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Separation Characteristics of Dimethylformamide/Water Mixtures through Alginate Membranes by Pervaporation, Vapor Permeation and Vapor Permeation with Temperature Difference Methods

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Abstract: In this study permeation and separation characteristics of dimethylformamide (DMF)/water mixtures were investigated by pervaporation (PV), vapor permeation (VP), and vapor permeation with temperature difference (TDVP) methods using alginate membranes crosslinked with calcium chloride. The effects of membrane thickness (30–90 μm), feed composition (0–100 wt%), operating temperature (30–50°C) on the permeation rates and separation factors were investigated. The permeation rate was found to be inversely proportional to the membrane thickness whereas separation factor increased as the membrane thickness was increased. It was observed that the permeation rates in VP and TDVP were lower than in PV however the highest separation factors were obtained with TDVP method. Alginate membranes gave permeation rates of 0.97–1.2 kg/m^2h and separation factors of 17–63 depending on the operation conditions and the method. In addition, 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 dominant factor for the separating of DMF/water mixtures.

Keywords: Membrane, separation, pervaporation, vapor permeation, organic-water mixtures, dimethylformamide

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INTRODUCTION

Pervaporation process is an important technology for the separation of organic compounds. Organic compounds can be easily separated from water or from other organic streams (1–11). It is a new membrane technology and more effective than other options, such as chemical oxidation or distillation from the energy saving point of view. In this method the membrane is in contact with the feed mixture and it is a barrier between two phases, the feed mixture and the vapor phase permeate. Because of this, some problems appear such as swelling or shrinking of the membrane. These problems are minimized with vapor permeation (VP) and vapor permeation with temperature difference (TDVP) methods (Fig. 1). In these methods membrane is in contact with the vapor of the feed mixture. Furthermore a temperature difference between the membrane surrounding and the feed mixture was establised in the vapor permeation with temperature difference method (12–14).

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. Recently the sodium alginate (NaAlg) membranes have been used in the separation of alcohol-water mixtures (16–22) by pervaporation.

DMF is an important solvent, it is primarily used as a solvent in the production of polyurethane products and acrylic fibers. These uses account for about 50% of the total demand. It is also used in the pharmaceutical industry, in the formulation of pesticides and in the manufacture of

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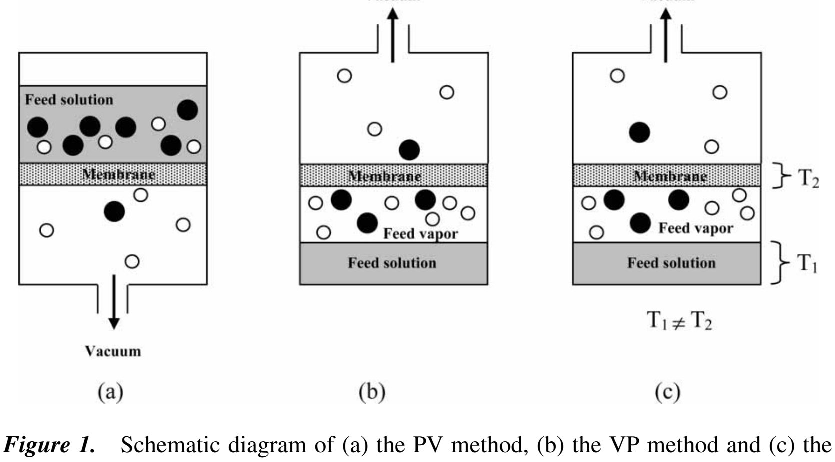

Figure 1. Schematic diagram of (a) the PV method, (b) the VP method and (c) the TDVP method.

synthetic leathers, fibers, films and surface coatings (23–25). DMF may be emitted to the environment as a result of its use in a variety of industries.

A few articles were found in the literature about the separation of DMF/water mixtures (26–28) which were related to the PV method. Shah and coworkers (26) prepared hydrophilic zeolite NaA membranes for the PV of alcohol-water and DMF-water mixtures. Aminabhavi and Naik (27) grafted PVA with acrylamide for separation of DMF/water mixtures. It was found that these membranes are more selective to water than DMF. Separation factors increased with grafting, but permeation flux did not change considerably with grafting. Kurkuri and Aminabhavi (28) grafted PVA with polyacrylonitrile and studied in the separation of DMF and water mixtures a range of 10 to 90 wt% in the feed at 25, 35, and 45°C. They have reported that by increasing the grafting of the membrane, flux decreased whereas selectivity increased slightly over that of pure PVP membrane.

