Liquid – liquid extraction (L.L.E.)

L.L.E. is a technique in which a solution (aqueous) is brought into contact with a second solvent (organic), essentially immiscible with the first. The solute is distributed between the two immiscible liquid phases, and the ratio of the concentrations of the solute in the two phases will be constant. The separation by solvent extraction is usually, simple, cleaner, rapid and convenient than the separation by means of precipitation in which the precipitate is usually contaminated by post precipitation, occlusion and surface adsorption.

Experiment No.1:

The Distribution Coefficient (D) of Acetic Acid between Water and Diethyl Ether

Theory:

The distribution coefficient or distribution ratio (D) of a solute is the solubility ratio of that solute between two immiscible solvents. The first one is generally an organic solvent immiscible with water and the second solvent is water. As a result of the difference in the solubility of the solute in the two immiscible solvents, separation (or extraction) can be achieved and simply by shaking the two solvents in a separatory funnel in order to increase the surface area between two phases. When the extraction is complete, the liquids are allowed to separate with the denser phase settling to the bottom of the separatory funnel. The distribution coefficient is characteristic of the solute and is a constant at constant temperature (It is independent on the initial concentration of solute).

The value of distribution coefficient is generally directly proportional to the ratio of solubilities of the solute in the two solvents. The solubilities, as is well known, are dependent on the polarities of both the solute and the solvent. A polar solute would be more soluble in a polar solvent and a non polar solute in a non-polar solvent.

Distribution coefficient can be represented by:

$$D = \frac{C_1(\text{ Solvent1})}{C_2(\text{ Solvent 2})}$$

Where C_1 is the concentration (g / L) of the solute in solvent 1 , which is an organic solvent immiscible with water.

C_2 is the concentration (g / L) of the solute in solvent 2 (water).

In this experiment, we shall determine the distribution ratio (D) of acetic acid between diethyl ether and water.

Apparatus:

100 ml separatory funnel, 25 ml, 10 ml transfer pipettes, and 100 ml conical flasks.

Chemicals :

Aqueous acetic acid (unknown), diethyl ether, and
0.05 N standard NaOH solution.

Procedure:

To the dry 100 ml separatory funnel, add (by a pipette) 5ml of the unknown aqueous acetic acid, and then 5 ml of diethyl ether (supply the pipette with a pipette filler in taking the ether). Stopper the funnel and shake gently the contents of the funnel frequently for at least 30 minutes the shaking should not be too vigorous since diethyl ether is volatile and its vapours tend to buildup within the funnel. The vapours should be relieved after each shaking by (slowly removing the stopper). After shaking time (30 minutes) has finished, settle for 2 minutes, remove the stopper, and separate the two layers in to two dry conical flasks.

Determination of acetic acid in the aqueous layer:

1. Add to the separated aqueous acetic acid (layer) in 100 ml conical flask; 2 drops of phenolphthalein indicator.
2. Titrate with standard 0.05 N NaOH solution to the pink colour of phenolphthalein indicator.
3. Calculate the strength (g/L) of acetic acid using the following relationship :

IL IN NaOH = 60.05 g CH_3COOH

Determination of acetic acid in the organic Layer:

1. Add to the separated organic layer in 100 ml conical flask, 20 ml of distilled water and shake (Why?), 2 drops of phenolphthalein indicator, and then titrate to the phenolphthalein pink colour.
2. Calculate the strength (g/L) of acetic acid by using the same relationship mentioned before .
3. Having thus found the conc. of acetic acid in both the aqueous and organic layers, calculate the value of D.

Questions and Problems:

1. Comment on the value of (D) you have attained.
2. Why acetic acid dissolves in both water and diethyl ether.
3. Calculate the distribution ratio of a solute (A), the solubility of which in the aqueous layer is five times its solubility in the organic layer. Predict the nature of the solute.

Experiment No. 2:

The Distribution Ratio of Ammonia between Water and Chloroform

Theory:

In the previous experiment, we have evaluated the value of (D) for an organic acid (acetic acid) in a water-ether system. The subject of this experiment will be the determination of the distribution ratio of an inorganic base (ammonia) in a water-chloroform system.

Apparatus:

The same as in the previous experiment.

