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Effect of novel Polysiloxane functionalized Poly(AMPS-co-CEA) membranes for base recovery from alkaline waste solution via diffusion dialysis

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In the modern arena of separation science and technology, cation exchange membrane (CEM) based diffusion dialysis (DD) has attracted remarkable attention due to their unique ion transport phenomena during the application for base recovery. In this manuscript, for the first time we are going to reveal novel Disodium 4-Formylbenzene-1,3-disulfonate modified polysiloxane (FSP) induced Poly(AMPS-co-CEA) based CEMs with polyvinyl alcohol (PVA) as a binder and tetraethoxysilane (TEOS) acting as a crosslinker for base recovery *via* diffusion dialysis. Synthesis of Poly(AMPS-co-CEA) involved classical free radical polymerization with azobisisobutyronitrile (AIBN) acted as an initiator. By regulating the dosage of FSP in membrane matrix, physiochemical as well as electrochemical properties of the prepared membranes can be modified. Prepared membranes were investigated comprehensively in terms of water uptake (W_R), ion exchange capacity (IEC) along with the thermo-mechanical measurements like DMA and TGA. The effect of FSP was discussed in brief to correlate the base recovery behaviour of prepared membranes. Prepared CEMs have the water uptakes (W_R) ranging 204.0–248.7%, ion exchange capacity (IEC) between 0.58–0.76 mmol/g, tensile strength (TS) varied between 9.3–15.9 MPa as well as elongation at break (E_b) of 125.6–236.7%. At 25 °C, the dialysis coefficients (U_{OH}) values appeared as high

as 0.0078-0.0112 m/h and the separation factors (S) ranged from 10.32 to 14.19. The membranes described in this manuscript could be a promising contender for base recovery via diffusion dialysis.

Keywords: Cation exchange membrane, Poly(AMPS-co-CEA), FSP, Diffusion dialysis, Base recovery.

Introduction

From the view point of metal finishing industries, ion exchange membrane (IEM) based separation methods have got remarkable attention during last two decades due to their exclusive potential selectivity for specific ions as well as the ability for acid and base recovery.¹⁻⁵ Traditionally, ion exchange membranes can be allocated into two major sections, namely as: i) cation exchange membrane (CEMs) and ii) anion exchange membrane (AEMs), depending upon the type of functional groups attached to the polymer backbone. IEMs were most widely used in different industries for various separation purposes via the membrane based available techniques such as diffusion dialysis (DD), electrodialysis (ED), donnan dialysis and electro-membrane reactors.⁴⁻¹⁰ In several industrial production houses like leather, paper, dyeing and printing, aluminium & tungsten ore smelting as well as man-made fiber industries, a great deal of alkaline waste solution is produced which is known to be a major concern from the environmental perspective.¹¹⁻¹² Thus base recovery from the aqueous waste solution became really crucial for pollution free environment. The ultimate goal of this method was to avoid the environmental pollution by recovering alkali from aqueous waste solution along with the financial benefits to industries.^{13,14}

Till date, different existing methods such as neutralization, concentration and burning (in paper industries) were applied to deal with alkaline wastes but demand for enormous amount

of acids or plenty of energy limits its application. Ion exchange resins based adsorption process was irregular due to the regeneration of resins after successive operation. Therefore, we certainly need to have a cleaner and more competent method to handle the alkaline wastes solution. Under these circumstances, where there was a severe need to cope up with the scarcity for available efficient methods for alkali recovery, DD process turned out to be the best one among all other separation based techniques due to its incomparable unique features.¹⁵⁻¹⁷ The exceptional features of DD process are lower energy intake, simple construction of the apparatus, no pollution, continuous operation and recoverable alkali or acid.¹⁸⁻²¹ DD is thus considered to be the most favorable separation technique known till date in which variation in concentration gradient plays the major role as solutes passed through an IEM from higher concentration side to the lower one.^{8,22-23} By this process, base recovery from aqueous waste solution was done so efficiently and has been reported in several literatures.^{4,12}

A superior diffusion dialysis membrane must possess the following requirements like high thermo-mechanical property, base resistance, base permeation as well as selectivity in order to demonstrate its authenticity for separation purpose.⁴² Therefore, membrane construction remains a challenging assignment as fabricated membrane needs to possess aforementioned criteria to be a deserving candidate for DD application.¹⁵⁻¹⁷ A number of different polymer backbone was used to prepare CEMs for base recovery from various resources like: poly vinyl alcohol (PVA), sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO), polyvinylidene fluoride (PVDF).^{4,12,24-25} In light of SPPO membrane, though it possesses high thermo-mechanical stability still the major issue remained its low base permeation therefore with this kind of membrane getting high base permeation value appeared as a real challenging issue. This low permeability factor gave us adequate ideas about moving towards different

polymer backbone and forced us to incorporate different functionality in membrane matrix to achieve better result than available one.²⁶

In view of the above fact kept under surveillance, we were mainly focused towards a polymer (PVA) which should be more hydrophilic in nature and different functionality, crosslinking agents were introduced inside polymer backbone for better stability and applications.^{27,28} Additionally, PVA based membranes showed better performance as well as thermo-mechanical stability. In view of the above mentioned facts related to alkali recovery via DD process PVA based membranes are considered to be a good choice.

Hence, to create the trend for CEMs based DD process, a well-organized technique was projected to prepare organic-inorganic nanocomposite cation exchange membrane relied on PVA, Poly(AMPS-co-CEA) and FSP (Disodium 4-Formylbenzene-1,3-disulfonate modified polysiloxane) in this manuscript. The synthesis of Poly(AMPS-co-CEA) and FSP were performed under mild conditions and for the first time reported in literature. The consequence of the membrane fabrication process *e.g.* the extent of FSP on membrane assembly and influence on membrane characteristic properties such as ion exchange, water uptake etc. has been thoroughly explored. With the fabricated membranes DD experiment was carried out using NaOH/Na₂WO₄ model aqueous waste mixture to intricate the separation capabilities as well as base recovery.

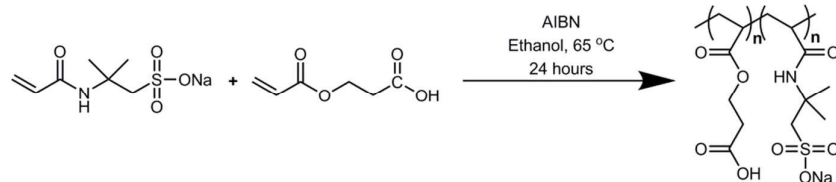
Experimental

Materials

Poly Vinyl Alcohol (PVA, average degree of polymerization: 1750±50) was purchased from Shanghai Yuanli Chemical Co. Ltd. (China). 2-Carboxyethyl acrylate (CEA) and 2-Acrylamido-2-methyl-1-propanesulfonic acid sodium salt solution (50 wt% in H₂O) (AMPS) were purchased from Sigma Aldrich. Disodium 4-Formylbenzene-1,3-disulfonate (FBDS) and 3-(Trimethoxysilyl)-1-propanamine were obtained from TCI Chemicals and Energy

Chemical, China respectively. Tetraorthoethoxy silane (TEOS) was purchased from domestic chemical company (China). Azobisisobutyronitrile (AIBN) was dissolved in hot methanol (40 °C) and recrystallized in an ice bath, finally dried in a vacuum oven at room temperature. All other reagents used here were of analytical grade and used without further purification. Deionized water (DI water) was used throughout the experiments.

