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Pervaporation Separation Using Sodium Alginate and Its Modified Membranes—A Review

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Abstract: Sodium alginate (NaAlg) and its modified forms have been widely used as membranes in pervaporation (PV) separation of aqueous-organic solutions because of the hydrophilic nature and versatility to modify/tune their structures to achieve the desired separation. A survey of the literature indicates that in recent years, NaAlg-based membranes have been reported to perform outstanding separation characteristics in dehydrating the aqueous-organic mixtures. In view of the availability of extensive data on the PV performance of NaAlg and its modified membranes, particularly in separating water-organic mixtures, we thought of compiling the available literature PV data on NaAlg membranes with an aim to assess their performances over other membranes. The present review addresses the application of PV technique using NaAlg membranes for dehydration of organic liquids of different kinds. Literature data on NaAlg-based membranes such as grafted NaAlg, blends of NaAlg, hybrid composites of NaAlg and mixed matrix membranes of NaAlg are widely scattered. Hence, this review compiles and critically evaluates such data. Literature data on modified NaAlg including blends, grafts, filled matrices, composites, etc., are discussed with respect to a variety of aqueous-organic mixtures. Factors such as effect of feed composition, membrane swelling, flux and selectivity are assessed with reference to solvents like ethanol, isopropanol, tetra-hydrofuran, 1,4-dioxane, acetic acid, and acetonitrile.

Keywords: Sodium alginate, membranes, pervaporation

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INTRODUCTION

Natural polysaccharides are among the most widely used biopolymers for various applications and also in developing membranes for pervaporation (PV) separation applications (1–11). Among the various natural polymers, sodium alginate (NaAlg) is a widely used water-soluble polysaccharide, next to chitosan, due to its good membrane forming properties. It can be readily cross-linked with glutaraldehyde or Ca^{2+} ions, etc., to form a stable membrane. It is a linear chain structure of (1-4)-linked β-D-mannuronic acid (M) and α-L-guluronic acid (G) residues arranged in a blockwise fashion. Its chemical structure is shown in Figure 1. These blocks are constructed in three different ways: homopolymeric MM blocks, homopolymeric GG blocks and heteropolymeric sequentially alternating MG blocks (12, 13). The presence of α-L-guluronic acid in various ratios and molecular weights alters the physicochemical properties of the polymer (14). NaAlg has been widely studied as a membrane due to its potential to dehydrate organic-aqueous solutions. Sometimes its performance exceeds those of poly(viny1 alcohol) (PVA) (15), ion-exchange resins (16) and other polysaccharides, such as chitosan (17) and cellulose (18). Therefore, NaAlg has been very popular as a membrane in PV dehydration studies of organic liquids.

Among many separation and purification technologies available in the literature, PV is considered to be the most simplest unit operations to separate azeotropic mixtures, closely boiling liquid mixtures, heat-sensitive biochemicals, liquid-liquid isomers, etc. PV is an energy saving method and is eco-friendly when compared to other separation techniques including conventional distillation (19–22). In PV, the feed stream is maintained in contact on one side of the membrane, while permeate is continuously extracted from the other side as a vapor by applying high vacuum (low pressure), thereby creating a pressure gradient that is large enough to initiate the phase change from liquid to vapor. The advantages of PV are its simplicity, low cost, in addition to acceptable values of flux and selectivity. Liquid transport in PV is generally described by the solution-diffusion model (23) wherein, sorption or permeation of molecules at the interface of the feed solution and the membrane, diffusion across the membrane due to concentration gradient (rate determining step), and desorption into vapor

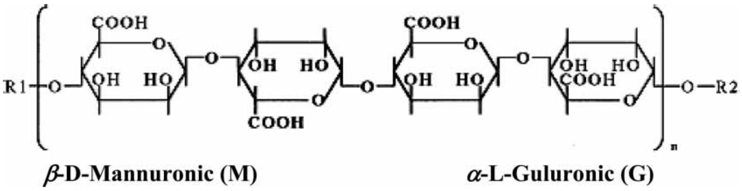

Figure 1. Structure of (M) β-D-mannuronic acid and (G) α-L-guluronic acid units of NaAlg (32).

phase on the permeate side of the membrane will take place. The first two steps are complimentary to each other, which are responsible to achieve membrane permselectivity. As the liquid passes through the membrane, “swelling” makes it more permeable, but less selective until a point of unacceptable selectivity is reached. Alternatively, to create a partial pressure gradient, an inert gas such as helium or nitrogen is swept over the permeate side of the membrane. Such methods are described as vacuum and sweep gas pervaporation, respectively.

Published literature on the use of NaAlg membrane and its various modified forms in PV dehydration studies have been increasing over the years. However, no comprehensive review is available on the use of NaAlg or NaAlg-based membranes in PV separation of water-aqueous mixtures. This review will address an update on the evaluation of PV dehydration data on aqueous-organic mixtures using NaAlg and/or modified NaAlg-based membranes. So far, only six binary aqueous-organic mixtures have been separated by the PV technique using NaAlg and/or NaAlg-based membranes. These are discussed with reference to other membranes used in the literature.

TYPES OF NaAlg-BASED MEMBRANES USED IN PERVAPORATION SEPARATION

In the reported literature, a variety of different types of NaAlg membranes have been employed in PV dehydration of organic liquids with an ultimate objective of achieving enhanced flux and selectivity to water. Efforts in this direction have lead to the development of various types of cross-linked dense NaAlg membranes, blend NaAlg membranes, particulate filled matrix membranes, hybrid composite membranes, and so on. Such developments of hybrid and other composite membranes have lead to improved mechanical strength/membrane performances over those of the plain cross-linked NaAlg membranes. Different types of membranes employed in the literature will be discussed in subsequent sections of this review with reference to different types of aqueous-organic feed mixtures.

The feed mixtures covered in this review include aqueous solutions of ethanol, isopropanol, 1,4-dioxane, tetrahydrofuran (THF), acetic acid and acetonitrile, since these are the mixtures that have been widely separated so far using NaAlg or NaAlg-based membranes. Isopropanol, 1,4-dioxane, THF, ethanol, and acetonitrile forms azeotrope at 12.5, 18.1, 6.7, 4, and 12.3 wt.% of water, respectively. These are the most commonly used solvents in chemical industries. Acetic acid is an important industrial commodity used in the chemical synthesis of vinyl acetate from ethylene as well as in the catalytic esterification of alcohols, wherein plant removal from the discharged water is necessary. Pervaporation has been efficiently used to dehydrate such solvents, because the method is more advantageous than conventional distillation. PV separation depends upon membrane morphology or its structure in addition to physicochemical characteristics of the liquid mixtures as well as their interactions with NaAlg. A listing of the available data on flux and selectivity for different types of NaAlg-based membranes used in PV separations of such mixtures are compiled in Tables 1–5.

