CHAPTER 1

Introduction
CHAPTER - 1

Introduction to Pervaporation

ABSTRACT:

This chapter deals with the history of membranes, classification of membranes, classification of membrane processes, Pervaporation mechanism, applications of membranes, advantages of membrane technology, factors affecting membrane performance, scope of the present investigation and the literature survey pertaining to the present investigation and recent developments in the field of Pervaporation, such as mixed matrix membranes with inorganic fillers. This chapter also includes the brief discussion about the factors affecting the membrane performance such as flux, selectivity and Pervaporation separation index (PSI) and enrichment factor etc. A brief discussion related to the present study is well defined in this chapter. It also covers the brief literature regarding the earlier studies related to the polymers, zeolites, Ethanol, Isopropanol and cross-linker used in the present study.
1.1: Introduction:

Most industrial scale separation processes are based on energy intensive methods such as distillation, evaporation, and freeze crystallization. Membrane separations offer significant advantages over existing separation processes. Current membrane separation technologies can offer energy savings, low-cost modular construction, high selectivity of separated materials, and processing of temperature-sensitive products [1-4]. Membranes separate mixtures by discriminating the components on the basis of physical or chemical attributes, such as molecular size, charge, or solubility [5]. By passing water and retaining salts, membranes are used to produce over half of the world's desalinated potable water. Membranes can also separate oxygen and nitrogen from air as well as hazardous organics from contaminated water in applications such as groundwater remediation.

The need for membrane separation technology increases as environmental requirements tighten, water circuits close, the recycling of wastes increase and the purity requirements for foodstuff and pharmaceuticals increase. Six major membrane processes (microfiltration, ultrafiltration, reverse osmosis, electrodialysis, gas separation and pervaporation) have found use in such application areas as water purification, chemical and food processing, drug delivery, bioseparations, and medical treatment [1-5].

In the present study we are mainly concerned with pervaporation and vapor permeation both particularly useful and relatively new membrane separation processes.
1.1 (a): Definition of Pervaporation Process:

Pervaporation is recognized as a separation process in which a binary or multicomponent liquid mixture is separated by partial vaporization through a dense non-porous membrane. During pervaporation, the feed mixture is in direct contact with one side of the liophilic membrane whereas the permeate is removed in a vapor state from the opposite side into a vacuum or sweeping gas (Fig. 1.1, Tab. 1) and then condense. Pervaporation is unique among membrane separations, involving the liquid-vapor phase change to achieve the separation [6, 7].

Fig. 1.1. Scheme of pervaporation process
Table 1.1: Overview of chosen membrane separation processes.

<table>
<thead>
<tr>
<th>Membrane process</th>
<th>Feed phase / permeate phase</th>
<th>Driving force</th>
<th>Membrane</th>
<th>Main applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pervaporation</td>
<td>Liquid/vapor</td>
<td>Chemical potential gradient</td>
<td>Dense, liophilic</td>
<td>Separation of liquid mixtures</td>
</tr>
<tr>
<td>Vapor permeation</td>
<td>Vapor/vapor</td>
<td>Chemical potential gradient</td>
<td>Dense, liophilic</td>
<td>Separation of vapor mixtures or vapors from gases</td>
</tr>
<tr>
<td>Pertraction</td>
<td>Liquid/liquid</td>
<td>Concentration gradient</td>
<td>Dense, liophilic</td>
<td>Separation of organic solutions</td>
</tr>
<tr>
<td>Gas separation</td>
<td>Gas/gas</td>
<td>Hydrostatic pressure gradient</td>
<td>Porous or dense</td>
<td>Separation of gaseous mixtures</td>
</tr>
<tr>
<td>Membrane distillation</td>
<td>Liquid/vapor</td>
<td>Vapor pressure gradient</td>
<td>Porous, liophobic</td>
<td>Ultrapure water, concentration of solutions</td>
</tr>
</tbody>
</table>

The driving force for the mass transfer of permeants from the feed side to the permeate side of the membrane is a gradient in chemical potential, which is established by applying a difference in partial pressure of the permeant across the membrane. The difference in partial pressures can be created either by reducing the total pressure on the permeate side of the membrane by using a vacuum pump system or by sweeping an inert gas on the permeate side of the membrane [6, 7].

1.1 (b): Definition of Vapor Permeation

Vapor permeation is similar in principle to pervaporation. The only difference concerns the feed, which is a mixture of vapors or vapors and gases [8]. As in pervaporation, the permeate partial pressure is maintained by use of a
vacuum or an inert sweep gas (Fig. 1.2, Tab. 1).

Fig. 1.2 Scheme of permeation process

There is no change of phase involved in its operation. Thus, compared to pervaporation, the addition of heat equivalent to the enthalpy of vaporization is not required in the membrane unit and there is no temperature drop along the membrane [9]. Operation in the vapor phase also eliminates the effect of the concentration polarization prevalent in liquid phase separations, such as pervaporation.

1.1 (c): Related Process:

Table 1 presents the main characteristics of chosen membrane processes which resemble pervaporation or vapor permeation concerning either the membranes applied or type of application. To avoid any misunderstandings it is quite important to know both the differences and similarities of these processes [7, 10].

1.1 (d): Performance Parameters of Membranes

The performance of a given membrane in pervaporation or vapor permeation is estimated in terms of its selectivity and the permeate flux. The assessment is
based on the mass transfer of the preferentially permeating species, regardless of whether the permeate or the retentate is the target product of the pervaporation process [10].

The selectivity of a given membrane can be estimated by using the following two dimensionless parameters [10]:

Separation factor or selectivity (α)

\[
\alpha = \frac{Y_A / Y_B}{Y_A / X_B} = \frac{Y_A / (1-Y_A)}{X_A / (1-X_A)}
\]  

(1)

Enrichment factor (β)

\[
\beta = \frac{Y_A}{X_A}
\]  

(2)

Where:

X_A - weight fraction of preferentially permeating species in the feed phase,
Y_A - weight fraction of preferentially permeating species in the permeate phase,
with X_A + X_B = 1 and Y_A + Y_B = 1.
Unfortunately, neither the separation factor nor the enrichment factor are constant. Both parameters are the strong function of the feed composition. Therefore, the McCabe-Thiele diagram, employed usually for the analysis of liquid-vapor equilibrium, is often used to the evaluation of pervaporation or vapor permeation selectivity. Fig. 1.3 compares the distillation and pervaporation through hydrophilic polyvinyl alcohol membrane of water-ethanol binary mixture. It is seen that pervaporation with highly hydrophilic membrane favors the transport of the higher boiling water. The high efficiency of pervaporation also occurs near the azeotropic composition of the water-ethanol system. The diagonal line in Fig. 1.3 represents azeotropic compositions, for which separation does not take place (compositions of the product and the feed mixture are the same, i.e. \( a = 1 \)).

The permeate flux (\( J \) [kg m\(^{-2}\) h\(^{-1}\)]) shows also a strong dependency on the feed composition, permeate pressure and temperature of the process. Temperature dependence is of the Arrhenius type, usually with doubling of flux at temperature increase of 10-12 K.
1.2: History of membranes:

Membranes have been widely used in various industrial separation applications for the last two decades. It is estimated that the annual revenue of the worldwide membrane industry is over a billion dollars, and an annual growth rate of about 10 percent has been forecasted for this industry [11]. Currently, the industry is dominated by polymeric membranes that have been used in a variety of applications ranging from food and beverage processing, desalination of seawater, and gas separations, to medical devices. Recently, research directed at the development and application of inorganic membranes is gaining momentum because of their high demand in the new application fields, such as fuel cells, membrane reactors, and other high-temperature separations. The annual growth rate of inorganic membranes is expected to be about 30 percent with almost 15 percent share of the total market volume [11].

