For the best and safest method of philosophizing seems to be, first diligently to investigate the properties of things and establish them by experiment, and then to seek hypotheses to explain them. For hypotheses ought to be fitted merely to explain the properties of things and not attempt to predetermine them except in so far as they can be an aid to experiments.

-Isaac Newton
CHAPTER-I

Introduction

1.1 SEPARATION PROCESSES

The separation of chemical mixtures into their constituents has been practiced, as an art, for millennia. Early civilizations developed techniques to: (i) extract metals from ores [1-4], perfumes from flowers [5], dyes from plants [6,7] and potash from the ashes of burnt plants [8]; (ii) evaporate sea water to obtain salt [9,10]; (iii) refine rock asphalt [11,12] and (iv) distill liquors [13,14]. The human body could not function for long if it had no kidney, a membrane that selectively removes water and waste products of metabolism from blood.

Separations, including enrichment, concentration, purification, refining and isolation, are important to chemists and chemical engineers [15]. The former estimate the compositions of complex mixtures quantitatively using analytical separation techniques such as chromatography. Chemists also use small-scale preparative separation techniques, often similar to analytical separation methods, to recover and purify chemicals. Chemical engineers are more concerned with the manufacture of chemicals using economical and large-scale separation methods, which may differ considerably from laboratory techniques.

*The information covered in this Chapter has been submitted to Journal of Membrane Science as a review article.*

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As industries move to incorporate pollution prevention principles into their production processes and attempt to remediate existing contaminated sites and waste streams, new cost-effective separation technologies are needed. In addition, for process retrofits, these separation technologies must be easily integrated into existing plant designs. Membrane technologies can be utilized to separate, fractionate and concentrate contaminants or process components. In general, they require minimal temperature changes and chemical addition, operate in either continuous or batch modes, consume significantly less energy than traditional separation processes and are easy to integrate into existing process due to their modular nature and compact size without altering the chemical structure of the processed materials [16].

Membranes for chemical separation applications constitute a relatively new area of Applied Chemistry and Chemical Engineering. During the past two decades, industrial membranes are being developed for a wide variety of chemical separation applications involving the treatment of industrial liquids, gases and vapours, such as those involved in waste water treatment [17], pollution control, water reuse and waste recovery, food processing, gas separations [18-20], petroleum engineering [21], biotechnology and biomedical devices [22-24]. As such, the field of industrial membranes is an emerging area of enormous industrial and public health significance. To make the fullest utilization of the potentialities of industrial membranes for practical applications requires intensive and extensive
research and development work. As it touches many vital areas of everyday life, the field of industrial membranes is second to none in terms of economic significance and social relevance [25].

Generally, membrane processes are classified based on various driving forces. Some use pressure difference (microfiltration, ultrafiltration, reverse osmosis and piezodialysis), while others use other driving forces such as concentration difference (gas separation, pervaporation, liquid membrane and dialysis), thermal (membrane-distillation, thermo-osmosis) and electric (electrodialysis) [26].

1.2 PERVAPORATION: AN OVERVIEW [27]

As a separation technique, pervaporation occupies a special niche in the chemical industry. It is the only membrane process primarily used to purify chemicals. Currently, about one hundred pervaporation units are operating worldwide; most of them are dehydrating solvents, such as ethanol and isopropanol. Now that pervaporation has been proven in these end-of-pipe applications, attention is turning to separations closer to the chemical reaction step — more critical to production and promising much greater benefits.

This shift in focus is accelerating the development of new, more-robust membranes with better performance that can be used at higher temperatures. Over the next few years, pervaporation will be used increasingly to enhance reactor performance, either by purifying feeds or separating reaction products. Because

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pervaporation is a membrane process, these separations can be integrated with the reaction step, promising quantum improvements in reaction efficiencies, yields and process economics.

In pressure-driven membrane processes, such as ultra, micro and nanofiltration, the bulk component is purified by passing it through a porous membrane that holds back the minor component. The membrane acts rather like a filter or strainer. Reverse osmosis (RO) is similar, but uses nonporous membranes. In this case, the major components selectively permeate through the membrane by preferential absorption, diffusion and desorption. The solute or minor component is held back.

Pervaporation and vapour permeation processes are used in the reverse situation, i.e., when the membrane is preferentially permeated by the minor component. The bulk fluid is held back by the membrane. To get a pure product stream in this situation, almost all of the permeating component has to pass through the membrane, so pervaporation and vapour permeation resort to application of vacuum to the permeate side of the membrane. Very high-pressure ratios can be achieved, so the minor component can be almost completely removed without excessive pressure difference across the membrane. Undue mechanical stresses on the membrane and equipment are avoided.

Because substances that permeate nonporous membranes are reasonably volatile, application of vacuum always causes the permeate to be desorbed from
the membrane in the vapour state. Hence, the term pervaporation is used if the feed to the membrane is liquid, since the contaminant appears to evaporate through the membrane. If the feed is vapour, or a gas/vapour mixture, the process is called vapour permeation.

The best performing industrial membranes permeate water in preference to other components, so filtration and RO processes are used typically to purify water. In contrast, pervaporation and vapour permeation are commonly used to remove water from organics.

Although pervaporation and vapour permeation require significant driving forces to transport components through the membrane, the processes do not depend on particular vapour/liquid equilibria. Water is preferentially permeated from a stream irrespective of the other components present. In practice, pervaporation and vapour permeation are only competitive where distillation is difficult or costly.

