

Activated Charcoal-Loaded Composite Membranes of Sodium Alginate in Pervaporation Separation of Water-Organic Azeotropes

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ABSTRACT: Composite membranes of sodium alginate prepared by incorporating nanosized-activated charcoal particles were prepared and characterized for the extent of cross-linking, thermal stability, and mechanical strength properties using Fourier transform infrared, differential scanning calorimetry, and universal testing machine, respectively. The membranes were tested for pervaporation (PV) dehydration of isopropanol (IPA), ethanol (EtOH), 1,4-dioxane (1,4-D), and tetrahydrofuran (THF) at their azeotropic compositions. Improved PV performances of the composite membranes were observed compared with plain sodium alginate membrane for all the azeotropes. Sorption was studied to evaluate the extent of interactions between liquids and membranes as well as

degree of swelling of the membranes in the chosen aqueous-organic mixtures. Adding different amounts of activated charcoal into NaAlg offered high water selectivity values of 99.7, 99.1, 99.4, and 99.41%, respectively, for IPA, THF, 1,4-D, and EtOH. Arrhenius activation parameters were computed from the temperature versus flux plots, which showed systematic trends for different liquids that depended upon their interactions with membranes. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 966–975, 2009

Key words: pervaporation; sodium alginate; charcoal; composite membrane; azeotropic mixture; aqueous-organic mixtures

INTRODUCTION

Pervaporation (PV) separation is an effective method of utilizing polymeric membranes in separating azeotropes^{1–5} and its success mainly depends on the development of novel type of polymeric membranes that can effectively separate water from organics. Since the PV separation through membranes is controlled by physical structure and morphology of the membrane, physicochemical properties of the feed mixtures, feed liquids in addition to liquid-membrane interactions,⁶ for successful applications, PV membranes should offer high flux and selectivity in addition to long-term stability in the desired media to maintain their integrity throughout the PV experiments. To meet these criteria, many efforts have been made to develop novel type of membranes for use in the PV separation of water-organic mixtures.^{7–10} In continuation of our earlier research efforts, we present here PV data on the composite membranes prepared by incorporating nanosized-

activated charcoal particles into sodium alginate (NaAlg) matrix that has a porous structure with an ability to absorb more water selectively than organics. The membranes prepared were cross-linked in the presence of glutaraldehyde to form the homogeneous membrane structures for PV applications.¹⁰

The activated charcoal particles used here were chosen in view of their hydrophilic nature and the high-value carbon products (e.g., activated carbon, electrode carbon, etc.) can be produced from charcoal. Environmental black carbon (BC) refers to carbonaceous residues of incomplete burning of fossil fuels and the biomass (soot and charcoal or char).^{11,12} BC tends to absorb organics more than other forms of natural organic matter (e.g., humic acids, etc.), especially at low solute concentration. The structure of activated carbon (AC), which is manufactured in large quantities for water and air purification, consist of short stacks of small graphite-like sheets arranged in a highly disordered fashion to form poorly interconnected microporous network.^{13–15} Since chars are ordinarily formed in air, the functionalities are groups such as —OH, —COOH, C—O—, C=O, and —CHO. These groups potentially can undergo specific or nonspecific physisorption interactions with the absorbed molecules.

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Naturally occurring BCs vary significantly in carbon source, temperature, and partial pressure of O₂ during its formation^{16,17} and hence, they are likely to vary considerably in O₂ content and distribution of functionality.

In this work, we have selected activated charcoal as a filler to NaAlg to develop novel type of composite membranes that can be effectively used in the PV separation of water from the mixed media containing organics like 1,4-dioxane (1,4-D), isopropanol (IPA), ethanol (EtOH), and tetrahydrofuran (THF), which are the well-known industrial solvents and would form azeotropes with water at certain compositions. Their separation by conventional distillation would be prohibitively expensive and an entrainer like benzene or toluene is required to achieve the separation, making the process more environmentally hazardous. Therefore, in this study, we have employed the composite membranes of NaAlg to achieve the separation of water from the azeotropic mixtures of IPA, 1,4-D, EtOH, and THF by the PV process. The membrane performance was studied in terms of flux and selectivity under varying temperatures. Arrhenius parameters have been estimated and the results have been discussed in terms of the solution-diffusion anomalies. To the best of our knowledge, this is the first kind of the composite NaAlg membranes developed for use in PV dehydration of organics at their azeotropic compositions.

EXPERIMENTAL

Materials

Sodium alginate of high viscosity grade sample was purchased from s.d. fine chemicals, Mumbai, India. Charcoal was obtained from Sigma Aldrich Co. Solvents IPA, 1,4-D, THF, and glutaraldehyde (GA) were purchased from s.d. fine chemicals, Mumbai, India. EtOH was procured from Changshu Yangyuan Chemicals, China.

Membrane fabrication

Charcoal used was an anatase-type powder (PC-101, Japan), having a high-specific surface area of 450 m²/g with an average particle size of 100 nm. Polymer membranes were prepared by dispersing charcoal powder (1, 5, and 10 wt % with respect to weight of the polymer, i.e., 40, 200, and 400 mg) in NaAlg solution (4 g in 80 mL of water) by ultrasonication in about 20 mL of water for about 160 min. The dispersion was carried out using an ultrasonicator (Grant Ultrasonic Bath, UK) at output amplitude of 35 W for about 120 min at ambient temperature (30°C). The sonicated solution was dispersed in NaAlg solution. The blend solution was stirred for

about 24 h to obtain a homogeneous dispersion of charcoal particles in the membrane matrix. The resulting viscous slurry was cast onto a clean glass plate using doctor's blade (with a gap of 400 μm) in a dry atmosphere. The self-supporting films were easily obtained with thicknesses ranging from 60 to 65 μm for all compositions of the charcoal content. The prepared membranes contained 5 and 10 wt % of the filler.

