This chapter deals with membrane technology in details with pervaporation and gas separation membranes. A thorough literature survey is conducted to report the performance of state of the art membranes for dehydration of aqueous-organic mixtures, natural gas and flue gas purification. The criteria for membrane selection, besides scope and objectives of the present study are stated.

I.1. DEFINITION OF MEMBRANE

The membrane can be defined essentially as a barrier, which separates two phases and restricts transport of various chemicals in a selective manner. A membrane can be homogenous or heterogeneous, symmetric or asymmetric in structure, solid or liquid, can carry a positive or negative charge or be neutral or bipolar [1, 2]. Transport through a membrane can be affected by convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient.

I.2. MEMBRANE BASED SEPARATION TECHNOLOGY

A membrane separation system separates an influent stream into two effluent streams known as the permeate and the concentrate. The permeate is the portion of the fluid that has passed through the semi-permeable membrane. Whereas the concentrate stream contains the constituents that have been rejected by the membrane. Table I.1 displays the wide range applications of membrane based separation technology.
Table I.1. Characteristics of membranes used in different membrane separation processes, process driving forces and applications of such processes.

<table>
<thead>
<tr>
<th>Process</th>
<th>Membrane Type and Pore Radius</th>
<th>Membrane Material</th>
<th>Process Diving Force</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Microfiltration</td>
<td>Symmetric microporous, 0.1-10 µm</td>
<td>Cellulose nitrate or acetate, Polyvinylidene difluoride (PVDF), Polyamides, Polysulfone, PTFE, Metal Oxides etc.</td>
<td>Hydrostatic pressure difference at approx. 10-500 kPa</td>
<td>Sterile filtration, Clarification</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>Asymmetric microporous, 1-10 nm</td>
<td>Polysulfone, Polypropylene, Nylon 6, PTFE, PVC, Acrylic Copolymer</td>
<td>Hydrostatic pressure difference at approx. 0.1-1.0 Mpa</td>
<td>Separation of macromolecular solutions</td>
</tr>
<tr>
<td>Reverse Osmosis</td>
<td>Asymmetric skin-type, 0.5-1.5 nm</td>
<td>Polymers, Cellulosic acetate, Aromatic Polyamide</td>
<td>Hydrostatic pressure difference at approx. 2-10 Mpa</td>
<td>Separation of salts and micro solutes from solutions</td>
</tr>
<tr>
<td>Electrodialysis</td>
<td>Cation and anion exchange membrane</td>
<td>Sulfonated cross-linked polystyrene</td>
<td>Electrical potential gradient</td>
<td>Desalting of ionic solutions</td>
</tr>
<tr>
<td>Gas Separation</td>
<td>Asymmetric homogenous polymer</td>
<td>Polymers &amp; copolymers</td>
<td>Hydrostatic pressure and concentration gradients</td>
<td>Separation of gas mixtures</td>
</tr>
<tr>
<td>Pervaporation</td>
<td>Asymmetric homogenous polymer (A non-porous membrane)</td>
<td>Polyacrylonitrile, Polymers</td>
<td>Vapour pressure gradient</td>
<td>Separation of azeotropic mixtures</td>
</tr>
<tr>
<td>Nanofiltration</td>
<td>Thin-film membranes</td>
<td>Cellulosic Acetate and Aromatic polyamide</td>
<td>9.3-15.9 bar</td>
<td>Removal of hardness and desalting</td>
</tr>
</tbody>
</table>

INTRODUCTION
I.3. TYPES OF MEMBRANES

The proper choice of a membrane should be determined by the specific application objective: particulate or dissolved solids removal, hardness reduction or ultra pure water production, removal of specific gases/chemicals etc. The end use may also dictate selection of membranes for industries such as potable water, effluent treatment, desalination or water supply for electronics or pharmaceutical manufacturing. The following section explains the types of membranes commonly used.