Chemicals:

Aqueous ammonia (unknown).
Chloroform.
0.05 N standard HC1solution.

Procedure:

To a dry 100ml separatory funnel, pipette (use a pipette filler for handling) 5 ml of chloroform and then5 ml of aqueous ammonia, stopper the funnel and gently shake the contents of the funnel frequently for 30 minutes. After shaking time has come to end, settle for two minutes, remove the stopper, and separate the two layers in to two dry conical flasks.

Determination of ammonia in the aqueous layer:

1. To the separated aqueous ammonia in 100 ml conical flask add 3 drops of methyl red indicator.
2. Titrate with standard 0.05 N HC1 solution to the pink-red colour of methyl red indicator.
3. Calculate the strength or conc. (glL) of ammonia in the aqueous layer using:

1L 1NHC1 = 17.03 g NH_3

Determination of ammonia in the chloroform layer:

1. Add 50 ml of distilled water to chloroform layer, shake (Why?); then 3 drops of methyl red indicator was added.
2. Titrate with standard 0.05 N HC1 solutions to the pink-red colour of the indicator.
3. Calculate the strength (g/L) of ammonia, using the relationship mentioned before.
4. Compute the value of (D).

Questions:

1. How do you explain the solubility of ammonia in water and chloroform? Which is more?
2. Compare this experiment with the preceding one.

Ion Exchange

Is a process by which ions held on a porous, essentially insoluble solid, are exchanged for ions in a solution that is brought in contact with the solid. The solid material is called ion exchange resin.

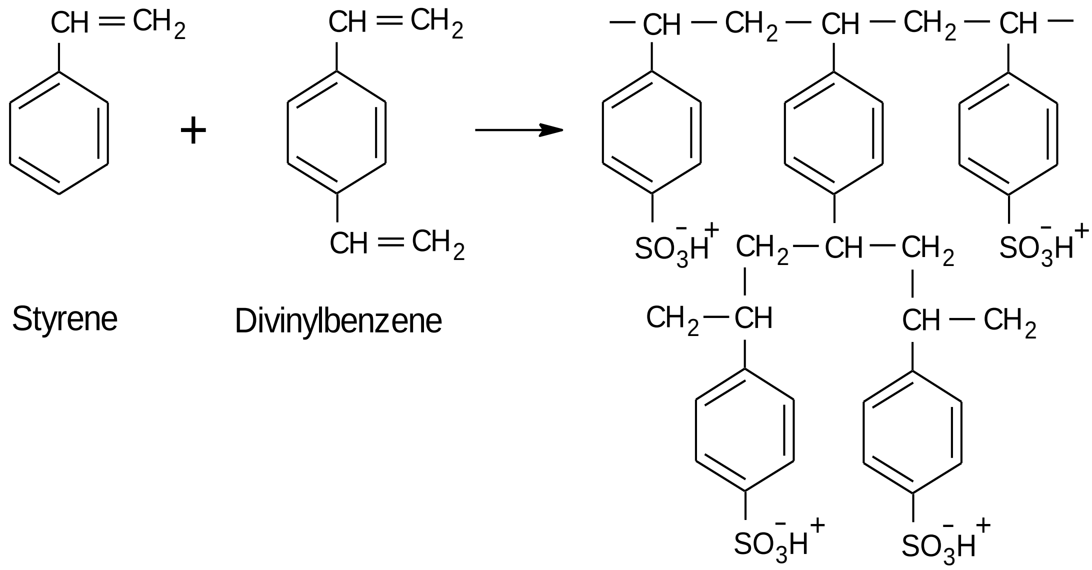
Ion Exchange Resins

Synthetic ion-exchange resins are high- molecular weight polymers that contain large numbers of an ionic functional groups per molecule. There are three types of ion exchange resin:

Cation exchange resins: these resins contain acidic functional groups . The strong–acid cation exchangers have sulfonic acid groups, ($-SO_3^- H^+$), which are strong acids. The weak-acid cation exchangers have carboxylic acid groups, ($-COOH$), which are only partially ionized. The protons on these groups can exchange with other cations. Cation–exchange resin is prepared by a polymerization of styrene and divinylbenzene , followed by sulfonation.

