Pervaporation-Aided Dehydration and Esterification of Acetic Acid with Ethanol Using 4A Zeolite-Filled Cross-linked Sodium Alginate-Mixed Matrix Membranes

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ABSTRACT: Filled mixed matrix membranes (MMM) of sodium alginate (NaAlg) were prepared by solution casting method and were filled with 4A zeolite particles in varying compositions from 0 to 10 wt % with respect to weight of NaAlg polymer. Membranes were cross-linked with glutaraldehyde and tested for pervaporation (PV) dehydration of acetic acid and ethanol in the temperature range from 30 to 70°C. Flux and selectivity data increased simultaneously for both feed mixtures at higher loadings of 4A zeolite, due to its high hydrophilic nature as well as molecular sieving effect in addition to its favorable interaction with hydrophilic NaAlg. At increasing temperature, flux increased, but selectivity decreased. Arrhenius activation parameters for permeation process were dependent upon the extent of filler content. Pervaporation-aided catalytic esterification of acetic acid with ethanol was attempted at 70°C, resulting in considerable increase of ethyl acetate conversion at reduced reaction time due to continuous removal of water by the membrane. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 157–168, 2009

Key words: sodium alginate; 4A zeolite; pervaporation; flux; selectivity; permeation; esterification reaction

INTRODUCTION

Use of dense mixed matrix membranes (MMM) in separation and purification of liquids has been widely investigated in membrane science literature,[1–4] since separation through such membranes can be achieved by selective permeation of a liquid from a mixture; MMMs could enhance the removal of one or more of the reactant or product species from the feed. In particular, zeolite-filled MMMs have been widely used in boosting the PV separation characteristics over neat polymer membranes. Earlier reports have been devoted to molecular-based separations using zeolite-filled polymeric membranes in liquid separations.[5–7] Zeolites have uniform molecular size pores and separation through them, particularly when they are incorporated into polymeric matrices, can be achieved due to combination of effects like molecular sieving, selective adsorption, and differences in diffusion rates between feed liquids. Particularly, type-A zeolites are ideally suited for organic PV dehydration since they are hydrophilic and their pore diameter (0.4 nm) is smaller than or equal to almost all organic molecules, but larger than water.[8] Thus, their presence in polymer matrices would help to enhance preferential permeation of water over the organic liquids, thereby increasing selectivity, a parameter that is sensitive to permeate concentration, since water concentrations are often higher than 98%.

In the previous literature, Okamoto et al.[9] and van den Berg et al.[10] have reported successful application of zeolite membranes for organic dehydration. One of the drawbacks of these membranes is high cost of preparation. Alternatively, zeolite-filled MMMs are nowadays widely used because these are cost-effective and small amount of zeolite is required as filler and are often easier to fabricate than plain zeolite membranes. Different mulitilayer copoyimide MMMs were also used in PV and gas separation work.[11–13] Our recent studies[14–19] on PV dehydration of organics have dealt with different types of MMMs containing zeolites, mesoporous materials, clays, and alumino-phosphates. These MMMs have offered higher selectivity and flux data than pristine polymer membranes.

In this work, we have chosen acetic acid and ethanol, since these are the major industrial solvents and

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their aqueous mixtures can be separated more effectively using PV technique than the conventional distillation. Earlier reports on PV separation of water-ethanol and water-acetic acid mixtures using different types of polymeric blend or composite membranes did not offer high flux and selectivity.[20–28] Some reports showed that for water-ethanol mixture, pristine NaAlg membrane had a selectivity of 414 with a flux of 0.035 kg/m^2 h,[21] but much lesser flux (0.025 kg/m^2 h) and selectivity (13.6) were observed for water-acetic acid mixture.[25] In an effort to increase the separation performance of plain NaAlg membrane, PV dehydration was attempted using 4A zeolite-loaded NaAlg membranes, which gave higher flux and selectivity simultaneously in dehydrating acetic acid and ethanol from their aqueous mixtures. Further, the temperature dependent PV results were used to compute Arrhenius activation parameters to understand these data in terms of interactions between solvent and membrane polymer.

There is an increasing trend now to use membrane reactors for catalytic dehydrogenation and decomposition reactions and PV seems to work best at low water concentration of the feed. Reversible reactions that produce water as a byproduct increase the PV performance. In particular, PV membrane reactors were used to investigate the esterification of oleic acid with ethanol,[29,30] propionic acid, and propanol,[31,32] etc. Waldburger et al.[33] studied heterogeneously catalyzed esterification of acetic acid and ethanol to propose cascade arrangements of membrane reactors. Realizing these studies, we felt it important to investigate the PV performance of MMMs of NaAlg membrane for water-acetic acid and water-ethanol separation as well as to study their feasibility for catalytic esterification of acetic acid with ethanol. Separation characteristics of catalytic membranes are assessed in a continuous membrane reactor to study the esterification of acetic acid with ethanol to afford ethyl acetate as per the following reaction:

$$CH_3COOH + C_2H_5\!-\!OH \rightleftarrows CH_3COOC_2H_5 + H_2O$$
$$(1)$$
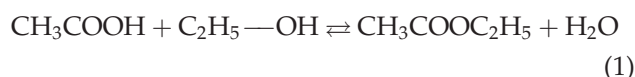
Thus, the study demonstrates the applicability of 4A zeolite-filled NaAlg MMMs to effectively dehydrate acetic acid and ethanol from their individual aqueous mixtures and to study the esterification of acetic acid with ethanol.

EXPERIMENTAL

Materials

Sodium alginate, acetic acid, ethanol, glutaraldehyde (GA), acetone, and hydrochloric acid were all purchased from s.d. fine Chemicals, Mumbai, India. Deionized double distilled water having a conduc-

tivity of 20 µS cm was produced in the laboratory itself using the Permionics pilot plant (Vadodara, India) by employing a reverse osmosis membrane module. The 4A zeolite samples were kindly supplied by Dr. S.B. Halligudi, Scientist, Catalysis Division, National Chemical Laboratory, Pune, India. 4A zeolite had a Na : Si : Al molar ratio of 1 : 1 : 1. Sulfonated cation exchange resin (Dowex-50) used in the esterification reaction was kindly provided by Dr. G.S. Gokavi, Shivaji University, Kolhapur, India.

