CHAPTER I

INTRODUCTION

TO PERVAPORATION
CHAPTER-1

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ABSTRACT

This chapter deals with the history and classification of membranes, about different 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 blending and filling the polymer matrices with inorganic fillers. This chapter also includes a brief discussion about the factors affecting the membrane performance such as flux, selectivity and pervaporation separation index (PSI) etc. It also covers a brief survey of literature regarding the earlier studies related to the polymers, zeolites, isopropyl alcohol and crosslinker used in the present study.
1.1 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 [1]. 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 is 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 [1].

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 Scivers 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>
<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 fur 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>
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</table>
1.2 Background

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 [2]

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 1.1 shows a schematic membrane process [2, 3]. 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 [4], but no extensive research was carried out until in the 1950s by Binning et al., [5]. 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 [6]. Currently, pervaporation membranes and processes are being studied in many laboratories and companies, such as Sulzer Chemtech, MTR, Exxon and Texaco [7, 8].
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.

![Schematic general membrane separation process](image)

**Fig 1.1:** Schematic general membrane separation process

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 [8, 9]. 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 Kværner). Later, Generon (now MG) introduced a membrane system to separate nitrogen from air, followed by the competitive membranes from Dow, Ube and Du Pont [10]. Applications of membrane gas separation technology keep
expanding, and further growth is likely to continue for the next decade [8]. 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 [11].

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 [12 -17]. Based on the experimental structure-property results, some mathematical methods were developed to predict the permeability of polymers to gases [18-22].

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.

1.3. Definition of membrane

Membrane is 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.

1.4. 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 1.2.
1.5. Classification of membrane processes

In membrane separation process separation is achieved due to the difference in rate of transport and diffusivities of different species through the membrane. Membrane is a highly selective and controls the transportation of the components from one side to other. Based on driving forces separation is broadly classified as follows and summary of membrane separation technologies is presented in Table 1.2.

a. Pressure driven process
b. Concentration driven process
c. Voltage driven process
Table 1.2 Summary of the established membrane separation technologies

<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>Steril filtration, Clarification</td>
</tr>
<tr>
<td>Ultrafiltration</td>
<td>Asymmetric microporous, 1-10 nm</td>
<td>Polysulfone, Polypropylene, Nylon6, 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, Cellulosicacetate, 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>
</tbody>
</table>
1.6 Advantages of membranes technologies

The technologies of membrane separation have been developing to be the top of process separation. The advantage of membrane separation has been found in certain processes such as producing, separation, recovering, and drying [11]. 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 cost effective and environment friendly.
- These polymers not only exhibit 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 used large or complex machine that have to more from a part of plant to another part of plant. It only consist some instrument that is easy to operate. This process can be continuously.

1.7. Pervaporation

Pervaporation is a membrane-based separation process that has elements in common with reverse osmosis and membrane-based gas separation, where liquid permeation through the membrane is followed by evaporation. In pervaporation, the liquid mixture to be separated (feed) is placed in contact with one side of a membrane and the permeate product is removed as a low-pressure vapor from the other side. The permeate vapor is then condensed and collected, or, released as a vapor product. The chemical potential gradient across the membrane is the driving
force for the mass transport which can be created by either a vacuum pump or an inert purge stream.

**Application of Pervaporation**

The applications of Pervaporation can be classified into three categories.

- Dehydration of organic solvents
- Removal of dilute organics from aqueous streams
- Separation of organic mixtures

1.8. Literature Survey

Isopropanol, a widely used solvent in chemical and pharmaceutical industries is known to form an azeotrope with water, at 85.3 mass % of IPA [23] a characteristic stage that creates difficulties in its recovery by the conventional distillation [24]. The application of PV as a means to achieve dehydration of solvents has received a wide spread attention from chemical, petrochemical and pharmaceutical industries. The IPA boiling point is 82.5°C and it forms azeotropic mixture at 85.3 mass% of IPA [23]. It can also be used in semiconductor and liquid crystal display industries as a water removing agent [24, 25]. IPA is an important organic solvent used in the commercial production of acetone through catalytic dehydrogenation process. It is also useful in the production of hydrogen peroxide as an anti-icing agent in gasoline and as extracting solvent in fish protein concentration process. In chemical process engineering areas, there is a need to concentrate/purify IPA from water.