In this article, sodium alginate membranes were prepared and crosslinked with calcium chloride resulting in the formation of insoluble calcium alginate. These membranes were used in the separation of DMF/water mixtures and the separation performance of the membranes as a function of membrane thickness, temperature, and feed composition were studied.

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EXPERIMENTAL

Materials

NaAlg was provided from Sigma (medium viscosity). DMF and calcium chloride were supplied by Merck.

Membrane Preparation

2 wt% solution of NaAlg was prepared in deionized water. The solutions of 80 ml were poured onto petri-dishes and the solvent was evaporated at 60°C to form the membrane. The dried membranes were crosslinked with calcium chloride (0, 1 M) for 24 h. The thickness of the membranes was 70 (±10) μm. Membranes prepared in this research were used at least 10 times without any deformation during the PV, VP, and TDVP processes.

Swelling Degree Measurements

The crosslinked membranes were immersed in different concentrations of dimethylformamide solutions in PV and were exposed to vapor of dimethylformamide mixtures in VP at 40°C for 48 h. The swollen membranes were wiped with cleansing tissue and weighed as quickly as possible. Then the membranes were dried at 60°C until they reached constant weight. The swelling degrees (SD) of membranes were calculated as:

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

where, W_S, W_D were the mass of the membranes before and after swelling, respectively.

Sorption Measurements

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

The sorption selectivity was calculated as:

$$\text{Sorption selectivity}(\alpha_{\text{sorp.W/DMF}}) = \frac{Y_W/Y_{DMF}}{X_W/X_{DMF}} \tag{2}$$

where; X_{DMF}, X_W and Y_{DMF}, Y_W are the mass fractions of DMF and water in the DMF solution (feed) and membrane (permeate), respectively.

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Scanning Electron Microscopy

The morphology of the NaAlg membranes were observed using scanning electron microscope (JEOL JSM-6400) (Fig. 2 (a,b)). It was seen from the SEM results that the uncrosslinked membrane surface (Fig. 2a) had a smoother and more homogenous appearence.

Pervaporation Experiments

Separation of DMF-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 Alg membranes. The membrane surface area was 16.5 cm^2 and pressure was kept at 0.6 mbar with a vacuum pump (Edwards). Feed mixture was circulated between PV cell and feed tank at constant temperature and permeate was collected in liquid nitrogen traps (Fig. 3). Composition of the permeate that was collected after steady state conditions attained was analyzed with Atago DD-5 type digital refractometer.

