

Separation of Water–Isopropyl Alcohol Mixtures with Novel Hybrid Composite Membranes

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ABSTRACT: New-fangled hybrid composite membranes were prepared by the incorporation of 5, 10, and 15 mass % NaY–zeolite particles into blend membranes of carboxymethyl cellulose (CMC)-*g*-acrylamide/sodium alginate (NaAlg) and crosslinked with glutaraldehyde. The pervaporation (PV) separation performance of the hybrid composite membranes was explored for the dehydration of isopropyl alcohol from their aqueous solutions at 30°C. The effect of NaY–zeolite in these blend membranes was investigated in PV dehydration. From the experimental results, we found that NaY particles could be intercalated in the aqueous polymer solution. The obtained results

show that both the flux and selectivity increased simultaneously with increasing zeolite content in the membrane. This was explained on the basis of an enhancement of the hydrophilicity, selective adsorption, and molecular sieving action by the creation of pores in the membrane matrix. The membranes were characterized by differential scanning calorimetry, scanning electron microscopy, and Fourier transform infrared spectroscopy. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

Key words: carbohydrate synthesis; membranes; polyaromatics; polysaccharides

INTRODUCTION

The pervaporation (PV) technique has a greater potential for saving energy than conventional distillation and has been recognized as an economically effective way to separate azeotropic mixtures. The use of low-performance natural polymers, such as sodium alginate (NaAlg), as membranes for PV has some drawbacks because of lower flux rates and separation factors, such as selectivity.^{1–3} There have been reports^{4–7} about the modification of membranes by blending, grafting, and dispersal of nanometer- or micrometer-size inorganic fillers, such as zeolites, clays, or mesoporous materials. These modifications have resulted in a marked increase in membrane performance. The graft copolymerization of vinyl monomers on carbohydrate polymers has been widely studied because radical sites can be generated on the cellulose backbone with chemical initiators. In 1958, Mino and Kaizerman⁸ grafted monomers such as acrylamide (AAm), acrylonitrile, and methyl methacrylate onto poly(vinyl alcohol) using a Ce⁴⁺ initiator. Earlier studies from the literature

have dealt with the use of hydrophilic membranes prepared from guar-gum-grafted AAm [poly(vinyl alcohol)-*g*-AAm] for the PV dehydration of acetic acid, and they have also dealt with the preparation of other membranes, namely, (HEC-*g*-AAm)/NaAlg blend membranes, and the use of the PV dehydration of acetic acid.⁹

Zeolites are highly crystalline inorganic structures having pores with uniform molecular size and are used in a variety of separation problems. Because of the small pore size, the diffusion rates of some molecules with different sizes and adsorption strengths of the zeolite crystals differ by orders of magnitude. Zeolites have been used as fillers to develop polymeric membranes to take advantage of the adsorption and diffusion differences to separate liquid mixtures.¹⁰ Zeolite-filled membranes for PV separation have been widely studied in recent years.^{11–14} Because of their unique structural properties, zeolites can selectively separate a wide range of compounds, depending on their size, shape, and chemical characteristics. During PV, the adsorbed coverages are higher than those present in gas separation studies, whereas with the liquid feed, the total coverage at the feed side of the membrane is usually near saturation.

Hydrophilic and hydrophobic membranes have been used to separate aqueous organic mixtures.^{15–19} In studies in the literature, a variety of zeolites have

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been used as fillers to overcome the problems associated with low flux, selectivity, and mechanical strength properties of pristine PV membranes.²⁰ The hydrophilicity and hydrophobicity of the membranes can be varied by the incorporation of zeolites of different polarities. This helps to increase the flux and selectivity simultaneously. However, the published data on clay-modified hybrid composites are rare when compared with those on zeolite-filled membranes.^{21,22} Earlier, Wang et al.²¹ prepared polyamide/sodium dodecyl sulfate–clay hybrid nanocomposite membranes and tested them for PV separation of water–ethanol mixtures.

Isopropyl alcohol (IPA) is an important solvent and is used on a large scale in the chemical industry and in pharmaceutical laboratories. Furthermore, it has also been used in the semiconductor and liquid crystal display industries as a water-removing agent.^{23,24} IPA and water form an azeotropic mixtures at 85.3 mass % of IPA,²⁵ and hence, the separation of these mixtures by conventional methods, such as solvent extraction and rotavapor, or by distillation could prove uneconomical. The purification of organic solvents, such as IPA, containing a small amount of water is of vital significance in the area of organic synthesis. In this study, we attempted to enhance the permeation flux and separation selectivity simultaneously by suitably modifying the NaAlg membrane by blending it with carboxymethyl cellulose (CMC; CMC-g-AAm 50 : 50) by incorporating NaY zeolite using a solution technique.

EXPERIMENTAL

Materials

NaAlg (extrapure grade), CMC (weight-average molecular weight \approx 457,000), AAm (analytical grade reagent), glutaraldehyde (GA; 25% content in water, extrapure grade), acetone (analytical-reagent grade), hydrochloric acid (HCl; 35% content, extrapure grade), and IPA were purchased from S. D. Fine Chemicals, Ltd. (Mumbai, India). NaY-zeolite was a kind gift from S. Sridhar of the Indian Institute of Chemical Technology (Hyderabad, India). All of the chemicals were reagent grade and were used without further purification. Double-distilled water was used throughout the research work.