The concept of the ideal semi permeable membrane able to separate two species with the theoretical minimum work has been used by thermodynamicists for more than 150 years, but attempts to use membranes for practical separations did not begin until the 1900s, when Bechhold devised a technique for preparing nitrocellulose membranes of graded pore size. Later workers, particularly Zsigmondy, Bachmann, Elford and Ferry, refined these preparative techniques and membranes were used to separate a variety of laboratory solutions by dialysis and micro-filtration. By the 1930s, micro porous membranes were produced commercially on a small scale. The first ion exchange membranes were made at about the same time; these were used by Teorell, Meyer and Seivers to develop their theory of ion transport. This work led eventually to the development of electro dialysis.
By 1960’s, the elements of modern membrane science had been developed, but membranes were only used in laboratories and in a few small, specialized industrial applications. There was no significant membrane industry, and total sales for all applications probably did not exceed 10 million US$. Membrane processes suffered from three problems that prohibited their widespread use: they were too slow, too expensive and too unselective. Partial solutions to each of these problems have since been developed, and sales of membranes and membrane separation equipment have grown several hundred-fold. Currently, several tens of millions of square meters of membranes are produced each year, and a membrane industry has been created.

The problem of slow permeation rates through membranes was largely overcome in the late 1960s and early 1970s by the development of imperfection free ultra thin membranes. These membranes are anisotropic structures and consist of a thin selective surface film supported by a much thicker microporous substrate to provide mechanical strength. Because the selective surface film is very thin, these membranes have high fluxes.

The problem of packing a large membrane area into a low-cost module has also been solved since the 1980s. The earliest module designs were plate-and frame or tubular units similar to conventional heat exchangers. These designs are still used in some processes, such as ultrafiltration, in which the ability to clean fouling deposits from the membrane surface is important. However, the cost of both designs is relatively high, and in most processes they have been displaced by capillary, hollow-fine-fibre and spiral wound module designs.

The problem of low selectivity remains one of the principal limitations of membrane processes. No general solution has been found, although substantial improvements have been made since the 1950s.
Table 1.2: Milestones in the development of membrane based separation

<table>
<thead>
<tr>
<th>Name of the Inventor</th>
<th>Year</th>
<th>Invention</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abbe Nollet</td>
<td>1748</td>
<td>Wine and water were separated with animal skin by reverse osmosis</td>
</tr>
<tr>
<td>J.K. Mitchell</td>
<td>1831</td>
<td>First scientific observation related to gas separation</td>
</tr>
<tr>
<td>Thomas Graham</td>
<td>1850</td>
<td>Graham’s Law of diffusion</td>
</tr>
<tr>
<td>L. Kahlenberg</td>
<td>1906</td>
<td>The separation of a mixture of a hydrocarbon and an alcohol through a rubber membrane</td>
</tr>
<tr>
<td>D. H. Hagerbaumer</td>
<td>1955</td>
<td>Conducted the first quantitative investigation with a microporous Vycor glass membrane with a high-pressure drop across it to allow for the separation of liquid-liquid mixtures.</td>
</tr>
<tr>
<td>Leob and Sourirajan</td>
<td>1961</td>
<td>Make the first anisotropic membrane</td>
</tr>
<tr>
<td>Binning et al.,</td>
<td>1965</td>
<td>Operation of separating a liquid-liquid mixture into a vapor mixture using a nonporous polymeric film.</td>
</tr>
<tr>
<td>Permea Inc.</td>
<td>1980</td>
<td>Launched its hydrogen separating Prism membrane</td>
</tr>
<tr>
<td>Gesellschaft für Trenntechnik</td>
<td>1982</td>
<td>Installed a pervaporation plant to separate water from concentrated alcohol solutions.</td>
</tr>
<tr>
<td>Exxon</td>
<td>1990</td>
<td>Pervaporation in its refineries to separate hydrocarbon mixtures containing aromatics and aliphatics.</td>
</tr>
</tbody>
</table>
1.3: Back ground

Compared with traditional separation processes, such as distillation, extraction and filtration, membrane technology is a relatively new method that has been developed in the past few decades, but it has been widely adopted in many industries. The membrane processes have the following distinguishing characteristics [12]

1) Continuity and simplicity of the processes,
2) Adjustability of the separation properties,
3) Feasibility of incorporation into hybrid processes,
4) Low energy consumption and moderate operating conditions

Developments in membrane formation techniques and material science accelerate the research and applications of membrane technology. Now commercial membrane applications have successfully displaced some conventional processes, and membrane technology has become an indispensable component in many industrial fields and in our daily life. Fig 6.1 shows a schematic membrane process [12, 13]. Separation membranes are located between the feed side and the permeate side. In most membrane processes, such as gas separation, reverse osmosis and ultrafiltration, both the feed and the permeate sides are in the same phases, gas or liquid, while in pervaporation, the liquid feed is separated into vaporous permeates with the aid of vacuum or a purge gas in the downstream side.

Pervaporation has become a very important technique to separate azeotropes, close-boiling mixtures, and recover volatile organic chemicals from liquid mixtures, and now it has emerged as a good choice for
separating heat sensitive products. The phenomenon of pervaporation was first discovered in 1917 by Kober [14], but no extensive research was carried out until in the 1950s by Binning *et al.*, [15]. In 1982, the first industrial application of the pervaporation process was launched by Gesellschaft Fuk Trenntechnik (GFT) mbH of Germany (now acquired by Sulzer Chemtech) for dehydration of ethanol using PVA/PAN composite membranes [16]. Currently, pervaporation membranes and processes are being studied in many laboratories and companies, such as Sulzer Chemtech, MTR, Exxon and Texaco [17, 18].

In pervaporation processes with functional polymer membranes, the non-porous dense membranes are essential. By choosing proper membranes, pervaporation has great advantages as an alternative separation method in the following separation tasks:

1) Dehydration of organic solvents,

2) Removal of organics from water,

3) Separation of organic liquids.

Non-porous dense membranes can also be applied in other separation processes such as gas separation. Furthermore, both gas separation and pervaporation can be interpreted with the solution diffusion mechanism for mass transport in membranes.
Gas permeation was first studied by Graham in 1860s, but it was not until the 1940s that Knudsen diffusion exploited in large scale use to separate U235F6 from U238F6 with finely micro porous metal membranes [18, 19]. Nevertheless, commercial gas separation membranes are based on the development of polymer membranes. In 1980, Permea (now Air Products and Chemicals) launched its hydrogen-separating Prism® membrane, after which cellulose acetate membranes for CO2/CH4 were developed by Cynara (now Natco), Separex (now UOP) and GMS (now Kvaerner). Later, Generon (now MG) introduced a membrane system to separate nitrogen from air, followed by the competitive membranes from Dow, Ube and Du Pont [20]. Applications of membrane gas separation technology keep expanding, and further growth is likely to continue for the next decade [18]. On the basis of the growing
industrial demand and new developments in polymer materials and membrane technologies, the next generation of membrane processes should maintain attractive economics associated with the current polymer-based membranes, while greatly extending performance properties [21].

Studies on the relationship between polymer materials and gas separation properties were carried out to understand membrane permeability and selectivity in order to maximize the membrane efficiency and to provide directions for new membranes or new processes [22-27]. Based on the experimental structure-property results, some mathematical methods were developed to predict the permeability of polymers to gases [28-32].

As mentioned before, pervaporation and gas separation, where non-porous membranes are used, follow the same mass transport mechanism. Therefore, it is possible to develop a theoretical or empirical method from the structure-property relationship, to interpret these results or predict membrane properties for both pervaporation and gas separation processes.