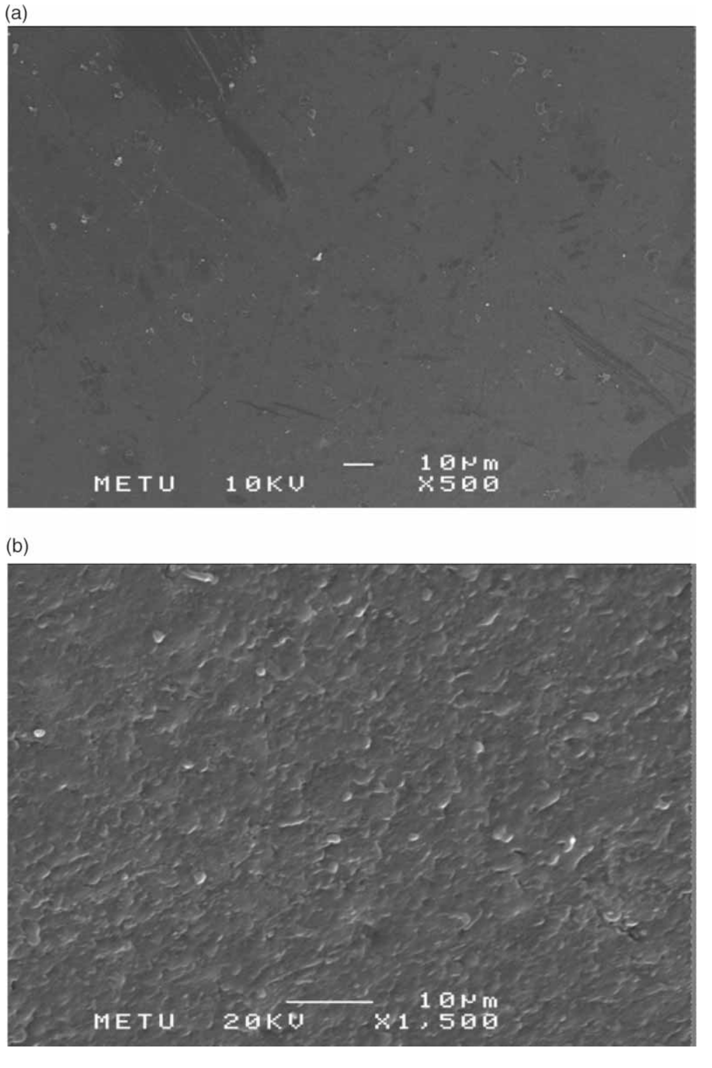

Figure 2. (a) Scanning electron microscopic picture of uncrosslinked NaAlg membrane. (b) Scanning electron microscopic picture of crosslinked NaAlg membrane.

VP and TDVP experiments were conducted similar to PV experiments. Temperature of the membrane surroundings is controlled by a cold medium in a permeation cell of a jacket type. The separation factor (permeation selectivity) ($\alpha_{sep.W/DMF}$), and permeation rate (J) of PV, VP and TDVP were calculated as follows:

$$\alpha_{sep.W/DMF} = \frac{P_W/P_{DMF}}{F_W/F_{DMF}} \qquad (3)$$

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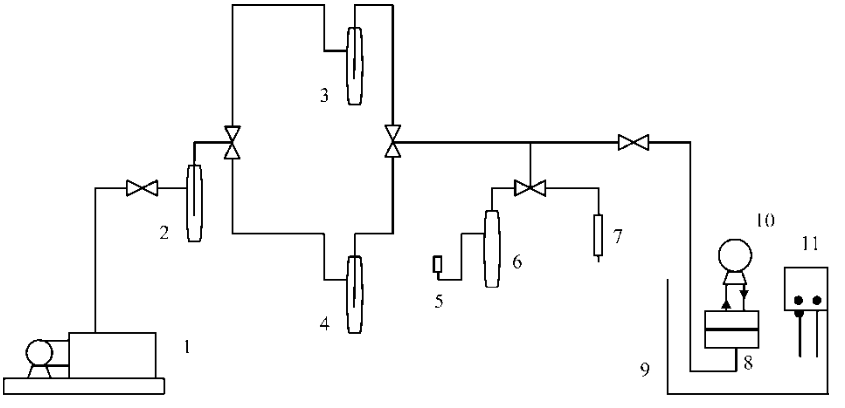

Figure 3. Schematic diagram of the pervaporation apparatus: (1) vacuum pump, (2–4, 6) permeation traps; (5) Mc Leod manometer; (7) vent; (8) permeation cell; (9) constant temperature water bath; (10) peristaltic pump; (11) temperature indicator.

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where P_W and P_{DMF}, F_W, and F_{DMF} are the mass fractions (wt%) of water and DMF components in the permeate and feed for PV, VP, and TDVP methods, respectively.

$$J = \frac{W}{A\,t} \tag{4}$$

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

Separation index was calculated by using the following equation (7, 29).

$$SI = J.\alpha \tag{5}$$

where J and α are the total permeation rate and separation factor, respectively.

The diffusion selectivity can be calculated from the separation factor and the sorption selectivity by Eq. 6 as follows (30):

$$\text{Diffusion selectivity}(\alpha_{\text{dif.W/DMF}}) = \frac{\alpha_{\text{sep.W/DMF}}}{\alpha_{\text{sorp.W/DMF}}} \tag{6}$$

RESULTS AND DISCUSSION

Effect of the Membrane Thickness

Membranes with varying thicknesses (30–90 μm) were prepared from the NaAlg solution by casting method. The separation factor and permeation rate as a function of membrane thickness were studied for the separation 20 wt% dimethylformamide mixture at 40°C and the results were presented in Fig. 4. As seen in the figure, the permeation rate decreases with 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. Figure 5 shows a linear relationship between the total permeation rate and the reciprocal of the membrane thickness as is predicted by solution-diffusion model (Fickian behavior).

Different results concerning the effect of membrane thickness were reported in the literature (2, 29, 31). Alghezawi et al. (2) studied the effect of membrane thickness on the separation factor and permeation rate for 20 wt% acetic acid solutions at 30°C. They have reported that as the membrane thickness increases permeation rate decreases whereas separation factor increases. Işklan and Şanlı (29) studied the separation characteristics of acetic acid-water mixtures by pervaporation using poly(vinyl alcohol) membranes modified with malic acid. They have reported that as the membrane thickness increases the permeation rate decreases whereas separation factor stays almost constant below a membrane thicknesses of 70 μm and then increases sharply between 70 and 100 μm membrane thickness. Koops et al. (31) investigated the pervaporation selectivity as a function of membrane thickness for the polysulfone, poly(vinyl chloride), and poly(acrylonitrile) membranes in the dehydration of acetic acid and reported that selectivity decreases with decreasing membrane thickness below a limiting value of about 15 μm.

