

**Module :**  
**8**  
**Chromatographic Separation  
and Ion Exchange**

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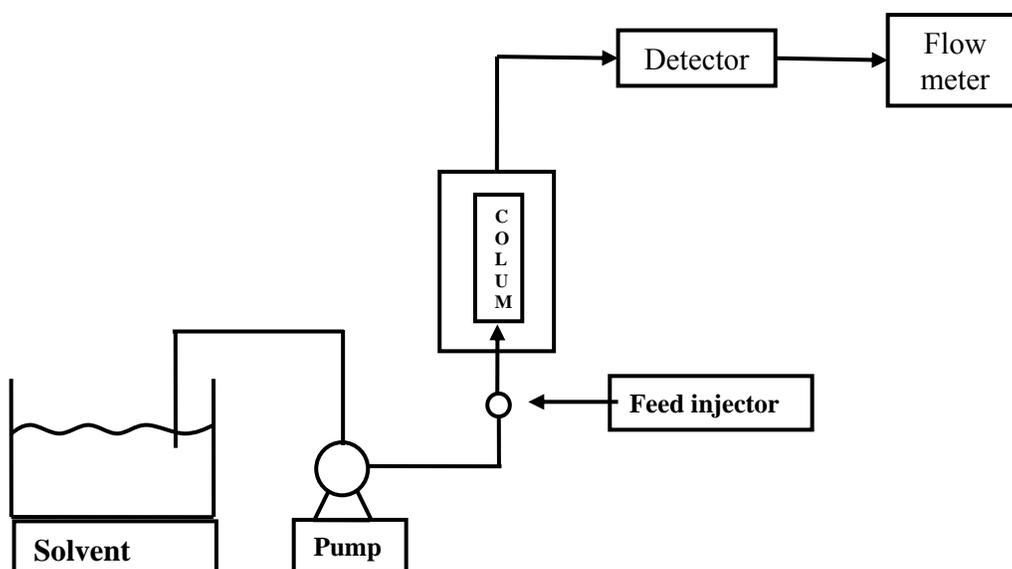
**Keywords:**

**Separation processes, membranes, electric field assisted separation, liquid membrane, cloud point extraction, electrophoretic separation, supercritical fluid extraction**

## Chromatographic Separation and Ion Exchange

Chromatography is an extremely powerful analytical tool for separating and analyzing complex mixture. The principle of chromatography is elaborated now. It constitutes a bed of particles through which a gas or liquid stream flows. The flowing phase is also known as carrier gas (in case of flowing phase is gas) or solvent (in case of flowing phase is liquid). A feed pulse (a small amount of feed) containing various solutes is introduced into the system. The solutes in the feed pulse are then separated by difference in their velocities. Therefore, the solutes emerging from the chromatographic column (the housing of the packed bed) are detected by refractive index or ultraviolet absorbance and that measurement is directly related to concentration of solutes. Based on this basic principle, chromatographic separation occurs.

A typical analytical chromatograph is shown in Fig. 8.1.



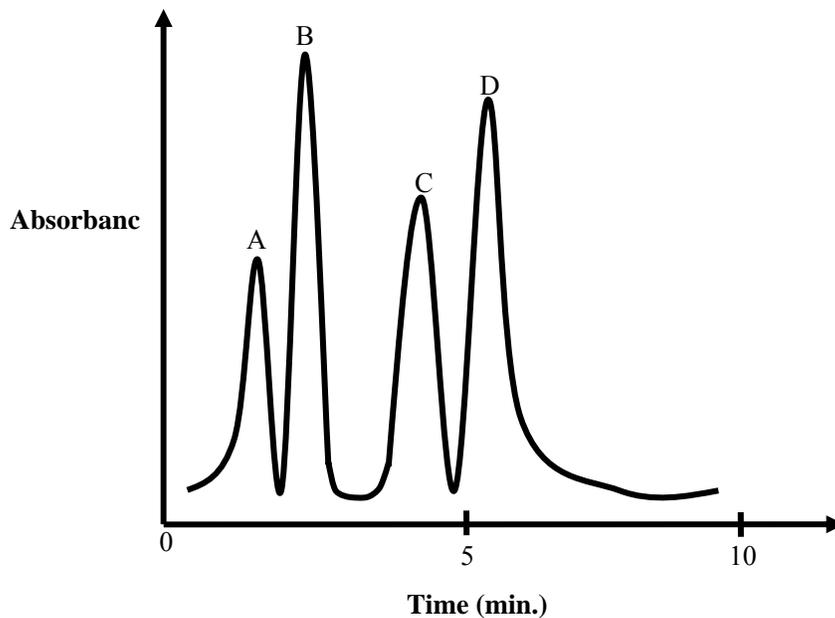
**Fig. 8.1:** Schematic of an analytical high pressure liquid chromatograph

It contains the following features:

- a) For liquid system, a pump is used to push the fluid through the column.
- b) A pulse of feed is injected into the system.
- c) The column is often enclosed in an oven to control temperature.
- d) Detector analyzes the stream for some properties like RI, UV absorbance, those can be related to concentration.

### Purpose of column:

The purpose of column is to separate the feed mixture into peaks that contain only one component in addition to solvent as shown in Fig. 8.2.



