CHAPTER - II

Theoretical Aspects, Experimental Methods and Materials

This chapter presents the details of theoretical aspects explored in pervaporation process, experimental methods and general properties of materials used in the research work. The experimental methods describe the details and importance of characterization techniques such as Fourier transform infrared (FTIR) spectroscopy, differential scanning calorimetry (DSC), wide-angle X-ray diffraction (WAXD), scanning electron microscopy (SEM) and refractometry.

II.1. THEORETICAL ASPECTS

II.1.1. Introduction

Pervaporation is a combination of preferential permeation followed by evaporation. It differs from other membrane separation processes in the fact that there is a phase change on the downstream side of the membrane. The components of the feed solution permeate through membrane and evaporate as a result of partial pressure on the permeate side being lower than the saturated vapour pressure. As a separation process, pervaporation relies on the difference in membrane permeabilities as well as on the thermodynamic activities of the components to be separated [1].
Mass transport in dense membranes has been usually quantified using the solution diffusion mechanism proposed by Binning et al. [2]. The assumptions in the model development are as follows:

i) Preferential sorption of the component occurs at the feed side of the membrane. This results in partitioning of the components between the feed mixture and feed side of the membrane, giving rise to selective sorption. It is basically controlled by the chemical nature of the membrane material and its interaction with the components of the feed solution.

ii) Diffusion of the sorbed solutes through the membrane. In this step separation is induced by the ability of the membrane to allow transport of one component more readily than the other even if the driving forces are equal, giving rise to selective diffusion.

iii) Desorption of the solutes on the downstream side of the membrane.

It has been established that sorption and diffusion of the components of the feed solution control the separation process. Desorption on the permeate side of the membrane is generally considered to be rapid and nonselective. Further, since the gas phase diffusivities in step (iii) are generally very high and this step offers the least resistance to the overall transport process. When both sorption and diffusion favour the same component through the membrane, a high selectivity with respect to that component can be achieved. Therefore, it is important to understand the role of sorption and diffusion in membranes.
II.1.2. Sorption in Membranes

Sorption is a general term used to describe the penetration and dispersion of penetrant molecules in the polymer matrix. Phenomenologically, it can be described as distribution of penetrants between two or more phases to include adsorption, absorption, incorporation into microvoids, etc.

The penetrant molecules may experience more than one sequential mode of sorption in a given polymer material. Furthermore, the distribution of penetrants between different modes of sorption may change with sorbed concentration, temperature, swelling induced structural states, time of sorption to equilibrium. The four possible types of sorption isotherms are given in Fig. II.1 [3,4].

The simplest case is that of ideal solution behaviour with sorbed molecules randomly dispersed in the polymer matrix, in accordance with the Henry’s law. The solubility coefficient is a constant independent of sorbed concentration at a given temperature. The sorption isotherm is a linear relation of feed concentration and weight fraction in the membrane. This type of sorption isotherm is obtained with dilute feed solutions as shown in Fig. II.1A.

In the second type of sorption (Fig. II.1B), there is a preference for the formation of polymer-penetrant solute pairs at low concentrations with a small amount of sorption of approximately ideal behaviour at higher concentrations. Thus, initially sorption occurs on some kind of specific sites. After exhaustion of
such sites a small amount of solute dissolves in the polymer in a randomly distributed manner.

Fig. II.1. Types of sorption isotherms.

In the third type of sorption (Fig. II.1C), penetrant-penetrant pair formation occurs, which leads to a continuous increase of the solubility coefficient with feed concentration. The first molecule sorbed tends to loosen the polymer structure locally and makes it easier for the subsequent molecules to enter in the neighbour-
hood of the first (i.e., the first molecule plasticizes the polymer). Another interpretation of the type III sorption is that it occurs when the cohesive forces between penetrant molecules are greater than the attractive forces between the penetrant and polymer. This strong penetrant-penetrant interactions lead to penetrant molecules forming cluster in the polymer matrix. In such a case, the sorbed concentration of penetrants increases within the polymer matrix. If so, the diffusivities of penetrants decrease with increasing concentration of the penetrants in the polymer matrix. This is because, the activation energy for the mobility of clusters is very high. Such a situation may arise during some stage of sorption in polymers with the following structural features:

i. high degree of crosslinking or crystallinity,

ii. stiff and inflexible chains,

iii. very strong cohesive forces between adjacent polymers, and

iv. microvoids/cavities/pores present in the polymer matrix.

