CHAPTER 3

Materials and Experimental Methods
3.1: INTRODUCTION

This chapter deals with the experimental procedures used in pervaporation separation studies of water Ethanol and Isopropanol mixtures. Chemicals and experimental techniques used in the present research work are well explained in this chapter. Various experimental and characterization techniques such as preparation of membranes and Mixed Matrix Membranes (MMM's), swelling studies, Fourier Transform Infrared (FTIR) Spectroscopy, Thermo Gravimetric Analysis (TGA) and Scanning Electron Microscope (SEM) studies. The methods employed to prepare membranes for preparation separation studies are also explained in this chapter.

3.2: Materials

Polymers, chemicals, solvents and their sources used for the present work along with their abbreviations are tabulated in Table 3.1. All the chemicals used were of analytical grade and hence no attempt was made to purify them. Double distilled water collected in the laboratory was used throughout this work.
Table 3.1: List of Chemicals and their sources with Abbreviations used in the present work

<table>
<thead>
<tr>
<th>S.No</th>
<th>Polymer</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Sodium Alginate (Medium Molecular Weight)</td>
<td>s.d. fine Chemicals, Mumbai, India</td>
</tr>
<tr>
<td>2.</td>
<td>HEC (High Viscosity)</td>
<td>Merck, Mumbai, India</td>
</tr>
<tr>
<td>3.</td>
<td>Poly (vinyl alcohol) (mol. wt ~ 70, 000) (PVA)</td>
<td>Hi-media Laboratories Pvt., Ltd., Mumbai, India</td>
</tr>
<tr>
<td>4.</td>
<td>Glycine</td>
<td>s.d. fine Chemicals, Mumbai, India</td>
</tr>
<tr>
<td>5.</td>
<td>ZSM-5 Zeolite (Particle Size-10Å°)</td>
<td>Gift Sample From Poorna Pragna Research Institute, Bangalore, India</td>
</tr>
<tr>
<td>6.</td>
<td>3A Zeolite (Particle Size-2.8Å°)</td>
<td>Gift Sample From Poorna Pragna Research Institute, Bangalore, India</td>
</tr>
<tr>
<td>7.</td>
<td>HY Zeolite (Particle Size)</td>
<td>Gift Sample From Poorna Pragna Research Institute, Bangalore, India</td>
</tr>
<tr>
<td>8.</td>
<td>Isopropyl alcohol (IPA) (AR)</td>
<td>s.d. fine Chemicals, Mumbai, India</td>
</tr>
<tr>
<td>9.</td>
<td>Ethanol (ET) (AR)</td>
<td>s.d. fine Chemicals, Mumbai, India</td>
</tr>
<tr>
<td>10.</td>
<td>Glutaraldehyde (GA)(AR)</td>
<td>s.d. fine Chemicals, Mumbai, India</td>
</tr>
<tr>
<td>11.</td>
<td>Acetone (AC) (AR)</td>
<td>s.d. fine Chemicals, Mumbai, India</td>
</tr>
<tr>
<td>12.</td>
<td>Hydrochloric acid (HCl)(AR)</td>
<td>s.d. fine Chemicals, Mumbai, India</td>
</tr>
<tr>
<td>13.</td>
<td>Double distilled water</td>
<td>Collected in Department Laboratory</td>
</tr>
</tbody>
</table>

3.3: Pervaporation Process

Schematic pervaporation experimental setup is shown in Fig 3.1. Photograph in Fig 3.2 shows the PV assembly built in the Dept. of Polymer Science, S.K. University and it was used elsewhere [2] and the procedure used in pervaporation has been described by many researchers [2-4]. The pervaporation cell consist of two bell-shaped B-24 size glass column reducers / couplers clamped together with external padded flanges by means of tie rods to give a vacuum tight arrangement. The top half is used as the feed chamber.
The membrane is supported by a stainless steel porous plate which is embedded with an SS mesh/screen. Teflon gaskets are fixed by means of high-vacuum silicone grease on either side of the membrane, and the sandwich is placed between the two glass column couplers and secured tightly. The effective membrane area in contact with feed is almost 20 cm\(^2\) in all cases. The feed side pressure is maintained at atmospheric pressure and the vacuum in the downstream side at about 0.5 mmHg using a vacuum pump (Ind high vac, ED-18 model Bangalore, India). The permeate was collected in liquid nitrogen cold traps for a period of 8 hrs followed by analyzing the compositions of the feed and permeate at 35°C using Abbe Refracto meter (Atago, Model: DR-A1, USA) shown in Fig 3.3.

**Fig 3.1: Schematic representation of laboratory pervaporation equipment**

**Legend:**
- SM: Stirring motor
- SR: Stirring rod
- FC: Feed chamber
- TV: Teflon Volve
- CT: Condenser trap
- MA: Membrane assembly
- PC: Permeate collector
- MG: McLeod Gauge
- DF: Dewar flask
- VP: Vacuum Pump
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Fig 3.2: Photograph of Pervaporation Equipment (S.K. University)

Fig 3.3: Photograph of Abee Refractometer (S.K. University)
The pervaporation performance of the membranes was evaluated in terms of permeation flux and selectivity and using the Eqn's. (3.1) and (3.2). In pervaporation, flux, $J_t$, is calculated as given below:

$$J_t = \left( \frac{W_t}{A_t} \right)$$

(3.1)

Here $W_t$ represents the mass of water in permeate (kg), $A$ is the membrane area (m$^2$) and $t$ represents the permeation time (h).