Membrane preparation

NaAlg (1.5 g) was dissolved in 40 mL of water under constant stirring. The 0.045, 0.075, 0.105, and 0.150 g of 4A zeolite particles were dispersed in 10 mL of water separately, sonicated for 30 min, added to the previously prepared NaAlg aqueous solution, and then the mixture was stirred for about 24 h. This mixture was poured onto a clean glass plate to cast the membranes. The membranes formed were allowed to dry at ambient temperature (30°C), peeled-off from the glass plate, and cross-linked by immersing in a solution of water and acetone taken in the volume ratio of 25 : 75 containing 1 vol % of GA and conc. HCl for 12 h in a cross-linking bath. Acetone being a nonsolvent prevented the initial dissolution of the membrane and water present in the feed mixture caused membrane to swell thereby facilitating an easy penetration of glutaraldehyde into the membrane matrix to establish an effective cross-linking. Cross-linking reaction took place between the —OH group of NaAlg and the —CHO group of glutaraldehyde because of the formation of ether linkage by eliminating water that is commonly observed with the cellulose-based hydrophilic polymers such as NaAlg. The crosslinked membranes were removed from the bath, washed repeatedly with deionized water, and then dried in a hot air oven at 40°C. The pristine NaAlg membrane was prepared in a similar manner without the addition of zeolite particles. Membrane thicknesses as measured by a micrometer screw gauge were around 30 ± 1.0 µm. The prepared MMMs were cloudy white in color and semitransparent. Filler loadings were limited to 10 wt % because membranes started to become brittle at loadings >10 wt %.

Particle size measurement of 4A zeolite

Particle size and size distributions of 4A zeolite have been measured using Zetasizer, Model 3000HS, Malvern, UK. Zeolite particles were dispersed in 10 mL of water. After sonicating for 1 h, the solution was taken in a couvette by subjecting to a laser beam radiation. Series of readings were taken, but average
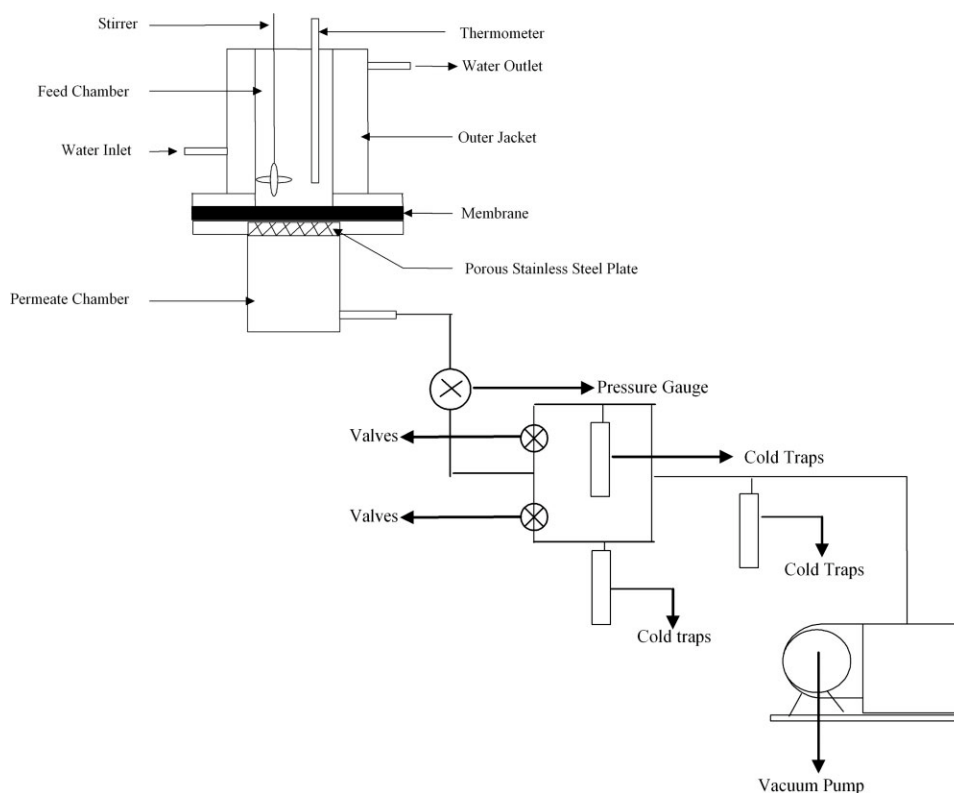
Figure 1 Schematics of pervaporation-aided esterification apparatus.

distribution histograms were considered in measuring the particle size range.

Mechanical properties

The equipment used to measure the mechanical properties of the membranes was that of universal testing machine (UTM) (Model H25 KS Hounsfield, Surrey, United Kingdom). Test specimens were prepared in the form of dumbbell shapes as per ASTM D-638 standards. Films of guage length of 50 mm and width of 10 mm were stretched out at the crosshead speed of 10 mm/min. Cross-sectional area of the sample of known width and thickness was calculated and tensile strength was calculated using the following:

Tensile strength

$$= [\text{maximum load}/\text{cross-sectional area}] \, (\text{N}/\text{mm}^2) \quad (2)$$

Scanning electron microscopic studies

Cross-sectional SEM micrograph of 10 wt % 4A-filled NaAlg MMM was obtained under high resolutions (Mag. 10 kV) using Leica Stereoscan-440 scanning electron microscope (SEM) equipped with Phoenix energy dispersive analysis of X-rays (EDAX). Since these films were nonconductive, gold coating (15-nm thickness) was done on samples. These measurements were done at Indian Institute of Science, Bangalore (courtesy of Mr. Deshpande, Materials Science Division).