Type IV sorption (Fig. II.1D) is the combination of type II sorption at low concentrations and type III sorption at high concentrations.

Various studies have shown that sorption selectivity is often a strong indicator of the overall pervaporation selectivity, especially if the preferentially permeating component is dilute. Most of the industrial applications, involving dehydration of organics or removal of organics from their dilute aqueous solutions, use a dilute feed solution, hence conforming with the case where sorption selectivity approximates the pervaporation selectivity. Therefore,
selection of polymers, which afford very high sorption selectivity, is very
important for the success of any given pervaporation application.

II.1.3. Diffusion in Membranes

The transport of a penetrant through a homogeneous membrane, in absence of
gross defects occurs by the solution-diffusion mechanism. Diffusion in polymers
is best described by free-volume theory [5,6]. According this theory, the
migration of a penetrant can be visualized as a sequence of unit diffusion steps or
jumps during which the particle passes over a potential barrier separating one
position from the next. The diffusion step involves a cooperative rearrangement
of the penetrant molecule and its surrounding polymer chain segments. A certain
number of van der Waals type or other interactions between the component
molecules and chain segments must be broken to allow a rearrangement of the
local structure. The amount of energy required for this rearrangement increases
with increasing penetrant size. This process requires localization of energy to be
available for diffusing molecules and its surrounding polymer chains to provide
the energy needed for the rearrangement against the cohesive forces of the
medium. Thus, diffusive motion depends on the relative mobilities of the
penetrant molecules and polymeric chain segments.

II.1.4. Performance Parameters

Performance of pervaporation is assessed in terms of flux, selectivity and energy
consumption. Assessment is based upon the mass transfer of the preferentially
permeating species.

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II.1.4.1. Pervaporation flux

According to a generalized Ohmic law [1]:

\[ \text{flux} = \text{permeability} \times \text{driving force} \]  \hspace{1cm} (II.1)

Permeability, being a function of permeant concentration and permeant diffusivity in the membrane, has SI dimensions of kg/ms. Dividing permeability by membrane thickness yields flux density, denoting the amount of permeates per unit area of membrane per unit time at given membrane thickness with the dimension of kg/m²s. The permeability, obtained by multiplying flux density with membrane thickness, may thus be viewed as a normalized flux density.

Knowing the composition of the permeate, the total flux density may be broken down into partial flux densities of the individual permeants, to be expressed in terms of mass units or molar units. Again, the partial flux densities may be converted to partial permeabilities being independent of membrane thickness. The partial permeabilities thus obtained, because of mutual interactions inherent to pervaporation, differ significantly from the corresponding single component permeabilities.

II.1.4.2. Pervaporation selectivity

There are two ways of expressing selectivity by comparing the analytical compositions of permeate and feed. The separation factor \( \alpha \) is a dimensionless quantity and is patterned after the relative volatility of the components of binary liquid mixtures as [1]:

\[ \text{Chapter-II} \]  \hspace{1cm} 46
\[ \alpha_i = \frac{(c_i/c_j)^*}{(c_i/c_j)^{*'}} = \frac{c_i^*/c_j^*}{c_i^{*'}/c_j^{*'}} = \frac{(p_i/p_j)^*}{(p_i/p_j)^{*'}} \]  

(II.2)

where \( i \) is the preferentially permeating species in permeate ('') and feed (''). As a ratio of ratios, the separation factor is independent of the concentration units used.

The enrichment factor \( \beta_i \) is simply the ratio of concentrations of the preferentially pervaporating species in permeate and feed [1]:

\[ \beta_i = c_i^*/c_j^* \]  

(II.3)

**II.1.5. Influence Parameters**

There are several factors affecting the membrane performance. They are:

**II.1.5.1. Feed composition and concentration**

A change in the feed composition directly affects the sorption phenomena (degree of swelling) at the liquid membrane interface, as proved by the solution-diffusion principle and as the diffusion of the components in the membrane is dependent on the concentration of the components (or the solubility of the components). Hence, the permeation characteristics are also dependant on the feed concentration. An example to prove this phenomenon is shown in Fig. II.2 [7].
**II.1.5.2. Activity coefficients**

Viewing sorption into the membrane as distribution equilibrium implies equality of activity of the solution components across the feed-membrane interface. The thermodynamic activity of a liquid solution component is manifested by its partial vapour pressure as follows:

\[ p^i = x_i \gamma_i, \quad p^i_0 = a_i p^i_0 \]  

\text{(II.4)}

The key quantity in assessing liquid solution behaviour is the activity coefficient, \( \gamma_i \geq 1 \) or \( \gamma_i \leq 1 \).

