Novel Pendant Benzene Disulfonic Acid Blended SPPO Membranes for Alkali Recovery: Fabrication and Properties

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Ⓢ *Supporting Information*

ABSTRACT: To reconcile the trade-off between separation performance and availability of desired material for cation exchange membranes (CEMs), we designed and successfully prepared a novel sulfonated aromatic backbone-based cation exchange precursor named sodium 4,4′-(((((3,3′-disulfo-[1,1′-biphenyl]-4,4′-diyl)bis(oxy)) bis(4,1-phenylene))bis(azanediyl))bis(methylene))bis(benzene-1,3-disulfonate) [DSBPB] from 4,4′-bis(4-aminophenoxy)-[1,1′-biphenyl]-3,3′-disulfonic acid [BAPBDS] by a three-step procedure that included sulfonation, Michael condensation followed by reduction. Prepared DSBPB was used to blend with sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) to get CEMs for alkali recovery via diffusion dialysis. Physiochemical properties and electrochemical performance of prepared membranes can be tuned by varying the dosage of DSBPB. All

the thermo-mechanical properties like DMA and TGA were investigated along with water uptake (W_R), ion exchange capacity (IEC), dimensional stability, etc. The effect of DSBPB was discussed in brief in connection with alkali recovery and ion conducting channels. The SPPO/DSBPB membranes possess both high water uptake as well as ion exchange capacity with high thermo-mechanical stability. At 25 °C the dialysis coefficients (U_{OH}) appeared to be in the range of 0.0048−0.00814 m/h, whereas the separation factor (S) ranged from 12.61 to 36.88 when the membranes were tested for base recovery in Na_2WO_4/NaOH waste solution. Prepared membranes showed much improved DD performances compared to traditional SPPO membrane and possess the potentiality to be a promising candidate for alkali recovery via diffusion dialysis.

KEYWORDS: *cation exchange membrane, DSBPB, SPPO, diffusion dialysis, alkali recovery*
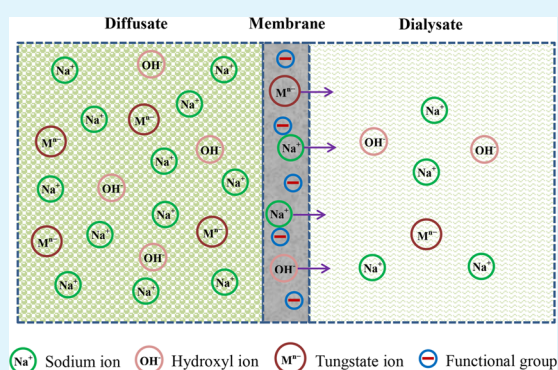
1. INTRODUCTION

There have been intensive research efforts rendered toward the development of cation exchange membranes (CEMs) for base recovery via diffusion dialysis (DD) process. Rapid advancement in the arena of modern industries like paper, leather, artificial fiber, dying, printing, aluminum, and tungsten ore processing as well as man-made fiber industries causes severe damage to the environment by discharging huge amounts of alkali wastewater.[1−5] The consequences of direct disposal of the wastewater into the environment became a severe issue and causes water pollution, harms wild life and plants, as well as intimidates human health.[1,3−8] Therefore, alkali recovery from the waste solutions took the major attention while dealing with the aqueous wastes. The major significance of this technique was to enhance the value of recycling alkaline and a pollution-free environment along with the economic benefits to enterprises.[9,10]

Nowadays, different methods are employed to encounter the aqueous alkaline waste solutions, which included the neutralization process, membrane technologies, concentration,

and burning (mainly used in the paper industries) as well.[1,5,13] Elaboration of the neutralization method suggested that this method always consumed huge quantities of acids and subsequently an enormous amount of sludge was generated afterward.[2] It is also quite well-known that waste treatment from the paper industry was always dealt with by the help of the concentration and burning method.[2] The raw materials used in the paper industry are often known as wood fiber as well as grass fiber. Hence, moderately high quantities of lignin, cellulose, alkali (pH 11−13), and high COD (chemical oxygen demand) content every now and then exists in the feed solution, which makes the waste treatment complex enough and far more difficult.[2] According to Luo et al., requirements related to the processing techniques as well as the waste feed quality are difficult and the consumption of energy is very high.[2] Among all other separation-based methods, diffusion

dialysis (DD) technology is well-established, recognized, and known to be the most effective one because of its unique features. DD is one of the most promising separation process known until date where the difference in concentration gradient plays the major role as the solutes effectively goes through a membrane from the direction of a higher concentrated compartment to the lower one.[11,12,44] It is a thermodynamically favorable process as during operation Gibbs free energy decreases and is superior to other available separation process in many aspects. Lower energy consumption, purification of wastewater, low operating cost, reliability during operation, and environmentally friendly nature is the main driving force of this process.[17,18]

Cation exchange membrane-based diffusion dialysis is an alternative attractive method to treat alkali wastes, which can make the recovery of alkali but its practical application in base recovery is still under big question and facing numerous number of difficulties, especially compared with acid recovery using anion exchange membranes because of the nonavailability of high-performance CEMs.[1] A superior DD membrane needs to fulfill the following requirements like: thermo-mechanical stability, alkali resistance, base permeation, as well as high selectivity in order to prove its suitability for practical DD application.[1] Therefore, fabricating membranes with superior stability and base resistance remains the most challenging issue in alkali recovery via DD process.[1−5] A number of different CEMs were prepared for alkali recovery from various resources, such as sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) (SPPO) and poly(vinyl alcohol) (PVA)-based (organic−inorganic hybrid) membranes.[19−25] Typically, all of these membranes showed acceptable thermo-mechanical properties along with potential character to serve as alkali recovery material. Out of these membranes, SPPO can provide better stability and alkali resistance but a problem associated with this kind of membrane is their low dialysis coefficient during the DD process compared to other polymers. This low permeability factor forced us to find a new way such that using SPPO as new polymer backbone can give us acceptable permeation and prompted us to incorporate different functionality in the membrane matrix such that it can provide better results than the available ones.

As an extrapolation of the above idea, we rendered our attention toward more hydrophilic polymer (SPPO)-based membranes and introduced different functionality, cross-linking agents inside the membrane matrix by different methods.[13,16] A major issue with SPPO-based membranes could be their high swelling nature in water, but on the other hand outstanding thermo-mechanical stability could be a promising phenomenon for the DD process. SPPO-based membranes showed improved U_{OH} values as well as separation behavior compared to other PVA-based membranes when blended with different active functionality and silica.[14,15] Hence, the above results suggest that blending could be a promising option for SPPO-based membranes to get high permeability as well as separation. As we know that during DD operation energy consumption is low and it is a cost-effective process, it could be highly possible to use this type of blend membranes for industrial purposes.