I.3.1. Microporous Membranes

The membrane behaves almost like a fibre filter and separates by a sieving mechanism determined by the pore diameter and particle size. Materials such as ceramics, graphite, metal oxides, polymers etc. are used in making such membranes. The pores in the membrane may vary between 1 nm-20 μm.

I.3.2. Homogeneous Membranes

This is a dense film through which a mixture of molecules is transported by pressure, concentration or electrical potential gradient. Using these membranes, chemical species of similar size and diffusivity can be separated efficiently when their concentrations differ significantly.

I.3.3. Asymmetric Membranes

An asymmetric membrane comprises a very thin (0.1-1.0 μm) skin layer on a highly porous (100-200 μm) thick substructure. The thin skin acts as the selective membrane. Its separation characteristics are determined by the nature of membrane material or pore size, and the mass transport rate is determined mainly by the skin thickness. Porous sublayer acts as a support for the thin, fragile skin and has little effect on the separation characteristics.
1.3.4. Electrically Charged Membranes

These are necessarily ion-exchange membranes consisting of highly swollen gels carrying fixed positive or negative charges. These are mainly used in the electrodialysis.

1.3.5. Liquid Membranes

A liquid membrane utilizes a carrier to selectively transport components such as metal ions at relatively high rate across the membrane interface.

1.4. MEMBRANE MODULES

The membranes can he cast as flat sheets, tubes and fine hollow fibers (see Figure I.1). For accommodating such shapes and structures, different types of membrane modules are available. The last decade of membrane and module development has lessened the effects of physical compaction and has brought forth spiral membrane modules (see Figure I.2) capable of operating at pressures in excess of 800 psig (55.2 bar). The techno-economic factors for the selection, design and operation of membrane modules include cost of supporting materials and enclosure (pressure vessels), power consumption in pumping and ease of replaceability. The following membrane modules are largely used for industrial applications namely (1) Plate and frame module, (2) Spiral wound module, (3) Tubular membrane module, (4) Capillary membrane module and (5) hollow fiber membrane module.
Figure 1.1. Schematic diagrams of tubular membrane module and capillary membrane module

Figure 1.2. Schematic diagrams of plate and frame membrane module and spiral-wound membrane module

INTRODUCTION
I.5. PERVAPORATION

Pervaporation is one of the most active areas in membrane research and the pervaporation process has been shown to be an indispensable component for chemical separations. In the present research work, recent development in pervaporation membranes and pervaporation processes is reviewed and some outstanding questions involved in membrane pervaporation are discussed with emphasis on the following issues: mass transport in the membrane, membrane material selection, concentration polarization in the boundary layer, semi-synthetic and composite membranes. We attempt to provide insight into this dynamic field and to highlight some of the outstanding problems yet to be solved or clarified.

I.5.1. Background

During the past decade, industrial membranes have established themselves as indispensable components of chemical processing industries. Membrane-based technology is currently regarded as a new frontier of chemical engineering and has been widely used for the purification, concentration and fractionation of fluid mixtures.

Pervaporation is a relatively new membrane separation process that has elements in common with reverse osmosis and membrane gas separation. In pervaporation, the liquid mixture to be separated (feed) is placed in contact with one side of a membrane and the permeated product (permeate) is removed as a low pressure vapor from the other side as shown in Figure 1.3. The permeate vapor can be condensed and collected or released as desired. The chemical potential gradient across the membrane is the driving force for the mass transport. Applying either a vacuum pump or an inert purge (normally air can create the driving force or steam) on the permeate side to maintain the permeate vapor pressure lower than the partial pressure of the feed liquid.
Vacuum pervaporation, which is customarily referred to as the standard pervaporation, is the most widely utilized mode of operation, while inert purge pervaporation is normally of interest if the permeate can be discharged without condensation. Besides these two modes of operation, there are several other process variants, including thermal pervaporation, perstraction or osmotic distillation, saturated vapor permeation and pressure-driven pervaporation [3-5]. Some of them are really process hybrids rather than process variants. Recently, electrically induced pervaporation has also been attempted by [6].