Homogeneous nonporous composite membranes were prepared by casting the respective polymer solutions containing filler particles followed by drying at ambient temperature for about 48 h. These composites were cross-linked in a bath containing methanol-water (90/10 vol %) mixture with 1 wt % GA for about 180 min to make them insoluble in water and to control membrane swelling. After cross-linking, membranes were washed with water to remove traces of impurities and to prevent further cross-linking.

Membrane characterization

Fourier transmission infrared (FTIR) spectral studies

FTIR spectra were taken for NaAlg before and after cross-linking. Samples were scanned to confirm the cross-linking of NaAlg with calcium chloride in NaAlg matrix using Nicolet-740 and Perkin-Elmer-283B FTIR spectrophotometers. Membrane samples were ground well with KBr to make pellets under a hydraulic pressure of 400–450 kg/cm².

Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) spectra of the uncross-linked and cross-linked NaAlg as well as uncross-linked and cross-linked NaAlg-charcoal filled composite membranes were obtained using Rheometric Scientific (Model DSC-SP, UK). Measurements were done over the temperature range of 30 to 400°C at the heating rate of 10°C/min in hermetically sealed aluminum pans.

Scanning electron microscopic (SEM) studies

Scanning electron microscopic (SEM) photograph of the charcoal-loaded NaAlg membrane cross-linked with GA was taken. Membrane was sputtered with gold to make it conducting and placed on a copper stub. Scanning was done using Leica 400, Cambridge, UK.

Particle size measurement of activated charcoal filler particles

Particle size was measured by Zetasizer (Model 3000HS, Malvern, U.K.). Sizes of the completely dried

activated charcoal particles were measured by wet sample technique using a wet sample adapter. Particles were dispersed in water and placed on the sample couvette. The zeta average diameter was recorded. After measurement of particle size, the sample couvette was cleaned thoroughly to avoid any cross contamination. Triplicate measurements were taken and the average value was considered in data analysis and graphical display.

Mechanical properties

Mechanical properties of the cross-linked plain NaAlg and cross-linked activated charcoal-loaded NaAlg membrane strips were evaluated using the universal testing machine (UTM) (Hounsfield, UK), model H 25 KS, with an operating head load of 5 kN, following the procedure outlined in ASTM D-638 test method. Cross-sectional area of the sample of known width and thickness was calculated. Membrane strips were placed between grips of the testing machine. The grip length was 5 cm; while the speed of testing was set at 5 mm/min. Tensile strength was calculated using the following equation:

$$\text{Tensile Strength} = \frac{\text{Max Load}}{\text{Cross Sectional Area}} \quad (1)$$

Pervaporation experiments

PV experiments were performed on a 100-mL batch level instrument with an indigenously constructed manifold operated at a vacuum level as low as 0.05 mmHg in the permeate line. The effective membrane area was 20 cm² and weight of the feed mixture taken in the PV cell was 70 g. Temperature of the feed mixture was maintained constant by a thermostatic water jacket. Before starting the PV experiment, the test membrane was equilibrated for about 2 to 4 h with the feed mixture. After establishment of a steady state, permeate vapors were collected in cold traps immersed in liquid nitrogen for up to 4–5 h. Weight of permeate collected was measured on Mettler balance (model B 204-S, Greifensee, Switzerland: accuracy 10⁻⁴ g) to determine the flux, J (kg m⁻² h⁻¹) using the weight of liquids permeated, W (kg), effective membrane area, A (m²), and measurement time, t (h) as follows:

$$J = \frac{W}{At} \quad (2)$$

The analysis of feed and permeate samples was done using Nucon Gas Chromatograph (model 5765) provided with Thermal Conductivity Detector (TCD) equipped with a DEGS or Tenax packed column of 1/8" ID and 2 m in length. 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 0.75 kg/cm². The GC response was calibrated for the column and for known compositions of IPA, EtOH, 1,4-D, and THF mixtures at their respective azeotropic compositions with water. Calibration factors were fed into the GC software to obtain the analysis for unknown samples. The PV selectivity, α_{PV} and pervaporation separation index (PSI) were calculated as follows:

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

$$\text{PSI} = J_p(\alpha_{\text{sep}} - 1) \quad (4)$$

where F_A is mass % of water in feed and P_A is mass % of water in permeate. A minimum of three independent measurements of flux and α_{PV} were taken under similar conditions of temperature and feed compositions to confirm the steady-state PV. The PV setup is the same as described earlier.^{11,18}

Sorption studies

To assess the interactions of the membranes with liquid penetrant molecules, the weighed samples of circularly cut membrane pieces (3 cm dia) have been soaked in water-IPA, water-EtOH, water-THF, and water-1,4-D mixtures at their respective azeotropic compositions. Membranes were weighed accurately (± 0.1 mg), kept in different soaking mixtures, and removed after 48 h by carefully blotting off the surface-adhered excess liquid droplets to estimate accurately the amount of liquid mixture sorbed at time, t . The % sorption was calculated as follows:

$$\text{Sorption (\%)} = \left(\frac{W_s - W_d}{W_d} \right) \times 100 \quad (5)$$

where W_s is weight (g) of the swollen membrane, and W_d is weight (g) of the dried membrane.