Pervaporation is now coming of age as a separation process. Industrially, it has been introduced in end-of-pipe application such as solvent recovery. As with other membrane processes, accumulated experience in both membrane fabrication, and design and operation of pervaporation units has matured the technology, such that it is now applied to separations that are integral to production. Although dehydrating the ethanol/water and isopropanol/water azeotropes account for the majority of all plants operating (roughly, four-fifths), most of the new plants being
installed are in quite different applications. The typical pervaporation units are shown in Figs. 1.1 - 1.3.

Fig. 1.1 Pervaporation plant designed for a few kg/h to 1000 tonns/year.

Fig. 1.2 Pervaporation unit (pilot scale) to demonstrate and optimize operating parameters.
1.2.1 Pervaporation (PV): History

As early as 1906, L. Kahlenberg reported a qualitative study on the separation of hydrocarbon and alcohol mixtures using rubber membrane. In 1955, D. H. Hagerbaumer and Brubaker conducted the first quantitative investigation with a microporous Vycor glass membrane using a high-pressure drop across it to separate liquid-liquid mixtures [28]. Later in 1965, Binning and Robert, at the American Oil Company studied the separation of liquid-liquid mixtures into a vapour mixture using nonporous polymeric membrane. This research yielded a high degree of separation along with high permeation rates. However, PV process did not come into commercial usage until 1982 when Gesellchaft Fur
Trenntechnik mbH (GFT) in Germany (now Sulzer Chemtech) installed the PV plant to separate water from concentrated alcohol mixtures. Since then, more than one hundred plants have been installed. Recently, Exxon used PV in its refinery to separate hydrocarbon mixtures containing aromatics and aliphatics [29].

1.2.2 Definition and Process Fundamentals

Pervaporation is a membrane process in which liquid mixture is maintained at the atmospheric pressure on the feed or upstream side of the membrane, while the permeate is removed as a vapour because of low vapour pressure existing on permeate or downstream side. This low vapour pressure can be achieved by employing a carrier gas or using a vacuum pump. The partial downstream pressure must be lower than the saturation pressure.

In the pervaporation process, typically a heated liquid phase mixture containing at least two components, for example, A and B, is fed to the membrane that has a higher permeation flux, for at least one of the components in the feed mixture. For example, the membrane in the illustration below has a higher flux for B. The driving force for permeation of the components is the difference in partial pressure between the feed side and the permeate side of the membrane. Therefore, the permeate side of the membrane is maintained under vacuum. The majority of component B and a small fraction of component A permeate through the membrane in the vapour phase. This is due to the phase change associated with pervaporation across the membrane.

*Chapter-I*
1.2.3 **Pervaporation: Principles**

Liquid transport in pervaporation is described by various solution-diffusion models [30-32]. The steps included are the sorption of the permeate at the interface of the solution feed and the membrane, diffusion across the membrane due to concentration gradients (rate determining steps), and finally desorption into a vapour phase at the permeate side of the membrane. The first two steps are primarily responsible for the permselectivity [30]. As material passes through the membrane a *swelling* effect makes the membrane more permeable, but less selective, until a point of unacceptable selectivity is reached and the membrane must be regenerated.
The other driving force for separation is the difference in partial pressures across the membrane. By reducing the pressure on the permeate side of the membrane, a driving force is created. Another method of inducing a partial pressure gradient is to sweep an inert gas over the permeate side of the membrane.

Pervaporation can be used for breaking azeotropes, dehydration of solvents and other volatile organics, organic/organic separations such as ethanol or methanol and wastewater purification. Characteristics of the pervaporation process include:

a) Low energy consumption.

b) No entrainer required, no contamination.

c) Permeate must be volatile at operating conditions.

d) Functions independent of vapour/liquid equilibrium.

1.2.4 Advantages

Comparing to the competing technologies, pervaporation features the following benefits.

a) Pervaporation is environmentally clean and energy efficient technology.

b) Simple equipment design and hence, involves low capital investment.

c) Process is completely enclosed thereby minimizing direct and fugitive emissions.

d) Suitable for concentrations ranging from ppb to g/l

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e) System is compact, modular and easily transportable.

f) Low operating cost, and easy to scale up for industrial use.

g) Reduces the energy demand because only the fraction of the liquid needs to be vapourized.

h) Opportunity for recovering concentrated organics.

1.2.5 Disadvantages

Besides the advantages describe above, PV process also posses several disadvantages. These includes:

a) Inadequate membrane material.

b) Fouling of the membrane.

c) Competition with established processes, which are seen as safe options.

1.2.6 Industrial Applications

Pervaporation offers significant capital and energy savings in applications that are difficult to separate by conventional techniques such as azeotropic mixtures or mixtures of close boiling components. The established industrial applications [33-36] of pervaporation include:

a) The treatment of wastewater contaminated with organics.

b) Pollution control applications.

c) Recovery of valuable organic compounds from process side streams.

d) Separation of 99.5% pure ethanol-water solutions.

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e) Harvesting of organic substances from fermented broth.

f) Other products separated or purified by pervaporation include:

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<thead>
<tr>
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<td></td>
<td>Perchloroethylene</td>
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</tbody>
</table>
1.2.7 Continuing Research on Pervaporation

1.2.7.1 Pervaporation of apple juice

Pervaporation is used to recover any lost juice solution during evaporation. The vapour from the evaporation process is further processed using pervaporation. The recovered, concentrated apple juice can be combined with the product solution to help the apple juice retain its aromatic and taste qualities.