**Fig. 8.2:** Peak separation in a typical chromatographic column for a mixture of various components present in the feed

Typical concentration of feed about 1 *mg/ml*. The typical column dimension is *10cm×4.6mm*, 7-5  $\mu\text{m}$  WCX with  $300\text{\AA}$  pore size. The possible mobile phase composition is 0.05(M) phosphate with NaCl. A typical flow rate is 1.5 *ml/min*. The detection mode is ultraviolet. For protein solution, the detection is done at wavelength of *280 nm*. Typically around *10  $\mu\text{l}$*  solution is injected. The peaks correspond to various components, present in the mixture. Area under the curve is then compared with calibration curve of each pure component.

### **Gas system:**

In case of analysis in a gaseous system, a carrier gas, e.g. helium/hydrogen is used and an adsorbent is used as column. Typical adsorbents are zeolite, silica gel, activated alumina, etc.

### **Gas Liquid Chromatography (GLC):**

An inert, porous solid is coated with viscous, high boiling liquid. This stationary liquid phase does the separation. The solid should be inert, porous and inexpensive, like, diatomaceous earth. Solute in feed can dissolve in stationary liquid phase and then vaporize in flowing gas. Separation is based on relative volatility and is essentially adsorption-stripping operation.

### **Disadvantages of GLC:**

Slow vaporization of stationary phase changes

- (i) Column criteria
- (ii) Contaminate the products

## Capillary gas Chromatography:

A glass/fused silica capillary with a coating of adsorbent or high boiling solvent on the wall is used. Since the amount of stationary phase is small, the capacity is limited. However, open capillary has little resistance to mass transfer and sharp separation is observed.

## Liquid-Liquid Chromatography (LLC):

Following are the salient features of a liquid-liquid chromatograph

- (i) A stationary liquid phase is coated over an inert, porous solid.
- (ii) Separation is essentially an extraction process.
- (iii) Useful for separating non-volatile solutes.

## Difference of LLC with modern high performance liquid chromatography (HPLC):

- (i) Inert solid is silica. Stationary liquid phase is chemically attached to the solid. Most common stationary phase is C8 or C18 compounds attached to the silica gel. Water is the common solvent. Therefore, there is no loss of stationary phase occurring by the flowing feed.
- (ii) Short column have very small diameter. Packings are operated at high velocity and high pressure drop. 10-25 cm long, 4-8 mm ID, packing is 3-9  $\mu\text{m}$  and  $\Delta P \sim 1000$  psi.

### **Advantage:**

Changing solvent has major effect on the distribution coefficient and hence on separation.

### **Size Exclusion Chromatography (SEC) (GPC):**

In this case, no adsorption takes place. Steric exclusion of the solutes plays the major role. This method is useful for separation of large molecules from smaller ones. The solid matrix is cross linked polymer gels like Agarose, polydextran (sephadex).

### **Principle of working:**

This is essentially a migration chromatography where solutes sorb and desorb and all solutes move at a finite but different velocity.

### **Solute movement:**

Solute movement depends on packing structure and nature of packing. Solid particles should be sorbents having high porosity, large surface area per gram of sorbent. Particles are porous. Let us define,  $\varepsilon_p$  is the porosity within particle and  $\varepsilon_e$  is the average interparticle porosity. Following are the definitions of two quantities:

$$\varepsilon_e = \frac{\text{volume between particles}}{\text{Total volume of packed bed}} \quad (8.1)$$

$$\varepsilon_p = \frac{\text{Volume of fluid inside all particles}}{\text{Total volume of all particles (solid + fluid)}} \quad (8.2)$$

Total bed porosity ( $\varepsilon_T$ ) is defined as,

$$\begin{aligned} \varepsilon_T &= \text{sum of voids within particles and between the particles} \\ &= \varepsilon_e + (1 - \varepsilon_e) \varepsilon_p \end{aligned} \quad (8.3)$$

Bulk density is defined as,

$$\rho_B = (1 - \varepsilon_e) \rho_p + \varepsilon_e \rho_f \quad (8.4)$$

Here,  $\rho_p$  is particle density and  $\rho_f$  is fluid density. Particle density is defined as

$$\rho_p = (1 - \varepsilon_p) \rho_s + \varepsilon_p \rho_f \quad (8.5)$$

Where,

$\rho_s$  is Crystalline density after crushing, compressed solid containing no pores and it is obvious that

$$\rho_f \ll \rho_s, \rho_p.$$

Pores are not uniform in size. Large molecules such as proteins/synthetic polymers may be sterically excluded from some of the pores. Fraction of volume of pores that a molecule can penetrate is  $K_d$ . For non-absorbing species,

$$K_d = \frac{V_e - V_0}{V_i} \quad (8.6)$$

Where,

$V_e$  = elution volume (volume of fluid at which species exit from the column)

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$V_0$  = external void volume between particles