Therefore, to improve the possibility of using cation exchange membranes via DD process, we extended our efforts to the fabrication of cation exchange membrane based on SPPO and a highly sulfonated monomer 4,4′-(((((3,3′-disulfo-[1,1′-biphenyl]-4,4′-diyl)bis(oxy))bis(4,1-phenylene))bis-(azanediyl)) bis(methylene)) bis(benzene-1,3-disulfonate)

[DSBPB] in this manuscript. Through a simple efficient blending technique, SPPO-based membrane was prepared. DSBPB (Scheme 1) was synthesized by three steps and all of

Scheme 1. Synthesis of Active Conducting Material (DSBPB) through Three Steps
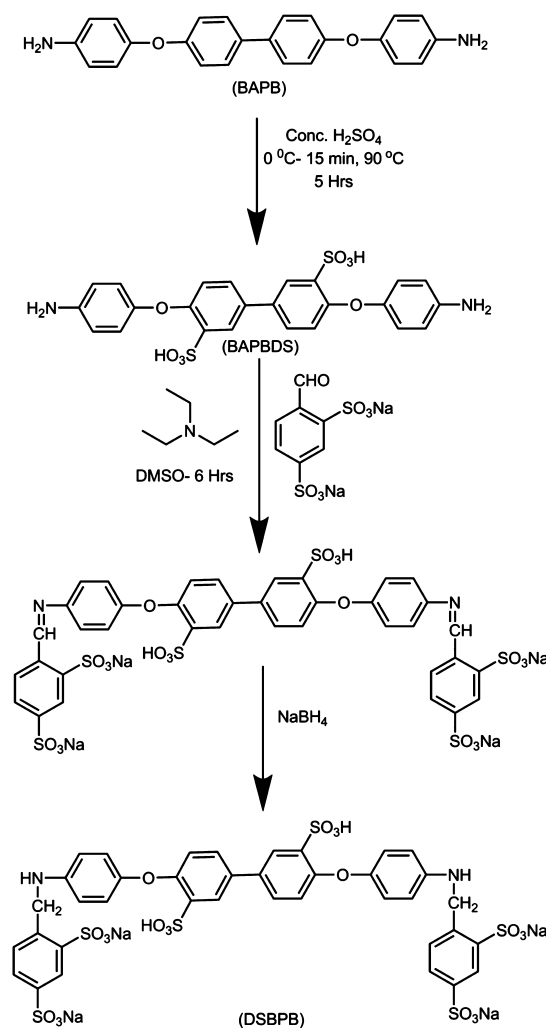
the reactions were conducted under mild conditions having high efficiency and good yield. The dosage of DSBPB on membrane structure and impact on membrane inherent properties such as IEC, water uptake (W_R), etc., has been thoroughly investigated. Moreover, with the prepared membranes, diffusion dialysis experiments were conducted for NaOH/Na$_2$WO$_4$ aqueous mixture to elaborate the separation performance and alkali recovery. The prepared CEMs were validated in terms of physicochemical and electrochemical properties while diffusion dialysis experiment was also performed to evaluate the base recovery as well as separation values.

2. EXPERIMENTAL SECTION

2.1. Materials. Tianwei Membrane Co. Ltd. (Shan-dong, China) supplied us Sulfonated poly(2,6-dimethyl-1,4-phenylene oxide) [SPPO] in Na$^+$ form with IEC around 2.25 mmol g^{-1}.[13] 4,4′-Bis(4-aminophenoxy)biphenyl (BAPB) and Disodium 4-Formylbenzene-1,3-disulfonate (FBDS) were obtained from TCI Chemicals. All other reagents like tetraorthoethoxysilane (TEOS), triethyl amine (TEA), sodium borohydride, etc., used during the experiment was obtained
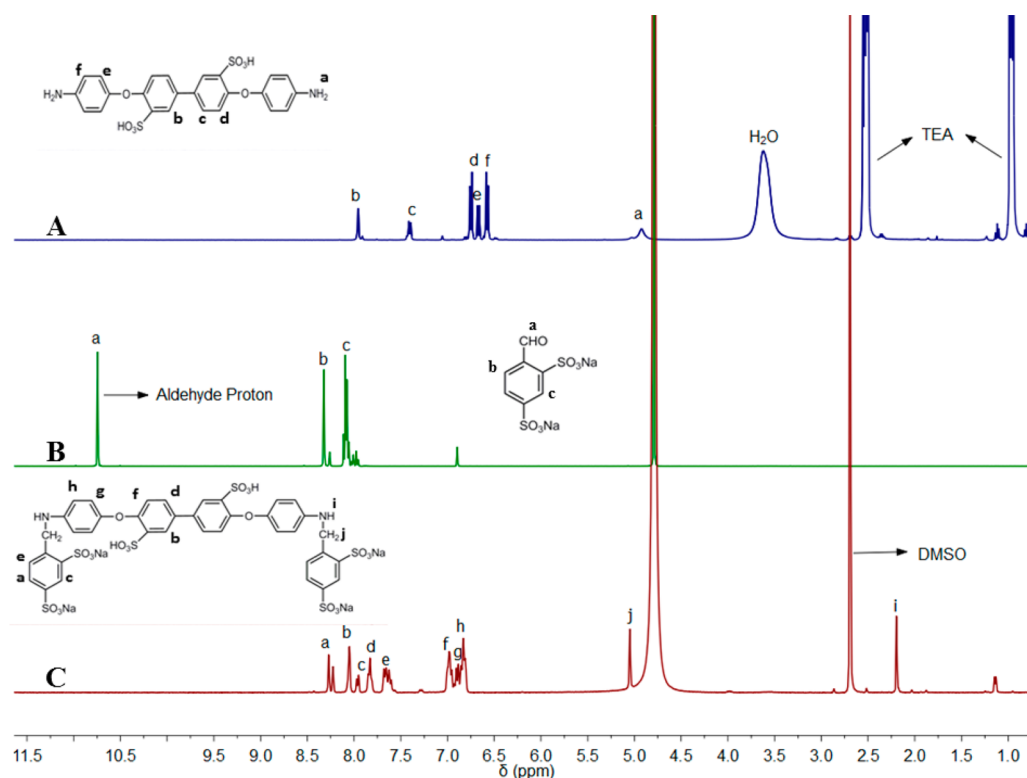
Figure 1. Comparative study of ^{1}H NMR spectra of synthesized (A) BAPBDS, (B) disodium 4-formylbenzene-1,3-disulfonate (FBDS), and (C) DSBPB.

from domestic chemical company (China). Reagents used in this manuscript were of analytical grade and no further purification was done prior to use. Deionized water (DI water) was used all throughout the experiments.

2.2. Synthesis of BAPBDS. BAPBDS was synthesized according to the literature in a modified synthetic approach stated below (Scheme 1).[26] Under constant nitrogen flow, 2.0 g (0.0054 mmol) of BAPB was added to a 50 mL oven-dried three-neck flask. Upon cooling the flask in an ice-bath, a required amount (6 mL) of conc. sulfuric acid (H_2SO_4) was slowly added to the reaction medium containing BAPB. Because of the exothermic nature of reaction during the addition of acid, a magnetic stirrer was always used to stir the reaction mixture slowly. The rest of the reaction procedure, process, and isolation of the product was done in the same way as previously reported in literature.[26] Finally after the reaction gets over we obtained 91% (2.62 g) of white desired product. ^{1}H NMR (DMSO-d_6 containing a drop of Et$_3$N, 400 MHz): δ 7.98 (d, 2H), δ 7.43 (dd, 2H), δ 6.77 (d, 4H), δ 6.69 (d, 2H), δ 6.59 (d, 4H), δ 4.92 (br, 4H) ppm.

