Pervaporation Separation of Water and Dioxane Mixtures with Sodium Alginate-*g*-Polyacrylamide Copolymeric Membranes

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ABSTRACT: Polyacrylamide (pAAm)-*grafted* sodium alginate (NaAlg) copolymeric membranes have been prepared and used in the pervaporation separation of dioxane mixtures containing 10–70 mass % water. Three different polymeric membranes have been prepared: neat NaAlg, 46% grafted pAAm-*g*-NaAlg, and 93% grafted pAAm-*g*-NaAlg. For reduced brittleness and increased flexibility of the membranes, 10 mass % poly(ethylene glycol) and 5 mass % poly(vinyl alcohol) were added to all three membranes. With the transport data for the mixtures through the membranes, the permeation flux, selectivity, pervaporation separation index, swelling index, and diffusion coefficients have been calculated at 30°C. The Arrhenius activation parameters for the transport processes have been calculated for 10 mass % water in the feed mixture with flux and diffusion data obtained at 30, 40, and 50°C. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 300–305, 2003

Key words: pervaporation; sodium alginate; polyacrylamide

INTRODUCTION

Pervaporation (PV) separation technique based on polymeric membranes has become popular in recent years for separating water from aqueous–organic mixtures.[1–5] In PV separation experiments, the simultaneous enhancement of the flux and selectivity has been a challenging task. For improving or optimizing the flux and selectivity, several techniques have been attempted, such as polymer crosslinking,[6–8] selective species grafting onto the polymer backbone,[9,10] copolymerization,[11] hydrophilic polymer blending with a hydrophobic polymer,[12,13] and composite membranes.[14] Among the many hydrophilic membranes, sodium alginate (NaAlg) membranes have been reported for the dehydration of aqueous–organic mixtures.[15,16] In our previous study,[17] we prepared NaAlg-grafted membranes of polyacrylamide (pAAm; i.e., pAAm-*g*-NaAlg) and used them to separate water–tetrahydrofuran mixtures. The same membranes are now tried for the separation of water–dioxane mixtures. In our earlier efforts, different hydrophilic membranes were prepared and used to separate different types of aqueous–organic mixtures.[17–23]

EXPERIMENTAL

Materials

NaAlg (LR), poly(vinyl alcohol) (molecular weight = 1,250,000), glutaraldehyde (GA; 25 mass % aqueous solution; LR), and acetone were obtained from s.d. Fine Chemicals, Ltd. (Mumbai, India). Analytical-reagent-grade dioxane was supplied by Spectrochemical Pvt., Ltd. (Mumbai, India). Poly(ethylene glycol) (PEG) and potassium persulfate were procured from Merck and Sisco-Chem Industries (Mumbai, India), respectively. All these chemicals were used as received, and mixtures were prepared from double-distilled water.

Preparation of grafted copolymers

The grafted copolymers were prepared according to the procedure published earlier.[17] An aqueous solution of 10 g of NaAlg in 100 mL of water at 60°C under an inert nitrogen atmosphere, 0.12M acrylamide (AAm), and 10 mL of 0.1M potassium persulfate were mixed and maintained between 50 and 60°C for 4 h. The polymer formed was precipitated by the addition of methanol, filtered, and dried. Two copolymers with grafting percentages of 46 and 93 (Copoly-1 and Copoly-2, respectively) were prepared with 5 and 10 g of AAm monomer, respectively. The grafting efficiency was 100% with a 92% conversion of AAm.

Membrane preparation

Membranes were prepared according to the procedure published earlier.[17] Three membranes were prepared:

(1) pure NaAlg, (2) Copoly-1, and (3) Copoly-2. The polymers were dissolved separately in distilled water at 50°C. To each of the three polymer solutions, 10 mass % PEG and 5 mass % poly(vinyl alcohol) were added to plasticize the membranes. These solutions were poured onto a clean glass plate and allowed to dry. The dried membranes were further crosslinked by immersion in an acetone : water (7:3) mixture containing 0.0062 mol of GA and 2 mL of HCl at room temperature for about 12 h. The membranes were repeatedly washed with distilled water for the removal of excess GA and HCl and then dried at room temperature for 24 h before being used in PV experiments.