Synthesis of Poly(AMPS-co-CEA)

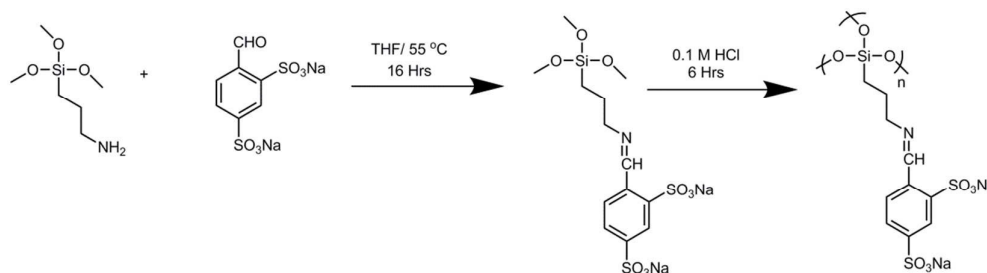


Scheme 1. Reaction scheme of synthesized Poly(AMPS-co-CEA).

Poly(AMPS-co-CEA) was synthesized by the reaction of 2-Carboxyethyl acrylate (CEA) and 2-Acrylamido-2-methyl-1-propanesulfonic acid sodium salt solution (AMPS) in the following manner (Scheme 1). In a typical synthetic procedure, a 50 mL oven-dried round bottom flask was taken with a required amount of CEA (1.0 g, 0.0069 mol). 10 mL of ethanol was added very carefully to the reaction medium. After stirring the complete reaction mixture for 15 minutes, a known amount of AMPS (3.18 g, 0.0069 mol of AMPS) was added to the reaction mixture. Finally, (0.023 g, 0.000138 mol) of AIBN was added to the reaction mixture as the free radical initiator while the mixture was stirred continuously at 65 °C for 24 hours in order to complete the polymerization reaction. Afterwards, the reaction mixture was poured into cold acetone and kept inside the freeze for overnight. Obtained precipitate was then carefully filtered and washed several times with acetone to remove impurities and other volatiles. Finally, the obtained polymer was dried in *vacuo* and the crude product appeared as white solid (2.412 g) which was further characterized by means of NMR and FT-IR spectroscopy. ¹H NMR (D₂O-*d*₂, 400 MHz): δ 1.16-2.20 (12H), δ 2.76 (2H), δ 3.38-3.83

(2H), δ 4.38 (2H) ppm.

Synthesis of Disodium 4-Formylbenzene-1,3-disulfonate modified polysiloxane (FSP)

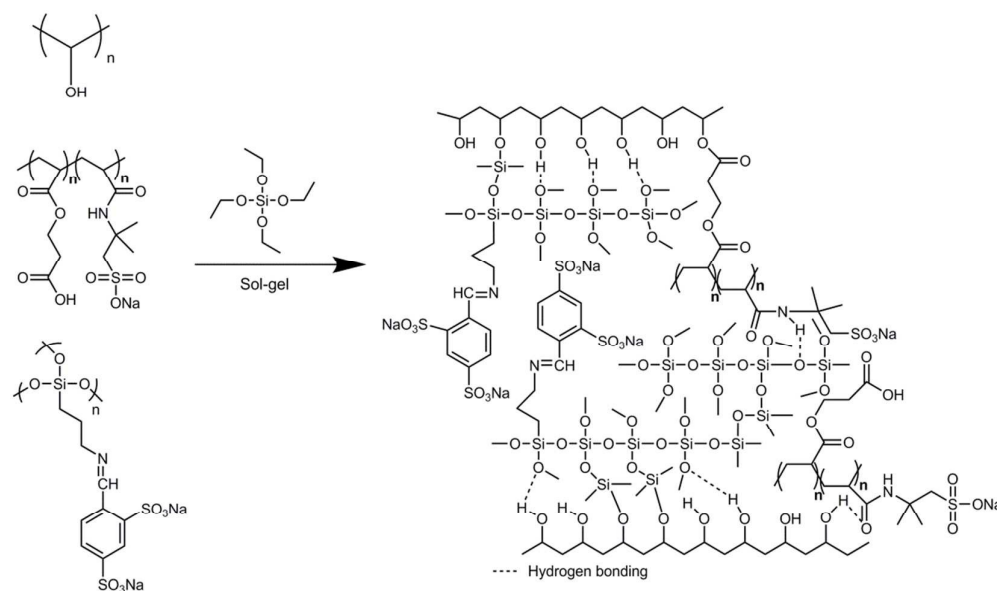


Scheme 2. Reaction scheme of synthesized FSP.

The typical synthetic procedure to prepare disodium 4-Formylbenzene-1,3-disulfonate (FBDS) substituted polysiloxane (FSP) is as follows and depicted in Scheme 2. Firstly, (4.4823 g, 0.025 mol) of 3-(Trimethoxysilyl)-1-propanamine was taken in a 100 mL round bottom flask containing 50 mL THF solution. Disodium 4-Formylbenzene-1,3-disulfonate (7.755 g, 0.025 mol) was dissolved separately in a 50 mL beaker containing 20 mL of (1:1) THF/H₂O mixture and added slowly in a dropwise manner to the reaction medium containing 3-(Trimethoxysilyl)-1-propanamine. Stirring of the reaction mixture was continued till 16 hours at 55 °C for the complete formation of imine linkage. Then, 5 mL of 0.1 (M) HCl was added to the reaction medium for the polymerization to occur. Again, the stirring was continued for further 6 hours. Finally, the solvent was evaporated through rotavapor to yield the desired modified polysiloxane as a straw yellow solid (8.514 g). Obtained polymer was further dried under vacuum. The prepared polymer was named as FSP and characterized in terms of FT-IR and ¹H NMR spectroscopy. ¹H NMR (D₂O-*d*₂, 400 MHz): δ 0.64 (2H), δ 1.82 (2H), δ 2.61 (1H), δ 3.69 (2H), δ 8.00 (1H), δ 8.30 (1H), δ 9.06 (1H) ppm.

Fabrication of the FSP induced Poly(AMPS-co-CEA) based PVA membranes

FSP induced Poly(AMPS-co-CEA)/PVA membranes were prepared through two steps via classic sol-gel process (Scheme 3). In the first step, a required amount of PVA (5 wt %) was thoroughly dissolved in dimethylsulfoxide (DMSO) at 100 °C. At the same time an appropriate amount of Poly(AMPS-co-CEA) was also separately dissolved in 6 mL of (1:1) DMSO/H₂O mixture which produced a highly viscous solution. Then, the viscous solution of Poly(AMPS-co-CEA) was slowly added to the PVA solution and stirred for additional one hour at room temperature. After stirring for one hour a fixed amount of FSP was added to the mixture and stirring was continued for another two hours. Later, predetermined amount of TEOS was also added for enhance crosslinking. The obtained solution was stirred for overnight at 60 °C temperature. The sol-gel process was achieved by hydrolysis of silanes. Thus the obtained gel was casted in a petridish and transformed into a thin film which was dried at 70 °C for 12 h followed by drying in *vacuo*. Afterwards in the second step, thermal crosslinking was attained by heating the membranes from 70 °C to 130 °C at the rate of 10 °C/h and kept at 130 °C for 4 h to form the hybrid membranes.²⁹ After complete drying, the membranes were converted into H⁺ form by equilibrating with 1.0 (M) HCl solution and the equilibrated membranes were washed several times with double distilled water to remove trace of acid, finally the membranes were kept in DI water for further characterizations. Obtained transparent membrane was designated as CEM-X, where X is the different wt % of FSP content in the membrane matrix and varied between 60-90 wt % of PVA content. The complete composition of the prepared membranes was depicted in Table 1.



