CHAPTER 5

Synthesis, characterization and electrochemical study of magnesium-strontium phosphate composite membrane
5.1 Introduction

Membrane separation processes stand out as an alternative to conventional processes in chemical, pharmaceutical, biotechnological and food industries. In many cases the low energy consumption, reduction in number of processing steps, greater separation efficiency and improved final product quality are the main attractions of these processes [1].

The electro chemical properties can exert profound influence on the nature and magnitude of the interaction between the membrane and liquid feed, thus affecting permeating fluxes of the solvent and solute through membrane pores [2, 3]. The surface charge properties of membrane materials are among the factors that influence membrane performances and electrical characterizations of the membranes. It also plays a very important role in understanding and predicting filtration properties of the membranes [4–6].

An inorganic precipitate ion-exchanger based on organic polymeric matrix must be an interesting material, as it should possess the mechanical stability due to the presence of organic polymeric species and the basic characteristics of an inorganic ion-exchanger regarding its selectivity for some particular metal ions [7–9], indicating its useful environmental applications [10,11]. Membrane systems also played a vital role in the purification of the earliest biotechnology products [12, 13] which were developed for the blood fractionation, food, dairy and distillery industries [14].
The current study is focused upon the synthesis and characterization of stable polystyrene based MSP composite membrane by sol-gel approach, involving polystyrene as a binder by the application of pressure. The values for the membrane potential are of the order of positive mV and increase with a decrease in external electrolytes’ concentration. This shows that the membrane is cation selective. Polystyrene based MSP composite membrane demonstrates a large number of applications, which makes them attractive in filtration tasks such as beverage, textile industry, medicine, pharmacy, chemical industry, waste water treatment and others. These applications are attributed to their high thermal resistance, chemical resistance and the mechanical strength.

The surface charge density ($\tilde{D}$) is the most effective parameter that controls the membrane phenomena and was calculated using the membrane potentials values for different electrolytes by using Teorell, Meyer, and Sievers (TMS) method [15-18]. Some other parameters including distribution coefficient, transport numbers, mobility ratio and charge effectiveness etc were also calculated for polystyrene-based MSP composite membranes. Membrane potential studies are commonly used in the electrochemical characterizations of membranes [19, 20].
5.2. Theoretical Aspects of the composite membrane

5.2.1 Fixed charge density theory of Teorell–Meyer–Sievers

In the Teorell–Meyer–Sievers theory there is an equilibrium process at each solution membrane interface which has a formal analogy with the Donnan equilibrium. The assumptions made are (a) the cation and anion mobilities, fixed charge concentration are constant throughout the membrane phase but are independent of the salt concentration (b) the transference of water may be neglected. The implications of these assumptions have been discussed [21]. Further assumption is that the activity coefficient of the salt is same in the membrane and solution phase at each interface must also be made. The introduction of activities for concentrations can only be corrected by the Donnan potential using either the integration of Planck or Henderson equation. According to TMS theory, the membrane potential (applicable to a highly idealized system) is given by the equation at 25 °C

\[
\Delta \Phi_m = 59.2 \left( \log \frac{C_2}{C_1} \sqrt{\frac{4C_1^2 + D^2 + D}{4C_2^2 + D^2 + D}} + \bar{U} \log \frac{4C_2^2 + D^2 + D\bar{U}}{4C_1^2 + D^2 + D\bar{U}} \right)
\]

where \( \bar{U} = (\bar{u} - \bar{v}) / (\bar{u} + \bar{v}) \)

where \( \bar{u} \) and \( \bar{v} \) are the ionic mobilities of cation and anion \( (m^2/v/s) \) respectively in the membrane phase, \( C_1 \) and \( C_2 \) are the concentrations of the membrane and \( D \) is the charge on the membrane expressed in equivalent per litre. The graphical method of TMS determines the fixed charge \( D \) in
equivalents/litre and the cation-to-anion mobility ratio in the membrane phase.