![Diagram of pervaporation process](image)

**Figure 1.3.** Schematic diagram of the pervaporation process. (a) Vacuum pervaporation, (b) purge gas pervaporation.

Though pervaporation is one of the most popular areas of current membrane research, the concept of pervaporation separation is not new. The phenomenon of pervaporation was first observed by [7], who originated the term in a publication reporting selective permeation of water from aqueous solutions of albumin and toluene through collodion (cellulose nitrate) films. The usefulness of pervaporation for separation and concentration was recognized in [8]. However, the first known quantitative work on
pervaporation was published by [9] for the separation of water/ethanol mixtures using a cellulose membrane. It was the work of [10-12] that established the principles and highlighted the potential of Pervaporation technology. Although the research work was continued for several years and many patents were obtained, the permeation flux was too low to be economically useful. A breakthrough was achieved in the early 1980’s when Gesellschaft fu¨r Trenntechnik (GFT) Co. in Germany has developed a composite membrane comprised of a thin layer of crosslinked poly(vinyl alcohol) supported on a porous poly(acrylonitrile) substrate. This is indeed the commercially successful membrane on large scale. The pervaporation separation process for dehydrating ethanol was then commercialized. In the following years, substantial work was done that widened the research scope to many liquid mixtures and a variety of membranes. Membranes made of both synthetic polymers and derivatives of natural polymers have been tested for the separation of various liquid mixtures including, for example, alcohols-water, acetone-water, methanol/methyl tert-butyl ether, methanol/pentane, toluene-heptane and isomeric xylenes.

The applications of pervaporation can be classified into three categories: (i) dehydration of organic solvents, (ii) removal of organic compounds from aqueous solutions and (iii) separation of anhydrous organic mixtures. Currently, pervaporation has been commercialized for two applications: one is the dehydration of alcohols and other solvents and the other is the removal of small amounts of organic compounds from contaminated waters. In the latter application, pollution control and solvent recovery are affected simultaneously. There are also some other promising applications such as aroma recovery and beer dealcoholization in the food industry [13-16] and product recovery from fermentation broths for enhanced bioconversions [17-22].

The separation of organic-organic mixtures is presently the least developed application of pervaporation because of the problems normally
associated with membrane stability under relatively harsh conditions, but it represents the largest opportunity for energy and cost savings. The separation of methanol/methyl tert-butyl ether/C₄’s azeotropes is now being actively investigated due to commercial interest of producing octane enhancers for gasolines [23-29]. Once a suitable membrane is available, pervaporation can also find a niche in some reversible reactions such as esterification and condensation reactions to remove one or more product species selectively, thereby shifting the equilibrium toward the product side [30-34]. The application of pervaporation has now been extended to include dehydration of aqueous electrolyte solutions [35]. Interestingly, membrane aided pervaporation is also being investigated as a chemical sensor in instrumental analysis [36-38].

The literature on pervaporation is extensive. Many reports and articles provide a substantial amount of information on the development of pervaporation technology [4, 39-40]. Among others, the book edited by Huang [41] provides an extensive treatment of theory and practice of the process.

**7.5.2. Characteristics of Pervaporation**

Pervaporation separation is governed by the chemical nature of the macromolecules that comprise the membrane, the physical structure of the membrane, the physicochemical properties of the mixtures to be separated and the liquid-liquid and liquid-membrane interactions. Pervaporation transport is usually described to be a three-step process: solution-diffusion-evaporation. The separation is based on the selective solution and diffusion, i.e., the physical-chemical interactions between the membrane material and the permeating molecules, not the relative volatility as in distillation. Therefore, pervaporation is commonly considered to be a profitable complement to distillation for the separation of azeotropic and close-boiling mixtures, which requires the use of energy-intensive processes.
Pervaporation can be operated at low feed pressures and at ambient temperature or even below this and no additional chemicals are needed for separation. Therefore, pervaporation can be applied in biotechnology to the concentration of sensitive biochemicals. The effectiveness of pervaporation was also demonstrated for concentrating dilute protein and enzyme solutions [42,43]. Compactness, flexibility, simplicity and versatility are some other strong points of the pervaporation process. In a comprehensive assessment of fluid separation techniques, pervaporation is ranked the third highest among the 31 techniques under evaluation [44].