Pervaporation-esterification coupling experiments

Pervaporation-esterification coupling experimental set up is the same as originally described before.[34] The schematic pervaporation-aided esterification apparatus is shown in Figure 1. The permeation cell was made of stainless steel and the effective membrane area of 20 cm^2 was sticked onto a porous stainless steel support plate using 704 silicone rubber. PV experiments were performed by maintaining on one side of the membrane (feed) a mixture of acetic acid-water or ethanol-water, either of which was fed batchwise at the atmospheric pressure and on the other (permeate or product) side, a reduced pressure of 6.66 Pa was maintained through a vacuum pump (Toshniwal, Mumbai, India). The capacity of PV cell is 250 mL but to start with, 50 g of the feed mixture was added on the upper side of the membrane and stirred at a constant temperature by circulating water through the thermostatic water jacket. Before starting the PV-esterification experiment, the test membrane was equilibrated for about 2–4 h with the feed mixture. After establishment of a steady state, permeate vapors were collected in cold

traps immersed in liquid nitrogen for about 4–5 h. Weight of the permeate collected was measured on a Mettler Balance (model B 204-S, Greifensee, Switzerland: accuracy 10^{-4} g) to determine flux, J (kg/m² h) using the weight of liquids permeated, W (kg), effective membrane area, A (m²), and measurement time, t (h) as follows:

$$J = \frac{W}{At} \qquad (3)$$

The analysis of feed and permeate samples was done using a Nucon Gas Chromatograph (GC) (Nucon, model 5765, Mumbai, India) provided with a Thermal Conductivity Detector (TCD) equipped with a DEGS or Tenax packed column of 1/8 in. internal diameter having 2 m length. The oven temperature was maintained at 70°C (isothermal), whereas injector and detector temperatures were maintained at 150°C. The sample injection volume was 1 μL. Pure hydrogen was used as a carrier gas at a pressure of 0.073 MPa. The GC response was calibrated for the column and for known compositions of water + organic (acetic acid or ethanol) mixtures. Calibration factors were fed into the GC software to obtain the analysis for unknown samples. Selectivity, α, was calculated as follows:

$$\alpha = \left(\frac{P_W}{P_{\text{org}}}\right)\left(\frac{F_{\text{org}}}{F_W}\right) \qquad (4)$$

Here, P_W and P_{org} are wt % of water and organic components, respectively, in permeate; F_W and F_{org} are wt % of water and organic components, respectively, in the feed. A minimum of three independent measurements of flux and selectivity were taken under similar set of conditions of temperature and feed compositions to confirm the steady-state pervaporation. Standard errors in computing different mixture compositions were less than 3%, since all the weight measurements were done within ±0.01 mg. Triplicate measurements of flux and selectivity were reproducible within 3% standard errors and average values were considered in all computations.

Esterification reaction accompanied by PV was carried out in the same membrane reactor using sulfonated cation exchange resin (Dowex-50) as the catalyst. Product samples were drawn periodically and analyzed to follow the reaction course. The conversion of membrane catalytic reaction was determined by ethanol conversion as follows:

$$\%\,\text{Conversion}(X) = \left[\frac{W - (W_1 + W_2)}{W}\right] \times 100 \qquad (5)$$

where, W is initial weight of alcohol (g), W_1 is weight of excess alcohol in the reaction mixture (g), and W_2 is weight of the permeated alcohol (g).

The general kinetic expression for the second-order reversible reaction was used to find the kinetic parameters of the esterification reaction. The reaction rate with respect to acetic acid can be written as follows:

$$-\,dC_a/dt = k_f C_a C_b - k_f C_c C_w / K_e \qquad (6)$$

where, C_a is molar concentration of acetic acid, C_b is molar concentration of ethanol, C_c is molar concentration of ethyl acetate, and C_w is molar concentration of water. The equilibrium constant, K_e was calculated from the equilibrium conversion using the equation:

$$K_e = X.X/(1 - X)(2.88 - X) \qquad (7)$$

Here, X represents the equilibrium conversion in terms of molar concentration. Under initial condition, $C_{b0} = 2.88 C_{a0}$ and $C_{c0} = C_{w0} = 0$ at $t = 0$. Then, by writing all concentrations in terms of conversion and initial concentration of acetic acid, we get the following,

$$C_a = C_{a0}(1 - X), \quad C_b = C_{a0}(2.88 - X),$$
$$C_c = C_w = C_{a0}X \qquad (8)$$

In this research, esterification of acetic acid ($1M$) with ethanol ($2.88M$) was studied in the membrane reactor below 70°C in the presence of 6 g of sulfonated cation exchange resin (Dowex-50).

Sorption experiments

Sorption experiments were performed gravimetrically[35] on membranes at the respective compositions (10 wt % water) of acetic acid and ethanol containing feeds at 30, 40, 50, 60, and 70°C. Sorption was also studied in water as well as in pure acetic acid or ethanol. Sorption with respect to feed composition was determined. Initial mass of the circularly cut (dia = 2.5 cm) pristine NaAlg and 4A incorporated NaAlg MMMs were placed on single-pan digital microbalance (model AE 240, Mettler, Switzerland) sensitive to ±0.01 mg. Samples were placed inside the specially designed airtight test bottles containing 20 cm³ of the test solvent. Test bottles were transferred to oven maintained at constant desired temperature. Dry membranes were equilibrated by soaking in different feed mixtures in sealed vessel for 48 h. The sorbed membranes were weighed immediately after blotting with soft tissue paper and % sorption was calculated as follows:

$$\%\,\text{Sorption} = \left(\frac{W_\infty - W_o}{W_o}\right) \times 100 \qquad (9)$$

where, W_∞ and W_o are the weights of sorbed and dry membranes, respectively.
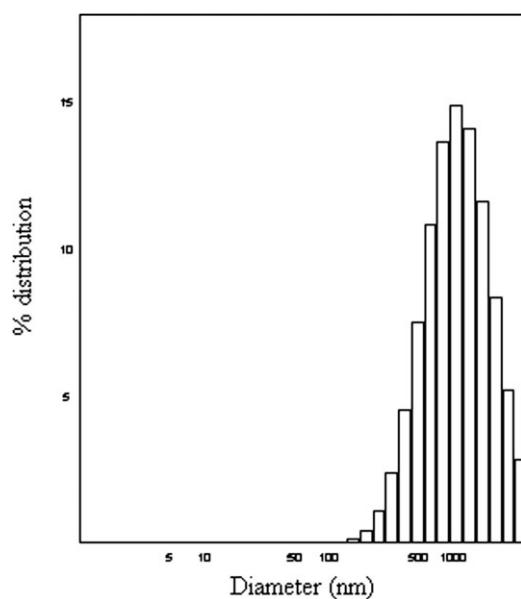
Figure 2 Number average particle size distribution histogram of 4A zeolite particles.