Cross-linked Dense Membranes of Sodium Alginate

Pure NaAlg by itself cannot be fabricated as a successful PV membrane. Therefore, its cross-linking is necessary to prepare the mechanically strong NaAlg membranes that can withstand the PV conditions. Different types of cross-linking agents have been used to prepare dense NaAlg membranes. The most common cross-linking agents used are: glutaraldehyde (GA),

Table 1. Isopropanol dehydration data for different types of NaAlg-based membranes with 10 wt.% feed water at 30°C

Membrane type	Normalized flux[a] J(10 μm thickness (kg/m^2 · h))	Selectivity α	Ref.
Pristine/blend/grafted NaAlg membranes			
Two-ply NaAlg/CS[b]	2.77	2010	(39)
pAAm-*g*-NaAlg[c]	0.441	100	(46)
NaAlg	0.204	650	(52)
NaAlg/PVA blend	0.207	580	
NaAlg	0.037	360	(49)
NaAlg/PVA blend	0.071	200	
NaAlg/pAAm-*g*-GG blend	0.129	890	(44)
NaAlg + 5 wt.% PVA + 10 wt.% PEG	0.150	3600	(34)
Mixed matrix membranes of NaAlg			
MCM-41 (10 wt.%) filled NaAlg	0.550	30,000	(56)
SBA-15 (10 wt.%) filled NaAlg	0.110	∞	(57)
Fe-SBA-15 (10 wt.%) filled NaAlg	0.175	∞	(57)
Na$^+$MMT (10 wt.%) filled NaAlg	0.250	∞	(58)
AlPO$_4$-5 (20 wt.%) filled NaAlg)[d]	0.386	69,000	(59)
Al-MCM-41 (20 wt.%) filled NaAlg	1.07	∞	(65)

NaAlg-Sodium alginate; Na$^+$MMT-Sodium montmorillonite; AlPO$_4$-5-Alumino-phosphate; pAAm-poly(acrylamide); PVA-Poly(vinyl alchol); PEG-Poly(ethylene glycol); GG-Guar gum.

[a] Flux values are normalized to 10 μm thickness.

[b] At temp of 60°C.

[c] At 20 wt.% of water in feed.

[d] At 12.6 wt.% of water in feed.

Table 2. 1,4-Dioxane dehydration data for different types of NaAlg-based membranes with 10 wt.% feed water at 30°C

Membrane type	Normalized flux[a] J (10 μm thickness (kg/m^2 · h))	α	Ref.
Pristine/blend/grafted NaAlg membranes			
5 wt.% PVA + 95 wt.% NaAlg blend	NA	63	(51)
pAAm-*g*-NaAlg	0.300	83	(47)
Dense NaAlg membrane[b]	1.526	1900	(29)
NaAlg (GA + UFS cross-linked)	0.460	270	(43)
NaAlg-HEC-5 blend	0.424	60	
Mixed matrix membranes of NaAlg			
SBA-15 (10 wt.%)-filled NaAlg	0.200	∞	(57)
Fe-SBA-15 (10 wt.%)-filled NaAlg	0.245	∞	
Na$^+$MMT (10 wt.%) filled NaAlg	0.445	∞	(58)
AlPO$_4$-5 (20 wt.%)-filled NaAlg[c]	0.517	45,000	(59)

NA-Not available; HEC-Hydroxyethylcellulose; GA-Glutaraldehyde; UFS-Urea formaldehyde-Sulfuric acid; AlPO$_4$-5-Alumino-phosphate.

[a] Flux values are normalized to 10 μm thickness.

[b] 5 wt.% of water in the feed at 60°C.

[c] 18.1 wt.% of water in the feed.

Table 3. THF dehydration data for different types of NaAlg-based membranes with 10 wt.% feed water at 30°C

Membrane type	Normalized flux[a] J (10 μm thickness (kg/m^2 · h))	α	Ref.
Pristine/blend/grafted NaAlg membranes			
5 wt.% PVA + 95 wt.% NaAlg blend	NA	216	(51)
pAAm-*g*-NaAlg	0.470	300	(48)
Dense NaAlg membrane[b]	1.800	∞	(29)
NaAlg-HEC-10 (GA + UFS cross-linked)	0.732	1500	(43)
PHEMA (20 wt.%)-NaAlg[d]	0.168	860	(71)
Mixed matrix membranes of NaAlg			
Na$^+$MMT (10 wt.%) filled NaAlg	0.590	∞	(58)
AlPO$_4$-5 (20 wt.%)-filled NaAlg)[c]	0.550	20,000	(59)

PHEMA-Poly(hydroxyethylmethacrylate); NA-Not available.

[a] Flux values are normalized to 10 μm thickness.

[b] 5 wt.% of water in the feed at 55°C.

[c] 6.7 wt.% of water in the feed.

[d] 5 wt.% of water in the feed at 30°C.

Table 4. Ethanol dehydration data for different types of NaAlg-based membranes with 10 wt.% feed water at 30°C

Membrane type	Normalized flux[a] J (10 μm thickness (kg/m^2 · h))	α	Ref.
Prisitne/blend/composite NaAlg membranes			
Two-ply composite NaAlg/CS[b]	0.350	1110	(39)
Cellulose/NaAlg (ca^{2+} cross-linked) blend[c]	0.170	1175	(38)
NaAlg dense membrane	0.228	7700	(30)
NaAlg dense membrane[d]	1.406	∞	(29)
NaAlg dense membrane[e] (cross-linked with Cr^{3+})	0.090	2000	(31)
NaAlg/CS blend	0.220	440	(42)
PHEMA (20 wt.%)-NaAlg[f]	0.132	570	(67)
Mixed matrix membranes of NaAlg			
Al-MCM-41 (20 wt.%)-NaAlg	0.645	1090	(65)
AlPO$_4$-5 (20 wt.%)-filled NaAlg[g]	0.104	980	(59)

[a] Flux values are normalized to 10 μm thickness.
[b] 5 wt.% of water in the feed at temperature of 60°C.
[c] At the temperature of 60°C.
[d] 20 wt.% of water in the feed at 70°C.
[e] 8.8 wt.% water at 70°C.
[f] 5 wt.% of water in the feed.
[g] 4 wt.% of water in the feed.

Table 5. Acetic acid dehydration data for different types of NaAlg-based membranes with 10 wt.% feed water at 30°C

Membrane type	Normalized flux[a] J (10 μm thickness (kg/m^2 · h))	α	Ref.
Pristine/blend/grafted NaAlg membranes			
NaAlg composite (cross-linked with HDM)[b]	0.262	160	(41)
NaAlg + 5 wt.% PVA + 10% wt.% PEG	0.071	40	(34)
NaAlg/pAAm-*g*-GG	0.400	7.4	(45)
NaAlg/HEC-*g*-AAm	0.290	28	(54)
Mixed matrix membranes of NaAlg			
Na-Y-filled NaAlg	0.190	43	(62)
Cobalt (III) (3-acetylpyridine-*o*-aminobenzoyl hydrazine)-filled NaAlg	0.123	174	(64)
STA (2 wt.%) filled NaAlg	0.950	22500	(66)

HDM-1,6-Hexanediamine, AAm-Acrylamide; STA-Silicotungstic acid.
[a] Flux values are normalized to 10 μm thickness.
[b] 15 wt.% of water in the feed at 70°C.

urea-formaldehyde-sulfuric acid (UFS) and 1,6-hexanediamine (HDM). Even though the technique of PV was known ever since its early introduction by Kober in 1917 (24), more research activities on the utilization of NaAlg membrane have started as late as 1989 by Uragami and Saito (25), who first used alginic acid membranes for the PV separation of ethanol-water mixtures. In 1990, Mochizuki et al. (26) studied the relationship between permselectivity of alginic acid membrane and its solid-state structure as well as the effect of counter cations on membrane performance to separate ethanol-water mixtures. Yeom and Lee (27, 28) developed glutaraldehyde cross-linked NaAlg membranes for the PV separation of ethanol-water mixtures.

