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Use of Sodium Alginate-Poly(vinyl pyrrolidone) Membranes for Pervaporation Separation of Acetone/Water Mixtures

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Pervaporative separation of acetone from water at a concentration range of 0–100 wt% were studied using sodium alginate (NaAlg)/Poly vinyl pyrrolidone (PVP) membranes. Membranes were prepared in different ratios (w/w) (100/0, 95/5, 90/10, 85/15, 80/20, 75/25) of NaAlg/PVP by crosslinking with $CaCl_2$. Experimental studies were carried out to investigate the effects of the operating temperature, feed composition, and membrane thickness on the pervaporation performance. The optimum operating temperature, membrane thickness, NaAlg/PVP ratio, and feed composition were determined as 40°C, 70 μm, 75/25 (w/w), and 20 wt% acetone, respectively. The effect of PVP content in the membranes was investigated on pervaporation performance. The permeation rate was increased with increasing the PVP content; however, there was no appreciable change about the separation factor. The permeation rate and separation factor values were found to be in the range of 0.304–1.023 kg/m^2h and 16–57, respectively. In addition, the sorption-diffusion properties of the alginate membranes were investigated at the operating temperature and the feed composition. It was found that the sorption selectivity was the dominant factor for the separation of acetone/water mixtures.

Keywords acetone; membrane; NaAlg; pervaporation; PVP

INTRODUCTION

Pervaporation (PV) is an important technology for the organic separation from organic-water mixtures (1–4). It is a new membrane technology and more effective than traditional separation techniques, such as chemical oxidation or distillation from the energy saving point of view. It has important advantages in azeotropic systems due to its mechanism of separation. In this method, the membrane is in contact with the feed mixture and it acts as a selective barrier between two phases. The feed mixture is placed in contact with one side of the membrane and the permeate is removed as vapor from the other side.

For dehydration of organic solvents and separation of alcohol-water mixtures, NaAlg based membranes and their modified forms are used in PV method (5–11). Alginic acid is a highly hydrophilic polymer used in biotechnology, pharmaceutical, and cosmetic industries. Although alginic acid can hardly dissolve in commercially available solvents, its alkali metal salt form (alginate), obtained by neutralizing the acidic functional groups with strong alkalis, is well soluble in water. Thus, a membrane can be easily prepared from an alginate aqueous solution. However, since it is a highly hydrophilic polymer and has poor stability in water, it should be insolubilized by blending, copolymerization, crosslinking, or grafting (12–17). In this study NaAlg/PVP membranes were prepared and successfully crosslinked with $CaCl_2$ (Scheme 1).

PVP is a hydrophilic polymer which is soluble in water and other polar solvents. It readily absorbs up to 18% of its weight in atmospheric water. In solution, it has excellent wetting properties and readily forms films. Although its monomer is carcinogenic and is extremely toxic to aquatic life, the polymer PVP in its pure form is so safe that not only it is edible by humans, but it was used as a blood plasma expander for trauma victims after the first half of twentieth century.

Acetone is a widely used chemical which is commonly used in the production of chemicals and plastics as well as a solvent in pharmaceutical industry. It does not form an azeotrope with water but a large reflux is required when attempting to distil a solution necessitating a large column and high-energy costs. Because of this PV is a good alternative method to be used for the concentrating of acetone.

Several articles were found in the literature about the separation of acetone/water mixtures (18–27) which were related to the PV method. Urtiaga and co-workers (22) used inorganic zeolite NaA membrane for dehydration of acetone. They reported that by increasing the temperature from 40 to 48°C, the flux was more than doubled when dehydrating acetone containing 3 wt% water. Burshe et al. (24) studied pervaporative dehydration of organic solvents by using PVA with different crosslinking agents; adipic acid, maleic acid, citric acid, and gluteraldehyde. They found that crosslinking with maleic acid produced the best separation characteristics in the membrane. Ray and Ray