Dehydration of isopropanol has received great attention from industries due to the price of isopropanol and its uses in various industries. It is generally used as solvent for oils, gums, waxes and variety of cosmetics and as a cleaning agent in the semi conductors. Due to its vital role in various industries such as pharmaceutical, paints, semi-conductor and LCD, most of the research efforts of the pervaporation have concentrated on the separation of alcohol-water system. IPA is an important basic solvent in the industry ranging among the top 10 organic intermediates. Because of the small difference in the volatility’s of water and IPA in dilute aqueous solutions, azeotropic distillation is used instead of normal binary solutions so that
the process in an energy intensive process. From this point of view the pervaporation separation of IPA/water mixture can be one of the alternative processes for saving energy.

The application of PV as a means to achieve dehydration of solvents has received a wide spread attention from chemical and pharmaceutical industries. However, the recent technology improvements have lead to a rapid commercialization of several novel membranes that are economical, safe and clean to be used in the separation of azeotropic and close boiling liquid mixtures by the PV technique [26].

Considerable literature on the successful dehydration of IPA using PV technique is available [25, 27-30]. Dehydration of IPA was attempted by Anjali devi et al., [32] using crosslinked chitosan membranes and obtained flux of 0.39Kg/m²h with a selectivity of 472. Moon et al., [25] used the two-ply composite membranes of CS and SA and obtained a flux of 554 g/m²h and separation factors of 2010 at 95% IPA in the feed. Recently, Veerapur et al., [32] obtained a flux ranging from 0.226 to 0.391Kg/m²h for CS-HPMC blend membrane containing 40% HPMC in the blend and the selectivity ranges from 453 to 80 over the composition range of 10-30 wt% water in the feed.

In another study Toti and Aminabhavi [29] obtained a highest flux of 74.7 g/m²h for 10%water in the feed and the separation selectivity obtained in this case is 5 in the dehydration studies of IPA using SA/PAAm-g-GG blend membranes. Membranes based on PAAm-g-SA have been prepared by Toti and Aminabhavi [33] for the dehydration of IPA. They reported the flux of 112.2 g/m²h where the water content in the feed is 70% and also found a separation selectivity of 10.9 at the same feed composition at 30°C. Kittur et al., [34] obtained a highest separation selectivity of 2620 with a substantial flux of 11.50X10⁻² Kg/m²h at 30°C. K. Mallikarjuna Reddy et.al. [35] developed the Sodium alginate - TiO₂ mixed matrix membranes for pervaporation dehydration of tetrahydrofuran and Isopropanol. Swayampakula Kalyani et.al.[36] conducted pervaporation studies for the dehydration of ethanol-water mixtures through sodium alginate membranes. R.S.Veerapur et.al.[37] prepared the Sodium alginate – magnesium aluminum silicate mixed matrix membranes for pervaporation separation of water – isopropanol mixtures. A
Krishnaiah et al., [38] studied the blend membranes of sodium alginate and hydroxyethylcellulose for pervaporation-based enrichment of t-butyl alcohol. Dachano Kunnakorn et al., [39] studied for the Optimization of synthesis time for high performance of NaA zeolite membranes synthesized via autoclave for water–ethanol separation.

Poly vinyl alcohol has received a great deal of attention due to its considerable application either pure or composite form with other materials. PVA is known for its excellent film forming properties, currently this polymer was chosen for the manufacture of membranes for PV dehydration studies [40]. These membranes were extensively used in many industrial dehydration units. They generally showed excellent selectivity towards water in organic solvents, but with rather low permeabilities, especially where the organic solvent are short chain alcohols. Although PVA is known as semi-crystalline polymer it seems that there were no detailed studies on the correlation between its crystallinity and its transport properties in PV.

PVA is a water-soluble bio-compatible polymer [41] consequently; much attention has been paid to the applications of PVA membranes for pervaporation [40,42] dehydration of organic solvents. PVA is the most selective polymer in PV with regard to the dehydration alcohol/water mixture [43]. PVA has been successfully utilized with the other polymer such as CS for PV separation of organic water mixtures [44,45]. Zhen Huang et al., [46] studied the dehydration of ethanol using various zeolite (3A, 4A, 5A NaX and NaY) filled PVA composite membranes and concluded that zeolite filled membranes showed higher separation factor, higher fluxes and higher selectivity than unfilled PVA membranes. Recent works [47-49] on IPA and butanol dehydration demonstrated with high water perm selectivity and durability suing commercial PVA based multi layer membranes. The crosslinked PVA membranes have been frequently investigated for membrane based separations because their hydroxyl groups have strong interactions with water through hydrogen bonding [50].