Membrane selectivity, $\alpha$, is the ratio of permeability coefficients of water to that of isopropanol, which is calculated from their respective concentrations in feed and permeate as given below:

$$\alpha = \left( \frac{y(1 - x)}{x(1 - y)} \right)$$

(3.2)

Where ‘y’ is the permeate weight fraction of water and ‘x’ is its feed weight fraction.

3.4: Swelling properties of the membranes

Interaction of the membranes with the pure liquid components of the feed mixture was determined by gravimetric sorption experiments at 35°C [1]. Weighed samples of circular pieces of crosslinked films (2 cm diameter) were soaked in pure distilled water as well as in their binary mixtures for 48 hrs, after completion of the specified time membranes were removed from the bottles and were quickly wiped to remove adhering liquid using tissue paper without applying much pressure and then weighed immediately. Degree of swelling was calculated using the Eq 3.3.
% Degree of Swelling = \left( \frac{W_s}{W_d} \right) \tag{3.3}

Where \( W_s \) is weight of the swollen polymer in (g) and \( W_d \) is weight of the dry polymer in (g).

The percent sorption was calculated using the equation:

\[
\% \text{Sorption} = \frac{W_s - W_d}{W_d} \times 100
\]

3.5: Characterization Techniques:

Polymer consists of chains of varying lengths, and each chain consists of monomer residues which affect its properties. A variety of instrumental techniques are used to determine the properties of polymers such as: FTIR, SEM and TGA.

3.5.1: Fourier Transform Infrared (FTIR) Measurements

Infrared spectroscopy is the most common spectroscopic method used to determine the types of chemical bonds and functional groups in a polymer sample. FTIR in an important record which gives sufficient information about the structure of a compound or it can be employed to establish compounds or to determine the structure of a new compound. The FTIR spectra result from energy changes arising due to different modes of characteristic stretching and bending vibrations. In the present thesis, FTIR analysis was done using Bomem MB-3000 (Make: Canada). The finely powdered and dried samples were mixed by crushing 3 mg of the polymer with 100 mg of KBr in a pestle and mortar. Pellets were prepared under a hydraulic pressure of 600 kg/cm². These pellets were again crushed and repelleted. This step was repeated 2-3 times to get better reproducibility. Spectra were taken in the wavelength range 600-4000 cm⁻¹. The photo graph of instrument is given. (See Photo graph 3.4.)
3.5.2: Scanning Electron Microscope (SEM)

The Scanning Electron Microscope (SEM) is a type of electron microscope capable of producing high resolution images of a sample surface. Due to the manner in which the image is created, SEM images have a characteristic three-dimensional appearance and are useful for judging the surface structure of the sample.

Scanning Electron Micrographs (SEM) of surface and cross section were taken for the pure and incorporated molecular sieves composite membranes, using software controlled digital scanning electron microscope JEOL JSM 5410 (Japan).

SEM micrographs of the membranes were obtained under high resolution (Mag 300X5kv) Using Joel Model JSM 840A, scanning electron microscope (SEM), equipped with phoenix energy dispersive analysis. SEM micrographs were taken at Anna University, Chennai.
3.5.3: Thermal Analysis (Differential Scanning Calorimeter (DSC) 
And TGA Studies)

Differential Scanning Calorimeter (DSC) is a thermo analytical 
technique in which the difference in the amount of heat required to increase the 
temperature of a sample and reference are measured as a function of temperature. Both the sample and reference are maintained at very nearly the same temperature throughout the experiment. Generally, the temperature program for a DSC analysis is designed such that the sample holder temperature increases linearly as a function of time. The reference sample should have a well-defined heat capacity over the range of temperatures to be scanned. The basic principle underlying this technique is that, when the sample undergoes a physical transformation such as phase transitions, more (or less) heat will need to flow to it than the reference to maintain both at the same temperature.

DSC thermograms of pure polymer, polymer composite membranes were recorded by using a Rheometric Scientific, Model DSC-SP, UK. DSC and TGA curves of NaAlg, PVA and their blend membranes of different compositions were recorded using TA instruments differential scanning calorimeter. The analysis of the samples was performed at heating rate of 10°C/min under N₂ atmosphere at a purging speed of 100mL/min. The photograph of the instrument is given (see photograph 3.5).
3.6: Mechanical properties

The equipment used for testing mechanical properties is Universal tensile testing machine (UTM) (Instron 3369) with an operating head load of 5kN. Cross-sectional area of the sample of known width and thickness was calculated. The films were then placed between the grips of the testing machine for a constant grip length of 5 cm. The speed of testing was set at the rate of 12.5 mm/min. A photograph of the UTM used for the present study is shown in Fig 3.6. Tensile strength was calculated using Eqn: 3.5.