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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. 6. From the figure, it is clear that as the concentration of DMF in the feed solution

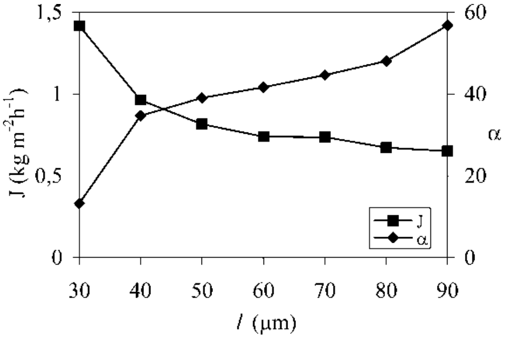

Figure 4. Effect of membrane thickness on the permeation rate and the separation factor.

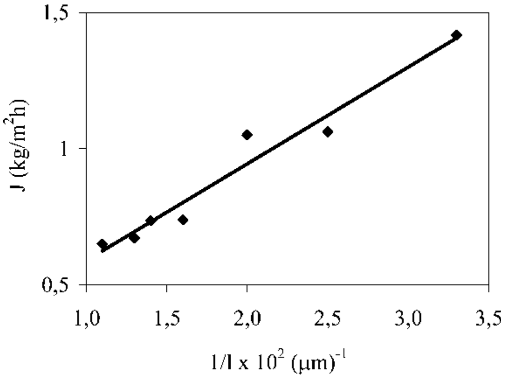

Figure 5. Permeation rate as a function of the reciprocal of the membrane thickness.

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increases, permeation rate decreases whereas the separation factor increases. 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 DMF concentrations. These results were supported by the swelling measurements (Fig. 7).

Similar results were obtained in the pervaporation separation of dimethylformamide/water mixtures using hydrophilic zeolite NaA membranes (26), poly(vinyl alcohol)-g-polyacrylamide copolymeric membranes (27) and polyacrylonitrile-g-poly(vinyl alcohol) membranes (28).

Permeation rates of individual components were shown in Fig. 8. As is seen from the figure, the permeation rate of water was much higher than the permeation rate of DMF. The permeation rate of water component decreased with the decrease in water content of the feed solution. These phenomena can be explained in terms of plasticizing effect of water.

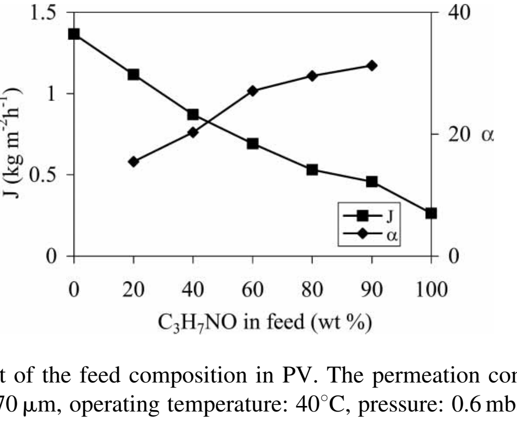

Figure 6. Effect of the feed composition in PV. The permeation conditions; membrane thickness: 70 μm, operating temperature: 40°C, pressure: 0.6 mbar.

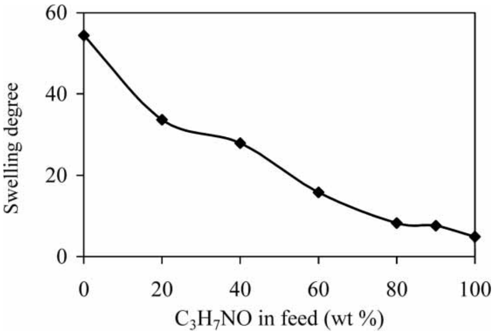

Figure 7. Change in the swelling degree with the feed composition.