The situation \( \gamma_i = 1 \) (\( a_i = x_i \)) signifies ideal solution behaviour (Raoult’s law), in addition to applying to the pure solution components (\( \gamma_i \to 1 \) for \( x_i \to 1 \)).
Dilute solution components are approximately represented by activity coefficients at infinite dilution, $\gamma_\infty$ [8].

In the situation $\gamma_i > 1$ (positive deviation from Raoult's law) the activity is higher than the analytical concentration, and increases with dilution. As a consequence, the pervaporative separation effect tends to increase with dilution.

In the situation $\gamma_i < 1$ (negative deviation from Raoult's law) the activity is lower than the analytical concentration, further decreasing with dilution. As overall result, polymer sorption of the target component is reduced beyond proportion, adversely affecting separation. The actual concentration dependence of polymer solubility is visualized by sorption isotherms (see Fig. II.1).

**II.1.5.3. Azeotropic mixtures**

Positive solution non-ideality ($\gamma_i > 1$) is associated with the occurrence of positive azeotropes, whereas negative solution non-ideality ($\gamma_i < 1$) is associated with negative azeotropes. In keeping with the relation, positive azeotropes are readily supported by pervaporation, whereas negative azeotropes are not [9].

**II.1.5.4. Concentration polarization**

In membrane processing, any departure of boundary layer composition from the analytical bulk composition is referred to as concentration polarization, $c_w \neq c_b$ [1]. In pervaporation, depletion of the preferentially permeating species near the membrane boundary is to be expected, limiting its polymer sorption. The effect is
modified by sign and concentration dependence of the activity coefficient of the depleted species in the boundary layer, requiring individual consideration.

Many investigators have dealt with problems related to concentration polarization in pervaporation separation of organic-water mixtures and have generally calculated that concentration polarization does not play a very significant role [10-15]. However, the role of concentration polarization in separation of organic mixtures is yet to be explored.

**II.1.5.5. Membrane thickness**

Membrane thickness in pervaporation (as in other membrane processes) is taken to be dry thickness, although the actual thickness depends on the swelling state of the membrane.

Flux is generally accepted to be inversely proportional to membrane thickness, suggesting thin membranes to realize high flux densities [16,17]. In multi-component pervaporation to separate liquid mixtures, flux enhancement, pertaining to all solution components, may adversely affect selectivity. The lower limit thus posed to practical membrane thickness depends on the extent of mutual interaction among the components of the pervaporation system. As a rule, highly swelling elastomeric membranes need to be thicker than low swelling glassy membranes in order to maintain selectivity.

The case of very thin membranes in pervaporation deserves consideration. As the diffusion resistance of the membrane diminishes, a downstream boundary
resistance to permeant transfer becomes relevant, resulting in a higher than vapour-phase equilibrium loading of the permeate interface of the membrane.

II.1.5.6. Permeate pressure

In vacuum pervaporation, the permeate pressure is the total pressure of the vapourized permeant(s) in contact with the membrane, ideally being devoid of non-condensable gases. Permeate pressure is a resultant pressure, being established as a balance between permeant vapour refurnished and permeant vapour transported to pump or condenser. For practical purposes, permeate pressure is taken to be the gauged downstream pressure.

Permeate pressure, translating into gaseous permeant activity, provides the driving force in pervaporation. In principle, the permeation rate of any one feed component increases as its partial permeates pressure is lowered [12,18]. The highest conceivable partial permeate pressure is the vapour pressure of the respective component in the liquid feed.

The effect of permeate pressure on pervaporation performance is dictated by the magnitude of the vapour pressures encountered, and by the difference in vapour pressure between them, taking note that pervaporation may favour the more volatile or less volatile liquid feed components.

II.1.5.7. Temperature

Temperature in pervaporation may mean the temperature of the feed entering the process, or some representative temperature intermediate between feed (inlet) and
retentate (outlet). Since the heat of vapourization of the permeate is withdrawn from the liquid feed stream, there is a temperature loss between the feed entering and the retentate exiting from the process, the membrane acting as a heat exchange barrier. Since, on the other hand, the liquid feed stream is the only carrier providing thermal energy to the process, there is an incentive to operate pervaporation at elevated feed temperature.

Temperature affects solubility and diffusivity of all permeants, as well as the extent of mutual interaction between them. As a result, both total and partial flux densities increase with temperature, with relatively minor effect on the selectivity [1,19]. Activation energies may be used to describe the temperature dependence of the flux of individual permeants.