\[
\text{Tensile Strength} = \left( \frac{\text{Max Load}}{\text{Cross-Sectional Area}} \right) \text{N/MM}^2 \quad (3.5)
\]
Fig 3.6: Photograph of Universal testing machine (Instron) (S.K. University)
3.7: Procedure adopted for membrane preparation

Membranes were prepared by “Solution casting and Solvent evaporation” method. The procedure followed for membrane preparation was similar for all the formulations under the present investigation. Required amount of the selected polymers were taken in a 100mL beaker, in which proportional amount of solvent (in present case water) is also taken. The mixture was allowed for stirring under magnetic stirrer (500rpm) to get homogeneous solution; this solution was then filtered to remove the impurities and bubbles.

The apparatus used for membrane casting is shown in Fig 3.7. The filtered solution was poured on to the cleaned glass plate. The thickness of the membranes can be fixed using doctor’s blades. These set consists of seven blades each of varying thickness. They can be used at a time or in conjugation with the others to give the desired thickness (present case 30±2μm). They are placed between the movable metallic bar and the glass plate containing the solution such that the bar was fixed at a height so that the plates could move freely between bar and plate. The glass plate is slided through the gap created between the metal bar and the base of the casting instrument. In order to obtain a suitable membrane, care must be taken to ensure the complete absence of air bubbles or voids in the solution while casting onto the glass plate.

In order to obtain a uniform membrane, the glass plate is placed in the oven. Drying was carried for about 24-36 h at 40°C, it can also be air dried (free from dust). The later process takes long time; the solvent evaporates leaving behind the polymer membranes after the drying process. After complete drying the membrane was peeled off from the glass plate and allowed to dry in oven (40°C).
3.7.1: Preparation of ZSM-5 Zeolite filled sodium alginate composite Membrane

NaAlg (4 g) was dissolved in 80mL of water under constant stirring. Then, respective amounts of ZSM-5 zeolite filler particles (5% and 10% wt% with respect to weight of NaAlg) were weighed separately and dispersed in 20mL of water, sonicated for 30 min, and added to NaAlg solution (already prepared) with further stirring for 24 h. The solution was poured on a glass plate to cast the membranes. Dried membranes were peeled off from the glass plate and immersed in a cross-linking bath containing (30:70) water:acetone mixture along with 2.5mL of GA and 2.5mL of conc. HCl. After keeping the membranes in a crosslinking bath for about 12–14 h, they were removed, washed repeatedly with deionized water and dried in an oven at 40°C. Acetone being a non-solvent prevented the initial dissolution of the membrane and water present in the feed mixture caused membrane to swell thereby facilitating an easy penetration of glutaraldehyde into the membrane matrix to establish an
effective cross-linking. Crosslinking reaction took place between the –OH group of NaAlg and the –CHO group of glutaraldehyde due to the formation of ether linkage by eliminating water. The pristine cross-linked NaAlg membrane was also prepared in the same manner except that no particles of zeolite 408 were added. Membranes with different thicknesses ranging from 5 to 10 within ±2μm were prepared. However, a thickness of 50±2μm was found to be ideal for performing the repetitive PV experiments, which withstood the high-vacuum pressures.

### 3.7.2: Preparation of 3A Zeolite filled sodium alginate composite Membrane

Zeolite-filled NaAlg and pure NaAlg membranes NaAlg (3 g) was dissolved in 80 mL of water with continuous stirring. 3A Zeolite (0.3 g) was dispersed in 20 mL of water, and the solution was sonicated for about 30 min. This was added to the already prepared NaAlg solution with continuous stirring for 24 h and poured on a dust-free flat glass plate to cast the membranes and dried overnight. The membranes were peeled off from the glass plate and immersed in a crosslinking bath containing a water–acetone mixture (30:70) with 2.5 mL of glutaraldehyde and 2.5 mL of concentrated HCl for about 12–14 h. The crosslinked membrane was removed from the bath and dried in an oven at 40°C. The pure NaAlg membrane was prepared in the same manner without the zeolite. The membrane thickness, as measured by a screw gauge, was 40 μm.
3.7.3: Preparation of HY Zeolite filled sodium alginate composite Membrane

4 g of NaAlg was dissolved in 80 mL of water with constant stirring. Then, respective amounts of HY zeolite filler particles [5, 10 and 15 wt% with respect to weight of NaAlg] were weighed separately and dispersed in 20 mL of water, sonicated for 30 min and then added to NaAlg solution with a further stirring up to 24 hrs. The solution was poured on a glass plate to cast the membranes, dried at room temperature and peeled off from the glass plate. The dried membranes immersed in a crosslinking bath containing 75% aqueous - acetone mixture along with 2.5mL of GA and 2.5mL of HCl. After keeping the membranes in a crosslinking bath for about 10-12 hrs, they were removed, washed repeatedly with deionised water and dried in an oven at 40ºC. Membrane thickness were measured by micrometer screw gauge at different positions with standard errors being <±1.0 µm.
REFERENCES