5.3. Experimental

5.3.1. Preparation of membrane

MSP precipitate was prepared by mixing 0.2M magnesium(II)chloride (99.98% purity, E. Merck, Mumbai, India) and 0.2M strontium(II) chloride (99.98% purity, E. Merck, Mumbai, India) with 0.2M tri-sodium phosphate (99.90% purity, E. Merck, Mumbai, India) solution. The precipitate was washed well with deionized water (Water purification system, ‘Integrate, whose RO conductivity 0−200 µs/cm and UP resistivity 1−18.3 M Ω-cm’) to remove free reactant and then dried and powdered. Membrane using suitable ratio of binder (1:3) was prepared [22]. The precipitate was ground into fine powder and was sieved through 200 mesh BSS standard (granule size <0.07 mm). Pure crystalline polystyrene (Otto Kemi, India, AR) was also ground and sieved through 200 mesh. The MSP along with appropriate amount of polystyrene powder was mixed thoroughly using mortar and pestle. The mixture was then kept into a cast die having a diameter of 2.45 cm and placed in an oven (Oven-Universal, Memmert Type) maintained at 200 °C for about an hour to equilibrate the reaction mixture [23, 24]. The die containing the mixture was then transferred to a pressure device (SL-89, UK), and a pressure such as 100 MPa was applied during the fabrication of the membrane.

Our effort has been to prepare the membrane of adequate chemical and mechanical stability. The membranes prepared by embedding 25%
polystyrene were found to be mechanically most stable and gave reproducible results. Those containing larger amount (>25%) of polystyrene did not give reproducible results, while the one containing smaller amount (<25%) was found unstable [25]. Thus, the total amount of the mixture utilized for the preparation of the membrane contained 0.125 gm polystyrene 200 mesh and 0.1875 gm magnesium phosphate and 0.1875 gm strontium phosphate (200 mesh). The membranes were subjected to microscopic and electrochemical examinations for cracks and homogeneity of the surface and only those which had smooth surface and generate reproducible potentials were considered.

5.3.2. Measurement of membrane potential

Membrane potential was measured by using digital potentiometer (Electronics India model 118). The freshly prepared charged membrane was installed at the centre of the measuring cell, which had two glass containers, on either side of the membrane. The various salt solutions (chlorides of K⁺, Na⁺, and Li⁺) were prepared from B.D.H. (A.R.) grade chemicals using deionized water. Both collared glass containers had cavity for introducing the electrolyte solution and saturated calomel electrodes. The half-cell contained 25 ml of the electrolyte solution while the capacity of each of the half cells holding the membrane was about 35 ml. The electrochemical setup used for uni-ionic potential and membrane potential measurements may be depicted as:
5.3.3. Characterization of membrane

The pre-requisite criterion for understanding the performance of an ion-exchange membrane is its complete physico-chemical characterization, which involves the determination of all such parameters that affects its electrochemical properties. These parameters include membrane water content, porosity, thickness and swelling etc. These were determined in accordance with the method described by [26, 27].

5.3.3.1. Water content (% total wet weight)

The conditional membrane was first soaked in water, blotted quickly with Whatmann filter paper to remove surface moisture and immediately weighed. These were further dried to a constant weight in a vacuum over P₂O₅ (dehydrating agent) for 24 hr. The water content (total wet weight) was calculated as:

\[
\% Total\,(weight_{\text{wet}}) = \frac{W_w - W_d}{W_w} \times 100
\]

Where \(W_w\) is the weight of the soaked or wet membrane and \(W_d\) the weight of the dry membrane.

5.3.3.2. Porosity

Porosity was determined as the volume of water incorporation in the cavities per unit membrane volume from the water content data:
\[
Porosity = \frac{W_w - W_d}{AL\rho_w}
\]

Where \(W_d\) is the weight of the dry membrane, \(W_w\) is the weight of the soaked or wet membrane, \(A\) is the area of the membrane, \(L\) is the thickness of the membrane and \(\rho_w\) is the density of water.

**5.3.3.3. Thickness**

The thickness of the membrane was measured by taking the average thickness of the membrane using screw gauze.

**5.3.3.4. Swelling**

Swelling was measured in accordance with the procedure described by Arfin and Rafiuddin [27]. It was calculated as the difference between the average thickness of the membrane equilibrated with 1M NaCl for 24 h and the dry membrane.

**5.3.3.5. Chemical stability**

Chemical stability was evaluated on the basis of ASTM D543-m95 method. Membrane was exposed to several media commonly used. Membrane was evaluated after 24, 48 and 168 h, analyzing alteration in colour, texture, brightness, decomposition, splits, holes, bubbles, curving and stickiness [28].