1.4: Definition of membrane

A membrane is a semipermeable barrier between two phases. It allows the passage of some molecules, called permeate, and reject the others, called retentate with the aid of a driving force such as pressure or concentration difference [33, 34]. The membrane performance depends on the physical and chemical properties of the membrane material and the permeating components. The permeability or flux through a membrane and the selectivity of the membrane to a component over another are the key parameters to evaluate the performance of a membrane [33, 34].
The important membrane parameters are:

- High Selectivity
- High Permeability
- Temperature Stability
- Chemical Resistance
- Mechanical Strength

### 1.5: Classification of membranes

Membranes are being developed from a wide range of materials including metals, polymers, ceramics and biological materials. Membrane morphology and structure can be manipulated by physical and chemical methods to bring the desired separation. However, the choice of method and material for separation is often dictated by the economics of the technology involved. Membranes can be classified based on the origin (Synthetic or Natural), Nature (organic and inorganic), structure, applications and the mechanism by which the separation is affected. Classification of membranes based on applications is presented in Fig 1.5.
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Symmetrical membranes

- Isotropic microporous membrane
- Nonporous dense membrane
- Electrically charged membrane

Anisotropic membranes

- Loeb-Sourirajan anisotropic membrane
- Thin-film composite anisotropic membrane
- Supported liquid membrane

Fig 1.5: Classification of Membranes

Ideal membrane characteristics:

1. High flux rates
2. High solute rejection
3. Resistance to chemical and biological attack
4. Resistance to fouling by colloidal and suspended materials
5. Mechanical and structural solubility over long operating periods
6. Easy to form into thin films or hollow fibers
7. Desired separation characteristics for each system
8. Low cost
1.6: Membrane module

Pervaporation is less familiar to the industry in comparison to the well-established mass exchange processes and is perceived to be expensive due to the phase change involved. The central part of any membrane plant is the module, i.e. the technical arrangement of the membranes. Some important aspects to be taken into consideration for the module design include packing density, cost-effective manufacture, easy access for cleaning and cost-effective membrane replacement. Based on the above, modules can be distinguished into five major types:

1.6 (a): Tubular module:

The membrane here is in hose form [35,36, 37] on the inside of pressure-tight tubes having 12–24mm internal diameter (Fig. 1.6[a]). If the material of the support tube is impermeable, then a thin porous tube is fitted between the support tube and the membrane. In many cases, several tubular membranes are assembled in a common support block to increase the packing density. Zeolite membranes for PV applications are generally fabricated in Tubular form. Though the manufacturing cost of these modules are high, these modules offer excellent resistance to fouling with low pressure drop and are not suitable for high pressure operations.

Fig. 1.6 [a]: Typical tubular membrane module
1.6 (b): Hollow fiber module:

Essentially this module consists of a pressure vessel containing a bundle of individual fibers (Fig. 1.6[b]). The open ends of the fibers are potted into a head plate. The feed solution flows radially or parallel to the hollow fibers. The permeate is collected at the open end of the fibers and hence the parallel flow can be cocurrent or countercurrent depending on the direction of permeate flow with respect to the feed. According to Gill and Bansal [38,39], countercurrent flow is always superior to cocurrent flow in parallel flow conditions. The module lends the membrane higher packing density, thus enabling production of modules at a lower cost per unit product. Also the unique ion-exchange structure is expected to enable organic–organic separations [40]. Pervaporation requires volatilization of a portion of liquid feed. In PV, the enthalpy of vaporization must be supplied by the feed. Due to this, a large thermal gradient is established across the membrane with continual heat loss to the permeate resulting in a reduction in flux. To compensate this heat loss, interstage heaters within the membrane module are required to reheat the feed. In case of hollow fiber modules, where the surface area/volume ratios are high, severe temperature losses are encountered that cannot be compensated with interstage heaters. Hollow fibers may have problems with longitudinal temperature drops and inefficient use of downstream surface area.

Fig. 1.6 [b]: Typical hollow fiber membrane module
1.6 (c): Plate and frame systems:

Here the feed solution flows through flat, rectangular channels (Fig. 1.6[c]). Packing densities of about 100–400 m² m⁻³ are achievable. For PV, plate and frame design has become the module of choice for two major reasons viz., firstly, the design allows the usage of gasketing materials that are resistant to the liquid organic solvents and secondly, this module allows high temperature operation with efficient interstage heating between stages [41,42].

![Plate and frame module](image)

Fig. 1.6 [c]: Plate and frame module

1.6 (d): Capillary module:

The capillary module has a tube bundle of fibers arranged parallel to each other with either end attached to a head plate. This module has a high packing density with higher mass transport resistance when compared to all the other modules, due to predominant laminar flow. Capillary module offers moderate pressure drop but is not suitable for high pressure operations. This module generally does not find application in PV despite its moderate manufacturing costs and good resistance to fouling [43].
1.6 (e): **Spiral wound module:**

These are characterized by high packing density (>900m² m³) and a simple design. Essentially, two or more membrane pockets are wound around a centrally located permeate collecting tube with a special mesh used as spacer (Fig. 16(b)). The membrane pocket consists of two membrane sheets with a highly porous material in between, which are glued together along three edges. The fourth edge of the pocket is connected to the collecting tube. Several such pockets are spirally wound around the perforated permeate tube with a feed-side spacer placed between the pockets [44]. Usually several such membrane elements are arranged in one pressure vessel. The feed-side flow is strictly axial while the permeate flows through the porous support inside the pocket, along the spiral pathway to the collecting tube [45,46]. A spiral wound unit for PV is difficult to develop because of the chemical susceptibility of the adhesives required.

![Spiral wound membrane module](image-url)

*Fig. 1.6 [d]: Spiral wound membrane module*
1.7: Applications of Membranes

The main domains of application of membrane techniques for liquids are reported in Fig 1.7. Among the major applications, are the water desalination (electro-dialysis or reverse osmosis), the production of tap water, the treatment of waste waters, the preparation of food, beverage, dairy or pharmaceutical products, the treatment and the recycling of industrial effluents. The mainly used membrane processes are micro-filtration and ultra-filtration. However the number of applications of Nano-filtration membranes is increasing more and more. For example, the plant of Mérysur Oise (France) produces tap water from the river Oise, using nano-filtration technology for a production capacity of 140000 m³ per day [47]. NF applications to non-aqueous liquids appear also as very promising for the recovery of organic solvents or of catalysts in fine chemistry synthesis.

Fig 1.7: Domains of Application of membrane techniques:
Data source: McIllyaine company [23]
1.8: Membrane Separation Process:

The driving force across a membrane can exist either as a pressure, concentration or voltage difference according to the driving force of the separation and to the physical size of the separated species, membrane process can be broadly classified as shown in the Table 1.3.

<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, Poly(Vinylidene 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 homogeneous 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>
1.9: Pervaporation Transport Models:

The transport theories described are general models, which can be applied to various membrane transport processes. In order to apply these models to pervaporation processes, an understanding of the various possible mechanisms of transport is necessary.

- Solution Diffusion Model
- Pore Flow Model
- Carrier Transport Mechanism

1.9.a: Solution diffusion model

The solution-diffusion model is the most widely accepted transport mechanism for many membrane processes, such as reverse osmosis, gas separation and pervaporation [18, 48]. The earliest application of the solution-diffusion model in pervaporation was proposed by Binning et al., [15], and he suggested that the selectivity took place in a boundary layer between the liquid zone and the gas zone in the membrane. Later, many researchers tried to interpret pervaporation processes based on the solution-diffusion model, and this model is now widely accepted. According to this model, the mass transport can be divided into three steps, as shown in Fig: 1.8

1) Sorption of liquids into the membrane at the feed side,
2) Diffusion of the sorbed components through the membrane,
3) Desorption/evaporation of the sorbed components at the permeate side.

Vaporization at the permeate side of the membrane is generally considered to be a fast and nonselective step if the partial pressure is kept low, i.e. far less than the saturated vapor pressure of the permeates [49]. The selectivity and permeability of a pervaporation membrane mainly depend on
the first two steps, that is, the solubility and diffusivity of the components in the membrane.

Fig. 1.8: Solution diffusion model for mass transport in membranes

1.9.b: Pore-flow model

Recently, Matsuura and co-workers have proposed a transport model applicable to pervaporation on the basis of the pore flow mechanism [50-52]. It is assumed that there are a bundle of straight cylindrical pores on the membrane surface. The mass transport by the pore flow mechanism consist of the following three steps:

- liquid transport from the pore inlet to a liquid-vapor phase boundary,
- evaporation at the phase boundary, and
- vapor transport from the boundary to the pore outlet

In Fig 1.9, the distinguishing feature of the pore flow model is that it assumes a liquid-vapor phase boundary inside the membrane, and
pervaporation is considered to be a combination of liquid transport and vapor transport in series.