Scheme 3. Membrane containing PVA, Poly(AMPS-co-CEA) and FSP as well as the analogous sol-gel reaction with TEOS.

Membrane Characterizations

NMR, FTIR spectra, thermal stability and mechanical properties

NMR spectra of prepared FSP and Poly(AMPS-co-CEA) was recorded with an AV III 400 NMR spectrometer (400 MHz, Bruker) using D₂O (with tetramethylsilane as an internal reference) as solvent. FTIR spectra of the synthesized FSP and Poly(AMPS-co-CEA) along with dried composite membranes were recorded by using the technique KBr and attenuated total reflectance (ATR) respectively with FTIR spectrometer (Vector 22, Bruker) with a resolution of 2 cm⁻¹ and a wide spectral range of 4000–400 cm⁻¹. Thermogravimetric analysis (TGA) for the as prepared membranes were carried out using a Shimadzu TGA-50H analyzer within the temperature ranging 40-800 °C under nitrogen flow, with a heating rate of 10 °C/min. Tensile strength (TS) and Elongation at break (E_b) measurements of the dry membranes were conducted using a Q800 dynamic mechanical analyzer (DMA, TA Instruments, USA) at a stretch rate of 0.5 N min⁻¹ at 25 °C.

Ion exchange capacity (IEC)

IEC denotes the amount of interchangeable ionic groups (equivalents) exist per dry membrane weight. IEC for the fabricated CEMs were estimated with the help of classical titration method by the below mentioned way: first of all, 1.0 (M) HCl solution was used to equilibrate the membrane samples for a span of 24 hours such that all charge sites were transformed into the H⁺ form. Membrane samples were then washed carefully with DI water to eliminate additional amount of HCl. For equilibration, the washed membranes were finally kept inside 50 mL of 2 (M) NaCl solutions for 48 hours. The amount of H⁺ ions liberated was estimated by acid–base titration with 0.01 (M) NaOH solution using phenolphthalein as an indicator. The ion-exchange capacity (*IEC*; mmol/g) of the membrane was calculated by the equation $IEC = ab/w$ where *w*, *a* and *b* represents the dry weight of the membrane, titre value during titration and the concentration of NaOH solution respectively.

Microscopic Characterizations for CEMs

Membrane morphological characterization was successfully done through a field emission scanning electron microscope (FE-SEM, Sirion200, FEI Company, USA). Surface and cross-sectional views of membranes were taken from dry membranes. The SEM images of membranes CEM-70, CEM-80 and CEM-90 were shown as the representative cases.

Water Uptake

Membrane hydrophilicity which in turn depends upon the availability of functionality was carefully monitored by the virtue of water uptake (W_R) experiment. Initially, membrane samples were oven dried at 60 °C and accurately weighed to confirm their dry weight. Afterwards, the samples were immersed in distilled water for 72 hours at 25 °C and wet weight of those membranes were recorded after removal of surface water through tissue

paper. By the difference in mass obtained before and after complete drying of the membrane samples, water uptake values were calculated as the relative weight gain per gram of the dry sample using the following equation (1).³⁰

$$W_R = \frac{(W_{wet} - W_{dry})}{W_{dry}} \times 100 \quad (1)$$

Dimensional Stability

Dimensional stability acknowledged as one of the key parameter of an ion exchange membrane was measured by the linear expansion ratio (LER) measurement. Firstly, all of the prepared membranes were cut into a desired size of 3 cm*3 cm. The main technique of the experiment remained the same as that of water uptake. Finally, LER was calculated according to the following equation:⁵

$$LER = \frac{(L_{wet} - L_{dry})}{L_{dry}} \times 100 \quad (2)$$

Here, L_{WET} and L_{DRY} treated as the length of wet and dry membrane samples respectively.

Diffusion dialysis of NaOH/Na₂WO₄ mixture

The most promising separation technique, diffusion dialysis (DD) experiment was carried out in a bi-compartment cell which was neatly divided by the membrane with an effective area of 5.3 cm². Before the commencement of the above test, prepared membranes were conditioned very cautiously in the feed solution (1 M NaOH + 0.1 M Na₂WO₄) for 1 hour, which can effectively stimulates waste base solution formed during tungsten metallurgical processes. When the experiment gets started, 100 mL aqueous waste solution was poured in to one side of the cell while the other side was filled with 100 mL distilled water. Both sides of the cell were stirred continuously so as to minimize the concentration polarization. Diffusion took place for 60 minutes and finally permeate and feed both solutions were taken out from both

sides. The OH⁻ concentrations was determined for both permeate as well as diffusate side by using aqueous 0.1 mol/L HCl via titration method while WO₄²⁻ concentration in the diffusate side was checked by ultraviolet (UV) spectrophotometry method. The above experiment was accomplished at 25 °C temperature.

The dialysis coefficients (U) can be calculated by using the below mentioned formula²⁹:

$$U = \frac{M}{At\Delta C} \quad (3)$$

where, M is the quantity of transported component in (mol), A is the operative membrane area (m²), t denotes the time (h), and ΔC is the logarithm average concentration between the two chambers (mol/m³).⁴² ΔC is calculated as below^{29,42}:

$$\Delta C = \frac{c_f^0 - (c_f^t - c_d^t)}{\ln[c_f^0 / (c_f^t - c_d^t)]} \quad (4)$$

C_f^0 , C_f^t are the feed concentrations at time 0 and t respectively and C_d^t is the dialysate concentration at time t.^{8,29,42}

By the help of the above mentioned equation (3) and (4), dialysis coefficient U_{OH} and $U_{WO_4^{2-}}$ can be easily calculated. The separation factor (S), which is well known as the ratio between dialysis coefficients (U) of the two species existing in the solution can also be calculated as stated below:⁴²

$$S = \frac{U_{OH}}{U_{WO_4^{2-}}} \quad (5)$$

Results and Discussion

NMR and FTIR spectra analysis

Poly(AMPS-co-CEA) was synthesized by the reaction of AMPS and CEA depicted in Scheme 1. ¹H NMR spectra of Poly(AMPS-co-CEA) in Fig. 1 showed the formation of the desired polymer as the chemical shift corresponding to olefinic double bonds present at δ

δ = 5.72, 6.23 ppm for AMPS and δ = 5.80, 5.99, 6.23 ppm for CEA was totally diminished after reaction. This observation suggested that olefinic double bonds were reacted with each other by the help of free radical initiator (AIBN) giving rise to a successful formation of Poly(AMPS-co-CEA) polymer. Rests of the other peaks around 1.16-2.20 ppm, 2.76 ppm, 3.38-3.83 ppm, 4.38 ppm are well in accordance with the synthesized Poly(AMPS-co-CEA) structure. Hence, the synthesis of the polymer Poly(AMPS-co-CEA) was confirmed through NMR spectroscopy. The IR spectrum of synthesized Poly(AMPS-co-CEA) was referred in Fig. 2 for further investigation of the polymer structure. The broad characteristic strong band in the range of 3150–3750 cm^{-1} can be mainly attributed to the stretching vibration of –OH groups present in the –(C=O)-OH group.²⁹ The band present in the region of 2850–2990 cm^{-1} raised from the stretching of –CH₂ group (ν).²⁴ Absorption bands with sharp intensity around ~1043 cm^{-1} (sym. SO₃ stretch) and ~1230 cm^{-1} (asym. SO₃ stretch) indicates strong presence of sulfonate group.³¹ The sharp intensity absorption band around ~1727 cm^{-1} confirmed the presence of carbonyl (-C=O) group in the polymer backbone.²⁹ The peak around ~1630 cm^{-1} is mainly due to the presence of N-H bending (scissoring) in the polymer Poly(AMPS-co-CEA).³²