Sorption experiments on neat zeolites were also carried out in the same manner as those of membranes for water and acetic acid or ethanol including their mixtures at 30, 40, 50, 60, and 70°C. Initial weight gain of the zeolite particles before attainment of equilibrium and the final weight gain after equilibrium were considered to calculate the % sorption. These data were collected to check or avoid any weight loss while decanting the zeolite dispersed solution by filtration.

RESULTS AND DISCUSSION

Particle size

Number average size distribution of 4A zeolite particles dispersed in water is around 1 μm. However, the particle size distribution histogram displayed in Figure 2 indicates the size distribution in the range of 150–1500 nm, but majority of particles have the average size in the range of around 1000 nm.

Mechanical properties

Tensile strength data at break for the 4A loaded NaAlg MMMs as well as pristine NaAlg in their dry states given in Table I suggest that MMMs exhibit higher tensile strengths than pristine NaAlg membrane, due to attainment of increased strength as result of physical interaction of filler with polymer. This would impose a restriction on the mobility of polymer chains to result in increased rigidity or tensile strength of MMMs with a reduction in % elongation at break.

TABLE I
Tensile Strength and % Elongation of Pristine NaAlg and 10 wt % 4A Zeolite-Filled NaAlg-Mixed Matrix Membranes

Membrane type	Tensile strength (N/mm^2)	Elongation at break (%)
Prisitne NaAlg	19.18	7.7
3 wt % 4A + NaAlg	30.27	7.3
5 wt % 4A + NaAlg	45.78	7.0
7 wt % 4A + NaAlg	60.22	6.8
10 wt % 4A + NaAlg	72.43	6.5

Membrane morphology

SEM of cross section image of 10 wt % 4A zeolite-loaded MMM shown in Figure 3 indicates that 4A zeolite particles are uniformly distributed in the void spaces of NaAlg matrix. However, interfacial voids and attachment between particles and polymer matrix are observed. Thus, in PV runs, the majority of water molecules get adsorbed onto 4A zeolite particle surfaces even though these are embedded inside the NaAlg matrix. It is thus necessary to have a uniform distribution of particles in NaAlg, such that MMMs will exhibit enhanced flux and selectivity.

Sorption

Liquid sorption through polymeric membranes has been well-documented.[36] PV results are greatly influenced by the sorption capacity of membranes. Figure 4 shows the sorption of neat zeolite 4A particles at 30, 40, 50, 60, and 70°C. For instance, sorption by zeolite 4A is more for water than for acetic acid, ethanol, and their feed mixtures at all the temperatures due to hydrophilic–hydrophilic interactions. Figure 5 displays the sorption capacity of MMMs as a
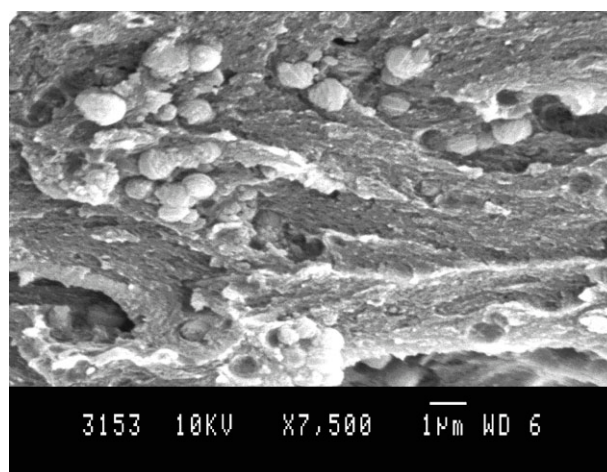

Figure 3 Cross-sectional SEM micrograph of 10 wt % 4A zeolite-filled NaAlg membrane.
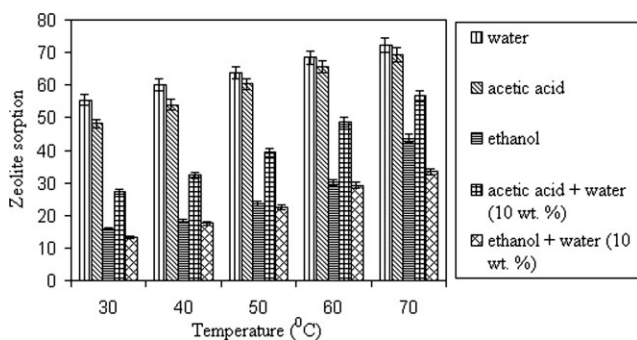
Figure 4 Zeolite 4A sorption versus temperature.

function of 4A zeolite loading at 30°C. Sorption of water increases, whereas for organic components, a decreasing sorption is observed with increasing loading of zeolite 4A due to the hydrophilic–hydrophilic interactions similar to increasing water flux and selectivity as discussed earlier. At increased temperature, permeation flux also increased giving a decrease in water selectivity due to thermal motions of polymer chain segments in response to chain relaxation in the presence of solvent. With increasing temperature, thermal motion of chain increases and more of organic components will diffuse through the membrane, thereby increasing the organic flux and sorption capacity of the membrane (Fig. 6).

Figure 7 illustrates the relationship between membrane sorption and feed composition at 30°C. The % sorption data for both feed mixtures are lower for pristine NaAlg membrane than for MMMs, a trend that is similar to flux. Higher-sorption would result in higher-specific interactions, but the extent of interaction between liquid molecules and membrane polymer depends upon the nature of the organic components of the feed. At increasing filler content, equilibrium total sorption also increases along with flux. These observations suggest that membranes of this study have higher affinity for water than organics, and hence will extract 99.33% water on permeate side.
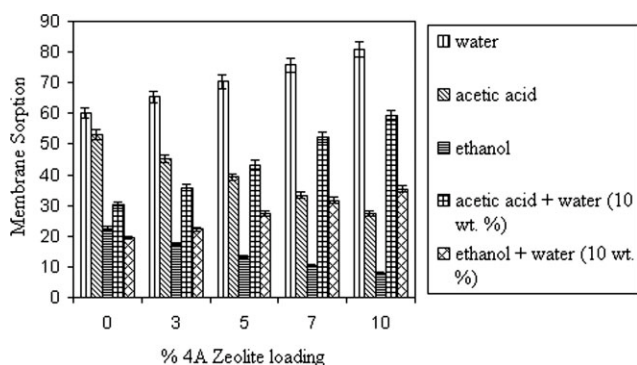

