1.1 Separation processes

Separation processes has importance in the manufacturing of the chemical process industries. They are used for important tasks as removal of contaminants from raw materials, recovery and purification of primary products and elimination of contaminants from effluent water and air streams. There are many types of separation processes viz., fractional distillation, solvent extraction, adsorption and membrane separations. The heart of the separating process is the mass-separating agent. In fractional distillation, it is heat; in solvent extraction, the solvent; in adsorption, the adsorbent; and in the membrane separation processes, the membrane material. Separation of solvents or gas mixture is of extreme importance in a variety of industries ranging from chemical, food and pharmaceutical.

Distillation and liquid-liquid extraction are two of the most common and traditional technologies used for solvent separations. Both of these technologies are mature and have been extensively used for commercial large-scale separations. However, these technologies have certain disadvantages associated with them. Distillation generally is an energy intensive process and since the basis of separation is the relative volatility of the compounds, the technique fails in the case of azeotropes i.e. mixtures wherein the relative volatility of the compounds is unity. Thus for azeotrope separation, one may have to resort to the use of more cost intensive processes such as azeotropic or vacuum distillation. Also, conventional distillation cannot be used for the separation of solvent mixtures, which contain a heat sensitive compound (commonly encountered in the food, perfumery and pharmaceutical industries). Liquid-liquid extraction, on the other hand suffers from the major drawback of enhanced downstream processing due to the presence of an additional solvent. In the food and pharmaceutical industries, the introduction of the liquid
extractant could also cause problems in terms of the purity of the final food or drug product. Thus in cases, where the conventional technologies would fail to meet the desired separation objectives, the use of alternate technologies may be required. Recently, membrane based separation techniques have got lot of attention from scientific community, due to their advantages in separation science.
1.2 Membrane Based Separation Processes

Membrane is 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, can carry a positive or negative charge or neutral or bipolar [1, 2]. Transport through a membrane can be affected by convection or by diffusion of individual molecules, induced by an electric field or concentration, pressure or temperature gradient.

In recent past, membrane based processes have become industrial products of substantial technical and commercial importance due to the wide range applications. Such methods can be useful to produce potable water from seawater, to treat industrial effluents [3], to recover hydrogen from off-gases or to fractionate [4] and in pharmaceutical industry [5]. Membranes are also key elements in artificial kidneys [6] and controlled drug delivery systems [7]. The growing significance of membranes and membrane processes as efficient tools for laboratory and industrial scale mass separations is based on the several properties, characteristic of all membrane separation processes, which make them superior to many conventional mass separation methods. The mass separation by means of a membrane is a physical procedure carried out at ambient temperature, thus the constituents to be separated are not exposed to thermal stress or chemical alteration. This is of particular importance for biochemical or microbiological applications where often mixtures of sensitive biological materials have to be separated. Furthermore, membrane processes are energy efficient and rather simple to operate in a continuous mode. Significant difference occurs in the membranes used viz., driving forces for the mass transport, the applications and also in their technical and economical significance. In some of the processes the membranes as well as the processes
have reached such a level that completely new developments cannot be expected. Some examples of this are in microfiltration, ultrafiltration, reverse osmosis, dialysis or electro-dialysis. In these processes only improvements and optimization of existing systems and their adaptation to special applications are to be expected. Other processes, such as pervaporation and vapor permeation, are in the very beginning of their industrial application and offer the possibility of totally new developments of membranes and modules.

### 1.2.1 Classification

Pressure driven membrane based processes can be classified into seven types based on the size of the permeable species and concentration of solute.

**A. Microfiltration:**

Microfiltration (MF) membranes are used for separation of fine particles from solutions. MF is a process mainly used for the separation of submicron size (< 0.1 µm) particulate matter from solution. This process also requires hydrostatic pressure gradient across the membrane and the pressure used is of the order of 100 kPa. The pore sizes of the membranes decide the size of the particulate matter retained. The process is similar to ultrafiltration and separation takes place by sieving. Most MF membranes are symmetric. Most commonly cellulose nitrate or acetate, poly vinylidene difluoride (PVDF), polyamides, polysulfone used as membrane material in MF processes. MF processes are generally applied in clarification, sterilization and slurry concentration. MF processes are typically applied in the removal of bacteria from water samples [8] and removal of submicron size suspended dust and particulate matters from gas streams [9]. Removal of chemical oxygen demand from effluent waters [10] is another important application of the MF process.
B. Ultrafiltration:

The ultrafiltration (UF) is a membrane based separation process wherein the solvent along with micro solutes permeates through the membrane and macro solutes are retained by the membranes. This process is similar to sieving and the driving force is the hydrostatic pressure across the membrane. Size or the molecular weight difference of the macro solute retained by the membrane depends upon the pore size of the membranes. Micro solutes whose effective sizes are smaller than the pore size of the membranes permeate along with the solvent whereas macro solutes whose effective sizes are larger than the pore size of the membranes are retained. The driving force used in ultrafiltration processes is of the order of 500 kPa or so. The membranes used in UF processes are asymmetric, microporous and having pore radius between 1 to 10 nm. UF processes are mostly used in separation of macromolecular solutions [11]. The major areas of application are in purification of proteins and nucleic acids [12] and virus removal from bio products [13]. UF is attractive because of the high throughput of product, low process cost and ease of scale-up. Commonly; polymers like polysulfone, polypropylene, nylon 6, PTFE and PVC are used as a membrane material in UF processes.