RESULTS AND DISCUSSION

Incorporation of activated charcoal as a filler into NaAlg matrix has resulted in improved membrane PV performance due to the formation of a dense homogeneous composite structure having good chemical stability as judged after keeping the membranes in soaked liquid solutions at ambient temperature (30°C) for up to 2–3 months. The membranes were thus stable as noted by mechanical strength data, which were restored upon bending the membranes and the membranes have reserved the PV performances even after bending. Morphological study of

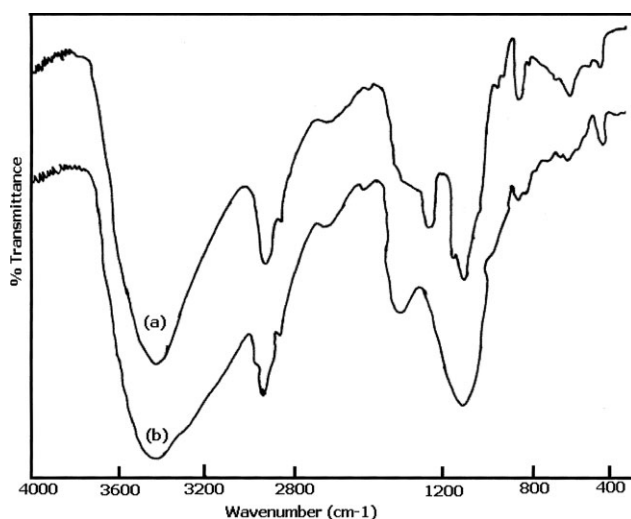


Figure 1 Tracings of FTIR of (a) cross-linked NaAlg and (b) uncross-linked NaAlg membranes.

the membranes was also done to ascertain uniform distribution of charcoal particles in the NaAlg matrix. The charcoal incorporated composite membranes were tested for sorption properties in water, IPA, EtOH, THF, 1,4-D, as well as in their binary mixtures at their respective azeotropic compositions to check for their suitability in PV experiments.

Membrane characterization

Fourier transform infrared spectral studies

Figure 1 shows the FTIR tracings for NaAlg-charcoal composite membranes before and after cross-linking. It can be seen that hydroxyl groups of NaAlg interacted with aldehydic groups of GA, resulting in the formation of acetal linkages (C—O—C). From the spectra of NaAlg-loaded charcoal, the formation of a peak at 1158 cm^{-1} suggests the successful cross-linking of composite NaAlg membrane with GA. Compared with the uncross-linked NaAlg membrane, the decrease in peak intensity around 3200 cm^{-1} for cross-linked membrane is due to the utilization of —OH groups to form the acetal linkage with GA during cross-linking reaction as can be seen in Figure 1 curves (a) and (b).

Differential scanning calorimetry

Noting the DSC curves of the composite membranes displayed in Figure 2, one can observe that the curve for uncross-linked NaAlg exhibits an endotherm with an onset at 60°C with a peak around 50°C due to melting. This endotherm has shifted to higher temperature in case of NaAlg-charcoal-loaded cross-linked membranes to about 100°C , indicating that ordered association of NaAlg chains has increased due to cross-linking in the presence of charcoal particles.

Scanning electron microscopy

Figure 3 shows the SEM morphology of NaAlg-charcoal-loaded versus unloaded membranes. For instance, in Figure 3(b), we can see that charcoal particles are distributed in the NaAlg matrix compared with the plain NaAlg membrane shown in Figure 3(a).

Particle size analysis

By measuring the particle size of activated charcoal in nonsolvent media, size of the particles was around 100 nm as can be observed from the histogram plot of Figure 4.

Mechanical properties

Tensile strength data of cross-linked plain NaAlg, charcoal-loaded NaAlg-charcoal-1%, NaAlg-charcoal-5%, and NaAlg-charcoal-10% composite membranes were presented in Table I. Of the four membranes tested, NaAlg-charcoal-10% exhibited highest tensile strength of 7.97 MPa . Consequently, tensile strength of NaAlg-charcoal-5% was smaller than NaAlg-charcoal-10% membrane, but that of cross-linked plain NaAlg showed the least tensile strength of 3.83 MPa . These data suggest that after addition of activated charcoal to NaAlg, the mechanical strengths of the composite NaAlg membranes were improved due to cross-linking between NaAlg chains. The tensile strengths of the membranes followed the trend: NaAlg-charcoal-10% > NaAlg-charcoal-5% > NaAlg-charcoal-1% > cross-linked plain NaAlg. Increased mechanical strength of the charcoal-reinforced NaAlg is the result of favorable

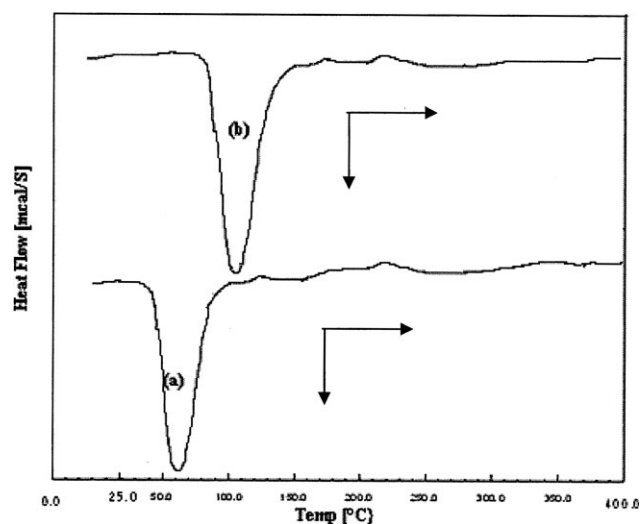


Figure 2 DSC curves of (a) uncross-linked NaAlg and (b) NaAlg-charcoal-loaded cross-linked membranes.