1.5.3. Mass Transport in Membranes

A proper understanding of the membrane separation mechanism may provide direct information on the research and development of an appropriate membrane. Because of the complicated penetrants-membrane interactions, it is difficult to formulate a single explanation for the complex transport process. There are principally two approaches to describe mass transport in pervaporation: (i) the solution-diffusion model and (ii) the pore flow model.

The solution-diffusion model is accepted by the majority of membrane researchers [45-47]. According to this mechanism, pervaporation consists of three consecutive steps: (i) sorption of the permeant from the feed liquid to the membrane, (ii) diffusion of the permeant in the membrane and (iii) desorption of the permeant to the vapor phase on the downstream side of the membrane (Figure 1.4). In general, solubility and diffusivity are concentration dependent. A number of mathematical equations for mass transport have been formulated on the basis of Fick’s diffusion equation using different empirical expressions of concentration dependence of solubility and/or diffusivity. However, these equations cannot be taken for granted unless they are used within the experimentally established range for which the relationships expressed for diffusion and thermodynamic equilibria are applicable.
The transport of a single component through a nonporous homogeneous membrane has been relatively well described. The concentration dependence of diffusivity is often expressed by exponential or linear forms [48-51]. Assuming thermodynamic equilibria exist at both membrane interfaces, the steady-state flux equation can be readily derived on the basis of Fick’s equation for one-dimensional diffusion normal to the membrane surface.

![Diagram of pervaporation transport mechanism](image)

**Figure I.4.** Schematic representation of the pervaporation transport mechanism. (a) Solution-diffusion model, (b) pore flow model.

For binary mixtures, the mass transport is complicated by the permeant-permeant and permeant membrane interactions and no overall explaining theory exists [52] and is used in concentration-independent diffusion coefficients and constant solubilities for both permeating species. As a result, it is derived that the permeation flux is a linear function of permeate pressure and the separation factor is essentially equal to the ratio of pure component permeabilities. This treatment is exactly the same as that used in the INTRODUCTION
permeation of noble gases through rubbery polymer membranes. Being the oversimplified version of the solution-diffusion model, it can hardly be applied to the pervaporation of liquid mixtures.

On the same basis the model was developed [53], but with the hypothesis that diffusivities are exponentially dependent on permeant concentration a "six-coefficient exponential model" was proposed [54]. The permeation flux is expressed by two complicated differential equations. All the model parameters are determined by fitting the flux equations to experimental data. Because of the large number of empirical parameters involved in the transport equations, many different sets of parameters can be fit to a given set of pervaporation data [55]. Consequently, the significance of a particular parameter becomes suspect and the model is of little predictive or interpretive value.

The uncertainty in the determination of the model parameters would be reduced by conducting sorption experiments in addition to pervaporation experiments so that the parameters related to membrane interface equilibrium could be determined independently. But this is only true for the case where liquid sorption in the membrane obeys Henry's law because a constant solubility was assumed in the model derivation. Therefore, the use of this model is restricted to such pervaporation systems where ideal sorption is expected but variation of diffusivity with concentration may nevertheless occur.

1.5.4. Polymers for Pervaporation Membranes

Polymeric materials are overwhelmingly utilized for pervaporation membranes. Three types of polymer membranes can be classified: glassy polymer membranes, rubbery polymer or elastomeric membranes and ionic polymer membranes.
By tendency, glassy polymers are suitable for making water-selective membranes used for solvent dehydration and rubbery polymer membranes are favorable to the selective removal of organic compounds from water. However, it is interesting to note the exception that some polyacetylene derivatives, which are glassy polymers, are preferentially permeable to organic compounds over water [56]. Poly(1-(trimethylsilyl)-1-propyne) [PTMSP] has been shown to be more alcohol selective than poly(dimethylsiloxane) [PDMS], a representative of organic-selective membranes. For the separation of organic mixtures, it is not yet very clear whether glassy or rubbery polymers are more appropriate and both types of polymers show some pervaporation selectivity.