C. Reverse Osmosis:

Reverse osmosis (RO) is a membrane-technology filtration method that removes many types of large molecules and ions from solutions [14] by applying pressure to the solution when it is on one side of a selective membrane. The result is that the solute is retained on the pressurized side of the membrane and the pure solvent is allowed to pass to the other side. To be "selective", this membrane should not allow large molecules or ions through the pores (holes), but should allow smaller components of the solution (such as the solvent) to pass freely. Membranes used in reverse osmosis are
asymmetric skin type and has pore radius ranging between 0.5 to 1.5 nm.

Process of RO is mainly used in separation of salts and micro solutes from solutions.

D. Electrodialysis:

Electrodialysis (ED) process is generally used for desalination of water. In ED electrolytes are removed from one solution to the other. The cations and anions permeate through cation selective and anion selective membranes, respectively as a result of applied electrical energy. Even though RO and ED are both useful for desalination, there is a fundamental difference between the two techniques. In RO, the solvent permeates through the membranes and solutes, both electrolytes and non-electrolytes, are retained by the membranes while In ED, electrolytes permeate through the membranes and, the solvent and non-electrolytes generally do not permeate through the membranes. The solution from which electrolytes are removed gets depleted of salt and the solution which receives the solute gets enriched with salt.

E. Nanofiltration:

The process of Nanofiltration (NF) is slightly different from the reverse osmosis process in the sense that the permeating species in this case is solvent as well as low molecular solutes or low valence solutes. This process also operates with hydrostatic pressure difference across a semi-permeable membrane having pore sizes which are slightly larger than that of reverse osmosis membranes. The pore sizes of NF membranes are in the range of 1 to 3 nm. The hydrostatic pressure used in this process can vary from 1.5 Mpa to 2 MPa. This process is essentially used to fractionate solutes based on valency of either cation or anion and also to separate various organic solutes of low molecular weights [15]. Membranes fabricated by using polymer; cellulose
acetate and aromatic polyamide are commonly used in NF for removal of hardness and desalting.

F. **Gas Separations:**

A typical membrane process for gas separation operates with hydrostatic or partial pressure and concentration gradient across the membrane. Gas separation membranes are asymmetric and homogeneous. The feed gas mixture is fed to the membrane at an elevated pressure, where it permeates across the membranes. The other side of the membranes is held at a lower pressure. Separation is achieved because of differences in the selective permeation rates of the feed gas components. Components that permeate more rapidly across the membranes become enriched in the permeate stream while the slower permeating components are concentrated in the residual at high pressure. Important applications of gas separation using membranes are in the production of high purity nitrogen from air, oxygen enrichment from air and recovery of helium from mixture of organic gases [15].

G. **Pervaporation:**

Pervaporation (PV), name originates from a combination of the terms permeation and vaporization; can be defined as, a membrane based separation process by which azeotropic, closely boiling mixtures or isomers can separated on their selective permeation followed by evaporation. PV is relatively new membrane separation process and it was first developed in 1917 by Kober. Now days, PV processes are generally used mainly in following applications:

a. Removal of water from organic solvent
b. Separation of closely boiling organic liquid mixtures
c. Separation of isomeric mixtures
d. Separation of azeotropic liquid mixtures
From above mentioned applications, separation of azeotropic mixtures is an important category as; azeotropic mixtures are cannot be separated by using conventional distillation method. For example; ethanol forms azeotropic mixture at 4% of its aqueous solution, isopropanol forms azeotropic mixture at 12.2% at its aqueous solution. Conventional distillation method is not able to separate such type of mixtures which can be efficiently separated by using PV technique.
1.3 History of Pervaporation

As stated above, PV technique was firstly used by scientist Kober in 1917. He observed selective permeation of water from an albumin/toluene solution through a collodion bag (cellulose nitrate) [17]. First PV plant was installed in Brazil for production of ethanol in 1982. Farber; in 1935, extended the PV studies by carrying some applications. PV study was first studied for dehydration of aqueous ethanol solutions in 1956, by Heisler and co-workers [18]. In 1961; Binning and his colleagues tried to work on separation of azeotropic mixtures by using PV technique, but due to the poor membrane selectivity and lower permeation flux [19] of membranes caused failure of their experiment as an application in industrial process. In the early 1980s, a German company Gesellschaft Fur Trenntechnik (GFT) has developed a composite membrane with a thin layer of cross-linked poly(vinyl alcohol) supported on a porous poly(acrylonitrile) substrate [20].