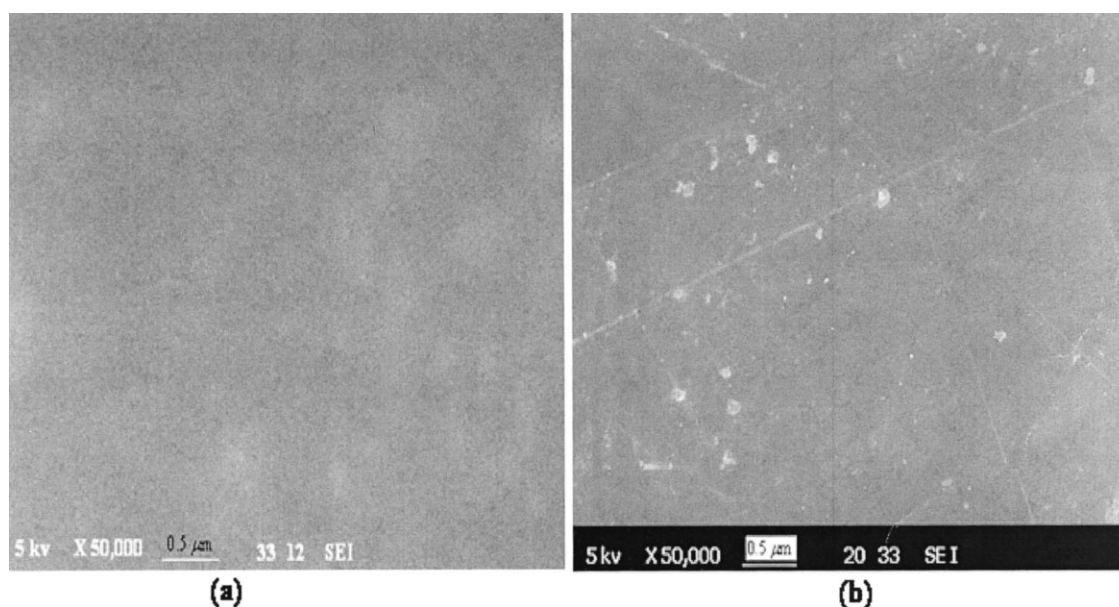


Figure 3 SEM Image of (a) plain NaAlg and (b) 5 wt % loaded NaAlg membranes.

physicochemical interactions between charcoal particles and the NaAlg matrix.

Effect of swelling

PV performance is influenced by the extent of membrane swelling that helps in absorbing water from the water-organic mixture due to hydrophilic interactions.¹⁹ However, the extent of swelling also determines the extent of water removal in a selective manner. It is also to be noted that the swelling should not be extensive enough to allow the membrane structure to rupture due to the aggressive nature of the organic component of the mixed media. Fig-

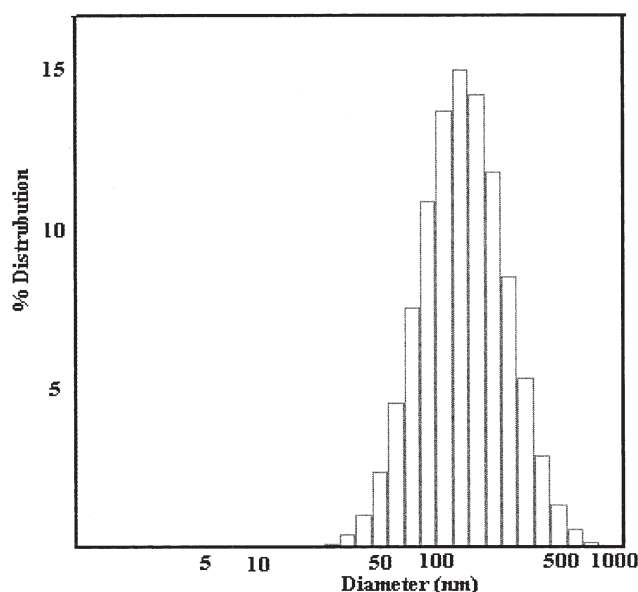


Figure 4 Histogram of activated charcoal particles.

ure 5 demonstrates % degree of swelling of NaAlg-charcoal composite membranes at 30°C for all the mixtures at azeotropic compositions. With increasing amount of charcoal in the NaAlg matrix, % degree of swelling also increased due to higher water uptake capacity of the combined effect of NaAlg as well as the activated charcoal particles. It can be seen from Figure 5 that membrane swelling depends upon the nature of the organic component of the azeotrope. For instance, with dipolar aprotic solvents like THF or 1,4-D, extent of swelling is higher than either polar solvents like IPA or EtOH for all composite NaAlg membranes. NaAlg itself is a hydrophilic polymer and after incorporating it with charcoal particles, the derived composite membranes have attained higher stability due to the intercalation of charcoal particles inside the interstices of NaAlg segments. This has further increased the hydrophilicity of NaAlg. Particularly, the optimum amount of 10 wt % of activated charcoal when incorporated into NaAlg matrix, we observed that extent of swelling has increased due to increased hydrophilic-hydrophilic interactions in the presence of higher amount of charcoal. Close inspection of the swelling data with reference to PV results indicate that water

TABLE I
Tensile Strength Properties of the Plain cross-linked NaAlg and Composite Membranes of NaAlg

Membrane type	Tensile strength (MPa)
Plain cross-linked NaAlg	3.83
NaAlg-charcoal-1	4.41
NaAlg-charcoal-5	5.34
NaAlg-charcoal-10	7.97