**5.3.4. SEM investigation of membrane morphology**

Scanning Electron Microscopic image was taken to confirm the microstructure of fabricated porous membrane. The membrane morphology was investigated by ZEISS EVO Series Scanning Electron Microscope EVO
50 at an accelerating voltage of 20 kV. Sample was mounted on a copper stub and sputter coated with gold to minimize the charging.

5.3.5 X-ray diffraction studies of the composite membrane

X-ray diffraction pattern of the composite ion-exchange membrane was recorded by Miniflex-II X-Ray diffractometer (Rigaku Corporation) with Cu Kα radiation.

5.3.6 FT-IR Spectra of membrane

The IR spectrum of Polystyrene based MSP composite membrane was done by Interspec 2020 FT-IR spectrometer, spectrolab (UK). The sample compartment was 200 mm wide, 290 mm deep and 255 mm high. The entrance and exit beam to the sample compartment was sealed with a coated KBr window and there was a hinged cover to seal it from the environment.

5.3.7 Antibacterial activity of membrane

The antibacterial study of Polystyrene based MSP composite membrane was tested in vitro against two Gram-positive bacteria *Staphylococcus aureus* (MSSA 22) and *Bacillus subtilis* (ATCC 6051) and two Gram-negative bacteria *Escherichia Coli* (K 12) and *Pseudomonas aeruginosa* (MTCC 2488) strains using disc diffusion method [29,30]. The discs measuring 5 mm in diameter were prepared from Whatmann No. 1 filter paper sterilized by dry heat at 140 °C for 1 hr after then discs were soaked in a 0.2M concentration of the test complex.

The screening was performed for 114.4 μg/ml concentration of test Polystyrene based MSP composite membrane and antibiotic discs.
Tetracycline (30 μg/disc, Hi- Media) was used as positive control. The discs were placed on the agar plates, which had previously been inoculated with the above testing organisms and incubated for 24 hr at 37 °C. After incubation inhibition zones appearing around the discs were measured and recorded in mm.

The nutrient broth which, logarithmic serially twofold diluted amount of test Polystyrene based MSP composite membrane and controls, was inoculated within the range 10^7–10^8 cfu/ml. The cultures were incubated for 24 hr at 37 °C and growth was monitored visually and spectrophotometrically like [31]. The lowest concentration (highest dilution) required to arrest the growth of bacteria is regarded as minimum inhibitory concentration. The number of colony forming units (cfu) was counted after 24 hr of incubation at 37 °C.

5.4 Results and discussion

The characterization of membrane morphology has been studied by a number of investigators using scanning electron microscopy [32, 33]. The surface morphologies of the membranes show uniform arrangement of particles while cross-sectional SEM image shows no visible cracks. The composite pore structure, micro/macro porosity, homogeneity, thickness, cracks and surface texture/morphology have been studied [34, 35]. The SEM, cross-sectional and surface images of the Polystyrene based MSP composite membrane prepared at 100 MPa applied pressure respectively are shown in Fig. 1(a) and Fig. 1(b). SEM images have provided ideas regarding the
preparation of well ordered crack free membranes. Membrane had random non-preferential orientation with no visible cracks and appeared to be composed of dense and loose aggregation of small particles. The SEM image is dense in nature and formed pores probably with non-linear channel but not fully interconnected. Particles are irregularly condensed and adopt a heterogeneous structure composed of masses of various sizes. Due to the strong interactions between the styrene particles and the membrane pore walls, the particles do not permeate through the membrane.

The distributions of charge density and mobile species within the pores are assumed to be uniform. The diameters of the polystyrene particles are clearly much smaller than the pore diameters of the membrane used [36].

The X-ray diffraction spectrum of the polystyrene based MSP composite membrane is shown in Fig. 2. The X-ray diffraction pattern of this material recorded in powdered sample exhibited strong intensities in the spectrum (2θ range) which suggest crystalline nature of the composite material. XRD results show the crystalline nature of polystyrene based MSP composite membrane.
Fig. 1  SEM images of polystyrene based MSP composite membrane at 100MPa and magnification of 5.00Kx (a). Cross-sectional view (b). Surface image
Fig. 2. X-Ray diffraction pattern of composite polystyrene based MSP composite membrane
Inorganic composite membranes have the ability to generate potential when two electrolyte solutions of unequal concentration are separated by a membrane and driven by different chemical potential acting across the membrane [37, 38]. The migration of charged species is regulated by the electrical behaviour of the membrane and diffusion of electrolytes from higher to lower concentration takes place through the charged membrane. Infact, the mobile species penetrate into the membrane at different magnitude and various transport phenomena, including the development of potential across it, are induced into the system [39].