Now days, PV process is commercially utilized in separation of organic solvents, removal of water from organic, dehydration of alcohol [21-23]. Recently, membranes made from synthetic polymer and derivatives of natural polymers have been tested for the PV separation of various liquid mixtures [24-33].
1.4 Principles of Pervaporation

As explained, pervaporation processes occur in two different phases in feed side and permeate side. To explain mass transport through pervaporation membranes some mass transport models have been developed as following:

1.4.1 Pore-flow model

1.4.2 Solution-diffusion model

1.4.1 Pore-flow model

Sourirajan and co-workers proposed the pore-flow model for pervaporation, later interpretation of this model for pervaporation observations is given by Okada et al. in 1991[34]. In pore flow model, there is no equivalent unified theory (like the Fick's Law in the solution-diffusion model) to describe mass transport through the membranes. In this model, it is supposed that there are bundle of straight cylindrical pores of specific lengths penetrating across the active surface layer of the membrane, and all pores are in an isothermal condition. The mass transport involves transport of liquid from the pore inlet to the liquid-vapor phase boundary, followed by its evaporation at the phase boundary and then vapors are transported from phase boundary to the pore outlet [see Figure 1.1(a) and (b)].

In the pore-flow model, the phase change occurs at a certain distance from the membrane surface contacting with the liquid feed and accordingly the transport mechanism changes from liquid permeation to vapor permeation at the liquid-vapor boundary. The pore-flow model is based on the presence of pores in the membranes, so whether the pores really exist or how small the pore size is remains hard to answer. Nonetheless, the theoretical calculations based on the pore flow model have been shown to be able to reproduce semi-empirical features of the experimental results.
Figure 1.1 (a): Schematics of pore-flow model.

Figure 1.1(b): Schematics of pore flow model.
1.4.2 Solution – Diffusion model:

A proper understanding of the membrane separation mechanism may provide direct information on the research and development of an appropriate membrane. The solution-diffusion model is a semi-empirical or phenomenological model originally developed by Graham in 1866 to describe gas permeation through rubber septa. Principle of PV can be best understood through sorption-diffusion model [35] consists of a three step process viz., sorption, diffusion and evaporation.

1. Sorption of penetrant molecules onto membrane surface.
2. Diffusion of penetrant molecules through the membrane.
3. Desorption of penetrant molecules, taking place at the downstream side of the membrane.

Mechanism of solution-diffusion process pervaporation can be well illustrated by using Figures 1.2(a) and 1.2(b).

In the first step i.e. in sorption, feed components get selectively sorbed on the surface membrane depending upon nature of membrane material used for PV experiment. On one hand, feed side of the membrane is maintained at atmospheric pressure, while on the other hand, permeate side of the membrane is maintained at lower pressure with the help of vacuum pump. A liquid feed is passed over the membrane surface and one component is able to pass through the membrane preferentially. The feed to the membrane is usually at a temperature close to that of its saturation temperature and this combined with the underside of the membrane being held under vacuum causes the liquid passing across the membrane to vaporize.

In the second process, the penetrating component diffuses from the feed side, across the membrane, to the permeate side. In general, solubility and diffusivity are concentration dependent terms. A number of mathematical
equations for mass transport have been formulated on the basis of Fick’s diffusion equation using different empirical expressions of concentration dependence of solubility and/or diffusivity.

For a component $i$ in a pervaporation system, the permeability can be expressed as follows:

$$ P_i = S_i \times D_i \tag{1.1} $$

where $P_i$ is the permeability coefficient, $S_i$ is the solubility coefficient, and $D_i$ is the diffusivity coefficient.

In order to understand permeation, we have calculated concentration-independent diffusion coefficient, $D_i$ of the permeating molecules using Fick’s diffusion equation:

$$ J_i = -D_i \left( \frac{dC_i}{dx} \right) \tag{1.2} $$

where $J_i$ is permeation flux/unit area (kg/m$^2$ s), $D_i$ is diffusion coefficient (m$^2$/s), $C_i$ is concentration of permeate (kg/m$^3$), subscript $i$ stands for aqueous or organic component. For simplicity, we assume that concentration profile along the diffusion pathway is linear and hence, concentration-independent, $D_i$ can be calculated using:

$$ D_i = \frac{J_i h}{C_i} \tag{1.3} $$

Where, $h$ is membrane thickness.