A complete survey of the literature for the preparation of NaCMC/PVA blend membranes has been widely collected. Many efforts have been made in the literature to increase the PVA membrane performance by blending it with different
natural polymer [30,51]. Lu et al., [52] prepared the PVA/CS hybrid membrane filled graphite for pervaporation of benzene and cyclohexane mixture and found the highest separation factor of 59.8 and permeation flux of 124.2 g/m²h containing 40% graphite in the blend membrane.

Sodium carboxymethyl cellulose (NaCMC) is a water soluble carbohydrate. It is a carboxymethylether of cellulose and is composed of β-(1→4) D-glucopyranose polymer. It is a non-toxic, biocompatible, bio-degradable and abundant [53-56]. It finds wide applications ranging from technological industries to the biological, pharmaceutical, petroleum and medical fields [57-60]. It is used as a bulk latexive and as an emulsifier, viscosity modifier and thickener in cosmetics and pharmaceuticals and as a stabilizer for reagents. NaCMC is used as a controlled drug release and biomedical membrane material [61-64].

Very limited studies on NaCMC membranes for pervaporation were reported in the literature. Liuyun et al., prepared the composite membrane by blending NaCMC with chitosan [65] filled with nano-hydroxyapatite. Blend membranes based on NaCMC/CS crosslinked with GA has shown good mechanical property and were used in the fields of pervaporation separation of water-ethanol mixture, separator in electro-generation, anti adhesion after operation [66-68]. Zhao et al., [69] prepared CS/NaCMC polyelectrolyte complex for pervaporation dehydration of their homogeneous membrane and obtained flux of 1.14 Kg/m²h, and selectivity of 1062.

Effort have also been made to increase the PVA membrane performance by blending it with different polymers like CS, SA for PV separation of organic-water mixtures [44, 45, 70] controlled drug release [71-73] and other biomedical applications [74]. Due to its crystalline nature PVA membranes give a low flux for water. To overcome this, blending of PVA with NaCMC was carried out by reducing crystallinity without significantly altering the selectivity; additionally, ionic interaction between PVA and NaCMC could probably improve the separation by reducing the organic sorption due to “salting out effect”.

NaCMC can be used to develop blends with PVA, since it can form highly selective and permeable blends with another hydrophilic polymer like PVA. Blends
of NaCMC with other polymers such as, PVA, gelatin etc., have been used in controlled drug release studies [61, 62]. In the earlier literature very few reports are available on NaCMC membranes for pervaporation of water-alcohol mixtures [65]. NaCMC has many bio-medical applications [63, 64], but in dehydration studies aqueous-organic mixture, its carboxyl group can be easily modified. NaCMC swell in water and hence, it can be crosslinked by a suitable agent to improve its mechanical strength and its selectivity during PV experiment. GA has been extensively used as a cross-linking agent for various polymeric membranes in pervaporation dehydrations of water alcohol mixtures [66].

It can be anticipated that a mixture of NaCMC and PVA probably will present the advantages of both components. However, application of NaCMC/PVA blends in the field of membrane separation is not reported in the earlier literature. In this study miscibility studies of NaCMC/PCA blends at various blend compositions was studied and were used for pervaporation dehydration of IPA/water mixture. These polymer blends have both inherently ionic-crosslinking structure and ionized carboxyl groups, which could be proved with good selectivity and hydrophilicity, respectively. So, it is expected that membranes made of NaCMC/PVA may be able to greatly improve its permeation flux in PV dehydration while maintaining its selectivity.

The key to the success of process is the fabrication of suitable membranes yielding both high permeability and selectivity [75]. Since most polymer membranes suffer from the inherent drawback of trade-off effect between permeability and selectivity [76, 77]. Many physical and chemical methods were introduced to modify the existing polymer material, trying to cross the trade off hurdle meet the practical application requirements. Among them, blending and incorporation of solid fillers are the two most frequently employed methods due to their simplicity and versatility. Blending one polymer into another polymer can significantly alter polymer chain mobility through the intermolecular interaction which results in the increase of the permeation flux and decreases the separation factor for blend membranes [44, 45, 69, 70]. On the other hand, incorporating solid filler into polymer can remarkably improve the solubility property through the preferential
adsorption which often results in the increase in separation factor and decrease the permeation flux.