$V_i$  = internal void volume

For small molecules that can penetrate the entire interparticle volume,

$$V_e = V_i + V_0 \text{ and } K_d = 1.0$$

When molecules are large and can penetrate none of interparticle volume,

$$V_e = V_0 \text{ and } K_d = 0.$$

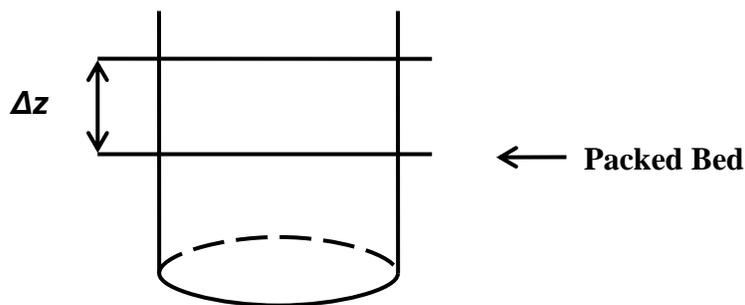
## Processes Involved:

Fluid containing solute flows in the void volume outside the particle. The following basic processes are involved:

- (i) Solute diffuses through an external film to the particle.
- (ii) Solute may sorb on external surface or diffuse through the stagnant fluid in the pores (most likely). If the pores are small, diffusion is hindered.
- (iii) Solute finds a vacant site and then sorbs by physical or electrical forces/chemical reactions.
- (iv) While sorbed, solute may diffuse along the surface, called surface diffusion.
- (v) Solute desorbs.
- (vi) Diffuses through the pores and diffuses back to external film and into moving fluid.

A given molecule can sorb and desorb number of times. While in moving fluid, solute is carried along the interstitial fluid velocity  $v$ , until it diffuses into another particle and whole process is repeated.

Migration of solute is function of  $f(\varepsilon_e, \varepsilon_p, K_d, v \text{ \& sorption equilibrium})$ .



**Fig. 8.3:** Schematic of the elemental area of the column

External void volume is  $\varepsilon_e A_c \Delta z$  ; Internal void volume (within particle) is  $(1 - \varepsilon_e) \varepsilon_p A_c \Delta z$  ;

Solute in the bed can be, (i) in the mobile fluid in external volume; (ii) in stagnant fluid inside the particle; (iii) sorbed to the particle. Solutes which are moving to column exit are in mobile phase.

Consider the movement of an incremental mass of solute added to the bed.

This will lead to change in fluid concentration  $\Delta C$  and change in amount absorbed  $\Delta q$

$$\begin{aligned} \text{Fraction of solute in mobile phase} &= \frac{\text{Amount of solute in mobile fluid}}{\text{Total amount of solute in segment}} \\ &= \frac{\text{Amount in mobile fluid}}{\text{Amount in (mobile fluid + stationary fluid + sorbed)}} \end{aligned}$$

Amount of solute increment in mobile fluid = (volume of segment)(fraction which is mobile fluid)  
(concentration in moles/litre)

$$= (\Delta z A_c) (\varepsilon_e) \Delta C$$

$$\frac{\text{Amount in mobile fluid}}{\text{Total amount of solute in segment}} = \frac{(\Delta z A_c) \varepsilon_e \Delta C}{(\Delta z A_c) \varepsilon_e \Delta C + (\Delta z A_c) (1 - \varepsilon_e) \varepsilon_p \Delta C K_d + (\Delta z A_c) (1 - \varepsilon_e) (1 - \varepsilon_p) \rho_s \Delta q}$$

Here,  $\rho_s$  is solid density .  $q, C$  are related to isotherm equilibrium.

If the fluid has a constant interstitial velocity  $v$ , then the average velocity of solute in the bed,  $u_s$  is

$$u_s = v \times (\text{fraction of solute in mobile phase})$$

So, solute wave velocity can be expressed as

$$u_s = v \times \frac{\text{Amount of solute in mobile phase}}{\text{Total amount of solute in column}}$$

$$u_s = \frac{v}{1 + \left(\frac{1 - \varepsilon_e}{\varepsilon_e}\right) \varepsilon_p K_d + \left(\frac{1 - \varepsilon_e}{\varepsilon_e}\right) (1 - \varepsilon_p) \rho_s \frac{\Delta q}{\Delta C}} \quad (8.7)$$

If isotherm is linear,

$$q = m(T)C \quad \text{or} \quad \frac{\Delta q}{\Delta C} = m \quad (8.8)$$

If isotherm is nonlinear,  $q = AC^n$  (8.9)

$$\lim_{C \rightarrow \infty} \frac{\Delta q}{\Delta C} = \frac{\partial q}{\partial C} = \frac{m(T)}{n} C^{\frac{1}{n}-1} \quad (8.10)$$