Membrane preparation

Preparation of a blend membrane from NaAlg and CMC-g-AAm

Blend membranes of NaAlg with CMC-g-AAm were prepared by solution casting. The required amount of NaAlg was dissolved in 100 mL of distilled water by stirring over a magnetic stirrer (Jenway, model

1103, Chelmsford, Essex, United Kingdom) for 24 h. To this, various amounts of CMC-g-AAm (25 and 50 wt %) were added. The solution was mixed uniformly and filtered to remove any suspended particles. It was then poured onto a clean glass plate leveled perfectly on a tabletop, kept in a dust-free atmosphere, and dried at room temperature. The dried membranes were peeled off carefully from the glass plate. We crosslinked the membranes by immersing them in 300 mL of a 70% aqueous–acetone mixture containing 2.5 mL of HCl and 2.5 mL of GA for up to 12 h. After the membrane was removed from the crosslinking bath, it was washed with water repeatedly and dried in an oven at 40°C. The measured membrane thickness was around 35–40 μ m. The membranes prepared with 25 and 50 wt % of CMC-g-AAm were designated as NaAlg–CMC-g-AAm-25 and NaAlg–CMC-g-AAm-50, respectively, whereas the plain NaAlg membrane was designated as NaAlg.

Preparation of NaY-zeolite-incorporated NaAlg/(CMC-g-AAm) composite membranes

NaAlg/(CMC-g-AAm) (75 : 25, 4 g) was dissolved in 80 mL of water with constant stirring. Then, respective amounts of NaY filler particles [5, 10, and 15 wt % with respect to the weight of NaAlg/(CMC-g-AAm)] were weighed separately, dispersed in 20 mL of water, sonicated for 30 min, and then added to the NaAlg/(CMC-g-AAm) solution with further stirring for 24 h. We used this solution to cast the membrane by pouring it onto a glass plate, drying it at room temperature, and peeling it off of the glass plate. The dried membranes were immersed in a crosslinking bath containing a 75% aqueous–acetone mixture, 2.5 mL of GA, and 2.5 mL of HCl and were kept in this bath for 10–12 h. The membranes were then removed, washed repeatedly with deionized water, and dried in an oven at 40°C. The membrane thickness was measured by a micrometer screw gauge at different positions with standard errors of less than ± 1.0 μ m.

Swelling experiments

The initial mass of these membranes was measured on a top-loading single-pan digital electronic microbalance (model AE 240, Mettler, Greifensee, Switzerland; sensitive to ± 0.01 mg). Swelling experiments for all of the membranes were performed gravimetrically at respective compositions of water and IPA mixtures at $30 \pm 0.5^\circ\text{C}$ and also in water and pure organic components in an electronically controlled hot-air oven (water tube boiler binder, Tuttingen, Germany). Circularly cut (diameter = 2.5 cm) disk-shaped membranes were placed in a vacuum oven at 30°C for 48 h before use. Membrane samples were then placed inside the specially designed airtight

test bottles containing 20 cm³ of the test solvent. Test bottles were then placed inside an oven maintained at a constant temperature of 30°C and were then equilibrated by soaking in different compositions of feed mixtures for 48 h. We weighed the swollen membranes immediately (by wiping the surface-adhered liquid droplets by gently pressing them between filter paper wraps) on a digital microbalance. To minimize the errors due to evaporation losses, this step was completed within 15–20 s. After complete swelling, equilibrium swelling (*S*) of the membrane was calculated from the initial dry mass (*W*₀) and equilibrium mass (*W*_∞) of the membrane with Eq. (1):

$$DS(\%) = \left(\frac{W_{\infty} - W_0}{W_0} \right) \times 100 \quad (1)$$

where DS is the degree of swelling and *W*_∞ and *W*₀ are the weights of the sorbed and dry membranes, respectively

PV experiments

The PV experiments were performed with an indigenously designed apparatus reported in the previous articles.^{26,27} The effective area of the membrane in contact with the feed stream was 32.43 cm², and the capacity of the feed compartment was about 250 cm³. The temperature of the feed mixture was maintained at a constant value by a thermostatic water jacket. The vacuum in the downstream side of the apparatus was maintained [1.34×10^3 Pa (10 Torr)] with a two-stage vacuum pump (Toshniwal, Mumbai, India). The test membrane was allowed to equilibrate for about 2 h while in contact with the feed mixture before the PV experiment was performed. The procedure used in the PV experiments was described by Chowdoji Rao and coworkers.^{27,28}

After a steady state was attained, the permeate was collected in a trap immersed in a liquid nitrogen jar on the downstream side at a fixed intervals. We calculated the flux by weighing the permeate on a digital microbalance (model AE 240, Mettler, Greifensee, Switzerland; accuracy = 10⁻⁴ g) to determine the flux (*J*; kg m⁻² h⁻¹) with the weight of liquids permeated (*W*; kg), effective membrane area (*A*; m²), and measurement time (*t*; h) as follows:

$$J_p = \frac{W_p}{At} \quad (2)$$

The selectivity (α_{PV}) was calculated as follows

$$\alpha_{PV} = \left(\frac{P_A}{1 - P_A} \right) \left(\frac{1 - F_A}{F_A} \right) \quad (3)$$

where *F*_A is the weight percentage of water in the feed and *P*_A is the weight percentage of water in the permeate. At least three independent measurements of flux and selectivity were made under the same conditions of temperature and feed composition to confirm the steady-state PV.