Shi et al. (29) investigated the PV separation of water-ethanol, water-1,4-dioxane and water-THF mixtures using dense NaAlg membrane. Their results demonstrated an exceptional ability of NaAlg membrane to offer high flux of $1.406\ \mathrm{kg/m^2 \cdot h}$ with an infinite selectivity to water at 70°C for feed containing 20 wt.% water and remaining ethanol. Shi et al. (29) also used NaAlg dense membrane for separating water from 1,4-dioxane with a water flux of $1.526\ \mathrm{kg/m^2 \cdot h}$ and a selectivity of 1900. Similarly, infinite selectivity to water was found with a flux of $1.8\ \mathrm{kg/m^2 \cdot h}$ for the dehydration of THF. These values are much superior to other membranes developed in the literature. Relaxation vs permeation trends have been investigated by Yeom et al. (30) in separating (90:10 wt.%) ethanol-water mixture using NaAlg membrane cross-linked with GA to obtain a water selectivity of 7700 with a flux of $0.228\ \mathrm{kg/m^2 \cdot h}$. However, under repeated temperature cycles, the relaxation of NaAlg chains was appreciable, resulting in a decreased water flux.

Shi et al. (31) studied the PV performance of modified NaAlg dense membranes prepared through an ion exchange of sodium with multivalent metal ions for ethanol dehydration. It was found that PV performance was optimum within 2 h when membranes were treated with Cr^{3+} ion. However, flux fluctuated between 0.090 and $0.104\ \mathrm{kg/m^2 \cdot h}$ with a selectivity of 2000, which remained constant for 91.2 wt.% of ethanol in aqueous mixture. Several dense NaAlg membranes, modified through ion exchange of sodium with multivalent metal ions like Al^{3+}, Cr^{3+}, Fe^{3+}, and Mg^{2+} have been reported, and their permselectivity properties have been tested for water-ethanol separation. Solutions of Mg^{2+}, Al^{3+}, Cr^{3+}, and Fe^{3+} salts were also chosen to cross-link NaAlg membranes. Nitrates were also considered because of their good solubility in organic aqueous solutions, wherein NaAlg did not dissolve, but was swollen.

Huang et al. (32) prepared cross-linked NaAlg membrane using divalent and trivalent metals like $Ca^{2+}$and Al^{3+} to study the PV separation of water-ethanol and water-isopropanol mixtures. Figure 2 displays the alginate gel network formation by multivalent ions. Ionic cross-linking of NaAlg membranes was also performed by submerging the membranes in 0.1 M solutions of various metal ions for 10 min in succession; they were then

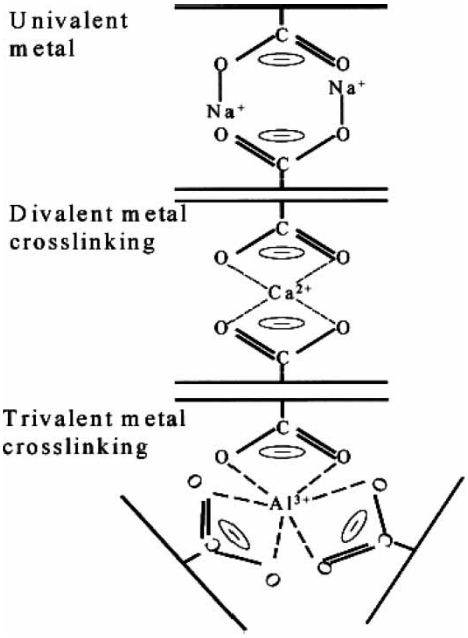

Figure 2. Alginate gel network formation by multivalent ions. From ref. (32), with permission, © 1999 Elsevier.

rinsed with water and dried at ambient temperature. Alginate membrane was then converted into a free alginic acid membrane by immersing in 0.1 M H_2SO_4 solution consisting of isopropanol/water mixture of 50/50 vol% (32). Considering the ion exchangeability of carboxyl groups in alginate, Na^+, a univalent cation, can be easily replaced by divalent or trivalent species. Replacement of Na^+ with multivalent cations actually has led to the cross-linked NaAlg network structure among alginic chains in the membrane, similar to what was found in calcium alginate (33).

Toti and Aminabhavi (34) prepared different viscosity grade NaAlg membranes modified by solution casting method and cross-linked with GA in methanol:water (75:25) mixture and used in PV dehydration of acetic acid and isopropanol mixtures for feeds ranging 10–50 wt.% of water at 30°C. Cross-linking reaction occurred between the -OH group of NaAlg and the -CHO group of GA due to the formation of ether linkage by eliminating water, which is commonly observed with most of the cellulose-based hydrophilic polymers (35, 36). In order to further increase the PV performance of the membrane, low viscosity grade NaAlg was modified by adding 10 wt.% of polyethyleneglycol (PEG) in the presence of varying amounts (5 to 20 wt.%) of PVA. Such modified membranes containing 10 wt.% PEG and 5 wt.% PVA showed the selectivity of 40 with a flux of 0.071 $kg/m^2 \cdot h$ for 10 wt.% water containing feed mixture of acetic acid. Thus, by increasing the amount of PVA from 10 to 20 wt.% and keeping 10 wt.% of PEG, selectivity has decreased from 40 to 11, but flux has increased from 0.071 $\mathrm{kg/m^2 \cdot h}$ to 0.221 $\mathrm{kg/m^2 \cdot h}$. In case of modified membranes of NaAlg with 5 wt.% of PVA and 10 wt.% polyethylene glycol, a flux of 0.150 $\mathrm{kg/m^2}$ h and a selectivity of 3600 were obtained for 10 wt.% water containing feed mixture of isopropanol. Thus, flux and selectivity values declined drastically with increasing water composition of the feed mixture.

Blend/Composite/Grafted Membranes of NaAlg

In an effort to increase the membrane performance of NaAlg, its blending with other hydrophilic polymers such as PVA, cellulose, guar gum (GG), etc., as well as preparation of asymmetric membranes using hydrophilic and hydrophobic supports (37–41) have been attempted. Yang et al. (38) developed blend membranes of NaAlg by coagulating a mixture of 8 wt.% cellulose cuoxam and 8 wt.% aqueous NaAlg solutions cross-linked with Ca^{2+} bridges in 5 wt.% $CaCl_2$ aqueous solution to study their PV performances for ethanol-water mixtures. These membranes due to strong hydrogen-bonding interactions with aqueous media, have exhibited good mechanical strength properties by giving a water selectivity of 1175 with a permeation flux of 0.170 $\mathrm{kg/m^2}$ h; these values are much better than the non-cross-linked NaAlg membrane.