Figure 5 Membrane sorption versus % zeolite 4A at 30°C.
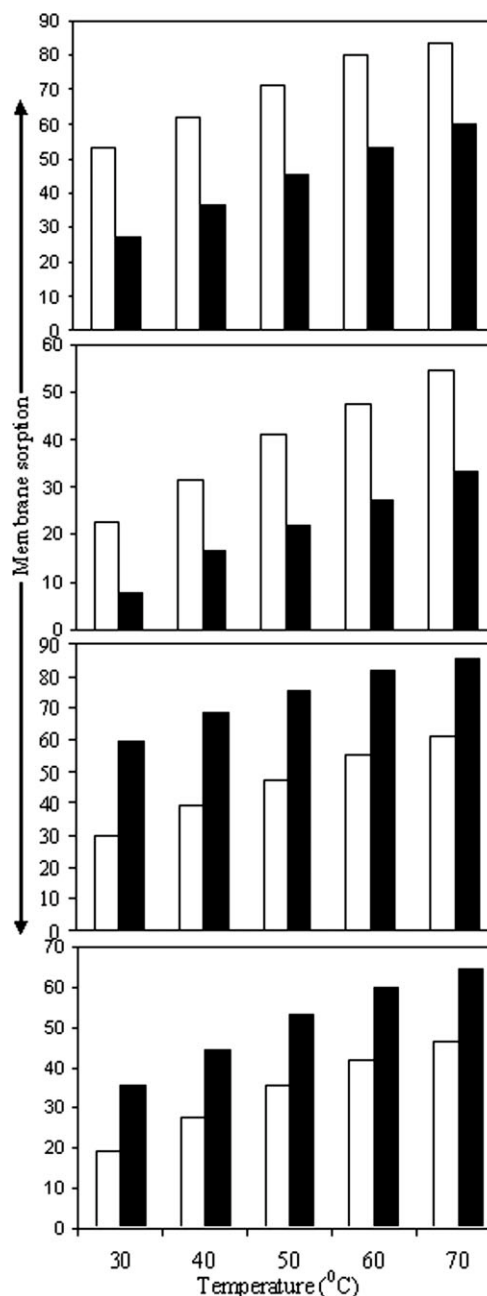
Figure 6 Membrane sorption versus temperature. Symbols: (□) Pristine NaAlg (■) 4A zeolite (10 wt %) filled NaAlg.

Pervaporation performance

The effect of zeolite loading between 0–5 and 5–10 wt % in NaAlg was tested, since addition of zeolite gave varying flux and selectivity data for the MMMs. The improvement of membrane performance shown by MMMs over that of pristine NaAlg membrane is due to filler-polymer and membrane-solvent interactions. The effect of filler content of NaAlg matrix was investigated for feed containing 10 wt % water and with increasing loading of 4A zeolite, both selectivity and flux were increased; the
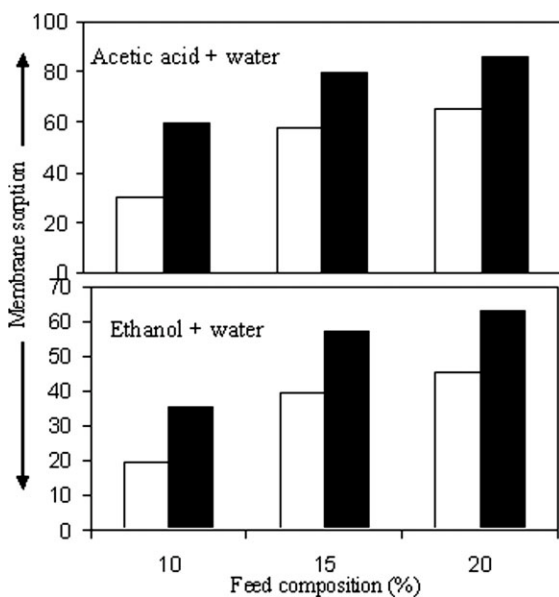
Figure 7 Membrane sorption versus wt % water in feed at 30°C. Symbols: (□) Pristine NaAlg (■) 4A zeolite (10 wt %) filled NaAlg.

reason would be the hydrophilic nature of 4A zeolite, which will adsorb large quantities of water through molecular size pores, thereby creating free channels for transporting water molecules through the membranes. Also, hydrophilic–hydrophilic interactions would reject the organic component of the feed, but allows only water molecules. This has resulted in increased flux with increasing zeolite loading for both feeds as shown in Table II. A strong interaction between hydrophilic 4A zeolite and water molecules would allow water to transport across the membrane but at high loading (10 wt %) of 4A zeolite in NaAlg, high water flux of 0.188 kg/m² h for water + acetic acid feed and 0.137 kg/m² h for water + ethanol feed are observed.

The selectivity for water + ethanol feed increased steadily with increasing loading of zeolite particles up to 7 wt %; but any further increase in selectivity was achieved when zeolite 4A loading was increased to 10 wt %. In case of water + acetic acid feeds, similar trends are observed as shown in Table II. The increased selectivity at higher loadings of 4A zeolite is due to good compatibility and/or adhesion between NaAlg chains and 4A zeolite particles. Notice that between the two feed mixtures of this study, water-acetic acid showed highest selectivity of 991 for 10 wt % 4A zeolite-loaded MMMs with an increase in flux. On the other hand, a selectivity of 1334 was observed for water-ethanol feed mixtures for MMM containing 10 wt % zeolite 4A loading, but flux values for water-ethanol are somewhat lower than those observed for water-acetic acid mixtures.