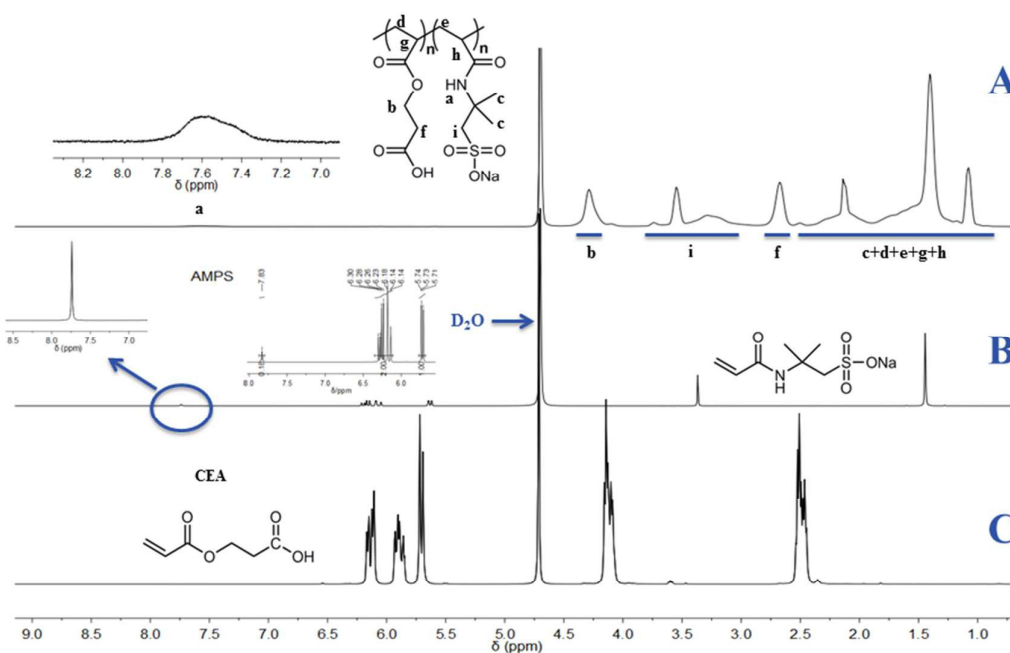


Fig. 1 (A) ^1H NMR spectra of synthesized Poly(AMPS-co-CEA) with (B) & (C) represents ^1H NMR spectra of corresponding monomers AMPS & CEA respectively.

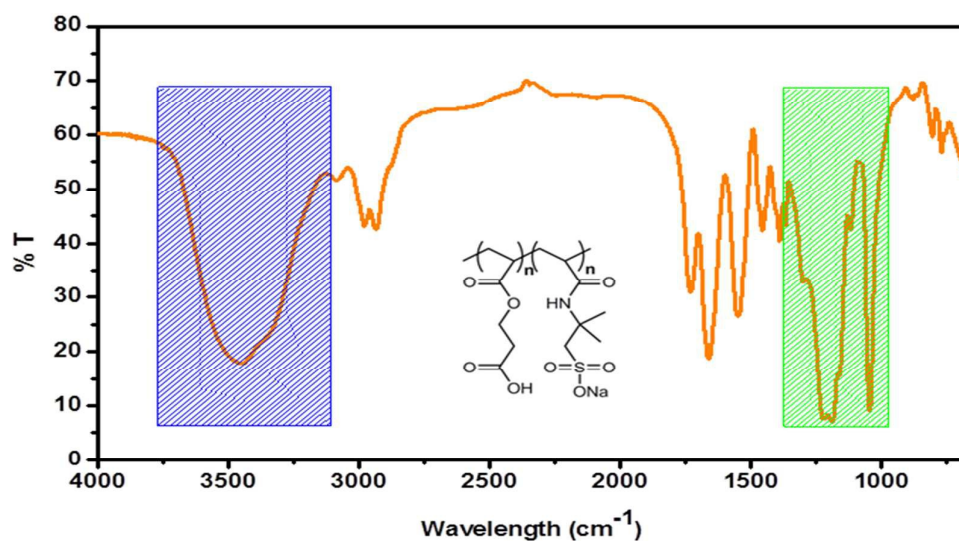


Fig. 2 FTIR spectrum of synthesized Poly(AMPS-co-CEA).

Disodium 4-Formylbenzene-1,3-disulfonate (FBDS) substituted polysiloxane (FSP) was synthesized by a well-known Schiff base reaction with the help of 3-(Trimethoxysilyl)-1-propanamine and FBDS depicted in Scheme 2. ^1H NMR spectrum of FSP in Fig. 3 showed

that after the completion of reaction successful formation of imine linkage was further proven and confirmed by the diminished chemical shift of the corresponding aldehyde proton present in FBDS moiety at 10.74 ppm. The peak around 0.64 ppm could be attributed for -Si-CH₂- protons while the chemical shifts corresponding to 8.00 ppm, 8.30 ppm, 9.06 ppm are the signals aroused from aromatic protons adjacent to the sulfonate group present in DSBPB moiety. This observation clearly suggested successful formation of FSP. The IR spectrum of the synthesized FSP in Fig. 4 showed characteristics peaks at anticipated wavelength. The absorption bands around ~1043 cm⁻¹ (sym. SO₃ stretch) and ~1230 cm⁻¹ (asym. SO₃ stretch) confirmed the strong presence of sulfonate group in FSP.³¹ The band around ~1100 cm⁻¹ is mainly due to the presence of Si-O-Si bonds inside FSP.²⁹ The bands around ~2920 cm⁻¹ and ~1650 cm⁻¹ originated from stretching of -CH₂ & -CH groups (ν and δ).⁵ Presence of a sharp band at 1460 cm⁻¹ is indicative of C-N stretching frequency.⁵ In the finger print region, the sharp peak around ~775 cm⁻¹ and 698 cm⁻¹ proved the existence of characteristic peaks aroused from benzene ring present in FSP.³³

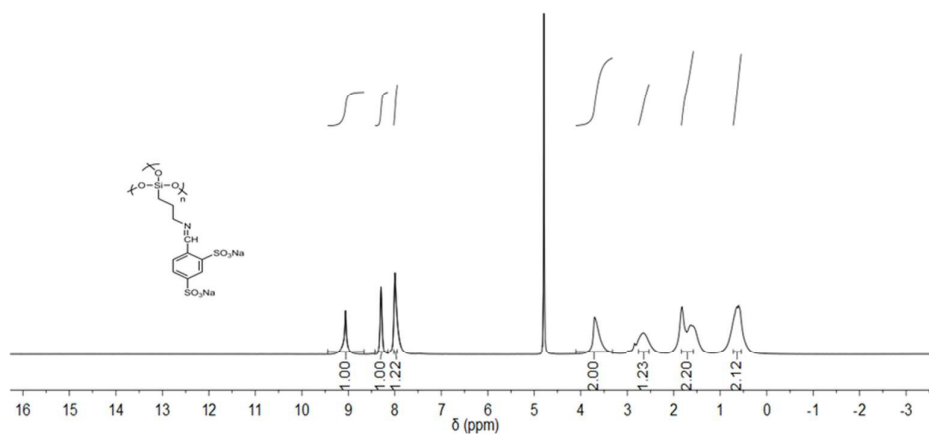


Fig. 3 ¹H NMR spectrum of synthesized FSP.