Sorption experiments

Swelling experiments were performed in water and dioxane mixtures of different compositions at 25 ± 0.5°C in an electronically controlled oven (model BD-53, WTB Binder, Germany) according to the procedures published earlier.[24] Circularly cut (surface area = 9.08 cm^2) disk-shaped membranes were kept in a desiccator over anhydrous calcium chloride and were maintained at 25°C for 48 h before use. The initial mass of the membranes was taken on a single-pan digital microbalance (model AE 240, Zurich, Switzerland) sensitive to ±0.01 mg. Polymer samples were placed inside air-tight test bottles containing different mixtures of water and dioxane. The test bottles were placed in the oven and maintained at 25°C. After 24 h (i.e., after the complete attainment of equilibrium), the membranes were removed, and the surface-adhered solvent drops were removed with soft filter papers and weighed immediately. The degree of swelling (DS) was calculated from the ratio of the equilibrium mass (W_∞) to the dry mass (W_0) of the membrane as follows:

$$DS = W_\infty / W_o \tag{1}$$

PV experiments

The PV experiments were carried out for water and dioxane mixtures with an apparatus designed indige-nously.[21] The composition of dioxane was varied from 30 to 90 mass %, and the temperature of the feed mixture in the PV apparatus was monitored with a calibrated thermometer. The membrane was placed on a porous stainless steel support of the PV apparatus and then secured firmly with bolts and nuts. After the mixture was poured into the feed compartment, about 30 min was allowed for equilibrium to be attained. The mixture in the PV cell was continuously stirred. The effective surface area of the membrane in contact with the feed mixture was 32 cm^2. A constant temperature was maintained by the circulation of water around the outer jacket of the PV cell assembly. A vacuum (10 Torr) was applied at the permeate side with a Tosh-niwal vacuum pump (Bangalore, India). The permeate was collected in glass ampules (traps) immersed in liquid nitrogen. The permeate in the cold trap was allowed to attain room temperature, removed, and weighed for the determination of the flux. The permeate composition was calculated by the measurement of the refractive index for a sodium-D line at 30°C with an Atago 3T refractometer (Tokyo, Japan). These data were used to compute the separation selectivity (α_{sep}).

RESULTS AND DISCUSSION

Liquid transport across a barrier membrane is governed by sorption–diffusion phenomena.[25] The transporting liquid is sorbed into the membrane and then diffuses into the membrane matrix because of the driving force created by the chemical potential difference, and preferential sorption of the solvent occurs at the feed side of the membrane. However, diffusion occurs until desorption takes place on the downstream side of the membrane. With these data, the permeation flux (J_p), α_{sep}, PV separation index (PSI), and enrichment factor (β), have been calculated as follows:

$$J_p = W_p / At \tag{2}$$

$$\alpha_{sep} = (P_{water}/P_{dioxane})/(F_{water}/F_{dioxane}) \tag{3}$$

$$PSI = J_p\,(\alpha_{sep} - 1) \tag{4}$$

TABLE I
Total J_p and α_{sep} Data for Different Mass Percentages of Water in the Feed Mixture at 30°C

Mass percentage water	$J_p\ 10^2$ (kg/m^{2}h)			α_{sep}		
	NaAlg	Copoly-1	Copoly-2	NaAlg	Copoly-1	Copoly-2
10	5.75	5.97	6.69	351	82.8	76.7
20	6.38	6.73	8.02	57.5	32.4	24.4
30	8.83	10.3	10.9	28.8	15.0	11.0
40	12.4	15.5	16.0	11.0	8.50	6.19
50	12.3	18.6	26.3	6.69	4.00	3.76
60	14.5	25.9	41.2	3.37	3.37	2.00
70	19.5	35.7	52.3	4.08	0.85	0.64

TABLE II
J_p **and** α_{sep} **at Different Temperatures for 10 Mass % Water in the Feed Mixture**

Temperature (°C)	J_p 10^2 (kg/m²h)			α_{sep}		
	NaAlg	Copoly-1	Copoly-2	NaAlg	Copoly-1	Copoly-2
30	5.75	5.97	6.69	351	82.84	76.71
40	6.52	6.82	6.93	104.92	66.63	62.43
50	6.91	7.13	7.31	82.84	45.88	42.43

$$\beta = \frac{C_W^P}{C_W^F} \tag{5}$$

where W_p is the mass of the permeate, A is the area of the membrane in contact with the feed mixture, and t is time. P_{water} and P_{dioxane} are the mass percentages of water and dioxane, respectively, in the permeate, and F_{water} and F_{dioxane} are the mass percentages of water and dioxane, respectively, in the feed. C_W^P and C_W^F are the concentrations of water at the permeate and feed sides, respectively. J_p and α_{sep} are presented in Table I. Similar data at different temperatures for dioxane mixtures containing 10 mass % water are presented in Table II. The results of PSI and β are displayed graphically.