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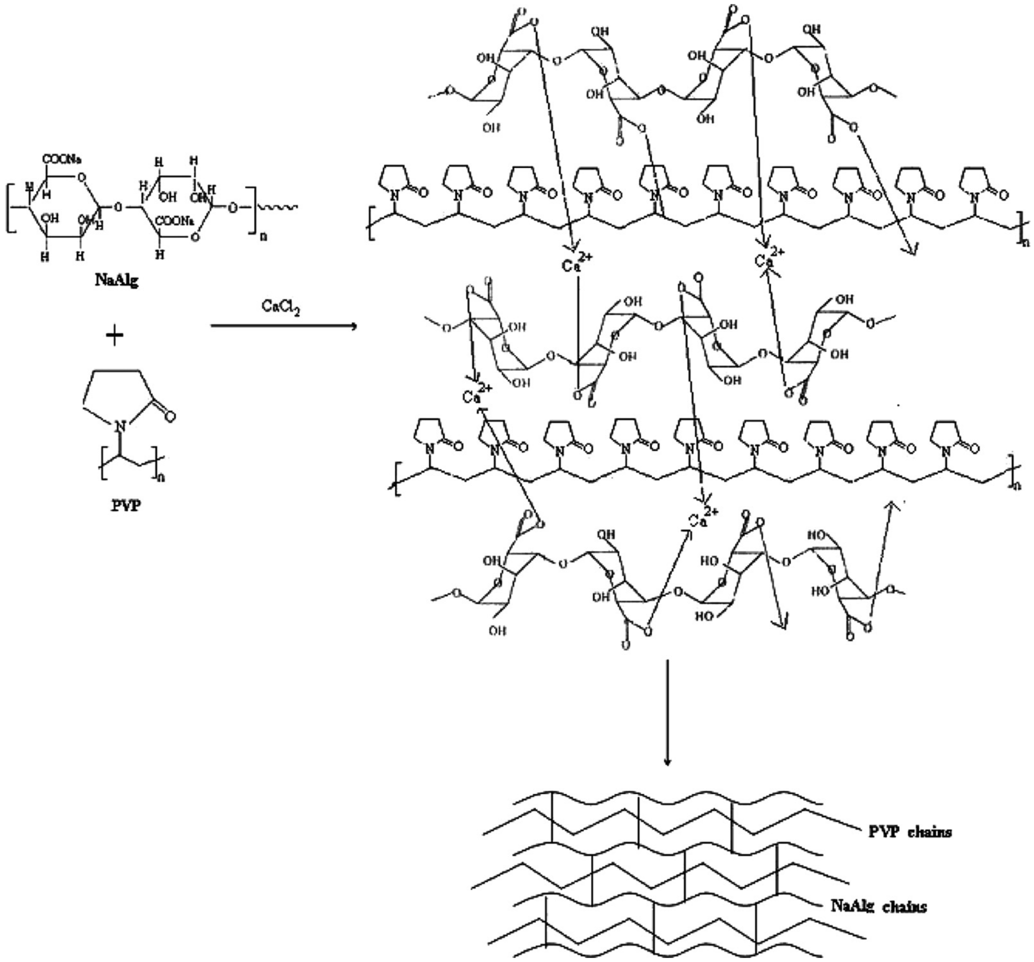


SCH. 1. Schematic representation of the polymer.

(27) synthesized different copolymer membranes for the separation of acetone-water mixtures. They found that acrylonitrile copolymer membranes showed maximum water flux and selectivity as 0.029 kg/m^{2}h and 16.73, respectively, for 2.5 wt% water in feed while styrene copolymer membranes showed maximum acetone selectivity and flux as 0.007 kg/m^{2}h and 12.61, respectively, for 1.6 wt% acetone in feed. As seen from the reported values flux and selectivity values are not high for the acetone-water separation, so further studies should be carried out on this separation using different polymeric systems because according to our literature survey there is no study about the separation of acetone-water mixtures using NaAlg/PVP membranes by PV. So this study pioneers on the separation of aqueous acetone solutions using NaAlg/PVP membranes.

EXPERIMENTAL

Materials

NaAlg was provided from Sigma with medium viscosity (Louis, USA). PVP, $CaCl_2$, and acetone were supplied by Merck (Darmstadt, Germany), and used as supplied.

Membrane Preparation

PVP (8 wt%) and NaAlg (2 wt%) were dissolved in water, mixed in different ratios (w/w), stirred, and then casted onto rimmed round glass dishes (10). The solvent was evaporated at 60°C to form the membrane. The dried membrane was crosslinked with $CaCl_2$ (0.1 M) for 24 h. The thickness of the membranes thus prepared was 70 (±10) μm.

Swelling Degree Experiments

The membrane was immersed in different concentrations of acetone solutions at 40°C for 48 h. The swollen membranes were wiped with cleansing tissue to remove the solvent mixture. Then the membranes were dried at 60°C until constant weight. The swelling degrees (SD) of membranes were calculated as;

$$SD = \frac{(W_S - W_D)}{W_D} \times 100 \qquad (1)$$

where W_S, W_D were the mass of the swollen membrane in the feed solution and dry membrane, respectively.

Pervaporation Experiments

The separation of acetone-water mixtures by using PV method was carried out over the full range of compositions (0–100 wt%) at temperatures varying from 30°C to 50°C by using NaAlg/PVP membrane. The membrane surface area was 16.5 cm^2 and pressure was kept at 0.6 mbar with a vacuum pump (Edwards). The feed mixture was circulated between PV cell and feed tank at constant temperature and permeate was collected in liquid nitrogen traps (Fig. 1). The composition of the permeate that was collected after steady state conditions attained analyzed with Atago DD-5 type digital refractometer.

The membrane performance was expressed by separation factor (α) and permeation rate (J).

The separation factor α was defined as follows:

$$\alpha = \frac{P_{Water}/P_{Acetone}}{F_{Water}/F_{Acetone}} \tag{2}$$

where P_{Water} and $P_{Acetone}$, F_{Water}, and $F_{Acetone}$ and are the mass fractions (wt%) of water and acetone components in the permeate and feed, respectively.

The permeation rate J was calculated as follows:

$$J = \frac{W}{A\,t} \tag{3}$$

where W is the mass of permeate (kg), A is membrane surface area (m^2), t is the time of experiment (h).