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The permeation rate of individual components was also studied by Alghezawi et al. (2). They have investigated the separation of acetic acid-water mixtures through acrylonitrile grafted poly(viyl alcohol)membranes by pervaporation and observed that the permeation rate of 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 9 shows the relationship between the sorption selectivity and the diffusion selectivity for NaAlg membrane at different DMF concentrations. The sorption selectivity and the diffusion selectivity slightly increased with increasing DMF concentration in the feed solution due to the decrease in the swelling degree at high DMF concentrations.

Chen et al. (15) have investigated the sorption-diffusion selectivity as a function of pervaporation properties for the polysulfone membrane in the pervaporation separation of water/ethanol mixture and reported that sorption

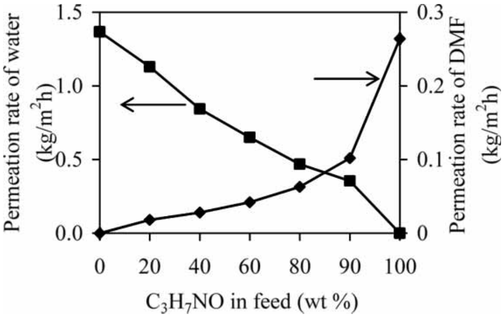

Figure 8. Variation of the permeation rate of water and dimethylformamide with the feed composition.

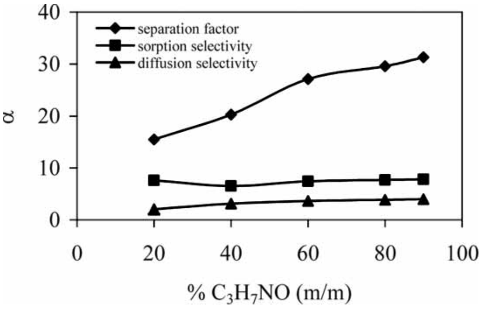

Figure 9. Relationship between the selectivities at different feed compositions.

selectivity increased and diffusion selectivity decreased with increasing ethanol composition in the feed.

Toti et al. (32) prepared Na-Alg and guar gum-grafted polyacrylamide membranes in different ratios and used in the pervaporation separation of acetic acid-water mixtures. They have also found that sorption selectivity increased with an increasing amount of acetic acid in the feed mixture.

Effect of the Operating Temperature in PV

The effect of the operating temperature on the separation performance of the membranes was shown in Fig. 10. Permeation rate increases whereas 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 DMF and water molecules pass through the membrane, resulting in increased total permeation rate with a decreased separation factor.

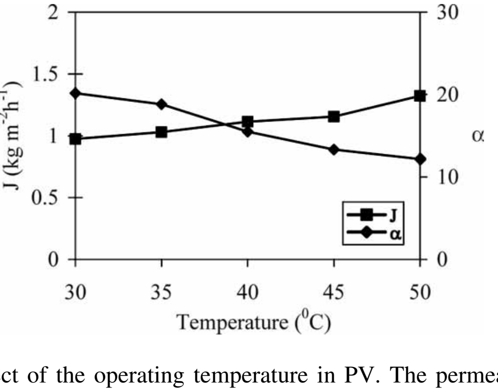

Figure 10. Effect of the operating temperature in PV. The permeation conditions; [C_3H_7NO]: 20 wt%, membrane thickness: 70 μm, pressure: 0.6 mbar.

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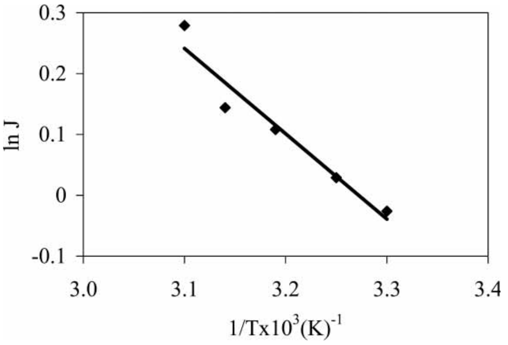

Figure 11. Arrhenius plot of lnJ versus 1/T for a NaAlg membrane in PV.

Figure 11 shows Arrhenius plot of the permeation rate for 20 wt% dimethylformamide mixtures. The temperature dependence of the permeation rates fittes with Arrhenius equation (33),

$$J = A_p \exp(-E_p/RT) \tag{7}$$

where A_p is permeation rate constant, E_p is activation energy for permeation. The activation energy of dimethylformamide-water mixture was calculated to be 4,0 kcal/mol.

Aminabhavi and Naik (27) obtained similar results in the pervaporation separation of water/dimetyhylformamide mixtures using poly(vinyl alcohol)-g-polyacrylamide copolymeric membranes. They have reported that as the amount of water varies between 10 and 90 mass % in the feed mixture, the separation factor decreased whereas permeation rate increased, as the temperature was increased.

