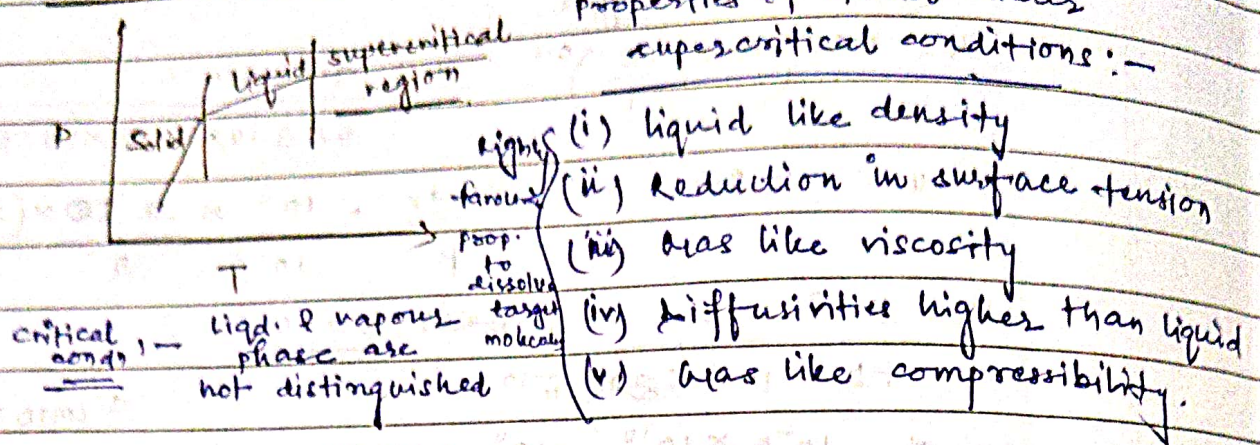


Supercritical fluid (SCF) extraction :-



Common super critical fluids :-

CO_2 , Ethylene, Propylene, ethanol.

Substance	T_c (K)	P_c (atm)	Density (g/cc)
CO_2	304	73	0.47
Ethane	305	48	0.2
Ethanol	516	63	0.3
Propane	370	42	0.22

CO_2 is common SCF :-

- (i) low P_c and low T_c
- (ii) Non Toxic
- (iii) Non-flammable
- (iv) Available in high purity
- (v) low cost

Disadv. :- Extraction of polar compounds is difficult in case of.

Co-solvents / modifiers is used.

CO_2 is mixed with 1% - 10% methanol.

Disadv. (i) $T_c > 374^\circ\text{C}$

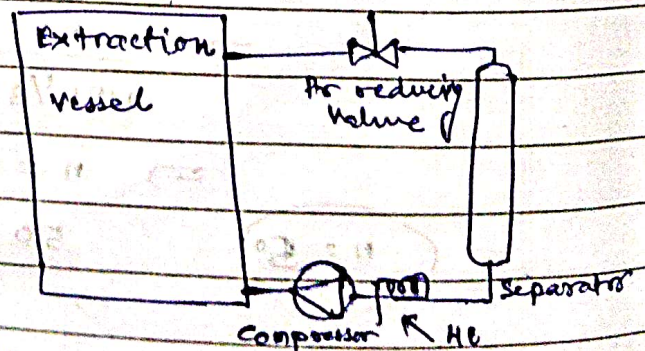
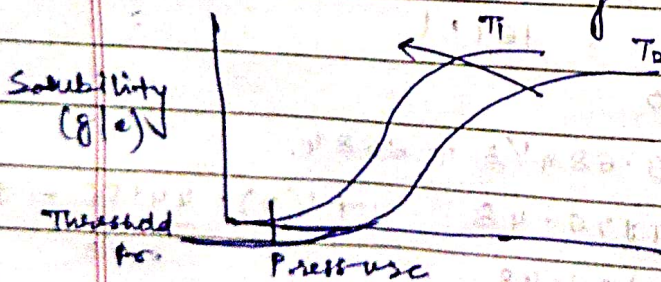
$P_c > 221 \text{ bar}$

(ii) Under SC condition water becomes corrosive



Working principle :-

based on solute solubility in SCF



→ removal of fat from - foods

→ Vit E extraction from natural sources

→ removal of alcohol from wine / beer

Electrophoretic Separation Process :-

colloidal macro molecules (nm) Charged properties of solutes / proteins / micelles / Pectin
Applications in pharmaceutical / ~~micelles~~ / ~~pectin~~ + bio medical

Isoelectric pH :

Compounds	PI (25°C)	Myoglobin - 7.33
Aspartic Acid	2.77	Cytochrome C → 9.28
Lysine	9.74	If $KR_p < 0.4 \Rightarrow u = \frac{2}{3} \frac{e\zeta}{\mu}$
Ovalbumin	4.7	$> 0.4 \Rightarrow u = \frac{e\zeta}{\mu}$
BSA	4.95	$(u = \frac{v_e \mu}{E})$

Complications of electrophoresis

Typical mobility :-

$10^{-8} \frac{m^2}{V.s} \rightarrow$ ions $10^{-5} \rightarrow$ m.s \rightarrow Proteins

Joule heating ($12RT$)

Methods to avoid convection

↑↑ Proteins may be denatured
mixing may lead to natural convection

- Adopt an efficient cooling method
- To maintain $4^\circ C$ in the cell.
- Height of the electrophoretic cell is kept small