Measurement of the refractive index (RI)

RI and nD (A refractive index measured using the D ray [wavelength: 589 nm] is expressed in units of nD.) for sodium-D line were measured with a thermostatically controlled Abbe refractometer (Atago 3T, Japan) with an accuracy of ±0.001. The refractometer was fitted with hollow prism casings, through which water was circulated. The temperature of the prism casing was observed with a digital display (±0.01°C). The instrument was provided with two prisms placed one above and the other in front of the telescope. When a drop of test liquid was inserted with a hypodermal syringe, the incident ray formed a line of demarcation between the light and dark portions of the field when viewed with a telescope, which moved with scale. The instrument directly gave the values of nD. The permeate composition was determined by the measurement of RI and its comparison with an established graph of RI versus mixture composition.

Characterization techniques

Fourier transform infrared (FTIR) measurements

The FTIR spectra of the uncrosslinked and crosslinked blend membranes were scanned in the range 400–4000 cm⁻¹ with a Nicolet-740 PerkinElmer 283B FTIR spectrophotometer (Waltham, USA) by the KBr pellet method.

Differential scanning calorimetry (DSC) studies

DSC thermograms of the pure polymer and polymer blend membranes were recorded with a Rheometric Scientific model DSC-SP (London, United Kingdom). Initially, the moisture was removed by the heating of the samples, and then, thermograms were recorded from 30 to 400°C at a heating rate of 10°C/min under a nitrogen atmosphere. The sample pan was conditioned in the instrument before the experiment was run.

Scanning electron microscopy (SEM)

SEM micrographs of the membranes were obtained under high resolution (Mag 300X5kv) with a JEOL model JSM 840A scanning electron microscope equipped with a phoenix energy-dispersive analyzer (Ottawa, Canada). SEM micrographs were taken at Anna University (Chennai, India).

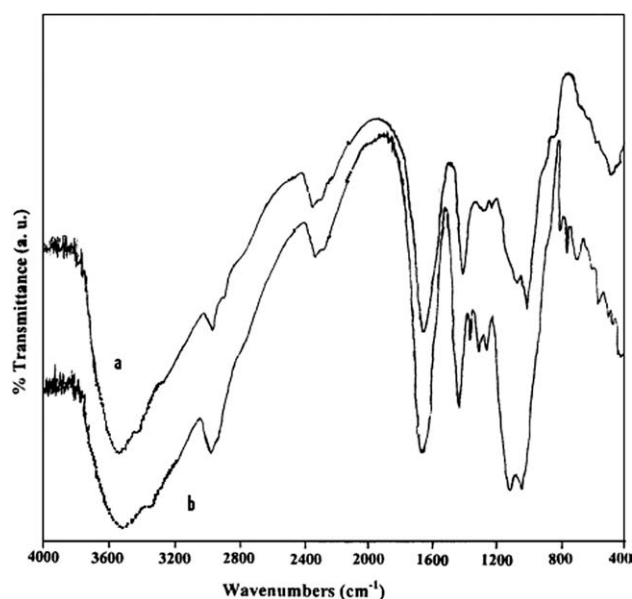


Figure 1 FTIR spectra of the (a) uncrosslinked and (b) crosslinked NaY-zeolite-filled NaAlg/(CMC-g-AAm) membranes.

RESULTS AND DISCUSSION

FTIR studies

The FTIR spectra of the uncrosslinked and crosslinked NaY-zeolite-filled NaAlg/(CMC-g-AAm) membranes are shown in Figure 1. The broad bands at 3443 and 3190 cm^{-1} represented the $-\text{OH}$ stretching of the hydroxyl and NH group stretching for NaAlg and CMC-g-AAm, respectively. The intensity of these bands did not change with the loading of different amounts of zeolite in the polymer matrix, and they indicated the OH and COO groups of the NaAlg/(CMC-g-AAm) membrane. The Si-O band also appeared at the same wavelength when zeolite was loaded into the polymer matrix, and hence, the C-O and Si-O bands at 1100 cm^{-1} almost overlapped in the spectra. The crosslinking reaction between the hydroxyl groups of NaAlg and CMC-g-AAm with the aldehydic groups of GA was confirmed by the increase in the peak intensity at 1097 cm^{-1} from the uncrosslinked polymer to the crosslinked matrix, which was due to the formation of an acetal ring and ether linkage.

