



CHAPTER II

BACKGROUND THEORY

2.1 Pervaporation

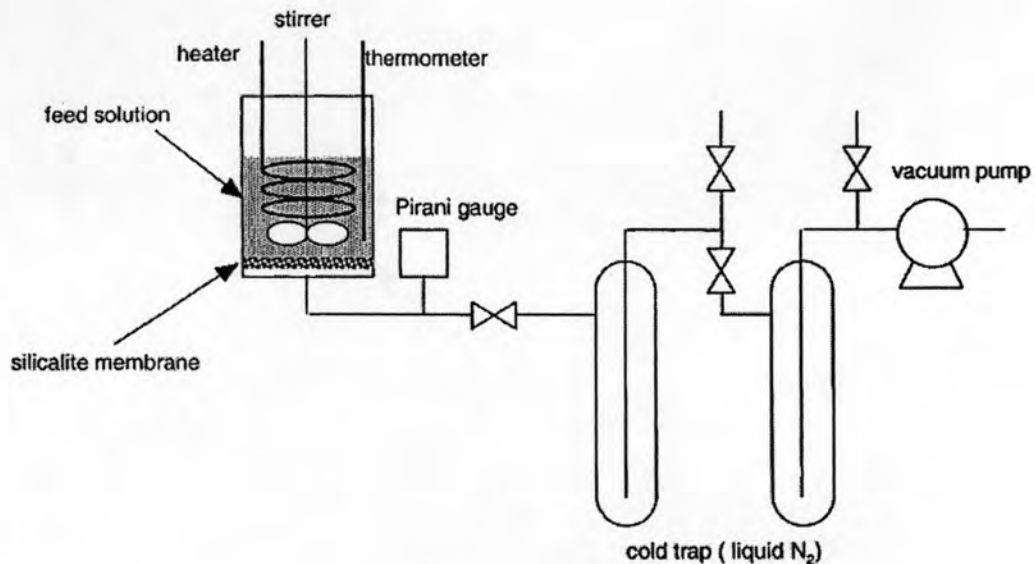


Figure 2.1 Pervaporation process (Nomura et al, 2002)

Pervaporation is a membrane separation process involving the partial vaporization of a liquid mixture through a dense membrane whose downstream side is usually kept under vacuum. A liquid feed mixture is in contact with one side of the membrane; the partial vapor pressure is at saturation. The gradient in partial pressure between the feed and the permeate side of the membrane is maintained by a reduction of the permeate side partial vapor pressure. The permeate leaves the membrane as a vapor and is usually condensed, and removed as a liquid. The heat necessary for the evaporation of the permeate has to be transported through the membrane, and this transport of energy is coupled to the transport of matter. The evaporation enthalpy is taken from the sensible heat of the liquid feed mixture, which leads to a reduction in feed side temperature.

According to the solution-diffusion model, transport and separation in pervaporation process occurs through 3 consecutive steps:

1. Sorption-components with a higher affinity to the membrane polymeric material are sorbed preferentially into the membrane from the feed solution.
2. Diffusion-component is transported through the membrane. Selectivity during diffusion step results from the differences in the permeation rates of the transported components.
3. Desorption-components are desorbed on the permeate side into the vacuum or sweeping gas. This is very fast and non-selective step

2.1.1 Estimate pervaporation system

- Flux

The flux of a component i in pervaporation process, J_i , can be described by the following general transport equation:

$$J_i = -L_i \nabla \mu_i \quad (1)$$

Where, L_i is phenomenological transport coefficient.
 μ_i is chemical potential of a component i .

Assuming that transport in the membrane system occurs only in the direction perpendicular to the membrane surface, equation (1) can be rearranged into :

$$J_i = -L_i \frac{d\mu_i}{dx} \quad (2)$$

Substituting:

$$d\mu_i = \frac{RT}{a_i} da_i \quad (3)$$

Where, a_i is activity of a component i .

Eq. (2) can be written in the form:

$$J_i = -\frac{L_i RT}{a_i^m} \frac{da_i}{dx} \quad (4)$$

Where, a_i^m denotes an activity of component i in the membrane phase.

