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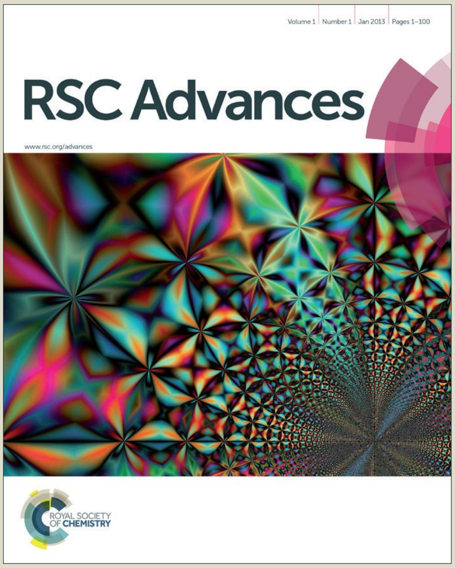

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Novel cross-linked anion exchange membrane based on hexaminium functionalized poly (vinylbenzyl chloride)

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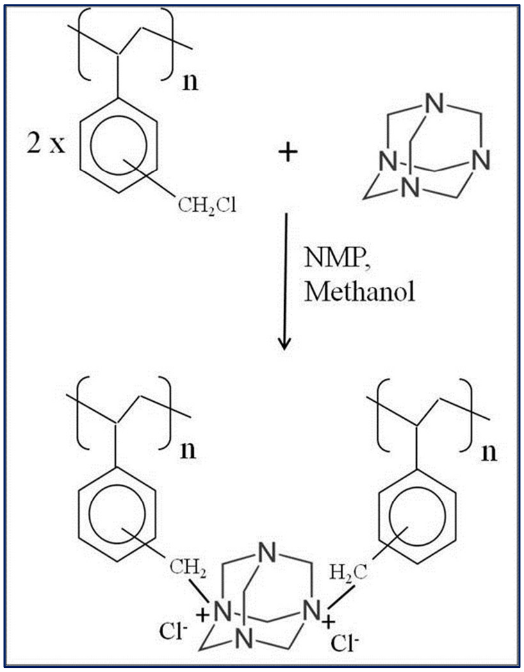
ABSTRACT

Hydroxide anion exchange membranes (HAEMs) are of recent research interest, since these membranes offer a great deal of replacing noble metal catalysts used in electro-chemical energy conversion systems such as fuel cells and electrolysers. The conductivity and stability of state-of-the-art anion exchange membranes are far below the realistic applications. Herein, we report a novel anion exchange membrane based on aminated and cross-linked poly (vinylbenzyl chloride) prepared by an easy, viable synthetic route. ß-hydrogen free, multi-nitrogen containing 'hexamethylenetetramine' is used and explored as an amination / cross-linking agent at first time in this study. FT-IR and ^{1}H-NMR analysis results confirms the successful quaternization of poly (vinylbenzyl chloride) with hexamine. TGA results show the degradation temperature of the quaternized polymer is as high as 160 ºC. AFM analysis reveals that the membrane possess phase separated morphology with hydrophobic and hydrophilic domains. The ionic conductivity of the membranes increases when the amine to polymer ratio is increased from 0.2 to 0.33, and the highest ionic conductivity achieved is 6.8 x 10^{-3} S cm^{-1}. The membrane acquires good chemical and alkaline stability which strongly suggests that the membrane would be a promising material for electrochemical energy conversion systems.

1. INTRODUCTION

Ion conducting solid polymer membranes finds diverse applications in fuel cells, electrolysis, de-salination, electro-dialysis, etc. Proton exchange membranes (PEMs) are extensively used in fuel cells and electrolysers, since these membranes acquire high ionic conductivity with good stability. Nevertheless, there are crucial problems, including the usage of expensive noble metal catalysts, perfluorinated membranes, catalyst poisoning, and complex water-management issues.[1-4] Hydroxide ion conducting alkaline anion exchange membranes (HAEMs) could unravel many of the limitations of PEM based membranes.[5, 6] Because electrochemical reactions are more facile in alkaline medium, non-noble metals can be used as catalysts, thus making the system more cost effective.[7-9] HAEMs predominantly contain fixed cationic groups, and mobile negatively charged OH^- ions. HAEM that contain different cationic groups such as ammonium, sulphonium, phosphonium, quanidinium, pyridinium , imidazolium, etc. have been extensively studied.[10-19] Among them, quaternary ammonium based HAEMs are mostly used in electrochemical systems due to their reasonable stability in alkaline conditions. The hydroxide ions move from the cathode to anode in an operating fuel cell or electrolyser, and the ionic conductivity is a decisive factor to decide the efficiency of these systems. Despite the intense research efforts on anion exchange membranes, their conductivities are not adequately high for realistic applications. One more challenge lies in their low stability under fuel cell working conditions, since the QA group decomposes *via* Hoffman elimination (due to presence of ß hydrogen) and / or S_N2 substitution reactions in strong basic environments.[20-22] The challenging feature of developing HAEMs is to improve the chemical stability of cationic groups by using QAs with no ß hydrogen. One more strategy in improving the membrane stability is chemical cross-linking of the polymer units.[23-27]