Ionic polymers contain ionic groups that are neutralized by counter ions. They may be viewed as crosslinked polyelectrolytes. Ionic membranes, which can be subdivided into cationic and anionic, are normally water selective due to their affinity to water. Ionic polysaccharides have been shown to be potential materials for making dehydration membranes.

A membrane with low hydrophilicity generally exhibits a low water flux in dehydration, but some membranes made of polymers with very high hydrophilicity such as poly(vinyl alcohol) [PVA] and poly(acrylic acid) [PAA] need crosslinking for improved stability and selectivity. The polymer materials for dehydration membranes should maintain a proper balance of hydrophilicity and hydrophobicity. The techniques of controlling the hydrophilicity-hydrophobicity balance have been discussed [57]. Improvement in membrane performance can often be achieved by polymer modification, for which several techniques have been developed, including crosslinking, grafting, blending, copolymerization and incorporation of adsorbent materials. Interpenetrating polymer networks (IPN’s) are a unique type of polymer blend. IPN membranes of hydrophilic/hydrophobic, cationic/anionic and glassy/rubbery constituents offer another way of improving membrane performance [58]. Such membranes can be prepared either by simultaneous polymerization of both networks or by
sequential polymerization in which a polymer is swollen in a monomer followed by in situ polymerization of the monomer.

Many polymers that can be formed into membranes have been investigated in terms of pervaporation properties and the list of polymer membrane materials is virtually endless so far as possible chemical varieties are concerned. An extensive survey of the pervaporation was conducted on membranes and different separation systems were also studied in the literature [59]. It is shown that currently silicone rubber based polymers primarily PDMS is mainly used for the selective permeation of organic compounds from aqueous solutions and PTMSP and other silicone containing polyacetylene derivatives are under development as potential membrane materials [60-63]. Generally, silicone rubber membranes exhibit limited selectivity for some mixtures such as lower alcohols-water and acetic acid-water. To improve permselectivity, it has been attempted to fill the membrane with organophilic adsorbent [64, 65]. As such, the sorption capacity and/or sorption selectivity will be enhanced due to the adsorbent fillers. However, strong adsorption will cause immobilization of the permeating species, leading to a reduction in permeation flux. Thus, suitable adsorbent filler should have proper organophilicity, hydrophobicity and pore size characteristics.

Poly(1-(trimethylsilyl)-1-propyne) is an extraordinary glassy polymer. It has ~25% voids which may be linked through chain-to-chain gaps at least ~3 Å wide [66]. Gas permeabilities through the polymer are orders of magnitude larger than in other glassy polymers due to its loose microstructure and high mobility of the pendant groups [67]. However, during pervaporation operations, both permeability and selectivity decline with operation time [68-70]. The problem associated with membrane stability sustained applicability of this unique material for producing industrial pervaporation membranes.

For making dehydration membranes, PVA and PAA based polymers are the most widely used materials, while chitosan and aromatic polyimide
materials are attracting great interest. PVA is a 1,3-diglycol polymer whose hydroxyl groups have strong interactions with water through hydrogen bonding. It is one of the very few high molecular weight water soluble resins and can easily be crosslinked either chemically or thermally. Of all the membranes for pervaporation separation of aqueous-organic mixtures, PVA based membranes have been studied most intensively. Most of the research is centered on modification of PVA for improved permselectivity and stability and performance testing for various perspective applications by incorporating nanoparticles, blending, grafting [71-73]. The commercial membrane of GFT Co. for solvent dehydration is made from chemically crosslinked PVA. PAA is another polymer suitable for preparing water selective membranes. It has a high charge density based on the carboxyl groups, which are readily available for crosslinking and salt formation with alkaline metals. Multivalent cations such as Al\(^{3+}\), Cr\(^{3+}\), Ca\(^{2+}\) and Mg\(^{2+}\) can be used to induce ionic crosslinking for improved resistance of PAA to dissociation in aqueous solutions and PAA can undergo ionization [74-79].