Evaporation (desorption) process, the temperature of the feed liquid is elevated to the point where a saturated vapors are formed. Vapors are cooled and the composition of permeated liquid can be analyzed by using refractometer and gas chromatography which will provide information about membrane selectivity.
Figure 1.2(a): schematics of pervaporation
Figure 1.2 (b): Principle of pervaporation (sorption-diffusion mechanism)
1.5 Pervaporation Membranes

The PV membranes must have a high permeation rate or flux and a large separation factor for the practical applications. Although a so-called trade-off relationship exists between permeability and selectivity, acceptable membrane materials with both high permeability and high selectivity may be synthesized by polymer design. Very selective and solvent stable membranes are commercially available, using materials such as poly(vinyl alcohol), chitosan, sodium alginate, poly(vinyl pyrrolidone), hydroxyethylcellulose, poly(acrylate), etc. At the same time, new membrane materials exhibiting good permselectivity are being developed for given separation problems.

1.5.1 Fabrication of Membranes

The capability of a membrane to normalize permeation lies not only in the selection of an appropriate membrane material, but also in the physical structure of the membrane. The physical structure and the physical properties of a membrane can be directly related to membrane preparation procedures.

A. Composite Membranes:

Two major steps are involved in the preparation of composite membranes: first, casting of the microporous support, followed by deposition of the selective dense layer on the surface of the porous support. One of the advantages of using the composite approach is that different polymers may be used as the barrier layer and the porous support, which allows a combination of properties that may not be available in a single material. The key to commercialization of PV on has been the development of asymmetric composite membranes. Several methods have been developed to prepare composite membranes and were described by Heinzelmann in 1991[36]. However, currently direct casting of polymer solution onto a porous support is the most widely used method for preparing composite membranes. A classic
example of composite membranes for pervaporation is the GFT membranes and it is believed that these membranes which are comprised of crosslinked PVA top skin layer and poly(acrylonitrile) (PAN) support, are manufactured by the direct casting technique. In this way, the PVA polymer solution was cast directly onto the PAN microporous support film.

B. Dense Membranes:

Dense homogeneous membranes are often used in research work to characterize membrane properties. These membranes can be prepared by solution casting and solvent evaporation technique. Since permeation is inversely related to membrane thickness, the concept of reducing the effective thickness of dense membranes has led to the development of thin asymmetric and composite membranes. In fact, dense homogeneous membranes are rarely used commercially in large scale industrial separation processes because the permeation rate or flux of such membranes is too low for practical applications.

C. Asymmetric Membranes:

Asymmetric membranes consist of a thin, relatively dense layer supported by a porous layer. The advantage of the asymmetric membranes over the homogeneous membrane lies in the extreme thinness of the top skin layer, and thus the ability to achieve high flux without any loss in selectivity. Whether the skin layer of a membrane is dense or finely porous often depends on the method of membrane preparation. The asymmetric membrane prepared from phase inversion process was first introduced by Loeb in 1960 [37]. Since then, various techniques have been developed to prepare this kind of membranes (Wijmans, 1986) [38]. Kesting, 1985 [39] discussed in detail the process variables involved in the procedure for membrane preparation and their effects on the structure of the resulting membranes. Skin layers deposited from solution or plasma onto a porous support are probably homogeneous, while
skin layers resulting from phase inversion processes may be finely porous or dense, depending upon casting solution composition, casting conditions and post-formation thermal or chemical treatment. Regardless of the origin or structure, it is the top skin layer which predominantly determines the permeation properties of the membrane. The top skin layer and the porous support layer may be comprised of the same material. In this case, the asymmetric membrane may be referred to as an integrally skinned asymmetric membrane.

1.5.2 Membrane Modification

Pristine pervaporation membranes have lower pervaporation performance with respect to separation factor and permeation flux, that’s why, cannot be used as successful PV membrane. In order to fabricate membranes with improved PV performance; post treatment membranes was needed. Various methods are reported in literature on membrane modification viz. annealing, blending or addition of filler.

A. Annealing:

As explained above, pristine polymer membranes cannot be successfully used in pervaporation of binary liquid mixtures. So in order to improve the PV performance of the membranes annealing treatment should be taken into consideration. By using this method one can control structural and morphological properties of the membrane. In this process, membrane is heated in vacuum oven at different temperatures. Annealing technique is simple and by varying the parameters like annealing temperature, annealing time or annealing rate; membrane properties can be designed to enhance PV performance. Annealing treatment will results into motion of the polymeric chains and rearrangement of the membrane structure.
Chapter 1

Introduction

Peng et al., [40] studied the annealing effect on pervaporation properties of PVA-GPTMS hybrid membranes for benzene/cyclohexane mixtures. They varied annealing temperature from 80°C to 120°C by keeping annealing time 1 hour. Increased annealing temperature from 80°C to 120°C resulted in increased separation factor from ~27 to ~120, while the permeation flux of the benzene decreased with increased annealing temperature.

