Novel Silica Functionalized Monosodium Glutamate/PVA Cross-Linked Membranes for Alkali Recovery by Diffusion Dialysis

Muhammad Adnan Ashraf¹ · Atif Islam¹ * · Muhammad Arif Butt²

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Abstract
In this work, two types of silica functionalized monosodium glutamate (GMSG and VMSG)/poly(vinyl alcohol) (PVA) were cross-linked by sol–gel process to prepare novel hybrid cation exchange membranes. The prepared membranes were systematically characterized by FTIR spectroscopy, SEM analysis, ion exchange capacity (IEC), TGA, water uptake, water swelling, mechanical strength and diffusion dialysis performance for alkali separation using NaOH/Na₂WO₄ solution. The FTIR peaks around 1260–1350 cm⁻¹ confirmed the secondary C–N linkages. The cross-linking between GMSG/VMSG and PVA was verified by the presence of stretching peaks of Si–O–C, Si–O–Si, C–O–C and –C(=O)–O–C groups between 1080 and 1120 cm⁻¹. SEM analysis confirmed dense structure and uniform distribution of silica particles in the membrane. TGA results indicated that GMSG membranes showed relatively high thermal stability as compared to VMSG membranes. Water uptake and degree of swelling decreased while IEC values increased with the increase of GMSG/VMSG content in membrane matrix. The mechanical properties of the membranes improved up to 40% GMSG/VMSG content. The NaOH dialysis coefficient (Uₐₒₙ) values improved while values of separation factor (S) declined with the increase of GMSG/VMSG content. Finally, the effect of temperature was studied and it was found that increase in temperature from 25 to 45 °C resulted in increase of diffusion coefficient and decrease of separation factor for both GMSG/VMSG crossed-linked with PVA membranes.

Keywords Silica functionalized · Monosodium glutamate · PVA · Diffusion dialysis · Alkali recovery

Introduction
It is a bitter fact that huge quantity of alkaline water is being produced from several industrial wastes like printing, paper, metal ores and leather industries which results in serious environment pollution [1–3]. The discharge of alkaline water without treatment process not only wastes useful substances but also disturbs the water pH of rivers which causes severe damage to aquatic life [4]. The traditional methods which have been applied for the treatment of alkaline waste are (a) neutralization of alkali substances with acids (b) lowering the concentration of alkali substances by diluting them and (c) directly burning these substances like in paper and pulp industry. These traditional processes are either energy extensive/require a large amount of commercial acids or a large amount of sludge is produced which poses disposal problems [5, 6]. In recent years, membrane-based alkali separation technology has been developed which includes nanofiltration, reverse osmosis, electro-dialysis, ultra-filtration and diffusion dialysis (DD) [3, 7]. DD is the most dominant process among all as it is environment friendly, requires less energy and has less installation cost as well. Other advantages include absence of pollution, simple construction of apparatus, recoverable alkali and continuous operation [6, 8]. The most important advantage of this process is that it does not require any external driving force as it is spontaneous separation process which relies on simple technique of ion diffusion (movement of ions from high to low concentration) [9]. The alkali separation properties of DD process are remarkably affected by cation exchange membranes (CEM). Recently, a lot of work on CEMs has been done
which focuses on various properties of these membranes like NaOH permeability, alkaline resistance, salt rejection, thermo-mechanical stability and selectivity [10]. A lot of polymeric materials have been used, for the development of cation exchange membranes for alkaline recovery, which include poly(vinylidene fluoride), polysulfone, polystyrene, polyetheretherketone, poly(ethylene oxide) and poly(vinyl alcohol) [11–14]. The most critical issues of CEMs having high IEC capacities are their low stability, high degree of swelling and permeability issues in alkaline conditions due to the lack of enough cross-linking [15]. By combining the properties of both inorganic and organic polymer materials, hybrid membranes can be prepared in which inorganic material is dispersed into the organic polymer matrix in order to obtain the required mechanical strength and separation properties [16]. These modifications have made most PVA based hybrid membranes [17, 18]. PVA has several advantages like high water solubility, low cost and excellent film forming properties [19]. PVA also possesses –OH groups in abundant which can facilitate extraordinary reaction with –Si-OCH3 group through sol–gel process. However, due to absence of cation exchange groups in PVA matrix, mixing with other materials having cation exchange group is required to obtain ion exchange capacities [20, 21]. Hao et al. studied the effect of carboxyl (–COOH) group content on PVA/SiO2 membranes prepared by sol–gel process for alkali recovery and found that separation factor was increased up to 36.2 [22]. Wu et al. prepared PVA hybrid membrane containing maleic anhydride for NaOH separation performance through DD process and observed noticeable increase in OH− transport, permeability and IEC values with the addition of maleic anhydride containing –COOH groups [23]. Wang et al. studied the influence of mesoporous silica functionalized phosphotungstic acid on PVA membranes for alkali recovery and observed improved thermo-mechanical properties along with improved values of IEC between 0.015 and 0.030 mmol/g [24]. Tong et al. studied separation properties of NaOH/Na2WO4 solution using un-charged PVA-silica hybrid membranes prepared by sol–gel process and found that alkoxysilanes significantly enhanced both mechanical properties and selectivity [2]. Gu et al. studied DD performance of NaOH/Na2WO4 solution using multisilicon copolymer/PVA hybrid membranes. The results indicated that the addition of Si-OH groups significantly improved the permeation of OH− ions [10]. Mondal et al. prepared silica functionalized aminosipthalic acid cross-linked PVA membranes through sol–gel process for the recovery of alkaline solution through DD process. The resulting membranes demonstrated high performance parameters like IEC values within 0.48–0.93 mmol/g, dialysis coefficient values between 0.0068 and 0.0097 m/h and separation factor reached to 31.79 [25]. Hence, PVA based hybrid membranes have been developed with different cross-linkers and cation exchange groups to improve the DD performance for alkali recovery [17]. The –Si-OCH3 cross-linked PVA based hybrid cation exchange membranes have been used in many DD applications for alkaline separation [26]. Monosodium glutamate (MSG) is environmentally friendly, easily available and cheap food additive having extremely hydrophilic nature due to the presence of –COOH group [27]. The –COOH or –COONa groups (cation exchange component) via ion exchange process can transfer Na+ ions, while OH− ions may be transferred through membrane via weak interactions such as hydrogen bonding with the hydroxyl (–OH) groups of PVA and also –Si-OH groups, presents in the membrane [11, 28].