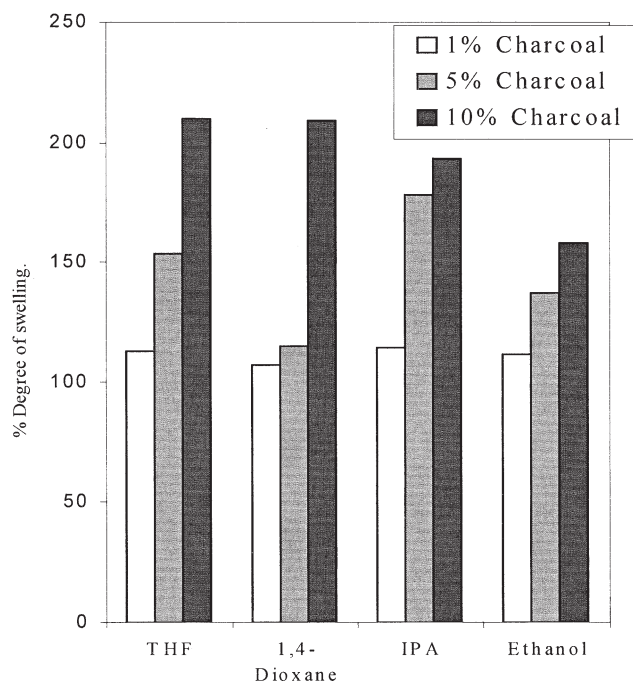


Figure 5 % Degree of swelling of activated charcoal-loaded NaAlg membrane at azeotropic mixtures of THF, 1,4-dioxane, IPA, and ethanol with water at 30°C.

selectivity decreased with increased flux for THF or 1,4-D containing mixtures, whereas a reverse trend is observed for IPA or EtOH containing mixtures.

Figure 6 shows the temperature effect (30, 40, and 50°C) on the extent of swelling of NaAlg-charcoal-10% membrane. As the temperature increased, swelling also increased. From Figure 7, it is observed that PSI values increased monotonically with increasing amount of activated charcoal in the membranes for all the aqueous-organic mixtures, signifi-

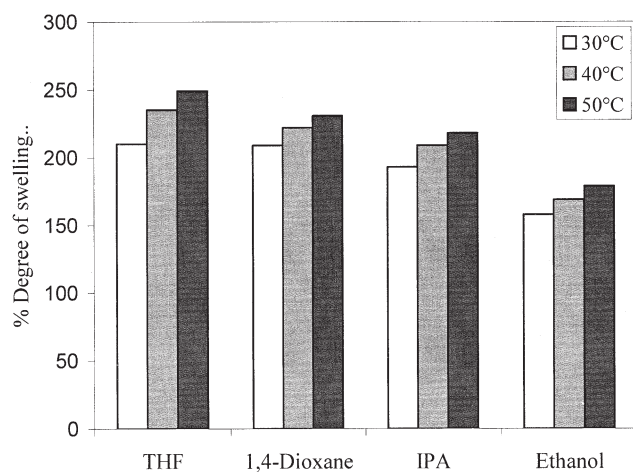


Figure 6 % Degree of swelling of activated charcoal-loaded NaAlg membrane at azeotropic composition of THF, 1,4-dioxane, IPA, and ethanol with water at 30, 40, and 50°C.

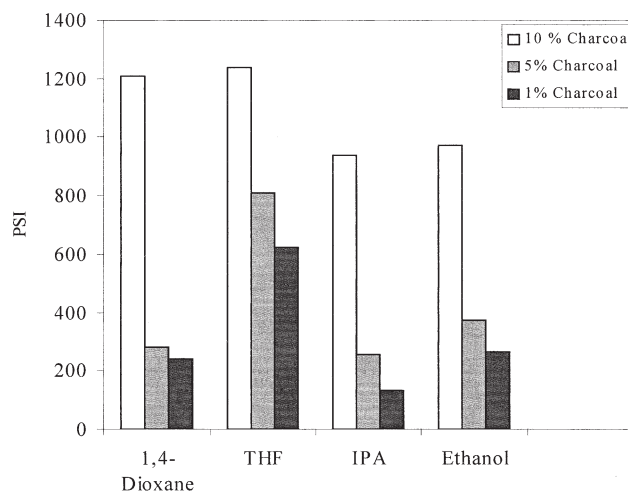


Figure 7 Pervaporation separation index (PSI) for different wt % activated charcoal-loaded NaAlg membrane.

ing that membranes incorporated with higher amount of activated charcoal showed improved PV performances, a trend that is similar to swelling data.

Effect of charcoal loading and azeotropic (Feed) composition on PV

Both extent of charcoal loading and azeotrope composition of the mixtures affected the PV results. However, our aim was not to investigate the effect water composition systematically as done before,^{11,18} but instead to obtain PV results at the azeotropic compositions of the chosen mixtures with an aim to assess the potentiality of PV technique in separating the azeotropes. Hence, results of this study are discussed in terms of improvements in flux and selectivity data of the composite membranes over that of the plain NaAlg membrane for the selected azeotropes. All the azeotropes have thermodynamically different values of azeotropic compositions and hence, our results cannot be compared directly with respect to varying feed water compositions. For instance, in case of water-IPA mixture, azeotrope exists at 12.5 wt % of water and for this mixture, all the membranes have shown higher values of selectivity with lower fluxes compared with 1,4-D azeotrope. On the other hand, azeotrope of THF has exhibited somewhat higher values of flux and selectivity compared 1,4-D azeotrope. With EtOH azeotrope, flux is lowest and selectivity is highest for all the membranes. In all the composite membranes, with increasing amount of charcoal loading, selectivity values increased, but fluxes varied depending upon the nature of the organic liquid (Table II) and are shown in Figure 11 and Figure 12 respectively.