![Diagram showing pervaporation process](image)

**Fig: 1.9.** Schematic representation of the transport mechanism of pore flow model.

There are different views regarding the existence of pores in pervaporation membranes. The solution-diffusion model considers the pores as passageways allowing communication between the upstream and the downstream membrane face by Knudsen flow or viscous flow mechanism. An effective solution-diffusion membrane has no pores but relies on the thermally agitated motion of chain segments comprising the polymer matrix to generate penetrant-scale transient gaps in the matrix, thereby allowing diffusion from the upstream to the downstream side of the membrane. The permeation is the net result of the random jumps of the penetrant in the membrane. On the other hand, the pores in the pore flow model are defined as the space between non bound material entities in the polymer matrix through which mass transfer takes place. The equivalent size of such a pore is expressed by any distance greater than zero [53]. The pores in the membranes effective for pervaporation and gas separation are angstrom sized, and these pores are thus not directly observable, making it difficult to physically see whether pervaporation
membranes have pores or not. However, it is clear that the pore concept in the pore flow model is not exactly the same as usually perceived from the standpoint of the solution-diffusion model. At present, it would be fair to recognize that the two models represent two different approaches to the description of pervaporation transport. Both models predict correctly that membranes with pores large enough for Knudsen or viscous flow to occur have no or little selectivity. The membrane pores in the pore flow model and transient gaps in the solution-diffusion model are both on the molecular scale, that describe essentially the same thing, that is, the two-dimensional space for the movement of penetrate molecules. In consideration

(i) The physical structure of the membrane is accounted for explicitly in the pore flow model,

(ii) The position of the phase change of permeant in the membrane is clearly addressed in the pore flow model,

(iii) Several main features of pervaporation observed experimentally can be explained semi quantitatively by the pore flow model, and

(iv) Good models that enable description and prediction of pervaporation transport are still lacking, the pore flow model should be appreciated.

It is important to investigate pervaporation from a study of diffusivities and sorption relations in order to elucidate the transport mechanism. However, the present knowledge on diffusivities and sorption properties is very limited, both experimentally and theoretically. Although numerous models have been proposed, many of them are solely based on qualitative observations, and vigorous verification by experimental data is lacking. Each model works for some systems, but none is general enough to make good descriptions and predictions for most systems. It is important to note that ideal sorption has
frequently been assumed in formulating the transport equations and the non ideal behavior in pervaporation has been attributed to the diffusivity aspect. It is thus irrelevant to incorporate a lot of parameters in an attempt to characterize non ideal diffusion without considering how non ideal sorption (e.g., preferential sorption) influences selective permeation. On the other hand, some researchers believe that preferential sorption is the prerequisite to preferential permeation, and the effect of diffusion aspect is overlooked. Comparison of preferential sorption with permeation results indicates that, while preferential sorption is favorable to preferential permeation, the separation can occur either through selective sorption or through diffusivity difference [54-57].

1.10: Types of Mechanisms:

Different mechanisms are postulated for diffusion of liquids through the membrane barriers. These are shown in figure 1.10.

1.10.a: Porous membranes:
Depending on the pore size, pores in membranes are classified as macropores (>50 nm), mesopores (2-50 nm) and micropores (<2 nm). Knudsen diffusion, surface diffusion, capillary condensation, and molecular sieving are the main transport mechanisms for microporous membranes. However, high selectivity cannot be achieved using porous polymer membranes, and the difficulty in fabricating membranes with uniform pores also restricts the applications of porous membranes in separation processes. As shown in Fig. 1.10, no apparent continuous passages exist in non-porous dense membranes, transport follows the solution-diffusion mechanism.
1.10.b: Knudsen’s diffusion

Knudsen diffusion is achieved when the pore dimension decreases (down to fractions of a micron) or when the mean free path of molecules increase, which can be achieved by lowering the pressure or raising the temperature. The molecules collide more frequently with the pore walls of the membrane rather with one another. The fluxes are then proportional to the square root of the molecular weight of the different gaseous compounds [57].

1.10.c: Solution diffusion

May also take place as a part of the diffusion process. It can contribute to the separation selectivity when one of the permeating adsorbed molecules can preferentially physisorb on the pore walls. By higher interactions between the adsorbed molecules themselves multilayer adsorption and hence multilayer diffusion occurs. The multilayer diffusion flux is generally much larger than the gas phase flux and can be considered as a two dimensional fluid ‘slipping’ over the surface [58].
1.10.d: Capillary diffusion

Capillary condensation is enabled when a pore is blocked by condensate. The condensed component evaporates at the permeate side, where a low pressure is imposed. The meniscus formed at the feed side promotes further condensation due to the decrease in vapor pressure that can be described by Kelvin equation [59].

1.10.e: Molecular sieving

Molecular sieving is achieved when pore diameters are small enough to let only smaller molecules permeate while mechanically preventing the bigger ones from getting in. Provided the pores are mono dispersed in dimension, selectivity may reach very high values.

1.11: Advantages of membrane technologies

The technologies of membrane separation have been developing to be the top of process separation. The advantage of membranes separation has been found in certain processes such as producing, separation, recovering, and drying [21]. The advantages are:

➢ The membranes are highly selective and so it has high effectiveness in separation process.

➢ Membrane processes are characterized by low energy consumption, possibility of different module design and easy scale up. These advantages make these processes superior to many other established separation processes.

➢ The membrane based separation processes are costly, effective and environmentally friendly.
These polymers not only exhibited better thermal and mechanical properties than natural polymers, but also present a wide range of gas transport and separation properties.

Membrane processes are able to recover minor but valuable components from a main stream without substantial costs.

The separation process of membrane do not use large or complex machine that have to move from one part of plant to another part of plant. It only consists of some instrument that is easy to operate. This process can be continuously.

1.12: Pervaporation

The term pervaporation is a combination of two terms Permeation and Evaporation. Pervaporation is a membrane based pressure – driven process in which the pressure is generally atmospheric on the feed side and low on the permeate side. It is generally employed for selective removal of one or more volatile species from the mixture of volatile liquids through perm selective nonporous membranes. The technique involves liquid mixture flow on the feed side and a vacuum on the permeate side followed by collection of permeate in condenser. As a result, permeate is collected in the vapor form, contrary to all other membrane processes (except gas permeation) where permeate is in the liquid form. Pervaporation involves phase transition from liquid to vapor. It is considered to be potentially useful in cases where distillation is not applicable, for example, separation of close boiling components, fractionation of mixtures containing components that decompose easily at temperatures close to the boiling point, separation of aqueous – organic liquid mixtures such as water – ethanol.
1.13: Applications of Pervaporation

The applications of Pervaporation can be classified into three categories.

1.13.a: Dehydration of organic solvents

Dehydration of organic solvents (e.g., alcohols, ethers, acids, and ketones) largely represents the applications of the pervaporation [60-64]. The materials used in earlier dehydration research were the naturally occurring polymers, e.g., cellulose and cellulose derivatives [64]. Synthetic polymers [65, 66], e.g., poly (acrylic acid) (PAA), poly (vinyl alcohol) (PVA), poly (acrylonitrile) (PAN), and nylon 6, were subsequently investigated, with a focus mainly on alcohol dehydration [66]. This endeavor did not gain success until the breakthrough achieved by GFT in 1980s. According to the incomplete statistics [67,68], there have been more than 60 pervaporation units operating around the world so far.