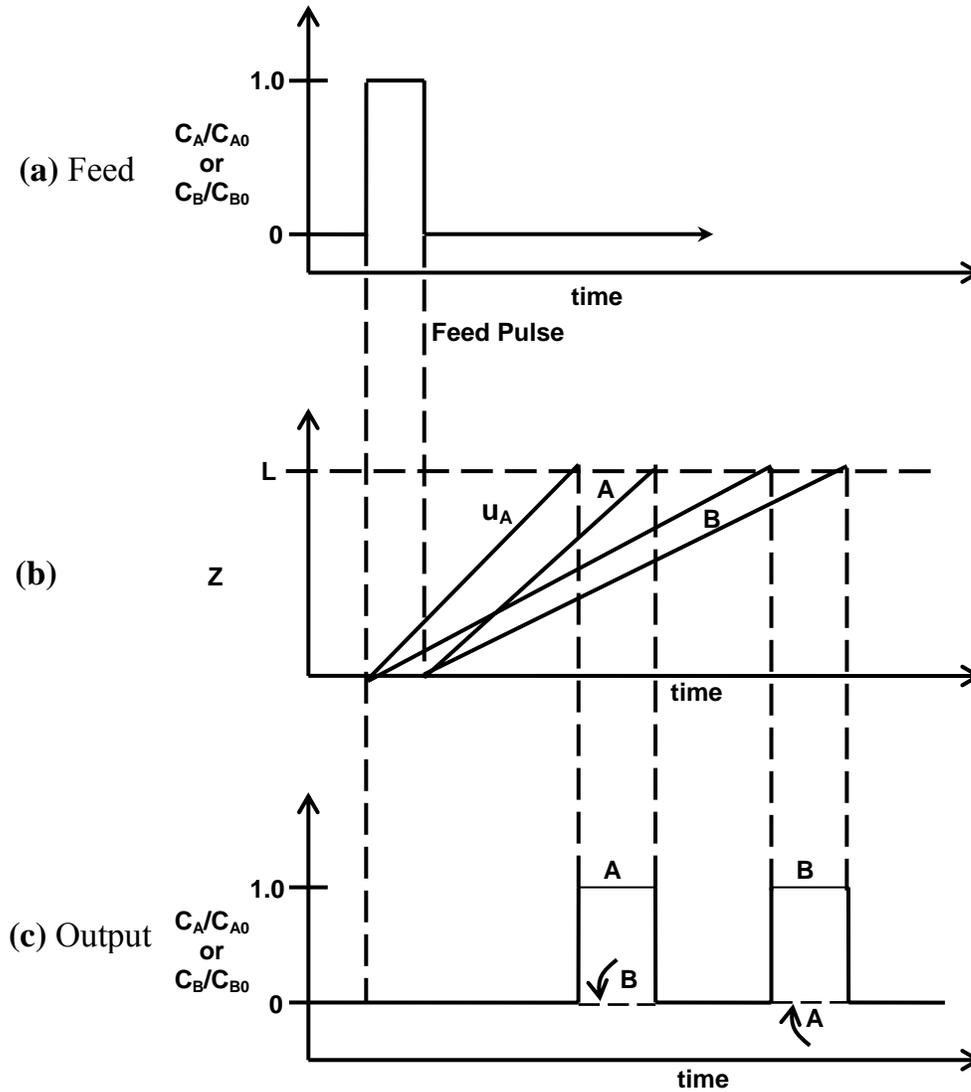
**Case 1:** For very large molecule,  $K_d = m(T) = 0$

**Case 2:** For small molecule,  $K_d = 1.0$ , thus smaller molecules move slower.

**Case 3:** In case of strong adsorption, molecules move slower as velocity decreases. In case of linear adsorption, solute velocity does not depend on solute concentration. In case of non-linear adsorption, solute velocity depends on solute concentration. But at low concentration linear adsorption is valid.

$$z = u_s t \quad (8.11)$$

So, if we plot  $z$  vs  $t$ , we get a linear with slope of  $u_s$ . By looking into  $z$  versus time curve one can interpret the separation efficiency (Fig. 8.4).



**Fig. 8.4:** Solute movement at various points in the column. (a). Feed pulse; (b). Solute movement in column; (c). Product concentration in the outlet

Fig. 8.4 (a) shows the feed pulse containing two components A and B, to be separated. Thus, the non-dimensional concentration in the feed looks like a rectangular pulse over a short duration, as shown in Fig. 8.4 (a). Now, the physico-chemical and adsorption parameters for the two solutes are different. Therefore, the velocities of these two solutes will be different. Thus, they will cover the column length (L) in different periods of time.

This is shown in Fig. 8.4 (b). If we now convert to concentration-time figure (as shown in Fig. 8.4c), we can observe that a product is obtained with component A at a time  $t_1$  that is earlier than component B. Thus, one can fractionate the products.