1.2.7.2 Pervaporation in the production of fuel ethanol

To establish a continuous fermentation process, the ethanol concentration within the fermentation vessel must be kept at 5% by weight or lower. Pervaporation has been used to maintain the necessary ethanol concentration in the broth. The advantages of using pervaporation in such a system include the ease of processing the clean, nearly pure ethanol extracted from the fermentation vessel and a significantly higher fermentation capacity or the reduction in fermentor size and costs.

1.3 MEMBRANES

Membrane plays a decisive role in PV process as it functions as a selective barrier for the mixture to be separated. The word membrane comes from Latin word, *membrana* that means a skin [37]. Today’s word *membrane* has been extended to describe a thin flexible sheet or film, acting as a selective boundary between two phases because of its semi permeable properties. History of synthetic membranes

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began in 1748 when French Abbe Nolet demonstrated semi permeability for the first time. After a century, Fick published his phenomenological law of diffusion, which we still use today as a first-order description of diffusion through membranes. It is an intervening phase separating two phases and/or acting as an active or passive barrier to the transport of matter between phases adjacent to it under a driving force. In other words, it is a discrete thin interface that controls the permeation of chemical species while in contact with it. This interface may be molecularly homogeneous, that is completely uniform in composition and structure or it may be chemically or physically heterogeneous.

1.3.1 Types of Membranes

As a first classification, membranes can be divided into two groups: biological and artificial membranes [38]. Artificial term can be applied to all membranes made by man with natural materials and with synthetic materials (synthetic membranes). Synthetic membrane can be divided further into organic (made up of polymers) and inorganic (made with metals, alumina, etc.) membranes. Since the effectiveness of the membranes in applications depends on the detailed morphology and microstructures of membrane systems, another possible classification of synthetic membranes can be made as shown in Fig. 1.5 [39].

Synthetic membranes can be classified as either symmetric or asymmetric. Symmetric membranes are comprised of one material of a single chemical composition and structural morphology. They are sometimes called isotropic.
Asymmetric membranes are constituted of two or more structural planes of different morphologies, and the size of the pores changes from one surface of the membrane to the other. Asymmetric membranes are sometimes called *anisotropic*.

**MEMBRANE STRUCTURES**

![Diagram of membrane structures](image)

Fig. I.5 Schematic classification of the structures of the synthetic membranes.

On the other hand, asymmetric membranes are characterized by a thin skin on the surface of the membrane. The method of membrane preparation can determine if the skin layer is porous or nonporous. Polymeric skin layers resulting from the phase-inversion process are generally dense and the obtained membranes
are called integrally skinned; those skin layers can also be deposited from the solution or plasma onto a porous support, in which case the membranes are called composite membranes.

The membranes used in PV processes are classified according to the nature of the separation being performed. Hydrophilic membranes are used to remove water from organic solutions. These types of membranes are typically made of polymers with glass transition temperatures above room temperatures. Poly(vinyl alcohol) is an example of a hydrophilic membrane material. Organophilic membranes are used to recover organics from solutions. These membranes are typically made up of elastomers with glass transition temperatures below room temperature. The flexible nature of these polymers makes them ideal for allowing organic liquids to pass through. Examples include nitrile, butadiene rubber and styrene butadiene rubber.

1.3.2 Membrane Modules

The first requirement in any membrane process is a membrane capable of the function needed, but successful implementation requires packaging the membrane in a module whose configuration is engineered for the specific application. [40]. 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, membrane modules can be distinguished into five major types [41]:
1.3.2.1 Tubular modules

In this module, membrane is case on the inside of a porous support plate, which is often housed in a perforated stainless steel pipe [42,43]. Individual modules contain a cluster of tubes in series held within stainless steel permeate shroud as shown in Fig.1.6.

![Diagram of tubular module membranes](image)

**Fig. 1.6** Schematic diagram of tubular module membranes.

Tubes generally 10-25 mm in diameter and 1-6 m in length. The feed is jumped through the tubes. They are easily cleaned and a good deal of operating data exists for them. These are widely used where it is advantageous to have a turbulent flow region. Their main disadvantages are the relatively low surface area and their high volumetric hold up. Zeolite membranes for PV applications are generally fabricated in Tubular form. Though the manufacturing cost of these modules are high, these modules offer an excellent resistance to fouling with low-pressure drop and are not suitable for high-pressure operations.
I.3.2.2 Hollow fiber modules

Essentially this module consists of a pressure vessel containing a bundle of individual fibers (Fig. I.7). 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 [44,45], 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.

Fig. I.7 Hollow-fiber membrane system.

Pervaporation requires volatilization of a portion of liquid feed. In PV, the enthalpy of vapourization 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.

I.3.2.3 Plate and frame systems

Here the feed solution flows through flat, rectangular channels (Fig. 1.8). Packing densities of about 100–400 m²/m³ 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 mixtures and secondly, this module allows high temperature operation with efficient interstage heating between stages [46].

Fig. 1.8 Flat asymmetric or thin composite membrane.
1.3.2.4 Spiral wound modules

These are characterized by high packing density (>900 m²/m³) and a simple design. Essentially, two or more membrane pockets are wound around a centrally located permeates collecting tube with a special mesh used as spacer (Fig. 1.9).

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 [47]. 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 [48,49]. A spiral wound unit for PV is difficult to develop because of the chemical susceptibility of the adhesives required.

