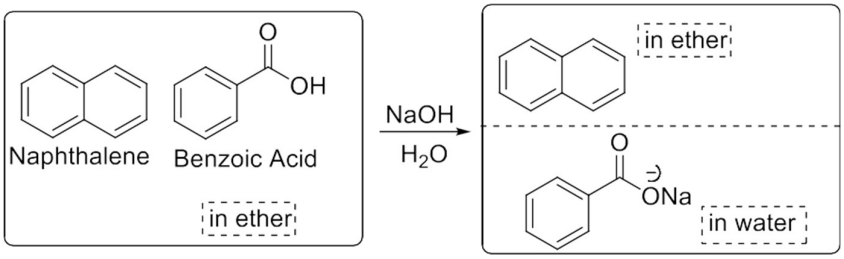


Fig: Basic Extraction of an Organic Acid

At this point, we can separate the organic ether layer and the aqueous layer. The aqueous layer can then be acidified and subsequently extracted with ether to obtain benzoic acid, separated from the naphthalene and aniline (figure).

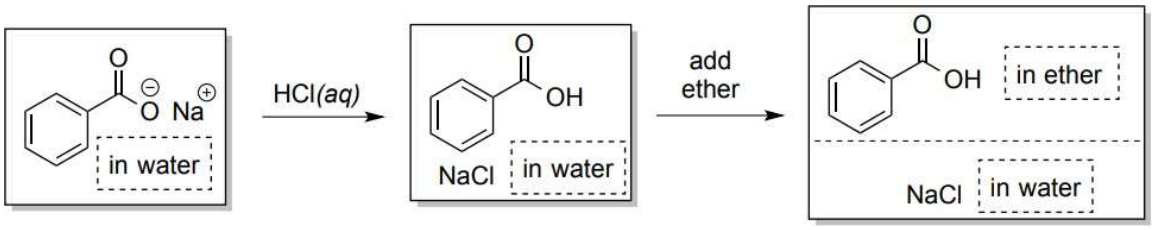
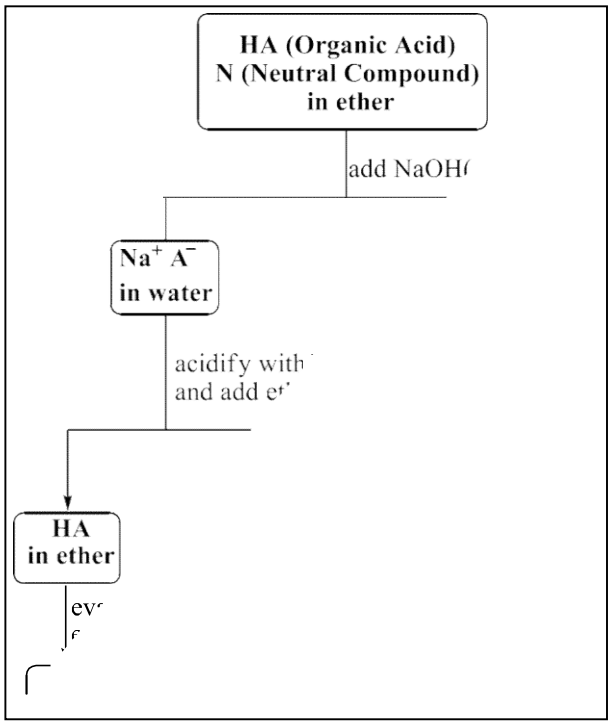


Fig: Acidification of the Basic Solution

The ether layer containing benzoic acid can be evaporated off to provide the solid benzoic acid.

EXTRACTION FLOW CHART: ORGANIC ACID-NEUTRAL MIXTURE



Base/Neutral Organic Compound Mixture Extraction/Separation:

In order to separate the naphthalene (neutral organic molecule) and aniline (organic base) we can employ an acidic extraction of the organic base. To the ether solution containing naphthalene and aniline, aqueous acid is added. This acid reacts with the amine to form an ammonium salt. The ammonium salt is water-soluble and goes into the aqueous layer. (Figure).