The results of thickness, swelling, porosity and water content capacity of Polystyrene based MSP composite membrane are summarized in Table 1. The water content of a membrane depends on the vapour pressure of the surroundings. In case of most of the transport measurements, only the membrane water content at saturation is needed, and that too mostly as a function of solute concentration. Thus, low order of water content, swelling and porosity with less thickness of membrane suggests that interstices are negligible and diffusion across the membrane would occur mainly through exchange sites [40].

Membrane was tested for chemical resistance in acidic, alkaline and strongly oxidant media. In acidic (1M H₂SO₄) and in alkaline media (1M NaOH) few significant modifications were observed after 24, 48 and 168 h, demonstrating that the membrane was quite effective in such media.
Table 1: Thickness, water content, porosity and swelling properties of polystyrene based MSP composite membrane at (100-160) MPa Pressure.

<table>
<thead>
<tr>
<th>Applied Pressure (MPa)</th>
<th>Thickness of the membrane (cm)</th>
<th>Water content as % weight of wet membrane</th>
<th>Porosity</th>
<th>Swelling of % weight wet membrane</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>0.090</td>
<td>0.07</td>
<td>0.082</td>
<td>No Swelling</td>
</tr>
<tr>
<td>120</td>
<td>0.085</td>
<td>0.06</td>
<td>0.071</td>
<td>No Swelling</td>
</tr>
<tr>
<td>140</td>
<td>0.080</td>
<td>0.05</td>
<td>0.059</td>
<td>No Swelling</td>
</tr>
<tr>
<td>160</td>
<td>0.075</td>
<td>0.04</td>
<td>0.053</td>
<td>No Swelling</td>
</tr>
</tbody>
</table>
However, in strong oxidant media the synthesized membrane became fragile in 48 h and broken after 168 h, losing mechanical strength. In general membranes having the same chemical composition were found to absorb same amount of water, where density ionisable groups are same throughout the membrane [41]. Moreover, in membrane transport phenomenon, membrane water content as a function of solute concentration at saturation is needed. Thus, low order of water content, swelling and porosity with less thickness of this membrane suggests that interstices are negligible and diffusion across the membrane would occur mainly through exchange sites.

The FTIR spectral technique has been used as a valuable tool to explain the binding sites of polystyrene based MSP composite membrane. The FTIR spectra indicates the various peaks (Fig. 3) of functional groups present in the composite containing polystyrene moiety with the metals i.e. magnesium and strontium. The aromatic peaks are well defined at the position 698, 754 and 869 cm\(^{-1}\) exhibiting the presence of an aromatic ring [42].

The C=C of the ring shows characteristics peak at 1650 and 1456 cm\(^{-1}\). The C-H stretching frequencies are shown as broad band at 2924 cm\(^{-1}\). The C-H bonding peak is at 1075 cm\(^{-1}\) as a broad band. The peaks in the spectra of polystyrene based MSP composite show a comparatively negative shift as compared to those of the free ligand (polystyrene), due to coordination with metal [42]. The phosphate group present in the composite material shows the peak at appropriate position in the spectra.
Fig. 3. FTIR Spectra of polystyrene based MSP composite membrane
The biological activity of Polystyrene based MSP composite membrane have been studied for its antibacterial activities using disc diffusion method [29, 30] in vitro against two Gram-positive bacteria Staphylococcus auras (MSSA 22) and B. subtilis (ATCC 6051) and two Gram-negative bacteria E. Coli (K 12) and P. aeruginosa at concentration of 114.4 μg/ml. Tetracycline was used as standard drug for the comparison of bacterial results and screening data are given in Table-2. The novel synthesized Polystyrene based MSP composite membrane have exerted noteworthy inhibitory activity against the growth of the tested bacterial strains and data reveal that Polystyrene based MSP composite membrane have good influence on the antibacterial profile of S. aureus and B. subtilis. The Polystyrene based MSP composite membrane show excellent inhibitory results against E. coli and P. aeruginosa as reported in Table 2.

