Functionalized silica–chitosan hybrid membrane for dehydration of ethanol/water azeotrope: Effect of cross-linking on structure and performance

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ABSTRACT

Sodium 2-formylbenzenesulfonatepolysiloxane (SBAPTS) was synthesized, while chitosan was modified to N-o-sulphonic acid benzyl chitosan (NSBC). NSBC–SBAPTS hybrid membranes were prepared for pervaporation (PV) dehydration of water–ethanol mixture. Grafting of –SO$_3$H groups was achieved on both segments (organic and inorganic) of hybrid membranes. Membrane composition and cross-linking density were systematically optimized to explore the effect of membrane structure on its PV performance. Most suitable hybrid membrane (CPS-a) showed 0.59 kg/l^2 h permeation flux and 5282 selectivity for dehydration of ethanol (90 wt%) at 30 °C.

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1. Introduction

Chitosan, a promising membrane material [1,2], has been widely studied for biomedical applications [3], drug delivery systems [4], sensors [5], solid polymer electrolytes [6], membranes for separations etc. [7]. The presence of hydroxyl and amino groups in glucosamine unit provides the cross-linking sites [8–12]. Cross-linked chitosan based PV membranes showed good stability and were anticipated to be suitable for the separation of alcohol/water azeotropic mixture [13–15]. However, excessive swelling and low water-permselectivity of chitosan based PV membrane are serious problems [16].

Diversified efforts, such as blending of chitosan with another polymer [17], doping of inorganic filler in the chitosan matrix [18], chitosan based organic–inorganic hybrid [19], or modification of chitosan, were reported [20]. Chitosan-hetropoly acid (H$_{14}$[NaP$_5$W$_{30}$O$_{110}$]) nanoparticle impregnated membrane with high water-permselectivity was also reported [21]. Blending or doping of inorganic filler in chitosan membrane leads to leaching-out problems. For good interaction between chitosan and inorganic part, chitosan was functionalized either by introducing quaternary ammonium groups [22] or carboxylic acid groups [23]. Although, functionalized silica nanoparticles were used to develop chitosan based organic–inorganic hybrid membranes [18], sulphonic acid functionalized chitosan has been not reported.

Silica nanoparticle derived membrane showed high permeability and permselectivity for small molecules (such as water (kinetic diameter 2.6 A°)), while relatively low permeability for larger molecules (> 3 Å) (such as ethanol) [24]. Sulphonic acid functionalized silica nanoparticles served as reactive sites for chitosan cross-linking resulting in homogeneous dispersion and swollen stability responsible for high water permselectivity [18]. The PV performances of sulphonic acid functionalized chitosan and silica precursor based organic–inorganic hybrid membranes are still unexplored. Attractive features of these membranes, such as arrangement of silica, interfacial junction between functionalized organic and inorganic segments and membrane hydrophilic nature, will be responsible for preferential sorption and diffusion of water across the membrane.

Herein, first time we are reporting NSBC–SBAPTS hybrid membrane with improved permeability and selectivity for dehydration of ethanol. Poly(vinyl alcohol) (PVA) was used as a plasticizer because of its alcohol impervious and stable nature. Acetalization of oxidative sensitive primary alcohol groups by formal reaction (cross-linking) leads to more stable ether-type linkages [25].

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2. Experimental

2.1. Materials

Deacetylated chitosan (100% deacetylated), 2-sulphonic acid benzaldehyde, and (3-Aminopropyl) triethoxysilane (APTES) were purchased from Sigma Aldrich chemicals and used without any purification. Poly(vinyl alcohol) (PVA; MW, 125 000; degree of polymerization, 1700; degree of hydrolysis, 88%), methanol, acetic acid, sodium borohydride, formaldehyde, hydrogen peroxide, etc., of AR grade were obtained from SD fine chemicals, India, and used with proper purification. In all experiments, milli-Q water was used.

2.2. Surface functionalization of silica nanoparticles

Preparation procedure for SBAPTS has been included in Scheme 1 [26]. 3-aminopropyltrimethoxysilane (APTES) (6 mL) was mixed with THF/isopopanol (2/1 mixture) (80 mL) in a round-bottom flask. Further, THF solution (30 mL) containing sodium 2-formylbenzenesulfonate (5.6 g) was added drop-wise under stirring for 6 h at 60 °C. Then, 0.1 M HCl (5 mL) was added for the polymerization. Further sodium borohydride (5% w/v) was added under stirred condition (4 h) to reduce the imine linkage. After complete evolution of hydrogen, suspended particles were filtered. Filtrate was added to 20-fold acetone to precipitate the polymer. Obtained precipitate was washed several times with acetone and dried under vacuum. The prepared polymer was named as (SBAPTS-X), where X stands for the degree of substitution of the polysiloxane by sodium 2-formylbenzenesulfonate.