Here, we report the preparation of anion exchange membranes with cross-linked structure (Scheme 1) by a one-step synthetic route. It mainly involves the preparation of quaternized poly (vinylbenzyl chloride) (PVBC) anion exchange polymer using an inexpensive amination / cross-linking reagent, hexamethylenetetramine (HMTA). HMTA, commonly known as 'Urotropine', is an amine base having cage like structure which finds various applications, especially in plastic and rubber industries as a hardener / binder. In literature, there have been different amination / cross-linking agents such as ethtylene diamine, hexamethylene diamine, tetramethylene pentamine, triethylene diamine used and most of them have ß hydrogen in their structure.[28-31] To be noted, *Pandey et al.* prepared highly cross-linked anion exchange membranes using 1, 4-diazabicyclo [2.2.2] octane as a cross-linker.[31] *Cao et al.* prepared a novel alkaline anion exchange membrane using methylated melamine as an amination / cross-linking agent.[32] Though the membrane afforded high ionic conductivity and stability, the methylation step



Scheme 1 Synthesis scheme of cross-linked anion exchange polymer.

described in their work is a particularly excessive pathway. However, the present work uses the amination agent, HMTA, taking advantage of its ß-hydrogen free structure which can circumvent the malefic elimination and / or substitution reactions. Moreover, this work involves a single step fabrication of the membrane by casting the viscous solution of the quaternization reaction mixture without further processing or modification.

2. EXPERIMENTAL SECTION

2.1 Materials

Poly (vinyl benzylchloride), (60/40 mixture of 3- and 4- isomers with average molecular weight of M_n 55,000) was purchased from Sigma Aldrich. Hexamethylenetetramine (99% purity) was purchased from Otto Chemika-Biochemika reagents and potassium hydroxide from Thermo Fischer Scientific India Pvt. Ltd. The other chemicals, namely, methanol, N-methyl pyrrolidone (NMP) and tetrahydrofuran (THF) were analytical grade and used as received. De-ionised water was used throughout this study.

2.2 Amination and membrane preparation

Poly (vinyl benzylchloride) was dissolved in NMP, and hexamethylenetetramine in methanol, separately. The polymer and amine solutions were mixed together and stirred at 60 ^oC for 30 min. This amination process would lead to quaternization of the PVBC polymer. After the amination step, the homogeneous mixture was casted on a glass plate by solution casting method. Then, the membrane was dried in a vacuum oven at 70 ºC for 30 min. and further cured at 120 ºC for 12h. The membrane was peeled-off from the glass plate and washed thoroughly with deionised water, further soaked in 0.5M KOH for 12h (to convert the membrane into OH^- form).

A series of membranes with various HMTA : PVBC weight ratios (0 : 1, 0.2 : 1, 0.25 : 1, 0.33 : 1, and 0.5 : 1) were prepared using the above procedure. For comparison, a PVBC membrane without quaternization was also prepared. The thickness of the membranes was 100 ± 5 µm in the dry form.

For the solubility test, the quaternized anion exchange polymers with HMTA : PVBC ratios of 0 : 1, 0.2 : 1, 0.33 : 1, 0.5 : 1 and 1 : 1 were also synthesized in tetrahydrofuran (replacing NMP and methanol in the previous procedure) at 60 ^{o}C .

2.3 Degree of quaternization

The degree of quaternization (DQ) of PVBC with various amount of HMTA was calculated from the exchangeable chloride content (using argentometric titration), and total nitrogen content (using CHNS analysis) of the quaternized membrane[33].

$$\% \mathrm{DQ} = \frac{\text{No. moles of chloride}}{\text{No. moles of nitrogen}} \times 100$$

2.4 Ionic conductivity

The ionic conductivity (IC) of the membranes in OH^- form was measured using AC impedance spectroscopy. To perform the impedance analysis, the electrochemical work station / multi-potentiostat (model: VMP3, Bio-logic SAS) was employed. A home-made four-electrode conductivity cell was used to assemble the membrane test samples.[34] The membrane sample was cut into 1 cm x 4 cm and the membrane clamped between current (Pd foil) and potential (Pt wire) probes. During the measurement, the conductivity cell was immersed in de-ionised water at 25 ^{o}C. The impedance measurements were carried out in galvanostatic mode over the frequency range from 1 MHz to 1Hz at the amplitude of 1 mA. The in-plane ionic conductivity (σ) was calculated using the eqn:

$$\sigma = \frac{L}{R \times A}$$

where L (cm) is the distance between two probes, R (Ω) is the resistance of the membrane, and A is the cross-sectional area [thickness (t) x width (w)].