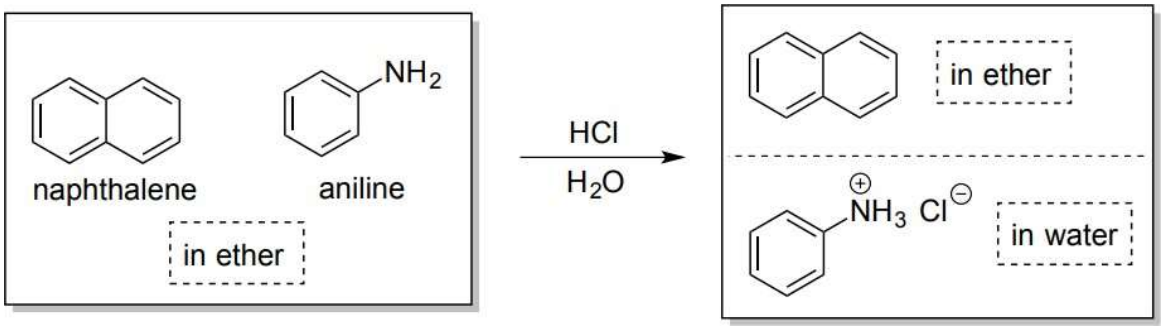


Fig: Acid Extraction of an Organic Base.

The organic and aqueous layers can then be separated. The organic layer contains pure naphthalene while the aqueous layer contains the ammonium ion of aniline. To isolate aniline, the acidic solution can be basified followed by the addition of ether to extract the neutral aniline into the organic solvent as shown in figure below.

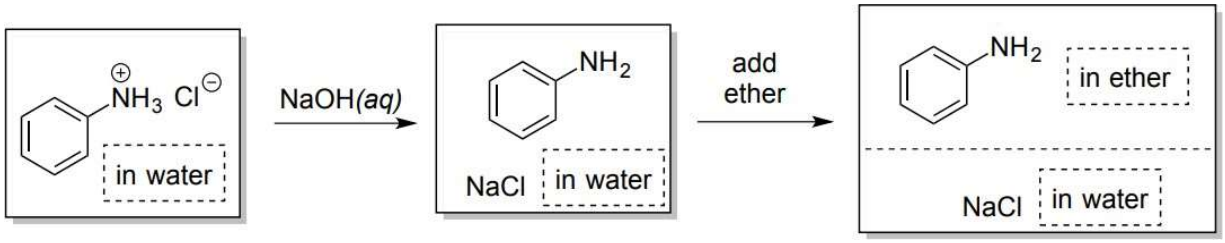
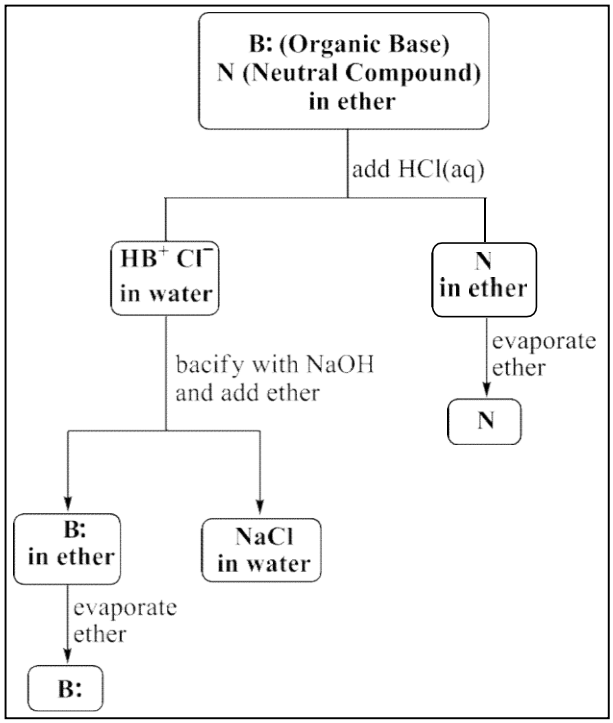


Fig: Basification of the Acidic Solution.

