



Separation of ethanol from water by pervaporation using mixed matrix copolymer membranes



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ABSTRACT

Several ethanol selective mixed matrix membranes were prepared from the copolymer of butyl acrylate and styrene and an organophilic nano size clay filler. The clay was incorporated in the polymer during its synthesis from the butyl acrylate and styrene monomer by emulsion polymerization in water. These membranes were characterized and used for the separation of 2.5–15 wt% ethanols from water by pervaporation. The mixed matrix copolymer membrane containing 2% (wt% of total polymer) clay was observed to yield the best result, i.e., a flux of 0.34 kg/m² h and an ethanol selectivity of 26.4 at 30 °C for 5 wt% ethanol in water. The permeability, intrinsic membrane selectivity and concentration average diffusion coefficients of the solvents were also determined.

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1. Introduction

More than 95% of total ethanol is globally prepared by fermentation of sugar or starch based bio mass using *Clostridium acetobutylicum* bacteria or other similar microorganisms [1]. However, fermentation exhibits strong product inhibition on alcohol production due to toxic effect of the alcohols on the bacteria used for the fermentation [2]. Product inhibition causes incomplete substrate utilization and low process yield in batch or continuous fermentation. Depending on the biomass source and the hydrolysis procedure the concentration of ethanol in the fermentation broth may be 1–15 wt% [3] while the maximum toleration limit of ethanol concentration in the broth without measurable product inhibition is around 6–10% depending on the microorganism [4]. Thus, in order to produce the fuel grade anhydrous ethanol, the water content of the ethanol produced by fermentation must be reduced from around 85 wt% to less than 1 wt% [3]. The conventional technology used for removing this huge amount of water from diluted ethanol is distillation followed by adsorption using molecular sieve to concentrate ethanol further to fuel grade containing less than 1.3 wt% water [5]. However, very high energy is consumed for the concentration of the diluted alcohol only by distillation which makes it economically unfavorable [6]. Thus, to make this bio production of ethanol economically feasible and also competitive with

the alternating petrochemical route, the fermentor is coupled to an effective product recovery technique to remove the inhibitory products [7].

Several product recovery techniques such as crystallization [8], adsorption [9], liquid–liquid extraction [10,11], gas stripping [12], membrane distillation [13], reverse osmosis [14], ultrafiltration [15], perstraction [16] and pervaporation [3,6,7,17] have been tried. Amongst these various separation techniques membrane based pervaporation is preferred because it is more selective than non membrane processes [2]. Pervaporation can be applied for ethanol production in two ways (1) using organophilic membranes for recovery of ethanol from fermentation broth and (2) using hydrophilic membranes for dehydration of ethanol near azeotrope point in a hybrid distillation–pervaporation process. There are many reports on ethanol dehydration by pervaporation using hydrophilic membranes [17]. In contrast it is difficult to find a suitable organophilic or hydrophobic membrane for the recovery of low concentration of ethanol from water by pervaporation. In general, poly (dimethyl siloxane) (PDMS) or silicon rubber membrane is used for the pervaporative recovery of organics including ethanol from water. However, pure PDMS rubber has been reported to give a poor ethanol–water separation factor of 2–8 [18]. Thus, for higher ethanol selectivity higher grade of silicone rubber [19] or ceramic supported PDMS membranes [20] were tried. However, solubility of the higher grade of silicone rubber containing substituted siloxane repeated units or the stability of the ceramic supported membrane is questionable. Other polymers were also tried as the membrane materials

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for the pervaporative recovery of ethanol from water. Schmidt et al. [21] tried substituted polyacetylene (PTMSP) membrane which yielded three fold higher flux and two fold higher concentration factor than the conventional PDMS membrane. Chang and Chang [22] tried a composite membrane of the copolymer of polysiloxane and phosphate ester coated on poly (vinylidene fluoride) (PVDF). This composite membrane gave high flux (2.8 kg/m² h) but very low ethanol selectivity (4.5) for 10 wt% ethanol in feed. Mixed matrix membranes (MMM) prepared by incorporating adsorptive filler in the matrix of a polymer are reported to give high flux and selectivity [23]. In this case the filler not only contribute to increased flux and selectivity but it also improves the mechanical stability of the membranes. These MMMs are easily prepared by adding a filler, usually a clay, carbon nano tube (CNT), carbon black, metal oxide or zeolite in the casting polymer solution. Thus, Vane et al. observed the highest ethanol selectivity of 3 with 60% zeolite loading in PDMS rubber [3]. Zhan et al. further modified ZSM-5 zeolite by etching it with HF acid and the MMM made of PDMS and this treated zeolite gave better flux and selectivity than the untreated zeolite filled PDMS membrane for the same ethanol–water mixtures [24]. Le et al. synthesized mixed matrix membrane by incorporating nano size polyhedral oligosilsesquioxane (POSS) in the matrix of the polyether-block-amide (PEBA) and the PEBA/POSS membrane containing 2 wt% POSS gave a flux of 0.18 kg/m² h and a selectivity of 4.6 for ethanol–water mixtures [25]. PEBA membrane filled with 2 wt% silcalite gave a flux of 0.83 kg/m² h and a selectivity of 3.6 for ethanol–water mixtures [26]. For an ideal MMM, there should be a uniform distribution of the adsorptive filler in the polymer matrix which is often difficult by simple mechanical stirring of the polymer solution containing the filler. For nano filler mixing is more difficult because of its agglomeration even at low concentration [23]. Thus, in the present work instead of the physical mixing of the filler and the polymer, in situ mixing of the filler was tried during the copolymerization of the styrene and the butyl acrylate monomer. The properties of the hydrophobic polystyrene plastic and the poly (butyl acrylate) rubber may be combined by making its copolymer and the organophilic character of this copolymer may further be improved by adding the adsorptive nano size organo clay during the copolymerization of the styrene and the butyl acrylate monomer by free radical emulsion polymerization. The membranes prepared from the copolymer containing the varied amount of the organophilic clay were used for the separation of ethanol from ethanol–water mixtures containing 2.5–15 wt% ethanols in water.