\textbf{II.1.5.8. Nature of penetrant}

The diffusion process involves the jumps of penetrants from one hole to the adjacent. This would mean that larger holes would be needed to accommodate bigger molecules. This will need a higher energy for their formation, and hence activation energy will be higher for diffusion of bigger molecules and as a result, diffusivity will be lower. The activation energy is expressed as an intermolecular term, \( E_i \), and an intramolecular term, \( E_b \) [20]:

\[ E_i = S \sigma_p \sigma_v N P_i \tag{II.5} \]
\[ E_b = 18 \frac{V_o \Lambda \sigma_p^2}{S^3} \tag{II.6} \]
For a particular polymer, the effect of penetrant molecular diameter should depend upon the relative magnitudes of the intermolecular and intramolecular energies. If the intermolecular energy is predominant, the activation energy would vary directly with the penetrant molecule diameter. If the intramolecular energy were predominant, it would vary as square of the diameter of penetrant molecule. Generally, in elastomeric polymers intermolecular energy is predominant whereas in glassy polymers, intramolecular energy is predominant.

**II. 1.5.9. Nature of polymer**

According to the hole theory of diffusion, the rate of diffusion depends on: i) the number and size distribution of pre-existing holes; and ii) the ease of hole formation. The number and size distribution of holes depend on the ease of hole formation and degree of packing of the chains and is related to the free volume and the density. The ease of hole formation depends on the segmental chain mobility and on the cohesive energy of the polymer. The introduction of unsaturation into the polymer backbone results in easier rotation of the chains leading to higher diffusivity [21]. The introduction of polar side-chains causes an increase in the cohesive energy of the polymer, thus causing a corresponding decrease in the diffusivities and permeability [22].

**II.1.5.10. Glass transition temperature**

The glass transition temperature is an important characteristic property of polymers, which would be expected to have a profound influence on transport
properties. The first systematic study of effect of glass transition temperature ($T_g$) on the diffusivities of penetrants in amorphous homopolymers was carried out by Mears [23] with poly(vinyl acetate). It was observed from the Arrhenius plots that there is a distinct slope change at the $T_g$, with lower activation energies beyond the $T_g$. Mears showed that in the glassy state, the jump lengths are small and the entropy of activation is less. Above the $T_g$, the segmental mobility increases, resulting in an increase in the activation energy as well as the entropy of activation. If the penetrant molecules were small, minor or no changes would be observed in their diffusivities above and below $T_g$, since the probability of the penetrants encountering a hole remains the same. However, for large penetrant molecules the changes in the diffusivities above and below $T_g$ is significant. Above the $T_g$, the hole size increases, resulting in an increased probability of the penetrant molecules encountering holes which can accommodate them and hence the inflection in the Arrhenius plot at $T_g$.

II.2. EXPERIMENTAL METHODS

II.2.1. Membrane Characterization Techniques

This section deals with a brief introduction to characterization techniques including general procedures for carrying out the measurements. However, specific procedures of these techniques are given in the corresponding chapters.
II.2.1.1. *Fourier transform infrared (FTIR) spectroscopy*

Infrared spectroscopy is extensively used for the investigation of polymer structure and the analysis of functional groups. It can also be used for the quantitative measurement of components in a complex mixture [24,25].

II.2.1.2. *Differential scanning calorimetry (DSC)*

Differential scanning calorimetry is used to measure the important physical changes in a polymer. These include the glass transition temperature \((T_g)\), the crystallization temperature \((T_c)\), the melt temperature \((T_m)\) and the degradation or decomposition temperature \((T_d)\). Chemical changes due to polymerization reactions, degradation reactions and other reactions affecting the sample can also be determined [26, 27].

II.2.1.3. *X-ray diffraction*

The diffraction of X-rays has become a powerful tool in the study of the structure of polymers. The wavelengths of X-rays are comparable to the inter-atomic distance in crystals (0.5-2.5 Å). The two primary diffractions are used to study polymers: (a) wide angle X-ray diffraction (WAXD) and (b) small angle X-ray diffraction (SAXD). WAXD has been used for decades to study the structural properties of the polymers [28,29]. The value of angles used in WAXD is from 5-120°. The primary information generally obtained from a diffraction experiment is the structure of semi crystalline polymers with a range of inter-atomic distances of 1-50 Å. As the crystallinity of the polymer is often low, the width of the
diffraction peaks in WAXD gives information on the size of the crystals. From the measurements of relative intensities of diffraction peaks in the crystalline part and the diffusion halo from the amorphous part, the crystalline content of the polymer may be deduced. WAXD has also been used to provide information on the number of repeat units per term in the helical structures that are typical of linear polymers, the length of the repeating unit along the fiber axis and degree of orientation [30]. However, SAXD provides information on greater inter-atomic distances (50-700 Å).