### Application of solute movement theory to chromatography:

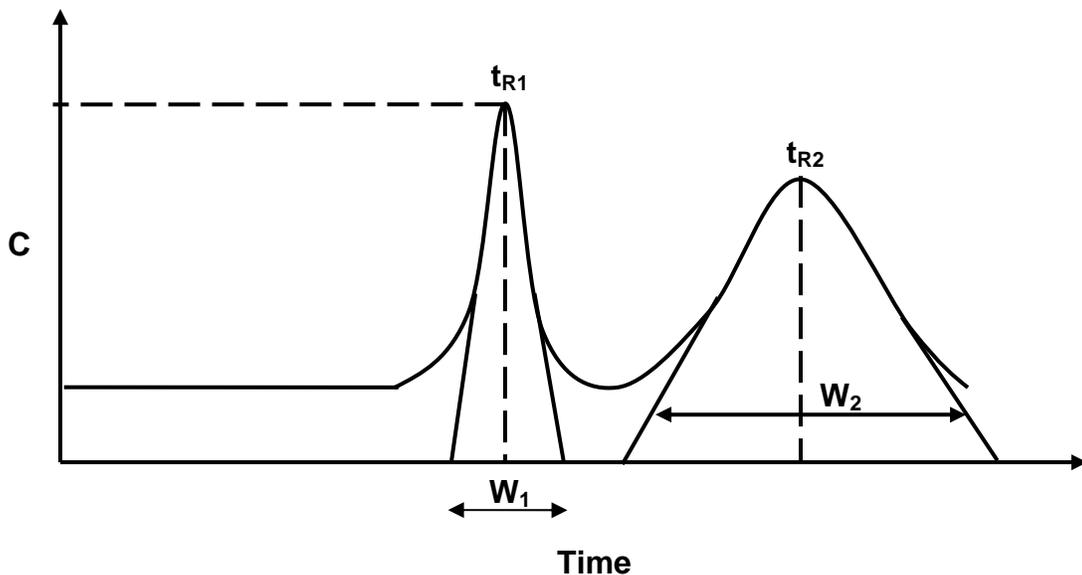
For a small feed pulse, the peak maximum exits at a retention time,  $t_{R,i}$

$$t_R = \frac{L}{u_s}$$

For fairly wide pulse the retention time is corrected.

$$t_R = \frac{L}{u_s} + \frac{t_F}{2}$$

Here,  $t_F$  = period of feed pulse



Widths,  $W_1 = 4\sigma_1$ ;  $W_2 = 4\sigma_2$

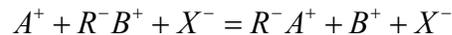
$\sigma_1, \sigma_2$  = standard deviations of peaks

## Ion Exchange

Ion exchange means exchange of ions from a medium. It has typical application in water softening by exchange of alkaline metal ions like  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  by  $\text{Na}^+$ . Other common applications are sugar processing, hydrometallurgical application, protein fractionation, biological separation, etc.

### **Fundamentals:**

Ion from a solution is removed when it is passed through a bed of exchangeable ions, called resins.



In this reaction,  $R^-$  is fixed negative charge on the resin.  $A^+$  and  $B^+$  are called counterions and  $X^-$  is called coion in resin phase. An example is addition of  $\text{KCl}$  to a resin having  $\text{Na}^+$  ions. Here,  $\text{K}^+$  and  $\text{Na}^+$  are counterions and  $\text{Cl}^-$  is the coion. Above example is for a monovalent cation exchange process. Anion exchange is similar, except anions are being exchanged. Ion concentration in the liquid and resin are expressed in terms of equiv/ $\text{m}^3$ , based on total column volume. In the solution, total ion concentration is

$$C_T = C_A + C_B \quad (8.12)$$

In the resin phase, total ion concentration is

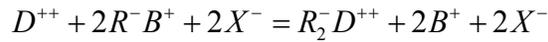
$$C_{RT} = C_{RA} + C_{RB} \quad (8.13)$$

Eqs. (8.12) and (8.13) are known as the electroneutrality conditions. These hold in both the phases. Thus, in the resin phase as counterion  $B^+$  leaves, equivalent  $A^+$  from the solution should join to maintain electroneutrality. After exchanging the ions, the resin is in the form of  $R^-A^+$  from  $R^-B^+$ . To regenerate the resin, a concentrated solution of  $B^+X^-$

has to be added in the column. Thus, a complete ion exchange cycle consists of three steps,

- (i) Loading  $\rightarrow A^+$  goes to resin from solution
- (ii) Regeneration  $\rightarrow A^+$  is removed from resin
- (iii) Washing  $\rightarrow$  washing of excess  $B^+X^-$  from the column

For a divalent cation with monovalent cation, the reaction becomes



Divalent ion occupies two sites o the resin. Example is removal of  $Ca^{2+}$  from aqueous solution using a resin having  $Na^+$ , as counterion. Electroneutrality conditions in resin and solution phase becomes,

$$C_T = C_B + C_D \quad (8.14)$$

$$C_{RT} = C_{RB} + C_{RD} \quad (8.15)$$

One can define equivalent fractions of ions in both phases as,

in solution phase:

$$x_i = \frac{C_i}{C_T} \quad (8.16)$$

in resin phase:

$$y_i = \frac{C_{Ri}}{C_{RT}} \quad (8.17)$$

It may be noted that,

$$\sum x_i = \sum y_i = 1 \quad (8.18)$$

It is also to be noted that concentration of coions ( $X^-$ ) in resin phase is less than in the solution. This is known as Donnan Exclusion. This occurs due to repulsion of coions, between fixed charges in resin.

### **Ion exchange resin:**

Most popular base for ion exchange resin is polystyrene. Cross linking with divinylbenzene (DVB) is done with resin to make it insoluble. About 2-10% DVB is used. Both (i) macroporous and (ii) gel type resin beads are used.

Macroporous beads have pores inside the beads where ions can go in or get out. Typical external porosity is about 0.40. Gel type resin have various degrees of swelling. These may be polystyrene-sulfuric acid resin with various % of DVB, polyacrylic acid resin, etc.

Acidic resins have negative fixed charges and can exchange cations. Basic resins have positive fixed charges and can exchange anions. Exchangers can also weak or strong. Strong resins are fully ionized and all the fixed groups are available to exchange cations. Strong base resins can degrade at higher pH and temperature.