2.3. Synthesis of DSBPB. DSBPB was synthesized by the reaction of BAPBDS and Disodium 4-Formylbenzene-1,3-disulfonate (FBDS) in the presence of triethylamine and sodium borohydride (Scheme 1). In a typical synthetic procedure, a 100 mL oven-dried round-bottom flask was taken with a stirbar and charged with BAPBDS (0.528 g, 1.0 mmol). Twenty-five milliliters of DMSO was added very carefully to the reaction medium. Upon addition of DMSO the solution becomes turbid and Triethyl amine (0.212 g, 2.1 mmol) was charged very slowly to the reaction medium. Finally, after complete dissolution of BAPBDS in DMSO, a required amount of disodium 4-formylbenzene-1,3-disulfonate (0.620 g, 2.0 mmol) was dissolved in DMSO: H_2O mixture (4:1 v/v) and added to the reaction mixture. Then stirring of whole solution was continued until 6 h at 80 ^{o}C in order to complete the imine formation. Finally, sodium borohydride was added in portion such that the imine linkage could be completely reduced and it was further confirmed via the disappearance of hydrogen gas evolution. After that, the complete reaction mixture was poured into cold acetone and kept inside the freeze for overnight. Filtration was performed in

order to obtain the crude precipitate followed by the subsequent washing with acetone (5−6 times) to remove impurities as well as any other volatiles. Finally, the crude product was dried in vacuo and appeared as a straw yellow solid in 86% yield (1.815 g). ^{1}H NMR (D_2O, 400 MHz): δ 8.27 (d, 2H), δ 8.05 (d, 2H), δ 7.96 (d, 2H), δ 7.85−7.80 (m, 2H), δ 7.69−7.61 (m, 2H), δ 7.01−6.95 (m, 4H), δ 6.87−6.92 (m, 2H), δ 6.85−6.80 (m, 4H), δ 5.05 (s, 4H), δ 2.20 (s, 2H) ppm.

2.4. General Procedure for Fabrication of the DSBPB/SPPO Blend Membranes. DSBPB/SPPO blend membranes were prepared using two steps by solvent casting technique and a typical procedure was as follows: First, a required amount of SPPO (20 wt %) was thoroughly dissolved in dimethylformamide (DMF) at room temperature for 6 h, meanwhile in second step an appropriate amount of DSBPB was also separately dissolved in DMF. Obtained solutions were mixed together while stirring was continued at room temperature for 24 h. Thus, the obtained dark brown colored homogeneous mixture was finally casted on top of a clean glass plate and transformed into a thin film which was dried for 12 h at 60 °C followed by further drying in vacuo. The obtained transparent membrane was represented as DSBPB-X, where X is the loading weight percentage of DSBPB content in the SPPO matrix and ranged between 20 and 60 wt % of SPPO content. Prepared membranes were further used for physiochemical and electrochemical characterizations.

For comparison, the conventional method was employed to prepare pristine SPPO membrane, i.e., a 20 wt % polymer solution of SPPO in DMF (dimethylformamide) was casted on top of a glass plate, whereas drying was done as mentioned above for the DSBPB/SPPO blend membranes.

2.5. Membrane Characterizations. Information on the detailed instrumental analysis, e.g., NMR spectroscopy, infrared spectroscopy, DMA, TGA, is represented in the Supporting Information, Section S1. Microscopic characterization of prepared membranes, i.e., SEM analysis, is included in the Supporting Information, Section S2.

2.5.1. Water Uptake (W_R) and Ion Exchange Capacity (IEC). Detailed procedures for the estimation of water uptake (W_R) and volume fraction of water in membrane matrix are included in the
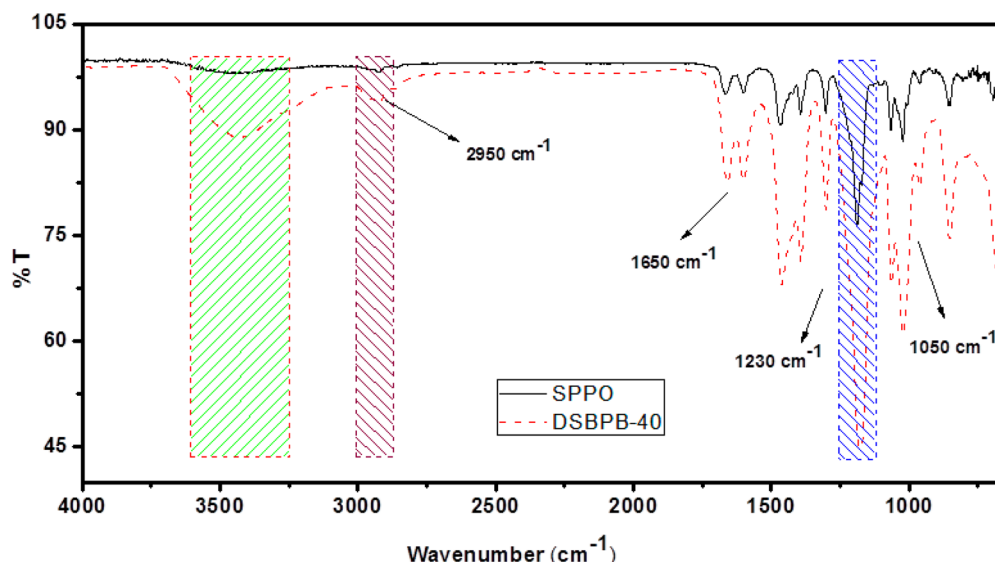
Figure 2. ATR-FTIR spectra of synthesized SPPO/DSBPB membrane (DSBPB-40 as reference) and comparative study with parent SPPO membrane.

Supporting Information, Section S4.[52] IEC was measured through the classical titration method and the exact procedure is included in the Supporting Information, Section S3.[41]

2.5.2. Diffusion Dialysis of NaOH/Na₂WO₄ Mixture. Diffusion dialysis (DD) tests were performed using a membrane of area 5.3 cm² in a cell consisting of two compartments. The cell was fabricated in such a way that the membrane used in the experiment can separate these two compartments of the cell evenly. Before performing the DD test, all of the prepared membranes were very carefully conditioned with the model waste solution (1 M NaOH + 0.1 M Na₂WO₄) for 2 h, which stimulates the waste base solution that is produced in metallurgical processes or its related products. During the experiment, one compartment of the cell was filled up using 100 mL of model waste solution while another side was filled with 100 mL of DI water. To minimize the concentration polarization, both sides were stirred vigorously. The reference experiment was carried out for 60 min, whereas after the experiment, both the feed as well as permeate solutions were taken out from either sides of the compartment.[50] Aqueous HCl solution (0.1 mol/L) was used to determine the concentration of OH⁻ from both sides (permeate as well as diffusate) by the titration method, whereas the ultraviolet spectrophotometry method was used to determine the concentration of WO_4^{2-} in the diffusate side.[24,32] All the experiments were conducted at 25 °C.

