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Permeation and separation characteristics of dimethylformamide/water mixtures by vapor permeation and vapor permeation with temperature difference methods through a sodium alginate-g-n-vinyl-2-pyrrolidone membrane

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ABSTRACT

The characteristics of separation of dimethylformamide (DMF)/water mixtures with sodium alginate-g-N-vinyl-2-pyrrolidone membranes were investigated by vapor permeation (VP) and vapor permeation with temperature difference (TDVP) methods. N-vinyl-2-pyrrolidone (NVP) was grafted on to sodium alginate (NaAlg) with benzophenon under atmosphere on N_2. The grafted NaAlg was characterized by Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM) and differential scanning calorimeter (DSC). The effects of the feed composition, operating temperature and temperature of the membrane surroundings on the separation characteristics (separation factor, permeation rate) were studied for the DMF/water mixtures. The separation factors decreased and permeation rates increased with an increase in permeation temperature for both VP and TDVP methods. With the TDVP method the separation factors increased and the permeation rates decreased as the temperature of the membrane surroundings decreased. The highest separation factor, 63, was obtained in TDVP for a 90 wt% DMF concentration in the feed. The activation energy of permeation was calculated to be 2.11 kcal/mol for 20 wt% DMF solution.

Keywords: Graft copolymers; Vapor permeation; Membrane; Dimethylformamide

1. Introduction

The vapor permeation (VP) and vapor permeation with temperature difference (TDVP) separation techniques were proposed by Uragami and coworkers [1–6]. 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 established in the TDVP method.

In VP (Fig.1a), swelling or shrinking of the membranes due to the feed mixtures can be largely prevented, and consequently improvement of membrane performance may be expected. In TDVP (Fig.1b), the temperature of the membrane surrounding and the feed mixture are different from each other.

DMF is a solvent that dissolves a wide variety of organics. It has been called the universal solvent because of its wide organic and inorganic solvency. DMF is completely miscible with water and is both chemically and thermodynamically stable. DMF is used primarily in the pharmaceutical processing and acrylic fiber production industries. These uses account for about 50% of the total demand. DMF is also used in various extraction and absorption processes as well as being extensively used as a solvent, reagent and catalyst in synthetic organic chemistry [7–10].

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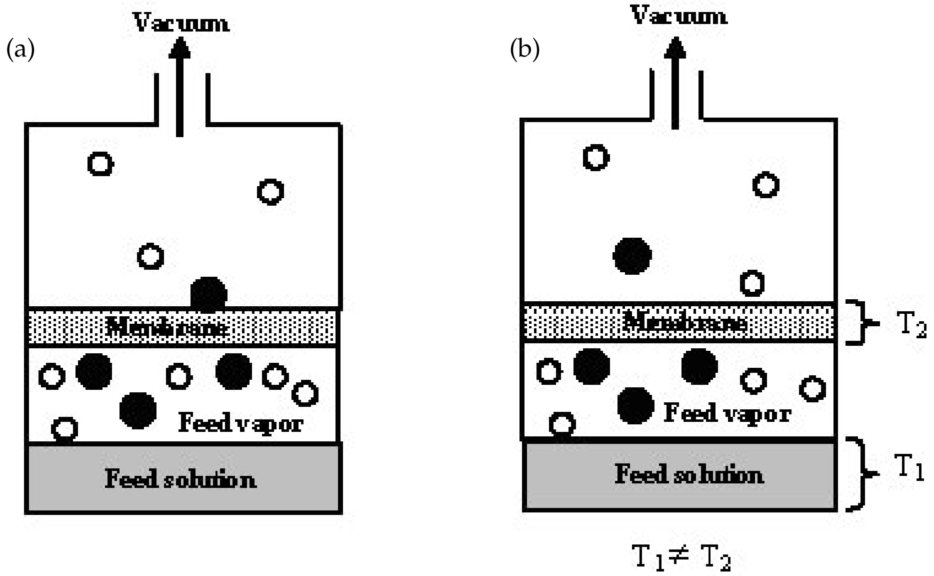


Fig. 1. Schematic diagram of (a) the VP method and (b) the TDVP method.