II.2.1.4. Scanning electron microscopy (SEM)

Scanning electron microscopy has been developed as a special technique in which a fine electron beam is scanned across the surface of an opaque and non-conducting polymer specimen coated with a conducting film of metals such as gold and copper. The sample is illuminated by parallel electron beams and the scattered electrons are measured by Gieger-Muller counters. The scattered electron intensities are then converted into cathode ray beam whose intensities vary with the initial intensity. This variation in the intensities develops a contrast and the image of the sample under observation is formed on the screen. The images formed have greater depth of field and excellent three-dimensional appearance. SEM method is used in the studies [31] of (i) phase morphology of polymer blends, graft and block copolymers, (ii) surface features of texture of natural and synthetic fibers, and (iii) monitoring the surface or fracture failure in
plastics, elastomers and composite materials under the applied mechanical stresses such as tensile, abrasion and dynamic loading etc.

II.2.1.5. Refractive index measurement

Refractive index $n_D$ for sodium-D line was measured using the thermostatically controlled Abbe's refractometer (Atago 3T, Tokyo, Japan). Precision of the instrument was ± 0.0001 units. Refractometer was fitted with hollow prism casings through which water was circulated. Temperature of the prism casings was observed with a digital display (± 0.1°C). The instrument was provided with two prisms placed one above the other in front of the telescope. Upon inserting a drop of the test liquid using a hypodermic syringe, the incident ray forms a line of demarcation between light and dark portions of the field. This was viewed with a telescope, which moves with the scale. The instrument directly gives the values of $n_D$.

Refractive index measurements have been carried out at 30°C by circulating water from a thermostat using a ¾ HP water pump. In order to obtain the precise data, refractometer was calibrated frequently using a glass piece of known refractive index supplied along with the instrument [32]. It was also double checked by measuring the refractive index of pure water. A built-in sodium-D lamp was used as a light source and an average of triplicate measurements was considered in all the calculations.
**II.2.2. Swelling Measurements**

Swelling of polymers is a slow process involving the penetration of solvent molecules into the polymer matrix there by increasing its mass and volume. The diffusion of solvents into polymer solute structure depends upon polymer-solvent interaction, which leads to the unwinding or expanding of the polymer surface and allows the penetration of solvent molecules. Thus, the polymer chain containing diffused solvent molecules is known as swollen chain. The swelling may reach a thermodynamic equilibrium. The swelling is unlimited for solutes, which forms molecular solutions in solvents. The swelling continues infinitely until the chains are completely separated from each other and finally acquire mobility and diffuse back into the bulk of solvent state (forming molecular solutions). For limited swelling i.e., when thermodynamic equilibrium exists between polymer-solvent systems, the polymer does not dissolve to form molecular solution [31].

The degree of membrane swelling was carried out with different compositions of aqueous-organic mixtures using an electronically controlled oven (WTB Binder, Jena, Germany). The masses of the dry membranes were first determined. The dry membranes were equilibrated by soaking in different compositions of the feed mixture in sealed vessels at 30°C for 24 h. The swollen membranes were weighed immediately after careful blotting on digital microbalance (Model B204-S, Mettler-Toledo International, Zurich, Switzerland).
having a sensitivity of ± 0.01 mg. The percentage degree of swelling (DS) was calculated as [33]:

\[
DS (\%) = \left( \frac{W_s - W_d}{W_d} \right) \times 100
\]

where \( W_s \) and \( W_d \) are the mass of the swollen and dry membranes, respectively.

**II.2.3. Pervaporation Experiment**

Pervaporation experiments have been carried out using an indigenously designed apparatus illustrated in Fig. II.3(A and B).