The dialysis coefficients (U) can be calculated by using the below mentioned formula[15,32]

$$U = \frac{M}{At\Delta C} \tag{3}$$

Where M represents as the amount of transported component in (mol), A is known as the effective surface area of the membrane (m²), time is represented by t (h), and ΔC corresponds to the logarithmic value of average concentration in between two different chambers (mol/m³).[56] ΔC is calculated as below[15]

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

C_f^0 and C_f^t represent concentrations of the feed solution at time 0 and t, respectively, whereas C_d^t is the concentration of the dialysate at time t.[24]

According to above eq 3 and 4, dialysis coefficient U_{OH} and $U_{WO_4^{2-}}$ can be calculated. The separation factor (S) corresponds to the ratio between dialysis coefficients (U) of two different species available inside the medium (solution) and estimated as mentioned below

$$S = \frac{U_{OH}}{U_{WO_4^{2-}}} \tag{5}$$

3. RESULTS AND DISCUSSION

3.1. NMR and FTIR Spectra Analysis. The synthesis of active cation exchange material, such as DSBPB in this study, involves the combination of a sulfonated aromatic backbone based amine named BAPBDS[26] (which is synthesized by the reaction of 4,4′-(1,1′-biphenyl-4,4′-diyldioxy)dianiline [BAPB] with conc. H₂SO₄ at 90 °C) as well as disulfonated aromatic aldehyde (Scheme 1).

The functionalized compound DSBPB, based on Schiff base formation reaction, was synthesized in a straightforward and high-yielding step. The chemical structures of the compounds at each step of the reaction were further confirmed by using ¹H NMR spectroscopy, as shown in Figure 1. The reaction of the corresponding amine and aldehyde which is well-known as Schiff base formation reaction was performed with the use of disulfonated aromatic aldehyde (FBDS) in dimethyl sulfoxide for 6 h at 80 °C. As shown in Figure 1, the chemical shift corresponding to aldehyde proton (present in FBDS) diminished from 10.74 ppm after reaction, indicating successful formation of imine linkage. Functionalization of 4,4′-bis(4-aminophenoxy)-[1,1′-biphenyl]-3,3′-disulfonic acid [BAPBDS] with the corresponding aldehyde was further proven by the addition of sodium borohydride. This addition leads to immediate effervescence of colorless gas, which supports our observation as reduction of imine linkage.

¹H NMR spectra of DSBPB in Figure 1 showed significant chemical shift around δ = 8.27 ppm, which can be attributed to the ortho protons with respect to the sulfonate group present in the aromatic backbone of FBDS. Peaks around 8.05, 7.96, 7.85−7.80, and 7.69−7.61 ppm are the signals aroused from aromatic protons that are adjacent to the sulfonate group present in DSBPB. The presence of the sulfonate group had a profound effect in chemical shift values. The presence of the sulfonate group adjacent to aromatic protons makes the environment less shielding and hence more down fielded. Significant shifts occurring around 7.01−6.95, 6.87−6.92, and

Table 1. Membrane Compositions and their Water Uptake (W_R), Volume Fraction in Water (φ_w), Ion Exchange Capacity (IEC) As Well As Number of Water Molecules per Ionic Site (λ_w) Values

membrane code	DSBPB of SPPO (%)	W_R (wt %)	φ_w (vol %)	IEC (mmol/g)	$\lambda_w/-SO_3^-$
SPPO		91.9 ± 0.67	49.4 ± 0.18	2.25 ± 0.01	22.61 ± 0.29
DSBPB-20	20	105.5 ± 1.9	52.8 ± 0.64	2.37 ± 0.02	24.74 ± 0.30
DSBPB-40	40	130.8 ± 1.02	57.7 ± 0.43	2.45 ± 0.01	29.69 ± 0.38
DSBPB-60	60	160.1 ± 5.21	60.7 ± 1.51	2.81 ± 0.01	31.72 ± 1.09

6.85−6.80 ppm can be correlated to the other aromatic protons that are away from sulfonate groups. Hence they became more shielded and showed upfield shift. Chemical shifts around δ = 5.05 ppm appeared as a singlet because of the presence of −CH$_2$ group, which in turn approved the complete reduction of imine linkage and incorporation of FBDS into BAPBDS backbone.

The IR spectrum of the synthesized DSBPB moiety and the comparison with BAPB & BAPBDS (in the Supporting Information, Figure S1) indicates the formation of DSBPB. DSBPB showed characteristics peaks at desired wavelength. The sharp intensity absorption band appeared around 1512−1465 cm^{-1} could be attributed to the C−C stretching vibration from the aromatic groups present in DSBPB where as the C−H stretching frequency of aromatic groups present in DSBPB skeleton could be confirmed by the medium intensity absorption peak appeared at 3012 cm^{-1}.[53] The absorption bands showed a strong −SO$_3$H stretching at ∼1050 (sym. SO$_3$ stretch), ∼1230 (asym. SO$_3$ stretch) cm^{-1} indicated a strong existence of −SO$_3$H group.[27] A sharp absorption peak around ∼1600 cm^{-1} is mainly due to the presence of N−H bending (scissoring) in the DSBPB as well as BAPB & BAPBDS.[51] Synthesis of DSBPB was done via Schiff base formation reaction using BAPBDS with FBDS, thus the sharp band at ∼2950 cm^{-1} confirmed the existence of −CH$_2$ groups from DSBPB unit.[28] The broad band ranging from 3200 to 3600 cm^{-1} also confirmed the existence of −OH stretching vibration in DSBPB skeleton, which was totally absent in BAPB moiety.[29] In the fingerprint region, the sharp peak around 820 cm^{-1} proved the existence of in plane and out of plane C−H bending for 1,4-disubstituted aromatic group present in DSBPB.[27]

The ATR-FTIR spectra of representative SPPO and DSBPB-40 membranes were represented in Figure 2 for detailed discussion. The main difference between SPPO and DSBPB incorporated SPPO membrane (DSBPB-40) was the presence of more sulfonic acid groups (as DSBPB contains six additional −SO$_3$H group) as well as −NH groups. Here we can see, because of the increased amount of −SO$_3$H groups present within the DSBPB-40 membrane, the peak intensity of −SO$_3$H group at 1050 and 1230 cm^{-1} increases sharply compared to pure SPPO-based membrane. The band at ∼2950 cm^{-1} confirmed the existence of −CH$_2$ groups from DSBPB unit. Another important finding to be considered here is the active presence of −NH group in DSBPB-40 membrane. Thus, according to our expectation in the DSBPB-40 membrane spectra, peaks at ∼1650 cm^{-1} confirmed the existence of −NH group, which suggests successful fabrication of DSBPB incorporated SPPO membrane.[30]

3.2. Water Uptake (W_R) and Ion Exchange Capacity (IEC). Water uptake (W_R) is considered as an important parameter of a membrane and has got a valuable effect on the separation phenomena; dimensional as well as mechanical properties.[31,32,46] Dissociation of the charged functional groups could be facilitated by the presence of water molecules inside

the membrane matrix and are very crucial for ion transport.[46] Another major importance is that ionic concentration, dimensional as well as thermo-mechanical stabilities of the membrane could be preferentially affected by the presence of large water volume fraction present within the membrane matrix.[45,46] We could expect our prepared CEMs to be more stable in terms of their dimension, strength as well as enough durable so that it can sustain for a long time..[53] The physiochemical stability of the as prepared SPPO/DSBPB blend membranes were assessed by the change in volume fraction in water along with water uptake (W_R) values (Table 1). SPPO/DSBPB membranes exhibited higher water uptake than pristine SPPO membrane. This crucial scenario can be elucidated in terms of formation of the increased volume of the hydrophilic domains. Obtained data presented in Table 1 revealed that the water uptake (W_R) values gradually increased with cation exchange content which may be accredited to the enhanced hydrophilic domains of the membrane matrix. Hydrophilicity of membrane matrix along with degree of plasticization plays an imperative role for water uptake (W_R).[46] At lower degree of plasticization (i.e., presence of high cation exchange content) flexibility of the polymer network allows increased water uptake.[33,46]