DSC analysis

The DSC curves of the crosslinked NaAlg and crosslinked NaAlg/(CMC-g-AAm) membranes containing 5, 10, and 15 mass % NaY-zeolite are displayed in Figure 2(a-d). Broad endotherms were absorbed in the region 30–100°C for all of the membranes because of the release of moisture from the membranes. The crosslinked NaAlg membrane had an endotherm with a peak position at 188°C; this shifted to a higher temperature region with increasing content of NaY in

the NaAlg/(CMC-g-AAm) blend membranes. This indicated that with a greater zeolite content, the mechanical strength of the blend membranes was greater; this, in turn, made it more stable for PV separation. Figure 3 gives a clear picture of the surface scanning electron micrographs of the pure (CMC-g-AAm)/NaAlg, 5% NaY-filled (CMC-g-AAm)/NaAlg, and 15% NaY-filled (CMC-g-AAm)/NaAlg.

SEM analysis

Figure 3(a) shows the SEM surface photograph of the pure (CMC-g-AAm)/NaAlg membrane, and Figure 3(b-d) show the surface of the 5, 10, and 15 wt % NaY-incorporated (CMC-g-AAm)/NaAlg membranes, respectively. As per the SEM analysis, a molecular-level distribution of NaY particles was observed in the (CMC-g-AAm)/NaAlg matrix. However, it was necessary for these particles to be uniformly dispersed in the membrane matrix so that the composite membrane could exhibit the enhanced effects of flux and selectivity. This type of morphology might have facilitated the higher amounts of water molecules to be transported through the membrane by restricting the transport of IPA.⁵⁻⁷

Swelling studies

Effects of the feed composition and zeolite loading on the membrane swelling

The membrane swelling in certain liquids depends on the chemical composition and microstructure of

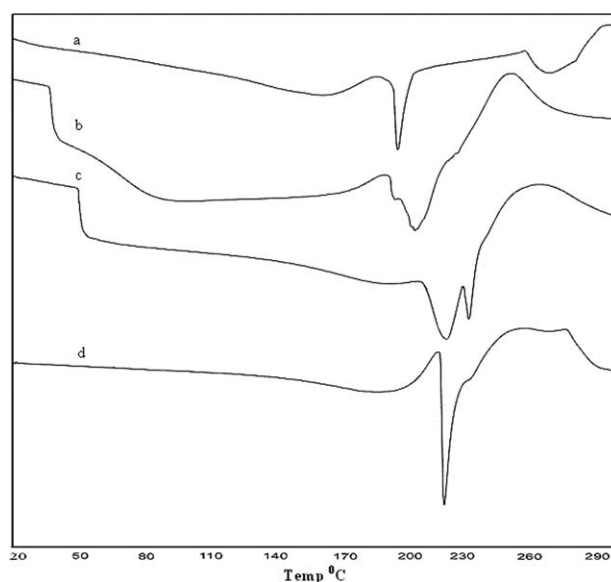


Figure 2 DSC thermograms for (a) crosslinked NaAlg, (b) crosslinked (CMC-g-AAm)/NaAlg-NaY (5 mass %), (c) crosslinked (CMC-g-AAm)/NaAlg-NaY (10 mass %), and (d) crosslinked (CMC-g-AAm)/NaAlg-NaY (15 mass %) membranes.