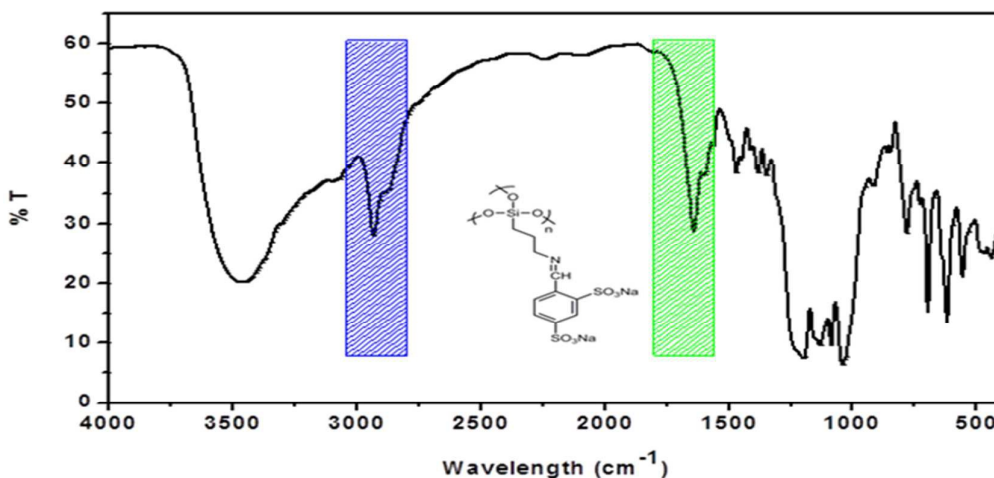


Fig. 4 FTIR spectrum of synthesized FSP.

The ATR-FTIR spectra of representative CEM-60 and CEM-90 membranes were shown in Fig. 5 for detailed discussion. Sulfonate group was confirmed by the existence of peaks in the regions of $\sim 1040\text{ cm}^{-1}$ and $\sim 1230\text{ cm}^{-1}$.³¹ A broad band prevailing in the region of $3050\text{--}3650\text{ cm}^{-1}$ revealed the active presence of -OH stretching vibration inside the membrane matrix.²⁹ In the IR spectra, the sharp peaks in the range of 1050 cm^{-1} and 1120 cm^{-1} strongly indicated the presence of Si-O-C, Si-O-Si as well as C(=O)-O-C groups in the membrane.^{29,31,34} It is highly possible that due to the polycondensation reaction occurred between hydrolyzed silanol (Si-OH) groups, Si-O-Si groups are generated and the Si-O-C groups might be the result of the condensation reaction happened between Si-OH groups and C-OH groups from PVA (Scheme 3) whereas C(=O)-O-C groups which is nothing but a ester bonding originated from the reaction between C-OH groups of PVA and -C(=O)-OH groups present in Poly(AMPS-co-CEA).²⁹ Hence, the presence of Si-O-Si, Si-O-C as well as C(=O)-O-C bonds established the existence of covalent linkage between organic groups and silica, which leads to a better compatible and crosslinked network between both organic and inorganic segments leading to a highly thermally and mechanically stable membrane.

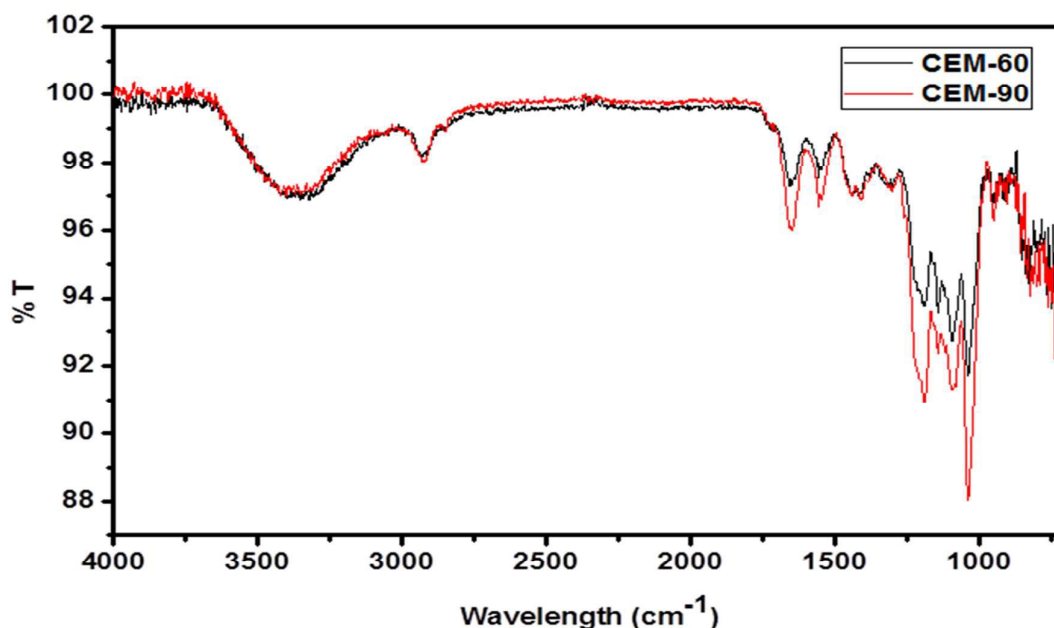


Fig. 5 ATR spectra of synthesized CEM-60 & CEM-90 membranes.

As the reaction time progressed, adequate numbers of interconnected Si-O-Si bonds are formed while they converted into sol by interacting with each other and additionally colloidal particles associated together for the formation of a three-dimensional cluster or a gel.³¹

Water Uptake and Ion exchange capacity (IEC)

Water uptake, the most essential parameter of an ion exchange membrane holds the key for various membrane based applications and therefore these applications can be significantly affected by the existence of water molecules inside the membrane matrix. As expected, water uptake of an IEM has got a huge influence over its separation performance, mechanical as well as dimensional stabilities.³⁵⁻³⁶ Prepared CEMs showed the W_R values varied in the range of 204.–248.7 % which clearly indicated formation of polyelectrolytes. Obtained data denoted in Table 1 revealed that water uptake values initially decreased from CEM-60 to CEM-70 and then showed an ascending trend from CEM-70 to CEM-90 with the increase in the amount of FSP content inside membrane matrix. This observation is of huge importance

as it revealed that the water uptake property of any membranes is not only the function of available functionality (charged groups) but crosslinking also got a decisive role.³⁷ With the lower amount of FSP content (60 and 70 wt.%), the W_R value of CEM-70 membrane appeared to be less in comparison with CEM-60, indicating that extensive crosslinking (interrelated Si-O-Si linkage, esterification reactions operative between -OH groups from PVA and -SO₃H groups of FSP) inside the matrix played a significant role in governing the water uptake.³⁷ The effect of crosslinking could be the formation of a stiffer and compact membrane structure and subsequently a reduction in chain mobility as well as empty spaces that accommodate water molecules in membrane are obtained.³⁷ With the higher FSP content (>70 wt.%), the W_R of the membranes gradually increased from 204 to 248.7% while FSP content was varied between 70 to 90 wt.%. This phenomenon may be attributed to the increasing hydrophilicity of the membrane matrix where presence of functional groups dominates the water absorption over the crosslinking.³⁷ Higher FSP content contained more polar groups which lead to the development of larger ion clusters and may permit more water sorption.³⁷

IEC values for different CEMs were estimated by the titration method and represented in Table 1. As shown in Scheme 3, IEC was contributed from both sulfonic acid as well as carboxylic acid groups. Obtained data revealed that IEC varied in the range of 0.58 mmol/g to 0.76 mmol/g for different CEMs. IEC value of any IEM solely depends upon the available functionality inside polymer matrix.^{8,42} Thus, increasing FSP content in polymer matrix leads to the increasing functionality inside membrane and hence it became responsible for an ascending IEC trend while moving from membrane CEM-60 to CEM-90. IEC results also established the charge nature of the fabricated CEMs.