Three types of water mainly found in the membrane matrix that can be classified as (1) free water (which has the same enthalpy of melting as well as temperature as bulk water), (2) freezing bound water (that is loosely held with the corresponding ionic as well as polar functional groups present in the polymer backbone and showed significant variation in enthalpy and temperature as compared to bulk water while DSC can be used to detect it), and (3) nonfreezing bound water (it is very strongly attached to the polar or ionic groups, respectively, and showed no phase change).[46] Eikerlings theory explained that,[34] usually charged ion exchange membrane contained two different types of water which are namely as bulk and bound water.[46] Bound water could be essential for the ionic groups solvation, whereas the bulk water is involved in filling up the void volume.[46] Values of water uptake can be used in order to estimate the total number of water molecules present per ionic site (λ_w)[36,46] (Table 1), which further supports the hydrophilic nature of the prepared membranes with high cation exchange component. The highest number of water molecules present per ionic site for membrane DSBPB-60 showed its hydrophilic character.

As the membrane possesses selective permeability, it is possible to separate salt as well as lower molecular organic constituent.[32] Particularly this phenomenon is very important for diffusion dialysis and thus prepared membranes are applicable for the DD process. Furthermore, water retention proficiency is an important character of an ion exchange membrane, which is often helpful to evaluate their appropriateness for different preferred applications.[46]

IEC depends on the density of functional group available in polymer backbone and hence plays a major role in

selectivity.[35,36] To assess the suitability of prepared membranes for ion exchange, we carried out corresponding experiments. It was evident that IEC observed for parent SPPO membrane (2.25 mmol g^{-1}) gradually increased with the incorporation of DSBPB (Table 1). Obtained increasing trend in IEC values could be clarified in context of availability of more number of cation exchange groups with higher loading of DSBPB in SPPO matrix. Titration method was employed in order to assess the IEC results for prepared CEMs and represented in Table 1. It is important to mention that DSBPB-60 membrane exhibited 2.81 mmol g^{-1} of IEC, which is highest among other prepared membranes. IEC studies revealed charged nature of developed CEMs. Figure 3 here represents a comparative study of water
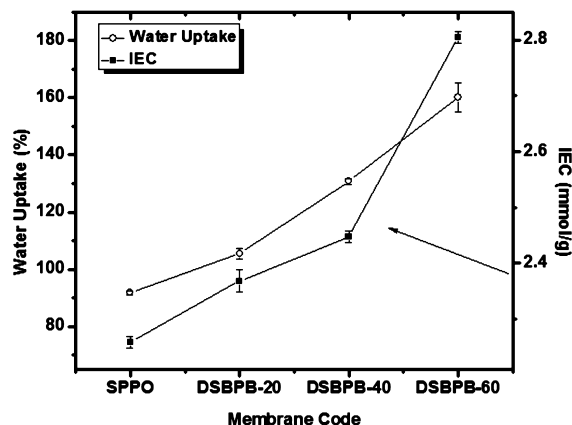

Figure 3. Variation in water uptake (W_R) and ion exchange capacity (IEC) of different DSBPB/SPPO blend membranes.

uptake and IEC of SPPO & different DSBPB blend SPPO membranes. It can be noted that with the increase in DSBPB content in the membrane matrix starting from DSBPB-20 to DSBPB-60, a gradual increase in IEC and W_R could be observed. It is possibly due to the availability of more functionality in the membrane matrix that is taking part to show a gradual increasing trend of water uptake (W_R) and IEC. Obviously, the sulfonate group is known to be extremely hydrophilic in nature and the gradually increasing content of sulfonate group can assist the increasing hydrophilicity of the membrane matrix.[22] The variation in the hydrophilicity of the

prepared membranes going from DSBPB-20 to DSBPB-60 is mainly governed by the gradual increase in the amount of sulfonate group. Therefore, the WU values represented an ascending trend going from membrane DSBPB-20 to DSBPB-60.
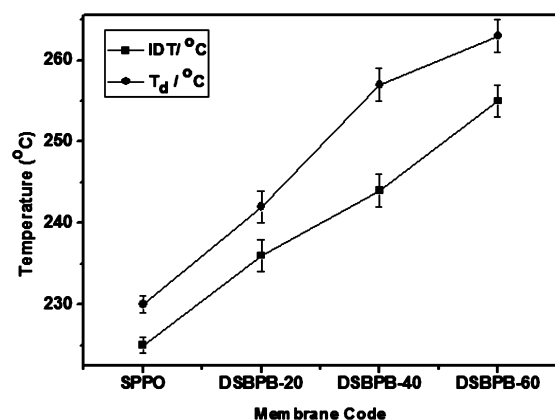
3.3. Thermal and Mechanical stability. Figure 4A shows reference TGA plots for the SPPO and SPPO/DSBPB blend membranes. Mainly, weight loss can be divided into three major steps over the entire temperature range starting from 30 to 800 °C. All of the above-mentioned steps appeared to be alike for pure SPPO as well as DSBPB blend SPPO membranes, though later ones always exhibited delayed degradation in each step. Thermal stability of the membranes can be clarified from two major aspects: the decomposition temperature as well as the remaining weight percentage. The first weight loss between 80 and 130 °C could be attributed to the loss of bound and hydrated water linked with the sulfonic acid groups.[37−40,42,53] Weight loss during the entire temperature range for pristine SPPO membrane was significantly much higher as compared to the SPPO/DSBPB blend membrane. Figure 4B showed the comparison of bound water content in different DSBPB blend membranes along with pristine SPPO. The second stage of weight loss can be ascribed as the degradation of the hydrophilic sulfonic acid groups available inside the membrane matrix.[38,39,53] The SPPO/DSBPB blend membranes displayed much higher decomposition temperature as well as lower mass loss as compared to pristine SPPO membrane. This observation can be explained in terms of different interactions present inside the membrane structure.[41] Hydrogen bonding present in the DSBPB blend SPPO membrane could be responsible for enhanced membrane stability, thus SPPO/DSBPB membranes behaved thermally more stable than pristine SPPO. Weight loss corresponding to the second stage for blend membranes was mainly ascribed to the decomposition of sulfonic acid groups and phenyl groups.[53] The final weight loss stage could be assigned to the degradation of the main polymer chain.[53] Here it is important to note that at around 420 °C for the SPPO membrane, a sharp decrease in membrane weight can be observed. This sharp decrease in weight loss corresponds to the decomposition of SPPO backbone. For SPPO/DSBPB blend membranes, because of better thermal stability, the percentage of weight loss was less and a delayed degradation was observed. The slower weight loss percentage also reflects the enhance-
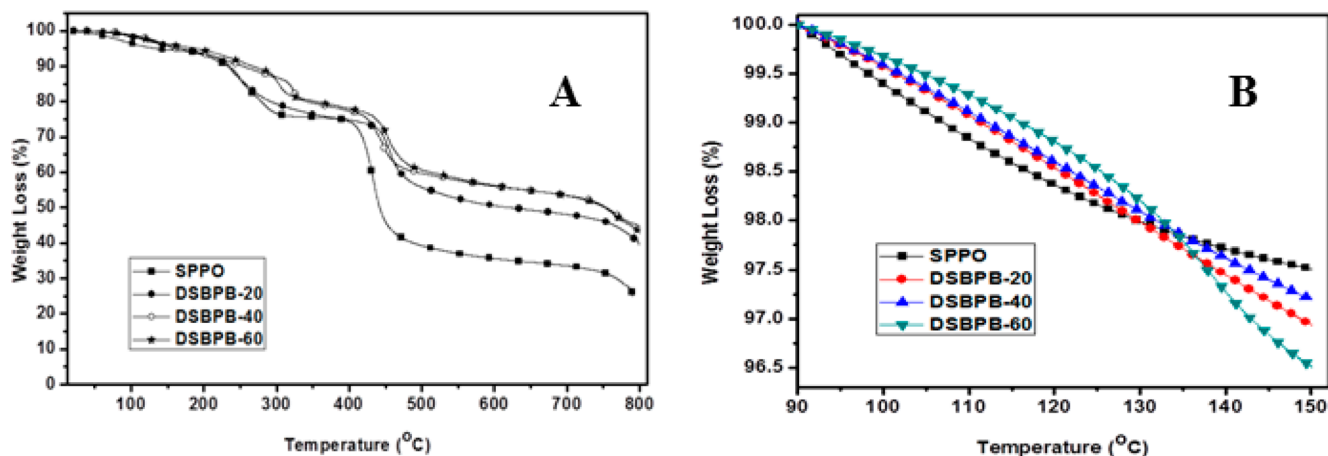
Figure 4. (A) TGA thermograms of different DSBPB/SPPO blend membranes and (B) comparison of bound water content of different DSBPB blend membranes with SPPO.