Sorption Measurements

The membranes were immersed in to the different concentration of acetone solutions for 48 h at 40°C. To remove the excess solvent, membranes were blotted between tissue paper, and then the membrane was placed into an empty pervaporation cell and the sorbed mixture was collected in the traps. The composition of the collected mixture was determined by an Atago DD-5 type digital refractometer (9–10).

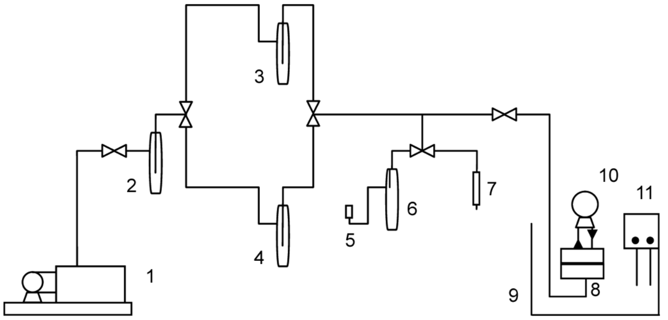


FIG. 1. Schematic diagram of the pervaporation apparatus: (1) vacuum pump, (2–4, 6) permeation traps; (5) Mc Leod manometer; (7) vent; (8) permeation cell; (9) constant temperature water bath; (10) peristaltic pump; (11) temperature indicator.

The sorption selectivity α_s was calculated as;

$$\text{Sorption selectivity } \alpha_s = \frac{Y_{Water}/Y_{Acetone}}{X_{Water}/X_{Acetone}} \tag{4}$$

where; $X_{Acetone}$, $X_{Acetone}$, and $Y_{Acetone}$, $Y_{Acetone}$ are the mass fractions of acetone and water in the acetone solution (feed) and membrane (permeate), respectively.

The diffusion selectivity α_d can be calculated from the separation factor and the sorption selectivity by Eq. (5) as follows;

$$\text{Diffusion selectivity } \alpha_d = \frac{\alpha_{sep.Water/Acetone}}{\alpha_{sorp.Water/Acetone}} \tag{5}$$

RESULTS AND DISCUSSION

Selection of NaAlg/PVP Ratio

The effect of NaAlg/PVP ratio was studied with 20 wt% acetone/water mixture in ratios of 100/0, 95/5, 90/10, 85/15, 80/20, 75/25 (NaAlg/PVP, w/w), and 40°C. The results were presented in Table 1. As it is seen from the table that the permeation rate increases whereas the separation factor decreases as the PVP content of the membrane increases. The results were supported by the swelling measurements (Fig. 2). The swelling measurements of membranes increased with the increase in the PVP content of the membrane. Similar results were found in the literature (28–29,3). Zhang and coworkers (29) studied the pervaporation dehydration of ethyl acetate/ethanol/water azeotrope using chitosan/poly(vinyl pyrrolidone) blend membranes. They observed that the permeation flux increased with increasing feed temperature and PVP content, while the separation factor decreased.

The blend ratio of 75/25 (NaAlg/PVP, w/w) was preferred in the rest of the study due to their mechanical resistance.

TABLE 1
Effect of the separation factor and permeation rate in different ratio of NaAlg/PVP. $[C_3H_6O]$: 20 wt%, membrane thickness: 70 μm, pressure: 0.6 mbar, operating temperature: 40°C

NaAlg/PVP ratio (w/w)	Separation factor (α)	Permeation rate (J, kg/m^2 h)
100/0	30.31	0.672
95/5	29.59	0.692
90/10	28.16	0.709
85/15	28.78	0.722
80/20	27.65	0.758
75/25	27.67	0.790

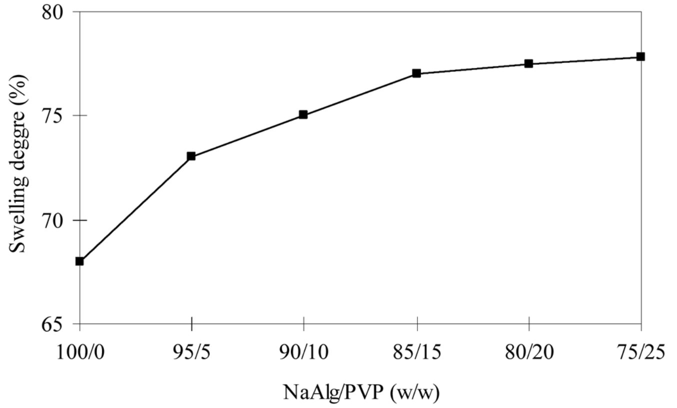


FIG. 2. Change in the swelling degree with the PVP content in the membrane. [C_3H_6O]: 20 wt%, membrane thickness: 70 μm, operating temperature: 40°C.