The estimation of L_i and a_i^m independently from each other would lead to the inaccurate result, so the term $\frac{L_i RT}{a_i^m}$ is summarized and described as a permeability of the membrane in the pervaporation process.

$$J_i = -P_i' \frac{da_i}{dx} \quad (5)$$

Integration of Eq.(5) over the membrane thickness, leads to the following expression for the permeate pervaporation flux:

$$J_i = -\frac{P_i'}{l} (a_{i,p} - a_{i,F}) \quad (6)$$

In pervaporation, the activity of components is very low on the permeate side ($a_{i,p} \approx 0$), so Eq.(6) can be rewritten as follows:

$$J_i = \frac{P_i'}{l} a_{i,F} \quad (7)$$

By including the membrane thickness into the permeability parameter, the final form of the transport equation for pervaporation flux can be presented:

$$J_i = P a_{i,F} \quad (8)$$

- Selectivity

Selectivity is indicated in different ways. Most commonly found in literature is the co-called α -value. This is calculated as the ratio of the better permeable component (organic) in the permeate divided by the respective ratio in the feed.

$$\alpha = \frac{(C_{water} / C_{org})_{Permeate}}{(C_{water} / C_{org})_{Feed}} \quad (9)$$

Although the α -value looks fairly simple, it is not very informative. For most dehydration membranes, the composition of the permeate is constant over a very broad range of feed compositions. As a consequence, the α -value is not constant but varies considerably, depending to which feed composition it is related (Kujawiki et al, 2007).

Secondly membrane selectivity is characterized by so-called β -value or enrichment factor. This is simply the concentration of water in the permeate divided by that in the feed.

$$\beta = C_{wp} / C_{wf} \quad (10)$$

or

$$\alpha = \beta C_{of} / C_{op} \quad (11)$$

Again this numerical value is informative for only one feed concentration and not very useful if different membranes have to be compared (Nunes and Peinemann, 2001).

2.1.2 Factors affecting membrane performance

There are several factors affecting the membrane performance, which have to be kept in mind before attempting to work on pervaporation. They are :

- Feed composition and concentration

A change in the feed composition directly affects the sorption phenomena (degree of swelling) at the liquid membrane interface, as proved by the solution-diffusion principle. The diffusion of the components in the membrane is dependant on the concentration of the components (or the solubility of the components). The permeation characteristics are hence dependant on the feed concentration as well. An example this phenomenon is shown in Figure 2.2.

- Feed and permeate pressure

The main driving force in pervaporation is the activity gradient of the components in the membrane. The permeate pressure is directly related to the activity of the components at the downstream side of the membrane and strongly influences the pervaporation characteristics. The maximum gradient can be obtained for zero permeate pressure and thus for higher permeate pressures, the feed pressure influences the pervaporation characteristics (Figure 2.3).

- Temperature

The temperature of the feed increases; the permeation rate generally follows an Arrhenius-type law $J = J_0 \exp(E_p/RT)$. The selectivity is strongly dependant on temperature; in most cases a small decrease in selectivity is observed with increasing temperature (Figure 2.4).