Table 1 Membrane compositions and their Water Uptake (W_R) as well as Ion Exchange Capacity (IEC) and Linear Expansion Ratio (LER) Values

| <i>Membrane code</i> | <i>PVA wt%</i> | <i>FSP of PVA</i> | <i>Poly(AMPS-co-CEA) of PVA</i> | <i>TEOS of FSP</i> | W_R (wt%) | <i>IEC (mmol./g)</i> | <i>LER (%)</i> |
|----------------------|----------------|-------------------|---------------------------------|--------------------|-------------|----------------------|----------------|
| CEM-60 | 5 | 60 % | 50 % | 10 % | 214.4 | 0.58 | 32.4 |
| CEM-70 | 5 | 70 % | 50 % | 10 % | 204.0 | 0.68 | 26.7 |
| CEM-80 | 5 | 80 % | 50 % | 10 % | 216.3 | 0.70 | 35.3 |
| CEM-90 | 5 | 90% | 50 % | 10 % | 248.7 | 0.76 | 45.2 |

Dimensional Stability

Dimensional stability of an ion exchange membrane is well known for its huge impact in different membrane based applications and processes. LER measurement was carried out to determine the dimensional stability of the as prepared membranes. Reference experiment result proposed in Table 1 revealed that, from membrane CEM-60 to CEM-70 LER values gradually decreased while moving from the membrane CEM-80 to CEM-90 displayed an increasing trend. It is an established fact that LER theoretically depends on degree of crosslinking.^{5,43} We observed that moving from CEM-60 to CEM-70 crosslinking predominates over functionality therefore CEM-70 shows lower LER value in comparison with CEM-60 although CEM-70 contained higher FSP loading. On the other hand with the higher FSP content (>70 wt.%) functionality predominates over crosslinking therefore LER value gradually increased from CEM-70 to CEM-90.

Thermal and Mechanical stability

Thermal stability of the prepared membranes was assessed by thermo-gravimetric analysis in the temperature range of 40 °C to 800 °C at a heating rate of 10 °C /min under nitrogen atmosphere. TGA thermograms for different prepared nanocomposite CEMs in H⁺ form were

represented in Fig. 6. Overall, the weight loss pattern of all membranes looks alike where initially associated water (which is a combination of both loose and bound water) lost from the membrane phase followed by decarboxylation,⁴⁴⁻⁴⁵ desulfonation occurred as the second step and finally membrane matrix degradation completes the entire process. Typically, the initial weight loss (step I) occurred due to the loss of bound water in the region of 100-140 °C which can be mainly attributed to the evaporation of residual water (bound water) from the membrane matrix whereas weight loss in the region of 190-250 °C could be assigned to the decarboxylation from the membrane matrix.^{38,44-45} In this step CEM-60 showed the lowest weight loss in comparison to the other membranes with high percentage loading of FSP content. In figure 6 inset diagram represented the decarboxylation step where it was clearly evident that CEM-60 showed significantly lesser weight loss character than that of CEM-90. Hence, in this step CEM-60 membrane undoubtedly appeared as thermally most stable one in comparison with other membranes. The second step (step II) of the weight loss could be ascribed to the decomposition of sulfonic acid groups around the region of 290-320 °C.^{39,46-47} During this step it was observed that the difference in weight loss between CEM-60 and CEM-90 was not that high like decarboxylation step. The last and final weight loss step comprised of the sharp rapid degradation of main polymer matrix beyond the temperature range 450 °C. Therefore, on the basis of the afore-mentioned observations we can conclude that introducing functionalization on the PVA polymer matrix leads us to achieve improved thermally stable membranes.

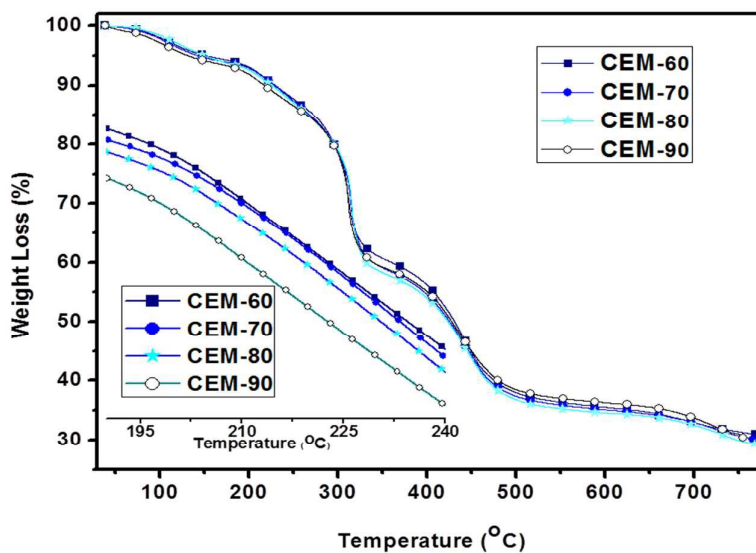


Fig. 6 TGA thermograms of different prepared membranes.

Table 2 TS and E_b values of different Composite membranes

| Membrane | CEM-60 | CEM-70 | CEM-80 | CEM-90 |
|-----------|--------|--------|--------|--------|
| TS (MPa) | 15.9 | 12.7 | 9.3 | 11.7 |
| E_b (%) | 236.7 | 187.6 | 125.6 | 168.3 |

Mechanical properties of the membranes (such as stress and strain), known as one of the most important factor of IEMs were measured by DMA curves (Fig. 7) and the corresponding TS and E_b (%) values were represented in Table 2. It has been observed that the TS (tensile strength) values of prepared CEMs varied in between 9.3–15.9 MPa while the E_b values of the prepared membranes are in the range of 125.6–236.7%. Obtained results can be explained in terms of miscibility and crosslinking nature of organic and inorganic moiety inside membrane matrix. Tensile strength of prepared membranes showed descending trends while going from CEM-60 to CEM-80 whereas CEM-60 showed maximum E_b value. Usually, the

elongation at break (E_b) value validates the flexibility behavior of the membrane.⁸ Now if we focus on the membrane fabrication process, it is noteworthy that there is condensation reaction happening between -OH group of PVA and FSP precursor. Therefore, with the gradual increase in the FSP content inside membrane matrix, the membrane gets hardened. This condensation degree known to be responsible for influence the membrane properties.⁴⁸ Hence, this is worthy to mention that CEM-60 to CEM-80 showed a decreasing trend reason being with the increasing amount of FSP precursor in membrane matrix polymer chain gets tightly held and relaxation of chain segments became more and more difficult which may be attributed to the gradual decrease in E_b values of the prepared membranes going from CEM-60 to CEM-80. For the membrane CEM-90, a reverse trend can be seen where E_b and TS both values increases. This phenomenon could be attributed to the maximum loading of FSP content in the membrane matrix. As, there are free FSP content which do not interfere in the condensation mechanism due to higher loading of FSP content in the membrane thus chain segments became little more relaxed in comparison with CEM-80 and hence E_b value shows reverse trend for CEM-90 membrane. Therefore, the maximum condensation should be restricted to CEM-80. Obtained E_b values appeared to be much higher than the previously reported ones, indicating higher flexibility of the prepared membranes.^{27,29} Hence, incorporation of FSP in PVA backbone leads to a mechanically stable membrane.