Anion exchange resins: anion exchangers contain quaternary ammonium [$-N(CH_3)_3^+ OH^-$] groups (strong-base). Whereas weak–base types contain secondary or tertiary amines.

Mixed exchange resins : these resins contain acidic and basic functional groups (HO-----R-----H).



The important properties which determine the behaviour of a resin can be summarized:

1. Size of particles – rate of exchange and permeability of packed column.
2. Degree of cross- linking – rigidity, porosity, swelling.
3. Nature of functional group – kind of ion exchanged.
4. Strength of functional group- distribution coefficient.
5. Number of functional groups- capacity of resin.

Ion – exchange chromatography is based on the fact that different cations or anions have different affinity to undergo exchange reaction on the surface of a given exchanger. It depends upon the charge and size of the hydrated ion in solution.

The factors determining the distribution of ions between an ion-exchange resin and a solution include:

a. The extent of exchange increases with increasing valency of the exchanging ion.

$$Na^{+} < Ca^{++} < Al^{3+} < Th^{+4}$$

The greater the charge on the ion, the greater the affinity for the resin.

b. For univalent ions the extent of exchange increases with decrease in size of the hydrated cation.

$$Li^{+} < H^{+} < Na^{+} < NH_4^{+} < K^{+} < Rb^{+} < Cs^{+}$$

The smaller the (hydrated) ion, the greater the affinity for the resin.

Experiment No. 3:

Determination of Water Regain and Total Capacity of a Strong Cation Exchange Resin (Zeo Karb-225).

Theory:

Zeo-Karb225 is the commercial name for the resin polystyrene sulphonic acid divinylbenzene. The general formula of the resin is RSO_3H (Where R is the resin matrix or the organic part of the resin, $-SO_3^-$ is active (ionized) group, and H^+ is the exchangeable ion). Zeo-Karb-225 is a strong cation exchange resin, "because it contains the highly ionized sulphonic group, and is a cation exchange resin, since the exchangeable ion is a cation (or hydrogen ion).This type of resin is used widely on both industrial as well as laboratory scales, so information about some of its properties is of importance.

Two, among other, important properties of ion exchange resins are the water regain and total capacity.

Water regain: is the amount of water absorbed by (l) g of a dry resin, usually in the hydrogen form or hydroxide form.

Total capacity: is a measure of the ion-active groups (milli- equivalents) in (l) g of a dry resin. The greater number of these groups, caused to greater value of capacity. It is expressed as meq/g of a dry resin.

Determination of water regain:

Weigh accurately about (l)g of wet resin (Zeo Karb-225, H-from). Dry it in the oven at 100 C° for 1 hour.

Determine the loss in weight which represents the amount of water taken by the resin.

Water regain is expressed as the amount of water gained by (l)g of a dry resin.

Water regain = wt. of wet resin – wt. of dry resin

Determination of total capacity:

Weigh accurately about (0.2) g of the dry resin (Zeo Karb-225, H-form). Place it in a 100 ml conical flask. Add 25 ml of distilled water and 2 drops of phenolphthalein indicator, then titrate (shake vigorously) with standard 0.05 N NaOH solution to a permanent pink colour of the indicator. Calculate the total capacity of the resin by applying the formula:

$$\boldsymbol{Total\ capcity\ (meq/g) = \frac{V_{NaOH} \times N_{NaOH}}{\text{wt of dry resin}}}$$

Questions and Problems:

1. Mention other important properties for the resin you have examined.
2. Mention other types of cation exchange resins.
3. The water regain of a strong cation (H-form) exchange resin is 0.1g Calculate the total capacity of this resin, if (0.5) g of the resin (wet) requires 11 ml of 0.1 N NaOH solution to give a permanent pink colour of phenolphthalein.

Experiment No. 4:

Efficiency of a Strong Cation Exchange Resin (Zeo-Karb 225, H-form).