Kurkuri and Aminabhavi (28) studied pervaporation separation of dimethylformamide and water mixtures through polyacrylonitrile-g-poly(vinyl alcohol) membranes. They have observed the same trend that

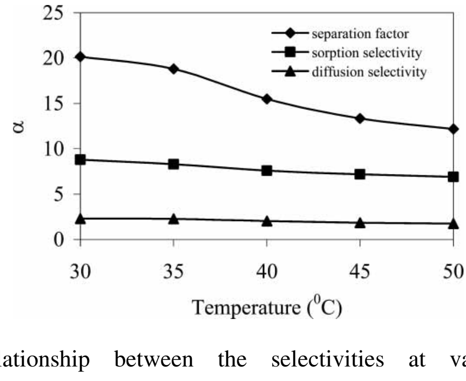

Figure 12. Relationship between the selectivities at various permeation temperatures.

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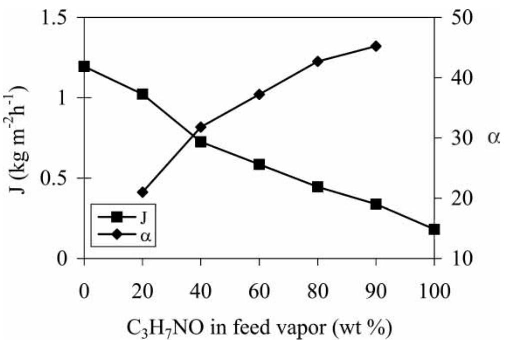

Figure 13. Effect of the feed vapor composition in VP. The permeation conditions; membrane thickness: 70 μm, operating temperature: 40°C, pressure: 0.6 mbar.

permeation rate increased whereas separation factor decreased with increasing temperature.

The relationship between the sorption selectivity and the diffusion selectivity for NaAlg membrane at various permeation temperatures by PV is shown in Fig. 12. The sorption selectivity and the diffusion selectivity of the NaAlg membrane was decreased with the increase in the permeation temperature. It is well known that the decrease of the sorption selectivity and the diffusion selectivity was due to the increase of membrane swelling with increasing feed temperature.

Inui et al. (30) have investigated the relationship among the separation factor, the sorption selectivity and the diffusion selectivity for a Benzene/cyclohexane (Bz/Chx) mixture of 10 wt% benzene through the nematic and smectic side-chain liquid-crystalline polymer (n- and s-LCP) membrane in the liquid-crystalline state at various permeation temperatures by PV. They have reported that the sorption selectivity of the n-LCP and s-LCP membranes was lowered with an increase in the permeation temperature.

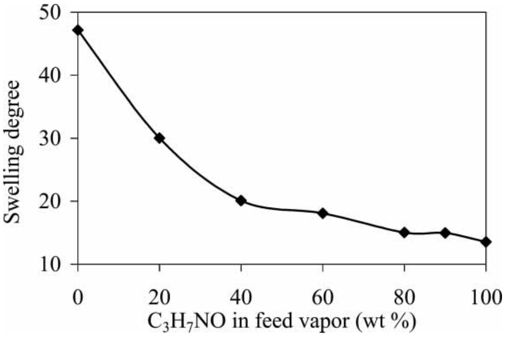

Figure 14. Change in the swelling degree with the feed vapor composition.

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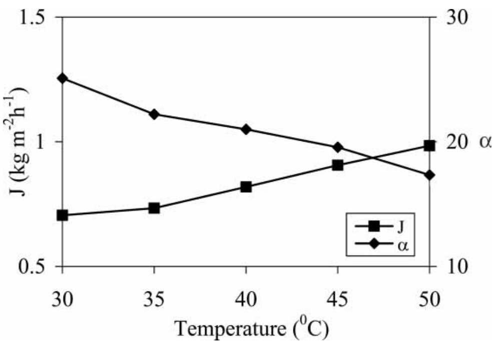

Figure 15. Effect of operating temperature in VP. The permeation conditions; [C_3H_7NO]: 20 wt%, membrane thickness: 70 μm, pressure: 0.6 mbar.

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On the other hand, though the diffusion selectivity of the n-LCP membrane was considerably lowered with an increase in the permeation temperature but that of the s-LCP membrane was almost constant.