After the success of GFT membranes based on the crosslinked PVA coated on PAN substrate, many other hydrophilic materials were studied, and some of them are sodium alginate, chitosan, nylon 6, polyethyleneimine (PEI), cellulose sulfate (CS), synthetic zeolites [69, 70], etc. Uragami and Saito [70] and Mochizuki et al., [71] were among the pioneers using sodium alginate membranes for alcohol dehydration. Sodium alginate is a polysaccharide obtained from seaweeds, and it shows excellent affinity for water. As a membrane material, it however lacks mechanical strength and stability in aqueous solutions. Yoom and co-workers [72-74] improved the membrane strength and stability by cross-linking using glutaraldehyde, or alternatively by thermal treatment of the membrane at 100 °C for hours. Huang et al., [75] also obtained stabilized sodium alginate membranes by using a relatively simple but quite effective method of ionic cross-linking, which results from the interaction between the multivalent metal ions (e.g., Ca²⁺, Al³⁺) and the carboxyl groups of
the polymer. It is well known that crosslinking limits mobility of the polymer chains, and thus excessive membrane swelling can be suppressed. However, the density of cross-linking should be well controlled; otherwise, membranes will become too brittle to be used.

Blending is also an effective approach for modifying membrane properties. It was found that blending of alginate with other polymers could increase both the mechanical strength and stability of the membrane in aqueous solutions. Zhang et al., [76] blended alginate with cellulose cuoxam; the increased mechanical strength of the blended membranes was attributed to the hydrogen bonding interactions between the hydroxyl groups of the two polymers. Yang et al., [77] blended alginate with cellulose, and further cross-linked the alginate using Ca\(^{2+}\). It was found that the tensile strength of the membrane was enhanced 12 folds, and more importantly, the good separating performance of alginate was retained.

Like sodium alginate, the chitosan membrane is extremely hydrophilic, and can lose membrane integrity in aqueous solutions. Accordingly, cross-linking and blending strategies [78, 79] were employed to suppress the excessive membrane swelling and achieve the enhanced membrane stability. Shieh and Huang [80] mixed a chitosan solution with that of polyacrylic acid, and very stable separating performance of the membrane was obtained. Earlier work in this regard was carried out by Richau et al., [81] using cellulose sulfate as a poly anion, which was mixed with various polycations, e.g., poly (ethyleneimine)(PEI), poly (dimethylallylaminechloride) (PDMDAAC), andpoly\((N,N\)-dimethyl-3,5-dimethylene-piperidiniumchloride)(PPIP), Pervaporation tests revealed that all these membranes demonstrated excellent membrane stability and dehydration performance.
1.13.b: Removal of dilute organics from aqueous streams

Removal of organics from water is a long-standing topic for environmental protection, and the adsorption technology plays a key role in this area. As pointed out previously, pervaporation demonstrates a competitive gap over the adsorption technology when multiple, or relatively high concentrations of organics are present in water, since pervaporation is a continuous process, and can offer the incomparable operation convenience than intermittent process. According to the literature, the crosslinked poly dimethylsiloxane membrane has found wide use in this application [82-84], since it shows high affinity and low transport resistance for organics, and is also very stable in the streams. Other rubbery materials were also attempted for the application, and showed all the materials [83, 85-87] demonstrated high selectivity for their respective organic(s).

Clearly, the challenge facing the pervaporation is not how to find the right material for specific applications, but how to fight against the concentration polarization to make full use of the good separating properties of the available membranes. Based on this understanding, some attempts have been directed to the concentration depolarization [88, 89]. The use of turbulence-promoting spacer in the membrane systems, and the introduction of the Dean vortices to the feed flow represent the two main strategies for coping with the challenge, the others also include two-phase feeding [90], and vibrating pervaporation modules [91].

1.13.c: Separation of organic mixtures

The org-org separation attracted lot of research interest from the very beginning of pervaporation [92], researchers have been motivated by the huge industrial needs of efficient methods for separating mixtures like benzene/cyclohexane, benzene/hexane, toluene/heptane, ethylbenzene/xylene,
p-xylene/o-xylene, etc. As it is known that the components in these pairs have similar physicochemical properties, and effective separation of these mixtures could be very difficult according to the solubility parameter theory. Even so, some attempts have been proved to be promising.

Ho et al., [93, 94] separated aromatics/saturate mixtures using the polyimide copolymer membranes, which contain both soft and hard segments. It is believed that the soft segments show preferential affinity for aromatics, are thus responsible for the selective performance of the membrane, while the hard segments provide mechanical integrity for the membrane. Based on this approach, Tanihara et al., [95, 96] used the polyetherimide segmented copolymer, and polyimide-co-polyphenylenediamine membranes for separating benzene/cyclohexane, benzene/heptane, and acetone/cyclohexane mixtures. The achieved separation factor of benzene to cyclohexane varied from 9 to 27, and the permeation rate varied from 0.4 to 2.7 kg/m² h.

Polymer blending was attempted by Neel et al. [97], Cabasso et al., [98, 99] for the separation of benzene/cyclohexane and other mixtures like methanol/hexane and styrene/ethyl benzene. The blended polymers are expected to demonstrate superior separating performance to the single materials. The difference is made by the resulting optimization in the blended polymer architectures through polymer chain entanglement and intermolecular interactions. The blended membranes showed very good balance between the permeation flux and the separation factor, while single polymers usually give either high permeation rate (e.g., polyphosphonates, polyethylene, polypropylene), but low separation factor, or fairly good separation factor, but very low productivity (e.g., cellulose acetate, poly(vinyl fluoride)) [99]. Cabasso et al., [98] blended cellulose acetate and polyphosphonates, and the achieved separation factors of benzene/cyclohexane ranged from 12 to 40, and
the permeation rates varied from 800 to 1000 ml/m² h. Similar results for the separation were also obtained by Acharya et al., [100] by using the blended membranes based on cellulose acetate and polybromophenylene oxide dimethylphosphonate ester. More recently, blending polymers with nanoparticles, or fine powders with nanostructures have been attempted by some researchers [101, 102] for the separations, and the preliminary results were quite encouraging. It is expected that nanotechnology will play an increased role in the near future. The complex interaction between olefins and silver ions (Ag⁺) was also utilized for separating olefin/paraffin mixtures. Koval et al., [103,104] used the perfluorosulfonate-Ag⁺ for the separation of styrene/ethyl benzene. The membrane was styrene-selective, and a selectivity of 36 was obtained while the permeation flux of the membrane was quite low, at the level of 10⁻¹⁰ mol/s cm².

Although some promising results have been achieved by using the above-mentioned approaches (e.g., copolymer, blending, and the complex interaction), the separating performance of the membranes is still below the standards expected by the industry. Research progress in this area advanced very slowly over the past decades, and more innovative efforts are thus needed to change this situation [97, 105-107].

Based on the Solution-Diffusion theory, Koros [108] pointed out that the advantage of the mobility difference of the organic species should also be taken for the efficient separation of the organic mixtures. For doing this, rigid glassy polymers or copolymers with cross-linkable segments should be selected since glassy polymers are generally more shape and size selective, and in order to suppress the plasticization effects of the penetrants for retaining or even improving the intrinsic mobility selectivity of the membrane, an appropriate degree of cross-linking of the glassy polymer should be performed. Xu et al.,
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[109] employed the rigid polyimide copolymer containing the cross-linkable functionality: 3, 5-diaminobenzoic acid, for separating toluene/iso-octane. The synergy between sorption and diffusion was also observed in membrane permeation, the sorption selectivity was increased from 3.5 to about 5.0 by introducing the cross-linkable segment into the polyimide chain, and a perm selectivity higher than 100 was achieved with the mobility selectivity being the main separation contributor.

The zeolite membrane represents another innovative approach for the organic–organic separation [110]. Compared with polymeric membranes, zeolite membranes can provide essentially non-swollen, well-defined, and molecular-sized pore structures. As such, zeolite membranes are particularly suited to separate organic mixtures with appreciable size differences although preferential sorption also plays an important role in the zeolite-resulting separations [111]. For the separation of organic mixtures like benzene / p-xylene, p-xylene/o-xylene, the uniform pore structures of silicalite-1 [112], Mordenite [113], and Ferrierite [114] zeolite membranes have demonstrated very good potential. At 303 K, with the 50/50 (mol) feed composition, the Ferrierite zeolite membrane [115] exhibited selectivity (benzene to p-xylene) of 100, and a benzene flux of 12 g/m2 h. Although synthesis of a thin yet perfect zeolite layer on support to ensure a satisfactory membrane flux is still a very complex process, with continued research efforts, the zeolite membrane will surely be able to play an important role in the organic–organic separation.