On the other hand, weak resins are only partially ionized at most pH values. They have lower exchange capacity but they are easier to regenerate. Weak resins require less regenerant than strong resins.

But weak resins swell or contract when ions are exchanged. They can rupture due to improper stress distribution of during expansion/contraction cycle. In weak resin also the ions diffuse slowly. So, mass transfer resistance is very high and time requirement is long.

## Binary ion exchange equilibrium:

Equilibrium equations can be written in terms of ion fractions, using equations (8.16) and (8.17) as

$$K_{AB} = \frac{y_A x_B}{y_B x_A}$$

$$= \frac{y_A (1 - x_A)}{(1 - y_A) x_A} \quad (8.19)$$

$y_A$  can be extracted and can be written in terms of  $x_A$  and  $K_{AB}$  as

$$y_A = \frac{K_{AB} x_A}{1 + (K_{AB} - 1) x_A} \quad (8.20)$$

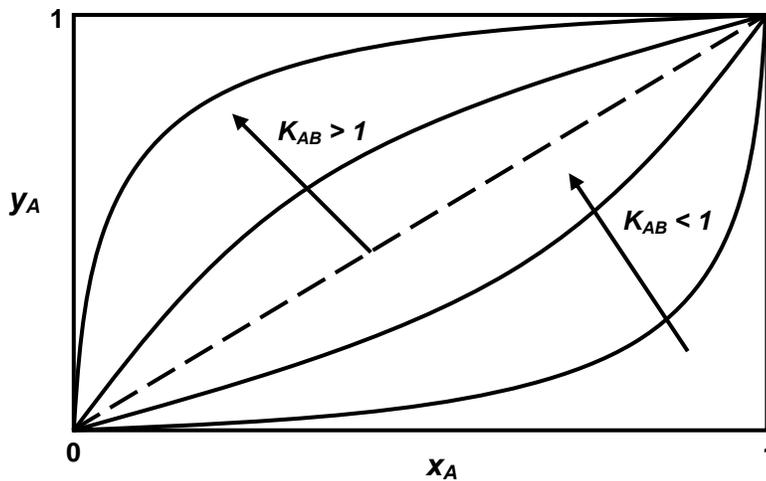
$K_{AB}$  is constant for dilute system. Generally,  $K_{AB}$  values are known.

For monovalent-divalent exchange the corresponding equation is,

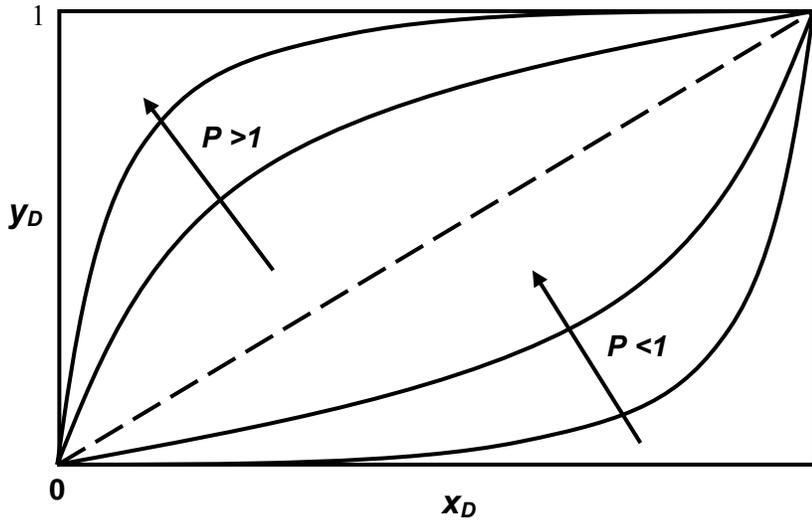
$$\frac{y_D}{(1 - y_D)^2} = \left( K_{DB} \frac{C_{RT}}{C_T} \right) \frac{x_D}{(1 - x_D)^2}$$

Or

$$\frac{y_B^2}{1 - y_B} = \frac{1}{\left( K_{DB} \frac{C_{RT}}{C_T} \right)} \frac{x_B^2}{(1 - x_B)} \quad (8.21)$$



**Fig. 8.16:** Equilibrium curve for monovalent - monovalent ion exchange



**Fig. 8.17:** Equilibrium curve for monovalent - divalent ion exchange

### Ion movement theory:

Result for any ion velocity is

$$u_{ion} = \frac{V}{1 + \frac{1}{\epsilon_e} \frac{C_{RT}}{C_T} \frac{\Delta y}{\Delta x} K_E} \quad (8.22)$$

Where,  $y, x$  = equivalent ion fraction;  $K_E$  = a factor to include effects of Donnan exclusion and electroneutrality.

If the ion is excluded  $K_E=0$ , else  $K_E=1$ .