In all the cases, water molecules interacted more favorably when compared with organic molecules

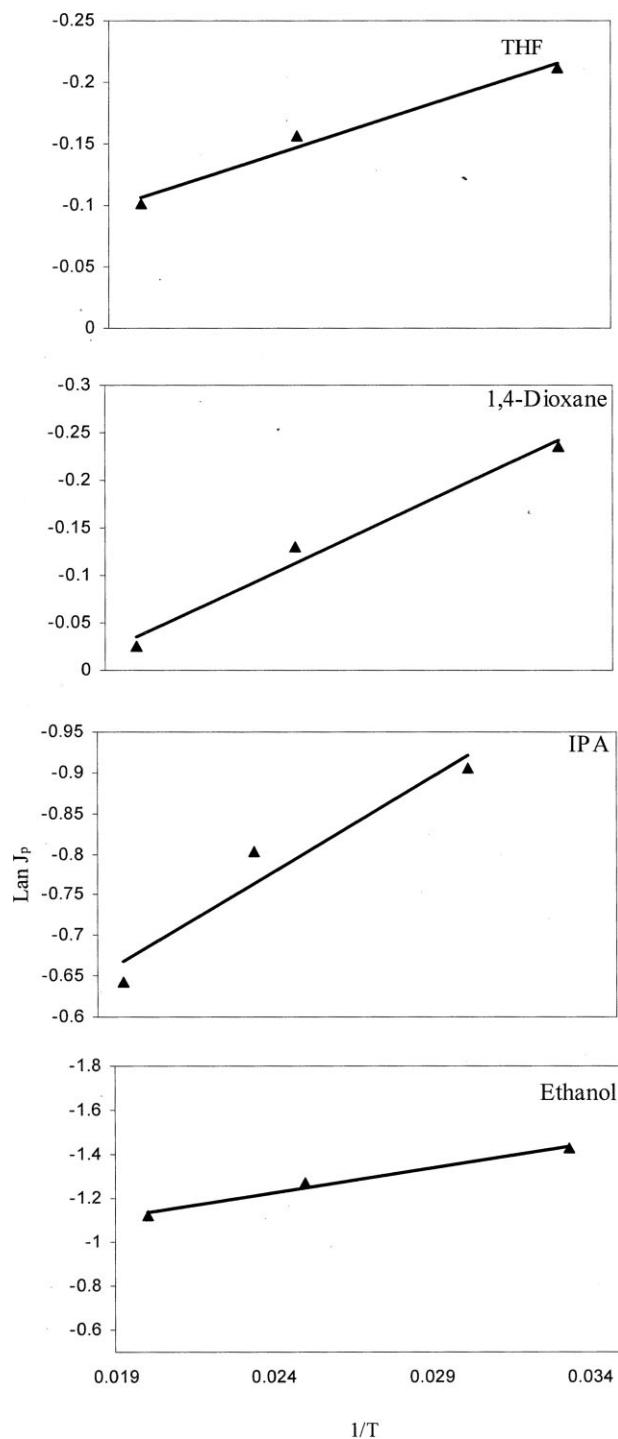


Figure 8 Archery plots of flux, i.e., in J_p versus $1/T$.

with NaAlg as well as the filler-loaded composite NaAlg membranes. A selectivity of 2326 for the azeotropic of IPA and a flux of $0.41 \text{ kg/m}^2 \text{ h}$ was observed for NaAlg-charcoal-10 membrane. Selectivities of 693, 382 and fluxes of 0.37 , $0.35 \text{ kg/m}^2 \text{ h}$ were observed for NaAlg-charcoal-5 and NaAlg-charcoal-1 membranes, respectively. In case of EtOH, selectivity values were 4044, 1976, 1822 and fluxes were 0.24 , 0.19 , and $0.14 \text{ kg/m}^2 \text{ h}$, respectively, for NaAlg-charcoal-10, NaAlg-charcoal-5, and

NaAlg-charcoal-1 membranes. For the azeotrope of THF, selectivity values were 1533, 1057, 856, whereas fluxes were 0.81 , 0.77 , $0.73 \text{ kg/m}^2 \text{ h}$ for NaAlg-charcoal-10, NaAlg-charcoal-5, and NaAlg-charcoal-1 membranes, respectively. Similar trends are observed for the azeotrope containing 1, 4-D. For instance, selectivity were 773, 403, 373 and fluxes were 0.79 , 0.70 , $0.65 \text{ kg/m}^2 \text{ h}$ for NaAlg-charcoal-10, NaAlg-charcoal-5, and NaAlg-charcoal-1 membranes, respectively. The membranes of this study were evaluated for water/organic azeotropic