The values of observed membrane potentials, measured across polystyrene based MSP composite membrane in contact with various uni-univalent electrolyte (KCl, NaCl, LiCl) solutions at different concentrations at 25±1 °C are given in Table-3. These values were found to be concentration dependent. At low concentration, the potential was found to be high, whereas on increasing concentration of electrolytes the potential decreased. The membrane potential offered by various 1:1 electrolytes followed the order LiCl > NaCl > KCl. The values for the membrane potential are of the order of
Table 2: Antibacterial activity of polystyrene based MSP composite membrane.

<table>
<thead>
<tr>
<th>Bacteria</th>
<th>MSP composite membrane</th>
<th>Tetracycline</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Staphylococcus aureus</em></td>
<td>30.4 (±1.37)</td>
<td>20 (± 0.23)</td>
</tr>
<tr>
<td><em>Bacillus subtilis</em></td>
<td>29.5 (±1.10)</td>
<td>21 (± 0.55)</td>
</tr>
<tr>
<td><em>Escherichia Coli</em></td>
<td>28.2 (±0.62)</td>
<td>25 (± 0.88)</td>
</tr>
<tr>
<td><em>Pseudomonas aeruginosa</em></td>
<td>26.6 (±1.26)</td>
<td>24 (± 0.63)</td>
</tr>
</tbody>
</table>
positive mV and increase with a decrease in external electrolytes’ concentration. This shows that the membrane is negatively charged (cation selective).

Inorganic precipitate membranes were found to have the ability to generate potentials when interpose between electrolyte solutions of different concentrations due to the presence of net charge on the membranes [43, 44]. These charges play crucial role in the transport of electrolytes [45]. The membrane potential data obtained with Polystyrene based MSP composite membrane using various 1:1 electrolytes are plotted as a function of $-\log C_2$ (Fig. 4).

The fixed charge concept of TMS model [15-18] for charged membrane is an appropriate starting point for the investigations of the actual mechanisms of ionic or molecular processes which occur in membrane phase. The membrane potential according to TMS applicable to an idealized system is represented in equation (1). The thickness of the polystyrene based MSP composite membrane is found to be 0.075 cm.
Table 3: Observed membrane potential in mV across the polystyrene based MSP composite membrane in contact with various 1:1 electrolytes at different concentrations and pressures at 25±1 °C.

<table>
<thead>
<tr>
<th>C₂ (mol/l)</th>
<th>100 (MPa)</th>
<th>120 (MPa)</th>
<th>140 (MPa)</th>
<th>160 (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>KCl</td>
<td>NaCl</td>
<td>LiCl</td>
<td>KCl</td>
</tr>
<tr>
<td>1</td>
<td>2.5</td>
<td>4.2</td>
<td>5.8</td>
<td>3.2</td>
</tr>
<tr>
<td>0.1</td>
<td>7.4</td>
<td>10.6</td>
<td>12.6</td>
<td>8.0</td>
</tr>
<tr>
<td>0.01</td>
<td>14.7</td>
<td>17.5</td>
<td>20.3</td>
<td>15.4</td>
</tr>
<tr>
<td>0.001</td>
<td>28.5</td>
<td>30.4</td>
<td>34.7</td>
<td>29.1</td>
</tr>
<tr>
<td>0.0001</td>
<td>42.3</td>
<td>44.8</td>
<td>47.5</td>
<td>43.5</td>
</tr>
</tbody>
</table>

Membrane Potential (mV)
Fig. 4. Plots of observed membrane potentials against logarithm of concentration for polystyrene based MSP composite membrane using various 1:1 electrolytes at 100 MPa pressure.
The charge densities of inorganic membranes were estimated from the membrane potential measurement and can also be estimated from the transport number. To evaluate this parameter for the simple case of a 1:1 electrolyte and a membrane carrying various charge density \( D \leq 1 \). The theoretical potential and observed potential were plotted as a function of \(-\log C_2\) as shown by solid and broken lines, respectively in Fig. 5. Thus, the coinciding curve for various electrolytes system gave the value of the charge density \( \bar{D} \) within the membrane phase as shown in Table-4. Thus order of charge density for electrolytes used were found to be \( \text{KCl} > \text{NaCl} > \text{LiCl} \). The charge density in the case of KCl is higher than in NaCl case due to the size factor (the smaller size, the larger ionic atmosphere).