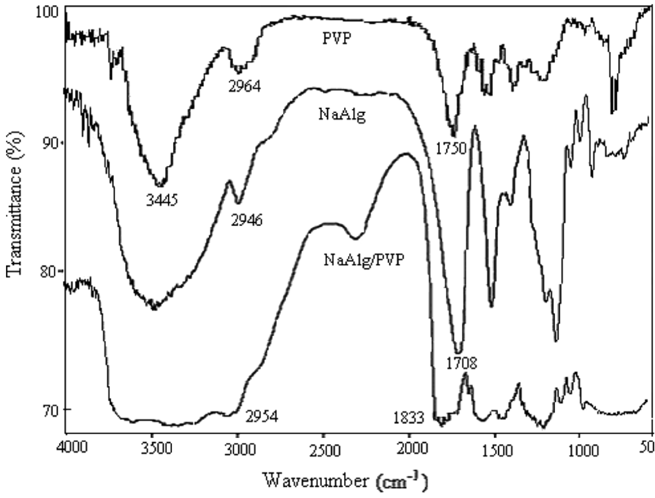


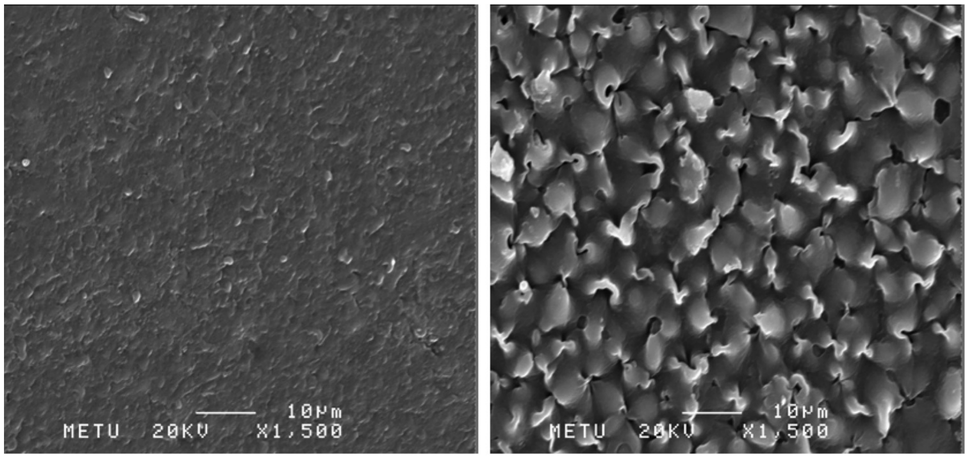
FIG. 4. IR spectra of NaAlg/PVP (75/25, w/w), PVP and NaAlg membranes.

Characterization of Membrane

The morphology of the NaAlg and NaAlg/PVP membranes was observed using Scanning Electron Microscopy (SEM, JEOL JSM-6400) (Fig. 3(a,b)). It was seen from the SEM results that the NaAlg membrane surface (Fig. 3a) had a smoother appearance than the membrane for the same magnification.

The membrane was scanned with Mattson 1000 Fourier Transfer Infrared Spectroscopy (FTIR) (Fig. 4). In the FTIR spectrum of NaAlg/PVP (75/25, w/w) and NaAlg, the peak at 3000–3500 cm^{-1} area presents the stretching vibration of the –OH band. In the FTIR spectrum of NaAlg/PVP these stretching vibrations appear as a wider band than the spectrum of NaAlg. This peak appears at 3445 cm^{-1} in the spectrum of PVP. The peak at 1708 cm^{-1} in the spectrum of NaAlg is due to the stretching band of C=O. The spectrum of PVP appears as a strong absorption band at 1750 cm^{-1}, due to the presence of the C=C−N group. In the FTIR spectrum of NaAlg/PVP, these bands were seen together at 1833 cm^{-1}. The spectrums of PVP, NaAlg, and NaAlg/PVP appear stretching bands of C−H group at 2964 cm^{-1}, 2946 cm^{-1}, and 2954 cm^{-1}, respectively.

The thermal analysis was performed with Differential Scanning Calorimeter (DSC, General V4.1C Dupont 2000) and results were illustrated in Fig. 5. The NaAlg polymer used in this study showed a T_g of 64°C; however, this value for NaAlg/PVP has been found to be 66°C. The increase in T_g could also be the evidence of the interaction between PVP and NaAlg in the membrane.



(a) (b)

FIG. 3. (a) Scanning electron microscopic picture of crosslinked NaAlg membrane, (b) Scanning electron microscopic picture of crosslinked NaAlg/PVP membrane.

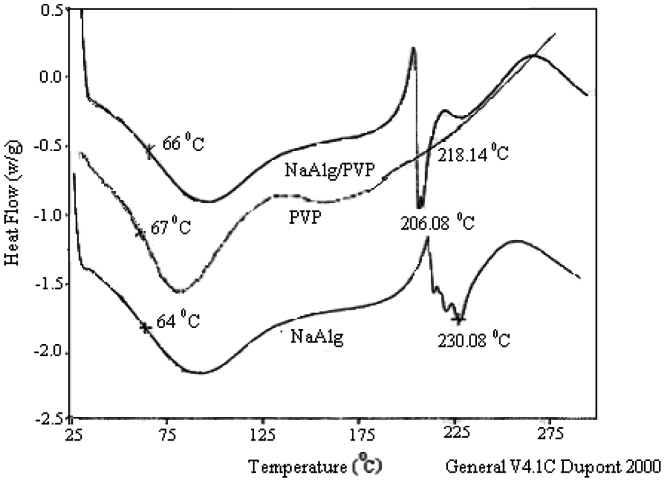


FIG. 5. Differential scanning calorimeter curves of NaAlg/PVP and NaAlg membranes.