In this work, two series of novel silica functionalized monosodium glutamate (GMSG, VMSG) cross-linked PVA hybrid cation exchange membranes have been synthesized which has never been synthesized and studied before for alkaline recovery, according to the best of our literature survey. Moreover, FTIR spectroscopy, IEC, SEM analysis, water uptake, swelling degree, thermo gravimetric analysis (TGA) and mechanical strength of the prepared membranes have been analysed. Finally DD performance properties in term of UOH and selectivity were evaluated via DD test at two different temperatures using NaOH/Na2WO4 solution as a model for alkali waste feed solution.

**Experimental**

**Materials**

Polyvinyl alcohol (Hydrolyzed 90%, Mw = 30,000–70,000 g/mol), 3-glycidoxypropyltrimethoxysilane, vinyltrimethoxysilane and sodium tungstate (Na2WO4) were purchased from Sigma Aldrich, USA. Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were purchased from Merck, Germany. Monosodium glutamate was purchased from Ajinomoto, China. Deionized water utilized as a solvent was prepared in our laboratory.

**Synthesis of Silica Functionalized Monosodium Glutamate (GMSG, VMSG)**

Two types of silica functionalized monosodium glutamate (GMSG, VMSG) were separately prepared by the reaction of monosodium glutamate with 3-glycidoxypropyltrimethoxysilane and vinyltrimethoxysilane, respectively. First, 1 g (5.9 mmol) of monosodium glutamate was added to 10 mL of deionized water with continuous stirring at 75 °C for 30 min in a 50 mL round bottom flask and then calculated amount of 3-glycidoxypropyltrimethoxysilane (1.39 g/5.9 mmol) was added to this mixture and stirring was continued on a hot plate for 5 h at 75 °C in order to complete the reaction and obtain viscous solution of GMSG. Similarly,
1 g (5.9 mmol) of monosodium glutamate and 0.87 g (5.9 mmol) of vinyltrimethoxysilane were processed to obtain viscous solution of VMSG.