2.5 Ion-exchange capacity

The ion-exchange capacity (IEC) of the anion exchange membranes was measured using Mohr's method.[35] The dry OH^- form of the membranes were soaked in 0.5M sodium chloride solution and equilibrated for 24h at 25 ^{o}C. The chloride form of the membrane was converted to a carbon trioxide form by immersion in 0.5M sodium carbonate solution. The solution was titrated against 0.1M silver nitrate using 5% solution of potassium chromate until brown sediment precipitated. The ion exchange capacity was calculated using the eqn:

$$\text{IEC (milliequiv./ g)} = \frac{V_{AgNO3} \times C_{AgNO3}}{W_{dry}}$$

where V_{AgNO3} is the volume of silver nitrate consumed, C_{AgNO3} is the milli molar concentration of the silver nitrate solution, and W_{dry} is the mass of the dried membrane (Cl^- form) in g.

2.6 Water Uptake

Water uptake of the membranes was measured using the procedure as follows: The anion exchange membrane (OH^- form) was cut into a piece (3 x 3cm) and then soaked in distilled water for 24h. The membrane's surface water was removed carefully using wipe and the wet weight

(W_{wet}) of the membrane measured. Then, the membrane was dried in vacuum oven at 60 °C for 24h. The dry membranes were transferred immediately to a desiccator before cooled to room temperature. The water uptake of the anion exchange membrane was calculated using the eqn:

$$\text{Water uptake (\%)} = \left\{ \frac{W_{wet} - W_{dry}}{W_{dry}} \right\} \times 100$$

where W_{dry} is weight of the dry membrane (g), and W_{wet} is the weight of the wet membrane (g).

2.7 Stability tests

The chemical stability of the anion exchange membranes was tested in both alkaline solution and Fenton's solution separately. The alkaline stability of the membrane was carried out by immersing a piece of membrane with known weight in 5M KOH solution for 10 days at 30 ^{o}C. The membrane was taken from the KOH solution and rinsed with de-ionised water several times. Then, the ionic conductivity and ion-exchange capacity of the alkaline treated membranes were measured using the standard protocols

The oxidation stability of the membranes was also tested in Fenton's solution. The Fenton's solution was prepared using ferrous sulphate ($FeSO_4$) and hydrogen hydroxide (H_2O_2) in the weight ratio 1: 8 at the acidic pH of 3. The membrane sample with known weight was immersed in the Fenton's solution for 10 days at 30 ^{o}C. Then, the membrane sample was taken from Fenton's solution and rinsed with de-ionised water, followed by drying in vacuum oven at 60 ^{o}C for 24h. From the above experiments, the weight loss of the membrane was calculated.

2.8 Characterisations

FT-IR spectra of poly (vinylbenzylchloride) and quaternized anion exchange polymer were recorded using Bruker 27 Tensor FT-IR spectrophotometer with a resolution range of 0.125cm^{-1}.

^{1}H-NMR analysis of the polymerisation products was performed on a Bruker Avance 400MHz instrument using dmso-d$_6$ as solvent and tetramethylsilane (TMS) as an internal reference. Thermal degradation and stability of the membranes were investigated using a simultaneous TGA / DTA analyser (model: SDT Q600, TA Instruments) from 30 to 700 °C at the heating rate of 5 °C / min under nitrogen atmosphere. The nitrogen content of the quaternized polymers were measured using CHNS elemental analyser (model: Vario EL III, Elementar, Germany).

The surface morphological features of the membrane were analysed using TESCAN scanning electron microscope (model: S-3000H, Hitachi, Japan). The localization of hydrophilic domains in the membrane were analysed using atomic force microscope (model: Picoscan 2100, Molecular imaging, USA).

3. RESULTS AND DISCUSSION

The quaternization of PVBC with HMTA was confirmed using FTIR spectrum shown in Fig. 1.

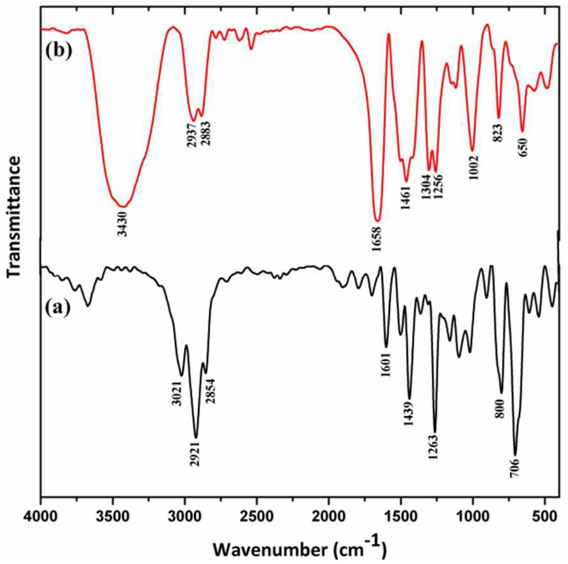


Fig. 1 FT-IR Spectra of (a) PVBC and (b) Quaternized PVBC in OH$^-$ form (HMTA / PVBC = 0.5 : 1).