Kondolot Solak and Şanlı [6] studied separation characteristics of DMF/water mixtures through alginate membranes by pervaporation, vapor permeation and vapor permeation with temperature difference methods. They found that an increase in the operating temperature in pervaporation and the VP method increased the permeation rate whereas it decreased the separation factor. However, permeation rate decreased whereas the separation factor increased as the DMF content of the feed increased in all of the methods. The highest separation factor (63) was found in the TDVP method whereas the highest permeation rate (1.2 kg $m^{-2}h^{-1}$) was observed in the PV method. Devi and coworkers [11] studied pervaporation separation of DMF/water mixtures through poly (vinyl alcohol)/poly (acrylic acid) blend membranes. They reported that membrane selectivities improved with the decreasing feed water concentration, but a simultaneous drop in overall permeation flux was observed. Increasing membrane thickness decreased the flux, whereas higher permeation pressure caused a fall in membrane performance. Shah and coworkers [12] prepared hydrophilic zeolite NaA membranes for the PV DMF/water mixtures. They have reported that the water flux for the DMF/water system decreases rapidly with an increase in the feed DMF concentration. Aminabhavi and Naik [13] grafted poly (vinyl alcohol) (PVA) with acrylamide for the separation of water/DMF 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 [14] grafted PVA with polyacrylonitrile and used in the separation of DMF and water mixtures in a range of 10 to 90 wt% in the feed at 25, 35 and 45 °C. They have reported that by the increase in the grafting percentage of the membrane, flux decreased whereas selectivity increased slightly over that of pure poly (vinyl pyrrolidone) (PVP) membrane.

NaAlg has a widespread application as a membrane material because it is a highly hydrophilic polymer [3–5, 15]. When a highly permeable polymer material is preferred, this membrane material should be modified to have the suitable combination of permeation rate and separation factor. To improve the separation performance of the alginate membrane, it is grafted with NVP and is crosslinked with calcium chloride.

In our previous study [16] we used the NaAlg-g-NVP membrane to determine membrane thickness for pervaporation of DMF/water mixtures. In this paper we aimed to investigate separation characteristics of DMF/water mixtures through NaAlg-g-NVP membranes by VP and TDVP methods.

2. Experimental

2.1. Materials

NaAlg was provided from Sigma (medium viscosity). DMF, calcium chloride, ethanol and acetone were obtained from Merck and used as supplied. NVP was also a product of Merck but it was vacuum distilled before its use.

2.2. Synthesis of grafting a copolymer

The graft copolymerization of NVP onto NaAlg was carried out in aqueous medium using benzophenon (10^{-3} M, 1.5 mL ethanol) as an photosynthesizer for a period of 3 h under N_2 atmosphere. The graft polymerization medium was irradiated by UV light. NaAlg (1 g) was dissolved in 100 mL of distilled water and stirred with NVP (1 M, 25 mL). Oxygen-free nitrogen was purged through the solution for 30 min. At this stage a benzophenon solution was added to the reaction mixture. After a specified time interval, the obtained polymers were precipitated out with an excess of acetone and then the copolymer was treated with ethanol. The grafted polymer was dried at 60°C for 48 h under vacuum and weighted. The graft percentage of the copolymer was found to be 33 using the following equation:

$$\text{Graft percentage (\%)} = \frac{\left(M_g - M_o\right)}{M_o} \times 100 \qquad (1)$$

where M_o and M_g are the mass of the original (ungrafted) and grafted NaAlg, respectively.

2.3. Membrane preparation

NaAlg-g-NVP (2 g) was dissolved in 100 mL of water. This solution was cast onto petri dishes, and the solvent was evaporated at 60°C to form the membrane. The dried membrane was crosslinked with calcium chloride (0.1 M) for 24 h. The thickness of the membranes was 70 (±10) µm. Membrane prepared in this research was used at least 10 times without any deformation during the VP and TDVP processes.