The thickness of the polystyrene based MSP composite membranes were diminished continuously from 0.090 cm to 0.075 cm with progressive increase in the applied pressure. The increase in the values of \( \bar{D} \) with higher applied pressure is due to the successive increase of charge per unit volume as well as the decrease in pore volume of polystyrene based MSP composite membrane and therefore, the degree of selectivity for ions is enhanced with the modification in surface microstructure of membrane. Surface charge density \( \bar{D} \) of membrane for 1:1 electrolytes (KCl, NaCl and LiCl) were plotted against pressures (Fig. 6) and the order of charge density for electrolytes used were found to be \( \text{KCl} > \text{NaCl} > \text{LiCl} \).
Fig. 5. Plots of membrane potential (theoretical and observed) (mV) versus $-\log C_2$(mol/l) at different concentrations of KCl electrolyte solution for polystyrene based MSP composite membrane prepared at pressure of 100 MPa.
Table 4: Derived values of membrane charge density ($\bar{D} \times 10^{-3}$ eq/l) of polystyrene based MSP composite membrane for various electrolyte system using TMS equation.

<table>
<thead>
<tr>
<th>Applied pressure (MPa)</th>
<th>KCl $\bar{D} \times 10^{-3}$</th>
<th>NaCl $\bar{D} \times 10^{-3}$</th>
<th>LiCl $\bar{D} \times 10^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100</td>
<td>9.83</td>
<td>7.70</td>
<td>5.78</td>
</tr>
<tr>
<td>120</td>
<td>10.20</td>
<td>6.90</td>
<td>5.29</td>
</tr>
<tr>
<td>140</td>
<td>10.80</td>
<td>7.56</td>
<td>6.08</td>
</tr>
<tr>
<td>160</td>
<td>11.10</td>
<td>8.22</td>
<td>7.30</td>
</tr>
</tbody>
</table>
Fig. 6. The plot of surface charge density $D$ of polystyrene based MSP composite membrane for 1:1 electrolytes (KCl, NaCl and LiCl) versus pressures.
The TMS Equation (1) can also be expressed by the sum of Donnan potential $\Delta \Psi_{Don}$, between the membrane surfaces and the external solutions, and the diffusion potential $\Delta \Psi_{diff}$ within the membrane \cite{46, 47}.

$$\Delta \Psi_{m,e} = \Delta \Psi_{Don} + \Delta \Psi_{diff}$$  \hspace{1cm} (2)

Where

$$\Delta \Psi_{Don} = -\frac{RT}{V_k F} \ln \left( \frac{\gamma_{2^+} C_2 \overline{C}_{2^+}}{\gamma_{1^+} C_1 \overline{C}_{1^+}} \right)$$  \hspace{1cm} (3)

The $R$, $T$ and $F$ have their usual significance; $\gamma_{1^\pm}$ and $\gamma_{2^\pm}$ are the mean ionic activity coefficients; $\overline{C}_{1^+}$ and $\overline{C}_{2^+}$ are the cation concentration in the membrane phase first and second, respectively. The cation concentration is given by the equation

$$\overline{C}_+ = \sqrt{\left( \frac{V_i D}{2V_k} \right)^2 + \left( \frac{\gamma_+ C}{q} \right)^2} - \frac{V_i D}{2V_k}$$  \hspace{1cm} (4)

where $V_k$ and $V_i$ refer to the valency of cation and fixed-charge group on the membrane matrix, $q$ is the charge effectiveness of the membrane and is defined by the equation

$$q = \sqrt{\frac{\gamma_\pm}{K_\pm}}$$  \hspace{1cm} (5)

where $K_\pm$ is the distribution coefficient expressed as;

$$K_\pm = \frac{\overline{C}_i}{C_i}, \quad \overline{C}_i = C_i - D$$  \hspace{1cm} (6)
Where \( C_i \) is the \( i^{th} \) ion concentration in the membrane phase and \( C_i \) is the \( i^{th} \) ion concentration of the external solution. The transport of electrolyte solutions in pressure-driven membrane has shown that the transport properties of membrane are also controlled by ion distribution coefficients. It appeared that utilizing the Equation (6) for evaluating the distribution coefficients were found to be low at lower concentration and as the concentration of electrolytes increases the value of distribution coefficients, sharply increases and thereafter, a stable trend was observed and is presented in the Table-5.