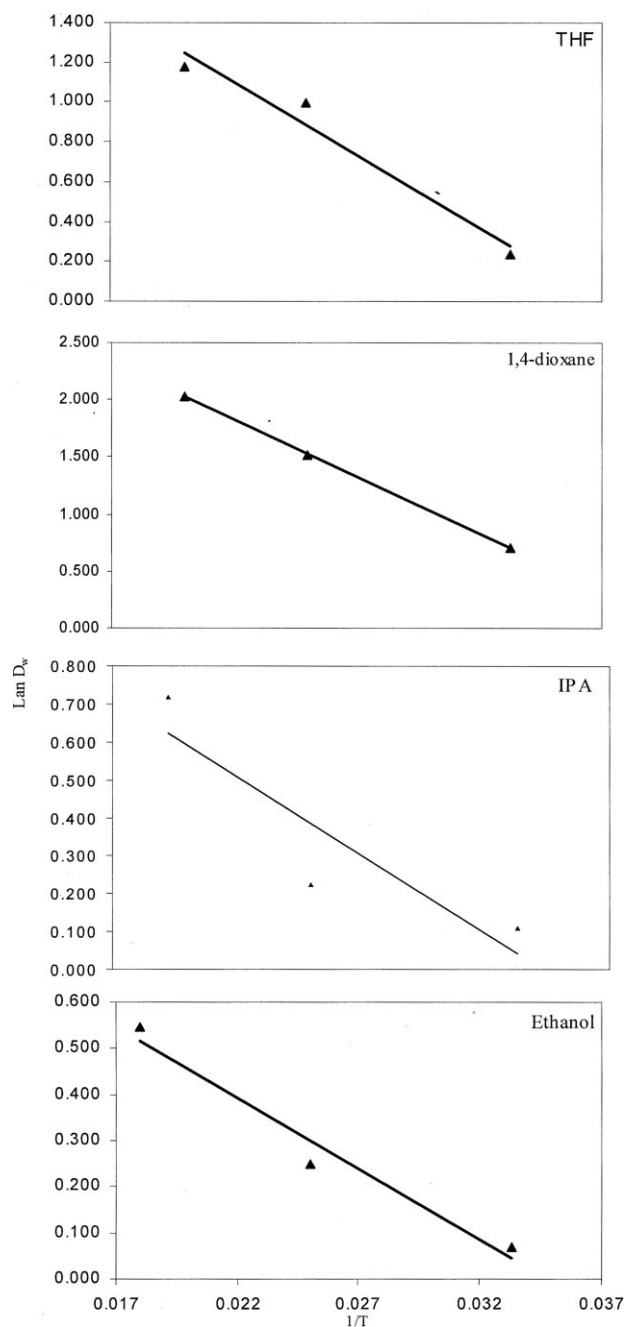


Figure 9 Diffusion coefficients of aqueous organic mixtures at their azeotropic compositions.

TABLE II
Selectivity and Flux Data of the Membrane at 30°C

Wt % Charcoal loading	Flux (kg/m ² h)	Selectivity
THF		
Plain NaAlg	0.05	300
1	0.73	856
5	0.77	1057
10	0.81	1533
1,4-Dioxane		
Plain NaAlg	0.15	190
1	0.65	373
5	0.70	403
10	0.79	773
IPA		
Plain NaAlg	0.04	360
1	0.35	382
5	0.37	693
10	0.41	2326
Ethanol		
Plain NaAlg	0.02	770
1	0.14	1822
5	0.19	1976
10	0.24	4044

separation and these results are much better than those observed for plain NaAlg membrane.

Diffusion coefficient

Transport of binary liquid mixtures through PV membranes can be explained by solution-diffusion mechanism, which occurs in three steps: sorption, diffusion, and evaporation. Permeation rates and selectivity are governed by solubility and diffusivity of the component of feed mixture to be separated. It is, therefore, important to estimate diffusion coefficient, D_i of the penetrating molecules to understand about the transport mechanism. Fick's first law of diffusion equation can be used to compute diffusion coefficient as follows:

$$J_i = -D_i \left(\frac{dC_i}{dx} \right) \quad (6)$$

where J_i is permeation flux per unit area (kg/m² s), D_i is diffusion coefficient (m²/s), C is concentration of the permeate (kg/m³), subscript i stands for water or organic, and x is the diffusion path length. For simplicity, it is assumed that the concentration profile along the diffusion pathway is linear and hence, concentration-independent D_i can be calculated as follows:

$$D_i = \frac{J_i h}{C_i} \quad (7)$$

where h is membrane thickness. Calculated values of D_i at different temperatures for different membranes are presented in Table III. Similar to PV results, diffusion coefficients of water and organics increased

TABLE III
Diffusion Coefficients of Water and Organics at Different Temperatures for 10 wt % of Water in Feed Mixture in NaAlg-charcoal-10 Membranes

Temperature (°C)	$D_w \times 10^{11}$ (m ² /s)	$D_o \times 10^{14}$ (m ² /s)
THF		
30	2.02	2.20
40	4.57	2.40
50	7.62	2.80
1,4-Dioxane		
30	1.27	2.50
40	2.71	3.30
50	3.25	3.60
IPA		
30	0.34	1.20
40	1.25	1.40
50	2.05	1.80
Ethanol		
30	0.39	1.10
40	0.94	1.30
50	1.72	1.60

with increasing temperature, due to increased segmental movements at higher temperatures, thereby leading to increased diffusivity. Diffusion coefficients of water increased with increasing temperature from 30 to 50°C, but those of the organic solvents increased to a smaller extent.

Effect of temperature

The effect of temperature on PV performance was studied typically for NaAlg-charcoal-10 membranes for 10 wt % water containing feed; the resulting flux values are shown in Figure 10. It is observed that flux increased with increasing temperature. The temperature dependency of permeation and diffusion for water were calculated using Arrhenius equation as follows:

$$X = X_o \exp\left(\frac{-E_x}{RT}\right) \quad (8)$$

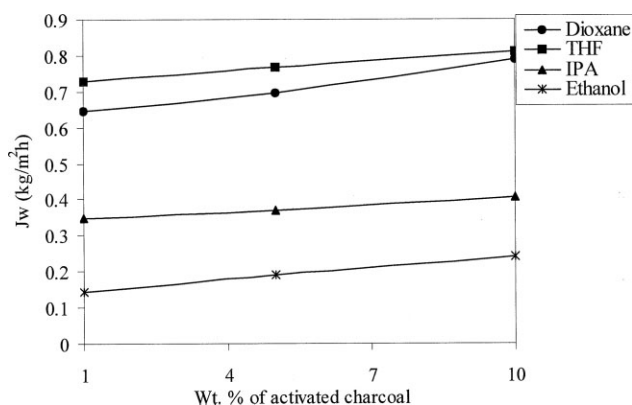


Figure 10 Effect of wt. % of activated charcoal loading on flux.