Zhang et al., [41] investigated Effects of annealing on the physico-chemical structure and permeation performance of novel hybrid membranes of poly(vinyl alcohol)/c-aminopropyl-triethoxysilane for ethanol-water mixtures. He observed increase in density of the membranes with increase in annealing temperature. He also observed increase in separation factor from 119 for 80°C to 200 for 160°C at 85 wt.% ethanol aqueous solutions in feed.

B. Blending of Polymers:

Cabasso et. al. [42] reported the blend system. They used successfully blend membranes of cellulose acetate/poly (phosphonate) alloys for the separation of benzene/cyclohexane and methanol/hexane mixtures [43].

Aminabhavi and his group have done enormous work on the PV separation of binary liquids by using membranes prepared by polymer blending. Adoor et.al [44] prepared Poly(vinyl alcohol)/poly(methyl methacrylate) (PVA/PMMA) blend membranes for pervaporation separation of water + isopropanol and water + 1,4-dioxane mixtures and observed higher PV selectivity for the PVA/PMMA blends than plane PVA membrane.

Naidu and Aminabhavi [45] prepared blends of sodium alginate and hydroxyethylcellulose for PV separation of isopropanol-water liquid mixtures, observed that blend membranes are quite efficient for PV dehydration of IPA.

The important task in fabrication of blend membranes is the miscibility of the polymers in the common solvents because only few blends are miscible
at the molecular level. Blend membranes can be prepared by dissolving the desired amounts of polymers in the common solvents followed by evaporation of solvent. Hydrogen bonding between blend polymers provides the driving force for the miscibility of polymers. Hence blending of polymers proves an excellent way for developing new materials with improved properties.

C. Addition of Filler:

Plane polymer membranes are suffered from various disadvantages, so to overcome this difficulty one should modify the membrane in order to enhance its performance. Such task can be achieved by incorporation of different types of fillers having particle size in micron or nanometers. Selection of the filler in mainly depends upon the nature of polymeric material. Incorporation of hydrophilic filler will enhance the hydrophilicity of membrane which in turns increases the degree of swelling of membrane. Increased swelling of membranes gives more permeation flux during the PV experiment and also increases the selectivity of membrane towards one of the components from the mixture.

In literature various reports are available on preparation and applications of polymeric membranes in PV incorporated with different types of filler. Generally; zeolites, carbonnanotubes, clay material, heteropolyacids, oxides, microporous and mesoporous materials are used as filler material in membrane preparation. PV results obtained by using zeolites and heteropolyacids gave the promising results, hence we have concentrated our study on PV separations

Heteropolyacids (HPAs) are the heteropolyanions of the transition metals having metal-oxygen octahedra as the basic structural unit. Out of various types of heteropolyanions Keggin heteropolyanion (shown in figure 1.3) is the well known and represented by formula $\text{X} M_{12}\text{O}_{40}^{x-8}$ where $X$ is the central atom ($\text{Si}^{4+}, \text{P}^{5+}, \text{etc.}$), $x$ is its oxidation state, and $M$ is the metal ion
which may be molybdenum or tungsten having +6 oxidation states. This KU consists of the central $\text{XO}_4$ tetrahedron surrounded by four $\text{W}_3\text{O}_{13}$ sets linked together through oxygen atoms. Four types of oxygen atoms can be distinguished. The central oxygen atom belonging to the $\text{XO}_4$ tetrahedron is shared by the three tungsten atoms of the set. The edge-sharing oxygen atoms bridge two metal atoms of the same set. The corner-sharing oxygen atoms bridge two metal atoms of different sets. The terminal oxygen atoms are associated with a single metal atom. The bridging and terminal oxygen atoms are on the periphery of the structure and therefore are available to associate with protons or water molecule to form hydrates that are thought to enhance selectivity to water. Also, hydrogen-bonding is likely to be established between HPA and polymer material hence, in the present study, HPA [e.g. phosphotungstic acid, phosphomolybdic acid, silicotungstic acid] loaded organic-inorganic hybrid membranes are studied and used in PV dehydrations of binary-liquid mixtures.

![Diagram of Keggin structure of heteropolyacid](image)

**Figure 1.3:** Keggin structure of heteropolyacid
1.6 Literature Review

To obtain the efficient PV performance, it is very important to choose the appropriate polymeric material for fabrication of the membranes. Material should have good film forming property, thermally and mechanically stable. In the literature, it is found that various types of hydrophilic and hydrophobic membranes are prepared and used for PV applications. Hydrophilic polymers like chitosan, poly(vinyl alcohol), sodium alginate, poly(vinyl pyrrolidone), hydroxyethylcellulose are extensively used in preparation of PV membranes. Improved PV performance is still expected than the reported PV membranes as per industrial requirements. So, we have concentrated on preparation of organic/inorganic hybrid membranes using these hydrophilic polymeric materials for application of PV separation of liquid mixtures in order to obtain better PV results as compared to literature. Detailed structural information of the individual polymers is given in this section with the brief literature review.