At lower loadings of zeolite 4A particles as well as with pristine NaAlg membrane, both selectivity and flux values are lower. On the other hand, MMMs have higher PV performances than pristine NaAlg membrane; thus, it would extract more amount of water compared with organics. Compared with pristine NaAlg membrane, MMMs have better PV performances due to the following: (i) adsorption and diffusion of water molecules through pores of 4A zeolite and (ii) transport along the boundaries between the molecular sieve crystals and the NaAlg matrix. The former process is more dominant than the later, since MMM would possess good interface contact, whereas in the latter, this contact may be less dominant if zeolite 4A-polymer interface is poor.[37] At any rate, the unique properties like molecular sieving effect and adsorption preference are important if zeolite 4A particles are compatible with NaAlg matrix. In addition, interfacial interactions between 4A zeolite and polymer are also critical to the optimum performance to the separation. Thus, zeolite 4A particles could discriminate components of the aqueous-organic mixtures either by exclusion of competing molecules on the basis of molecular

TABLE II
Pervaporation Results of Water + Acetic Acid and Water + Ethanol Mixtures for Pristine NaAlg and 4A Zeolite-Filled NaAlg-Mixed Matrix Membranes at 300°C for 10 wt % of Water in the Feed

Membrane type	Wt of permeate (gm)	Wt % of water in permeate	Wt % of organic in permeate	Total flux (kg/m² h)	Water flux J (kg/m² h)	Organic flux (kg/m² h)	Selectivity (α)
Water (10 wt %) + Acetic acid							
Pristine NaAlg	0.356	94.9	5.0	0.126	0.119	0.006	169
3 wt % 4A + NaAlg	0.428	96.7	3.3	0.151	0.146	0.005	264
5 wt % 4A + NaAlg	0.474	97.8	2.1	0.167	0.164	0.004	404
7 wt % 4A + NaAlg	0.504	98.3	1.7	0.178	0.175	0.003	520
10 wt % 4A + NaAlg	0.536	99.1	0.9	0.190	0.188	0.002	991
Water (10 wt %) + Ethanol							
Pristine NaAlg	0.192	96.7	3.2	0.068	0.066	0.002	266
3 wt % 4A + NaAlg	0.247	98.1	1.8	0.087	0.086	0.002	467
5 wt % 4A + NaAlg	0.285	98.4	1.5	0.101	0.099	0.002	575
7 wt % 4A + NaAlg	0.325	98.9	1.0	0.115	0.114	0.001	873
10 wt % 4A + NaAlg	0.389	99.3	0.6	0.138	0.137	0.001	1334

TABLE III
Pervaporation Results of Water + Acetic Acid and Water + Ethanol Mixtures for Pristine NaAlg and 10 wt % 4A
Zeolite-Filled NaAlg-Mixed Matrix Membranes at 300°C at Different Feed Compositions

Feed composition (wt %)	Wt of permeate (gm)	Wt % of water in permeate	Wt % of organic in permeate	Total flux (kg/m^2 h)	Water flux J (kg/m^2 h)	Organic flux (kg/m^2 h)	Selectivity (α)
A. Water + Acetic acid							
Pristine NaAlg membrane							
10	0.356	94.9	5.1	0.126	0.119	0.006	169
15	0.382	94.6	5.3	0.135	0.128	0.007	100
20	0.393	94.3	5.7	0.139	0.131	0.008	66
4A zeolite (10 wt %)-filled NaAlg membrane							
10	0.536	99.1	0.9	0.190	0.188	0.002	991
15	0.565	98.7	1.2	0.200	0.197	0.002	455
20	0.578	98.5	1.4	0.204	0.202	0.003	276
B. Water + Ethanol							
Pristine NaAlg membrane							
10	0.192	96.7	3.3	0.068	0.066	0.002	266
15	0.205	96.4	3.5	0.073	0.070	0.003	155
20	0.227	94.3	5.7	0.080	0.076	0.004	66
4A zeolite (10 wt %)-filled NaAlg membrane							
10	0.389	99.3	0.7	0.138	0.137	0.001	1334
15	0.409	99.0	1.0	0.145	0.143	0.001	579
20	0.427	98.7	1.2	0.151	0.149	0.002	321

size and shape or by adsorption preference; hence, by incorporating zeolite 4A particles, it is expected to enhance the separation performance of NaAlg. Zeolite 4A has a pore size of (0.4 nm), which is larger than the kinetic diameter of water (0.296 nm) and this value is much smaller than acetic acid (0.436 nm) as well as ethanol (0.430 nm). Thus, viewed from any angle, i.e., either through polymer-solvent or through polymer-filler interactions, as well as based on size exclusion effect, it is obvious that incorporation of zeolite 4A into NaAlg would boost the PV performance over that of plain NaAlg membrane. Even on the basis of sorption and diffusion principles also, the separation efficiency of membranes is higher for water than organics. Sorption is usually favored by specific type of hydrophilic–hydrophilic interactions, whereas diffusion is affected by membrane morphology (amorphous or crystalline) in addition to chain mobility. The improvement in selectivity and flux data of MMMs is affected due to the presence of 4A zeolite particles in NaAlg.

Flux for pristine NaAlg membrane is lower than MMMs for the studied feed compositions. For instance, with water + acetic acid feeds, flux is higher than water + ethanol feeds and this is indicative of the fact that liquid–liquid interactions might vary depending upon the nature of the membrane. In addition, plasticization of membrane polymer in the presence of different media and chain mobility would also influence membrane performance. Plastisization of membrane is higher for water + acetic acid feeds than water + ethanol feeds and this might be responsible for a reduction in selectivity and increase in permeation flux. On the other hand,

polymer chain mobility is higher in case of water + ethanol feeds and this is due to increased selectivity and reduced flux. Such an effect would be more favorable for water transport than organics, because water will occupy free channels created within MMMs and thus, the recovery of water will be more on permeate side. In both the mixtures, flux increased systematically with increasing loadings of 4A zeolite. The minimum value of J observed for 3 wt % 4A zeolite-loaded NaAlg membrane is due to lesser surface diffusion and activated transport of water through the pores of MMMs, but at 10 wt % 4A zeolite loading, adsorption capacity of zeolite particles would increase due to increased hydrophilicity of MMM, thereby offering higher permeation flux.

Table III illustrates the relationship between membrane performance and water composition for both the mixtures in case of pristine NaAlg and 10 wt % 4A zeolite-loaded MMM at 30°C. Flux increases with increasing water content of the feed, which is caused by higher concentration of water in the membrane, but selectivity decreased for both the feeds. This reduction is more at 20 wt % of water and is attributed to plasticizing effect as well as specific molecular interactions between feed components themselves. For all feed mixtures, fluxes of MMMs are higher than found for pristine NaAlg membrane.