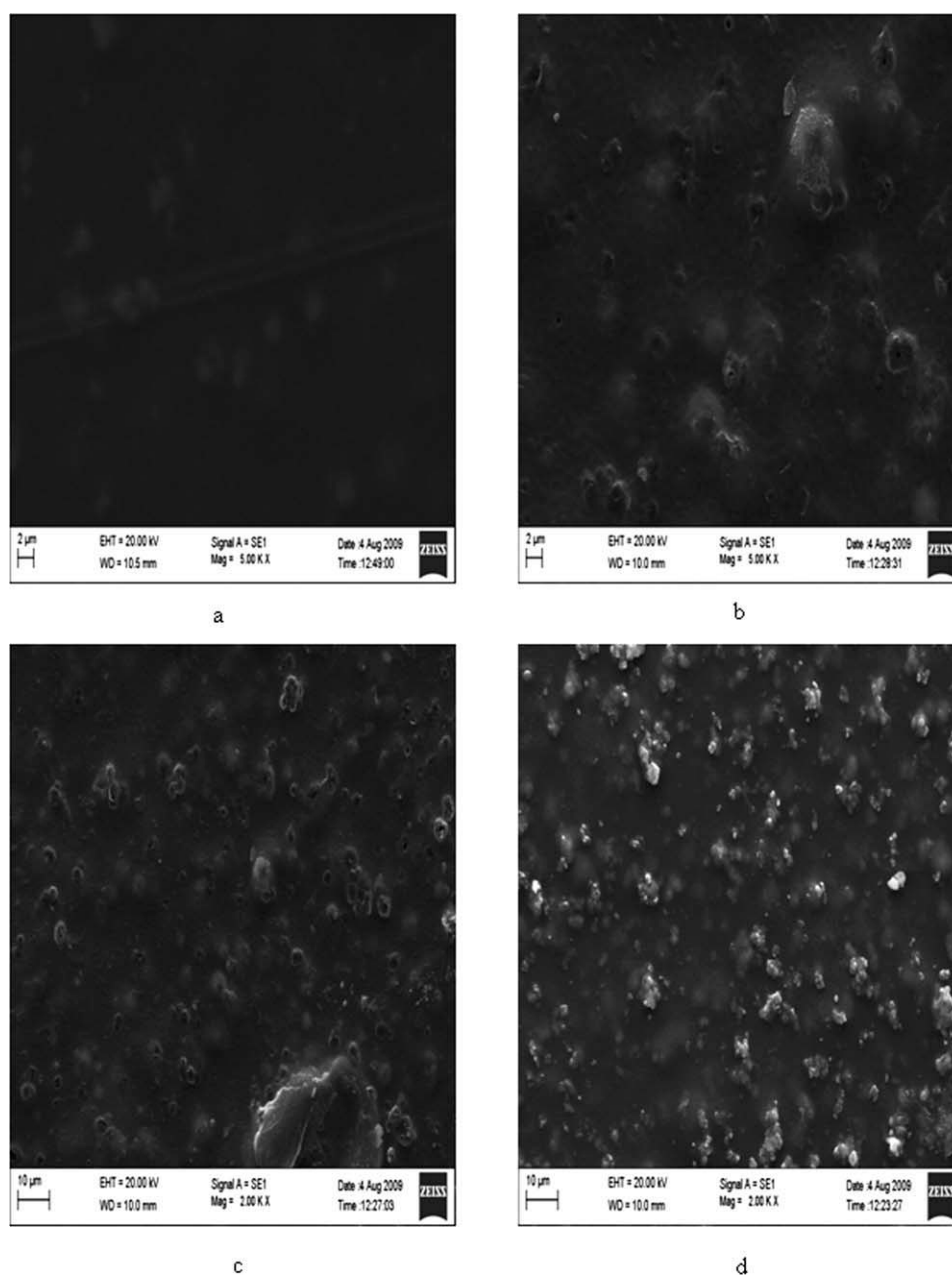


Figure 3 Surface scanning electron micrographs of (a) pure (CMC-g-AAm)/NaAlg membrane, (b) 5% NaY-filled (CMC-g-AAm)/NaAlg membrane, (c) 10% NaY-filled (CMC-g-AAm)/NaAlg membrane, and (d) 15% NaY-filled (CMC-g-AAm)/NaAlg membrane.

the polymer and the incorporated moiety.²⁹ In PV experiments, membrane swelling is an important factor and controls the transport of permeating molecules under the chemical potential gradient. To study the effects of the feed composition and zeolite loading on the membrane swelling, the DS (%) data obtained from the swelling experiments at 30°C for (CMC-g-AAm)/NaAlg and 5, 50, and 15 mass % NaY-zeolite-filled (CMC-g-AAm)/NaAlg membranes, measured as a function of the mass percentage of water in the feed mixture, are displayed in Figure 4. Swelling kinetics depend on the mutual

diffusion of solvent molecules in response to polymer-chain relaxation processes.²⁴ In this study, the swelling increased with an increase in the loading of the zeolite particles. For instance, the swelling was higher for the 15% NaY-zeolite-filled (CMC-g-AAm)/NaAlg membrane than for the 10 and 5% zeolite-filled (CMC-g-AAm)/NaAlg and (CMC-g-AAm)/NaAlg membranes. These data further indicated that water molecules were sorbed preferentially and then diffused more easily through the hybrid mixed-matrix composite membranes than through the unfilled (CMC-g-AAm)/NaAlg

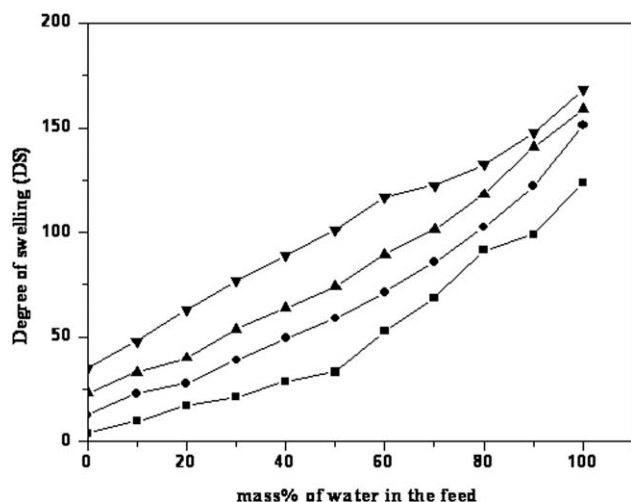


Figure 4 DS versus the mass percentage of water in the feed for (■) NaAlg/(CMC-g-AAm), (●) (CMC-g-AAm)/NaAlg-NaY, (▲) (CMC-g-AAm)/NaAlg-NaY (10 mass %), and (▼) (CMC-g-AAm)/NaAlg-NaY (15 mass %) membranes at 30°C.

membrane because of the availability of pores created by the zeolite particles. The efficiency of a membrane depends on its selectivity to the preferred liquid component, namely, water from the mixture, which depends on the extent of membrane swelling. The (CMC-g-AAm)/NaAlg hybrid mixed-matrix composite membranes showed a higher degree of swelling than the unfilled (CMC-g-AAm)/NaAlg membrane because of their high hydrophilic interaction with water molecules.