The crosslinking density of the membrane was determined from the swelling studies. For this purpose the molecular weight between the crosslinks (M_C) of the polymer was determined by using the Flory-Rehner Eq. (30) as given below:

$$M_C = -\delta_p V_S \phi^{1/3}\left[\ln(1-\phi) + \phi + \chi\phi^2\right]^{-1} \tag{6}$$

ϕ is the volume fraction of the polymer in the swollen state and can be calculated as:

$$\phi = \left[1 + \frac{\delta_P}{\delta_S}\left(\frac{M_a}{M_b}\right) - \frac{\delta_P}{\delta_S}\right]^{-1} \tag{7}$$

where δ_P and δ_S are the densities of the polymer and solvent, respectively. M_a and M_b are the mass of the polymer before and after swelling, respectively. V_s is the molar volume fraction of the polymer in the swollen state.

Interaction parameter, χ can be calculated from following equation.

$$\begin{aligned}\chi = {} & [\phi(1-\phi)^{-1} + N\ln(1-\phi) + N\phi]\cdot \\ & [2\phi - \phi^2 N - \phi^2 T^{-1}\cdot(\partial\phi/\partial T)^{-1}]^{-1}\end{aligned} \tag{8}$$

where $N = (\phi^{2/3}/3 - 2/3)(\phi^{1/3} - 2\phi/3)^{-1}$ and temperature is taken as Kelvin.

For the NaAlg/PVP beads, the M_C value was found to be 885.

Finally cross-link density, δ_X;

$$\delta_X = \delta_P / M_c \tag{9}$$

In our study the cross-link density of NaAlg/PVP (75/25, w/w) membranes was found as 1.01×10^{-3} mol/cm^3 taking the χ (acetone-water) as 0.7959.

Diffusion Coefficient

In the pervaporation method, the mass transport of liquid molecules is generally described by using the solution-diffusion mechanism. This mechanism involves sorption, diffusion, and evaporation steps. The permeation performance is affected both preferential sorption in the membrane and the diffusion of each component of the feed mixture through the membrane. So it is important to estimate the diffusion coefficient, *Di* of penetrating molecules to understand the transport mechanism.

The flux of component *i*, J_i, can be given by using Fick's first law (28,31);

$$Ji = -Di(dCi)/dx) \tag{10}$$

Here, *J* is the permeation flux of component i (kg/m^2 s), *Di* is the Fickian diffusion coefficient (m^2/s), *Ci* is the penetrate concentration in the membrane (kg/m^3), *x* is the diffusion lengh (m). For simplicity, it is assumed that the concentration profile along the diffusion lengh is linear. So, the diffusion coefficient can be calculated using the following equation;

$$D_i = J_i\delta / C_i \tag{11}$$

δ is the membrane thickness; *C* is the concentration of component *i* at the membrane surface of the feed side. The results were shown in Fig. 6. As it was seen from the figure, the diffusion coefficients increased with an increasing amount of water in the feed mixture. Increase in D_{water} values with an increasing amount of water in the feed mixture was attributed to the increasing free volume in the membrane. As a result the transport of more water molecules was facilitated through the free volume spaces.

Effect of the Membrane Thickness

Membranes with varying thicknesses (30–90 μm) were prepared from the NaAlg/PVP solution by casting

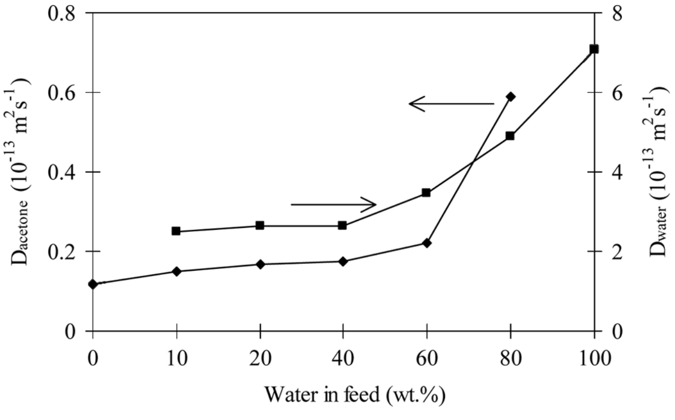


FIG. 6. Effect of the feed composition on the diffusion coefficients of NaAlg/PVP membranes.