The spectrum of PVBC has an absorption band at 1263 cm^{-1} that attributes to CH_2Cl wagging,[36] the region of 750 - 800cm^{-1} is assigned to C-Cl stretching.[37] The bands at 2921, 2854 cm^{-1} are related to symmetric and asymmetric CH_2 stretching, and at 1601cm^{-1} is due to aromatic C=C stretching. The quaternized PVBC polymer shows two major peaks at 1002 and 1304 cm^{-1}, which is assigned for C-N stretching vibrations.[36] Also, the C-Cl stretching vibration (800 cm^{-1}) is disappeared in the quaternized PVBC spectrum that confirms the quaternization reaction. The broad peak appears at 3430 cm^{-1} is due to the O-H vibrations. Additionally, the intense peaks at 1461 and 1658 cm^{-1} indicate the presence of quaternary ammonium groups as reported in the literature.[32] Notably, the intensity of the stretching band at 1658 cm^{-1} increased in the quaternized PVBC spectrum which might arise from the cross-linking of PVBC polymer.

Fig. 2 represents the NMR spectra of PVBC, HMTA and quaternized PVBC. From the NMR spectra, the aliphatic protons ($-CH_2$ and -CH) of PVBC appear at around 1 to 2 ppm, whereas the

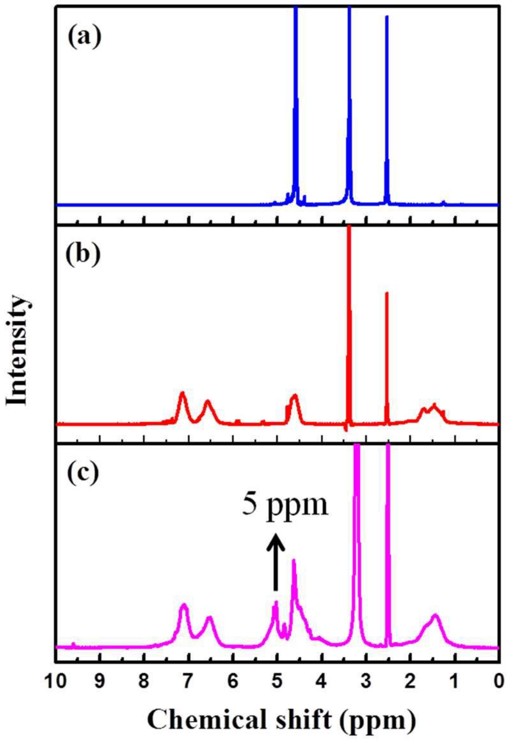


Fig. 2 ^{1}H-NMR Spectra of (a) HMTA; (b) PVBC and (C) Quaternized PVBC in Cl$^-$form (HMTA / PVBC = 0.5 : 1)

aromatic ring protons appear at 6.5 and 7.2 ppm. The peak at around 4.6 ppm is assigned to CH_2Cl group. On the other hand, hexamine spectrum shows a single peak at 4.55 ppm which corresponds to six equivalent methylene ($-CH_2$) protons. The peaks appear at around 2.5 and 3.3 ppm in all the three spectra is the signal from dmso-d6 and moisture present in dmso-d6, respectively. In case of quaternized PVBC spectrum, a new peak appears at 5.0 ppm in addition to the peak at 4.6 ppm. The new peak which appears in the downfield region is assigned to the quaternized CH_2Cl group. This result confirms the quaternisation of PVBC with hexamine.

Fig. 3 shows the photograph of the anion exchange polymers synthesized with different amine / polymer ratios in THF solvent. The solution opacity changes as the amine content is increased in the PVBC polymer, and it converts into a viscous gel (0.5 : 1 ratio) and a solid precipitate (1 : 1 ratio) at high amine concentrations. This reveals that the PVBC was aminated and cross-linked by HMTA which increases the solution viscosity and reduces the solubility of