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 proposed in 1987 by the UOP researchers for gas separation [78] and the Netherlands Scientist for liquid separation [79].

Zeolite filled membranes were introduced by Hennepe et al., [79]. He found the improved flux and selectivity on addition of silicate to silicone rubber membrane in the separation of alcohols from dilute mixtures. Gao et al [80] prepared various types of zeolite filled hydrophilic membranes with PVA as a polymer matrix were prepared and investigated the composite membrane performance and compared with un-filled membranes. An extensive summary of current advance and potential application of pervaporation through zeolite membranes has been made recently by Okamoto et al., [81], Van de Berg et al., [82] have reported successful application of zeolite membranes for organic dehydration. One of the drawbacks of these pure zeolite membranes is high cost and more brittle. Alternatively, zeolite filled MMM’s are now-a-days widely used because these are cost-effective, small amount of zeolite is enough for the Job and often easier to fabricate than plain zeolite membranes. Recent studies [83-88] on PV dehydration of organics have dealt with different types of MMM’s containing Zeolites, mesoporous materials, clays and Alumino-phosphates. These MMM have offered high selectivity and flux than pristine polymer membranes.

Experimental studies have shown that the incorporation of Zeolites usually results in an increase of either separation factor [89-91] or flux [80, 92, 93] for many liquid separations. Expect a few systems where both separation factors and flux have risen [79, 93 - 97]. Okumus et al., [92, 93]. have reported that the incorporation of zeolite A and 13 X into cellulose acetate (CA) or poly (acrylonitrile) (PAN) have caused a decrease rather than an increase in separation factor, SEM results indicate that increased porosity subsequently lead to an increase in the flux Goa et al., [80]
have fabricated hydrophilic composite membranes that consist of A-type and X-type zeolites and PVA and noticed that an enhanced permeation flux could be obtained with little or no decrease in separation factor and also observed flux increased with increasing zeolite pore size.

Pioneer works on mixed matrix membranes have clarified the importance of the proper choice of polymer materials and zeolites for different pervaporation requirements [80, 89-97]. Hydrophilic polymer and filler membrane appropriate for dehydration purposes [97]. High perm selectivity and durability could be achieved as demonstrated by recent works on Iso-propanol and butanol dehydration using PVA-based multi layer membranes [47-49]. Guan et al developed PV-PAN filled with KA zeolite for dehydration from aqueous alcohol solution [98] and observed that flux and selectivity increased on addition of KA zeolite. Hung et al., [99], used various zeolites [KA, NaA, NaX, NaY] silicalite-I and beta zeolite for the dehydration of ethanol/water mixture and observed the enhancement in separation factor, flux and high selectivity on addition of various Zeolites.

1.9 Aim and Scope of the Present work

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.

a) Very economical
b) Low capital, maintenance costs
c) High safety and environmentally clean
d) 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, blending and incorporation of inorganic fillers are used to create a stable NaAlg membrane with good
mechanical properties and selective permeability to water. Current NaAlg-HPC blending membranes used for PV were cross-linked with GA. The hydroxyl groups in blending NaAlg-HPC membrane 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 Ethanol / Isopropanol, due to low selectivities and flux. Selective separations of water from Ethanol / water and IPA / water mixtures using the NaAlg-HPC blending membranes have been attempted.

In the present investigation, we have prepared blend membranes for the dehydration of water-Ethanol and water - Isopropanol. This will impart excellent transport characteristics to the blend membranes for an effective separation of 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 excel 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 entertainer as well as large amount of energy.

Also, in the present study, blend membrane NaAlg – HPC were prepared to overcome the drawbacks of pristine NaAlg membrane. Since separation through such blend membranes can achieved by selective permeation of a liquid mixture. 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 blend membranes 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). Thermal stability and
morphological properties of the membranes was investigated using, Thermo gravimetric analysis (TGA) and Scanning electron microscopy (SEM), respectively.

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° C. The influence of HPC content and feed composition on membrane performance like flux and selectivity was also investigated.
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