Effect of the Feed Composition in VP

The permeation performance of NaAlg membrane in VP was investigated at 40°C and the results were shown in Fig. 13. As the amount of DMF in the feed vapor decreases membrane material becomes more swollen (Fig. 14), DMF molecules which have larger moleculer size than that of water molecules (5) diffuse easily through the swollen membrane, permeation rate increases so the separation factor decreases. However the permeation rates with VP was lower than that with PV. These results might be due to the fact that the membranes were in direct contact with the feed solution and were more swollen in PV than in VP. Thus the diffusivity of the permeating species in VP was lower than PV.

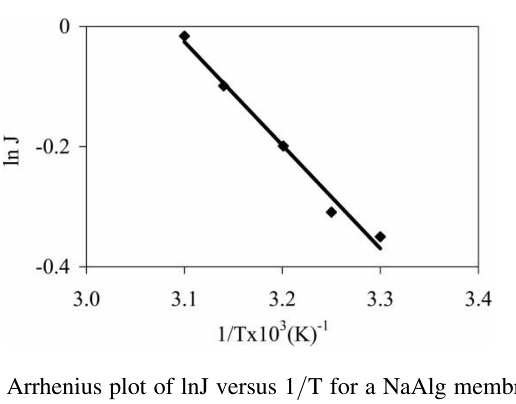

Figure 16. Arrhenius plot of lnJ versus 1/T for a NaAlg membrane in VP.

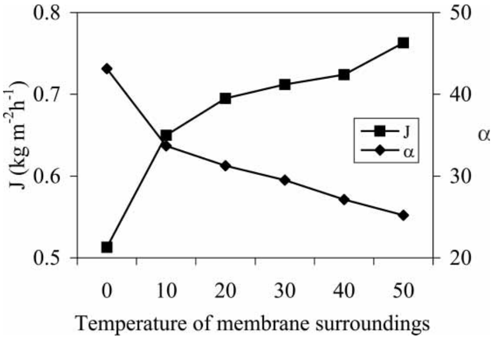

Figure 17. Effect of the temperature of the membrane surroundings on the permeation rate and separation factor. The permeation conditions; membrane thickness: 70 μm, temperature of the feed solution: 40°C, pressure: 0.6 mbar.

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Effect of the Operating Temperature in VP

The change of the permeation rate and separation factor with the temperature in VP for 20 wt% dimethylformamide was shown in Fig. 15. The permeation rate increased as the operating temperature increased whereas the separation factors decreased as expected.

Uragami et al. (13), Fialova et al. (34), Sommer and Melin (35, 36), Uragami and Shinomiya (37), Işıklan and Şanlı (29, 38) have also investigated the effect of permeation temperature on the permeation rate and separation factor in vapor permeation and found similar results.

In Fig. 16, the change of the permeation rate with the inverse of the temperature was shown. The activation energy was calculated as 2.6 kcal/mol. The PV activation energy was found to be higher than in VP. In PV method the membrane is directly in contact with the feed mixture. So the permeation

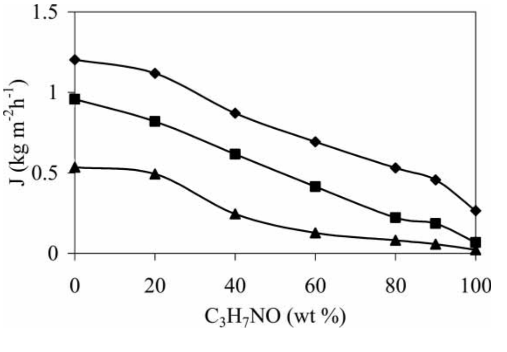

Figure 18. Change in the permeation rate in PV (◆), VP (■) and TDVP (▲) methods. The permeation conditions were as follows; membrane thickness: 70 μm, operating temperature: 40°C, pressure: 0.6 mbar, membrane surrounding temperature: 10°C.

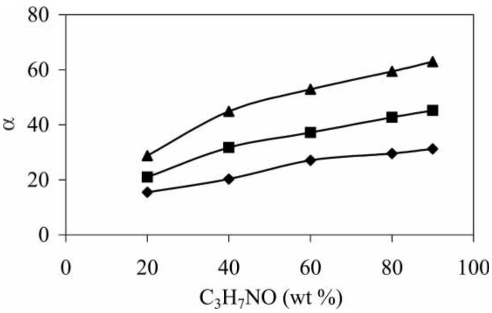

Figure 19. Change in the separation factor in PV (◆), VP (■) and TDVP (▲) methods. The permeation conditions; membrane thickness: 70 μm, operating temperature: 40°C, pressure: 0.6 mbar, membrane surrounding temperature: 10°C.