1.6.1 Chitosan

Chitosan (CS), a natural biomaterial, has recently attracted much attention from scientists in different parts of the world [46-48]. It is principle derivative of chitin derive by alkaline deacetylation [49]. Chitosan may be regarded as a binary heteropolysaccharide containing $\beta(1-4)$ linked 2-acetamido-2-deoxy-$\beta$-D-glucopyranose and 2-amino-2-deoxy- $\beta$ -d-glucopyranose residues [50]. CS has been evaluated for various uses in the food, medical, pharmaceutical, agricultural, and chemical industries because of its nontoxic, biocompatible, mucoadhesive and biodegradable properties [50-52]. Dissolved CS has antimicrobial and metal-binding properties and has been used as an antimicrobial additive to bind metals from food-processing wastewaters [53-55]. In addition, because of its free amino groups, CS can be
dissolved in acidic aqueous solutions and form gels, films, sutures, beads, and fibers. CS has wide applications in membrane based separation technology like PV. It has amino groups and hydroxyl groups on its backbone that, on the one hand, make CS itself hydrophilic and on the other hand, impart weak basic property to CS. The amino and hydroxyl groups of CS give rise to it being easily chemically modified. Several efforts have been made are found in literature for modification of CS, including it’s blending [56] with other natural or synthetic polymers or by crosslinking [57] using various reagents, including gluteraldehyde [58], sulfuric acid[59], epoxy compound [60] dialdehyde starch [61] and nontoxic nature agents [62-64] etc., have been used as crosslinkers for CS. More recently, irradiation is also used to cross-link CS [65].

![Figure 1.4: Structure of Chitosan](image)

CS has attracted many researchers for the use in PV due to it’s favorable properties. Various reports are observed in literature on PV separation of binary liquid mixtures by using CS membranes. In (1999) Jiraratananon et al., prepared chitosan/hydroxyethylcellulose blend membranes [66] and utilized successfully in the PV assisted separation of water-ethanol liquid mixtures. He also analyzed the mechanism of mass transport [67] and effect of operating conditions [68] on pervaporation of chitosan/hydroxyethylcellulose blend membranes. Cao et al., (1999) successfully used chitosan/poly (N-vinyl-2-
1.6.2 Polyvinyl alcohol:

Polyvinyl alcohol (PVA) was first prepared by Hermann and Haehnel in 1924 by hydrolyzing polyvinyl acetate in ethanol with potassium hydroxide [81]. PVA is produced commercially from polyvinyl acetate, usually by a continuous process. PVA is fully degradable and dissolves quickly. PVA has a melting point of 230 °C and 180–190 °C for the fully hydrolysed and partially hydrolysed grades, respectively. It decomposes rapidly above 200 °C as it can undergo pyrolysis at high temperatures. PVA is also used in pains, coatings [82] adhesives [83, 84] as it has good film-forming nature and mechanical, chemical stability [85, 86].

![Figure 1.5: Structure of poly(vinyl alcohol)](image)

Since PVA has poor stability in aqueous solution, several techniques such as cross-linking [87,88] used to create a stable PVA membrane with good mechanical properties and selective permeability. Currently PVA membranes are used for PV are cross-linked with glutaraldehyde, poly(acrylic acid), citric acid etc. The hydroxyl groups of PVA react readily with aldehydes and hence, they can be cross-linked easily. Since glutaraldehyde is a dialdehyde; chemical cross-linking reaction would be more effective and membrane would be more resistant than that obtained by heat treatment.

In literature, PVA is one of the extensively used polymeric materials for application in PV. C. K. Yeom and K. H. Lee (1997) developed blend membranes of poly(vinyl alcohol) [89] for PV assisted separation of ethanol –

1.6.3 Sodium Alginate:

Naturally occurring polysaccharides are among the most extensively used biopolymers for different applications. These polysaccharides are also useful in development of membranes for pervaporation (PV) separation applications [98-107]. Among the various natural polymers, sodium alginate
(NaAlg) is a widely used water-soluble polysaccharide, due to its good membrane forming properties, high thermal stability and greater mechanical stability. Sodium alginate obtained by extraction of seaweeds such as *Laminaria digitata* as well as from fermentation broths of bacteria such as *Azotobacter vinelandii*. NaAlg has been widely studied in PV separations of the organic-aqueous solutions. Sometimes its performance exceeds those of poly(vinylalcohol) (PVA) [108], ion-exchange resins [109] and other polysaccharides, such as chitosan [110] and cellulose [111]. Therefore, NaAlg has been very popular as a membrane in PV dehydration studies of organic liquids.