**Fabrication of GMSG and VMSG Cross-Linked PVA Hybrid Membranes**

GMSG and VMSG cross-linked PVA hybrid cation exchange membranes were synthesized through sol–gel process without using any hazardous chemical and organic solvent. For this purpose, 10 g of PVA was dissolved in 90 mL of deionized water with continuous stirring for 4 h at 90 °C till clear solution was obtained which was then cooled down to 65 °C. To prepare GMSG/VMSG cross-linked PVA hybrid membranes, the calculated amount of GMSG/VMSG solutions were added carefully to the PVA solutions. A little amount of 1 M HCl solution was then added to this mixture and the solution was stirred at 65 °C for 24 h to complete the cross-linking reaction as per proposed reaction scheme as shown in Scheme 1. As per the suggested reaction scheme, hydrolysed silanol (Si–OH) undergo sol–gel reaction to form Si–O–Si linkages, Si–OH react with PVA through cross-linking reaction to form Si–O–C linkages and self-condensation of the –C–OH groups of PVA to form C–O–C linkages. The development of –C(=O)–O–C linkage is the result of reaction between –COOH groups present in GMSG/VMSG and –OH groups of PVA.

The resulting gel mixtures were casted on petri dishes and dried at room temperature for about four days. The obtained membranes were carefully peeled off from the petri dishes with the help of knife blade. The membranes were then processed for thermal treatment in a vacuum oven for 5 h at 120 °C to ensure the complete reaction conversion into the hybrid membranes [29]. The obtained membranes were labelled as GMSG20, GMSG40, GMSG60 and VMSG20, VMSG40, VMSG60 series with different wt% content of GMSG and VMSG inside the membrane matrix, which were 20, 40 and 60 wt% of PVA as shown in Table 1. The thickness of the membranes was maintained to around 120 to 150 μm.

**Membrane Characterization**

**Fourier Transform Infrared (FTIR) Spectroscopy**

FTIR spectroscopic analysis of the PVA hybrid membrane was performed using IR Shimadzu, Prestige-21 (Japan) spectrometer equipped with Horizontal Attenuated Total Reflectance (HATR) accessory. The experiment was performed in the wave number range of 4000–400 cm⁻¹ and 100 scans were collected per spectrum at the resolution of 4 cm⁻¹ with air as its background.

**Ion Exchange Capacity (IEC)**

Membrane IEC value was calculated to investigate the content of interchangeable ionic (–COOH or –COONa) group in membrane using acid base titration method. The dried
sample was weighed \((W_{\text{dry}})\) and soaked in 1.0 M HCl solution for two days at room temperature to convert the ion exchange groups into \(H^+\) form. Afterwards, the sample was washed with plenty of deionized water to ensure the complete removal of acid residues and immersed in 0.05 M solution of NaOH for 48 h. This NaOH solution was titrated against 0.05 M HCl solution with phenolphthalein as an indicator to determine the decreased amount of NaOH. The IEC (mmol/g) was measured by the amount of HCl per dry weight of membrane by Eq. 1 [30, 31].

\[
\text{IEC} = \frac{C_{\text{HCl}} \cdot V_{\text{HCl}}}{W_{\text{dry}}}
\]

where IEC is the Ion exchange capacity (mmol/g), \(C_{\text{HCl}}\), \(V_{\text{HCl}}\) and \(W_{\text{dry}}\) represent the molar concentration of HCl solution, volume of HCl consumed and dry membrane weight (g), respectively. Each measurement was taken at least thrice and the results were reported in the form of error bars.

**SEM Analysis**

SEM analysis was performed to study the surface morphology of the membranes using JEOL Microscope. The images were taken at 5KV between 500 and 5000 resolutions.

**Thermal Gravimetric Analysis (TGA)**

TGA was performed using Mettler Toledo analyser at a heating rate of 10 °C/min and over a temperature range from room temperature to 800 °C. Nitrogen gas at a flow rate of 15 mL/min was supplied to obtain the inert atmosphere.

**Mechanical Properties**

Mechanical properties like tensile strength and elongation at break of the hybrid membranes were determined using U-CAN Dynatex, tensile tester (UT-2080, Taiwan) having crosshead speed of 100 mm/min. The experiment was performed at 25 ± 2% relative humidity and 25 °C using dumbbell shaped sample having 25 mm length and 5 mm width.