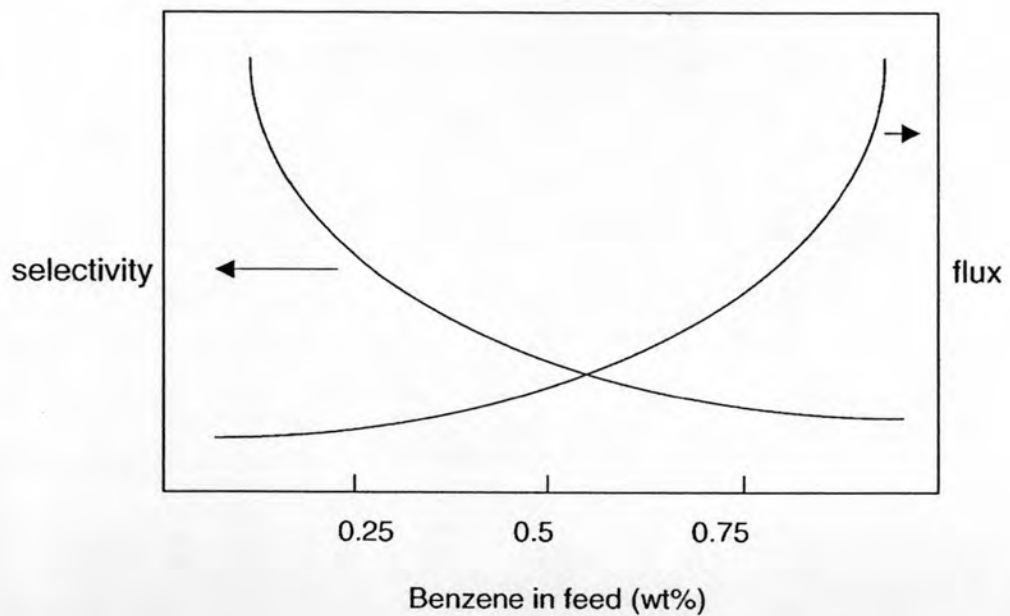


Figure 2.2 Effect of feed concentration on organic–organic pervaporation separation of benzene–cyclohexane mixture (Smitha et al, 2004).

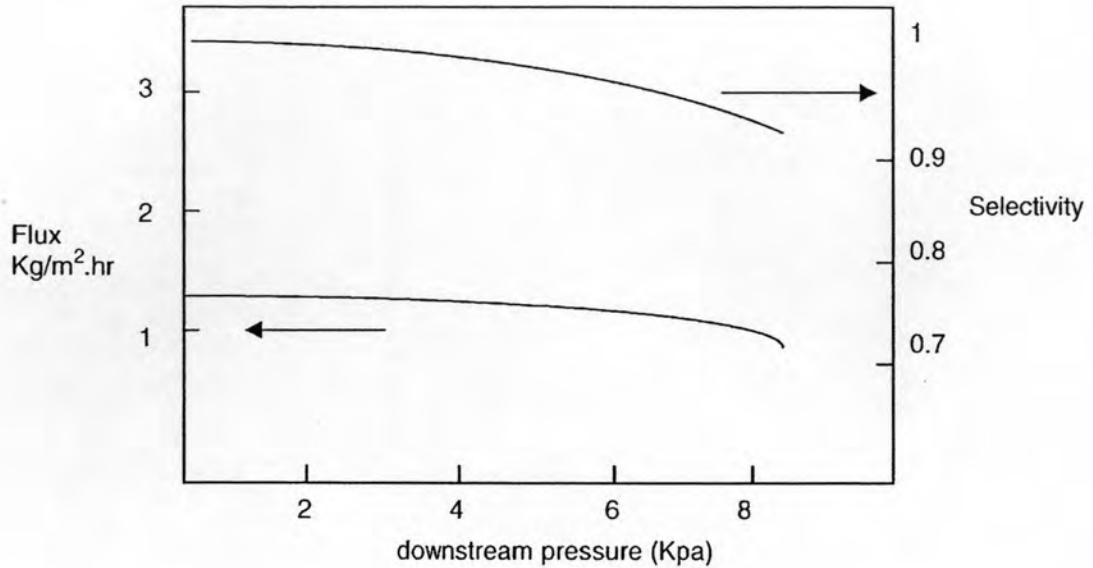


Figure 2.3 Effect of pressure on pervaporation (for ethanol/benzene mixture)
(Smitha et al, 2004).

- Concentration polarization (CP)

When a binary liquid mixture is permeating through a semi-permeable membrane, with different individual component permeation rates, an increase of the less permeable component in the boundary layer near the membrane surface occurs. This concentration gradient between the more concentrated boundary solution and the less concentrated bulk is termed as concentration polarization. Researchers have dealt with problems related to concentration polarization in pervaporation of organic–water mixtures and have generally concluded that CP does not play a very significant role. However, the role of CP in separation of organic mixtures is yet to be explored (Smitha et al, 2004).