DS as a function of the mass percentage of water in the feed mixture is displayed in Figure 1. DS generally increases with an increasing mass percentage of water in the feed mixture for all three membranes; this may be due to an increase in the hydrogen-bonding interactions between the membrane and water molecules with an increasing amount of water in the mixture. In the entire mixture composition, swelling is smaller for pure NaAlg than that for Copoly-1 and Copoly-2 membranes. The highest swelling observed for Copoly-2 may be due to higher hydrophilic interactions between the membrane and the water molecules of the mixture. The increase in the hydrophilicity of the membrane might be due to an increase in the grafting

percentage of pAAm to the NaAlg backbone, which facilitates the hydrophilic interactions.

Figure 2 shows the dependency of α_{sep} as a function of the mass percentage of water in the feed mixture. α_{sep} is quite high at 10 mass % water in the feed mixture for all three membranes. For the pure NaAlg membrane, α_{sep} is 351 at 10 mass % water in the feed, whereas for Copoly-1 and Copoly-2 membranes, the α_{sep} values are 82.8 and 76.7, respectively. The α_{sep} value for the pure alginate membrane decreases drastically from 10 to 20 mass % water in the feed. For Copoly-1 and Copoly-2 membranes, the decrease in α_{sep} is not so dramatic with the mass percentage of water in the feed mixture increasing from 20 to 70. However, with an increase in the mass percentage of water in the feed mixture, the membrane swelling increases because more dioxane molecules might have sorbed along with the water molecules, and this results in a decrease of α_{sep}.[15] α_{sep} also decreases with an increasing grafting percentage, and this is attributed to the fact that with an increase in the grafting percentage, hydrophilicity increases; this leads to higher swelling of the membrane and a reduction in the selectivity. For Copoly-1 and Copoly-2 membranes, α_{sep} remains almost identical over the entire range of mixture compositions.

Figure 3 shows the variation of the total flux with the mass percentage of water in the feed mixture. For all three membranes, the total flux increases with an
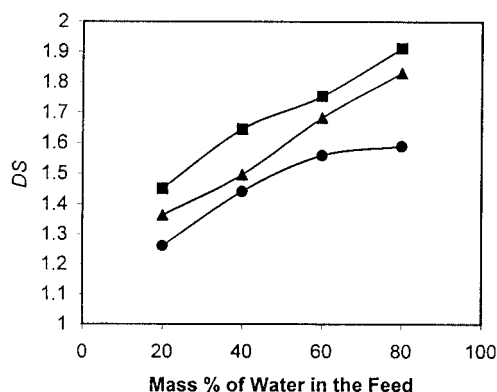

Figure 1 Plot of DS versus the mass percentage of water in the feed mixture for (●) NaAlg, (▲) Copoly-1, and (■) Copoly-2 membranes.
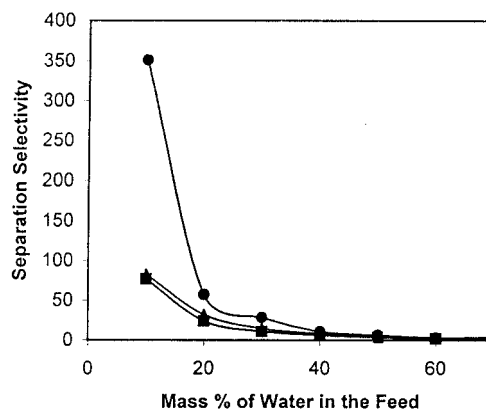