**Water Uptake and Swelling Degree**

Water uptake was measured to investigate the hydrophilicity of membrane. Small pieces of membranes were dried in a vacuum oven at 75 °C for 24 h. The dried pieces of membranes were weighed and soaked in deionized water at room temperature for 72 h. Afterwards, the pieces were withdrawn, wiped out with blotting paper to remove extra water and weighed again. Water uptake (%) was determined [32] using Eq. 2.

\[
\text{Water uptake(\%)} = \frac{W_2 - W_1}{W_1} \times 100
\]

where \(W_1\) and \(W_2\) represent dried membranes weight and wet membrane weight respectively. Swelling degree is used to investigate the stability of membrane in hot water. Degree of swelling of the membrane was determined using water immersion method, by membrane swelling behaviour in water. The weight gain of the dry membrane was measured for a certain time after immersed in water at 65 °C [23]. Pre-weighed dry membrane pieces \((W_1)\) was dipped in water at 65 °C and then taken out after 72 h. As a final point, the extra surface water from the membrane was wiped dry quickly with blotting paper and then wet piece of membrane was weighed \((W_3)\). Swelling degree (%) was measured using the following Eq.

![Scheme 2 Schematic diagram of two compartment diffusion dialysis cell](image)
Diffusion Dialysis

To investigate the potential application of the membrane for alkali recovery, DD experiment was performed using NaOH/Na₂WO₄ aqueous solution [33] in a cell of two compartments separated by the prepared membrane having an effective area of about 6.2 cm² as shown schematically in Scheme 2. The feed side of the dialysis cell was filled with 100 mL of 1 M NaOH and 0.1 M Na₂WO₄ aqueous solution as model aqueous waste feed solution and permeate side was filled with 100 mL of deionized water as dialysate. The membrane was immersed in the feed solution for 1 h before the test. Both sides of the dialysis cell were mechanical stirred continuously at equal speed to avoid concentration polarization. The experiment was performed at 25 or 45 °C for 1 h and then from both compartments of the cell, feed and permeate solutions were removed. The concentration of OH⁻ ions in feed and permeate sides were measured by titration method using 0.1 M HCl solution, while ultraviolet spectrophotometry method was used to measure the WO₄²⁻-concentration [23].

The dialysis coefficient (U) was calculated using Eq. 4 [31, 34].

\[
U = \frac{M}{A \Delta C} \tag{4}
\]

where M represents the amount of substance transported in moles, A is the effective area of membrane (m²), t stands for time in h and \( \Delta C \) is the logarithm average concentration difference (mol/m³) between the two compartments which was calculated using Eq. 5 [13, 35].

\[
\Delta C = \frac{C^0_f - (C^t_f - C^t_d)}{\ln[C^0_f/(C^t_f - C^t_d)]} \tag{5}
\]

where \( C^0_f \) and \( C^t_f \) are the concentrations of feed solutions at time 0 and t, respectively and concentration of dialysate at t time is \( C^t_d \).

The separation factor (S) determined by the ratio of (two dialysis coefficients) \( U_{OH} \) and \( U_{WO_4^{2-}} \) in the solution and was calculated using Eq. 6 [36].

\[
S = \frac{U_{OH}}{U_{WO_4^{2-}}} \tag{6}
\]

Results and Discussions

FTIR Spectra Analysis

The FTIR spectra of GMSG and VMSG cross-linked PVA hybrid membranes are demonstrated in Fig. 1. Absorption band between 1260 and 1350 cm⁻¹ represents the stretching vibration of secondary C–N group [25, 37] which confirms the formation of GMSG/VMSG (Scheme 1). The broad band around 3300 cm⁻¹ is assigned to stretching vibration of –OH
group of PVA and cross-linker [38]. The peaks appearing at 2930 cm$^{-1}$ and 1427 cm$^{-1}$ represent –CH stretching and bending vibrations, respectively [39–46]. The characteristics sharp peak at 1723 cm$^{-1}$ is attributed to stretching vibration of carbonyl (–C=O) group from GMSG/VMSG [47, 48], the intensity of which increases with the increase of GMSG/VMSG contents in the membrane matrix. The small peak at 1645 cm$^{-1}$ is attributed to the stretching vibration of C=C [49], which becomes gradually stronger by increasing content of VMSG. The stretching peaks of Si–O–C, Si–O–Si, ether linkages (C–O–C), and ester linkages (–C(=O)–O–C) are observed between 1050 and 1170 cm$^{-1}$ which confirm the cross-linking reactions [23, 50–52].