Moon et al. (39) prepared two-ply dense composite membranes using successive castings of NaAlg and chitosan (CS) solutions and used them for PV dehydration of ethanol and isopropanol. Operating parameters such as polymer type facing to the feed stream, NaOH treatment for the regeneration of chitosan and cross-linking system types have been investigated using factorial design method. These parameters were critical to the performance of the membrane. For instance, when PV performance of the two-ply membrane with its NaAlg layer facing the feed side and cross-linked or insolubilized in sulfuric acid solution was compared with plain NaAlg and CS membranes for flux and selectivity, it was found that two-ply membrane had a flux of 0.350 $\mathrm{kg/m^2 \cdot h}$ with a selectivity of 1110 at 95% ethanol in the feed, with better mechanical strength properties than the plain NaAlg membrane. PV performance of two-ply membrane that was moderately cross-linked with formaldehyde almost matched with the performance of pristine NaAlg membrane. Two-ply membrane had a flux of 2.77 $\mathrm{kg/m^2 \cdot h}$ with a selectivity of 2010 for 10 wt.% water containing isopropanol mixture, a value that is much higher than observed for pristine NaAlg membrane.

Composite membranes consisting of an active alginate layer and supporting chitosan layer on top of the base porous blended polyvinylidene fluoride (PVDF) membrane were prepared and tested for PV dehydration of ethanol and isopropanol (40). Surface properties of PVDF were enhanced by blending with polymethyl methacrylate (PMMA). Various modifications of alginate/chitosan composite membranes such as converting to free acid form and cross-linking with cobalt ion were also investigated to compare the PV dehydration data of the mixtures in addition to study the temperature effect on permeation flux. NaAlg composite membranes cross-linked with 1,6-hexanediamine (HDM) or PVA were prepared by casting an aqueous solution of alginate and HDM or PVA onto hydrolyzed microporous polyacrylonitrile (PAN) membrane and were used in PV dehydration of acetic acid. Influence of hydrolysis of PAN support layer and HDM content in the dense layer on PV separation performance of the composite membrane improved the flux and selectivity greatly (41). The counter cation of NaAlg coatings as dense separating layer influenced the PV properties of the membrane; flux was higher for K^+ than for Na^+ at 50°C, while selectivity showed an opposite trend. When the NaAlg composite membrane was cross-linked with HDM, its selectivity was 161 and flux was $0.262\,\mathrm{kg/m^2 \cdot h}$ for 85 wt.% acetic acid-water solution at 70°C. In this work, both selectivity and flux were increased with increasing amount of water in the feed. Cross-linked NaAlg composite membrane prepared with PVA exhibited much lower PV separation characteristics. NaAlg will not dissolve in acetic acid, but it dissolves in water and hence, its swelling decreases with increasing acetic acid concentration of the feed with a decrease in flux. Variation of selectivity with feed water concentration was attributed to extraordinary permselectivity of NaAlg membrane to water during the sorption step.

Kanti et al. (42) prepared polyion complex membranes by blending 84% deacetylated CS and NaAlg followed by cross-linking with GA and tested for the PV dehydration of ethanol. The membrane formed was washed with deionized water up to 4–5 h followed by vacuum drying up to 5 h at 60°C. Figure 3 displays the ionic complexation reaction between cationic group ($\text{-NH}_3^+\text{C}$) of CS and anionic group (-COO^-) of NaAlg as well as covalent cross-linking induced by the addition of GA. Cross-linked blend membranes could break the azeotrope containing 0.135 mol fraction of water from the feed mixture giving a selectivity of 436 and a flux of $0.220\,\mathrm{kg/m^2 \cdot h}$. Membrane selectivities were improved with a decrease in pressure, but remained relatively constant for variable membrane thicknesses. Increasing the membrane thickness decreased the flux, but higher permeate pressures caused reductions in flux and selectivity. With increasing feed water concentration, membrane performance was affected substantially due to increased swelling of the polymer, resulting in an increase of flux with a reduction in selectivity. The increase in flux and the corresponding increase in concentration of water is due to the availability of free water molecules for sorption and diffusion to take place. However, preferential interaction of water molecules with the membrane material would cause the membrane to swell due to absorption of liquid molecules in NaAlg matrix as well as membrane plasticization effect, thereby allowing the unrestricted transport of both ethanol and water molecules through the upstream layer. Swelling

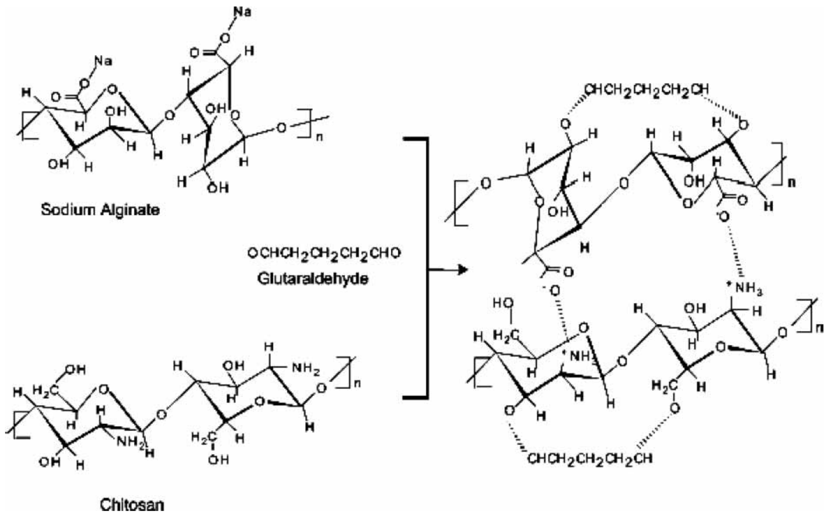

Figure 3. Ionic complexation reaction between cationic group of chitosan and the anionic group of NaAlg. From ref. (42), with permission, © 2004 Elsevier.

has increased with increasing water concentration, thereby sacrificing the selectivity.

NaAlg and hydroxyethylcellulose (HEC) blend membranes have been prepared by solution casting and cross-linked with GA and urea-formaldehyde-sulfuric acid (UFS) mixture to study their PV dehydrations of 1,4-dioxane and tetrahydrofuran (THF) (43). NaAlg membranes cross-linked with UFS and GA offered a selectivity of 268 with a flux of $0.460\,\mathrm{kg/m^2 \cdot h}$. Blend membranes of NaAlg/HEC were also prepared to improve the membrane performance in dehydrating 1,4-dioxane. A flux of $0.424\,\mathrm{kg/m^2 \cdot h}$ with a selectivity of 60 was observed. The blend membranes cross-linked with GA and UFS mixture were also studied for PV dehydration of THF at 30°C; these offered a flux of $0.732\,\mathrm{kg/m^2 \cdot h}$ with a selectivity of 1500. The model structure of cross-linked blend membrane of NaAlg and HEC is shown in Figure 4.