In the literature, different types of modified membranes NaAlg have been employed in PV assisted separation of aqueous-organic liquid mixtures. Efforts have been made in order to increase the selectivity of the membranes, achieved by Blending, crosslinking or by preparing mixed matrix membranes by loading fillers.

![Figure 1.6: Structure of sodium alginate.](image)

Such modification leads to enhanced mechanical stability of the membrane as compared to plane NaAlg membrane. Different types of membranes employed in the literature will be discussed in subsequent sections of this review with reference to different types of aqueous-organic feed
mixtures. Yeom et al., (1998) studied PV performance of glutaraldehyde crosslinked sodium alginate membranes [112] for PV. Moon et al., (1999) reported two ply composite membranes [113] of chitosan and alginate for the PV dehydration of ethanol and isopropanol. Huang et al., (1999) studied the characteristics of alginate membranes [114] for PV dehydration of ethanol-water and isopropanol-water mixtures. Aminabhavi and his group have done enormous work on the use of alginate based membranes for PV separation. Kurkuri et al., reported sodium alginate-g-polyacrylamide, polyacrylamide-grafted sodium alginate copolymeric membranes and blend membranes of sodium alginate and poly(vinyl alcohol) for PV separation of aqueous-organic mixtures [115-117]. Toti and T.M. Aminabhavi reported different viscosity grade NaAlg membranes [118] for PV dehydration of isopropanol and acetic acid. Naidu et al., (2005) reported blend membranes of sodium alginate and (hydroxyl ethyl) cellulose [119] for the PV dehydration of isopropanol. S.D. Bhat et al., prepared MCM-41 [120] and Na\textsuperscript{+}MMT [121] clay, SBA-15 molecular sieves [122], Zeolite K-LTL [123] and Microporous aluminophosphate (AlPO\textsubscript{4}-5) [124] molecular sieve incorporated sodium alginate membranes for PV mediated separation of different aqueous-organic mixtures. Teli et al., reported highly water selective silicotungstic acid loaded [125] and sodium alginate-poly(N-isopropylacrylamide) semi-interpenetrating [126] NaAlg membranes for the PV separation. Adoor et al., prepared Aluminum-rich zeolite beta [127], silicalite-1 [128] incorporated sodium alginate mixed matrix membranes for pervaporation dehydration. In this way, literature survey shows the importance of sodium alginate membranes in PV separations of liquid mixtures. So, we thought to use membranes prepared from NaAlg.
1.6.4 Poly(vinyl pyrrolidone):

Poly(vinyl pyrrolidone) (PVP) is a nonionic water soluble polymer with excellent adsorption, adhesion capacity, biocompatibility, and good thermal stability, PVP exhibits good miscibility with other polymers [129]. It readily absorbs up to 18% of its weight in atmospheric water. In solution, it has excellent wetting properties and readily forms films. Although its monomer is carcinogenic and is extremely toxic to aquatic life, the polymer PVP in its pure form is so safe that not only it is edible by humans, but it was used as a blood plasma expander for trauma victims after the first half of twentieth century [130]. The structure of PVP is shown in figure 1.7 below.

PVP attracted researchers worldwide for its applications in pervaporation separations. PVP in used in PV applications by preparing its blend with the other polymers. Due to miscibility in other polymers; PVP arises as important material in PV membranes. In the literature various reports found on use of PVP in preparation of PV membranes.


![Structure of Poly(vinyl pyrrolidone)](image)

**Figure 1.7:** Structure of Poly(vinyl pyrrolidone)

1.6.5 Hydroxyethylcellulose:

Hydroxyethylcellulose (HEC), is one of the water-soluble cellulose derivatives, a nonionic fiber or powder solid carbohydrate polymer with white or lightly yellow color, stable chemical structure, and good biological compatibility [137]. It has good thickening, suspension, dispersity, emulsification and water protection properties [66]. It has many biotechnological, biophysical, and industrial applications [138], such as oil exploitation, papermaking, coating, and polymerization [139]. It is a commercially important polymer that has many uses, for example, as a thickener in latex paints and paper finishes [140]. It is also useful in application for protein separation in capillary electrophoresis [141]. HEC is non-ionic polymer that is miscible in various polymers [66]. Such property of HEC is beneficial for its use in preparation of PV membranes. In literature, some
reports are available on preparation of PV membranes using blend mixtures of HEC with other synthetic or natural polymer. Figure 1.8 displays structure of HEC.