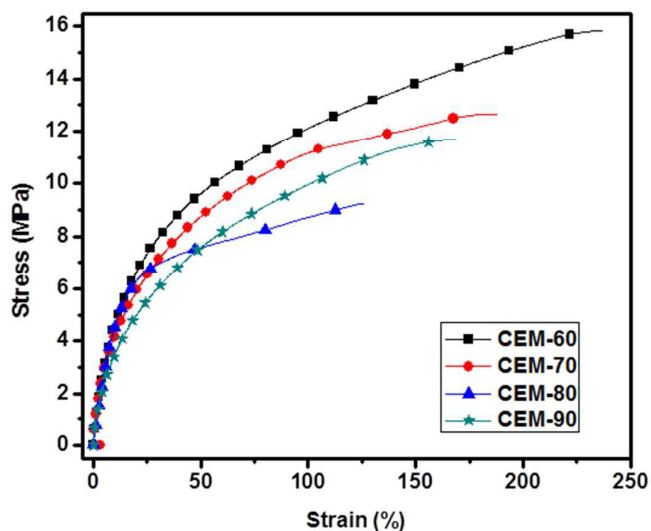


Fig. 7 Tensile Strength vs Elongation at break (E_b) of different prepared membranes.

Membrane morphologies

Morphologies of membrane surface and cross-sections have been studied through SEM micrographs and were represented in Fig. 8. The SEM images of CEM-60, CEM-70, CEM-80 and CEM-90 were demonstrated as a representative case. Overall membrane surface look homogeneous, dense and compact in nature though little surface aggregations was still observed for CEM-90 membrane. Membrane homogeneity could be attributed to the presence of covalent and hydrogen bonds in membrane matrix whereas aggregations on the surface of CEM-90 membrane could be due to the accelerated hydrolysis of silica precursor with the increase in FSP content. Another remarkable factor to note here was the presence of non-penetrating holes in membrane cross-sections. Possibly due to the enhance cluster formation of silica inside membrane matrix, membrane structure became very compact and showed non-penetrating areas. On the other hand presence of small phase separation was also a prominent factor for CEM-90 membrane though overall absence of cracks or holes on the membrane surface suggested homogeneous and dense nature of prepared CEM.

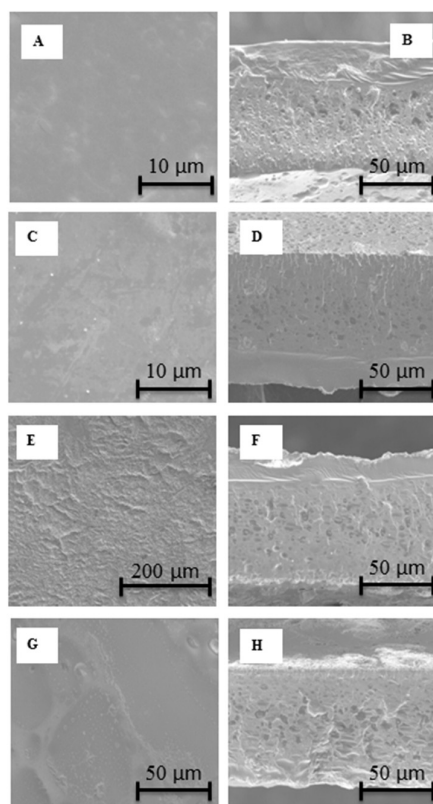


Fig. 8 (A) & (B) corresponds to the surface & cross-section of the CEM-60 membrane, (C) & (D) corresponds to the surface & cross-section of the CEM-70 membrane whereas (E) & (F) represents surface & cross-section of the CEM-80 membrane and (G) & (H) represents surface & cross-section of the CEM-90 membrane.

DD for NaOH/Na₂WO₄ solution

Diffusion dialysis performance including dialysis coefficient (U) and separation factor (S) of the prepared membranes are evaluated by using NaOH/Na₂WO₄ mixture (1.0 M NaOH+0.1 M Na₂WO₄) as a model feed solution and membrane potential applications in base recovery process was monitored. Obtained DD experiment results were represented in Fig. 9 for further clarification.

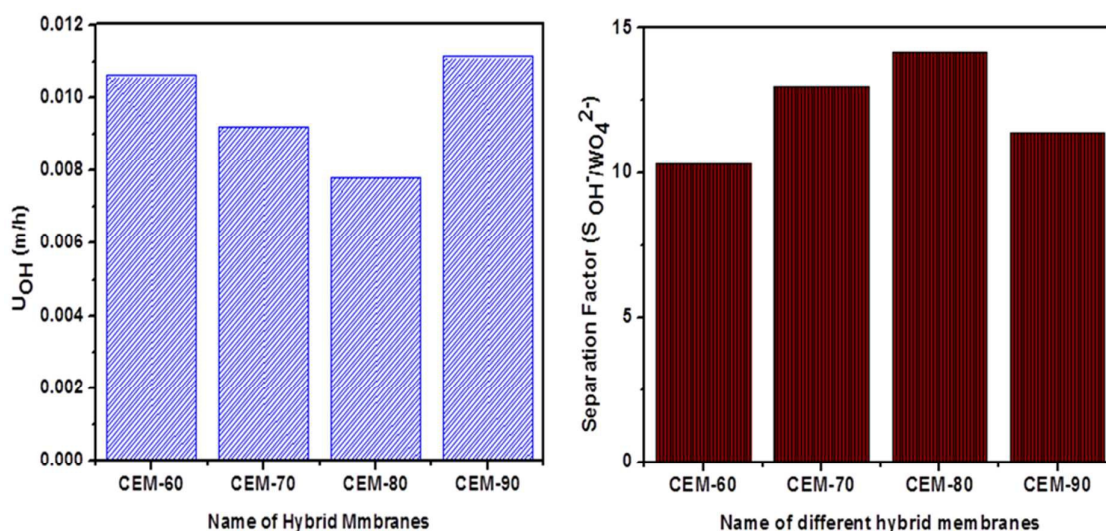


Fig. 9 Base dialysis coefficients (U_{OH}) and separation factor (S) for different prepared membranes at 25 °C.

Obtained results from Fig. 9 revealed that increases in the FSP content in membrane matrix leads to the decrease in U_{OH} values (CEM-60 to CEM-80) and the variation in the U_{OH} values ranged from 0.0078-0.0112 m/h. A few significant references can be drawn from the above observation. First of all, PVA-based hybrid membranes, though with lower IECs exhibited higher U_{OH} in comparison with SPPO-based membranes. The U_{OH} values of SPPO-based membranes at 25 °C are around 0.0022 m/h, whereas the obtained values of PVA-based membranes here are slightly higher than 0.01 m/h.^{24,40} Secondly, CEM-90 showed maximum U_{OH} values (0.0112 m/h) among all prepared membranes which is moderately much higher

than that of SPPO/SiO₂ membranes (around 0.002 m/h at 25 °C),⁴⁰ SPPO/DSBPB blend membranes (around 0.0048-0.00814 m/h at 25 °C)⁴² and almost same as that of PVA/SiO₂ membrane.^{25,28,29} Hence, it can be claimed that the prepared membranes have got the high potentiality to serve as the deserving candidate for base recovery.