Figure 2 α_{sep} versus the mass percentage of water in the feed mixture for (●) NaAlg, (▲) Copoly-1, and (■) Copoly-2 membranes.
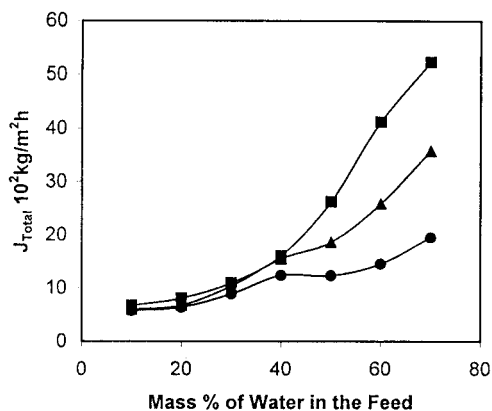
Figure 3 Plot of the total flux (J_{total}) versus the mass percentage of water in the feed mixture for (●) NaAlg, (▲) Copoly-1, and (■) Copoly-2 membranes.
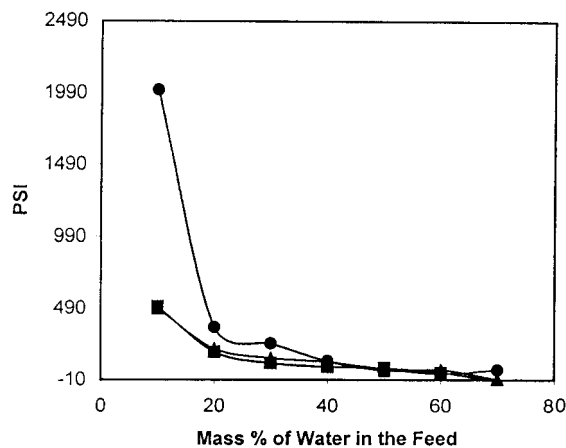

Figure 5 Plot of PSI versus the mass percentage of water in the feed mixture for (●) NaAlg, (▲) Copoly-1, and (■) Copoly-2 membranes.

increase in the mass percentage of water in the feed. This is because with an increase in the mass percentage of water in the feed, membrane swelling increases, and this creates more free volume, which results in an

increase in the total permeate flux. However, the difference in the total flux values for all three membranes is not considerable up to 30 mass % water in the feed mixture, but a noticeable increase in the total flux values can be observed for Copoly-1 and Copoly-2 membranes after 30 mass % water in the feed. The highest total flux of 0.523 kg/m^2 h is observed for Copoly-2 membrane at 70 mass % water in the feed, whereas Copoly-1 and pure NaAlg membranes have shown flux values of 0.357 and 0.195 kg/m^{2}h, respectively, at 70 mass % water in the feed. For all compositions of water in the feed mixture, higher flux values are observed with Copoly-2, whereas lower values are observed for the pure NaAlg membrane; intermediate values are observed for the Copoly-1 membrane. This could be due to the fact that with an increase in the grafting percentage of pAAm on NaAlg, more of the free amide groups are available,[26] and this results in an increase in the hydrophilicity of the membrane,
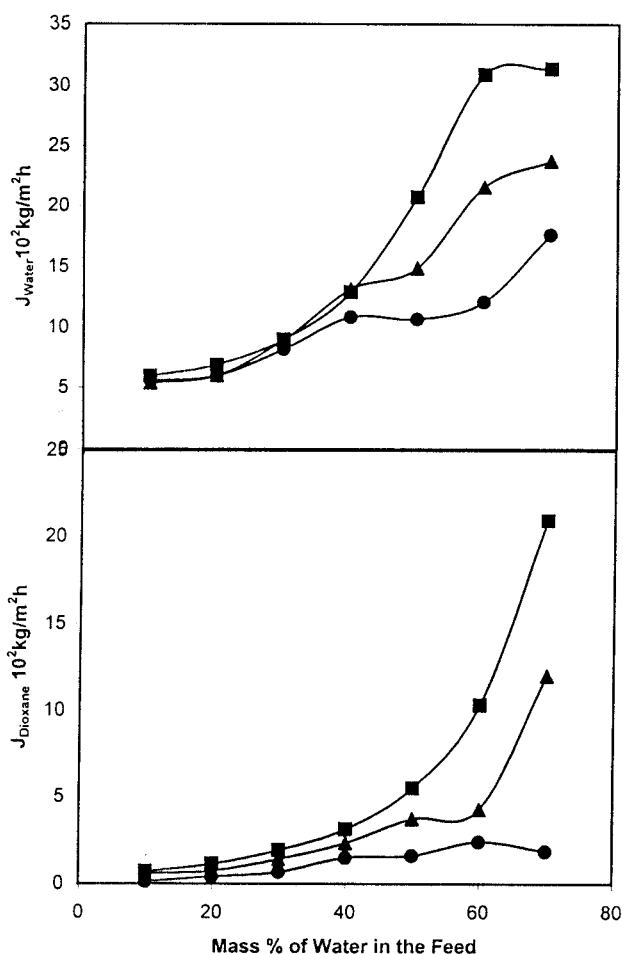