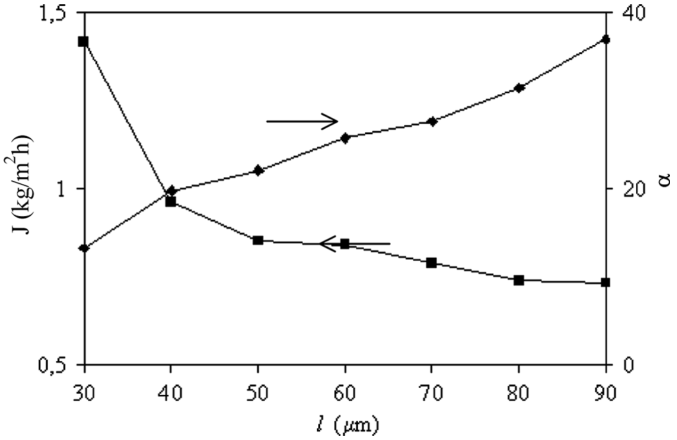


FIG. 7. Effect of membrane thickness on the permeation rate and the separation factor.

method. The separation factor and permeation rate as a function of membrane thickness were studied for the 20 wt% acetone mixture at 40°C and the results were presented in Fig. 7. As is seen from the figure, the permeation rate decreases with the membrane thickness whereas the separation factor increases. Membranes of 70 µm thicknesses were preferred in the rest of the study due to their acceptable flux and separation factor.

Different results concerning the effect of membrane thickness were reported in the literature (9–10,32–33). Liu and coworkers (32) studied the separation of acetone–butanol–ethanol (ABE) from dilute aqueous solutions by pervaporation. They observed that the thinner membrane exhibited a higher permeation flux (permeation rate) and a lower selectivity than the thicker membrane.

Effect of the Feed Composition in PV

The effect of the feed composition on the permeation rate and the separation factor was investigated at 40°C. The results were given in Fig. 8. From the figure, it is clear that as the concentration of acetone in the feed solution increases, the permeation rate decreases whereas the separation factor increases. Similar results were found in literature (33). In this research Zhao et al. focused on studies on pervaporation characteristics of polyacrylonitrile–*b*-poly(ethylene glycol)–*b*-polyacrylonitrile block copolymer membrane for dehydration of aqueous acetone solutions. They observed that the separation factor decreases with the increasing water concentration in the feed.

As the water concentration in the feed increases, the amorphous regions of the membrane becomes more swollen; hence the flexibility of polymer chains increases, the energy required for diffusive transport through the membrane decreases resulting in low separation factors at low acetone concentrations. These results were supported by the swelling measurements (Fig. 9).

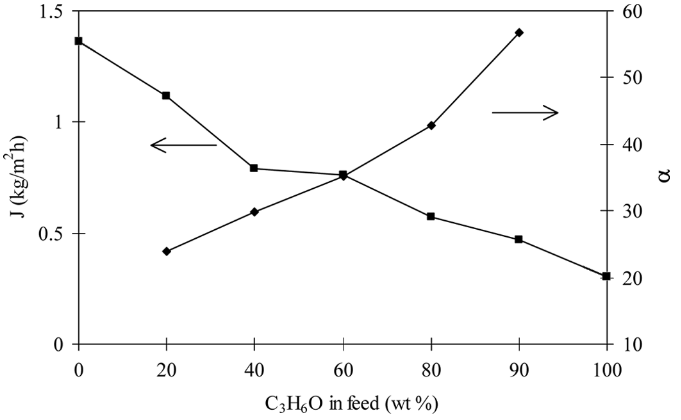


FIG. 8. Effect of the feed composition in PV. The permeation conditions; membrane thickness: 70 µm, operating temperature: 40°C, pressure: 0.6 mbar.

The permeation rates of induvidual components were shown in Fig. 10. As is seen from the figure, the permeation rate of water was much higher than the permeation rate of acetone. The permeation rate of the water component decreased with the decrease in water content of the feed solution. These phenomena can be explained in terms of the plasticizing effect of water.

The permeation rate of individual components was also studied by Alghezawi et al. (34). They have investigated the separation of acetic acid-water mixtures through acrylonitrile grafted poly(vinyl alcohol) membranes by pervaporation and observed that the permeation rate of the water component decreases with the decrease in the water content of the feed solution and the permeation rate of water is higher than that of acetic acid regardless of feed composition.

Figure 11 shows the relationship between the sorption selectivity and the diffusion selectivity for the membrane

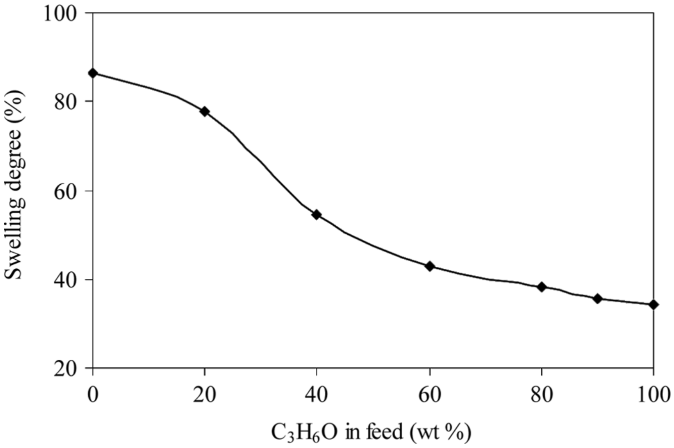


FIG. 9. Change in the swelling degree with the feed composition.