Sodium alginate [NaAlg] is one of the most popular polymer widely used in pervaporation experiments. Several researchers prepared modified NaAlg to improve membrane performance in PV experiments [80-86]. Polyelectrolyte complex [PEC] membranes were also prepared by the complexation of protonated chitosan with sodium alginate doped on a porous, polysulfone supporting membrane for PV dehydration of various alcohol/water mixtures [87] and, zeolite filler incorporated to enhance the PV performances.

1.6. GAS SEPARATION

1.6.1. Theory of Gas Separation

Permeation of a gas through a dense homogeneous membrane occurs via solution-diffusion mechanism. Figure 1.5 gives the schematics of gas separation. The permeability coefficient of a gas is a function of its solubility
in the membrane and its diffusion through the membrane. Transport across the membrane involves: (i) diffusion through the boundary layer at the membrane-feed gas interface, (ii) sorption into the upstream face of the membrane, (iii) diffusion through the thickness, (iv) desorption from the downstream face of the membrane and (v) diffusion from the boundary layer facing the permeate side. Each of these steps constitutes resistance to mass transport. The gas at high pressure \(P_H\) in contact with the membrane is sorbed by the polymer [88].

The amount of gas dissolved is directly proportional to the applied pressure and the proportionality constant is termed as sorption coefficient \(S\). The sorbed gas then diffuses through the membrane by virtue of its chemical potential gradient (i.e., concentration difference) across the membrane and gets desorbed at the downstream side, which is maintained at a lower pressure \(P_L\). Under steady state conditions, transport rate (flux) is calculated as:

\[
F = \frac{DS(P_H - P_L)}{h}
\]  (I.1)

where \(h\) is the effective membrane thickness and \(D\), the diffusion coefficient. The product \(DS\) is called the permeability coefficient \(P\), which is usually expressed in terms of Barrers (\(= 10^{-10}\) cc (STP) cm / cm\(^2\) s. cmHg). On the other hand, if the feed is a mixture of gases, the sorption of each gas molecule is proportional to its partial pressure, which depends upon the partial pressures of other components also. In such a case, sorption becomes competitive and diffusion process would be a complex coupled phenomenon [89].

The separation of a binary feed mixture, for example, can be described by an overall selectivity coefficient, \(\alpha_{1,2}\) given by:

\[
\alpha_{12} = \frac{S_1D_1}{S_2D_2} = \frac{P_1}{P_2}
\]  (I.2)

where the subscripts 1 and 2 represent the faster and slower permeating gases, respectively and \(P_1\) and \(P_2\) are their permeability coefficients. For a multi-
component mixture, a similar expression can be derived between any two components \((i\) and \(j)\), but often, for the sake of convenience, selectivities are expressed with respect to the least or slowest permeating component [90].

\[
\begin{align*}
Q_f &= \text{Flow Rate} \\
x &= \text{CO}_2 \text{ Conc} \\
1-x &= \text{CH}_4 \text{ Conc} \\
\end{align*}
\]

\[
\begin{align*}
\text{CO}_2 \text{ Partial Pressure Gradient } \Delta P &= x (P_{H}) - y (P_{L}) \\
\text{Membrane Thickness} &= \delta
\end{align*}
\]

\[
\begin{align*}
Q_r &= \text{Conc. Flow Rate} \\
z &= \text{CO}_2 \text{ Conc} \\
1-z &= \text{CH}_4 \text{ Conc} \\
\end{align*}
\]

\[
\begin{align*}
Q_p &= \text{Permeate Flow Rate} \\
J_{\text{m2}} &= -D \left( \frac{dc}{d\delta} \right) \text{ [cc/cm}^2\text{.sec]} \\
\text{Permeability } K &= \left( \frac{J \delta}{\Delta P} \right) \text{ [Barrer]} \\
\text{Selectivity } \alpha &= \frac{y(1-x)}{x(1-y)}
\end{align*}
\]

