Development of PVA/MIDA based hybrid cation exchange membranes for alkali recovery via Diffusion Dialysis

Noor Ul Afsar, Jibin Miao, Abhishek N. Mondal, Zhengjin Yang, Dongbo Yu, Wu Bin, Kamana Emmanuel, Liang Ge, Tongwen Xu *

CAS Key Laboratory of Soft Matter Chemistry, Collaborative Innovation Center of Chemistry for Energy Materials, School of Chemistry and Material Science, University of Science and Technology of China, Hefei 230026, PR China

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ABSTRACT

We report poly vinyl alcohol (PVA) based hybrid membranes composed of methyl iminodiacetic acid (MIDA) and tetraorthoethoxysilane (TEOS) prepared by classical sol–gel process. MIDA was prepared via N-methylation of iminodiacetic acid and then successfully incorporated into the PVA backbone. The concentration of MIDA with respect to PVA was varied from 10 to 40 wt%. These hybrid membranes showed water uptake (W_U) in the range of 106–125%, ion exchange capacities (IECs) of 1.14–2.13 mmol/g, dialysis coefficient (U_{OH}) from 0.009 to 0.012 m/h as well as selectivity (S) from 16.0 to 19.9. These obtained results revealed that MIDA. It controls the hydrophilicity and ion exchange capacity by providing channels for the transportation of ions through carboxylate sites. PVA/MIDA hybrid membranes also showed good thermal stability with the initial thermal decomposition temperature (IDT) ranging around 150–160 °C and excellent mechanical properties such as tensile strength (T_S) of 9–25 MPa and elongation at break (E_b) of 32–150%.

1. Introduction

Diffusion Dialysis (DD) is a promising separation technique. Due to the difference in concentration gradient, solute moves across higher concentration side to the lower one at ambient temperature and pressure [1]. It consumes lower energy and has a lower cost of installation and easy operational procedure that makes it distinct from all other relevant processes. It has been widely applied in acid or alkali recovery through an anion exchange membrane or a cation exchange membrane. Compared with acid recovery with a anion exchange membrane (AEM) which occurred in the early of 1980 [2], alkali recovery through a cation exchange membrane (CEM) is relatively less and late pronounced. The first sight of DD plant was installed in California Caspian in the year of 1991 for alkali (NaOH) recovery [3]. One striking factor observed could be the slow development in CEMs as compared to AEMs. A major reason of this drawback is the unavailability of appropriate CEMs for alkali recovery. CEMs require high chemical stability in alkaline solutions in order to get optimum performance.

Hybrid membranes are good combination of organic and inorganic components that can excel the mechanical as well as

chemical stability of CEMs. PVA has large number of –OH groups and has high water swelling capacity that makes it an incompatible candidate for membrane fabrication. Therefore, different cross linkers have been tried to increase the mechanical and chemical stability such as small molecules of alkoxysilanes [4] and aldehyde compounds such as glutaraldehyde. These alterations have been made mostly for PVA based hybrid membranes [4,5]. In present research, a modified organic compound, iminodiacetic acid (IDA), i.e., the di-carboxylic acid based amine ($C_4H_5O_4N$) (IDA), has been used for the fabrication of hybrid cation exchange membranes.

Previously, the selective removal of transition metals ions from water was done with chelating resins [6]. Keeping in view, the same, we chose IDA here. There are two carboxylic acid and nitrogen functional groups present in IDA. These groups can boost the selective removal of alkali, alkaline earth metals and transition metals on the basis of host–guest concept [7]. It has been reported that alkaline earth metals can bind easily with chelating agents and the binding energy is around 5000 times higher than alkali metals, hence making a stable coordination complex [6]. By looking at the structure, we can see that it is a secondary amine that acts as tridentate ligand; the hydrogen present on the nitrogen can be replaced to make an ion exchange resin such as Chelex 100 [8] and DOWEX M 4195 [9]. Two carboxylic acid groups attached with nitrogen through –CH$_2$– unit are responsible for

the exchange of ions. We modified IDA with N-methylation and converted it to methyl iminodiacetic acid (MIDA), as it is more soluble in PVA–DMSO (dimethyl sulfoxide) solution, due to the fact that it has an electron donating effect toward nitrogen which makes nitrogen more nucleophilic toward electrophile. Afterwards, MIDA was successfully incorporated into PVA through a sol gel process using tetramethylsilane (TEOS) as a cross-linking agent. The reaction was confirmed by FTIR and NMR spectroscopy. The effect of the MIDA quantity on membrane structure and inherent properties such as IECs, water uptake (W_U), etc. have been investigated. Moreover, with the prepared membranes, diffusion Dialysis experiments were conducted for simulated waste containing with 1.0 M NaOH and 0.1 M Na_2WO_4 to elaborate the separation performance and alkali recovery.

2. Experimental

2.1. Chemicals

All the chemicals and materials, such as Polyvinyl alcohol (PVA, Avg. degree of Poly. 1750 ± 50), dimethyl sulfoxide (DMSO), tetraethoxysilane (TEOS), iminodiacetic acid, and HCl were purchased from domestic store and used without further purification. Distilled water was used as per requirement.