Fig. II.3. (A) Schematic representation of pervaporation apparatus: (1) pervaporation cell; (2) vacuum control valve; (3) permeate cold trap; (4) moisture cold trap; (5) pressure sensor; (6) vacuum pump.
Fig II.3.(B) Schematic diagram of pervaporation cell: (1) water inlet; (2) water outlet; (3) feed inlet; (4) thermometer jacket; (5) stirrer; (6) O-ring; (7) membrane; (8) sintered disk; (9) permeate outlet.
The effective area of the membrane in contact with the feed stream was 34.23 cm² and the capacity of the PV cell was about 250 cm³. The vacuum in the downstream side of the apparatus was maintained $[1.333224 \times 10^3 \text{ pa (10 Torr)}]$ by a two-stage vacuum pump (Toshniwal, Chennai, India). The test membranes were allowed to equilibrate for about 1 h in contact with the feed mixtures before performing the experiment. The experiments were carried out at 30, 40 and 50°C by varying the feed composition. After a steady state was attained, permeate was collected in trap immersed in liquid nitrogen jar on the downstream side at a fixed time of intervals. The flux was calculated by weighing the permeate on a digital microbalance. The percentage composition of permeate was estimated by measuring the refractive index within an accuracy of ± 0.0001 units, using a refractometer and by comparing it with a standard plot of refractive index versus percent composition of aqueous-organic mixture, that was established with the known quantities of mixture components.

Membrane performance in PV experiments was studied by calculating the total flux ($J$), separation factor ($\alpha_{sep}$) and pervaporation separation index ($PSI$). These were calculated, respectively using the following simplified equations.

$$J = \frac{W}{A.t} \quad \text{(II.8)}$$

$$\alpha_{sep} = \frac{P_w}{P_o} \frac{F_o}{F_w} \quad \text{(II.9)}$$

$$PSI = J(\alpha_{sep} - 1) \quad \text{(II.10)}$$
In the above equations, $W$ is the mass of permeate (kg); $A$ is the effective membrane area ($m^2$); $t$ is the permeation time (h); $P$ and $F$ are the mass percentages of permeate and feed, respectively; subscripts $w$ and $o$, denote water and acetic acid or isopropanol, respectively.

II.3. Materials

II.3.1. Poly(vinyl alcohol) (PVA)

Poly(vinyl alcohol) is a well-known hydrophilic polymer, containing -OH groups as pendant moieties on the ethylene units. Its chemical formula is $(C_2H_4O)_n$. It is prepared by the hydrolysis of poly(vinyl acetate). The solubility and hydrophilicity of PVA can be varied depending on the percentage of hydrolysis of poly(vinyl acetate). Changes occurring in the properties of poly(vinyl alcohol) with respect to the degree of hydrolysis and molecular weight change is presented below:

Source: http://www.celaneschemicals.us/structure-c/pvoh

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It is a non-toxic, water soluble, biocompatible and biodegradable synthetic polymer, which can be widely used in biochemical and biomedical materials. The hydroxy groups of PVA reacts readily with aldehydes and hence, it gets cross-linked easily. Good crosslinking agents for PVA are formaldehyde and glutaraldehyde. PVA has good film forming properties, highly hydrophilic with good mechanical strength and as a result, it has been studied in various fields as a membrane. It is affected less at lower concentration but at higher water concentration it swells substantially [34].

\[
\begin{array}{c}
\text{H}_2\text{C} - \text{CH} \\
\text{OH}
\end{array}
\]

Fig. II.4 Structure of PVA

II.3.2. Sodium Alginate

Alginates are hydrophilic polysaccharides found in brown seaweeds (phaeophycota), comprising up to 40 wt % of the dry matter. They are well known for their ability to form a gel in contact with most divalent cations, and this property has been widely used in the food and drinks industry, as well as in the pharmaceutical sector. In contact with blood, calcium alginate will rapidly release Ca\(^{2+}\) ions in exchange for Na\(^{+}\) ions, stimulating blood coagulation and making it an ideal choice for wound dressing applications.
Sodium alginate is the sodium salt of alginic acid and its chemical formula is \((\text{C}_6\text{H}_7\text{NaO}_6)_n\). It occurs as a white to yellowish brown filamentous, grainy, granular or powdered forms. It is soluble slowly in water, forming a viscous solution; but insoluble in ethanol and ether, forms precipitate with calcium chloride.

Among the natural polymers, sodium alginate is a water-soluble polysaccharide extracted from the seaweed, having good membrane forming properties, which can be readily gelled by acid treatment or by crosslinking with glutaraldehyde or \(\text{Ca}^{2+}\) ions [35, 36]. Basically, it is a copolymer composed of \((1\rightarrow 4)\)-linked \(\beta\)-D-mannuronic acid (M) and \(\alpha\)-L-guluronic acid (G) residues arranged in a block wise fashion structures of M and G are shown in Fig.II.5. These blocks are constructed in three different ways: homopolymeric MM blocks, homopolymeric GG blocks and heteropolymeric sequentially alternating MG blocks [37]. Properties of the polymer are attributed to the presence of various amounts of \(\alpha\)-L-guluronic acid [38].