Blend membranes of NaAlg and poly(acrylamide)-*grafted*-guar gum (pAAm-*g*-GG) in the ratios of 3:1 and 1:1 were prepared by Toti et al. (44, 45) and used in PV dehydration of isopropanol and acetic acid. The flux of $0.129\,\mathrm{kg/m^2}$ h and a selectivity of 891 were observed for 1:1 blend of NaAlg and pAAm-*g*-GG for water-isopropanol mixture, whereas a flux of $0.400\,\mathrm{kg/m^2 \cdot h}$ with a low selectivity of 7.4 was observed for water-acetic acid mixture. Thus, flux can be enhanced by polymer modification, but selectivity enhancement was not possible. Toti and Aminabhavi (46) also prepared pAAm-*g*-NaAlg copolymers by persulfate induced radical polymerization using polymer-to-monomer ratios of 2:1 and 1:1. The

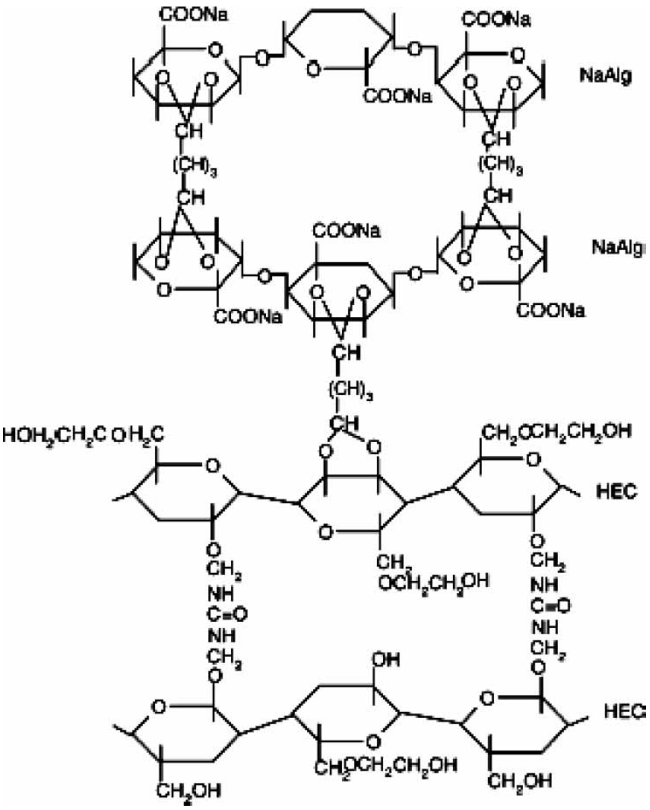

Figure 4. Structure of blend membranes of NaAlg and HEC. From ref. (43), with permission, © 2005 Elsevier.

pAAm-*g*-NaAlg membranes exhibited poor mechanical strength and barrier properties when compared to pristine NaAlg membrane; however, flux was improved to 0.441 kg/m^2 h with increasing grafting of the membrane at the expense of low selectivity of 96. Thus, these membranes were not able to improve the PV performance over that of pristine NaAlg membrane for 10 wt.% water containing feed with isopropanol.

Additional work using the above-mentioned membranes was continued for water-dioxane and water-THF mixtures. For instance, Kurkuri et al. (47) prepared pAAm-*g*-NaAlg copolymeric membranes for PV dehydration of 1,4-dioxane that contained 10–70 wt.% of water; the PV performance was studied as a function of grafting ratio and water composition of the feed mixture. Membranes could effectively dehydrate 1,4-dioxane with a flux of 0.300 $kg/m^2 \cdot h$ and a low selectivity of 83 at 30°C for 10 wt.% water in the feed. Kurkuri et al. (48) also used pAAm-*g*-NaAlg copolymeric membranes for the PV dehydration of 10–80 wt.% water containing THF mixtures. Three membranes were prepared: (1) by taking plain NaAlg with 10 wt.% of PEG and 5 wt.% of PVA, (2) 46% grafted pAAm-*g*-NaAlg membrane containing 10 wt.% of PEG and 5 wt.% of PVA and (3) 93% grafted pAAm-*g*-NaAlg membrane containing 10 wt.% of PEG and 5 wt.% of PVA. Selectivity of these membranes did not improve much, as these data ranged between 216 and 590. On the other hand, flux was improved considerably, which ranged from 0.456 to 0.654 $kg/m^2 \cdot h$ at 10 wt.% of water in the feed. This clearly indicated that an increase in % *grafting* resulted in membranes with higher fluxes than plain NaAlg membrane.

Blend membranes of NaAlg and PVA have also been studied for PV dehydration of isopropanol, ethanol, 1,4-dioxane and THF (49–51). Membranes were prepared by solution casting and cross-linked with GA, which offered a selectivity of 63 for the blend membrane of 5 wt.% PVA + 95 wt.% NaAlg in dehydrating 1,4-dioxane. A selectivity of 216 for 5 wt.% PVA + 95 wt.% NaAlg blend membrane was found for the dehydration of THF. These results are somewhat inferior compared to blend membranes of NaAlg and HEC (43). Sorption/diffusion characteristics (51), modeling and computer simulation approaches were attempted on these membranes to understand membrane area requirement and stage cut values required in engineering design applications (52, 53). In a further study, Aminabhavi et al. (52), investigated the PV performance of pristine NaAlg, pristine PVA and their blend membranes containing 10 and 20 wt.% of PVA with 10 wt.% water containing isopropanol feed mixture. Water flux of 0.207 $kg/m^2 \cdot h$ and selectivity of 580 were observed for NaAlg (90%) + PVA (10%) blend membrane when compared to pristine NaAlg membrane for which selectivity was 653 with almost a similar flux value of 0.204 $kg/m^2 \cdot h$ at 30°C as observed before, but selectivity declined, whereas flux improved at higher feed water concentrations due to increased plasticization and/or swelling effects. Blend membranes containing higher amount of PVA did not show any improvement in membrane performance. Pristine PVA showed a better flux with a much poor selectivity than plain NaAlg or its blend membranes at all compositions of feed mixtures. These results are much superior to similar type of blend membranes with different ratios studied before (49) i.e., a flux of 0.071 $kg/m^2 \cdot h$ and selectivity of 196 were observed for NaAlg (75%) + PVA (25%) blend membrane.

Krishna Rao et al. (54) prepared NaAlg/HEC-*g*-acrylamide (AAm) blend membranes to study the PV dehydration of acetic acid. These hydrophilic membranes could recover only up to 89% of water from acetic acid for feed mixtures containing 10 to 50 wt.% of water. Flux and selectivity to water have increased with increasing amount of HEC-*g*-AAm grafted copolymer in the mixed blend of NaAlg (54). A flux of 0.290 $kg/m^2 \cdot h$ and a selectivity of 28 were obtained, but these data are quite inferior to those found for other membranes.

Mixed Matrix Membranes of NaAlg

In recent years, mixed matrix membranes of NaAlg incorporated with zeolites or other similar type of particulate fillers such as clay or metal complexes are being developed (55–59). Utilizing such membranes enhanced the PV dehydration of acetonitrile, isopropanol, 1,4-dioxane, THF and ethanol. The most widely used fillers are: zeolites, clays, mesoporous molecular sieves, alumino-phosphates, metal complexes, etc. (55–59). PV separation of water-ACN mixture was attempted by Naidu et al. (55), using ZSM-5 and Na-Y-type zeolite-filled NaAlg membranes, whose performances were better than the plain NaAlg membrane. However, the performance of such mixed matrix membranes depends upon the nature of the zeolites incorporated. For instance, variation in the acidity function of ZSM-5 zeolite had an influence on flux and selectivity when compared to the unfilled NaAlg membrane. Plain NaAlg membrane had a selectivity of 414 for 30 wt.% water in the feed; whereas Na-Y and ZSM-5(40)-filled NaAlg mixed matrix membranes exhibited much lower values of selectivities i.e., 7.3 and 4.3, respectively for 30 wt.% water in the feed. By comparing the flux and selectivity data of ZSM-5(40)-filled NaAlg membranes with those of Na-Y or ZSM-5250-filled NaAlg membranes, a noticeable increase in selectivity i.e., 127 for ZSM-5(40)-filled composite NaAlg membrane with a sacrifice in flux compared to plain NaAlg membrane.