ment in thermal resistance. Considering all the features of prepared membranes, we can conclude that the blend membranes showed enhance thermal stability. Therefore, the obtained results suggest its outstanding thermal resistance potentiality for alkali recovery via DD process.

In Figure 5, we can observe the comparison of initial decomposition temperature (IDT) and thermal degradation

Figure 5. Initial decomposition temperature (IDT) and thermal degradation temperature (T_d) of different SPPO/DSBPB membranes.

temperature (T_d) of different prepared SPPO/DSBPB membranes obtained from TGA analysis where T_d known as the reference temperature at which 5% weight loss occurred. Presence of DSBPB in SPPO matrix proved to be beneficial for the fabrication of thermally stable membranes.

Figure 6 represented the mechanical properties of the prepared membranes (such as stress and strength) measured by
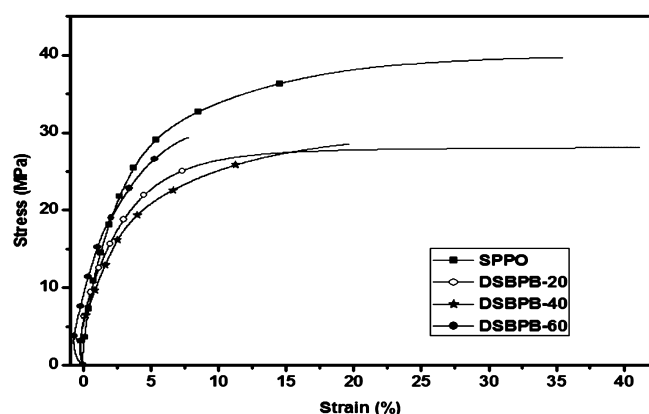
Figure 6. Tensile strength (TS) vs elongation at break (E_b) plot of different prepared SPPO/DSBPB blend membranes.

DMA curves. The corresponding TS (tensile strength) values ranging from 28.08- 29.33 MPa and E_b values ranging from 8 to 41% evaluated from the plot and compared with pure SPPO membrane. These results can be clarified in the context of better miscibility of DSBPB inside membrane matrix. Tensile strength of membranes gradually increased with DSBPB content, whereas DSBPB-60 showed maximum TS value, which may be attributed to the maximum amount of DSBPB content present in the DSBPB-60 membrane, indicating the increase in membrane flexibility. Hence we can claim that blending of DSBPB moiety with SPPO enhances the membrane mechanical stability and flexibility.

3.4. Membrane Morphologies. The morphological view of the parent and blend membranes named as SPPO and DSBPB-20 and 60, respectively, were assessed by the SEM technique and shown in Figure 7. The incorporation of DSBPB
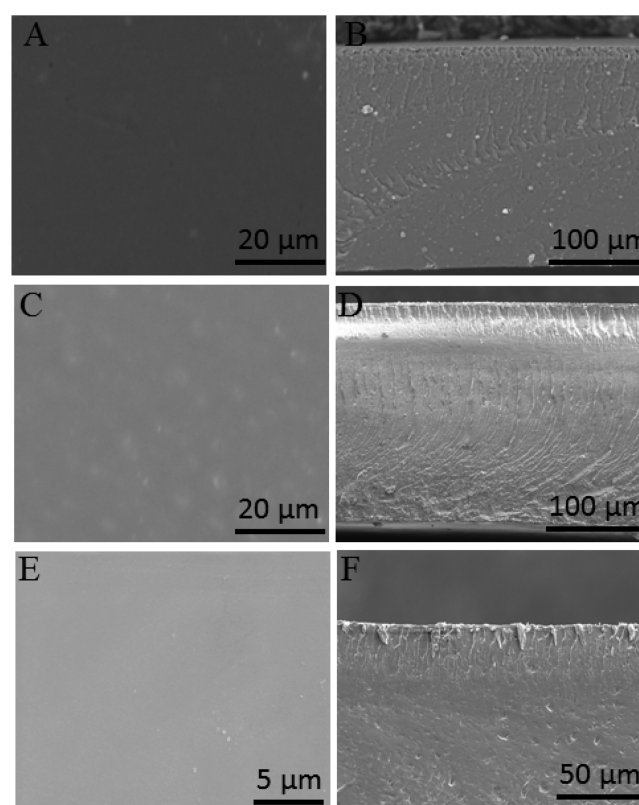
Figure 7. (A, B) Surface and cross-section of the SPPO membrane, (C, D) represents surface and cross-section of the DSBPB-20 membrane, whereas (E, F) represents surface and cross-section of the DSBPB-60 membrane.

moiety inside the SPPO backbone is visibly reflected by the surface images. Figure 7 represented low-magnified surface images of SPPO as well as SPPO/DSBPB blend membranes, where both types of membrane showed identical morphological features comprising smooth homogeneous surface attributed to the better compatibility between SPPO and DSBPB occurred through hydrogen bonding. A comparative study between SPPO and DSBPB incorporated SPPO clearly revealed that blend membranes are appreciably much more compact in comparison with parent one and showed no serious phase separation at lower loading of DSBPB into SPPO matrix. Some aggregations on the membrane surface with DSBPB-60 membrane were observed with the increase in DSBPB content. Therefore, blending with DSBPB makes the membrane highly compact and denser with moderate DSBPB content. Excellent compatibility between SPPO and DSBPB can be further verified by the cross-sectional views (B, D, and F) obtained from the blend membranes. Little phase separation was also observed with DSBPB-60, but overall, absence of any small holes and cracks on top of the membrane surface proved the compact and homogeneous nature of the prepared CEMs.