Ion Exchange Capacity (IEC)

The IEC value was measured using the titration method to confirm the charged nature of the CEMs and results are shown in Fig. 2. The IEC was mainly contributed from the –COOH/–COONa groups (Scheme 1a, b) present inside membrane matrix. By increasing GMSG and VMSG amount, the –COOH/–COONa content increases which results in gradual increase of both theoretical and experimental IEC values as shown in Table 1. Hence, GMSG, VMSG can be applied as new types of cross-linking agents for the synthesis of hybrid cation exchange membranes.

The experimental IEC values increases from 0.47 mmol/g to 1.05 mmol/g, which is slightly higher than the reported hybrid PVA/poly(AA-co-γ-MPS) membrane having IEC value 0.76 mmol/g to 0.90 mmol/g [11]. The higher experimental IEC values of membranes are due to having –COOH and –COONa groups present in GMSG/VMSG cross-linked membranes. It is also interesting to note that –COOH/–COONa groups remain stable during the sol–gel reaction and only –Si–O–CH$_3$ groups react with –OH groups of PVA [53]. The experimental IEC values depend upon the amount of fixed charge groups in membranes so it can also be claimed that increasing the amount of GMSG, VMSG in the membranes result in increase of IEC values.

TGA Analysis

The thermal stability of the prepared membranes was determined using TGA and the results are reported in the form of thermograms as shown in Fig. 3. Each thermogram shows following degradation steps. The first step, from room temperature to 190 °C is attributed to dehydration and removal of bounded and unbounded water molecules from membrane [40]. The second step from 190 to 370 °C is due to the degradation of the –COOH and –COONa groups [54]. The next step from 370 to 490 °C is attributed to the elimination of –OH groups from the PVA [55]. Final degradation stage occurring from 490 to 800 °C is due to the carbonization of degraded product into ash residue by the degradation of main polymer backbones [56]. It has been observed that by increasing GMSG/VMSG content in the membrane, the weight loss keeps on increasing due to increase of cross-linked and compact structure owing as a result of abundance of –COOH/–COONa groups concentration inside the membrane matrix.

The experimental data indicated that the temperature at which degradation initiated (T$_d$) values were 242–257 °C and temperature at 10% weight loss (T$_{10\%}$) values of membrane were 286–306 °C. The T$_d$ and T$_{10\%}$ values gradually decreased by increasing the amount of GMSG/VMSG in the membrane, the weight loss keeps on increasing due to the increasing amount of cross-linked and compact structure owing as a result of abundance of –COOH/–COONa groups concentration inside the membrane matrix. The experimental data indicated that the temperature at which degradation initiated (T$_d$) values were 242–257 °C and temperature at 10% weight loss (T$_{10\%}$) values of membrane were 286–306 °C. The T$_d$ and T$_{10\%}$ values gradually decreased by increasing the amount of GMSG/VMSG content from 20 to 60 wt% in membrane as indicated in Table 2. This is due to the increasing amount of –COOH/–COONa function groups which starts to degrade at relatively lower temperature. It was also noted that temperature at 50% weight loss (T$_{50\%}$) was 382, 437, 383 and 417 °C for GMSG20, GMSG60, VMSG40, and VMSG60 membranes, respectively. The enhancement in T$_{50\%}$ by increasing the amount

| Membrane type | T$_d$ (°C) | T$_{10\%}$ (°C) | T$_{50\%}$ (°C) | Residue at end (%) |
|---------------|------------|----------------|----------------|-------------------|
| GMSG20        | 257        | 306            | 382            | 15.8              |
| GMSG40        | 254        | 299            | 413            | 20.6              |
| GMSG60        | 251        | 297            | 437            | 23.1              |
| VMSG20        | 246        | 300            | 383            | 15.4              |
| VMSG40        | 243        | 293            | 394            | 18.6              |
| VMSG60        | 242        | 286            | 417            | 22.6              |
of GMSG and VMSG loading is due to increase of silica linkages which offer resistance to degradation.