Fig. 9 also revealed that there was a decreasing trend in U_{OH} values with the increasing FSP content which should be mainly attributed to the membrane cross-linking degree. It can be seen that with the increasing FSP content cross-linking degree gradually increases and the enhanced cross-linking degree is unfavorable for the transportation of OH⁻ ions due to membrane physical block-effecting from cross-linking network.²⁴ Hence, the U_{OH} values gradually decreases with increasing FSP content from CEM-60 to CEM-80. On the other hand, while going from membrane CEM-80 to CEM-90 phase separation played the decisive role. Incorporation of maximum amount of FSP in CEM-90 membrane leads to the phase separation hence more OH⁻ ions can be transported to the dialysate side leading to the high U_{OH} value which is in contrary to the previous trend.

The high U_{OH} values could be attributed for the following reasons: the existence of -OH groups and the phase separation observed with high FSP content in membrane matrix. It has been already well recognized that -OH groups are operating as an assistant functional group.^{21,28,41} Therefore, presence of huge number of -OH groups inside the PVA chain makes it highly hydrophilic and hydrogen bonded network formed between the -OH groups with OH⁻ ion. Therefore, the entire polymer matrix become friendly for the transportation of OH⁻ ion and U_{OH} can stretch up to relatively higher value in spite of lower IEC value. From Fig.8 H, phase separation can be observed by the SEM graphs and the presence of the phase separation can be beneficial for sodium ion transport. The inimitability of PVA-based membranes is the existence of huge extent of hydrophilic C-OH and Si-OH groups through the membrane matrix. Therefore, they cannot be classified into typical “three-phase”

structure membranes membrane.^{28,41} Ion transportation across the membrane could be assisted by the active manifestation of the multifunctional groups. Prepared CEMs contains different functional groups e.g. $-\text{SO}_3\text{Na}$, $-\text{COOH}$ and $-\text{OH}$ groups. The $-\text{SO}_3\text{Na}$ groups act as a strong ion exchange sites to endorse the transportation of counter-ions (Na^+). The $-\text{OH}$ groups (both Si-OH and C-OH) can form hydrogen bonding with the co-ions (OH^-). The $-\text{COOH}$ groups are known as weak acidic and can act as both weak ion exchanger and hydrogen bonding provider.¹¹ Presence of hydrogen bonding should be favorable for the transportation of OH^- ions.⁴¹ With the hydrogen bond formation between $-\text{OH}$ groups and OH^- ions, the OH^- ions can be adsorbed into the membrane; when the hydrogen bonding is broken, the OH^- ions can be desorbed out of the membrane. Hence, by the help of adsorption–desorption mechanism it is highly possible that part of the OH^- ions are transported through the membrane. It is also important to state that the synergistic effects arising out of the multifunctional groups present inside membrane matrix lead to the moderately higher U_{OH} values.⁴¹

Separation factors (S) can be defined as the ratio between U_{OH} and $U_{\text{WO}_4^{2-}}$. The obtained S values appeared in the range of 10.3–14.2 which were little less than that of PVA-based hybrid membranes (16.9–18.5) at 25 °C,²⁸ (11.6–20.2) at 25 °C.²⁴ Separation factor trend is also affected by the membrane physical block effecting. This physical block-effecting is advantageous to the membrane selectivity. The physical block-effecting along with the repulsive force arising from fixed groups may be much stronger for the WO_4^{2-} ions as the WO_4^{2-} ions have higher volume and valence in comparison to the OH^- ions.²⁴ Consequently, the transport of WO_4^{2-} ions may be more significantly restrained with increasing FSP content and the S values increase from membranes CEM-60 to CEM-80. Also, on the other hand, huge phase separation is not likely for high selectivity as both OH^- ions and WO_4^{2-} ions can transport through the membrane matrix without much resistance, which in turn can decrease S values.²⁹ Thus, going from membrane CEM-80 to CEM-90 due to phase separation, the

separation factor value decreases.

Conclusions

This study reports a novel multifunctional polymer and polysiloxane based cation exchange membrane which was further used for base recovery via DD process. Free radical polymerization and Schiff base reaction were performed to synthesize the novel multifunctional polymer as well as functionalized polysiloxane. Prepared materials were used for the preparation of stable organic-inorganic nano structured membranes using PVA as the polymer backbone. Obtained membranes were characterized in terms of different physiochemical and electrochemical properties. Membrane characterization studies revealed that membrane (CEM-90; water uptake: 248.7 %; IEC: 0.76 mmol. g⁻¹) with high FSP content was more probably used as DD material. Good mechanical properties with TS varying around 9.3-15.9 MPa and E_b ranging from 125.6–236.7 % could be an additional advantage for the aforementioned membranes. Reported FSP could be a promising starting point for the preparation of more highly conducting CEMs. Prepared membranes have been successfully applied to DD process for base recovery and the obtained values at 25 °C showed moderate OH⁻ permeability (0.0078-0.0112 m/h). Additionally, membrane selectivity showed acceptable values (10.32-14.19) which in turn proved the potential applications for these membranes for base recovery from metal refining industries.

Acknowledgments

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Nomenclature

| | |
|-----------------|--|
| IEM | Ion exchange membrane |
| PVA | Polyvinyl alcohol |
| IDT | Initial decomposition temperature |
| T_d | Thermal degradation temperature |
| FSP | Disodium 4-Formylbenzene-1,3-disulfonate modified polysiloxane |
| DMSO | Dimethyl sulfoxide |
| IEC | Ion exchange capacity |
| W_R | Water uptake |
| TGA | Thermo gravimetric analysis |
| DMA | Dynamic mechanical analysis |
| TS | Tensile strength |
| E_b | Elongation at break |
| SEM | Scanning electron microscopy |
| U_{OH} | Dialysis coefficient of NaOH |
| $U_{WO_4^{2-}}$ | Dialysis coefficient of Na_2WO_4 |
| S | Separation factor |

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Captions of Figures and Tables

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- Fig.1 ^1H NMR spectra of synthesized Poly(AMPS-co-CEA) along with AMPS & CEA.
- Fig.2 FTIR spectrum of synthesized Poly(AMPS-co-CEA).
- Fig.3 ^1H NMR spectrum of synthesized FSP.
- Fig.4 FTIR spectrum of synthesized FSP.
- Fig.5 ATR spectra of synthesized CEM-60 & CEM-90 membranes.
- Fig.6 TGA thermograms of different prepared membranes.
- Fig.7 Tensile Strength vs Elongation at break (E_b) of different prepared membranes.
- Fig.8 Surface & cross-section images of the CEM-60, CEM-70, CEM-80 and CEM-90 membrane.
- Fig.9 Base dialysis coefficients (U_{OH}) and separation factor (S) for different prepared membranes at 25 °C.
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Table 1 Represents membrane compositions, Water uptake, Ion exchange capacity and Linear Expansion Ratio values of different prepared membranes.

Table 2 Represents TS & E_b values of different prepared membranes.