3.5. Diffusion Dialysis for NaOH/Na$_2$WO$_4$ mixture. An excessive amount of alkaline wastewater is produced in alumina and tungsten ore smelting industry, where the key components are known as sodium hydroxide (NaOH) and (Na$_2$WO$_4$).[22]
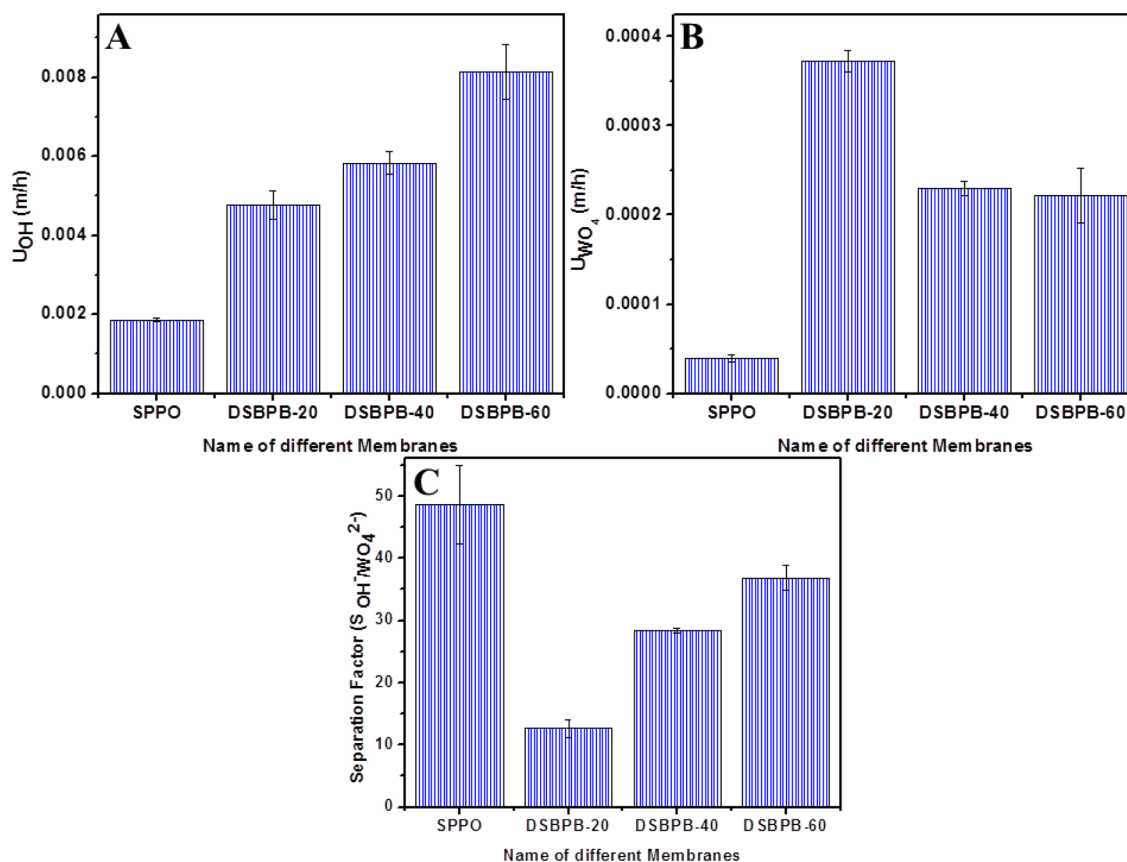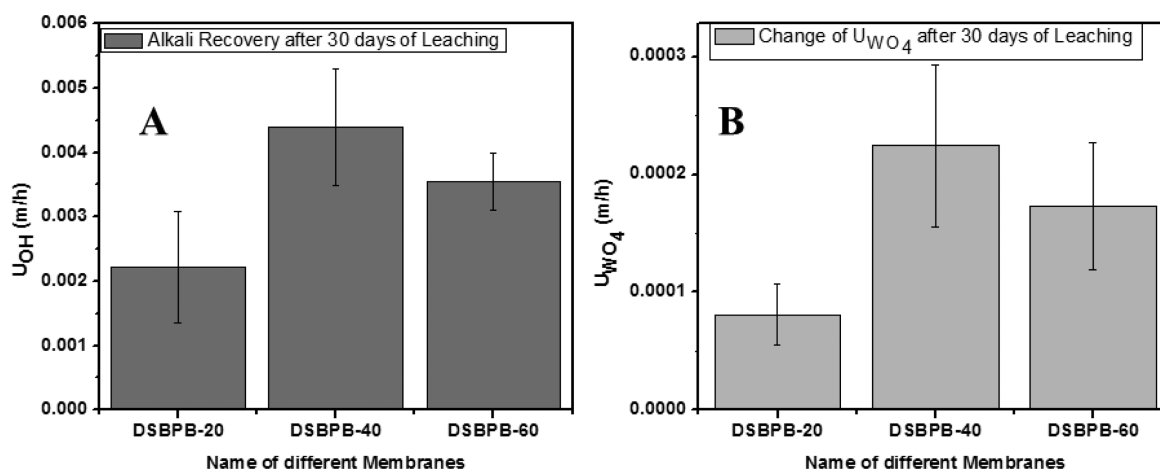
Figure 8. (A) Alkali dialysis coefficients (U_{OH}), (B) Change of U_{WO4}, and (C) separation factor (S) for SPPO and different SPPO/DSBPB blend membranes at 25 °C.

Therefore, to determine the base recovery and separation factor values of as-prepared membranes, we carried out the experiment by using NaOH/Na$_2$WO$_4$ mixture (1 M NaOH + 0.1 M Na$_2$WO$_4$) as a model feed and evaluated the membrane potential applications in alkali recovery process. Obtained DD experimental results along with dialysis coefficient values of NaOH (which is referred to U_{OH}) as well as separation factor (S) are represented in Figure 8.

Results obtained from Figure 8 showed that an increase in DSBPB (cation exchange precursor) content in membrane matrix can enhance the U_{OH} values rapidly from 0.00186 m/h (SPPO) to 0.00814 m/h (DSBPB-60). Hence, from the aforementioned observation, two different references can be drawn. DSBPB incorporated membranes (DSBPB 20−60) exhibited almost three times higher U$_{OH}$ values compared to pure SPPO membrane at 25 °C indicating facilitated OH$^-$ transport. This facilitated OH$^-$ transport can be attributed to the available extra ion conducting channels present between DSBPB and SPPO matrix. The association plus self-aggregation of DSBPB moiety is facilitated inside membrane matrix which can gave rise to high OH$^-$ transport. The enhanced hydrophilicity of the membrane matrix could be favorable for the ionic transportation across membranes[47] since higher hydrophilicity effectively leads to decrease the frictions between ions (OH$^-$ and Na$^+$) and polymer (membrane) matrix.[25,48] On the other hand, electrostatic repulsions acting between hydroxyl ions and sulfonate groups present in SPPO backbone gets reduced and enhanced uninterrupted ion transmitting channels.[25,49]