Theory:

This experiment illustrates the use of ion exchange resin in column and it can be called column chromatography (chromatography≡ separation process). Ion exchange chromatography for separation ions both cation and anion because the separation is based on exchange of ions in the stationary phase. The ion exchange resin is packed in the column and covered with a liquid. The resin is called the stationary phase (immobile phase) and the liquid covering it is called the mobile (moving) phase. This experiment will further illustrate one of the many applications of ion exchange methods; and that is the preparation of standard (HC1, in our case) solutions. A standard solution is passed through the resin in the column and ion exchange process occurs to give, after washing, another solution, For example:

$RSO_3^-H^+ + Na^+CL^- \longrightarrow RSO_3^-Na^+ + H^+Cl^-$ exchange process

Zeo-Karb standard Standard

and the efficiency (E) here is expressed as:

$$\boldsymbol{E} = \frac{\textbf{Number of millimoles of HCl}}{\textbf{Number of millimoles of NaCl}} \times \mathbf{100}$$

The resin can be regenerated to its original hydrogen form so it must be immersed in dilute hydrochloric acid 2 M with occasional stirring and then rinsing with distilled water until washings are neutral.

Apparatus: 35 cm glass chromatographic column.

Chemicals: Zeo Karb-225 (H-form).

Unknown Standard 0.05 N NaOH solution.

aqueous NaCl solution.

Procedure:

Preparation of the column:

1. Clean the supplied glass column with distilled water. Close the tap and fill the distance between the tap and (2-3)cm above the glass disc with distilled water.
2. Cover the glass disc with a layer (~0.5 cm thickness) of glass wool, or cotton to support the resin bed then add distilled water in the column to give a water depth of (15) cm.
3. Now, pour the supplied resin (H- form) in the column until a length of about (7) cm is obtained. The resin packed as an aqueous slurry and allowed to settle, then open the tap at a rate of 2 ml/min, and add water to remove the excess acid present with the resin (Why?)Repeat the addition of water until the elute is free from acid (does not change the colour of methyl orange indicator). Now the column is ready for operation. When tap is closed, leave always (2-3) cm liquid over the resin. The level of liquid should never be allowed to drain lower than the top resin bed or air bubbles will be entrapped and cause channeling.

Efficiency of the exchange process:

1. Pipette (5) ml of the unknown NaCl solution. Open the tap at a rate of 2 ml/min and then collect the eluate in 250 ml conical flask, add distilled water to wash the liberated HC1.
2. Add 2 drops of phenolphthalein, and titrate the total eluate with standard 0.05 N NaOH solution.
3. Determine the normality of HC1 obtained.

Questions and Problems:

1. How can standard NaOH solution be prepared using ion exchange method? Describe briefly the method.
2. Mention other applications for the ion exchange methods, and give example for each application.
3. A standard solution of HC1 (5×10^{-2}M, 100 ml) is to be prepared by passing a standard solution of NaCl through a strong cation exchange resin in its hydrogen form 25 ml of the standard NaCl are passed through the column, followed by 50 ml of distilled water, and the total eluate is diluted to 100 ml. How many grams of NaCl should be dissolved in volume of distilled water to produce the required HC1 solution?

Chromatography

Chromatography is an important technique for the separation, isolation and identification of the constituents of a mixture. Chromatography is a physical method of separation in which the components to be separated are distributed between two phases , one of which is stationary while the other (the mobile phase) moves in a definite direction .

What is column chromatography?

Column chromatography is a separation process involving the uniform percolation of a liquid solute through a column packed with finely divided material.

The separation in the column is effected either by direct interaction between the solute components and surface of the stationary phase or by adsorption of solute by the stationary phase. Column chromatography involves adsorption, partition or ion – exchange phenomenon.

In adsorption column chromatography, the substances are preferentially adsorbed by adsorbent packed in the column, while in partition column chromatography the separation of components of a mixture distribute themselves in different ratios between two different solvents.

Experiment No. 5:

Ion Exchange Chromatography-The Stepwise Elution of Iron (III) and Cu (II).

Theory:

Ion exchange chromatography is the separation of ionic substances which range from simple inorganic and organic ions to such large molecules as enzymes, proteins, nucleic acids...... etc.

In this type of chromatography, the use of a resin (the stationary solid phase) is used to covalently attach anions or cations onto it. Solute ions of the opposite charge in the mobile liquid phase are attracted to the resin by electrostatic forces.