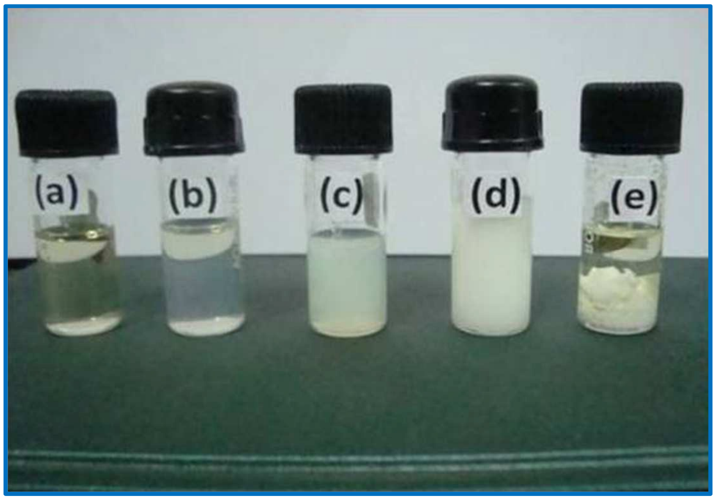


Fig. 3 Photograph of the quaternized anion exchange polymers with different HMTA / PVBC ratios (a) 0 : 1; (b) 0.2 : 1; (c) 0.33 : 1; (d) 0.5 : 1; (e) 1 : 1 in THF.

the quaternized polymer. Besides, cross-linking of polymer chains would also increase the molecular weight and reduces the solubility of the quaternized polymer. The degree of quaternization of PVBC with various amount of HMTA was calculated from chloride content of the membrane. The calculated DQ (%) of the membrane with HMTA / PVBC ratios of 0.2, 0.25, 0.33, and 0.5 are 27.2, 36.3, 47.2 and 61.6%, respectively. From these results, it is clear that the degree of quaternization increases with increasing amount of HMTA.

Thermo-gravimetric analysis was performed to estimate the thermal stability of the quaternized anion exchange polymer. The TGA curves of PVBC and quaternized PVBC polymer are shown in Fig. 4. The PVBC polymer shows two major degradation steps: the polymer

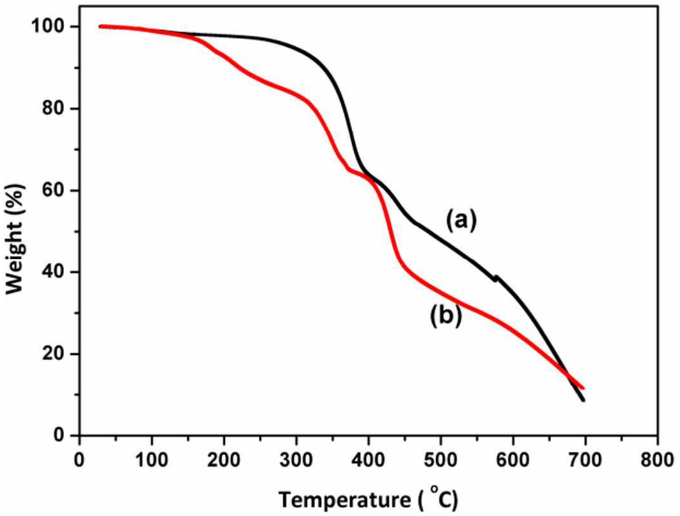


Fig. 4 Thermo-gravimetric curves of (a) PVBC and (b) Quaternized PVBC in Cl^- form (HMTA / PVBC = 0.25 : 1).

backbone degradation from 310 °C to 410 °C, and carbonization from 420 °C to 700 °C. However, the quaternized PVBC polymer shows three distinct degradation steps: the quaternary ammonium group degradation from 160 ^{o}C to 250 ^{o}C, polymer degradation from 310 ^{o}C to 400 ^{o}C, and carbonization from 410 ^{o}C to 700 ^{o}C. The TGA results are in well agreement with the literature results reported for quaternary ammonium containing anion exchange polymers.[32]

The membranes with different HMTA / PVBC ratios were fabricated using the quaternized PVBC (Cl^{-} form) in NMP solution, except for the ratio of 1 : 1. The 1 : 1 membrane can't be achieved due to the formation of solid precipitate before casting the reaction mixture. The optical image of the anion exchange membrane is depicted in Fig. 5a which displays a yellowish