Fig. 1.9 Spiral-wound membrane module.
1.3.3 Membrane Material Selection

In separating liquid mixtures by pervaporation, an array of feed streams must be dealt with. For which, three relevant areas such as material selection, membrane synthesis and system configuration must be integrated. Right from the early 1960, when work on membrane separations began, a wide range of materials including dense metals, zeolites, polymers, ceramics and biological materials are being used for the manufacturing of membranes. However, polymers are the most widely used materials for membrane manufacturing at present.

A major consideration in this section will be the theory behind the selection of polymer materials, membrane structures, modifications that can be made to such structures and the effect of process conditions that have enabled them in being the most appropriate membranes for separating liquid mixtures.

1.3.3.1 Polymer selection for development of membranes

Selection of the polymer materials for separation is based mainly on three important features: high chemical resistance, sorption capacity and good mechanical strength of the polymer film in the solution. It should have good interaction preferably with one of the components of the mixture for separation. Hence, the solubility parameter [50] and membrane polarity [51,52] are the indices of interest in the development of novel membrane materials.

Figure I.10 shows an example of solubility parameter as an index for membrane development [52]. As indicated from the figure, methanol is a good
solvent for poly(propylene oxide) PPO (B) membrane, while hexane is a poor solvent. In the sorption experiment, more methanol was sorbed into the membrane than hexane and as expected, exceptionally high selectivity was obtained with this membrane to separate methanol from its hexane mixture. This result suggests that the solubility parameter is one of the plausible yard-stick for membrane material selection. However, it is necessary to know the precise polymer structure to calculate the solubility parameter.

![Fig. 1.10 Solubility parameter of PPO membrane as plotted on two-dimensional grid.](image)

The membrane polarity also contributes to its separation performance. In order to separate a particular component from feed mixture, the polarity of one of the components must be close to the polarity of the membrane. For example, Shimidzu and Yoshikawa [53], investigated the separation of water–ethanol mixture using polystyrene membrane. The membrane polarity (31.7 kcal/mol) was close to the polarity of ethanol (30 kcal/mol) and as expected the membrane preferably permeated ethanol compared to water (63.1 kcal/mol).
In general, selection of polymers compatible with the mixtures for separation is based on the Hansen solubility parameters (Δ) and Flory–Huggins interaction parameter (χ). The compatibility among components ‘1’ and ‘2’, which are the liquids in major and minor quantities, respectively, and polymer ‘3’ is indicated by the relationship [54]:

\[
\Delta_{i,3} = \sqrt{\left((\delta_{d,i} - \delta_{d,3})^2 + (\delta_{p,i} - \delta_{p,3})^2 + (\delta_{h,i} - \delta_{h,3})^2\right)}
\]  

(1.1)

where \(\delta_d\), \(\delta_p\) and \(\delta_h\) are the dispersive, polar and hydrogen bonding contributions and Δ is the magnitude of the vectorial distance as shown in three dimensional diagram of \(\delta_d\), \(\delta_p\) and \(\delta_h\) on x, y and z axes, respectively (Fig. I.11), \(i\) represents 1 or 2. The greater the compatibility between any two components, the smaller will be the magnitude of Δ.

![Fig. I.11 Schematic representation of solubility parameter using vectors.](image)

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Flory-Huggins interaction parameter (χ) also signifies the compatibility of components with the polymer. The binary interaction parameters, χ_{1,3} and χ_{2,3} between the components and the polymer can be determined from

\[ \chi_{i,3} = \frac{-[\ln(1-v_3) + v_3]}{v_3^2} \]  

(I.2)

where \( v_3 \) is volume fraction of the polymer 3 and \( i \) again represents component 1 or 2. Again the smaller the value of \( \chi \) (close to 0.5 but not below), the greater will be the interaction.

I.3.3.2 Membrane structure

Several membrane structures like porous, dense and asymmetric, exist. The choice for the selection of a good membrane requires a sound knowledge of the same. In the development of high performance membranes, there arises a need to adjust the swelling extent occurring within the membrane while in contact with the feed solution. To achieve this, the membrane must be crosslinked and the crosslinking degree be thoroughly controlled. Especially, in the case of a composite membrane it is rather difficult to ensure controlled crosslinking as composite membranes are produced by the usual coating-evaporation technique and chemical crosslinking is achieved during the evaporation period only. Hence, definite crosslinked polymer networks of appropriate chemical nature could be realized by means of physical crosslinking. Promising results concerning the separation of aromatics and
saturates using physical crosslinking has been reported by Koenitzer [55]. The membranes used were made of multiblock copolycondensates comprising alternate flexible (soft) and rigid (hard) sequences.

Highly crystalline polymers do not dissolve easily in many solvents and furthermore, crystallites due to the lack of flexible groups act as physical crosslinks which prevent high degree of swelling and thereby show a lower permeability compared to the amorphous polymer. In pervaporation, degree of crystallinity also has great influence on the dissolution of the feed mixture in the membrane, because dissolution generally occurs in the amorphous part of the polymer. In polymers of the type (-CH₂-CHR-)ₙ the size of the side group -R plays an important role in knowing the crystallizability of the polymer. The presence of polar groups enables the polymer to absorb water preferentially compared to organic liquids. Membranes of this kind are excellent candidates for the separation of aqueous organic mixtures. Hydrophilic polymers fall into this category.