2. Experimental

2.1. Materials

High purity analytical grade ethanol used for this study was purchased from M/s. E. Merck (India) Ltd, Mumbai. The monomers used for the membrane synthesis, i.e., the laboratory reagent grade styrene and butyl acrylate monomer, emulsifier sodium lauryl sulfonate and the initiator potassium peroxodisulfate were also obtained from the same company. Organically modified montmorillonite clays (OMMTs), Cloisite 15A was kindly gifted by Southern Clay Products Inc., Kolkata. The specification of the filler is given in Table 1.

2.2. Methods

2.2.1. Synthesis of the membrane polymer

The copolymerization of butyl acrylate (BA) and styrene was carried out by emulsion polymerization in a three-necked reactor at 70 °C for about 6 h. The reactor was fitted with a stirrer, a thermometer pocket and a condenser. Water was used as the dispersion medium. Sodium lauryl sulfonate and potassium peroxodisulfate was

Table 1
Specification of the organoclay (Cloisite 15A).

Organic modifier	Dimethyl-dihydrogenated tallow quaternary ammonium salt
Modifier concentration	125 meq/100 g clay
Particle size of clay	90–95 nm
Density	1.66 g/cm ³
Basal spacing	<i>d</i> ₀₀₁ is 3.15 nm

used as the emulsifier and initiator, respectively. The required amount of the cloisite 15A clay was mixed in the reactor during polymerization. After polymerization the emulsion was broken by adding common salt to precipitate the polymer. It was then repeatedly washed with distilled water, methanol and ethyl acetate to remove the unreacted monomer and the emulsifier. The polymer was then dried at 70 °C for 4 h in a vacuum drier.

2.2.2. Casting and characterization of the membranes

Around 2.5 g of the dry polymer was dissolved in 50 ml tetrahydrofuran (THF) (~5%, w/v) in a 100 ml beaker with continuous mechanical stirring till a clear viscous solution is obtained. This solution was then cast on a clean and smooth glass plate to obtain the filled copolymer membrane. The unfilled and filled copolymer membranes were characterized by mechanical properties, i.e., by measuring tensile strength and elongation at break of the membranes in a universal testing machine (Lloyd UTM, England), Fourier transform Infrared spectroscopy (FTIR, Perkin Elmer, model-Spectrum-2, Singapore), scanning electron microscopy (SEM, model-S3400N, VP SEM, Type-II Hitachi, Japan), X-ray diffraction profile (XRD, PAN analytical B.V., model-X'Pert PRO, The Netherlands), differential thermal analysis and also the thermogravimetric analysis (DTA-TGA, Perkin Elmer).

2.2.3. Sorption and permeation study

For the sorption experiments the membranes samples of known weight were immersed in ethanol–water mixtures (2.5–15 wt% ethanols) and the membranes were allowed to equilibrate for 96 h at 30 °C. Each sample was weighed periodically until no weight change was observed. The membranes were then taken out from the solution and weighed after the superfluous liquid was wiped out with tissue paper. The increment in weight is equal to the total sorption (*S*) of the ethanol–water mixtures. For sorption selectivity, the swelled membranes were taken in a conical flask connected to a vacuum pump [27]. The solvent mixtures evaporating at low pressure from the swelled membranes were collected in a glass trap immersed in liquid nitrogen. It was analyzed by gas chromatography (GC-FID, model-GC 2025AF, Shimadzu, Singapur, column-Stabilwax-DAGC, EB624). The molar sorption (*N_t*) by these membranes were determined using the following Eq. (1) [28]

$$N_t = \frac{S}{x_{1m}M_1 + (1 - x_{1m})M_j} \quad (1)$$

Here *M*₁ and *x*_{1m} are the molecular weight and the mole fraction of the component 1 (ethanol) in the membrane, respectively. The sorption selectivity (*α_s*) for ethanol was obtained from the membrane phase and feed concentration of ethanol using the following Eq. (2)

$$\alpha_s = \frac{\frac{y_{1m}}{x_{1f}}}{\frac{y_{1f}}{x_{1f}}} \quad (2)$$

Here *y*_{1m} and *x*_{1f} are the weight fraction of the component 1 in the membrane and feed, respectively. The permeation studies were carried out by pervaporation experiments in a batch stirred cell [29] with adjustable downstream pressure that was maintained at

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