Attempts were also made to utilize MCM-41 molecular sieve as filler particles into NaAlg to develop mixed matrix membranes used in PV dehydration of isopropanol (56). Different filler loadings were attempted, but NaAlg membrane containing 20 wt.% of MCM-41 gave a selectivity of 30 for feed containing 10 wt.% of water, while flux for 20 wt.% MCM-41 filled NaAlg membrane was $0.550\,\mathrm{kg/m^2 \cdot h}$. For MCM-41 filled mixed matrix membranes, water permeated more preferentially through molecular sieve pores due to the small size of water than isopropanol, resulting in higher flux and selectivity values than observed for pristine NaAlg membrane. Compared to other similar studies in the literature, flux and selectivity values are much better when tested for 10 wt.% water containing feed. Flux of all the mixed matrix as well as pristine membranes have increased with increasing amount of feed water with a reduction in selectivity to water for membranes that contained a lower amount of MCM-41 ($<$20 wt.%). The precise pore structure of MCM-41 (due to its molecular sieving effect) was responsible for such a simultaneous increase in selectivity and flux. Additionally, mixed matrix membranes were mechanically strong and chemically inert. At any rate, detailed mechanistic interpretation of PV results on such systems would require a thorough understanding of the true microcavity uptake affects in relation to interstitially held water molecules between crystallites of the membrane. However, this aspect is beyond the scope of this review.

The crystalline ordered structure of hydrophilic zeolites with a narrow size distribution has a higher resistivity to organic liquids than water. By dispersing such particulate fillers into NaAlg would naturally increase permeation flux due to the preferential interaction of water molecules with the mixed matrix membrane, since more water molecules are accommodated into the membrane pores. This could be due to: (i) strong adsorptive hydrophilic interaction of water molecules onto zeolite particles, (ii) surface diffusion from cage to cage and (iii) vaporization on permeate side. Here, the physical adsorption involves both van der Waals-type dispersion-repulsive and electrostatic interactions due to the polarization effect as well as dipole and quadrupole type interactions. The complimentary effects of molecular sieve present in the NaAlg matrix on water transport has helped to improve the membrane performance. Variations in flux and selectivity data depend upon the amount of zeolite present in the NaAlg matrix as studied before (55, 56).

SBA-15, Fe-SBA-15 and sodium montmorillonite (Na^+MMT)-loaded mixed matrix membranes of NaAlg offered infinite selectivity data to water with a slight sacrifice in flux (57, 58) for water-isopropanol, water-1,4-dioxane and water-THF mixtures. However, selectivity to water was 69,358 for an azeotrope of water (i.e., 12.6 wt.%) with isopropanol for aluminophosphate ($AlPO_4$-5)-loaded NaAlg membrane (59). SBA-15 and Fe-SBA-15 loaded matrix membranes of NaAlg (57) could dehydrate 1,4-dioxane offering an infinite selectivity value with moderate fluxes of 0.200 $kg/m^2 \cdot h$ and 0.245 $kg/m^2 \cdot h$, respectively. This type of high PV performance of SBA-15 and Fe-SBA-15-loaded mixed matrix NaAlg membranes was explained as due to the type and nature of interactions of dual pore filler systems after incorporation into the hydrophilic NaAlg membrane. Sodium montmorillonite (Na^+MMT)-loaded NaAlg membranes have been tested for dehydrating 1,4-dioxane from water (58) for which infinite value of selectivity was found with somewhat high flux of 0.445 $kg/m^2 \cdot h$. For $AlPO_4$-5-containing mixed matrix NaAlg membranes, a selectivity of 45 was observed for the azeotrope of water (18.1 wt.%) with 1,4-dioxane (59). The Na^+MMT-filled NaAlg membranes also gave an infinite selectivity to water (i.e., 100% water removed on permeate line) with a moderate flux of 0.590 $kg/m^2 \cdot h$ for THF dehydration for 10 wt.% Na^+MMT loaded NaAlg membrane (58). The $AlPO_4$-5-loaded NaAlg mixed matrix membrane exhibited a selectivity of 20000 for the azeotrope of water (6.7 wt.%) with THF giving a flux of 0.550 $kg/m^2 \cdot h$ (59). The same $AlPO_4$-5-loaded NaAlg mixed matrix membrane was also tested for the dehydration of azeotrope of water (4 wt.%) in ethanol (59), which gave a selectivity of 980 with a flux of 0.104 $kg/m^2 \cdot h$ for 20 wt.% $AlPO_4$-5-loading. Further increasing $AlPO_4$-5 loading into the NaAlg matrix has increased both flux and selectivity values simultaneously due to higher number of free channels created that facilitated an easier transport of water molecules than ethanol. High performance of such mixed matrix membranes could also be attributed to specific-type of interactions between feed components of the mixtures.

Increased selectivity of the filled NaAlg mixed matrix membranes are due to the adsorptive nature of the fillers as well as the -OH group of NaAlg, resulting in higher preferential interactions with water than the organic component. Particularly, in the presence of adsorptive fillers like SBA-15, Na^+MMT or $AlPO_4$-5, such interactions would help to enhance their selectivity to water as compared to organic component. Sorption and diffusion are the dominating factors in PV separation. Sorption is usually favored by hydrophilic-hydrophilic interactions, whereas diffusion is affected by the nature (amorphous or crystalline) and flexibility of the membrane as well as filler particles. Thus, selectivity and flux values would determine the efficiency of the PV process. Higher the flux, lower will be the capital cost of the membrane system, while in the absence of any defects, selectivity is a function of material properties.

Hennepe et al. (60) proposed the concept that membrane performance can be enhanced by adding the selective fillers due to their high sorption capacities for water due to sorption-diffusion principles. Therefore, distribution of microporous and mesoporous adsorbents with high sorption capacities into NaAlg would help to enhance the overall selectivity of the mixed matrix membranes. Another observation is that the concentration difference of organic component between the feed and permeate sides of the mixed matrix membranes is higher than that observed for the unfilled (pristine) membrane. This is attributed to extra sorption capacity of the zeolite-filled mixed matrix membrane, which would affect the diffusive trends of water as well as organic components of the feed mixture, since the selective sorption of feed components are mainly governed by the presence of active centers in the NaAlg matrix that are capable of specific (hydrophilic-hydrophilic) type of interactions with the selectively permeating water molecules. These effects have been generalized by the adsorption-diffusion-desorption concepts as discussed by Feng and Huang (61). Separation occurs due to the selective adsorption of water onto the zeolite micropores or clay channels, which will further diffuse through the NaAlg membrane (hydrophilic) by inhibiting the transport of organic components. Such an increased flux is due to increased driving force for molecular transport to occur in addition to the faster desorption rate of water molecules on the permeate side. This type of effect is more beneficial for water transport, since these will occupy all the channels in the hydrophilic molecular sieve regions of the membrane. This further justifies the observed marked increase in selectivity to infinity, with a recovery of 100% of water on the permeate side.