1.3.4 Modification of Membranes

There are several methods, which are being used to modify the membranes to improve the separation performance. They are:
1.3.4.1 Crosslinking

In membrane technology, there are two reasons to crosslink a polymer. The first
reason is to make the polymer insoluble in the feed mixture and the second reason
is to decrease the degree of swelling of a polymer in order to derive good
selectivity. Crosslinking can be executed in three ways. One is via chemical
reaction by using a compound to connect two polymer chains, the second by
irradiation and third, is a physical crosslinking [56,57]. A good example of this is
the chemically crosslinked PVA top layer of the GFT composite membrane which
shows excellent resistance to many solvents. On the other hand, excessive
crosslinking has to be avoided as it renders the polymer membrane brittle with a
loss in the dimensional stability thereby making it unsuitable for pervaporation
applications.

1.3.4.2 Grafting

Grafting is a polymer modification technique where oligomeric chains are attached
as side chain branches irregularly to the polymer main chain. This again can be
done by chemical reaction or by irradiation. If the molecules to be grafted contain
a functional group that is able to react with a functional group of the polymer,
grafting by chemical reaction can occur. Grafting by irradiation is a versatile
technique for the modification of insoluble polymer films. Polymers with good
chemical resistance can be made into films by melt extrusion/calendaring followed
by modification through irradiation-based grafting. Neel and co-workers [58] and
Ellinghorst et al. [59] have performed a lot of research on grafting films by irradiation. They used poly(vinylidene fluoride) (PVDF), poly(vinyl fluoride) (PVF) and poly(tetrafluoroethylene) (PTFE) as basic polymers and N-vinylpyrrolidone, 4-vinylpyridine, vinyl acetate, acrylic acid, N-vinylimidazole as grafting monomers.

I.3.4.3 Blending

A mixture of two polymers, which are not covalently bonded, is called a polymer blend. In principle, blending is an ideal technique for creating optimum hydrophilicity in the hydrophobic membrane. The optimum-blending ratio can be determined by mixing the hydrophilic polymer with a hydrophobic one at various compositions and measuring the permeability and selectivity. Two types of blends can be distinguished: homogeneous blends, in which the two polymers are miscible on a molecular scale for all compositions and heterogeneous blends, in which the two polymers are not totally miscible. In the latter case, domains of one polymer distributed within the matrix of the other polymer can be observed. However, homogeneous blends are considered as potential membrane materials for PV as heterogeneous blends will not give enough mechanical strength to the thin membranes [60-62].
I.3.4.4 Copolymerization

Copolymerization can be applied for the same reason as the blends are used, but unlike in blends the two polymers are covalently bonded which increases the mechanical stability of the membrane. Besides grafted copolymers, block and random copolymers can be formed by this technique. An important aspect in copolymerization is the degree of crystallinity. Random copolymers might be fully amorphous while graft copolymers contain a certain degree of crystallinity. Membrane made of random copolymers cannot be used for PV applications, as a certain degree of crystallinity is required for the membrane to show preferable sorption towards one of the components [56,63].

I.3.4.5 Hybrid networking

Recently, organic-inorganic hybrid materials have been attracted considerable attentions as potential membrane materials for many applications due to their extraordinary properties arising from the synergism between the properties of these two different building blocks. This organic-inorganic hybridization is dependent on the sol-gel method in which the starting materials are in solution and synthesis at a low temperature is possible. The hybrid materials involving the sol-gel process permit growth of the inorganic phase into an organic polymeric matrix. A highly dispersed, homogeneous system of organic and inorganic phases at a nanoscale level could be achieved by specific molecular interaction or covalent linkage between the phases via sol-gel chemistry. Since our research mainly...
focuses on development of hybrid membranes and their modifications, a brief review of sol-gel and its chemistry is discussed below.

A sol is a colloidal dispersion of 1-100 nm solid particles within a liquid medium and a gel is defined as a colloidal system that is more like a solid than a sol [64, 65]. Sol-gel chemistry is the process in which a sol agglomerates to form a gel. Sols create by acid hydrolysis of silicate inorganic alkoxides and gelations of these sols occur by condensation reactions. These condensation reactions produce large molecular weight molecules that continually combine to form an infinite molecular weight network that is characterized by a gel-point [66-68]. The gel-point occurs when an infinite molecular weight molecule is formed throughout a reaction medium. When inorganic alkoxides are used for sol-gel chemistry, the sol of interest is a partially hydrolyzed inorganic alkoxide generated from acid catalyzed reactions that later condenses to from a gel. Depending on the sol reaction conditions, polymer-like chains or colloidal particles will form prior to gelation. The morphology formed during the condensation of the sol has a direct relationship to the final physical properties of the gel [69-73]. It should be noted that hydrolysis and condensation reactions occur concurrently, but one reaction can be favoured over the other depending on the reaction conditions. This simple definition of sol-gel chemistry underestimates its complexity and the many variables controlling the final morphology and physical properties. Table I.1 lists
several of the important variables that affect the final structure and physical properties.

Table I.1 Sol-gel chemistry variables.