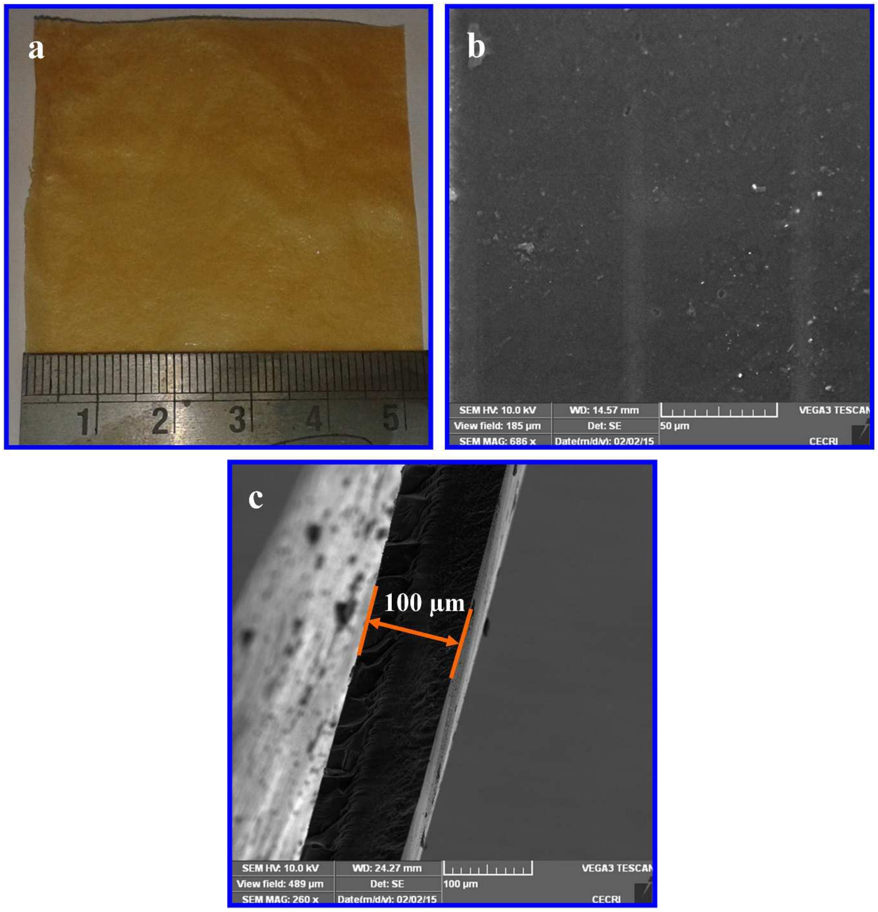


Fig. 5 (a) Optical image; (b) Surface and (c) cross-sectional SEM images of the quaternized PVBC membrane (HMTA / PVBC = 0.33 : 1).

membrane with smooth surface. Fig. 5b and 5c provide the SEM illustrations of the surface and cross-sectional morphological features of the membrane. The membrane shows no signs of cracks and/or voids. The cross-section of the membrane (Fig. 5c) appears smooth without any perforations or defects.

Fig. 6 shows the ionic conductivity and ion-exchange capacity of the membranes in their OH^- form. The PVBC only membrane exhibits very low ionic conductivity in the order of 10^{-7} S cm^{-1} (data not shown here). A quantum jump in conductivity is observed, once the PVBC is quaternized with HMTA, i.e. 10^{-7} S cm^{-1} to 10^{-3} S cm^{-1}. The conductivity rises exponentially as the HMTA / PVBC ratio is increased from 0.2 to 0.33 which reflects the vital role of amination agent in the quaternization of PVBC polymer. However, further increase in HMTA / PVBC ratio from 0.33 to 0.5 produces decrease in conductivity. This observed phenomenon is due to high level of polymer cross-linking as the amine content increased to a greater extent. As reported by *Xiong et al.,* [38] high level of cross-linking reduces the membrane conductivity due to the

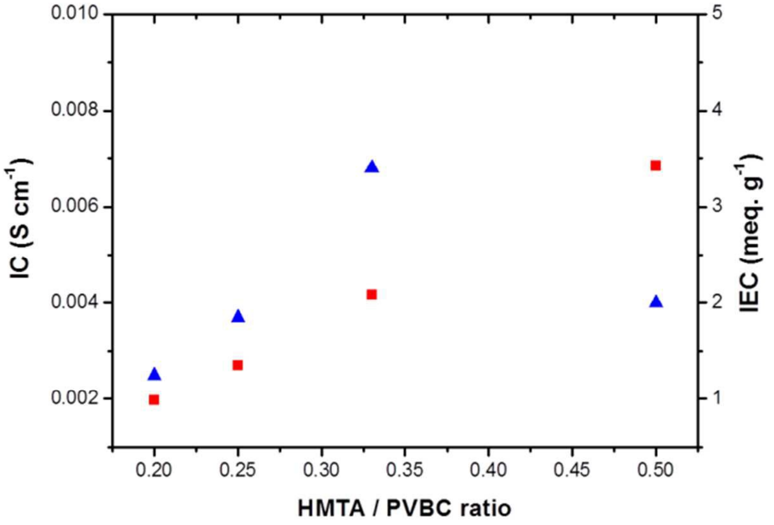


Fig. 6 Ionic conductivity (▲) and Ion-exchange capacity (■) of anion exchange membranes with different HMTA / PVBC ratios at 25 °C.

formation of membrane compact structure that narrows the anion transfer channels. From the figure, the ion exchange capacity of the membranes also shows linear increasing trend with increase in amine / polymer ratios. The IEC increases from 0.99 to 3.42 meq. g^{-1} (Table 1) as the amine / polymer ratio is increased from 0.2 to 0.5. It is apparent that more number of ion exchange groups can be introduced during the quaternization process, since the amination agent, HMTA possess multi-nitrogen centres in its structure. The nitrogen content of the membranes obtained from elemental analysis (Table 1) shows that the membrane acquires significant amount of nitrogen in its composition, and it increases as the amine to polymer ratio is increased.