**Figure I.5.** Principles of gas separation

**I.7. FACTORS AFFECTING MEMBRANE PERFORMANCE**

There are several factors affecting the membrane performance in a gas permeation process, which needs to be addressed by the researcher:

**I.7.1. Feed composition**

A change in feed composition will directly affect the sorption phenomena (degree of swelling) at the gas membrane interface as envisaged by the sorption-diffusion principles. Since diffusion of gaseous components in the
membrane is dependent upon the concentration of the components (or solubility of the components), permeation characteristics are greatly influenced by the feed composition [91]. Coupling effects between two or more species could occur in multicomponent feeds, which may considerably influence the selectivity. Similarly, higher concentration of condensable species plasticizes the membrane.

1.7.2. Feed and Permeate Pressures

The driving force in gas separation is the partial pressure gradient across the membrane [92]. The flow of a component, say $i$, across the membrane can occur only if the partial pressure (product of mole fraction and total pressure) of component, $i$ at the feed side of the membrane is greater than the partial pressure of the same component at the permeate side.

1.7.3. Temperature

In general, solubility decreases with increasing temperature, while diffusivity coefficients increase with temperature [93,94]. However, increased diffusivity offsets the decrease in solubility. Figure 1.6 shows that increasing the temperature will cause the selectivity to decrease, with an enhancement in the rate of permeation. Thus, membranes possessing high selectivity at room temperature may yield poor separation at elevated temperatures.
I.7.4. Concentration Polarization (CP)

For reverse osmosis liquid and pervaporation feeds, different individual component permeation rates generally cause an increase of the less permeable component in the boundary layer near the membrane surface [95]. This inhibits the rate of transport of more permeable species and subsequently, the selectivity. However, such effects are rare or nonexistent for gas separations due to the much greater gas phase (vs. liquid phase) external diffusion coefficients found in gases as against liquid feeds.

I.8. POLYMER SELECTION FOR MEMBRANE DEVELOPMENT

Preliminary criteria for the selection of polymeric materials for gas separation is based on chemical resistance, sorption capacity and good mechanical strength. However, the key important factors are: (a) intrinsic membrane permselectivity, (b) ability of the polymer to resist swelling induced plasticization (not chemical attack, which is more rare) and (c) ability to process the polymer into a useful asymmetric morphology. The polymer should have good interaction, preferably with one of the components of the...
mixture, for an effective separation. Molecular structure, specific nature of the material, crystallinity and membrane polarity are also some of the important factors, which affect the membrane performance [96,97].

1.8.1. Molecular Structure

It is well established that the chemical structures coupled with the subtle physical properties of the membrane material influence permeability and selectivity. Studies indicate that permeability and selectivity of polymeric membranes cannot be drastically improved by incorporating variations in the basic structure of a particular polymer [98,99]. Such efforts only shift the compromise between permeability coefficient and selectivity, but do not constitute a concrete improvement. Therefore, the dependence of permeability on chemical structure can only be a rough approximation, because the chemical structure is only one of the determinants for assessing membrane properties [91].

1.8.2. Specific Nature of the Material

Rubbery materials have high permeabilities, but poor selectivities due to the paucity of polar groups, absence of crystallinity and low degree of cross-linking [100]. Glassy polymers have higher permselectivity and are thus, suitable in gas separation studies [101]. Density of the glassy polymer increases by annealing or plasticization. Hence, high permselectivity can only be obtained with polymers of rigid backbone structures having small inter-segmental gaps i.e., high $T_g$ and resistance to plasticization [102]. In general, any glassy polymer is a combination of amorphous and crystalline phases and the knowledge of how crystallinity influences the separation would be essential in choosing the right kind of the membrane material.
1.8.3. Crystallinity