2.2. N-methylation of iminodiacetic acid (MIDA)

Iminodiacetic acid was methylated by using a modified reported method [10] and the route was shown in Scheme 1. IDA (6.65 g or 0.05 mol) was added to round bottom flask containing 7 mL water and 3.8 mL formic acid. Formaldehyde 7.5 mL was added drop wise to this mixture. The mixture was heated at 80 °C for 24 h. After cooling to 25 °C, 50 mL acetone was added to the reaction mixture and left for 24 h until the formation of white crystals of MIDA (Methyl Iminodicarboxylic acid). The sample was checked by NMR (^{1}H NMR (300 MHz, Deuterium Oxide) δ 3.97 (s, 4H), 2.99 (s, 3H) (Fig. 1).

2.3. Membrane preparation

1 g of PVA was dissolved in 20 mL DMSO at 103 °C for 2.5 h. The temperature was lowered to 90 °C and MIDA x% was added to PVA solution and stirred for 3 h. After homogeneous mixing of PVA–MIDA, the mixture was cooled to 60 °C followed by the addition of TEOS and 1 mL of 1 M HCl and was continuously stirred at 60 °C for 24 h. After that, this homogenous solution was cast on a glass plate over night at 60 °C. After peeling off, the membranes were cross-linked by heat treatment from 70 °C to 130 °C @ 10 °C/h and for 4 h at 130 °C. Four different membranes were synthesized by altering the quantity of MIDA from 10% to 40% and assigned as MIDA-1, MIDA-2, MIDA-3 and MIDA-4. Chemical compositions, water uptake and ion exchange capacity are summarized in Table 1. The proposed reaction scheme for membrane fabrication was shown as Scheme 2.
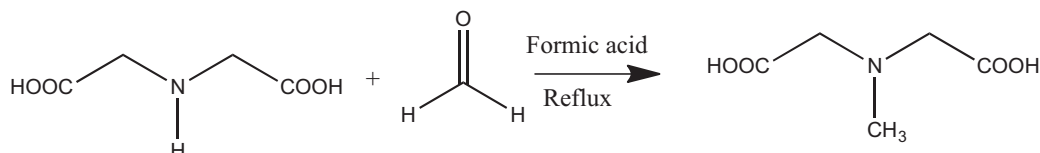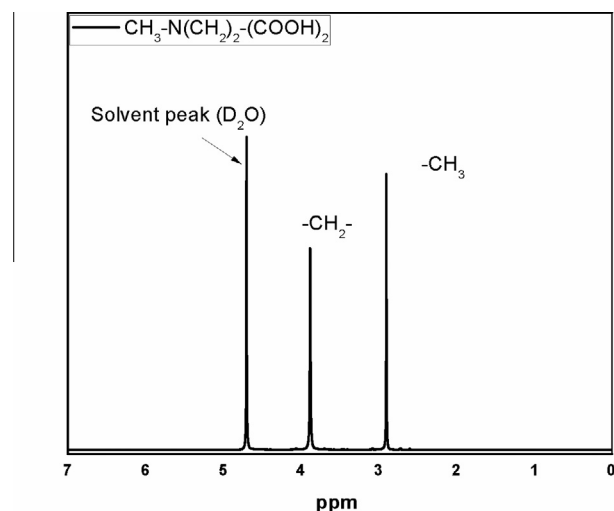

Fig. 1. NMR spectrum of MIDA.

Table 1
Summary of membrane ion exchange capacity and water uptake as well as chemical composition.

Membranes	PVA %	MIDA %	TEOS %	IEC$_{Theo}$ (mmol/g)	IEC$_{Exp}$ (mmol/g)	W_u (%)
MIDA-1	5	10	30	0.96	1.14	83
MIDA-2	5	20	30	1.80	1.23	81
MIDA-3	5	30	30	2.54	2.00	73
MIDA-4	5	40	30	3.19	2.13	97

2.4. Characterization of membranes

The spectroscopic characterization was carried out by FT-IR spectrophotometer (Bruker-Vector 22) having resolution 2 cm^{-1}, in the range of 4000–625 cm^{-1}. The peaks were interpreted and results were summarized. Thermal stability of MIDA membranes were checked using TGA (TGA Q5000 V3.15 Build 263) with heating rate@10 °C/min, in air medium. The elongation at break (E_b) and strain were checked by dynamic mechanical analyzer (Q-800, V20.24 Build43) with a measurement capacity of 500 N. The crosshead elongation gradient was 25 mm/min. In order to determine the number of exchangeable groups in MIDA membranes, ion exchange capacity (IEC) test was performed according to the procedure mentioned in the literature [11]. The dry weight of membrane having functional groups –COO– were converted to –H$^+$ form by immersing in 0.1 M HCl solution for two days. The membranes were washed 2–3 times with distilled water for 1 day to remove excess HCl from membranes. Then MIDA membranes were dipped in 0.05 M NaOH solution for two days to replace –COOH to –COONa. The remaining solution was titrated against standard solution of 0.05 M H$_2$SO$_4$ solution. The IECs mmol/g of membranes were calculated. The phase separation and homogeneity of membranes were analyzed by Electron microscope (XL30 ESEM-TMP PHILIP). The water uptake was determined by simple weight difference between wet and dry membrane using the following formula;

Scheme 1. Reaction scheme for N-methylation of Iminodiacteic acid (MIDA).