Effect of temperature

Temperature influences the PV separation characteristics and in this study, we have studied PV performances at 30, 40, 50, 60, and 70°C for pristine and 10 wt % zeolite-loaded MMMs for 10 wt % water

TABLE IV
Pervaporation Results of Water + Acetic Acid and Water + Ethanol Mixtures for Pristine NaAlg and 4A Zeolite-Filled NaAlg-Mixed Matrix Membranes at Different Temperatures for 10 wt % Water in the Feed

Temperature (°C) of feed mixture	Wt of permeate (gm)	Wt % of water in permeate	Wt % of organic in permeate	Total flux kg/m² h)	Water flux J (kg/m² h)	Organic flux (kg/m² h)	Selectivity (α)
A. Water (10 wt %) + Acetic acid							
Pristine NaAlg membrane							
30	0.356	94.9	5.0	0.126	0.119	0.006	169
40	0.373	93.8	6.1	0.132	0.124	0.008	137
50	0.387	92.9	7.0	0.137	0.127	0.010	119
60	0.413	91.6	8.3	0.146	0.134	0.012	99
70	0.423	90.7	9.2	0.150	0.136	0.014	88
4A zeolite (10 wt %)-filled NaAlg membrane							
30	0.536	99.1	0.9	0.190	0.188	0.002	991
40	0.570	98.2	1.7	0.202	0.198	0.003	511
50	0.582	97.7	2.2	0.206	0.201	0.005	387
60	0.591	96.5	3.4	0.209	0.202	0.007	253
70	0.603	95.8	4.1	0.213	0.205	0.009	210
B. Water (10 wt %) + Ethanol							
Pristine NaAlg membrane							
30	0.190	96.7	3.2	0.067	0.065	0.002	266
40	0.197	95.9	4.0	0.070	0.067	0.003	214
50	0.205	94.7	5.2	0.073	0.069	0.004	164
60	0.217	93.8	6.1	0.077	0.072	0.005	138
70	0.233	92.6	7.3	0.082	0.076	0.006	114
4A zeolite (10 wt %)-filled NaAlg membrane							
30	0.389	99.3	0.6	0.138	0.137	0.001	1334
40	0.407	98.5	1.4	0.144	0.142	0.002	620
50	0.423	97.9	2.0	0.150	0.147	0.003	426
60	0.445	97.2	2.7	0.157	0.153	0.004	316
70	0.460	96.8	3.1	0.163	0.158	0.005	279

containing feed. Flux, selectivity, and amount of water extracted on permeate side are all given in Table IV. Variation of flux, J with temperature is expressed by Arrhenius relationship[18,19]:

$$J = J_0 \exp(-E_J/RT) \tag{10}$$

where, J_0, E_J, R, and T are the pre-exponential factor, apparent activation energy (kJ/mol) for permeation flux, molar gas constant, and feed temperature (T) in Kelvin, respectively. From eq. (10), permeation activation energy was evaluated, while from the respective fluxes obtained at 30, 40, 50, 60, and 70°C, the E_J values for water were calculated from the slopes of Arrhenius plots of ln J versus 1000/T (Fig. 8). The E_J values calculated from the least-squares estimations (at 95% confidence limit), compiled in Table V, suggest that activation energies for pristine NaAlg membrane are higher than those of MMMs for both feed mixtures in the studied feed mixture compositions. Thus, temperature exhibited a significant effect on flux. The smaller activation energies were observed for MMMs than pristine NaAlg membrane, suggesting that lesser barrier energy is required for transport to take place and *vice versa*. After the addition of 4A zeolite particles in NaAlg, the energy barrier has decreased, since larger number of water molecules than organics from the feed mixtures
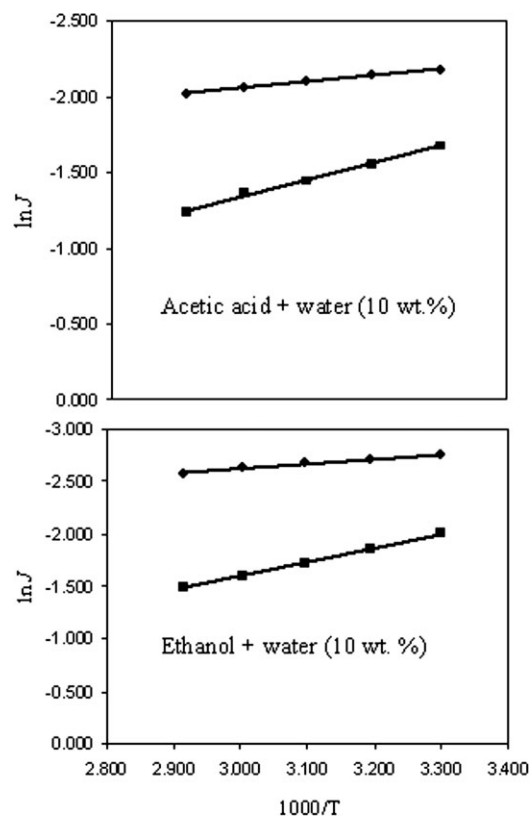

Figure 8 ln J versus 1000/T. Symbols: (●) Pristine NaAlg, (■) 10 wt % 4A-filled NaAlg membranes.

TABLE V
Permeation Activation Energy (E_J) for Pristine NaAlg and 4A Zeolite-Filled Composite NaAlg Membranes

Membranes	Permeation activation energy (E_J) (kJ/mol)
A. Water (10 wt %) + Acetic acid	
Pristine NaAlg membrane	36.44
4A zeolite (10 wt %)-filled NaAlg membrane	27.32
B. Water (10 wt %) +Ethanol	
Pristine NaAlg membrane	34.02
4A zeolite (10 wt %)-filled NaAlg membrane	20.27

have transported through the interstices of zeolite particles and NaAlg segments. Notice that E_J values for 10 wt % 4A zeolite-loaded NaAlg membrane are lower than those found for pristine NaAlg membrane.