When the polymer matrices were filled with NaY-zeolite, DS increased more than that of the virgin membrane. This effect became almost linear when the zeolite content in the membrane was increased and is clearly seen in Figure 4. This may have been due to the fact that zeolite had cationic particles in its cages, which tended to cause a greater electrostatic force of attraction between the water molecules and membranes. As a result, the adsorption of water molecules increased remarkably, and this, in turn, became responsible for the enhanced swelling with an increase of zeolite content in the membrane.

PV studies

Effect of zeolite-NaY on the membrane performance

The PV separation data calculated in terms of flux and selectivity of all of the membranes for water and IPA feed mixtures containing 10–50 mass % water are summarized in Table I. The flux and selectivity results of the zeolite-NaY hybrid composition membranes increased systematically with increased loading of zeolite-NaY into the (CMC-g-AAm)/NaAlg, respectively. The membranes were quite sta-

ble up to a 15% zeolite-NaY loading, and hence, this study was limited to the addition of up to 15 mass % zeolite-NaY particles in the (CMC-g-AAm)/NaAlg matrix. The observed increase in selectivity was attributed to polymer-filler contact and adhesion. By comparison with the PV performances of the (CMC-g-AAm)/NaAlg membrane, we found that the (CMC-g-AAm)/NaAlg membrane containing 15% zeolite particles exhibited improved PV performance over that of the (CMC-g-AAm)/NaAlg membrane and other (CMC-g-AAm)/NaAlg hybrid mixed-matrix composition membranes with lower loadings of zeolite-NaY. The permeation flux data of all of the (CMC-g-AAm)/NaAlg hybrid mixed-matrix composition membranes increased more than that of the unfilled (CMC-g-AAm)/NaAlg membrane with increasing amount of water in the feed mixture. This indicated that after the addition of zeolite-NaY (5 and 10% only) particles into the (CMC-g-AAm)/NaAlg matrix, the separation characteristics of the membranes improved considerably over those of the unfilled (CMC-g-AAm)/NaAlg membrane.

In this investigation, both the permeation flux and selectivity values increased simultaneously with increasing amount of zeolite-NaY in the (CMC-g-AAm)/NaAlg matrix, a phenomena that is more desired in PV separation. This was mainly possible

TABLE I
PV Results of the NaY-Zeolite-Filled (CMC-g-AAm)/NaAlg Mixed-Matrix Membranes in the Water and IPA Mixtures

Sample	Water in the feed (mass %)	J ($\text{kg m}^{-2} \text{h}^{-1}$)	α_{PV}	Water in the permeate (mass %)
(CMC-g-AAm)/NaAlg blend membrane				
1	10	0.211	29991	99.97
2	20	0.264	13329	99.97
3	30	0.314	7770	99.96
4	40	0.361	2998	99.95
5	50	0.449	1249	99.92
NaY (5 mass %)-filled (CMC-g-AAm)/NaAlg membrane				
1	10	0.223	44991	99.98
2	20	0.291	19996	99.98
3	30	0.354	7775	99.97
4	40	0.442	2998	99.95
5	50	0.522	1427	99.93
NaY (10 mass %)-filled (CMC-g-AAm)/NaAlg membrane				
1	10	0.251	∞	100.00
2	20	0.324	∞	100.00
3	30	0.404	11,664	99.98
4	40	0.501	3,748	99.96
5	50	0.549	1,665	99.94
NaY (15 mass %)-filled (CMC-g-AAm)/NaAlg membrane				
1	10	0.268	∞	100.00
2	20	0.349	∞	100.00
3	30	0.4211	∞	100.00
4	40	0.526	7,498	99.98
5	50	0.572	2,499	99.96

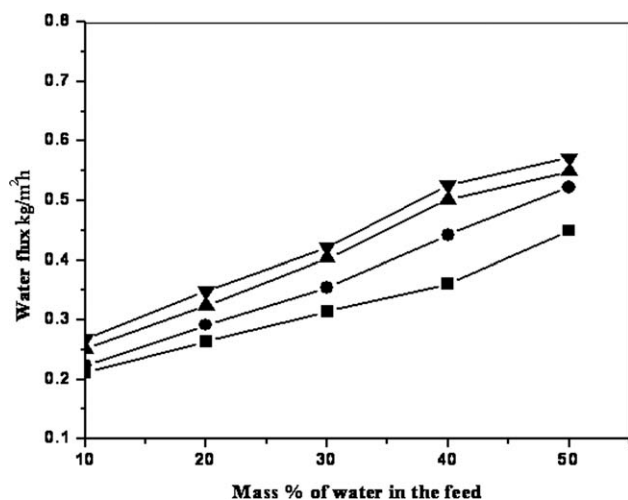


Figure 5 Water flux versus mass percentage of water in the feed for (■) NaAlg/(CMC-g-AAm), (●) (CMC-g-AAm)/NaAlg-NaY (5 mass %), (◄) (CMC-g-AAm)/NaAlg-NaY (10 mass %), and (►) (CMC-g-AAm)/NaAlg-NaY (15 mass %) membranes at 30°C.

because of the hydrophilic-hydrophilic interactions between the polymer and the filler, which further enhanced the hydrophilicity of the (CMC-g-AAm)/NaAlg hybrid mixed-matrix composition membranes. Additionally, the presence of zeolite-NaY particles would have created the free-volume channels throughout the matrix and, thus, preferentially allowed water molecules to transport through the membrane because of increased permeation flux.