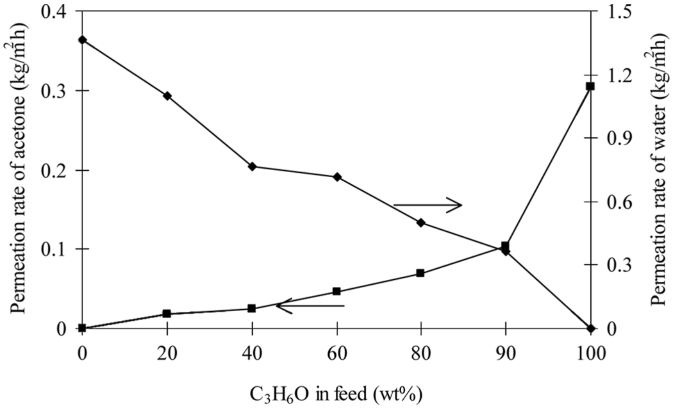


FIG. 10. Variation of the permeation rate of water and acetone with the feed composition.

at different acetone concentrations. The sorption selectivity and the diffusion selectivity increased with increasing acetone concentration in the feed solution due to the decrease in the swelling degree at high acetone concentrations. It was seen that the sorption selectivity was higher than the diffusion selectivity.

Effect of the Operating Temperature in PV

The effect of the operating temperature on the separation performance of the membranes was shown in Fig. 12. The permeation rate increases whereas the separation factor decreases with the increase in temperature. As the temperature increases the frequency and the amplitude of chain jumping increase so the free volume become larger, both acetone and water molecules pass through the membrane, resulting in increased total permeation rate whereas the decreased separation factor (32,34). 40°C can be selected as the advisable temperature for the operation due to its acceptable flux and selectivity.

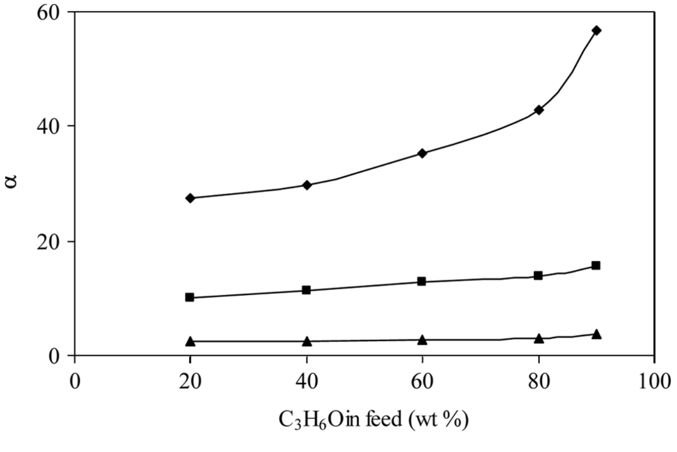


FIG. 11. Relationship between the selectivities at different feed compositions. Operating temperature: 40°C. Separation selectivity: (◆), sorption selectivity: (■) and diffusion selectivity: (▲).

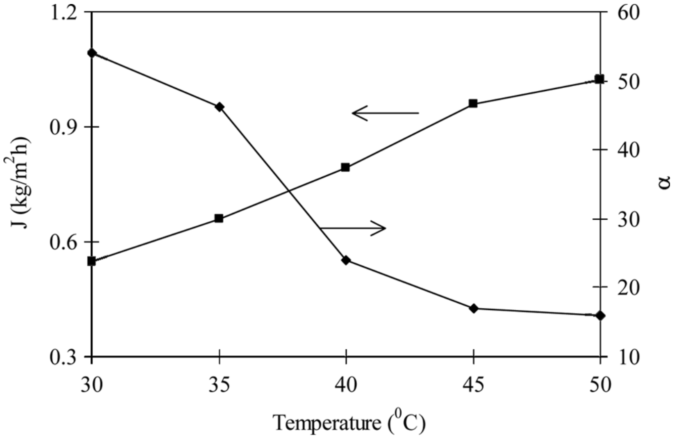


FIG. 12. Effect of the operating temperature in PV. The permeation conditions; [C_3H_6O]: 20 wt%, membrane thickness: 70 μm, pressure: 0.6 mbar.

Figure 13 shows the Arrhenius plot of the permeation rate for 20 wt% acetone mixtures. The temperature dependence of the permeation rates fits with the Arrhenius equation (9–10,31).

$$\mathrm{Ji} = \mathrm{Jpi}_0 \exp(-\mathrm{E_p}/\mathrm{RT}) \tag{12}$$

$$\mathrm{D_i} = \mathrm{Di}_0 \exp(-\mathrm{E_D}/\mathrm{RT}) \tag{13}$$

In the above equations E_P and E_D represent activation energies for permeation and diffusion. Jpi_0 and Di_0 are the permeation and diffusion rate constants, R is the gas constant, and T is the temperature in Kelvin.