Table 1 Physico-chemical properties of quaternized anion exchange membrane

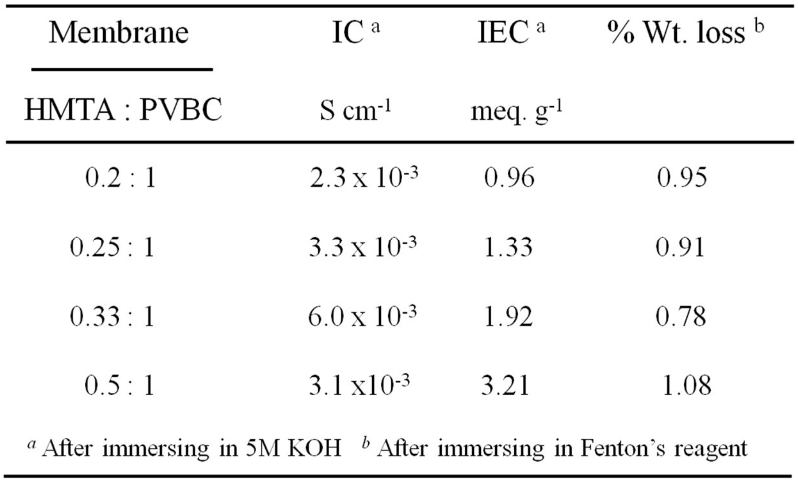
Membrane HMTA : PVBC	Nitrogen content [a] (%)	IC S cm^{-1}	IEC meq. g^{-1}	Water uptake (%)
0.2 : 1	5.09	2.5×10^{-3}	0.99	7.50
0.25 : 1	5.21	3.7×10^{-3}	1.35	11.57
0.33 : 1	6.17	6.8×10^{-3}	2.08	16.39
0.5 : 1	7.77	4.0×10^{-3}	3.42	21.86

[a] From elemental analysis

In general, ion exchange membranes have the tendency to absorb water, since they possess high density of hydrophilic ionic groups. Moreover, the water content of the membrane also plays a vital role in the ion conduction process. Therefore, the water uptake of the prepared anion exchange membranes were measured in OH^- form and given in Table 1. The water uptake data of membranes show that the uptake increases, as the amine to polymer ratio is increased. This is mainly attributed to the high level of quaternization as the amine content is increased. The high level of quaternization is likely to introduce more number of ionic groups in the anion exchange polymer and increases the water absorption capacity of the membrane.

The chemical stability of membrane is very crucial for long term operations, and the stability of anion exchange membranes were performed under strong alkaline and oxidizing conditions. The membranes were immersed in 5M KOH, Fenton's solution separately for 10 days at 30 ^{o}C and the stability test results are shown in table 2. The alkaline stability of the membranes is evaluated in terms of IC and IEC values. From the table, the membrane's IC and IEC decrease very marginally when compared to the untreated membranes (Table 1). Notably, the membranes with high amine concentration (0.33 and 0.5) comparatively exhibit low alkaline stability than low amine concentration (0.2 and 0.25). Also, the membranes after immersing in Fenton's solution show negligible weight loss (~ 1 %). Fenton's test was performed especially to see the oxidation stability of the anion exchange membrane in presence of sensitive OH radicals. These results reveal that the membranes are chemically stable.

Table 2 Stability of anion exchange membrane in 5M KOH, and Fenton's reagent at 30 ^{o}C



Membrane HMTA : PVBC	IC [a] S cm^{-1}	IEC [a] meq. g^{-1}	% Wt. loss [b]
0.2 : 1	2.3×10^{-3}	0.96	0.95
0.25 : 1	3.3×10^{-3}	1.33	0.91
0.33 : 1	6.0×10^{-3}	1.92	0.78
0.5 : 1	3.1×10^{-3}	3.21	1.08