(B) Electroosmosis should be avoided (iv) Porous gel is introduced

Coating of wall surface by materials like : methyl cellulose

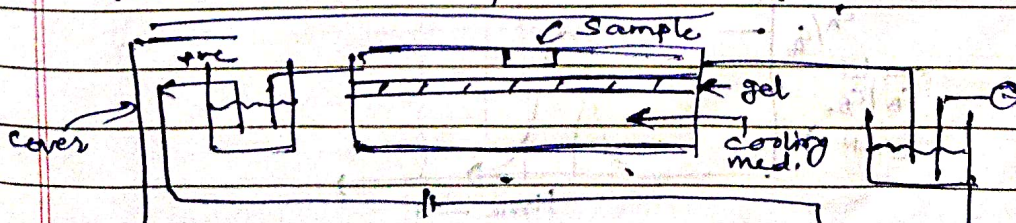
Gels - electrophoresis

- gel \rightarrow
- 1) Inert (should not react with species)
 - 2) No residual charge on the gel material.
 - 3) Gel pore size much higher than size of macromolecule.

⊕ Typical gel material - Polyacrylamide gel assisted electrophoresis

Advantages :- (i) Excellent anti-convective
(ii) can polymerise on glass surface

Schematic of electrophoretic cell :-



7/04/20

Novel Separation Processes

Chromatographic Separation Processes :-

→ Principle : Based on residence time of a solute in the column.
Residence time is different for different solutes due to different extents of transport.

Features :-

- * High pressure pump is needed to inject liq. sample
- * A pulse of sample is injected.
- * Column is enclosed to maintain temperature.
- * Detector (UV/RI) detects the solutes at elutant
- * Conc is measured by absorbance value.

Typ. Op. Condition :-

Feed conc : 1 mg/l

Col. dimension : $10 \text{ cm} \times 4.6 \text{ mm}$

Packing : Weak cation exchange beads

Pore size of solid matrix $\sim 300 \text{ \AA}$

Typical flow rate : 1.5 ml/min.

Volume of injection : 10 \mu l

Gas Sys. : - carrier gas is He

Adsorbent is used \rightarrow Alumina, zeolite

Gas-liq. Chromatograph (GLC)

1) Inert, porous solid beads are coated with viscous high boiling liq.

2) liq. 1) should be selected so that it does not create contamination.

Stationary phase causes desorption

3) Evaporation of the liq. should be very slow

liq. liq. chromatography (LLC) :-

* A stationary liq. phase is coated on the inert porous solid beads

* Separation is based on extraction

High pressure liquid chromatography (HPLC) :-

* Solids silica

* Stationary liq. HCs (C8 or C18 compound)

* $\Delta P \sim 1000 \text{ psi}$

Size exclusion chromatography (SEC)

No Adsorpⁿ / Diffⁿ, Sepⁿ is purely by size exclusion, larger size solutes are separated from smaller ones.

Solid matrix :- ~~liel~~, Sephadex, Agarose

Solute movement through the Col. :-

$$\epsilon_e = \frac{\text{Avg. Inter-particle porosity} = \text{Vol. b/w particles}}{\text{Total Vol. of packed bed}}$$

$$\epsilon_p = \frac{\text{Avg. Intraparticle porosity} = \text{Vol. inside particles}}{\text{Total vol. of all particles}}$$

$$\text{Total bed porosity} = \epsilon_T = \text{Sum of voids within \& b/w particles} = \epsilon_e + (1 - \epsilon_e)\epsilon_p$$

$$\text{Bulk density: } \rho_b = (1 - \epsilon_e)\rho_p + \epsilon_e\rho_f$$

$\rho_p \rightarrow$ particle density

$\rho_f \rightarrow$ fluid density

$$\rho_p = (1 - \epsilon_p)\rho_s + \epsilon_p\rho_f \quad \rho_s \rightarrow \text{crystalline density of solid after crushing}$$

Pores are not uniform in size \rightarrow size distribution

Larger particles are sterically hindered

$$K_d = \frac{\text{fraction of vol. of pores that a molecule can penetrate}}{\text{}} = \frac{V_e - V_o}{V_i}$$

$V_e \rightarrow$ elution vol. $V_o \rightarrow$ ext. void vol. b/w particles

$V_i \rightarrow$ internal void vol. within

for small particles \rightarrow \bullet

$$V_e = V_i + V_o \quad K_d = 1.0$$

Physical processes involved in solute transport :-

- (i) Solute diffuses through external liq. film to particles
- (ii) Solute reaching the surf can be adsorbed on ext. surf or can diffuse
- (iii) through liq. filled in pores. There may be surf. diffusion as well.
- (iv) Solute finds an active site & gets adsorbed.
- (v) Solute desorbs.

$$\text{vel. of solute} = f(\epsilon_e, \epsilon_p, K_d, \text{sorption equal})$$

$$\begin{array}{l} \text{change in conc } \Delta c \\ \text{change in solid phase } \Delta q \end{array} \left\{ \begin{array}{l} \text{Ext. void vol.} = \epsilon_e A_c \Delta z \quad \text{Area of Cs} \\ \text{Internal void vol.} = (1 - \epsilon_e) \epsilon_p A_c \Delta z \\ \text{Packed bed} \end{array} \right.$$

- Solute in bed can be (i) in the mobile fluid in ext. void vol. (ii) in stagnant liq. inside particle (iii) Adsorbed state on the particle