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<thead>
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<td>Alkoxide</td>
</tr>
<tr>
<td>Temperature</td>
<td></td>
</tr>
<tr>
<td>Pressure</td>
<td></td>
</tr>
</tbody>
</table>

These variables have been categorized into two areas, one related to the synthesis variables and the second related to structural factors. Because of the extensive complexity associated with the sol-gel technique, these are the only variables that will be considered. Brinker and Scherer provide an excellent review detailing many of these variables in their book titled Sol-Gel Science [69]. Figure I.12 illustrates hydrolysis and condensation reactions for the sol-gel process of an arbitrary silicon alkoxide. Although these reactions demonstrate the use of an acid or base, temperature and pressure are also driving forces for these reactions. Hydrolysis and condensation reactions for an alkoxide are governed by a $S_{N2}$
(substitution, nucleophilic, bimolecular) mechanism, but the actual nucleophile in these reactions is dependent on the catalysis method [69-72, 74-76]. The sol to gel transition for an arbitrary silicon alkoxide shown Figure I.12 can be divided into three reversible reactions.

**Hydrolysis and Esterification**

\[
\text{RO-Si-OR + H-OH} \rightleftharpoons \text{RO-Si-OH + ROH}
\]

Acid or Base Catalysed

**Alcohol Condensation and Alcoholysis**

\[
\text{RO-Si-OR + HO-Si-OR} \rightleftharpoons \text{RO-Si-O-Si-OR + ROH}
\]

**Water Condensation and Hydrolysis**

\[
\text{RO-Si-OH + HO-Si-OR} \rightleftharpoons \text{RO-Si-O-Si-OR + H-OH}
\]

Fig. I.12 Hydrolysis and condensation for an arbitrary silicon alkoxide.
The first reaction step involves the reversible hydrolysis and esterification of the alkoxide and the rate of hydrolysis and condensation are a function of the variables listed in Table I.1, which occur concurrently. As soon as the alkoxide becomes hydrolyzed, two reversible condensation reactions can occur; the first condensation reaction forms an alcohol and the second condensation reaction forms water. Complete hydrolysis of the alkoxide is not necessary for condensation reactions to occur that was demonstrated in many different studies [69,77-92]. The reverse reactions of condensation are known as alcoholysis and hydrolysis. These reactions result in the cleavage of a SiO₂ bond from a nucleophilic attack of alcohol or water [69]. The chemistry of sol-gel processing is of interest to both academia and industry. It has led to the creation of specialized piezoelectric, pyroelectric, and superconducting ceramics, and major advances in contact lenses, filters, catalyst supports, membranes, and novel glasses [93-104]. With this brief introduction to sol-gel, the rest of this section is devoted to provide further details regarding this unique chemistry.

a) Organic-inorganic monomers

Inorganic-organic monomers are molecules containing a metal core such as a silicon bonded to reactive alkoxy groups and/or organic groups. These monomers, when assembled together, form organic-inorganic siloxane materials. There are two distinctive types of inorganic-organic monomers: organically modified silicate
(ORMOSIL) monomers and silsesquioxane-type monomers. These monomers are typically used in the synthesis of controlled porosity materials.

i) **ORMOSIL monomers**

In the mid-1980s a flurry of research was conducted in the field of ORMOSIL chemistry [105-114]. ORMOSILs are derived from tetrafunctional silicone alkoxides such as tetraethylorthosilicate (TEOS) shown in Fig. 1.13

\[
\begin{align*}
\text{CH}_2\text{CH}_2\text{O} & \quad \text{Si} \quad \text{OCH}_2\text{CH}_3 \\
\text{OCH}_2\text{CH}_3 & \quad \text{CH}_2\text{CH}_2\text{O} \quad \text{Si} \quad \text{OCH}_2\text{CH}_3
\end{align*}
\]

**Fig. I.13 Tetraethylorthosilicate.**

Organic modification may take place at any one of the reactive alkoxide arms as shown in Fig. 1.14.

\[
\begin{align*}
\text{R} & \quad \text{Si} \quad \text{R} \\
\text{OCH}_2\text{CH}_3 & \quad \text{OCH}_2\text{CH}_3 \\
\text{OCH}_2\text{CH}_3 & \quad \text{OCH}_2\text{CH}_3 \\
\text{OCH}_2\text{CH}_3 & \quad \text{OCH}_2\text{CH}_3
\end{align*}
\]

**Fig. I.14 The ORMOSIL functionality spectrum.**
Here, \( n \) is representative of the number of organic moiety connected to the silicon molecule and \( f \) is representative of the number of reactive alkoxy groups connected to the silicon molecule. For a mono-functional silicon alkoxide \((f = 1, n = 3)\), the monomer 'terminates' the polymer chain since there is only 1 reaction site on the molecule. A di-functional silicon alkoxide \((f = 2, n = 2)\) behaves as a 'bridging' agent, connecting molecules in a linear fashion. A tri-functional silicon alkoxide \((f = 3, n = 1)\) behaves as a 'crosslinker', allowing for branching in the network. A tetra-functional silicon alkoxide \((f = 4, n = 0)\) behaves as a 'networking' agent, allowing for complete connectivity between all functional groups of the molecule.

\[
\begin{align*}
  &\text{OCH}_2\text{CH}_3 \\
  &\text{CH}_3\text{CH}_2\text{O} \quad \text{Si} \quad \text{OCH}_2\text{CH}_3 \\
  &\text{OCH}_2\text{CH}_3
\end{align*}
\]

\[
\begin{align*}
  &\text{OCH}_2\text{CH}_3 \\
  &\text{H}_2\text{C} \quad \text{Si} \quad \text{CH}_3
\end{align*}
\]

\[
\begin{align*}
  &\text{OCH}_2\text{CH}_3 \\
  &\text{H}_2\text{O} \quad \text{H}^+ \\
  &\text{OCH}_2\text{CH}_3
\end{align*}
\]

\[
\begin{align*}
  &\text{O} \\
  &\text{OCH}_2\text{CH}_3
\end{align*}
\]

\[
\begin{align*}
  &\text{O} \\
  &\text{OCH}_2\text{CH}_3
\end{align*}
\]

\[
\begin{align*}
  &\text{O} \\
  &\text{OCH}_2\text{CH}_3
\end{align*}
\]

\[
\begin{align*}
  &\text{O} \\
  &\text{OCH}_2\text{CH}_3
\end{align*}
\]

\[
\begin{align*}
  &\text{O} \\
  &\text{OCH}_2\text{CH}_3
\end{align*}
\]

Fig. I.15 ORMOSIL connectivity through sol-gel chemistry.