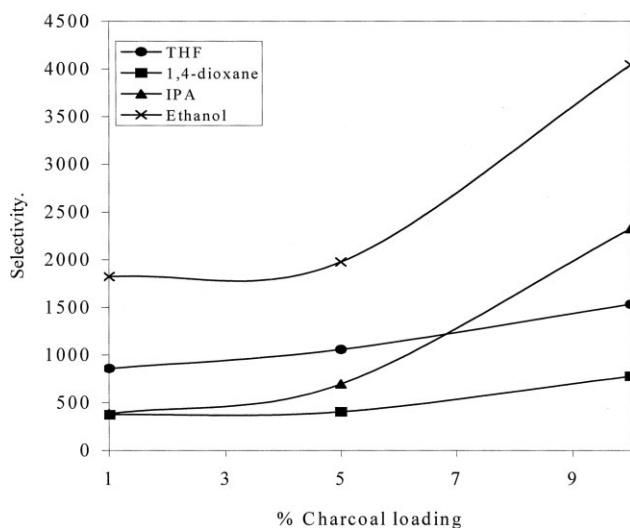


Figure 11 Effect of wt. % of activated charcoal loading on selectivity.

where X represents the diffusion coefficient (D) or permeation flux (J_p), X_o is a constant representing the pre-exponential factor of D_o or J_o , and E_x represents activation energy for permeation or diffusion, depending upon the transport process under consideration and RT is the usual energy term. As the feed temperature increases, vapor pressure in the feed compartment also increases, but vapor pressure on permeate side is not affected. This would result in increased driving force.

Arrhenius plots of $\ln J_p$ versus $1/T$ and $\ln D$ versus $1/T$ shown, respectively, in Figures 8 and 9 for flux and diffusion exhibited linear behaviors, suggesting that permeability and diffusivity follow the Arrhenius trend. From the least squares fit of these linear plots, the activation energies for permeability (E_J) and diffusivity (E_D) were estimated and the results presented in Table IV indicating that EtOH-water mixture has higher E_J values than other mix-

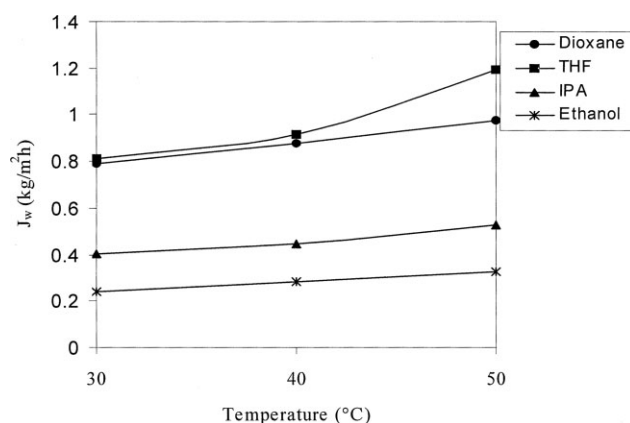


Figure 12 Diffusion coefficients of aqueous-organic mixtures at their azeotropic compositions.

TABLE IV
Arrhenius Activation Parameters for Permeation, Diffusion, and Heat of Sorption and Energy Difference Values for Water

Parameters	THF	1,4-Dioxane	IPA	Ethanol
E_J (kJ/mol)	8.15	15.48	19.1	22.7
E_D (kJ/mol)	72.56	99.41	41.2	30.8
ΔH_s (kJ/mol)	-69.86	-85.23	-23.2	-7.79

tures, suggesting that both permeating and diffusing molecules require higher energy for the transport to take place through the membrane.

In all cases, E_D values are higher than those of E_J values, yet the difference is not much, indicating that both permeation and diffusion almost equally contribute to the PV process. The E_J and E_D values ranged from 8.15–22.7 kJ/mol and 30.8–99.41 kJ/mol, respectively. Using these values, we have calculated the heat of sorption as follows:

$$\Delta H_s = E_J - E_D \quad (9)$$

The resulting ΔH_s values included in Table IV give information on the transport mechanism of liquids through the membrane, since it involves contributions from Henry's and Langmuir's type sorption. Henry's law states that heat of sorption is positive for liquid transport thereby, leading to the dissolution of chemical species into that site within the membrane, giving an endothermic contribution to sorption process. On the other hand, Langmuir's sorption requires the pre-existence of a site in which sorption occurs by hole filling, giving an exothermic contribution. In this study, ΔH_s values are negative for all membranes, suggesting that Langmuir's sorption is predominant with an endothermic contribution.

CONCLUSIONS

Composite membranes of sodium alginate have been developed by incorporating nanosized-activated charcoal particles. The composite membranes showed significant improvements in their performances over that of plain sodium alginate membrane in terms of flux and selectivity for all mixtures of this study at their azeotropic compositions. The membrane performance was studied in terms of % loading of activated charcoal as well as the nature of liquid organic molecules. Of all the membranes studied, NaAlg-charcoal-10 membrane, i.e., membrane with highest loading of charcoal showed highest selectivity and lowest flux data for all the aqueous-organic azeotropic mixtures. From the analysis of the data, the results of E_J and E_D indicate that both diffusion and permeation processes contribute toward the PV separation process. For all composite membranes,

Langmuir's mode of sorption seems to dominate the transport process, giving an exothermic contribution. The authors are thankful to University Grants Commission, New Delhi for funding to establish Center of Excellence in Polymer Science at Karnatak University, Dharwad during the period 2002-2007.

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