This experiment illustrates the separation of iron (III) from copper (II) by the use of phosphoric acid and then hydrochloric acid for copper ions from a strongly acidic cation exchange resin (Zeo Karb-225). If hydrochloric acid is used alone, the order of removal of the ions from the column is reversed, and a poorer separation is obtained.

Chemicals:

Zeo Karb-225 (H-form) resin.

Unknown mixture solution of Fe (III) & Cu (II) ions.

15% H_3PO_4 solution.

(1:1) HC1 solution.

Procedure:

1. Make up a column about (7) cm long using Zeo Karb (H-form) as the packing material.
2. Wash the column until eluate is acid—free. (check the eluate by using methyl orange indicator).

3. Introduce (5) ml of the unknown solution, containing Fe (III) and Cu (II) ions to the column.
4. Wash with distilled water to remove the liberated acid (from where and how?) at a flow rate of 2 ml/min.
5. When the eluate is acid free, elute iron (III) with 15%phosphoric acid solution at a rate of 2 ml/min. Test for iron with potassium ferrocyanide.
6. When all iron (III) has passed through the column, change the eluent to (1:1) HC1 to remove copper. Test for copper with potassium ferrocyanide.
7. Volumetric methods are suitable for the analysis of iron (III) and copper (II). (see Vogel p.305 & P-358, respectively).

Questions & Problems:

1. Why phosphoric acid elutes iron (III)?
2. Specify the stationary phase, the mobile phase, & the eluting solution for ferric & cupric ions.
3. A 10 ml cupric ion solution was diluted to 100 ml. A 25 ml portion of the diluted solution, to which solid KI was added, after iodometric titration needs 10 ml of 0.05 M thiosulfate solution to change starch indicator from blue to colourless.
    - **a.** Write the balanced equations of the reactions involved in the titration.
    - **b.** Calculate the strength of cupric ion solution.

Experiment No. 6:

Adsorption Column Chromatography the Separation of Permanganate and Dichromate

Theory:

Adsorption chromatography or Liquid – solid chromatography:

Is a technique in which small differences in the adsorption behavior of substances between a moving solvent (liquid) and a stationary solid phase are utilized to achieve the separation.

Adsorption is a process occurring at the surface of a solid or a liquid as a result of the attractive forces between the adsorbent and the solute. These may be physical, such as Van Der Waals forces or chemical electrostatic forces. The surface layer of a solid particle is at a higher energy level and is described as having surface activity. A good adsorbent should possess a large surface area containing many chemically active sites.

In practice the term “adsorption chromatography" is restricted to cases where adsorptions principally by Van Der Waals forces, and "ion exchange chromatography" is used when the packing is an ion exchange material and adsorption is principally by electrostatic forces.

In adsorption column chromatography, a solution of the mixture to be separated is run onto a column of adsorbent (powder form). Solvent is then allowed to flow through the column slowly; The rate of movement of a given component, of the mixture, depends on its affinity for the adsorbent and so the chromatogram develops. Weakly adsorbed substance travels more rapidly than a strongly adsorbed one. By continued elution, the separated solutes may be washed from the column into the eluate which is collected in separate portions. This experiment deals with such phenomenon in the separation of permanganate from dichromate, using alumina as the packing material and the separation may be due to a molecular type of adsorption.

Alumina is a strong adsorbent , three types of alumina are commercially available :

(i) Aluminum oxide. (neutral PH= 6.9 to 7.1) . it is a suitable adsorbent for hydrocarbons , esters, carbonyl compounds , nitro – compounds , organic acids and bases . It is often used with non- aqueous solvents.

(ii) Basic aluminum oxide. (pH= 10 to 10.5) . It is used for samples such as acetals , glycosides, …………etc.

(iii) Acid – alumina (pH= 3.5 to 4.5) . It acts as an anion exchanger. It is often used for separating both inorganic anions and acid organic molecules.

An adsorbent should have the following characteristics:

1. It should have high surface area and selective adsorption power.
2. It should be chemically inert.

It should be finely divided to hold the substance but not so fine that passage through the column is greatly retarded.

Chemicals:

Alumina (acid alumina).
0.5 M HNO_3 solution.
Unknown permanganate and dichromate solution.
1 M H_2SO_4 solution.