[a] After immersing in 5M KOH [b] After immersing in Fenton's reagent

To observe the morphological features of the membrane thoroughly, AFM analysis was performed in tapping mode and the results are shown in Fig. 7. The topography image (Fig. 7a) of the membrane shows microphase separated morphology and the microphase separation mainly occurs between the hydrophobic backbone and hydrophilic graft chains.[39] The 3D phase image (Fig. 7b) of the membrane shows the distribution of peak and valley regions. Earlier, *Luo et al*. studied the poly (vinyl benzylchloride–methylmethacrylate) copolymer based anion exchange membrane using AFM and identified that the peak regions mostly arise from the hydrophobic domains and the valley regions from the hydrophilic ionic domains.[40] It can be predicted from the above results that the membrane developed in the present work possesses the phase separated morphology which is typically found in Nafion® based membranes.[41]

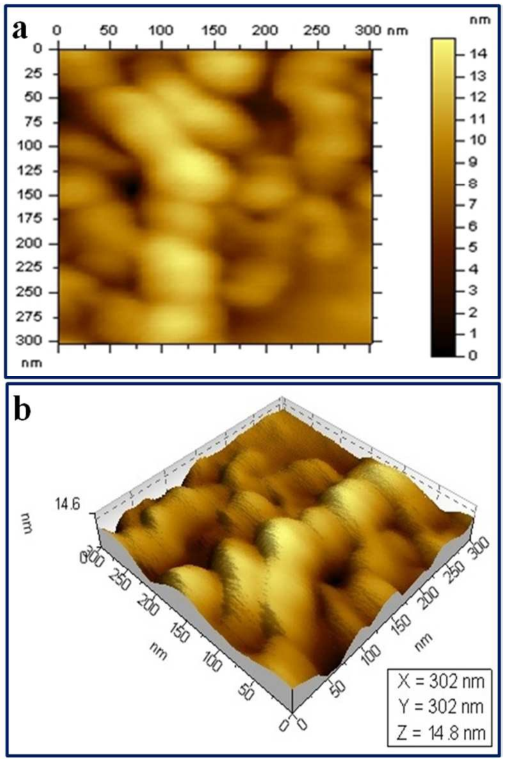


Fig. 7 AFM tapping mode: (a) topography image and (b) 3D phase image of anion exchange membrane (HMTA / PVBC = 0.33 : 1).

Quaternization of alkyl halides with HMTA was reported earlier by *Vidal et al.,*[42] in the preparation of QA functionalised silica sorbents for solid-phase extraction. However, we report for the first time the simultaneous amination and cross-linking of chloropolymer using HMTA, and explored the applicability of the QA functionalized polymer as an anion exchange membrane. Moreover, this work constitutes with its uniqueness of preparing anion exchange membrane in a single step using inexpensive amination / cross-linking agent. Further, the absence of ß-hydrogen in the amination agent eliminates the possible degradation of anion exchange membranes by Hoffman elimination and/or substitution reactions. Though the developed membranes were chemically stable, their mechanical flexibility is poor due to high cross-linking and rigidity of aromatic polymer that hampers the application in real systems.

4. CONCLUSION

A novel anion exchange membrane was successfully prepared using poly (vinylbenzyl chloride), and hexamethylenetetramine as an amination as well as cross-linking agent. The IC and IEC of the membranes increased with increase in amine / polymer ratio which emphasized the role of amination agent in the architecture of the membrane. The membrane's water uptake was comparatively low due to high cross-linking of polymer units during quaternization process.

TGA results showed thermoplastic behaviour of quaternized polymer which mainly occurs due to the incorporation of hydrophilic QA groups into the hydrophobic aromatic polymer backbone. AFM analysis revealed the presence of well defined hydrophobic, hydrophilic phase separation within the membrane. The chemical stability of the membranes was superior in alkaline and oxidizing environments, whereas the mechanical properties have to be improved for practical application of the membranes in real electrochemical systems.

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Notes

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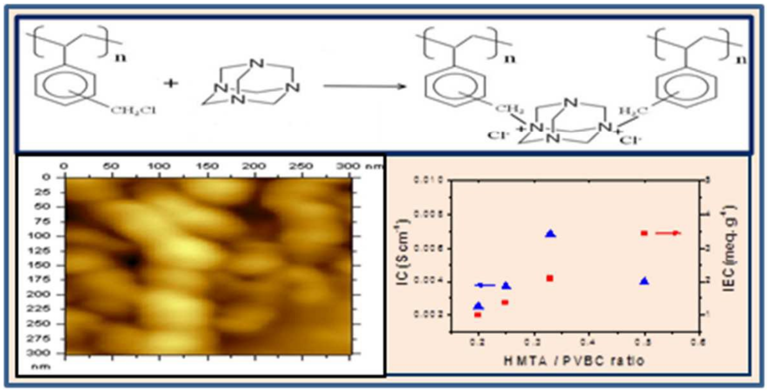
Table of contents graphic



- A novel cross-linked poly (vinylbenzyl chloride) anion exchange membrane is prepared using ß-hydrogen free 'hexamine' as an amination agent.