For counterions  $A^+, B^+, D^{++}$   $K_E=1$

For coions  $X^-$ ,  $K_E=0$

For  $K_{AB} > 1$  (monovalent exchange) or  $K_{DB} \frac{C_{RT}}{C_T} > 1$  (monovalent-divalent exchange),

shock wave results if a solution with low fraction of species A (or D) is displaced by a concentrated solution of A (or D). Thus,

$$u_{sh} = \frac{V}{1 + \frac{1}{\epsilon_e} \frac{C_{RT}}{C_T} K_E \left( \frac{y_a - y_b}{x_a - x_b} \right)} \quad (8.23)$$

'a' refers to after and 'b' refers to before shock wave. In both cases, resin and liquid are in equilibrium.

Diffused wave results if solution of high fraction A (or D) is displaced by a solution of low fraction A (or D). In this case, velocity is

$$u_s = \frac{V}{1 + \frac{1}{\epsilon_e} \frac{C_{RT}}{C_T} K_E \left( \frac{dy}{dx} \right)} \quad (8.24)$$

## Solved Problems

### 1. Ion Exchange:

#### Analysis of water softening cycle:

We wish to soften water having 2 meq/L  $\text{Ca}^{2+}$  and 9 meq/L  $\text{Na}^+$  with superficial velocity of feed 10 cm/min., 2 m. column is used.  $C_{RT} = 2$  eq/L

(a). Determine feed period:

#### Solution:

$$C_T = 2 + 9 = 11 \text{ meq/L}$$

$$x_{F,Ca} = 2/11 = 0.1818; \quad x_{F,Na} = 1 - x_{F,Ca} = 0.8182$$

$$v = \frac{v_{\text{super}}}{\varepsilon_e} = \frac{10}{0.4} = 25 \text{ cm/min}$$

$$K_{CaNa} = 1.3$$

$$K_{CaNa} \frac{C_{RT}}{C_T} = 1.3 \times \frac{2}{11 \times 10^{-3}} = 236.4 \gg 1.0$$

So, shock wave.

After the shock wave,

$$x_{a,Ca} = x_{F,Ca} = 0.1818$$

$y_{a,Ca}$  is calculated from equilibrium relation,

$$\begin{aligned} \frac{y_{a,Ca}}{(1-y_{a,Ca})^2} &= \left( K_{CaNa} \frac{C_{RT}}{C_T} \right) \frac{x_{a,Ca}}{(1-x_{a,Ca})^2} \\ &= 236.4 \frac{0.1818}{(1-0.1818)^2} = 64.2 \end{aligned}$$

$$y_{a,Ca} = 0.8827$$

Resin contains higher concentration of  $Ca^{2+}$  after the shock wave.

$$u_{sh} = \frac{V}{1 + \frac{1}{\varepsilon_e} \frac{C_{RT}}{C_T} K_E \left( \frac{y_{a,Ca} - y_{b,Ca}}{x_{a,Ca} - x_{b,Ca}} \right)}$$

$$y_{b,Ca} = x_{b,Ca} = 0$$

$$\begin{aligned} u_{sh} &= \frac{25}{1 + \frac{1}{0.4} \left( \frac{2}{1.1 \times 10^{-2}} \right) (1) \left( \frac{0.8827}{0.1818} \right)} \\ &= 0.0113 \text{ cm/min} \end{aligned}$$

$K_E = 1.0$ , Since ions are not excluded.

Low velocity of shock wave is due to the resin has a high capacity compared to liquid concentration and it is selective for  $\text{Ca}^{2+}$ .

$$t_F = \frac{200 \text{ cm}}{0.113 \text{ cm/min}} = 294.4 \text{ hrs.}$$

**(b).** Bed is regenerated by 25% (wt.) NaCl at a superficial velocity 0.5 cm/min.

Find time required to regenerate the bed ?

*Solution:*

$$v = \frac{v_{\text{super}}}{\epsilon_e} = \frac{0.5}{0.4} = 1.25 \text{ cm/min}$$

At  $25^\circ\text{C}$ ,  $\rho_L = 1.194 \text{ g/cc}$

$$\text{So, } 25\% \text{ NaCl} = \frac{0.25 \times 1.194 \times 1000}{58.415} = 5.311 \frac{\text{mol}}{\text{liter}} = 5.311 \text{ equiv.}$$

$$\text{So, } C_T = 5.311 \text{ equiv/liter}$$

$x_{\text{Ca,Reg.}} = 0$  as regeneration liquid is totally NaCl.

$$K_{\text{CaNa}} \frac{C_{RT}}{C_T} = 1.3 \times \frac{2}{5.311} = 0.49 < 1.0$$

So, we get a shock wave when material concentrated with in  $\text{Ca}^{2+}$  is removed with regenerate.

$t =$  time required of ion wave to go to the column exit

$$= \frac{200 \text{ cm}}{1.25 \text{ cm/min}} = 160 \text{ min.}$$

When ion wave passes,  $y_{a,Ca} = y_{b,Ca} = 0.8827$

$x_{Ca}$  changes since  $C_T$  changes.

$$\frac{x_{a,Ca}}{(1-x_{a,Ca})^2} = \frac{y_{a,Ca}}{(1-y_{a,Ca})^2} \frac{1}{K_{CaNa} \frac{C_{RT}}{C_T}}$$

$$= \frac{0.8827}{(0.1173)^2} \frac{1}{0.49} = 130.92$$

$$x_{a,Ca} = 0.9167$$

Before ion wave, fluid exits with  $C_T = 1.1 \times 10^{-2}$  and  $x_{b,Ca} = 0.1818$ . Immediately after wave, fluid exits with  $C_T = 5.311$  and  $x_{a,Ca} = 0.9167$

This continues until shock wave where  $x_{Ca}$  reaches to zero ( $x_{Ca} \rightarrow 0$ ).