The diffusion potential \( \Delta \Psi_{diff} \), is expressed in the form

\[
\Delta \Psi_{diff} = - \frac{RT}{V_k F} \frac{\overline{\omega} - 1}{\overline{\omega} + 1} \times \ln \left( \frac{\eta + 1}{\eta + 1} \times \frac{\gamma_{2+} C_2}{\gamma_{1+} C_1} \right) \quad (7)
\]

where \( \overline{\omega} = \frac{\eta}{\nu} \) is the mobility ratio of the cation to the anion in the membrane phase. The total membrane potential \( \Delta \Psi_{m,e} \), was thus obtained by simple addition of Eqs. (3) and (7).

\[
\Delta \Psi_{m,e} = - \frac{RT}{V_k F} \ln \left( \frac{\gamma_{2+} C_2}{\gamma_{1+} C_1} \right) - \frac{RT}{V_k F} \frac{\overline{\omega} - 1}{\overline{\omega} + 1} \times \ln \left( \frac{\eta + 1}{\eta + 1} \times \frac{\gamma_{2+} C_2}{\gamma_{1+} C_1} \right) \quad (8)
\]

In order to test the applicability of these theoretical equations for the system under investigation, the Donnan potential and diffusion potential were separately calculated from the membrane parameters obtained from membrane potential measurements using a typical membrane prepared at a pressure of 100 MPa.
The transport properties of the membrane in various electrolyte solutions are important parameters to further investigate the membrane phenomena as shown in Equation (9)

$$\Delta \bar{\psi}_m = \frac{RT}{F} \ln \frac{C_2}{C_1} \left( t_+ \ln \frac{C_2}{C_1} + \frac{t_-}{t_+} \right)$$

Equation (9) was first used to get the values of transport numbers $t_+$ and $t_-$ from experimental membrane potential data and consequently, the mobility ratio $\frac{\bar{\nu}}{\bar{\upsilon}} = \frac{t_+}{t_-}$ and $U$ were calculated. The mobility $\bar{\omega}$ of the electrolyte in the membrane phase were found to be high and the order is LiCl>NaCl>KCl and shown in Fig.7.

The high mobility is attributed to higher transport number of comparatively free cations of electrolyte which was also found to have the similar trend as the mobility in least concentrated solution.

The transport number of cation of the various electrolytes (KCl, NaCl, LiCl) increases with decreasing the concentration of electrolytes and follows the increasing order KCl<NaCl<LiCl shown in Fig. 8.

Donnan and diffusion potential at various electrolyte concentrations can be calculated from the parameters $\gamma_{1\pm}$, $\gamma_{2\pm}$, $\bar{C}_{1\pm}$, $\bar{C}_{2\pm}$, $\bar{\omega}$, $V_x$, $V_k$ and the experimentally derived values of charge density $\bar{D}$ by using Equations (3) and (7). The values of the parameters $K_{\pm}$, $q$ and $\bar{C}_+$ derived for the system are also shown in Table 5. The values of $\gamma_{\pm}$ were the usual charted values for electrolyte (KCl, NaCl and LiCl).
Fig. 7. The plot of mobility ratio of polystyrene based MSP composite membrane for 1:1 electrolytes (KCl, NaCl and LiCl) versus concentrations
Fig. 8. The plot of transport number of cation of polystyrene based MSP composite membrane for 1:1 electrolytes (KCl, NaCl and LiCl) versus concentrations
Table 5: The values of $t_\infty$, $\bar{U}$, $\bar{\omega}$ and $K_\infty$, $q$, $\bar{C}_+$ evaluated using Eq. (9), (6), (5) and Eqs. (4) respectively, from observed membrane potentials for various electrolytes at different concentrations for polystyrene based MSP composite membrane prepared at 100 MPa pressure.