Figure I.15 depicts ORMOSIL connectivity achieved through sol-gel polymerization. It is reasonable to expect that variation of the number and type of organic moieties included on the silicon monomer, results in a variety of pore sizes that can be created in the sol-gel network. The pore size corresponds to the physical size of the organic substituent. These pores, due to their organic nature,
can attract or divert various organic or gas molecules. In essence, ORMOSILs form well defined porous networks, each possessing unique physical and chemical properties.

b) Silsesquioxane-type monomers

The general structures of silsesquioxane-type monomers are shown in Fig. 1.16.

![Fig. 1.16 Silsesquioxane-type monomers.](image)

Here the organic substituent behaves as a spacer unit (bridging functionality) that resides between two reactive di- or tri-alkoxysilane endgroups. These spacer units have traditionally been methyl or benzyl groups stranded together but can be synthesized to have any number of organic spacer functionalities. Upon initial sol-gel network formation, porosity is limited due to the presence of the bridged organic groups. Limiting porosity through usage of a spacer unit, with its specific organic character, can be beneficial for specific gas or liquid permeation. However, limited porosity systems can be modified to form well-defined porous systems through removal of the spacer units by ozonolysis (see Fig. 1.17)
By removing the spacer units after the network formation, well-defined pores corresponding to the organic spacer are built into the sol-gel network.

\[
\begin{align*}
\text{EtO} & \quad \text{Si--[O--Si]
\text{EtO[O--Et]} + \text{CH}_2\text{CH}_2\text{O} \quad \text{Si--[O--OCH}_3\text{CH}_3} \\
& \quad \text{H}^+ \quad \text{H}_2\text{O} \\
\text{O} & \quad \text{Si--[O--Si]} \\
\text{O} & \quad \text{Si--[O--OCH}_3\text{CH}_3} \\
\end{align*}
\]

Fig. 1.17 Formation of precise porosity through usage of bridged aryl silsesquioxanes.

c) Catalyst and pH

Catalyst type and pH of the reaction determine the resulting morphology and growth model in sol-gel chemistry. Slow hydrolysis, fast condensation rates, and colloidal structures are characteristic of base catalyzed systems, which is described by a Monomer-Cluster growth model [117,118]. Fast hydrolysis, and slow condensation rates characterize an acid catalyzed system, which produces linear-like polymer structures that is described by a Cluster-Cluster growth model [117,118].
The Monomer-Cluster and Cluster-Cluster growth models are shown in Fig. 1.18. Cluster-Cluster and Monomer-Cluster growth models have variations in their overall structure, which is dependent on the reaction conditions employed. These reaction conditions determine if the condensation process is Reaction-Limited, Ballistic, or a Diffusion-Limited process.

These limitations in the condensation reaction result in a variety of structures for acid and base catalyzed systems. Because the reaction conditions

<table>
<thead>
<tr>
<th>Reaction-Limited</th>
<th>Ballistic</th>
<th>Diffusion-Limited</th>
</tr>
</thead>
<tbody>
<tr>
<td>Monomer-Cluster</td>
<td>Eden</td>
<td>Vold</td>
</tr>
<tr>
<td></td>
<td>RLCA</td>
<td>Sutherland</td>
</tr>
</tbody>
</table>

Fig. 1.18 Simulated structures resulting from the various kinetic growth models.

control the final gel morphology, final densification and mechanical properties are dependent on whether the skeletal structure is produced from linear-like polymer
structures, or colloidal particles. The final microstructure that evolves after densification of an acid or base catalyzed sol-gel reaction is schematically represented in Fig. 1.19. From this, it is apparent that the synthesis variables are extremely important when tailoring a system for the production of a monolithic film or fiber. In order to gain additional insight on the affect of pH and catalyst type on sol-gel processing, the following examples are provided from an acid or base catalyzed system [119].

Fig. 1.19 Schematic representation of an arbitrary gel densification.
Zeolite incorporation into a polymer matrix is another way for modification of membrane. Because, the incorporation of a suitable zeolite in dense membranes improves a significant performance of membrane in both gas and pervaporation separation processes [120-122]. This is possible due to combined effects of molecular sieving action, selective adsorption and difference in diffusion rates. In addition, zeolites have a high mechanical strength, good thermal and chemical stability and thus, the membranes incorporated with these fillers can be used over a wide range of operating conditions.

Zeolites are three-dimensional, microporous crystalline solids with well-defined structures. Generally they contain aluminium, silicon and oxygen in their regular framework and cations, water and/or other molecules within their pores. They are found in rocks of volcanic origin and were first described in 1756 by a Swedish Mineralogist, A. F. Cronstedt.