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rate through a membrane is determined by both the solubility and diffusivity of the permeant. The E_p value should be dependent on both the diffusive activation energy (E_d) in the diffusion step and heat of sorption (ΔH) in the sorption step. However in the VP only the energy required is for diffusive transport. This could be the reason for high activation energy in PV.

Effect of the Membrane Surrounding Temperature in TDVP

Figure 17 reflects the effect of temperature of the membrane surroundings on the permeation rate and the separation factor in TDVP. The temperature of the feed solution was kept constant at 40°C and the temperature of the membrane surrounding was changed in the range of 0–50°C. The permeation rate increases with the increase in temperature of the membrane surroundings so the separation factor decreases.

In Figs. 18 and 19 is shown the comparison of the three methods. As is seen from the figures, the highest permeation rates obtained in PV method whereas separation factors obtained in TDVP method were higher than PV and VP

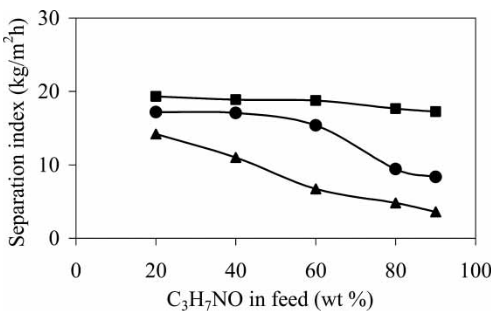

Figure 20. Change of separation index in PV (■), VP (●) and TDVP (▲) methods.

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Table 1. Comparison of the performance of the membranes for separation of dimethylformamide-water mixtures

Membrane	Feed composition (%) (w/w)	Temperature (°C)	Permeation rate (J) (kg/m^2 h)	Separation factor (α)	Separation method	Reference
PVA	10–90	25–45	0.016–0.403	6.5–28.5	PV	(27)
PVA-g-polyacrylamide (48%)	10–90	25–45	0.070–0.266	11.0–49.1	PV	(27)
PVA-g-polyacrylamide (93%)	10–90	25–45	0.013–0.459	22.0–65.2	PV	(27)
PVA	10–90	25	0.016–0.200	11.0–28.5	PV	(28)
PAN-g-PVA (46%)	10–90	25	0.090–0.164	15.0–32.1	PV	(28)
PAN-g-PVA (93%)	10–90	25	0.018–0.108	23.0–36.7	PV	(28)
NaAlg	0–100	40	0.264–1.200	17.4–37.8	PV	This study
NaAlg	0–100	40	0.067–0.957	21.0–45.2	VP	This study
NaAlg	0–100	40 10[a]	0.021–0.534	28.8–63.0	TDVP	This study

[a]Membrane surrounding temperature.

methods. The highest separation factors obtained in TDEV method may be attributed to temperature difference between the feed mixture and the membrane surrounding. When the dimethylformamide and water molecules are vaporized, these vaporized molecules come close to the membrane surrounding kept at a lower temperature, the dimethylformamide molecules are liable to be aggregated more than the water molecules [the freezing point of dimethylformamide (-16°C) is lower than that of water (0°C)]. This aggregation of dimethylformamide is responsible for the increase of separation water factor.

In order to estimate the performance of the alginate membranes, SI values were calculated by Eq. (5) and presented in Fig. 20. As is seen from the figure that separation indexes of PV method are much higher than VP and TDVP methods especially at low DMF concentrations.

Results of the studies reported in the literature on the separation of dimethylformamide-water mixtures were listed in Table 1 for comparison purposes. As can be seen from the Table, the best separation factor was obtained in the TDVP method.

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CONCLUSIONS

The following conclusions can be drawn from the study on the separation of DMF-water mixtures using alginate membranes crosslinked with calcium chloride.

1. Increase in the operating temperature in PV and VP method increased the permeation rate whereas decreased the separation factor.
2. As the membrane thickness increased permeation rate decreased whereas separation factor increased.
3. The diffusion selectivity and the sorption selectivity slightly increased with increasing dimethylformamide composition in feed in PV.
4. Permeation rate decreased whereas separation factor increased as the DMF content of the feed increased in all of the methods.
5. The highest separation factor (63) was found in TDVP method whereas highest permeation rate ($1.2\,\mathrm{kg\,m^{-2}\,h^{-1}}$) was observed in PV method.

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