Before shock wave,  $y_{b,Ca} = 0.8827$  &  $x_{b,Ca} = 0.9167$

After shock wave,  $y_{a,Ca} = x_{a,Ca} = 0$

$$u_{sh} = \frac{V}{1 + \frac{1}{\epsilon_e} \frac{C_{RT}}{C_T} K_E \left( \frac{y_{a,Ca} - y_{b,Ca}}{x_{a,Ca} - x_{b,Ca}} \right)}$$

$$= \frac{1.25}{1 + \left( \frac{1}{0.4} \right) \left( \frac{2}{5.311} \right) \left[ \frac{0 - 0.8827}{0 - 0.9167} \right]}$$

$$= 0.656 \text{ cm/min}$$

$$t = \text{time required} = \frac{200}{0.656} = 305 \text{ min}$$

This time is 145 minutes after the total ion wave exits.

Thus, solution with  $C_T = 5.311$  and  $x_{Ca} = 0.9167$  exits for 145 (305-160) mins.

**(c). Washing:**

Wash step has,  $v = 1.25$  cm/min

Since, salt in void volume is excluded,

$$K_E = 0; \quad u_{wash} = v = 1.25$$

$$t = \frac{200}{1.25} = 160 \text{ mins}$$

**2. Chromatographic Separation:**

In a chromatographic column, an organic acid is passed. The properties of various parameters of the solid matrix are listed as:

$$\rho_s = 1.5 \text{ g/cc}; \quad \kappa_d = 1.0; \quad \varepsilon_e = 0.4; \quad \varepsilon_p = 0.6. \text{ Adsorption isotherm is } q = 2.5C^{0.4},$$

where,  $C$  is in molar concentration and  $q$  has unit *gmol/kg dry bed*.

- a. An initially clean column ( $C=0$ ,  $q=0$ ) is fed with organic acid solution containing 0.2 (M) concentration. Superficial velocity is 5 cm/min, and column length is 2 m. Find the residence time of shock wave?
- b. After the column is saturated with  $C=0.2$  (M) solution, organic acid is removed with an aqueous solution at a superficial velocity 20 cm/min. Predict the shape and time distribution of the solute wave at the outlet of column?

**Solution:**

- (i) Interstitial velocity:

$$v = \frac{v_{\text{super}}}{\varepsilon_e} = \frac{5}{0.4} = 11.52 \text{ cm / min}$$

$$q_2 = 2.5C^{0.4} = 2.5 \times (0.2)^{0.4} = 1.313 \text{ gmol / kg}$$

$$\begin{aligned} u_{sh} &= \frac{v}{1 + \frac{1-\varepsilon_e}{\varepsilon_e} \varepsilon_p \kappa_d + \left(\frac{1-\varepsilon_e}{\varepsilon_e}\right) (1-\varepsilon_p) \rho_s \left(\frac{q_2 - q_1}{C_2 - C_1}\right)} \\ &= \frac{11.52}{1 + \left(\frac{1-0.4}{0.4}\right) \times 0.6 \times 1 + \left(\frac{1-0.4}{0.4}\right) (1-0.6) \times 1.5 \times \left(\frac{1.313-0}{0.2-0}\right)} \\ &= \frac{11.52}{7.81} = 1.475 \text{ cm / min} \end{aligned}$$

$$t_{\text{out}} = t_{\text{res}} = \frac{L}{u_{sh}} = \frac{200}{1.475} = 136 \text{ min}$$

c. Diffused wave:

$$v = \text{interstitial velocity} = \frac{v_{\text{super}}}{\varepsilon_e} = \frac{20}{0.4} = 50 \frac{\text{cm}}{\text{min}}$$

$$u_{sh} = \frac{v}{1 + \left(\frac{1-\varepsilon_e}{\varepsilon_e}\right) \varepsilon_p \kappa_d + \left(\frac{1-\varepsilon_e}{\varepsilon_e}\right) (1-\varepsilon_p) \rho_s \frac{dq}{dC}}$$

$$q = 2.5C^{0.4}$$

$$\frac{dq}{dC} = C^{-0.6}$$

$$\begin{aligned} u_{sh} &= \frac{50}{1 + \left(\frac{0.6}{0.4}\right) \times 0.6 \times 1 + \left(\frac{0.6}{0.4}\right) \times (1-0.6) \times 1.5 \times C^{-0.6}} \\ &= \frac{50}{1.9 + 0.9C^{-0.6}} \end{aligned}$$

<i>C</i>	<i>u<sub>s</sub> (cm/min)</i>	<i>t = L/u<sub>s</sub> = 200/u<sub>s</sub></i>
0.2	11.73	17 min
0.1	9.12	22 min
0.05	6.82	29 min

### References:

1. P. C. Wankat, Rate Controlled Separations, Springer, New Delhi, 2005.