**SEM Analysis**

Figure 4 shows the surface SEM images of best performing GMSG40 membrane at different resolutions. It is clear that membrane structure is compact and dense without having any pores or free volume. It has also been observed that silica particles are uniformly distributed to give homogeneous structure without any evidence of phase separation which proves that successful cross-linking has been done.

**Mechanical Strength**

Mechanical properties of membranes such as tensile strength (TS) and elongation at break (Eb) were determined and obtained results are shown in Table 3 and exhibited in Fig. 5. The TS values of the cation exchange membranes are in the range of 36.8–49.3 MPa, whereas the Eb values are in the range of 54–192%. These values are much higher than those of PVDF based hybrid membranes (TS: 7.5–13 MPa, Eb: 47–123%) [57] and PVA/multi-alkoxy silicon copolymer membranes (17.4–44.4 MPa, 33.4–114.0%) [22] which proves the superior mechanical properties of our membranes as compared to other similar membranes as reported in the literature. It was found that addition of the GMSG and VMSG up to 40 wt% results in improvement of both TS and Eb values and further addition results in decrease of these properties. The increase in the mechanical properties with the addition of GMSG, VMSG is due to cross-linking of GMSG/VMSG with PVA through sol–gel reaction resulting in the formation of covalent bonding, hydrogen bonding and homogeneous dispersion of silica throughout the polymer matrix causing superior mechanical properties. However, at higher GMSG and VMSG content (60 wt%), the high amount of silica disturbs the homogeneity of the membrane [58] and results in the decline of mechanical strength.

It can also be observed from Fig. 5 that membranes cross-linked with GMSG show higher strength than the corresponding VMSG cross-linked membranes; whereas, membranes cross-linked with VMSG show higher flexibility as compared to corresponding GMSG membranes.

**Table 3** Mechanical properties, water uptake and swelling degree of (GMSG/VMSG)/PVA cross-linked membranes

| Membrane | TS (MPa) | Eb (%) | Swelling degree (%) | Water uptake (%) |
|----------|----------|--------|---------------------|------------------|
| GMSG20   | 41.2     | 54     | 394.2               | 76.1             |
| GMSG40   | 49.3     | 151    | 346.3               | 63.5             |
| GMSG60   | 46.4     | 124    | 267.9               | 61.7             |
| VMSG20   | 36.8     | 67     | 424.2               | 158.3            |
| VMSG40   | 44.5     | 192    | 402.7               | 97.8             |
| VMSG60   | 38.9     | 176    | 371.1               | 72.7             |
increased strength of GMSG membrane is due to the formation of Si–O–C linkages (Scheme 1a) as a result of cross-linking reaction of hydrolyzed Si-OH groups of GMSG and –OH groups of PVA; as well as hydrogen bonding interaction between –OH groups of GMSG and –OH groups of PVA. The increased flexibility of VMSG cross-linked membranes is due to the unreacted C=C groups (Scheme 1b) which provide extra flexibility to the membranes.

**Water Uptake and Swelling Degree**

The water uptake and swelling degree values of the prepared membranes are shown in Table 3 and shown in Fig. 6. Water uptake values of prepared membranes were in the range of 61.7–158.3%. Moreover, the results show that the water uptake values of prepared membranes decreased by increasing the contents of GMSG/VMSG in PVA blend matrix. This could be due to the extensive cross-linking nature of GMSG/VMSG which causes the reduction of water uptake. The cross-linking of GMSG/VMSG with PVA leads to the formation of Si–O–Si groups and ester linkages which results in enhanced compact structure [20, 25, 40] as shown in Scheme 1. The compact membrane structure ultimately reduces the free spaces between the polymer chain molecules which can accommodate the water molecules [59, 60]. It is interesting to note that VMSG-based membranes demonstrate higher water uptake values as compared to GMSG based membranes (Fig. 6) due to the presence of polar hydrophilic (–COOH and –COONa) groups character in of in higher content as compared to that in GMSG based membranes. It can be seen from Fig. 6 that by increasing the concentration of GMSG and VMSG from 20 to 60 wt%, the swelling degree was decreased from 394.2 to 267.9% and 424.2 to 371.1%, respectively. The decrease

in swelling degree with increase of GMSG/VMSG loading is due to presence of –COOH and –Si-OCH 3 groups in GMSG/VMSG.