Procedure:

1. Make up a column of alumina about(8) cm long using 0.5 M HNO_3 solution as the solvent.
2. Wash the packed column with (15) ml of the same acid at a rate of 2 ml/min.
3. Carefully introduce 5 ml of the unknown solution and maintain the rate of flow at 2 ml/min.
4. The dichromate is adsorbed at the top of the column, and the permanganate passes through as a diffuse band.
5. When the permanganate band is near the bottom (see from the colour), start collecting the eluate until all the permanganate has passed through.
6. Now change the eluting solution to 1M H_2SO_4, to elute the dichromate.
7. To determine the permanganate, add (20) ml of 1M H_2SO_4 to the whole eluate and titrate against standard ferrous ammonium sulphate solution to a colourless end point.

To determine the dichromate, add a known excess of standard ferrous ammonium sulphate to it and back-titration with standard $KMnO_4$ solution.

Questions and Problems:

1. State the stationary phase, the mobile phase and the eluant for each permanganate and dichromate species.
2. A 20 ml of dichromate solution was diluted to 50 ml. A 25 ml of the diluted dichromate solution was added to 20 ml of 0.02 N acidic iron (II) solution. Back titration with standard 0.03 N permanganate solution needs 10 ml for a permanent pink colour end point.

i. Write the balanced equations of the reactions involved in the titration.

ii. Will you think, the reaction will trace the same path if the titration medium is made alkaline or neutral. Why?

iii. Calculate the strength of dichromate solution.

Experiment No. 7:

Partition Column Chromatography-The Separation of Cobalt (II) and Nickel (II) Ions.

Theory:

The technique of column chromatography is much the same whether the separations are based on adsorption or on partition, the difference lies only in the packing material. adsorbent powders are replaced by silica gel or cellulose .

Partition chromatography is a method of separation brought about by the partition (distribution) of the components of a mixture between a moving liquid and a stationary liquid held on a suitable solid support. when the solvent (moving phase) is a liquid, it is called liquid–liquid chromatography, when it is a gas the technique is known a gas–liquid chromatography. The liquid–liquid separations are carried out on cellulose packed into columns. This method is widely used for the separation of organic as well as inorganic species.

Chemicals:

Acetone/conc. HC1 (98:2by volume).
Unknown aqueous mixture of Co(II) and Ni(II) ions.
Cellulose powder.
Hydrochloric acid (4:1) and 1 M solution.

Procedure:

1. Prepare a column of cellulose powder about (8) cm long, using as solvent: acetone/conc.HCl 98:2 (v/v).
2. Wash the column by allowing about (50) ml of solvent to flow through at a rate of 2 ml/min. leave always (2-3) cm solvent above the cellulose layer.

3. By a pipette, take (5) ml of the unknown solution and place in (25) ml beaker, evaporate almost to dryness and to the resulting mixture solution add (2) ml of (4:1) HC1.
4. To the above solution, add about (1.5)g of cellulose powder which makes friable mass (homogenous mass).
5. Transfer to the top of the column and add (5) ml of solvent.
6. Stir up and then gently press down to form a homogeneous compact column.
7. Allow solvent to flow at 2 ml/min (wash the beaker with the solvent and add the washings to the column).
8. The cobalt will be eluted as a light blue solution of a complex ion, collect the cobalt until all the light blue solution has passed through the column.
9. Now change the eluent to 1 M HC1 to elute nickel (retained as a pale green band in the column). Test for nickel with dimethyl-glyoxime in ammonia solution. The presence of nickel gives a pink-red colour.
10. Collect the nickel solution.
11. Complexometric (back titration) with ethylenediamine tetra acetic acid (EDTA) is a convenient method for determination of cobalt and nickel ions.

Question and problems:

1. In this experiment, specify the stationary phase, the mobile phase and the eluant for cobalt ion for nickel ion.
2. 10 ml cobalt (II) ion solution was diluted to100 ml and to the whole solution was added 20 ml of 0.02M EDTA solution. Back titration with 0.03 M magnesium sulphate solution needs 5 ml for Eriochrom black T to change colour from blue to red.

a. Write equations for the reactions involved the processes above.

b. Calculate the strength of cobalt ion solution.

c. Is a direct titration in this case feasible? Why?

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