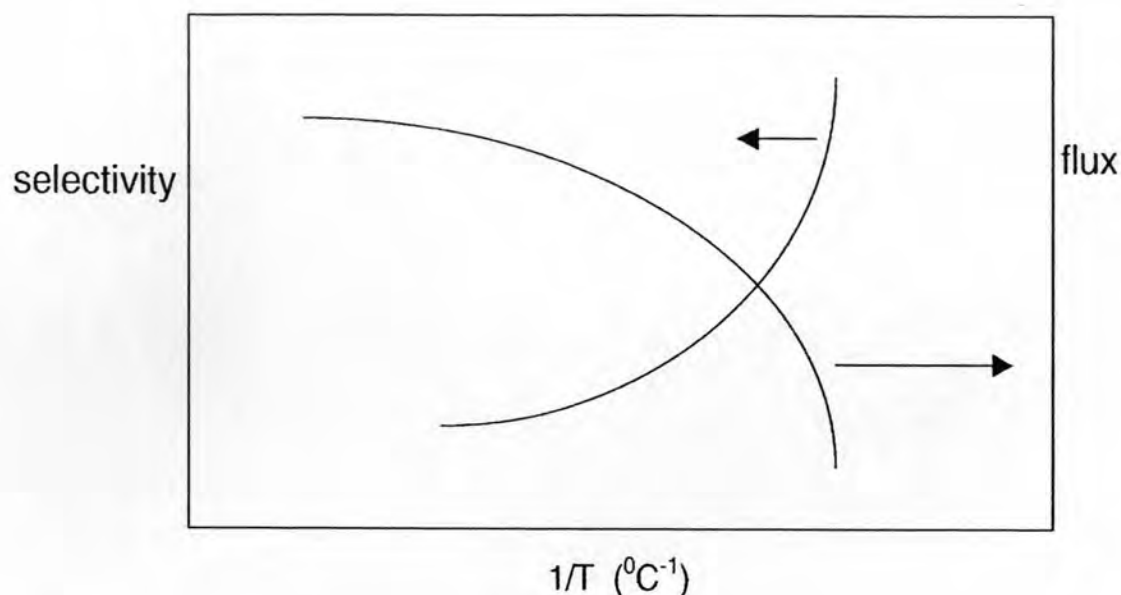


Figure 2.4 General trend of flux and selectivity with varying temperature for benzene/cyclohexane (Smitha et al, 2004).

2.2 Type of membrane for pervaporation

There are two different types of pervaporation membrane based on polymeric material:

2.2.1 Hydrophilic membrane, with a preferential permeation for water, utilized mainly for the removal of water from organic solvents and solvent mixtures, with an emphasis on azeotropic mixtures. Membrane for the removal of small alcohol molecules like methanol and/or ethanol are of hydrophilic nature as well.

2.2.2 Hydrophobic membrane with a preferential permeation for non-polar compounds, utilized for the removal of volatile organic component from aqueous and gas streams.

In both applications, a composite membrane structure is preferred, allowing for very thin defect free separation layers, but with sufficient chemical, mechanical, and thermal stability. Due to the composite structure, flat sheet configurations are preferred, too. The substructure of both types of flat sheet pervaporation membrane is very similar: A porous support membrane with an asymmetric pore structure is laid onto a carrier layer of a woven or non-woven textile fabric and a basic ultrafiltration membrane is formed. On the free side of this asymmetric porous substructure, the

pores have diameters in the order of 20 to 50 nanometers which widen up to the fabric side to the micrometer range. Polyester, polypropylene, polyphenylene sulfide, polytetrafluor ethylene, and similar fibers are used for the textile carrier layer. Structural polymers with high resistance against chemical attack and good thermal and mechanical properties like polyacrylonitrile, polyetherimide, polysulfone, polyethersulfone, and polyvinylidene fluoride form the porous support. All these structural polymers have already a certain intrinsic separation characteristic, they generally have a high permeability for polar substances like water.

On this substructure a thin dense layer (in the range of 0.5 to 10 micrometers thick) is coated which has a very good separation capability. Different coating techniques are in use, most commonly a solution of the respective polymer in an appropriate solvent is spread onto the porous substructure. The solvent is evaporated, followed by further treatment to effect cross-linking of the polymer.

The dense defect-free separating layer of hydrophilic membrane is made from different polymers which have a high affinity towards water. These polymers contain ions, oxygen functions like hydroxyl-, ester-, ether-, or carboxylic moieties, or nitrogen as imino- or imido- groups. They must be cross-linked in order to render them insoluble after the coating process. Preferred hydrophilic polymers are polyvinylalcohol (PVA), polyimides, natural polymers like chitosan blended with other polymers, or cellulose acetate (CA), or alginates, which are cross-linked by various chemical reactions. Other techniques are the deposition of thin layers from a vapour by means of cold plasmas where at least one of the gaseous components contains the above mentioned groups.

Hydrophobic membranes have the same structure as hydrophilic ones. The dense separating layer is formed by cross-linked silicones, mostly polydimethyl siloxane (PDMS) or polymethyl octyl siloxane (POMS). The methods to apply the dense layer on the porous substructure are similar to those used for hydrophilic membranes (Nunes and Peinemann, 2001).