1.13.d: MOLECULAR SIEVES:

Molecular sieves are zeolites (a zeolite is a synthetic, highly ordered aluminosilicate) which have very precise pore sizes and are processed into small beads or pellets about the size of a garden pea. The pores openings are very small (openings generally measured in Angstroms or nanometers) but lead
to an internal structure which is much larger (similar to doorway leading to a much larger room). The molecular sieves used in IPA dehydration have pore sizes generally around 3 Angstroms in diameter. This opening is too small for ethanol molecules to enter as ethanol is 4.4 Angstroms in diameter. Water molecules are 2.8 Angstroms in diameter and can fit into the sieve pores. It is this size sorting property of the zeolite that is responsible for the "sieve" term in the descriptive name molecular sieve.

1.13.e: An introduction to molecular sieves [zolites]:

Zeolites are porous crystalline aluminosilicates and are widely used in applications such as catalysts in the refining of petroleum or as ion exchangers in detergents. Zeolite membranes are commercially interesting due to the potential ability to separate molecules in continuous processes in industry. Advantages compared to other membrane types are high flux and selectivity due to well defined pores and thermal and chemical stability. In high quality membranes the zeolite film must be thin for high flux and free from defects for high selectivity. To achieve high quality membranes, parameters controlling the properties of zeolite membranes must be understood.

A molecular sieve is a material that can separate molecules based on size and shape. A subgroup of molecular sieves is zeolites. Zeolites are natural and synthetic microporous aluminosilicates. The Swede Cronstedt reported for the first time about this new class of minerals in the 18th century and denoted it "zeolites" from the Greek word "zeo" and "litos" which means a boiling stone [116, 117]. The zeolite framework is a three-dimensional network of oxygen ions with either Si$^{4+}$ or Al$^{3+}$ situated in the tetrahedral sites. This framework may be described with the following formula:
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M<sub>2/n</sub>O. Al<sub>2</sub>O<sub>3</sub>. xSiO<sub>2</sub>. yH<sub>2</sub>O [71]
M: exchangeable cation for example Li<sup>+</sup>, Na<sup>+</sup> or NH<sub>4</sub><sup>+</sup>
n: cation valance
y: degree of hydration

All known zeolite frameworks have been assigned with a three-letter code. Today there are more than 170 known framework structures [118]. For a given framework, the chemical composition can be varied significantly by varying Si/Al ratio and cations. Zeolites can also be depicted as a network of channels were the dimensions of the channel openings vary from zeolite to zeolite, ranging from 3 to 13 Å [117]. Zeolites are used in applications in primarily three areas; adsorption, catalysis and ion exchange. The most common application for zeolites is as water softener in detergents. Other applications are gas separation and as catalysts in the refining of petroleum [119, 120].

Zeolites are commonly prepared by hydrothermal treatment. The synthesis mixture mostly contains water, a silica source, an alumina source, a mineralizing agent and a templating agent. The synthesis mixture is heated and the composition of the synthesis solution, synthesis time and synthesis temperature determines which zeolite that will crystallize. To remove the templating agent, the zeolite must be calcined after synthesis; a procedure where the zeolite is heated in air to decompose and burn the templating agent that is blocking the pores.

The Si/Al ratio is an important characteristic of zeolites. Zeolites are classified as low Si/Al zeolites [1 ≤ Si/Al < 2], intermediate Si/Al zeolites [2 < Si/Al ≤ 5], high Si/Al zeolites [Si/Al >5] and pure silica molecular sieves. As the Si/Al ratio increases, the properties of the zeolite are modified. The lower the Si/Al ratio, the more cations will be required to balance the framework
charge. Large cations will decrease the effective pore opening. When the Si/Al ration is increased, the acid strength, thermal stability and hydrophobicity are increased, whereas the catalytic activity and the ion-exchange capacity are decreased.

As a consequence of these achievements, the classical definition of zeolites is no longer applied. Instead, the term “zeolitic” or “zeolite type materials” is now commonly used to cover both conventional and new structures and compositions.

1.14: Polymeric materials for Pervaporation membranes

There are many kinds of polymeric materials which may be called glassy polymers, rubbery polymers, and ionic polymers. A polymer is considered as a glassy polymer/rubbery polymer if it is in a glassy state/amorphous state at room temperature. A polymer is considered as an ionic polymer when it carries ionic groups. Ionic polymers can be either glassy or rubbery.

The choice of the polymer depends strongly on the type of application. Glassy polymers with hydrophilic functional groups are suitable for making water-selective membranes used for solvent dehydration, and rubbery polymer membranes normally do not contain hydrophilic functional groups. Therefore, they are favorable for the removal of organic compounds from water. However, there are some exceptions. 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 cross-linked 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 chitosan (CS), sodium alginate (SA) / gelatin (GL) and sodium alginate (SA) need cross-linking for improved stability and selectivity. The polymer materials for dehydration membranes should maintain a proper balance of hydrophilicity and hydrophobicity.

Polymers with high selectivity and low permeability are often preferred for further study over membranes with low selectivity and high permeability, since the disadvantage associated with low permeability can be partly overcome by introducing asymmetry to the membrane structure.

Improvement in membrane performance can often be achieved by polymer modification, for which several techniques have been developed, including cross-linking, grafting, blending, copolymerization, and incorporation of molecular sieve materials (Zeolites and CNTs). For making dehydration membranes, chitosan (CS), sodium alginate (SA)/gelatin (GL) and sodium alginate (SA), Sodium carboxymethyl cellulose (NaCMC) based polymers are the most widely used materials. The modifications of above said polymers are necessary for improved selectivity, stability and performance testing for various perspective applications.

1.15: Literature Survey

The PV technique has widely been used in many industrial areas, such as in the dehydration of alcohols [63, 121-122]. Isopropyl alcohol (Iso-OH) is an important organic solvent used in the commercial production of acetone and
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also used on a large scale in chemical industry as well as in pharmaceutical laboratories. Further, it has also been used in semiconductor and liquid crystal display industries as a water-removing agent [123]. Isopropanol and water form an azeotropic mixtures at 85.3 mass% of Isopropanol concentration.

Toti et al. [124] prepared the blend membranes of SA and Acryl amide grafted guar gum in the ratios of 3:1 and 1:1 and studied the pervaporative separation of water isopropyl alcohol mixtures over the entire range of mixture composition at 30°C. Liu et al. [125] used poly (ether-block-amide) (PEBAX 2533) membrane for the study of the separation of acetone/butanol/ethanol from dilute aqueous solutions by PV. Toutianoush et al. [126] used polyelectrolyte ultra thin multi layer composite membranes for pervaporative separation of alcohol mixtures. The optical resolution of α–amino acids including tryptophan and tyrosine are studied by a pressure driven separation process, using self supporting crosslinked SA membranes [127]. Studies on the synthesis and characterization of polyacrylamide grafted SA membranes for pervaporative separation of water/isopropanol mixtures are carried out by Toti et al. [128]. Thermal, viscoelastic, solution and membrane properties of SA/HEC blends have been evaluated by Naidu et al. [129].