<table>
<thead>
<tr>
<th>KCl (Electrolyte)</th>
<th>C_2 (mol/l)</th>
<th>$t_\infty$</th>
<th>$\bar{U}$</th>
<th>$\bar{\omega}$</th>
<th>$K_\infty$</th>
<th>$q$</th>
<th>$\bar{C}_+$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1.000</td>
<td>0.53</td>
<td>0.06</td>
<td>1.12</td>
<td>0.9902</td>
<td>1.0049</td>
<td>0.9895</td>
</tr>
<tr>
<td></td>
<td>0.100</td>
<td>0.57</td>
<td>0.14</td>
<td>1.32</td>
<td>0.9020</td>
<td>1.0529</td>
<td>0.0899</td>
</tr>
<tr>
<td></td>
<td>0.0100</td>
<td>0.63</td>
<td>0.26</td>
<td>1.70</td>
<td>0.0200</td>
<td>7.0710</td>
<td>0.00364</td>
</tr>
<tr>
<td></td>
<td>0.0010</td>
<td>0.75</td>
<td>0.50</td>
<td>3.00</td>
<td>-8.8000</td>
<td>0.3370</td>
<td>0.00002</td>
</tr>
<tr>
<td></td>
<td>0.0001</td>
<td>0.86</td>
<td>0.72</td>
<td>6.14</td>
<td>-97.0000</td>
<td>0.1015</td>
<td>0.000007</td>
</tr>
<tr>
<td>NaCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.000</td>
<td>0.54</td>
<td>0.08</td>
<td>1.17</td>
<td>0.9923</td>
<td>1.0038</td>
<td>0.9916</td>
</tr>
<tr>
<td></td>
<td>0.100</td>
<td>0.59</td>
<td>0.18</td>
<td>1.43</td>
<td>0.9230</td>
<td>1.0408</td>
<td>0.0918</td>
</tr>
<tr>
<td></td>
<td>0.0100</td>
<td>0.65</td>
<td>0.30</td>
<td>1.85</td>
<td>0.2300</td>
<td>2.0851</td>
<td>0.0042</td>
</tr>
<tr>
<td></td>
<td>0.0010</td>
<td>0.76</td>
<td>0.52</td>
<td>3.16</td>
<td>-6.7000</td>
<td>0.3863</td>
<td>0.00003</td>
</tr>
<tr>
<td></td>
<td>0.0001</td>
<td>0.88</td>
<td>0.76</td>
<td>7.33</td>
<td>-76.0000</td>
<td>0.1144</td>
<td>0.000009</td>
</tr>
<tr>
<td>LiCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>1.000</td>
<td>0.55</td>
<td>0.10</td>
<td>1.22</td>
<td>0.9943</td>
<td>1.0028</td>
<td>0.9936</td>
</tr>
<tr>
<td></td>
<td>0.100</td>
<td>0.61</td>
<td>0.22</td>
<td>1.56</td>
<td>0.9430</td>
<td>1.0297</td>
<td>0.0936</td>
</tr>
<tr>
<td></td>
<td>0.0100</td>
<td>0.68</td>
<td>0.36</td>
<td>2.12</td>
<td>0.4300</td>
<td>1.5249</td>
<td>0.0051</td>
</tr>
<tr>
<td></td>
<td>0.0010</td>
<td>0.80</td>
<td>0.60</td>
<td>4.00</td>
<td>-4.7000</td>
<td>0.4612</td>
<td>0.00004</td>
</tr>
<tr>
<td></td>
<td>0.0001</td>
<td>0.91</td>
<td>0.82</td>
<td>10.11</td>
<td>-56.0000</td>
<td>0.1336</td>
<td>0.00001</td>
</tr>
</tbody>
</table>
5.5 Conclusion

The polystyrene based MSP composite membrane was prepared after preliminary investigations, the binder polystyrene was selected because its cross-linked rigid framework provides an adequate adhesion to the MSP composite, which accounts for the mechanical stability to the membrane. Particles are irregularly condensed and adopt a heterogeneous structure composed of masses of various sizes and membrane is crystalline in nature.

The membrane potential of polystyrene based MSP composite membranes for different uni-univalent electrolytes was found to follow an increasing order $\text{KCl}<\text{NaCl}<\text{LiCl}$. The result indicates that the behaviour of investigated membrane is cation selective.

Fixed charge density is the central parameter governing transport phenomena in membrane and depends upon the feed composition. The order of surface charge density for uni-univalent electrolytes solution was found to be $\text{LiCl}<\text{NaCl}<\text{KCl}$. 
5.6 References


[14]. F.V. Kosikowski, Membrane separations in food processing, in: W.C. McGregor (Ed.), Membrane Separations in Biotechnology, Marcel Dekker, Inc., New York,