Effect of the feed composition

The flux and selectivity results of this investigation are displayed in Table I. The flux of the (CMC-g-AAm)/NaAlg membrane increased from 0.211 to 0.449 kg m⁻² h⁻¹ for feeds containing 10–50 mass % water. With increasing water content of the feed mixture from 10 to 50 mass %, the selectivity of the (CMC-g-AAm)/NaAlg membrane decreased from 29,991 to 1249. Parallel to this effect, the mass percentage of water in the permeate also decreased from 99.97 to 99.92%. The increase in flux with increasing amount of water in the feed was attributed to the plasticization effect of the membrane due to membrane swelling. On the other hand, the PV performance of (CMC-g-AAm)/NaAlg was improved by the addition of different amounts of zeolite-NaY particles (i.e., 5, 10, and 15 mass %). For instance, the flux for the 5 mass % NaY-filled (CMC-g-AAm)/NaAlg membrane increased from 0.223 to 0.522 kg m⁻² h⁻¹, whereas for the 10 mass % NaY-filled (CMC-g-AAm)/NaAlg membrane, it further increased from 0.251 to 0.549 kg m⁻² h⁻¹ with increasing amount of water in the feed from 10

to 50 mass %. In the case of the 15 mass % NaY-filled (CMC-g-AAm)/NaAlg membrane, the flux increased from 0.268 to 0.572 kg m⁻² h⁻¹ (Table I and Fig 5).

The amount of water removed on the permeate side in the case of the 5 mass % NaY-filled (CMC-g-AAm)/NaAlg membrane ranged between 99.98 and 99.93%, whereas for the 10 mass % NaY-filled (CMC-g-AAm)/NaAlg membrane, it ranged between 100 and 99.94%. On the other hand, for the 15 mass % NaY-filled (CMC-g-AAm)/NaAlg membrane, the amount of water extracted in the permeate side was quite high, that is, it ranged between 100 and 99.96% over the studied water compositions of the feed mixtures. This was due to the increased hydrophilicity of the hybrid mixed-matrix composite (CMC-g-AAm)/NaAlg membrane in the presence of hydrophilic zeolite-NaY particles. The significant enhancement of hydrophilicity, selective adsorption, and molecular sieving action overcame the situation by introducing porous zeolite-containing ionic particles into the membrane matrix. Moreover, these particles might have occupied the free-volume spaces in the (CMC-g-AAm)/NaAlg matrix; otherwise, they would have been held by the hydroxyl groups of the (CMC-g-AAm)/NaAlg polymer. The free volume inside the membrane matrix could have been in the form of static holes (unfilled spaces) or could have been created or destroyed as a result of molecular motions (dynamic free volumes) in the polymer network or in the form of connected free volumes known as *pores*. Principally, there are two mechanistic models that can influence the PV results: (1) the solution-diffusion model and (2) the

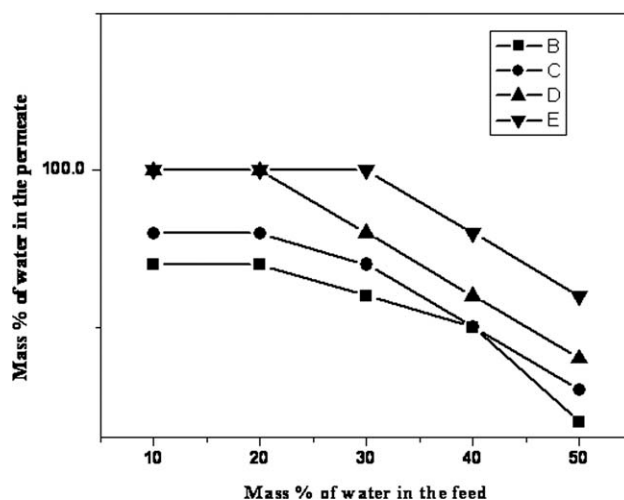


Figure 6 Mass percentage of water in the permeate versus mass percentage of water in the feed for (■) NaAlg/(CMC-g-AAm), (●) (CMC-g-AAm)/NaAlg-NaY (5 mass %), (◄) (CMC-g-AAm)/NaAlg-NaY (10 mass %), and (►) (CMC-g-AAm)/NaAlg-NaY (15 mass %) membranes at 30°C.