2.3. Synthesis of N-o-sulphonic acid benzyl chitosan

N-o-sulphonic acid benzyl chitosan (NSBC) was synthesized by Schiff base formation reaction (Scheme S1, (Supporting information)) [6]. In a typical synthetic procedure, chitosan (high viscosity grade) was dissolved in aq. acetic acid solution (0.7 wt %) at pH 3. After complete dissolution of chitosan, sodium 2-formylbenzenesulfonate (3 equiv.) was added. Obtained mixture was refluxed at 60 °C under 4–7 h constant stirring. After completion of reaction, pH was slowly increased up to 4–5. Further aqueous solution of sodium borohydride (5% w/v) was added drop-wise to complete reduction of imine linkage (assured by disappearance of gases evolution). Reduced product was precipitated with methanol and washed by ethyl alcohol and deionized water to remove the last trace of un-reacted sodium borohydride. The prepared polymer was named as (NSBC-X), where X stands for the degree of substitution of the chitosan by sodium 2-formylbenzenesulfonate.

2.4. Membrane preparation

NSBC–SBAPTS hybrid membranes were prepared by sol–gel in two steps (Fig. S1 (Supporting information)). NSBC (2.0 g) was dissolved in hot deionized water (50 mL) in presence of HCl (0.1 M) under constant stirring, to obtain a highly viscous solution. PVA (2.0 g in 20 mL) solution was prepared in deionized water at 70 °C separately, while polysiloxane (2.0 mL) solution in deionized water (20 mL) under constant stirring was also prepared separately. All these solutions were mixed under stirred conditions at room temperature and kept overnight to obtain a clear solution. Obtained solution was transformed into a thin film and dried at ambient temperature for 24 h followed by keeping it in vacuum oven at 60 °C for another 24 h. These membranes were cross-linked under different conditions (varied time, concentration of formal solution (HCHO+H_2SO_4) and temperature). Resultant membranes were designated as CPS-X, where X is the cross-linking condition. Eight membranes were prepared under different cross-linking conditions for further characterization.

2.5. Instrumental characterization of the membranes

FTIR spectra of dried membrane samples were recorded by Spectrum GX series 49387 spectrometer in the range of 4000–450 cm^{-1}. The IR spectrum for synthesized intermediate was obtained by the KBr pellet method. Wide angle X-ray diffractograms of the hybrid membranes were recorded using Philips Xpert X-ray diffractometer with Cu Kα (1.54056) radiation. ^{1}H and ^{13}C were used to characterize the synthesized material by NMR spectrometer (Bruker500 MHz) in a D_2O and d_6-DMSO solvent.

Thermal stability of the membranes was investigated by thermogravimetric analyzer (Mettler Toledo TGA/SDTA851 with *Star* software) under a nitrogen atmosphere with a heating rate of 10 °C/min from 30 to 450 °C. Differential scanning calorimetry (DSC) measurements were carried out between 30 and 450 °C with 5 °C/min heating rate. The dynamic mechanical stability of hybrid membranes was evaluated by using a Mettler Toledo dynamic mechanical analyzer 861 instruments with Star^c software under nitrogen with 10 °C/min heating rate from 30 to 320 °C.

The surface morphology of dried membranes was studied by a JEOL 1200EX transmission electron microscope (TEM) with tungsten, and electron source operated at an accelerating voltage of up to 120 kV. Atomic force microscopy (AFM) images of dried membranes were recorded using NTEGRA AURA (NTMDT). Semi-contact mode SPM NSG 01 tip (radius of curvature: 10 nm, and frequency for cantilever: 300 kHz) was used to determine the surface roughness. Tip was located with cantilever, and oscillates with natural frequency, while sample topography was obtained from the subsequent changes in the oscillation amplitude. Differences in viscoelastic properties were detected by the change in the oscillation phase. For scanning electron microscopy (SEM), gold sputter coating was carried out on desired membrane samples at pressure ranging in between 1 and 0.1 Pa. Sample was loaded in the machine, which was operated at 10^{-2}–10^{-3} Pa with EHT 15.00 kv with 300 V collector bias using Leo microscope. SEMs were recorded.

2.6. Membrane swelling

Dry membrane samples of known weight were equilibrated in pure solvent for 72 h. The swollen membrane was wiped with tissue paper to remove adherent solvent and weighed for the estimation of swelling ratio using the equation [23]:

$$S(\%) = \frac{W_s - W_d}{W_d} \times 100 \qquad (1)$$

where, W_d denotes the weight of the dry membrane and W_s denotes the weight of solvent swollen membrane.

2.7. Pervaporation experiments

Pervaporation apparatus has been schematically described in Fig. S2 (Supporting information). The cell assembled for two half cells of column couplers were made of steel and fastened with bolts. The capacity of each cell was about 50 mL and the effective area of the membrane was 12.56 cm^2. The membrane was supported on a finely porous copper plate with 100 μm porosity. Vacuum in the down-stream side was measured with a vacuum gauge. The membrane was equilibrated for 2 h in the cell before experiments and the permeated samples were collected after 2 h. In the permeate side, vapours were completely condensed in a trap placed in a liq. nitrogen cylinder. Permeate and feed