EXTRACTION FLOW CHART: ORGANIC BASE-NEUTRAL MIXTURE



Continuous extraction of Liquids

When the organic compound to be extracted his more soluble in water then in the organic solvent then the extraction by the usual method of shaking with an organic solvent in a separating funnel will require large quantities of the solvent and even the quantitative extraction of the compound will remain doubtful. To overcome this difficulty such materials are extracted in special apparatus called the liquid-liquid extractor is called **Soxhlet extractor**. These operators are designed in such a manner that only small amount of solvent is needed for a complete and continuous extraction of the material.

Liquid- liquid extraction two types

Two types of apparatus one meant for those solvents which are lighter than water and the other forthose solvents which are heavier than water are commonly used.

Apparatus for solvents lighter than water-

This consists of a round-bottomed flask A and a long wide tube B containing two side arms C and D. Both the side arms C and D unite at the lower end and lead into a single tube, as shown in Fig.

Another long glass tube E, whose upper end is widened to give the shape of a funnel, is placed vertically inside the wide tube B. At the upper open end of tube B, a reflux water condenser F is fitted in such a manner that the drops of the condensed organic solvent fall directly into the funnel of tube E The solvent is filled in the round-bottomed flask to half its volume. The aqueous layer is cautiously filled into the wide tube B up to a level much below the opening of tube D and a small quantity of the solvent is also placed over it. Flask A containing the solvent is heated either on a hot water-bath or a heating mantle. The solvent vapours reach the con- denser through the side tube C, get condensed, fall directly into the central vertical tube E, reach the bottom of the aqueous layer in B, and while going up (being lighter than water) through the aqueous layer extract some of the solute. In this process, the solvent above the aqueous layer continuously increases in bull. The excess solvent (now containing the solute) is sent back to flask A through the side tube D where it isagain vaporized.

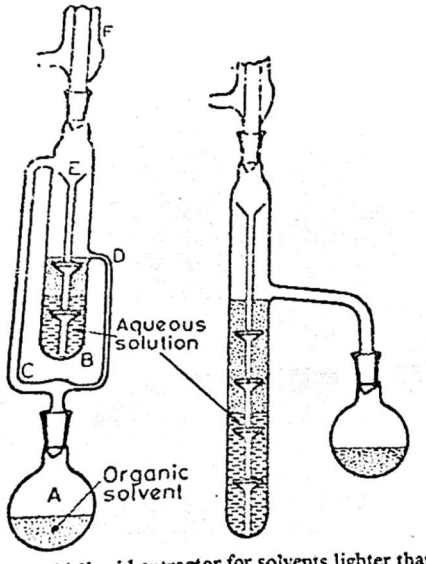


Fig. 5.1 Liquid-liquid extractor for solvents lighter than water.

leaving the solute in flask A In his way the cycle continues after many such cycles. The solute will gradually accumulate in the solvent in flask A and when it is judged that the whole of the solute has come to flask A the extraction is stopped. The solute can be recovered the solution in flask A in the usual manner. If the solution in flask. A becomes too concentrated and the extraction is not yet complete, then the contents of flask A are removed and replaced by a fresh solvent and extraction is continued until it is completed.

Apparatus for solvents heavier than water.

The apparatus, as shown in Fig. consists of a round-bottomed flask A and a long wide tube B containing one side arm C and an arm D emerging from the lower open end of tube B. Both the arms C and D unite at their far end and form a single tube, as shown in the figure. At the upper open end of tube B, a reflux water condenser E is fitted in such a manner that the condensed solvent falls directly on to the liquid contained in tube B. The solvent, e.g. chloroform, is taken in flask A to less than half its volume. The same solvent is also filled in tube B to a very small height and then the aqueous solution containing the solute is poured slowly and continuously into tube B. Take care that the upper level of the liquid remains below the side arm C when the extracting solvent level is equal to the level of arm D. The solvent is boiled in flask A, its vapours reach the condenser through the side arm C, get conde- used and fall as droplets on the aqueous layer in tube B. While going down through the aqueous phase the solvent droplets take a small amount of the solute with them and when the lower solvent layer reaches a certain height much of it is siphoned through D back into A. The cycle continues it this way, and after many such cycles, when it is judged all of the solute has come in to flask A. Extraction is stopped and the solution in flask A in processed in the same manner to recover the solute as is mentioned for solvents lighter than water.