TABLE II
Comparison of the PV Performance Data of the Crosslinked Blend Membranes with Literature Data for Water and IPA Mixtures at 30°C

Membrane	Water in the feed (mass %)	J (kg m ⁻² h ⁻¹)	α_{PV}	Reference
5 mass % NaY-zeolite-filled NaAlg/(CMC-g-AAm)	10	0.223	44,991	This study
10 mass % NaY-zeolite-filled NaAlg/(CMC-g-AAm)	10	0.251	∞	
15 mass % NaY-zeolite-filled NaAlg/(CMC-g-AAm)	10	0.268	∞	
NaAlg/(guar gum-g-AAm) (75 : 25)	10	0.062	711	29
NaAlg/(guar gum-g-AAm) (50 : 50)	10	0.123	891	
5 mass % NaY-zeolite-filled NaAlg	10	0.1419	191	30
15 mass % NaY-zeolite-filled NaAlg	10	0.1607	210.51	
30 mass % NaY-zeolite-filled NaAlg	10	0.2325	272.25	
5 mass % Na ⁺ MMT zeolite-filled NaAlg	10	0.038	∞	31
10 mass % Na ⁺ MMT zeolite-filled NaAlg	10	0.050	∞	

Na⁺-MMT, sodium montmorillonite.

pore-flow model. The former model is widely accepted. Hence, these PV results were more appropriately explained by the solution-diffusion concepts. With increasing concentration of zeolite-NaY, the (CMC-g-AAm)/NaAlg membrane tended to absorb an increasing amount of water because of a higher adsorption of water molecules in the porous structure of the zeolite-NaY particles. Hence, the uptake of water by the membrane was enhanced. The flux increased because of an increase in the driving force of permeation in addition to a faster desorption rate at the permeate side. The effect was more favorable for water transport because water molecules occupied most of the free channels in the hydrophilic clay region of the composite membranes.

This further justified the marked increase in selectivity to infinite with a recovery of 100 mass % of water on the permeate side for the composite membranes. The composite membrane of this study was, thus, highly water-selective, but small differences in the zeolite compositions led to high selectivity values. The mass percentage of water in the permeate versus the mass percentage of water in the feed is displayed in Figure 6. The decrease in selectivity in all of the membranes with increasing water content of the feed depended on the amount of NaY-zeolite filler added to (CMC-g-AAm)/NaAlg. For instance, the selectivity of the (CMC-g-AAm)/NaAlg and 5 mass % NaY-zeolite-filled (CMC-g-AAm)/NaAlg membranes decreased from 29,991 to 1249 and from 44,991 to 1427, respectively, with increasing feed water composition from 10 to 50 mass % water. The selectivities of the 15 mass % NaY-zeolite-filled (CMC-g-AAm)/NaAlg and 10 mass % NaY-zeolite-filled (CMC-g-AAm)/NaAlg membranes decreased from infinite to 2499 and from infinite to 1665, respectively, with increasing feed water composition from 10 to 50 mass % water. The composite membrane performance increased dramatically for the

dehydration of IPA with infinite selectivities to water. In this study, separation depended on the interaction between the polymer matrix and selectivity molecules in addition to filler particles (NaY), which had a the dual pore nature and hydrophilic functions that played independently within the membrane matrix. Moreover, these data depended on the percentage loading of NaY-zeolite into the (CMC-g-AAm)/NaAlg matrix and on the hydrophilic nature of NaY, which further interacted with the hydrophilic (CMC-g-AAm)/NaAlg matrix and, thus, increased its affinity to water molecules over the organic components because water is more polar than organic components.

Comparison of the PV results with the literature

In the literature, several reports are available on the successful dehydration of IPA by the PV technique. Table II compares the flux and selectivity data with literature data.³⁰⁻³² A comparison of all of the membranes was made under similar feed conditions. By comparison, we found that these membranes offered the highest selectivity and flux values for water, and hence, these could be effective in dehydrating IPA from aqueous streams.

CONCLUSIONS

We prepared novel hybrid composite membranes by incorporating NaY-zeolite in NaAlg/(CMC-g-AAm). These composite membranes showed a significant improvement in the membrane performance while separating water-IPA mixtures. An increase in the zeolite content in the membrane resulted in simultaneous increases in both the permeation flux and selectivity. This was explained on the basis of a significant increase in the hydrophilic character, selective adsorption, and molecular sieving action, including a reduction in the pore size of the

polymer matrix, as evidenced by a swelling study. This zeolite-based hybrid polymer composite is an attractive alternative over the conventional type of membrane because it provided better PV separation performance over the NaAlg/(CMC-g-AAm) membrane for the PV separation of aqueous-organic mixtures. The zeolite particles used here were interesting fillers for incorporation into hydrophilic polymers, such as NaAlg/(CMC-g-AAm), to develop hydrophilic PV hybrid composite membranes. The PV performance of the zeolite-filled membranes followed adsorption-diffusion-desorption principles. Because of the hydrophilic nature of the NaY particles, preferential water adsorption occurred; this hindered the transport of organic components from the feed streams through the zeolite portion of the matrix, in addition to the already existing small zeolite pores. These conditions were favorable for the adsorption of water and/or mobility of the absorbed molecules and led to increased selectivity. This work also demonstrated the possibility of achieving infinite selectivity to water from the feed mixture selected in this study. The hybrid composite membranes in this study were mechanically strong and were able to withstand PV conditions.

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