Among the natural polymers, chitosan, sodium alginate and cellulose have been commonly used. Of these, Sodium alginate is a naturally abundant polysaccharide extracted from seaweeds and has good water selectivity. Yeom and Lee [72, 130] prepared nascent and crosslinked (glutaraldehyde) sodium alginate (SA) membranes to study the effect of feed temperature, cell temperature and crosslinking density in the membrane, for the vapour permeation of ethanol/water mixtures. Such membranes were used for the PV dehydration of alcohols. Mochizuki et al. [71] studied the relationship between permselectivity of alginic acid membrane and its solid-state structure as well as
the effect of counter cations on membrane performance. However the high hydrophilic nature of the membrane due to the presence of hydroxyl and carboxyl groups made it mechanically less stable when compared to other hydrophilic membranes. Haung and co-workers [131] prepared a novel two-ply dense composite membranes using successive casting of sodium alginate and chitosan for the dehydration of Isopropanol and ethanol. Uragami and Saito [70] used alginic acid membranes for the PV separation of alcohol-water mixtures. Aminabhavi and co-worker [125, 132], prepared the blend membranes of sodium alginate with poly (vinyl alcohol) and were employed to separate water-Isopropanol mixtures. Preparation and characterization of filled matrix membranes of sodium alginate incorporated with aluminum-containing mesoporous silica for pervaporation dehydration of alcohols was carried out by Patil et.al. [133].

Yang et al. [77] prepared cellulose / alginate blend membranes and evaluated the effects of Ca²⁺ crosslinking and operating temperature on the permeation flux and separation factor. Aminabhavi et al. [134] worked on computer simulation and comparative study on the PV separation characteristics of SA and its blend membranes with PVA to separate aqueous mixtures of 1,4-Dioxane or terahydrofuran (THF). Toti and Aminabhavi [135] studied the different viscosity grades of SA and modified SA membranes in pervaporative separation of water/acetic acid and water/isopropanol mixtures. Bhat et.al. [136] studied the Pervaporation-aided dehydration and esterification of acetic acid with ethanol using 4A zeolite-filled cross-linked sodium alginate-mixed matrix membranes.

Efforts have also been made to increase the membrane performance of sodium alginate by blending, grafting with different hydrophilic polymers like poly (vinyl alcohol) and cellulose [137-138] for the dehydration of alcohol,
with gaur gum-grafted-poly (acrylamide) [139] for the PV separation of water-acetic acid mixtures and with hydroxyethylcellulose [140] for separation of water-1,4-dioxane and water-THF. Mino and Kaizerman (1958) grafted monomers like acrylamide, acrylo nitrile and methyl methacrylate on poly (vinyl alcohol) using Ce⁺⁴ initiator. Due to the presence of carboxylic groups, sodium alginate acts as a polyelectrolyte and hence it was proposed for use as a thin layer coating in many polyelectrolyte composite membranes [141-142]. Other composite membranes [143-144] of sodium alginate with different hydrophilic and hydrophobic supports also exhibit good PV performance. Aminabhavi et al. prepared blends membranes of NaAlg with PVA [145] and graft copolymeric membranes of PAAm with NaAlg [146]. The blend membranes of NaAlg with PVA [147, 148] and PAAm-g-guar gum [126] have also been used for the PV separation of water + isopropanol mixtures. Apart from these membranes, a variety of cellulose-based membranes have been used [149-155] in the PV dehydration studies. Naidu, Boya Vijaya Kumar et.al. [156] studied Pervaporation Separation of Water/2-Propanol Mixtures by Use of the Blend Membranes of Sodium Alginate and (Hydroxyethyl) cellulose: In this study they discussed the role of Permeate Membrane Interactions, Zeolite Filling, and Membrane Swelling on flux and selectivity of the dehydration of alcohol.

Savage and Thers, 1971; Dalal and Narukar, 1991; Naidu, Sai ram et al. 2005 have widely tested natural polymers as PV membranes in liquid separations. The other natural polymers, Methyl cellulose, Carboxy Methyl Cellulose and Dextrin are water soluble and water swellable cellulose ether, which were compatible with a wide range of water-soluble polymers [157-159]. The Characteristics of alginate membranes for the PV dehydration of ethanol/water and isopropanol/water mixtures are tested by Hung et al. [75].
Dong et al. [160] showed high selectivity and promising permeability for PV dehydration of isopropanol, n-butanol, tert-butanol and ethanol aqueous solutions using a poly (vinyl alcohol)/sodium alginate blend membranes supported by polysulfone and crosslinked with maleic acid. Lu et al. [161] synthesized the novel interpenetrating polymer network membranes from poly (vinyl alcohol) (PAV)/poly (vinyl pyrrolidone) (PVP) blends of different compositions. The two polymer components are independently crosslinked chemically with glutaraldehyde and photochemically with $4,4' -$ diazostilbene-2, 2$'$ - disulfonic acid isodium salt. The membrane performances are studied in PV of tetrahydrofuran (THF)/water and THF/methanol mixtures. Kittur et al. [162] analyzed swelling behavior of SA and its zeolite-incorporated membranes and the PV separation of water/acetic acid mixtures. Aminabhavi et al. [149] prepared SA/PVA blend membranes for PV separation of water/isopropanol mixture and studied the modeling and simulation aspects of the membranes. Biduru et al. [163] prepared crosslinked membranes of deacetylated chitosan biopolymer using 2, 4-tolylene diisocynates (TDI) and tested for the separation of t-butanol/water mixtures for PV. Kurkuri et al. [132] synthesized the blend membranes of SA and PVA for the PV separation of water/isopropanol mixtures. Adoor et al. [164] studies the pervaporation dehydration and esterification of ethanol and acetic acid by using matrix membranes.

Aminabhavi et al. [165] synthesized the grafted co polymeric membranes, of poly (vinyl alcohol) PVA and polyacrylamide (PAAm), for the separation of water/acetic acid mixtures. Mandal and Pangarkar [166] explained the membrane selection criteria based on solubility parameter, structural impact for a particular component separation with the help of pervaporative dehydration of water form a mixture of water and 1 – methoxy propanol. Urtiaga et al.
[167] looked at dehydrating THF using zeolite based membrane from the SMART chemical company. Baleen et al. [168] performed pervaporative experiments with alcohol/water and acetic acid/water mixtures to investigate the influence of molecular weight and polarity on the permeation behavior. [Y.Q. Dong et al. [169] prepared and characterized the poly(vinyl alcohol)-sodium alginate hollow-fiber composite membranes and used for the pervaporation dehydration characterization of aqueous alcohol mixtures.

The effects of feed temperature, feed concentration and carbon molecular sieve (CMS) content on the PV process for acetic acid/water has been investigated with carbon molecular sieve (CMS)-filled poly (dimethyl siloxane) (PDMS) membranes by Lei et al. [170]. Bhat et al. [171] studied Zeolite K-LTL-loaded sodium alginate mixed matrix membranes for pervaporation dehydration of aqueous–organic mixtures.

In recent years, the trend has been shifted towards developing a variety of modified forms of NaAlg. Such modified membranes have shown the superior separation performances over the pristine NaAlg membranes. Particularly, mixed matrix membranes have been studied. NaAlg, being hydrophilic, could help to extract more of water molecules than the organic component from a mixed water-organic media. In the reported literature, isopropanol, 1, 4-dixane, tetrahydrofuran (THF), acetonitrile, ethanol and acetic acid have been successfully dehydrated using variety of NaAlg or NaAlg-based membranes. In earlier studies, dehydration of organic solvents has yielded poor selectivities. Earlier, Wang et al. [172] prepared the polyamide/SDS-clay hybrid nanocomposite membranes and tested for PV separation of water-ethanol mixtures and found that SDS-clay content has an effect (when dispersed in to a hydrophobic polyamide) on its PV performance. Bhattacharyya et al. [173]
studied the pervaporation of water form an aqueous alcohol solution with Mitsui Engineering and Shipbuilding’s NaAlg Zeolite membrane.

Zeolite membranes have advantages over polymer membranes, such as better chemical and thermal stability, and have the great potential to separate the mixtures of molecules through both the adsorption and molecular sieving because zeolite material have uniform, molecular-sized pores. The idea of adding adsorptive filler to the polymer matrix to enhance membrane separation performance was in proposed in 1987 by the UOP researchers for gas separation [174] and the Netherlands Scientist for liquid separation [175]. K. Mallikarjuna Reddy et.al. [176] developed the Sodium alginate-TiO₂ mixed matrix membranes for pervaporation dehydration of tetrahydrofuran and Isopropanol.