![Fig. II.5 Structures of (M) \(\beta\)-D-mannuronic acid and (G) \(\alpha\)-L-guluronic acid.](image-url)
Sodium alginate and polypropylene glycol alginate are commonly used as thickeners in foods such as ice cream and fruit-filled snacks, coffee and cheese spread. It is also used for dental impression materials, drug encapsulation, wound dressings and as a component of the antacid.

II.3.3. Chitosan

Chitosan is considered to be a random copolymer comprised primarily of repeating sugar units. Chitosan [poly-β(1→4)-D-glucosamine] is a partially deacetylated polymer of chitin [poly-β(1→4)-N-acetyl-D-glucosamine], which is found in a wide range of natural sources like crab, lobster and shrimp shells. It is a white powder, harmless, odorless, non-pollutive, non-corrosive, non-burnable and non-explosive [40-42]. Chemically it is named as poly(1-4)-2-amino-2-deoxy-β-D-glucan, having chemical formula \( (C_6H_{11}O_4N)_n \).

![Fig. II.6 Structure of chitosan.](image)

*Fig. II.6 Structure of chitosan.*
It has good film forming properties, good mechanical and chemical stability and functional groups that can be easily modified. The advantage of chitosan in the presence of free amine group is that it not only renders a polyelectrolytic effect to the polymer backbone, but also presents an active site upon which many chemical reactions may be applied. The development of commercial applications for chitosan has expanded rapidly in recent years. There is a great potential for exploitation in numerous markets. It is used in wound dressings, gauzes, medical structures and in artificial hair. It is also used in microcapsules for drug delivery systems, wastewater flocculation and industrial dyestuff recovery from textile products with antimicrobial capabilities [Source: http://www.Wellable.com marine biological and chemical company].

II.3.4. Poly(dimethyl siloxane) (PDMS)

Silicones or (polysiloxanes) are polymers having a silicon-oxygen backbone. They have a glass transition temperature ($T_g$) below the ambient temperature. The polymer chains of the polysiloxanes contain rather small side groups, which are non-polar. This results in a flexible structure, which preferentially permeates organic liquids. Therefore, the membranes made up of elastomeric material are best suited for the selective removal of organics from water. One of the most common polysiloxanes is PDMS and is widely accepted as membrane material for the pervaporation separation of organics from their aqueous streams [12].
Polysiloxanes are extremely employed in biomedical devices. These have low toxicity, high gas permeability, good mechanical properties and wide range of fabrication processes that can be used in coating, encapsulation, casting, molding, sealing and extrusion. Furthermore, they are generally inert to the body and to the immune system. These are about 10 times more permeable to oxygen than low density polyethylene (LDPE) and a hundred times more permeable than nylon or butyl rubber [43]. They have high tear strength and permeability, have been used in oxygenation, dialysis and micro-electrode materials [44-46].

**II.3.5. ZSM-5 Zeolite**

It is a silicone-rich zeolite having MFI type. Its aluminium content can be varied by several orders of magnitude, but it is always smaller than the content of silicone. This fact is responsible for the hydrophobic property of the zeolite causing hydrophobic molecules to be adsorbed preferentially [47]. Furthermore, the pore size and structure of ZSM-5 has an effect on the sorption behaviour [48]. The framework of ZSM-5 is shown in Fig. II.8 contains two intersecting channel
systems with cross-sections of 0.5-0.6 nm. The elliptical ring openings controlling
the channels also have an effective diameter between 0.5-0.6 nm [49].

![Three-dimensional structure of ZSM-5 zeolite.](image)

**Fig. II. 8** Three-dimensional structure of ZSM-5 zeolite.

### II.3.6. NaY Zeolite

It is hydrophilic in nature and its structure is isomorphous to the mineral faujasite,
as determined by X-ray [50,51] and neutron powder diffraction [52]. The
structure of NaY zeolite is shown in Fig. II.9.

![Three-dimensional structure of NaY zeolite.](image)

**Fig. II. 9** Three-dimensional structure of NaY zeolite.
The framework is composed of cubo-octahedral sodalite cages linked together in a tetrahedral arrangement by six membered rings of oxygen atoms to form large cavities, called supercages. The supercages are interconnected by 12-ring windows, consisting of 12 Si/Al and 12 oxygen atoms. A single unit cell contains eight sodalite cages and eight supercages.