They combine rarity, beauty, complexity and unique crystal habits. Zeolites are the result of very low-grade metamorphism, typically forming in the cavities or vesicles of volcanic rocks. Some form from just subtle amounts of heat and pressure and can just barely be called metamorphic, while others are found in obviously metamorphic regimes. Zeolite crystals have been grown on board the space shuttle and are undergoing extensive research into their formation and unique properties.
Because of their unique porous properties, zeolites are used in a variety of applications with a global market of several million tones per annum. In the western world, major uses are in petrochemical cracking, ion-exchange (water softening and purification), and in the separation and removal of gases and solvents. Other applications are in agriculture, animal husbandry and construction. They are also often referred to as molecular sieves.

A defining feature of zeolites is that their frameworks are made up of 4-connected network of atoms. One way of thinking about this is in terms of tetrahedral, with a silicon atom in the middle and oxygen atoms at the corners. These tetrahedral can then link together by their corners (Fig. 1.20) to form a rich variety of beautiful structures. The framework structure may contain linked cages, cavities or channels, which are of the right size to allow small molecules to enter. The limiting pore sizes are roughly between 3 and 10 Å in diameter.
The shape-selective properties of zeolites are also the basis for their use in molecular adsorption. The ability preferentially to adsorb certain molecules, while excluding others, has opened up a wide range of molecular sieving applications. Sometimes it is simply a matter of the size and shape of pores controlling access into the zeolite. In other cases different types of molecule enter the zeolite, but some diffuse through the channels more quickly, leaving others stuck behind, as in the purification of \textit{para}-xylene by silicalite (Fig. I.21).

\textbf{Fig. I.21} Diffusion of \textit{p}-xylene in the channels of silicalite.

Cation-containing zeolites are extensively used as desiccants due to their high affinity for water, and also find application in PV and gas separation, where molecules are differentiated on the basis of their electrostatic interactions with the metal ions. Conversely, hydrophobic silica zeolites preferentially absorb organic solvents. Zeolite-membranes can thus separate molecules based on differences of size, shape and polarity.
Generally, these zeolites are classified into small, medium large and ultra-large pore materials. Small pore structures have pore aperture consisting of six, eight or nine tetrahedral (6, 8 and 9 membered ring), medium pore framework materials have 10 membered rings, large have 12 and ultra-large have 14, 18 or 20 membered rings [39].

The combination of many properties such as microporous character with uniform pore dimensions, accessibility of the internal part of the materials, high and stable surface area, shape selectivity, the ion-exchange property, the ability to develop internal acidity, high thermal stability and high internal surface area make the zeolites unique among other inorganic substances and also led to unique activity and selectivity [123-129].

1.4 LITERATURE SURVEY

Over the past two decades, innumerable research papers have been published on pervaporation. In this Chapter, literature related to separation processes, principles and history of pervaporation, and fundamentals of pervaporation including advantages, disadvantages and industrial applications, are discussed at length. As membrane plays a key role in membrane separation technology, a detailed account on membrane materials and their selections, membrane modules and modification of membranes, is also given. However, a detail literature pertaining to theoretical aspects, membrane materials and systems chosen for the study, is discussed in their respective Chapters.
1.5 MOTIVATION AND GOAL OF RESEARCH WORK

With respect to the aforementioned discussions, it can be noted that despite the apparent proliferation of membrane processes, the Science and Technology of Membrane Separations is still in its early stages of development. Tremendous opportunities exist and will continue to exist, for the penetration of membrane processes in every facet of chemical process engineering and environmental protection through intensive research and development. The level of research and developmental activity in the general field of Membrane Science and Technology has been rising dramatically all over the world during the past two decades. This is happening not only because of the growing recognition of the commercial potentialities of membrane separations, but also because of the growing realization of the international scientific and engineering community that synthetic membranes are capable of playing tremendously beneficial roles in society and industry far more than what has hitherto been appreciated. This is particularly a significant and welcome realization for the health and well-being of all humanity. The fullest potentialities and practical utilization of membrane applications in everyday life can be realized only through a fundamental understanding of the physicochemical basis of membrane separations. This has prompted me to undertake research work on membrane separation area.

Among the membrane separation processes, the pervaporation process attracted me as it is considered as the so-called Clean Technology and well-suited
alternative to many conventional energy intensive technologies for the separation of azeotropic mixtures, close boiling liquids and isomers. Besides the advantages described earlier, pervaporation process also poses several disadvantages, such as optimization of flux and selectivity, fouling and dependability. Among these, flux and selectivity of a membrane are prime deciding factors in mass transport so as to make the process more economical. Therefore, development of a new polymeric membrane is a key research area in membrane technology. The aim in the development of new pervaporation membranes is either to increase the flux, keeping the selectivity constant or aiming for higher selectivities at constant flux or to increase both.

In PV process, the simultaneous enhancement of both parameters is a big challenge due to a trade-off phenomenon, existing between flux and separation factor. However, present study aims to increase the flux and selectivity or both simultaneously by selecting suitable polymer with an appropriate crosslinking material, and by judiciously incorporating an appropriate amount of selective zeolite into a suitable polymer matrix and by modifying the membrane matrix with hydrophilic polymer. The polymers and aqueous-organic mixtures have been chosen based on their engineering properties and industrial importance, respectively. Such study on the type of polymer membranes for the separation of water-isopropanol and water-acetic acid mixtures has not been noticed in the
literature. Further, the study mainly emphasizes on the development of new membranes keeping the above systems constant.

I.6 REFERENCES


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