Pervaporation-aided catalytic esterification

Since PV performance of MMMs was higher than pristine NaAlg membrane, permeation flux increased as the temperature increased, but selectivity decreased. Therefore, MMM with higher selectivity was selected, since its permeation flux was not very low for studying PV-esterification that has industrial importance. Esters are widely used as solvents, extractants, and diluents.[38] Esterification reactions are equilibrium-limited, but different possibilities exist to achieve higher conversions of the required product. By using large excess of one of the reac-
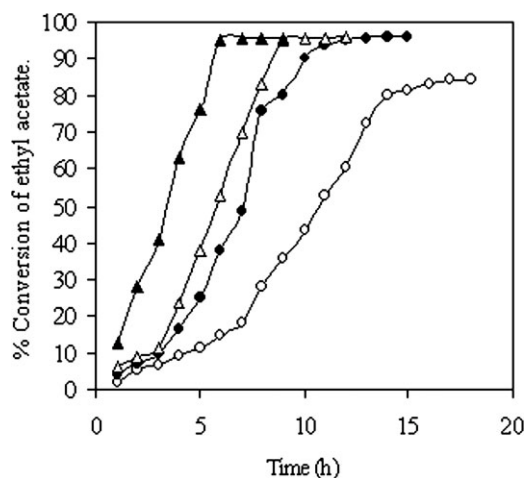

Figure 9 % Conversion of ethyl acetate versus time for esterification of acetic acid with ethanol at 70°C. Symbols: (○) blank reaction, (●) pristine NaAlg, (△) 4A zeolite (5 wt %)-filled NaAlg and (▲) 4A zeolite (10 wt %) filled NaAlg membranes.

tants, usually alcohol, the reaction yield of the other component can be enhanced. Because of the presence of large excess of one of the reactants, the product recovery becomes quite expensive, but for PV-aided esterification, catalytic membrane can be used to overcome these limitations.

In acid-catalyzed esterification of acetic acid with ethanol, the use of PV to preferentially remove water from the reaction system favored the forward reaction, which substantially enhanced the yields of ethyl acetate as shown in Figure 9 for MMMs. However, continuous removal of water from the system

TABLE VI
Comparison of PV Data with Literature at 30°C

Membrane type	Flux J (kg/m^2 h)	α	Ref.
Water + Ethanol			
4A (10 wt %) filled NaAlg[a]	0.137	1,334	Present work
Two-ply composite NaAlg/CS[b]	0.070	1,110	22
Cellulose/NaAlg (ca^{2+} crosslinked) blend[c]	0.068	1,175	21
NaAlg/CS blend	0.220	436	23
PHEMA (20 wt %)-NaAlg[d]	0.132	571	20
AlPO$_4$-5 (20 wt %)-filled NaAlg[e]	0.104	980	18
Water + Acetic acid			
4A (10 wt %) filled NaAlg	0.188	991	Present work
NaAlg composite (crosslinked with HDM)[f]	0.262	161	24
NaAlg + 5 wt % PVA + 10 wt % PEG	0.024	40	27
NaAlg/pAAm-g-GG	0.029	15	25
Cobolt (III) (3-acetylpyridine-o-aminobenzoyl hydrazine)-filled NaAlg	0.123	174	28

CS, Chitosan, PHEMA, Poly(hydroxyethylmethacrylate); HDM, 1,6-Hexanediamine; pAAm, Poly(acrylamide); GG, guar gum; PEG, Poly(ethylene glycol).
[a] 10 wt % water in the feed.
[b] 5 wt % of water in the feed.
[c] At temperature of 60°C.
[d] 5 wt % of water in the feed.
[e] 4 wt % of water in the feed.
[f] 15 wt % of water in the feed at 70°C.

makes it possible to pass over the equilibrium limit (80%) that was approached rather slowly as displayed by the blank reaction data at 18 h in the absence of membrane. The time required for reaction to attain 90% conversion for pristine NaAlg, 4A zeolite (5 wt %)-filled NaAlg, and 4A zeolite (10 wt %)-filled NaAlg membranes are 12, 9, and 6 h, respectively. The equilibrium constants, K_e calculated using eq. (7) are 2.2 for blank reaction (in the absence of membrane) and 10.7 for pristine NaAlg membrane (in the absence of filler). However, in case of 5 wt % and 10 wt % 4A zeolite-filled MMMs, the K_e values are 11.5 and 11.9, respectively, indicating that preferential permeation through hydrophilic membranes has greatly influenced the esterification reaction by shifting the chemical equilibrium for the conversion of ethyl acetate form ethanol and acetic acid. Promotion in the forward direction, due to the presence of 4A zeolite particles can be explained as due to increased water transport rates through zeolite cage crystals such that the membrane with higher permeation flux, such as 4A zeolite (10 wt %)-filled NaAlg, is more favorable to the reaction.

Comparison with literature data

From a comparison of present PV data with published results shown in Table VI, there is a good improvement in selectivity of water for both mixtures for all the MMMs compared with similar type of data published in the literature. In general, one could see a good improvement in both flux and selectivity data and the differences are attributed to different experimental conditions employed by different authors, which is hard to maintain.

CONCLUSIONS

MMMs of this study are novel for an effective PV dehydration of ethanol and acetic acid with high selectivity and flux; the use of 4A zeolite particles in NaAlg seems to facilitate permeation of water, but hindering the transport of acetic acid and ethanol. Overall results of this study are better than the published reports. Increased loadings of 4A into NaAlg matrix have increased the efficiency of the membranes due to available free channels. The efficiency of MMMs is quite high in case of water-ethanol mixtures, since selectivity for water is high, whereas it is less for water-acetic acid mixtures. At higher temperatures, an increase in permeation flux for both the mixtures occurred with a decrease in water selectivity. The present data are in agreement with the sorption results. The E_J values range from 20 to 37 kJ/mol and these depend upon the thermodynamic interactions of the components in the feed mixture. The continuous removal of water from the reacting

system has lead to an increase in conversion of acid into ester with a reduction in conversion time. The 4A zeolite-filled membranes performed better in PV-aided esterification reactions because of the enhancement of water transport through the membranes. Pervaporation-aided catalytic esterification of acetic acid and ethanol at 70°C showed the conversion of ethyl acetate of >90% for MMMs, a favorable factor for esterification reactions. The increase of ethyl acetate conversion was due to continuous removal of water from the system by MMMs due to the chemical equilibrium that was shifted in the forward direction.

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