Basically, the difference in the membrane structure is known to be liable for elucidating the ionic transportation phenomena related to DSBPB blend SPPO membranes in comparison with pure SPPO. It is quite well-known that, as per the membrane three-phase model, IEM comprised of three main phases i.e. (i). a polymer which is hydrophobic in nature, (ii) an active region (together with the exchange fixed sites as well as the counterions) and (iii) an interstitial zone.[24,43] The transportation of the counterions preferentially occurred through an active region with the help of hopping mechanism whereas the minimal repulsive force arising out of dragging mechanism solely became responsible for the transportation of co-ions which generally leaked through the interstitial region.[24,44] Here, the structure of SPPO-based membranes represented a classical three-phase membrane model.[24] In the membrane phase, mainly by the help of a hopping mechanism, Na$^+$ diffusion occurred alongside the active region, whereas the interstitial zone acted as the preferential gateway for the transportation of OH$^-$ & WO$_4^{2-}$ ions.[44] In our case related to base recovery, it is important to note that sodium ions moving inside the membrane matrix are assisted by the attractive forces originating from sulfonic acid moieties present with in the membrane which actually promotes the transportation of counterions (Na$^+$) through active regions and hence the junction between the two phases, named as "polymer phase" and "interstitial phase", became less distinctive.[24,50] The chain containing consecutive sulfonic acid group is known to be responsible for the transportation of sodium ions to the dialysate side due to its high ionic content in membrane phase. Meanwhile, during the whole process the electrical neutrality

Figure 9. (A) Alkali dialysis coefficients (U_{OH}) and (B) change of U_{WO4} for different SPPO/DSBPB blend membranes at 25 °C after 30 days of leaching.

should be maintained therefore after the transportation of Na^+ ions, OH^- ions must need to diffuse to the dialysate side along with the sodium ions so that it can retain the electrical neutrality requirement.[12,50] The second probable reason could be the increase in free volume and interstitial region as the incorporation of DSBPB in SPPO matrix. Hence, this phenomena leads to the increase in OH^- transport channel and the U_{OH} values gradually becomes higher and higher.

Separation factors can be represented as a ratio between U_{OH} and U_{WO_4}. The obtained S values are in the range of 12.61−36.88 which are appreciably much higher than that of PVA-based hybrid membranes (11.6−20.6) at 25 °C and almost similar to the PVA/SiO₂ membranes (12.2−36.2) at 25 °C.[22,24] A gradual increase in the amount of DSBPB in membrane matrix leads to the ascending trend of the IECs as well as water uptake of the corresponding membranes. These increases in IECs are beneficial and essential to obtain high S values for alkali recovery process. Therefore, the high content of DSBPB has a profound effect on obtaining high S values.

On the other hand, huge phase separation is not likely for high selectivity, as both OH^- and WO_4^{2-} ions can pass freely through the polymer matrix without facing much resistance; however, small phase separation is more resistive to WO_4^{2-} rather than OH^- ions, which in turn can enhance S values.[25,55]

3.6. DD Performance after the Leaching of DSBPB. All of the prepared membranes were used to investigate the DD performance after the leaching of DSBPB. The experiment was performed at room temperature and all of the prepared membranes were dipped in DI water for 30 days and then DD performance was again evaluated to obtain dialysis coefficient and separation factor values. Finally, the U_{OH} and S values were obtained accordingly. This particular test is of high importance related to the long-term alkali recovery performance of the prepared membranes.[53] After 30 days of leaching in water, the range of U_{OH} values appeared to be on the order of 0.0022−0.0044 m/h (Figure 9) along with the S value varied from 20.2 to 26.8 (Figure 10). These values are lower than the values before leaching (0.0048−0.00814 m/h, S = 12.61−36.88), indicating that the result of the diffusion dialysis experiment is usually stable, although the performance can still be effected by the leaching.[54] The slight loss in alkali recovery as well as separation factor may be explained on the basis of leaching of DSBPB. The loss of −SO₃H group from the membrane was
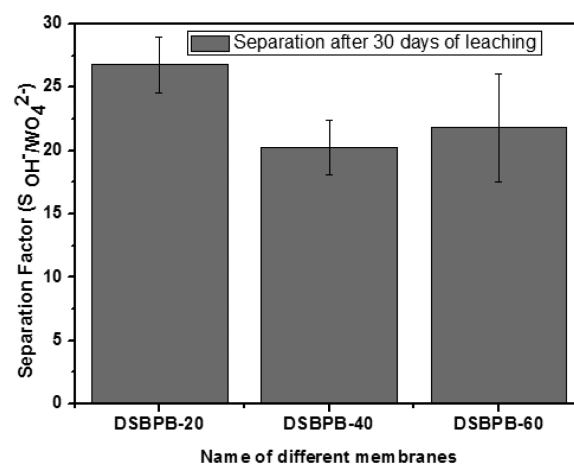
Figure 10. Separation factor (S) for different SPPO/DSBPB blend membranes at 25 °C after 30 days of leaching.

responsible for the small decrease in alkali recovery values, as mainly the transportation of sodium ions inside the membrane are governed by the force of attraction from sulfonic acid moieties present within the membrane.[1,24]

Membranes having high DSBPB loading showed higher U_{OH} loss in comparison with low DSBPB containing membrane after 30 days. The leached amounts of DSBPB from membrane matrix depend highly on the DSBPB loading weight percentage in SPPO matrix. Apparently, U_{OH} loss was found to be at a maximum for the DSBPB-60 membrane, whereas DSBPB-20 showed least loss in comparison with the unleached one. Therefore, separation values follow the expected trend while going from membrane DSBPB-20 to DSBPB-40 after 30 days of leaching in comparison with the unleached one. Overall, prepared membranes were stable and moderate leaching difference was observed going from DSBPB-20 to DSBPB-60, and thus the separation value gradually decreases from DSBPB-20 to DSBPB-40.

4. CONCLUSIONS

A novel cation exchange material DSBPB-based CEMs with SPPO backbone was designed and successfully synthesized. Incorporation of DSBPB is shown to effectively promote ionic conduction in CEMs. On the basis of membrane character-

ization studies, highly efficient membrane (DSBPB-60; IEC: 2.81 mmol g^{-1}) with high cation exchange precursor was used as DD material. The membranes possess good thermo-mechanical stabilities with (T_d) ranging from 242−263 °C and (IDT) ranging around 236−255 °C. The obtained membranes showed a significant higher diffusion coefficient [U_{OH} = 0.00814 m/h; S = 36.88 (for DSBPB-60)] at 25 °C. The methodology is likely to be versatile, as confirmed by the preparation of three CEMs with different weight percentage of loading of DSBPB. The whole experimental setup, e.g., stack used during the DD experiment, is very simple and the entire set up cost is very cheap. At the same time, all of the raw materials used during this study are easily available and the cost is low. From the viewpoint of base recovery, it appeared that the obtained alkaline diffusivity is much better than parent SPPO during experiment. Also, SPPO-based membranes got an additional advantage of high thermo-mechanical stability, which makes them promising candidates for base recovery via the DD process. Therefore, moderate process cost and high stability of membrane life makes this type of membrane a solid potent candidate for industrial application. In fact, these days, modern researchers render their effort toward these kinds of membrane for base recovery. Further investigation into DSBPB with SPPO is expected to have an impact on separation science, especially the potential applications for these membranes for alkali recovery from tungsten ore smelting industries.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Information on the detailed instrumental analysis, e.g., NMR spectroscopy, infrared spectroscopy, DMA, TGA, SEM, IEC, water uptake (W_R) details. IR spectra of BAPB, BAPBDS, and DSBPB also incorporated in Figure S1. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b04018.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

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