Figures 13 and 14 show the Arrhenius plot of the individual permeation rate and diffusion of water which are used to calculate the permeation activation energies. The permeation activation energy of water, acetone, and diffusivity of water are calculated to be 3.48 kcal/mol, 11.03 kcal/mol, and 47.08 kcal/mol, respectively. It is observed that the activation energy values of water

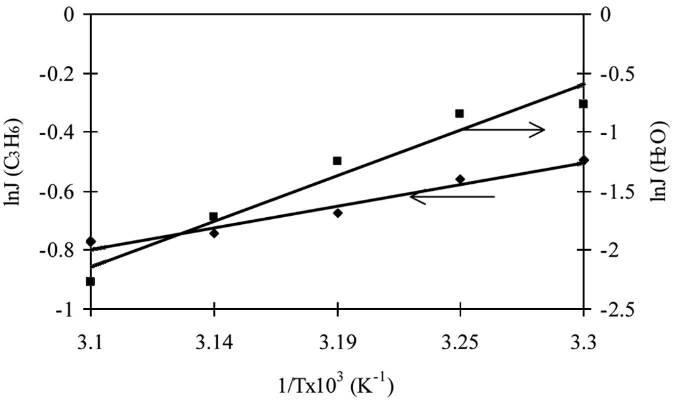


FIG. 13. Arrhenius plot of ln (acetone permeation rate) (■) and ln (water permeation rate) (◆) with 1/T for membrane in PV.

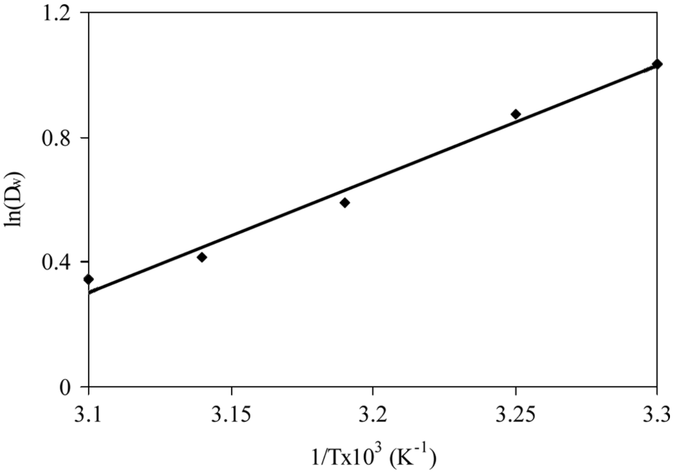


FIG. 14. Arrhenius plot of $\ln D_w$ with 1/T for membrane in PV.

permeation are lower than acetone permeation, suggesting a higher separation efficiency of the membrane. Using these values we have calculated the heat of sorption as (35);

$$Ep = \Delta H + Ed \tag{14}$$

The resulting ΔH value is found to be −43.60 kcal/mol. The ΔH value gives the additional information about the transport of the molecules through the polymer. If ΔH has negative value sorption is the dominant process (31).

The relationship between the sorption selectivity and the diffusion selectivity for the membrane at various permeation temperatures in PV is shown in Fig. 15. The sorption selectivity and the diffusion selectivity of the membrane was decreased with the increase in the permeation temperature. It is well known that the decrease in the sorption selectivity and the diffusion selectivity was due to the increase of membrane swelling with increasing feed temperature. Sorption selectivity was found to be higher than the diffusion selectivity and the difference between these two selectivities decreases as the temperature decreases.

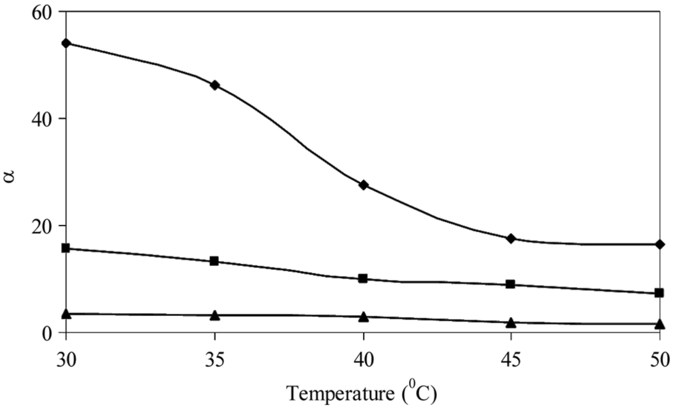


FIG. 15. Relationship between the selectivities at various permeation temperatures. Separation selectivity: (◆), sorption selectivity: (■) and diffusion selectivity: (▲).

CONCLUSIONS

NaAlg/PVP membranes with different PVP content were prepared and employed for the separation of acetone-water mixture by using the pervaporation method. It was seen that the permeation rate increases as the PVP content of the membrane increases. The performance of the membranes was explained with the permeation rate, the separation factor, the sorption-diffusion selectivity, and the diffusion coefficient. The membrane containing 75/25 (w/w) of NaAlg/PVP showed the highest separation factor of 57 with a permeation rate of 1.023 kg/m^{2}h at 40°C for 20 wt% acetone in the feed. The sorption and diffusion selectivity values show that the sorption selectivity slightly higher than diffusion selectivity. In addition the ΔH value supported the fact that the sorption is the dominant factor in this pervaporation process.

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