As per proposed reaction scheme, –COOH groups react with –OH group of PVA by esterification reaction (formation of ester–C(=O)–O–C group), while Si–OCH 3 groups react with –OH group of PVA via sol–gel reaction (formation of Si–O–Si and Si–O–C linkages) which can significantly improve the membrane stability [11, 22]. Hence, increased linkages provide strength to resist the swelling degree. GMSG (20–60) membranes exhibit lesser degree of swelling as compared to that of the VMSG (20–60) membranes, which is due to the low content of (–COOH/–COONa) of ion exchange groups and greater cross-linking ability of GMSG. The favourable swelling resistance in the GMSG membrane is attributed to the advantages of GMSG over VMSG.

**Diffusion Dialysis (DD) Analysis**

**DD Performance at 25 °C**

The prepared membranes were employed to separate NaOH/Na 2WO 4 aqueous solution (1 M NaOH/0.1 M Na 2WO 4) as model aqueous waste feed for analyzing the DD performance and their potential use for application in alkali recovery. The dialysis coefficient of NaOH (U OH) and separation factor (S) results at 25 °C for membranes having different wt% of GMSG or VMSG in PVA matrix are shown in Fig. 7.

It has been observed that U OH values increase gradually by increasing GMSG/VMSG amount, which is attributed to –COOH/–COONa groups in membrane matrix which are necessary for the DD process as they are able to migrate Na+ ions through membrane to dialysate, therefore the available OH– ions also transfer through membrane.
from feed side to dialysate side in order to keep the solution electrically neutral. The $U_{OH}$ values obtained are in the range of 0.0061–0.0092 m/h, which are greater than that of SPPO-based hybrid cation exchange membrane having $U_{OH}$ value 0.0022 m/h at 25 °C [33]. It has been found that the membranes having 60 wt% of GMSG/VMSG exhibit $U_{OH}$ values of 0.0088 m/h and 0.0092 m/h, respectively which exceeds the $U_{OH}$ value of SPPO-DSBPB based membranes (0.0081 m/h at 25 °C) [36] and PVA/SiO$_2$ hybrid membrane [61].

The GMSG and VMSG-based PVA hybrid membranes possess $-\text{COOH}/-\text{COONa}$ functional groups which act as ion exchange sites to facilitate the migration of $\text{Na}^+$ ions. The transfer of $\text{OH}^-$ ions through the membrane takes place due to hydrogen bonding between hydroxyl groups of solution and $-\text{OH}$ groups of PVA chain/ Si-OH group/$-\text{COOH}$ group present in the membrane. The existence of hydrogen bonding is beneficial for the migration of $\text{OH}^-$ ions through the membrane matrix [62]. The transport mechanism of $\text{OH}^-$ ions through the PVA membrane can be better explained on the basis of adsorption-desorption mechanism. This mechanism involves three steps: adsorption of $\text{OH}^-$ ions into the membrane by making the hydrogen bond with the $-\text{OH}$ groups presents in the membrane, breaking the hydrogen bond and desorption of $\text{OH}^-$ ions from the membrane [25]. The complementary effect of $-\text{OH}$ group of PVA and $-\text{COOH}$ group from GMSG, VMSG form a network of hydrogen bonding with the $\text{OH}^-$ ion, enhance the permeability of $\text{OH}^-$ ions.

The VMSG membrane series showed higher $U_{OH}$ values (due to its higher swelling) as compared to corresponding GMSG cross-linked membrane series as indicated in Fig. 7. These results were in agreement with low cross-linking and high IEC values which are beneficial to transport $\text{OH}^-$ ions. Furthermore, IEC of membranes highly influences $U_{OH}$ values.

The separation factor (S) is the ratio of $U_{OH}$ and $U_{WO_4^{2-}}$ values. The separation factor values obtained are in the range of 18.24–34.76 at 25 °C and these values are higher than the reported value of PVA cross-linked silicon copolymer cation exchange membranes (16.9–18.5) at 25 °C [10] and are also comparable with other PVA hybrid membranes (11.6–20.2) at 25 °C [63]. The higher separation factor values are credited to the amplified selective interaction between $\text{OH}^-$ ions and the membranes matrix (Fig. 7).