Suzuki [177] patented the first preparation of zeolite membranes in 1987. Since then, small pore, medium pore and large pore zeolite membranes have been prepared on metallic supports for different applications. Yeh et al. [178] studied the dehydration of water-alcohol mixtures by vapor permeation through PVA/clay nanocomposite membranes and found that permeation rate has decreased, but selectivity increased as the clay content increased. Kita et al. [179] synthesized NaY zeolite membranes for water/ethanol pervaporation. Recently, Bhat and Aminabhavi [180-184] studied the PV separation performance of novel hybrid composite membrane prepared by incorporating various types of zeolites like NaY,4A, AIPO₄-5, MCM-41 and sodium montmorillonite particles in to sodium alginate crosslinked with glutaraldehyde has been investigated for the dehydration of isopropanol, 1,4-dioxane and tetrahydrofuran from their aqueous solutions have shown the pronounced increase in membrane performance. M.Y. Kriduraganavar et al. [185-186] prepared mixed matrix membranes of NaY zeolite filled chitosan and sodium
Alginate membranes for the dehydration of water-isopropanol mixture shown the best and most stable PV separation characteristics. Z. Gao et.al [187] has reviewed different Application of zeolite-filled pervaporation membrane.

Lizon et al. [188] investigated the performance of commercially available polymeric, microporous silica and zeolite PV membranes with respect to the dehydration of binary mixtures of t-butanol/water. Lizon et al. [189] made a comparative study of commercially available polymeric and microporous silica membranes for the dehydration of isopropyl alcohol/water mixtures by vapour permeation. The permeation and separation characteristics of poly (vinyl alcohol) grafted acrylonitrile (PVA-g-AN) membranes are studied as a function of membrane thickness, feed composition, operating temperature and pressure for the pervaporative separation of acetic acid/water mixtures by Alghezawi et al. [190]. The influence of operating parameters such as feed composition, membrane thickness and permeate pressure on flux and selectivity of pure and crosslinked chitosan membrane performance is investigated in dehydration of isopropanol by Anjali et al. [191]. Kujawski [192] studied the effect of feed composition on flux and selectivity for three hydrophobic membranes for the separation of organic solvents from their aqueous solutions. Rezac et al. [193] addressed the effect of copolymer composition of the solubility and diffusivity of water and methanol in a series of polyether amides. H. Sudhakar et.al. [194] prepared 4A Zeolite-filled sodium alginate membranes and characterized them. These membranes utilized for Pervaporation separation of IPA-water mixtures.

1.16: Today’s pervaporation

Pervaporation is often used when the molecule sizes that need to be separated are relatively small such as between low-molecular weight solvents and water, where traditional separation processes such as distillation are not
effective due to azeotropy or the energy costs of running a traditional style separation process are extremely high.

There are different types of membranes available today which can be used in a wide range of applications depending on the individual characteristics of the membrane. In the case of solvent dehydration where there is a low concentration of water that needs to be separated from a solvent, hydrophilic membranes are often used as they preferentially allow water to permeate through, producing a permeate with a high-water content and dehydrating the solvent in the retentate. Hydrophilic membranes are designed to incorporate attractive interactions between water and the membrane material such as dipole-dipole interactions, hydrogen bonding and ion-dipole interactions [191]. Conversely, when a small amount of solvent is required to be removed from a stream comprising mostly of water, hydrophobic membranes can be used that will leave water in the retentate whilst allowing the solvents to pass across. To have still better results with higher flux and selectivity today's Pervaporation studies on dehydration of organic liquids are being conducted with zeolite filled hydrophilic polymer membranes. Because of introduction of zeolite the hydrophilic still enhanced and more flux and selectivity can be obtained.

1.17: Importance of NaAlg based membrane for Pervaporation Studies:

Ethanol /Isopropanol is widely used in chemical industries. A large amount of high purity Ethanol/ isopropanol is always in demand for cleansing in industries, especially in the electronics, paint industry, in many more pharmaceutical industries. However, isopropanol and water form an azeotrope (water ~12.6 w%/w) in common distillation. Separation/purification of Ethanol / isopropanol from water by traditional distillation is difficult, and alternative
methods are needed. Because of its outstanding characteristics, pervaporation has become one of the promising techniques that can be used for dehydration of Ethanol/ isopropanol. A part of this thesis, therefore, is aimed at developing new pervaporation membranes and also trying to understand the relationship between membrane materials and separation performance.

1.18: Scope of the present investigation

There is a huge demand for alternative separation technologies, which are more economical and safe than ordinary and extractive distillation for the separation of aqueous-organic azeotropes. The study attains a great deal of significance since the proposed PV technique posses the following advantages over conventional separation technologies.

- Very economical
- Low capital, maintenance costs
- High safety and environmentally clean
- Membrane modules can be arranged and replace as per need

The scope of the present study is to prepare pure membranes and zeolite filled composite membranes for the dehydration of water-Ethanol and water-Isopropanol. NaAlg is an effective polymer material for PV dehydration because of its high hydrophilicity and good chemical resistance. Since NaAlg has poor stability in aqueous sol's several techniques such as crosslinking, and incorporation of inorganic fillers are used to create a stable NaAlg membrane with good mechanical properties and selective permeability to water. Current NaAlg membranes used for PV were cross-linked with GA. The hydroxyl groups of NaAlg react readily with aldehydes and hence crosslinking reaction takes place easily. Since GA an aldehyde is useful in chemical crosslinking reaction and would be more effective with more resistant membrane.
Though pristine NaAlg membranes are proven materials for the dehydration of alcohols, their performance has not been satisfactory for the separation of water from organics such as Ethanol /Isopropanol, due to low selectivities and flux. Selective separation of water from Ethanol/water and IPA/water mixtures using the zeolite filled NaAlg membranes have been attempted.

In the present investigation, we have prepared mixed matrix membranes for the dehydration of water-Ethanol and water-Isopropanol. This will impart excellent transport characteristics to the membranes for an effective separation of water-Ethanol and water-Isopropanol from the aqueous mixture. In water-Ethanol and water-Isopropanol, there exists a strong intermolecular interaction between the components due to the presence of dipole-dipole interactions as evidenced by a large negative excess volume data. Such mixtures are difficult to separate by conventional techniques, because they form azeotropic mixtures at lower composition of water inhibiting their separation by conventional methods. Separation of such mixtures by simple distillation requires entertainers as well as large amount of energy.

Also, in the present study, mixed matrix NaAlg membrane (MMM's) filled with ZSM-5 zeolite, 3A zeolite and HY zeolite were prepared to overcome the drawbacks of pristine NaAlg membrane. Since separation through such mixed matrix membranes can be achieved by selective permeation of a liquid mixture, MMM's could enhance the removal of one or more of the reactant or product species from the feed. In particular, zeolite filled mixed matrix membranes have been widely used in boosting the PV separation characteristics over neat and blended membranes. This was followed by crosslinking of the membranes with GA to reduce swelling and introduce
specific properties such as structural strength along with thermal and mechanical stability.

The present research also explores the separation performance for varying water composition in the binary feed mixture, and mixed matrix membranes (MMM's) respectively. Further all the membranes were characterized using various techniques. Formation of ionic interactions and the constituents present in the membrane was analyzed by Fourier transform infrared spectroscopy (FT-IR) spectroscopy. Thermal stability and morphological properties of the membranes was investigated using, Thermogravimetric analysis (TGA) and Scanning electron microscopy (SEM), respectively. Mechanical stability of the membranes was assessed by Universal testing machine (Make: Instron, UK).

Membranes were subjected to sorption studies to evaluate the extent of interaction and degree of swelling in different compositions of water/IPA and water/ethanol mixtures ranging from 5 to 20 wt% of water in the feed at different temperatures 30, 40 and 50$^\circ$ C. The influence of the zeolite content and feed composition on membrane performance like flux and selectivity was also investigated.
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