Figure 4 Plot of the individual fluxes of water and dioxane versus the mass percentage of water in the feed mixture for (●) NaAlg, (▲) Copoly-1, and (■) Copoly-2 membranes.
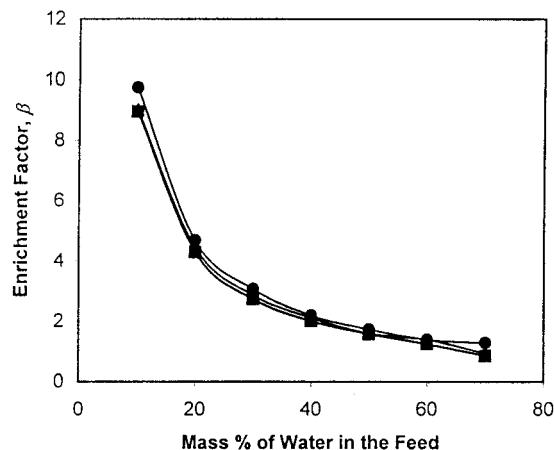

Figure 6 Plot of β versus the mass percentage of water in the feed mixture for (●) NaAlg, (▲) Copoly-1, and (■) Copoly-2 membranes.

TABLE III
Diffusion Coefficients of Water and Dioxane Calculated From Eq. (6) at 30°C

Mass percentage water	$D_{water} \times 10^9$ (m²/s)			$D_{dioxane} \times 10^{10}$ (m²/s)		
	NaAlg	Copoly-1	Copoly-2	NaAlg	Copoly-1	Copoly-2
10	2.49	2.61	2.93	0.64	2.84	3.44
20	3.16	3.38	4.06	2.19	4.17	6.67
30	5.08	6.15	6.67	4.12	9.60	14.2
40	8.81	11.4	12.4	12.0	20.1	30.0
50	11.2	19.3	27.8	16.0	48.3	74.0
60	20.0	35.8	80.2	39.6	70.7	267
70	33.8	264	122	35.1	1330	814

which increases the flux. In general, total flux values increase because of grafting of the membranes over that of the pure NaAlg membrane. Figure 4 displays the dependence of individual fluxes of dioxane and water as a function of the mass percentage of water in the feed. Flux values of water are higher than those observed for dioxane over the entire range of water in the feed mixture.

Membrane performance in PV separation can be influenced by several process parameters, such as the feed composition and temperature, in addition to polymer chain relaxation due to solvent diffusion and morphology of the membranes.[27] Both PSI and β are important for membrane performance, and these have been calculated with eqs. (4) and (5), respectively. Their dependencies are displayed in Figures 5 and 6, respectively. Both parameters show a decreasing trend with an increasing amount of water in the feed mixture. However, the β values for all the membranes decrease systematically in an identical manner with an increasing composition of water in the feed mixture, whereas the PSI values of pure NaAlg vary quite differently than those of Copoly-1 and Copoly-2 membranes.

The diffusion coefficient (D_i) of liquids through membranes has been calculated with the PV data as follows:

$$J_i = P_i[P_{i(feed)} - P_{i(permeate)}] = (D_i/(h)) [C_{i(feed)} - C_{i(permeate)}]$$
(6)

Here D_i is assumed to be constant across the effective membrane thickness (h); J_i is flux; C_i(feed) and C_i(permeate) are mixture compositions in the feed and permeate, respectively. The computed values of D_i

(where subscript i stands for either water or dioxane) at 30°C are presented in Table III, whereas the computed values of D_i at 30, 40, and 50°C are presented in Table IV.

The diffusion coefficients of water and dioxane increase systematically from pure NaAlg to the grafted membranes. With increased grafting, the diffusion values also increase for all the membranes at all compositions. Similarly, the diffusion coefficients increase with an increasing amount of water in the feed mixture for all three membranes. From the data presented in Table III, it is difficult to study the dependence of the D_i values as a function of the feed mixture composition with reference to individual membranes. For all the membranes at all the mass percentages of water, the D_i values for water are higher than those observed for dioxane. This is due to the membrane selectivity toward water molecules.