The Na-Y type zeolite-filled NaAlg membranes, when tested for PV dehydration of acetic acid and isopropanol (62, 63), did not offer much improvement over other reported values of the mixed matrix NaAlg membranes. For instance, Na-Y-filled NaAlg mixed matrix membranes when tested for PV dehydration of acetic acid (62), a flux of $0.190\ kg/m^2 \cdot h$ with a selectivity of 43 were obtained for 10 wt.% of water in the feed at 30°C. Similarly, cobalt (III) (3-acetylpyridine-*o*-aminobenzoyl hydrazine) complex-incorporated NaAlg mixed matrix membranes prepared by the solution casting technique, when tested for PV dehydration of acetic acid (64), offered the flux and selectivity values of $0.123\ kg/m^2 \cdot h$ and 174, respectively for 10 wt.% water in the feed. The interaction of cobalt complex with hydrophilic NaAlg was responsible for such enhanced effects of flux and selectivity. Recently, Patil et al. (65) developed the mixed matrix membranes of NaAlg containing aluminum-MCM-41 particles and tested them for the PV dehydration of isopropanol and ethanol. Flux and selectivity to water increased simultaneously with increasing loadings of the filler particles. Selectivity to water was infinite for isopropanol for mixed matrix NaAlg membrane containing 20 wt.% of Al-MCM-41 with the flux of $1.07\,\text{kg/m}^2 \cdot \text{h}$. Flux and selectivity of water increased simultaneously with increasing loadings of the filler particles. Selectivity to water was 1090, while flux was $0.645\,\text{kg/m}^2 \cdot \text{h}$ for 20 wt.% of Al-MCM-41-loaded NaAlg mixed matrix membrane. Highly water selective silicotungstic acid ($H_4SiW_{12}O_{40}$) (STA) incorporated NaAlg mixed matrix membranes prepared by solution casting technique, when tested for PV dehydration of acetic acid (66), gave infinite selectivity for loading of 1 wt.% of STA for feed water compositions varying from 10 to 25 wt.%. By further increasing the loadings of STA from 2, 3, and 5 wt.%, selectivities were ranged from 22.5 to 288, 12.8 to 190 and 6.9 to 108, respectively, for different feed compositions.

Interpenetrating Network Membranes of NaAlg

Veerapur et al. (67) prepared the semi-IPN membranes of poly(hydroxyethylmethacrylate) (PHEMA)/NaAlg and obtained a selectivity of 570 with a flux of $0.132\,\text{kg/m}^2 \cdot \text{h}$ for 5 wt.% water containing isopropanol feed. Not much improvement in flux and selectivity was obtained as compared to other membranes discussed before. On the other hand, in the case of THF dehydration, a selectivity of 860 and a flux of $0.168\,\text{kg/m}^2 \cdot \text{h}$ were obtained. These values are somewhat inferior when compared to the blend membranes of NaAlg/HEC, but superior to those of grafted membranes of pAAm discussed before (43, 48). The presence of hydrophilic PHEMA in the IPN matrix was responsible to increase the selectivity to water. NaAlg-PHEMA IPN membrane containing 20 wt.% PHEMA was found to be effective for the PV separation of water-ethanol and water-THF mixtures. These data are indeed better than the pristine NaAlg membrane. The flux of IPN membranes was smaller than observed for the pristine NaAlg membrane. Comparatively, higher flux values were observed for water-THF mixture than for water-ethanol mixture.

INFLUENCE OF OPERATING PARAMETERS ON PERVAPORATION SEPARATION

Effect of Feed Composition

In PV dehydration studies, generally flux increases with increasing water content of the feed due to increased concentration of water in the membrane matrix. However, the wt.% of water in permeate was decreased. Polymer plasticization also plays a major role on the permeability characteristics of NaAlg membrane, leading to specific interactions between feed components and the membrane polymer. For all the feed mixtures, fluxes of the composite NaAlg membranes were higher than the pristine NaAlg membrane. Hydrophilic NaAlg and its composites preferentially interacted in close proximity with water molecules, which was dependent upon the type of the organic component of the feed mixture. For instance, in case of water + 1,4-dioxane feed, flux values were higher than those observed for water + ethanol and water + isopropanol feed mixtures. Similarly, for water + THF feeds, fluxes were higher than those observed for other mixtures. Thermodynamic interactions between the organic components as well as water molecules of the feed mixtures are responsible for such varying flux data (59).

Flux and selectivity also depend upon the extent of sorption, which can be influenced by the feed composition of the mixture. Sorption by the membrane occurs due to the interaction of the penetrating species with the NaAlg membrane. Water sorption capacity of the pristine NaAlg membrane for almost all aqueous-organic mixtures increased with increasing water content of the mixture. In the case of water-organic feed, ethanol allowed only a small fraction of water to permeate through, whereas the less polar 1,4-dioxane would preferentially allow more of water to permeate. A somewhat less polar isopropanol than ethanol would allow a large amount of water to preferentially permeate through with a slight increase in flux, but with considerable increase in water selectivity. In case of composite membranes, the total equilibrium sorption increases along with flux. Thus, sorption tendencies of organic components of the feed mixtures through the membranes would decrease with filler loadings in NaAlg matrix (59).

Effect of Temperature

Temperature is an important variable affecting the membrane performance. Published reports (32, 34, 59) suggest that the variation of flux, J with temperature can be expressed by the Arrhenius type relationship, from which activation energy (kJ/mol) for permeation flux, E_p can be calculated. Permeation activation energy represents the energy required for the species to transport across the membrane. It has been demonstrated (32, 34, 59) that flux values obtained at different temperatures would generally follow the linear Arrhenius trends. It is obvious that the activation energy of pristine NaAlg membrane would be higher than those of the composite NaAlg membranes for almost all of the feed mixtures including their azeotropic compositions (59). Therefore, more energy is required for molecules to transport across the membrane under similar conditions. The smaller activation energy values observed for mixed matrix NaAlg membranes than those of the pristine NaAlg membrane suggests that the energy barrier would decrease and that the feed mixtures would readily transport across the barrier membrane. However, due to the addition of molecular sieves, greater amount of water molecules than organics can transverse across the membrane per unit time, thereby extracting more amount of water on the permeate side. At any rate, fluxes and selectivities are strongly dependent upon the feed temperature (59).

Effect of Membrane Thickness

Membrane thickness has shown an effect on flux data (42). Membranes of thicknesses of 25 to 200 μm were prepared to study their effect for PV dehydration of ethanol. A decrease in flux was observed with an increase in membrane thickness. In PV, diffusion is the rate-controlling step, which would decrease with an increasing membrane thickness, thereby causing a reduction in flux. Correspondingly, selectivity would also increase. During the PV process, upstream layer of the NaAlg membrane could be swollen and plasticized due to the absorption of feed liquid molecules, thereby allowing the unrestricted transport of feed components. In contrast, the downstream layer is virtually dry due to the continuous evacuation on the permeate side and hence, this layer would form a restrictive barrier, which allows only certain species to pass through, but not all. It is expected that thickness of the dry layer would increase with increasing membrane thickness, resulting in improved selectivity.