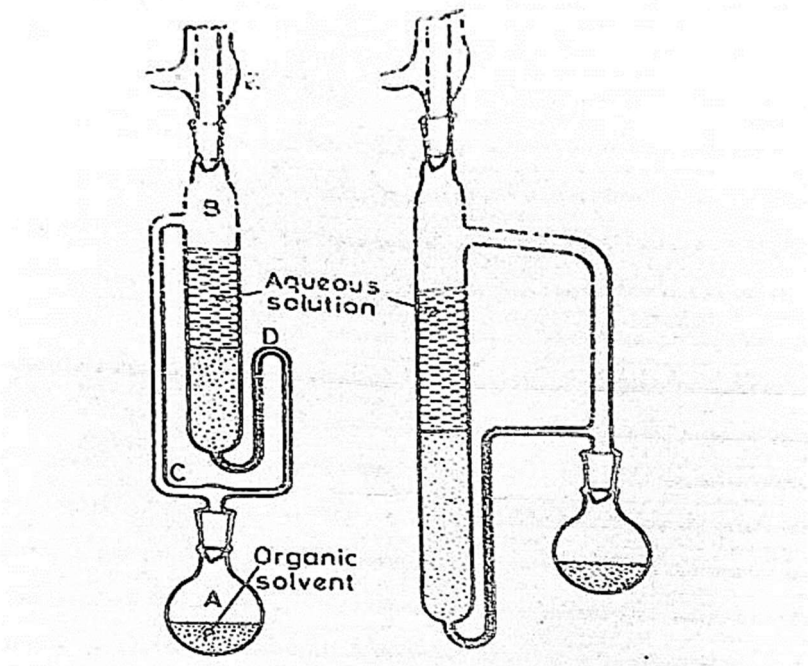
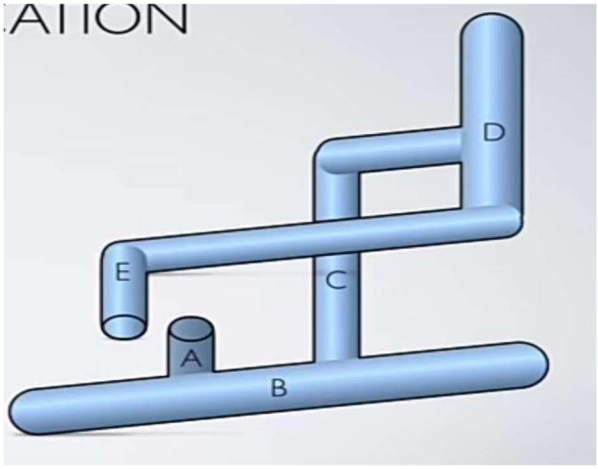


Fig. 5.2 Liquid-liquid extractor for solvents heavier than water.

Counter Current Extraction:

The method was discovered by craig and post. It consists of 300-400 such chambers. The organic solvent and the aqueous solution is introduced to tube A and then it passes to B. it is shaken and is allowed to attain the equilibrium. Now the apparatus is tilted so that the upper layer gets decanted through C and is collected in D. When the apparatus is again made vertical the liquid passes to D to E in the next chamber of A and then to B. The process is repeated till the two liquids get almost separated.



Counter Current extractor

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APPLICATIONS

• With the help of this method we can have accurate quantitative analysis of a single as well as the mixture of the components.

• In this case apparatus required are very simple (separating funnel burette pipets conical flask etc.)

• Time required for analysis is very small.

The method is very well used for detection of traces quantity of substance where precipitation method (Gravimetry) is not possible.

• The phenomenon is widely applied in drug analysis.

• The solvent extraction is used in clinical laboratory.

• Metal chelates are more soluble in non-polar solvents. Thus Ni(II) in its tetra co-ordinate complex with dimethyl glyoxime can be extracted into chloroform. In presence of citrate or tartrate the precipitation of Fe(III) and Cr(III) can be avoided.