The effect of temperature on flux and diffusion is systematic, as expected. An increase in the feed temperature increases the thermal mobility of the polymer chains, thereby increasing the diffusion rate. The results for J_p and α_{sep} for 10 mass % water in the feed mixture at 30, 40, and 50°C are presented in Table II. With an increase in temperature, the free volume of the membrane increases, thereby increasing the flux values, but α_{sep} decreases.

The temperature dependency of flux and diffusion has been analyzed with the following Arrhenius relationships:

$$J_p = J_{po} \exp(-Ep/RT)$$
(7)

$$D_i = D_{io} \exp(-Ed/RT)$$
(8)

TABLE IV
Diffusion Coefficients of Water and Dioxane Calculated from Eq. (6) at Different Temperatures for 10 Mass % Water in the Feed Mixture

Temperature (°C)	$D_{water} \times 10^9$ (m²/s)			$D_{dioxane} \times 10^{10}$ (m²/s)		
	NaAlg	Copoly-1	Copoly-2	NaAlg	Copoly-1	Copoly-2
30	2.49	2.61	2.93	0.64	2.84	3.44
40	2.84	2.99	3.05	2.44	4.04	4.39
50	3.02	3.15	3.24	3.28	6.17	6.86

TABLE V
E_p, E_d, ΔH_s, and $E_{\text{dioxane}} - E_{\text{water}}$ Values

Parameter	NaAlg	Copoly-1	Copoly-2
E_p (kJ/mol), eq. (7)	4.3423	4.1678	0.3256
E_d (kJ/mol), eq. (8)	7.8823	7.6976	4.0848
ΔH_s (kJ/mol)	−3.54	−3.5298	−3.7592
($E_{\text{dioxane}} - E_{\text{water}}$) (kJ/mol)	59.192	23.992	24.035

where E_d and E_p are the energies of activation for diffusion and permeation, respectively; J_{po} and D_{io} are the permeation and diffusion rate constants, respectively; R is the gas constant; and T is the temperature (K). The E_d and E_p values, estimated by the method of least squares, are presented in Table V. If the activation energy is positive, J_p increases with increasing temperature; a phenomenon that is most common in PV separation experiments. This further increases the driving force for mass transport because it represents the concentration gradient due to the differential vapor pressure of the permeant molecules between feed and permeate mixtures. As the feed temperature increases, the vapor pressure in the feed compartment also increases, but the vapor pressure at the permeate side is not affected. Therefore, with an increasing temperature, the driving force for molecular transport also increases. With the calculated values of E_p and E_d for water, the heat of sorption (ΔH_s) for water permeation has been calculated ($\Delta H_s = E_p - E_d$), and these data are also included in Table V. The ΔH_s values are negative for all the membranes, suggesting that sorption follows an endothermic process.

The temperature dependency of α_{sep} has also been studied with an equation proposed by Ping et al.:[28]

$$Y_{\text{water}} = \cfrac{1}{1 + \left(\cfrac{J_{\text{dioxane}}}{J_{\text{water}}}\right)\exp\left(\cfrac{-(E_{\text{dioxane}} + E_{\text{water}})}{RT}\right)} \quad (9)$$

where Y_{water} is the water composition in the permeate; J_{water} and J_{dioxane} are the permeation fluxes for water and dioxane, respectively; and E_{water} and E_{dioxane} are the Arrhenius activation energies for water and dioxane, respectively, at the average energy level. The positive values of $E_{\text{dioxane}} - E_{\text{water}}$ indicate that α_{sep} decreases with an increase in temperature, but the negative values indicate that α_{sep} increases with increasing temperature.[29] In this study, the difference ($E_{\text{dioxane}} - E_{\text{water}}$) is positive, indicating that α_{sep} decreases with increasing temperature (see Table V). The results presented in Table II also support the idea that α_{sep} decreases with the temperature increasing from 30 to 50°C.

CONCLUSIONS

NaAlg and its grafted membranes with AAm have been prepared and used in the PV separation of water–dioxane mixtures. The membrane performance varies, depending on the nature of the polymer, the water composition of the feed mixture, and the experimental conditions. These membranes are effective in separating water–dioxane mixtures.

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