Effect of Permeate Pressure

Permeate pressure also has an effect on the PV separation characteristics (42). For instance, when pressure was varied from 0.05 to 10 mmHg, with crosslinked NaAlg membranes at constant thickness and at the azeotropic feed composition of water-ethanol, at lower pressures (high vacuum), the driving force for diffusing molecules would be high, resulting in the components to be swept out from the permeate side due to high mass transfer rates. On the other hand, selectivity decreased. Diffusion through membrane is the rate-determining step in PV process and diffusing water molecules would experience a larger driving force under high vacuum, which would enhance the desorption rate at the downstream side. Lower vacuum would reduce the driving force, thus slowing down the desorption of molecules. In such cases, relative volatilities of two components of the feed mixture would govern the membrane permselectivity. For example, ethanol being more volatile than water, would permeate competitively with the latter, thereby lowering the water concentration on the permeate side (42).

PERVAPORATION SEPARATION OF ORGANIC-ORGANIC MIXTURES

PV is also an important technique used widely in separating organic-organic mixtures (68). This is possible because of the resistivity of NaAlg towards many organic liquids that makes it a viable polymer for use in PV separation of organic-organic mixtures. Even though extensive research has not occurred on this aspect, yet literature survey indicated that some reports are available on the organic-organic mixture separation using NaAlg- based membranes (69–71). For instance, Kim et al. (69) dealt with the separation of methanol/methyl tertiary butyl ether (MTBE) mixtures using NaAlg/chitosan polyion complex (PIC) membranes prepared by the complexation reaction of ionic groups of NaAlg with chitosan. Using this membrane, PV separation was attempted for MTBE/methanol mixtures. The PIC reaction occurred by ionic cross-linking reaction between carboxylate groups ($-COO^-$) of NaAlg and protonated amine groups ($-NH_3^+$) of chitosan. However, the polyion complexation depends upon the amount of counter ions present. Such membranes have shown excellent PV separation characteristics for MTBE/methanol mixtures. The PIC membrane prepared from 2 wt.% NaAlg and 2 wt.% chitosan solutions permeated only methanol with a flux of $0.240\,kg/m^2 \cdot h$. By increasing the temperature of the feed from 40° to 55°C, methanol permeation rate also increased, while that of MTBE decreased. These results were explained on the basis of physicochemical and structural properties of the PIC membranes.

COMPARISON OF NaAlg-BASED MEMBRANES WITH OTHER COMMERCIAL MEMBRANES FOR PERVAPORATION DEHYDRATION

NaAlg membrane performance is comparable with those of several commercial membranes and hence, it can be suggested for commercial exploitation. Some comparisons are made in Table 6. Only the selectivity data are compared, since flux data varied, depending upon the thickness of the membranes. Composite NaAlg membranes seemed to offer enhanced PV performances with high selectivity data that are comparable to the commercial membranes.

COMMERCIALIZATION AND FUTURE PROSPECTS

Currently, NaAlg membranes are available in dense forms with thicknesses ranging from 10 to 50 μm. Therefore, the rate of mass transport through NaAlg membranes is low. On a commercial scale, NaAlg membrane can be cast in the form of a thin film composite comprising of a thin selective

Table 6. Pervaporation performance of NaAlg-based membranes compared to commercial membranes

Membrane type	Wt.% of water in the feed	Selectivity	Operation temperature (°C)
Water + Ethanol			
Sulzer 2200[a]	5	170	(80)
Sulzer 2210[a]	10	80	(80)
GFT-1000 PVA	5	225	(70)
GFT-100 PVA	5	350	(80)
$AlPO_4$-5 (20 wt.%)-filled NaAlg[b]	4	220	(70)
Water + Isopropanol			
Sulzer 2510[a]	10	170	(80)
$AlPO_4$-5 (20 wt.%)-filled NaAlg	12.5	220	(70)
Water + THF			
CMC-CF-23[a]	7	630	(65)
$AlPO_4$-5 (20 wt.%)-filled NaAlg	6.7	260	(60)
Water + Acetic acid			
Sulzer pervap 2205[a]	8	60	(30)
STA (1 wt.%)-NaAlg[c]	10	820	(70)

[a] Specification obtained from commercial membranes.

[b] Data from reference (59).

[c] Data from reference (66).

layer of NaAlg (≈2 μm thick) on a porous substrate such as polyacrylonitrile (PAN). The ultraporous substrate can be cast on the nonwoven polyester fabric for better mechanical stability of the membrane. NaAlg layer would be nonporous and be easily cross-linked. Such a membrane can yield appropriate flux values without any sacrifice in selectivity. It may be noted that despite the excellent performance of NaAlg membranes on a laboratory scale, its commercialization would pose problems due to its weak mechanical stability, similar to chitosan membranes. Therefore, mixed matrix membranes of NaAlg prepared by incorporating different molecular sieves or zeolites (56–59) seem to provide better mechanical stability and would enhance flux as well as selectivity to water for their commercial exploitations. Blends of NaAlg with different zeolites and with different hollow fiber supports such as polysulfone (PS) can be used for developing new types of membranes that can be successfully used in mixture separation problems; yet, there are only very few reports available in the literature on this aspect (72, 73).

CONCLUSIONS

NaAlg is the widely studied membrane in PV separation and particularly, in dehydrating industrial solvents like ethanol, isopropanol, 1,4-dioxane, tetrahydrofuran, acetic acid, acetonitrile, etc. Efforts in these directions have been focused mainly on the use of pristine NaAlg membrane, but in recent years, the trend has shifted towards developing different types of modified forms of NaAlg. Such modified NaAlg membranes have shown superior separation performances over the pristine NaAlg membrane. Particularly, blend membranes, interpenetrating network membranes with a variety of other polymers and mixed matrix membranes of NaAlg have been studied. NaAlg is hydrophilic, and hence it could extract more water from the organic component of the mixed media. In the reported literature, isopropanol, 1,4-dioxane, tetrahydrofuran (THF), acetonitrile, ethanol and acetic acid have been successfully dehydrated using different types of NaAlg or NaAlg-based membranes.

In the earlier reports, even though acetic acid and acetonitrile separations have yielded poor selectivities with NaAlg, but improvements were made by incorporating NaAlg with fillers like ZSM-5(40), Co(III) complex, silicotungstic acid (STA), etc., to enhance flux and selectivity to water. Even though a compromise between flux and selectivity is a formidable task, yet the mixed matrix NaAlg membranes have demonstrated their superior abilities to overcome these problems to be on par with other better membranes in the literature. Organic liquid separation using NaAlg membrane is somewhat rare, yet efforts are increasing in recent years. The main drawback here is the low flux, which would require further study to develop novel membranes. The recently developed NaAlg-based membranes containing different types of zeolites, mesoporous molecular sieves/metal complexes, clays and alumino-phosphates are particularly interesting in boosting the flux and selectivity values to water. The molecular sieving effect of the zeolites or other fillers in addition to their interactions with NaAlg membrane appears to be responsible to produce such effects. Due to its polar nature, membranes based on NaAlg could be a viable alternative for the separation of polar organics from a nonpolar media such as in MTBE/methanol mixtures.

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