The mechanism of selectivity can be depicted by the action of hydrophilic matrix and the presence of cation exchange functional groups. The prepared PVA based membranes are hydrophilic in nature due to large amount of $-\text{OH}$ groups; which present a strong driving force for $\text{OH}^-$ ions. Therefore, $\text{OH}^-$ ions transport through the hydrophilic membrane matrix preferentially, due to its ability to form hydrogen bonding and being smaller in size. On the other hand, the transport of $\text{WO}_4^{2-}$ ions becomes difficult due to its bigger size and higher valence state [22].

The S values were found to have decreasing trend by increasing the amount of GMSG/VMSG in the membranes. This decrease is mainly due to increase of phase separation at higher GMSG/VMSG content resulting in the transport of $\text{WO}_4^{2-}$ ions through phase separation area of the membrane without much resistance. The free transport of $\text{WO}_4^{2-}$ ions to dialysate is not favourable for membrane selectivity. It is also interesting to note that GMSG cross-linked membranes exhibit higher values of separation factor than that of VMSG membranes due to higher cross-linking degree and formation of more compact structure. A clear trade-off relation between $U_{OH}$ and selectivity can be observed. For example, GMSG20 membrane exhibits maximum S value of 34.76, while it exhibits minimum $U_{OH}$ value of 0.0061 m/h while VMSG60 exhibit lowest S value (18.24) and highest $U_{OH}$ values (0.0092 m/h).

**DD Performance at 45 °C**

DD performances of GMSG/VMSG membranes were also studied at 45 °C and results are shown in Fig. 8. The obtained $U_{OH}$ values are between 0.0086 and 0.01117 m/h at 45 °C, which are around 30% greater than the $U_{OH}$ values at 25 °C. This indicates that the permeability of $\text{OH}^-$ ions increases significantly by increasing temperature proving that the membranes are thermo sensitive. With the increase of temperature, the polymer chain mobility increases which causes in increase of free volume [19, 64]. This results, in increased activity of ions in the solution for enhanced permeation of $\text{OH}^-$ ion through the membranes and causes increase in $U_{OH}$ values.
It is also interesting to that with the increase in temperature to 45 °C; S values obtained are lower than the values obtained at 25 °C. The decrease in S values is due to the different diffusion mechanism of OH− and WO4^{2−} ions at high temperature. The diffusivity of WO4^{2−} ion is very low at normal temperature for its large size and higher valence. However, increase in temperature can accelerate the diffusion of both OH− and WO4^{2−} ions. The increase in diffusivity of WO4^{2−} ions with temperature is more significant than OH− ions [11, 33] resulting in decrease of membrane selectivity at high temperature.

Finally, the comparison of our work was done with other similar membranes reported in the literature for alkali separation as shown in Table 4. From the comparison, it can be easily seen that our membranes perform better than many other membranes and can be potential candidates for alkali separation applications in the industry.

### Conclusions

Novel and high performance hybrid cation exchange membranes were synthesized by cross-linking two types of silica functionalized mono sodium glutamate (GMSG/VMSG) with PVA by varying the GMSG/VMSG content from 20 to 60 wt%. The FTIR spectra confirm successful crosslinking of GMSG/VMSG with PVA through covalent bonding via sol–gel reaction. SEM analysis confirmed dense structure and uniform distribution of silica particles in the membrane. The prepared membranes demonstrated good thermo-mechanical properties. The obtained tensile strength values were in the range of 36.8 MPa to 49.3 MPa and flexibility observed was 54 to 192%. Water uptake (61.7–158.3%) and water swelling degree (267.9–424.2%) decreased while IEC increased (0.47–1.05 mmol/g) with the increase of GMSG, VMSG content in membrane matrix. The obtained U_{OH} values (0.0061–0.0092 m/h) increased while S values (18.24–34.76) decreased with the increase of GMSG, VMSG content. Finally, the influence of temperature on the DD process was also evaluated. It was observed that NaOH dialysis coefficient (U_{OH}) values enhanced and selectivity reduced with the increase in temperature from 25 to 45 °C. The GMSG series of membranes demonstrated relatively lower permeability and higher selectivity values as compared to VMSG series. From the above results, GMSG40 membrane can be termed as the best performing membrane having optimum separation factor and optimum diffusion coefficient. Hence, (GMSG/VMSG) cross-linked PVA membranes demonstrated excellent permeability and selectivity along with high thermo-mechanical properties, indicating their great potential for industrial applications particularly for recovery of alkali from waste water by DD.

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