In the separation of gases, degree of crystallinity also exerts a great influence on permeability of gas through the membrane, because diffusion generally occurs in the amorphous part of the polymer [103]. Highly crystalline polymers do not contribute in enhancing permeabilities and furthermore, crystallites due to the lack of flexible groups, act as physical crosslinks, which prevent the high-degree of swelling and thereby, show lower permeability compared to amorphous polymers. Indeed, poly(phenylene oxide) [PPO], which can be prepared by melt processing as an amorphous thick film, typically tends to crystallize when formed in solvent-nonsolvent induced asymmetric form. While PPO has good separation properties in the amorphous dense film form, the complications with crystallization of casting dopes for this material has prevented its large scale practical usage.

1.8.4. Membrane Polarity

Membrane polarity also contributes considerably to its separation performance. In order to separate a particular component in an organic feed mixture, the polarity of one of the components must be close to the polarity of the membrane. Generally, all chemical differences between various polymeric materials are due to differences in polarity and steric effects caused by the attached side groups. Polarity strongly influences solubility and subsequently the permeability, which is demonstrated aptly by the Hildebrand solubility parameter, $\delta$ [104, 105]. Therefore, it is possible that selectivity of a polar gas in the feed gas stream may be improved with membrane polarity i.e., hydrogen bonding groups present in the polymer matrix. Table 1.3 shows some of the important polar groups.
Table 1.3. Polar groups responsible for intermolecular attraction

<table>
<thead>
<tr>
<th>Polar group (+ - -)</th>
<th>Dipole moment (Debye units)</th>
<th>Polar group (N[^+])</th>
<th>Dipole moment (Debye units)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H-F</td>
<td>1.9</td>
<td>C=NH</td>
<td>2.5</td>
</tr>
<tr>
<td>H-Cl</td>
<td>1.1</td>
<td>N\equiv O</td>
<td>3.9</td>
</tr>
<tr>
<td>H-O</td>
<td>1.6</td>
<td>C≡N</td>
<td>3.8</td>
</tr>
<tr>
<td>H-S-</td>
<td>0.9</td>
<td>C≡N</td>
<td>0.9</td>
</tr>
<tr>
<td>C-Cl</td>
<td>1.7</td>
<td>C\equiv N=O</td>
<td>1.9</td>
</tr>
<tr>
<td>H-C</td>
<td></td>
<td>C\equiv N</td>
<td></td>
</tr>
<tr>
<td>C=O</td>
<td>2.5</td>
<td>C\equiv S</td>
<td>3.0</td>
</tr>
<tr>
<td>C-F</td>
<td>1.5</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1.9. SCOPE AND OBJECTIVES OF THE THESIS

There are very few companies they are fabricating pervaporation membranes and no company in India so far, which has the capability to fabricate gas-separating membranes. Moreover, there are no imported plants installed in India for the separation of gaseous mixtures. This means that there is a tremendous scope and opportunity for developing this technology in India.

1.9.1. The objectives of the present study are listed below:

- Synthesis/preparation of various polymer membranes and to purify the organic solvents by dehydration, separation of alcohols from toluene and generation of basic permeation data with CO₂ and CH₄, N₂ gases for identification of the most suitable membrane material.
- Characterization of membranes by Fourier transform infrared spectroscopy (FTIR), X-ray diffraction studies (X-RD), scanning electron microscopy (SEM), particle size analysis, differential scanning calorimetry (DSC),
thermogravimetric analysis (TGA) and tensile strength measurements to understand intermolecular interactions, degree of crystallinity, membrane morphology, thermal and mechanical stability aspects.

- Modification of the best membranes by crosslinking, surface modification and incorporation of inorganic fillers, zeolites to improve their performance.
- Development of ceramic polymeric composite membranes for the effective separation of CO₂ from its binary mixtures.
- Studies with binary mixtures of CO₂/CH₄ and CO₂/N₂ gas mixtures with the most promising membranes to optimize the operating parameters such as membrane thickness, feed composition and pressure.
1.10. REFERENCES


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