![Figure 1.8: Structure of hydroxyethylcellulose.](image)

Chanachai et al., (2000) reported the blend membranes of CS and HEC for pervaporation separation study of ethanol-water mixtures [66] and extended their study to study effect of operating conditions on PV separation [68]. They also investigated mass transport in pervaporation dehydration of ethanol–water mixture with CS/HEC composite membrane [67]. Naidu et al., (2005) studied pervaporation separation of water + 1,4-dioxane and water + tetrahydrofuran mixtures using sodium alginate and its blend membranes with hydroxyethylcellulose[139] and also studied Thermal, viscoelastic, solution and membrane properties of same blends [142]. Kalyani et al., (2006) reported blend membranes of sodium alginate and hydroxyethylcellulose for pervaporation based enrichment of t-buty alcohol [143]. Qu et al., (2010) studied effect of crosslinking on sorption, diffusion and pervaporation of gasoline components in hydroxyethylcellulose membranes [144].
1.7 PV performance

PV performance of the membranes is generally determined by selectivity and permeation flux. There are several factors that influence the membrane performance in a gas permeation process [145].

1.7.1 Influence of Feed Composition:

A change in feed composition will directly affect the (sorption) degree of swelling of the membranes as envisaged by the sorption-diffusion principles. Since diffusion of gaseous components in the membrane is dependent upon the concentration of the components; permeation characteristics are greatly influenced by the feed composition [146]. Coupling effects between two or more species could occur in multicomponent feeds, which may considerably influence the selectivity. Similarly, higher concentration of condensable species plasticizes the membrane.

1.7.2 Influence of Feed and Permeate Pressures:

The driving force in gas separation is the partial pressure gradient across the membrane [147]. The flow of a component, say $i$, across the membrane can occur only if the partial pressure (product of mole fraction and total pressure) of component, $i$ at the feed side of the membrane is greater than the partial pressure of the same component at the permeate side.

1.7.3 Influence of Feed Temperature:

In general, solubility decreases with increasing temperature, while diffusivity coefficients increase with temperature [148, 149]. However, increased diffusivity offsets the decrease in solubility. Figure 1.7 shows that increasing the temperature will cause the selectivity to decrease, with an enhancement in the rate of permeation. Thus, membranes possessing high
selectivity at room temperature may yield poor separation at elevated temperatures.

Figure 1.9: Graphical representation of dependence of permselectivity on temperature (selectivity-dots, permeability-dashes, permselectivity-solid line)
1.8 **Scope and Objectives of Thesis**

Different organic/inorganic hybrid composite membranes based on sodium alginate, poly(vinyl alcohol), Chitosan etc. were prepared by using heteropolyacids as a filler to study the PV characteristic of aqueous-organic liquid mixtures. Blend membranes incorporated with heteropolyacid were also prepared to test the PV dehydration characteristic. Nowadays, heteropolyacids are used as an efficient filler due to its higher hydrophilic properties. PV technique is quite useful in separation of the aqueous-organic binary liquid mixtures as compared to common distillation. Therefore, this thesis focuses on PV performance of new organic/inorganic hybrid membranes to be used in dehydration of organic solvents. Chapter scheme is given below.

1.8.1 **Chapter Scheme:**

**Chapter 1** provides formation about the membrane based separation processes, history of PV, principles of PV viz., pore flow model and solution-diffusion model. Chapter also gives information about membrane fabrication and modification. Role of heteropolyacid is also explained. Detail information of membrane material and corresponding literature as also provided. Factor which affects the PV performance of the membranes is also explained.

**Chapter 2** describes the experimental techniques used in the entire research progress. The materials used, membrane preparation procedures, pervaporation experiments and membrane characterization are addressed in detail.

**Chapter 3** explores fabrication, characterization and PV application of poly(vinyl alcohol)/poly(vinyl pyrrolidone) blend hybrid membranes loaded with phosphomolybdic acid. This chapter is divided into three parts, **Chapter 3A:** PV separation of isopropanol-water mixtures.
Chapter 3B: PV separation of acetic acid-water mixtures.

Chapter 3C: PV assisted esterification reaction between ethanol and acetic acid.

Chapter 4 deals with fabrication, characterization of Preyssler type heteropolyacid incorporated nanocomposite hybrid membranes of sodium alginate. These membranes were utilized for sorption and permeation studies of water + isopropanol mixtures.

Chapter 5 provides information about dehydration of ethanol by using organic/inorganic hybrid blend membranes prepared from Chitosan/hydroxyethylcellulose loaded with phosphotungstic acid. Details of characterization and different factor affecting PV separation are explained in thus chapter.

Chapter 6 gives information about preparation, characterization and PV separation characteristic of poly(vinyl alcohol)/tetraethylorthosilicate composite membranes loaded with silicotungstic acid.

Chapter 7 provides summary of the thesis.
1.9 References


Chapter 1

Introduction


81. W. Haehnel, W.O. Herrmann, German Pat. 450.286 to consort F elektrochem Inc. G.m.b.H., (1924).


Chapter 1