II.3.7. Isopropanol (IPA)

Isopropanol is widely used in electronic and liquid crystal display industries for cleaning and drying operations during the production of semiconductors, flat panel displays, disks, opto-electronic and other electronic components [53,54].

Table II.1. Properties of isopropanol

<table>
<thead>
<tr>
<th>Appearance</th>
<th>Colourless liquid at room temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Odour</td>
<td>Pleasant</td>
</tr>
<tr>
<td>Taste</td>
<td>Slightly bitter</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C₃H₈O</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>60.09</td>
</tr>
<tr>
<td>Boiling point</td>
<td>82.5°C</td>
</tr>
<tr>
<td>Vapour pressure</td>
<td>44 torr at 25°C</td>
</tr>
<tr>
<td>Solubility</td>
<td>Miscible in water and most of the organic solvents, insoluble in salt solutions</td>
</tr>
</tbody>
</table>

Source: http://www.ee.byu.edu.cleanroom/gloves.html
Because of escalating virgin chemicals costs, disposal costs, safety and other environmental concerns, reprocessing of IPA has become an attractive, practical and cost-effective source for recycling ultra pure IPA. The availability of IPA in its pure form is difficult as it forms an azeotrope at 14.7 mass % of water concentration [55]. Hence, its separation by conventional distillation methods, such as solvent extraction and rotavapor or by distillation could prove un-economic.

II.3.8. Acetic Acid

It is a carboxylic acid with chemical formula C₂H₄O₂. Acetic acid is a molecule central to biochemistry and is produced in some amount by nearly all forms of life. The acetobacter genus of bacteria is named for its tendency to produce acetic acid, and these bacteria are found universally in foodstuffs, water and soil. As such, acetic acid is produced naturally as fruits and some other foods spoil, and it is one of the oldest chemicals known to humanity.

It is an important basic chemical in the chemical industry, ranking among the top 20 organic intermediates. In the form of vinegar, acetic acid is used directly as a condiment, and also in pickling of vegetables and other foodstuffs. Acetic acid is also sprayed onto silage as a preservative to discourage bacterial and fungal growth. The glacial acetic acid produced by the chemical industry is used in the manufacture of photographic films and sometimes in the production of the plastic polyethylene terphthalate (PET). It is also used as an intermediate for the
production of vinyl acetate, an important chemical in the paint and adhesives industry, and for cellulose acetate, a synthetic textile. Some of the esters of acetic acid are commonly used as solvents and artificial flavorings.

The current processes for acetic acid production include the carbonylation of methanol, the liquid-phase oxidation of hydrocarbons and the oxidation of acetaldehyde. One process for reducing the cost of acetic acid is fermentation of biomass, forestry residues, municipal wastes and other byproducts [56].

Table II.2 Properties of acetic acid

<table>
<thead>
<tr>
<th>Appearance</th>
<th>Colourless liquid, corrosive and flammable</th>
</tr>
</thead>
<tbody>
<tr>
<td>Odour</td>
<td>Unpleasant</td>
</tr>
<tr>
<td>Taste</td>
<td>Slightly bitter</td>
</tr>
<tr>
<td>Molecular formula</td>
<td>C₂H₄O₂</td>
</tr>
<tr>
<td>Molecular weight</td>
<td>60.05</td>
</tr>
<tr>
<td>Boiling point</td>
<td>118.1°C</td>
</tr>
<tr>
<td>Liquid density</td>
<td>1.05 ×10³ kg/m³</td>
</tr>
<tr>
<td>pKa</td>
<td>4.76</td>
</tr>
<tr>
<td>Explosive limits</td>
<td>5-16%</td>
</tr>
<tr>
<td>Solubility</td>
<td>Miscible in water and most of the organic solvents, insoluble in salt solutions</td>
</tr>
<tr>
<td>Chronic effects</td>
<td>Corrosive. Contact with concentrated vapours or solution can cause blistering and severe chemical burns. Repeated skin exposure can result in an allergic reaction.</td>
</tr>
</tbody>
</table>

Source: http://www.wordiq.com/definition/Acetic acid/html
The concentration of acetic acid obtained in this process is usually lower than 5 wt % [57,58]. Azeotropic distillation and extractive distillation have been developed for acetic acid recovery, but distillation is energy-intensive because of the small differences in the volatilities of water and acetic acid in dilute aqueous solution [59,60].

II.4. REFERENCES


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