2.4. Analyses

Infrared spectra of NaAlg-g-NVP membranes was measured with FTIR from Unicam, model Mattson 1000. The thermal analysis was done with a V4.1C Dupont 2000 differantial scanning calorimeter. For SEM analysis, the dried membranes were sputtered with gold in vacuum before viewing under a JEOL, model JSM-6400, electron microscope.

2.5. Swelling degree measurements

The dried membranes were immersed in different concentrations of DMF/water mixtures at 40°C for 48 h. The membranes were wiped with cleansing tissue to remove the excess solvent mixture. These samples were dried at 60°C until a constant weight. The swelling percentage was calculated as

$$\text{Swelling percentage (\%)} = \frac{(M_S - M_D)}{M_D} \times 100 \qquad (2)$$

where M_S is the mass of the swollen membrane in the feed solution and M_D is the mass of the dried membrane.

2.6. Vapor permeation and vapor permeation with temperature difference experiments

VP and TDVP experiments were carried out using the apparatus shown in Fig. 2. The capacity of the permeation cell made up of glass with jacket was about 150 mL. It was assembled from two half-cells fastened together with joints [6,16]. Membranes were placed on to the porous glass support in the cell. Effective membrane area was 16.5 cm^2 and pressure was kept at 0.6 mbar with a vacuum pump (Edward). The mixture of dimethylformamide and water which was used as a feed solution placed into the lower part of the permeation cell, permeation side of the cell (upper part) was kept under vacuum. The feed mixture was circulated between the permeation cell and the feed tank at constant temperature and permeate was collected in liquid nitrogen traps.

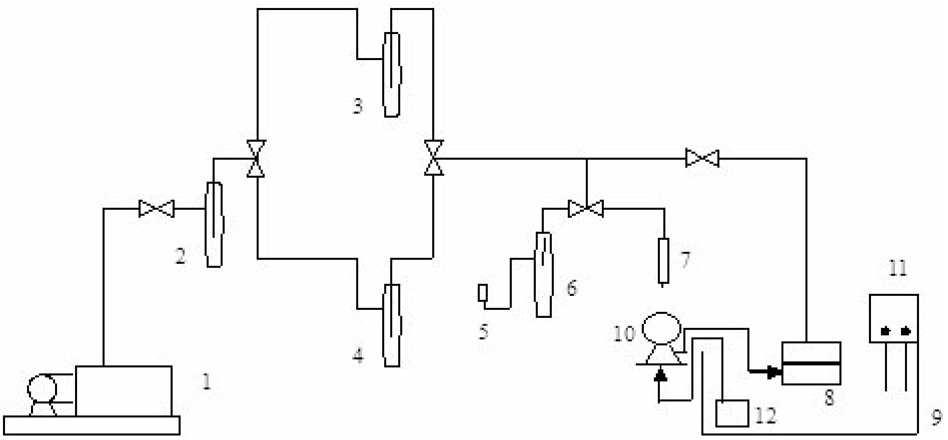


Fig. 2. Schematic diagram of the vapor permeation and vapor permeation with temperature difference apparatus used in this study: (1) vacuum pump, (2–4,6) permeation traps; (5) McLeod manometer; (7) vent; (8) permeation cell; (9) constant temperature water bath; (10) peristaltic pump; (11) temperature indicator; (12) feed tank.

In the TDVP method while the temperature of the feed solution was kept constant (40 °C) temperature of the membrane surrounding (0–50 °C) was controlled by a cold medium in a permeation cell of a jacket type.

Upon reaching steady-state conditions, the permeate vapor was collected in liquid nitrogen traps and weighed. The composition of permeate was found by means of refractive index values measured with an Atago DD-5 type digital refractometer.

The membrane performance was expressed by the separation factor (α), permeation rate (*J*) and separation index (SI). The separation factor was defined as follows [17,18]:

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

where P_W and P_{DMF}, F_W and F_{DMF} and are the mass fractions of water and DMF components in the permeate and feed vapor (measured by the isoteniscope method) respectively. The permeation rate was calculated using Eq. (4).

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

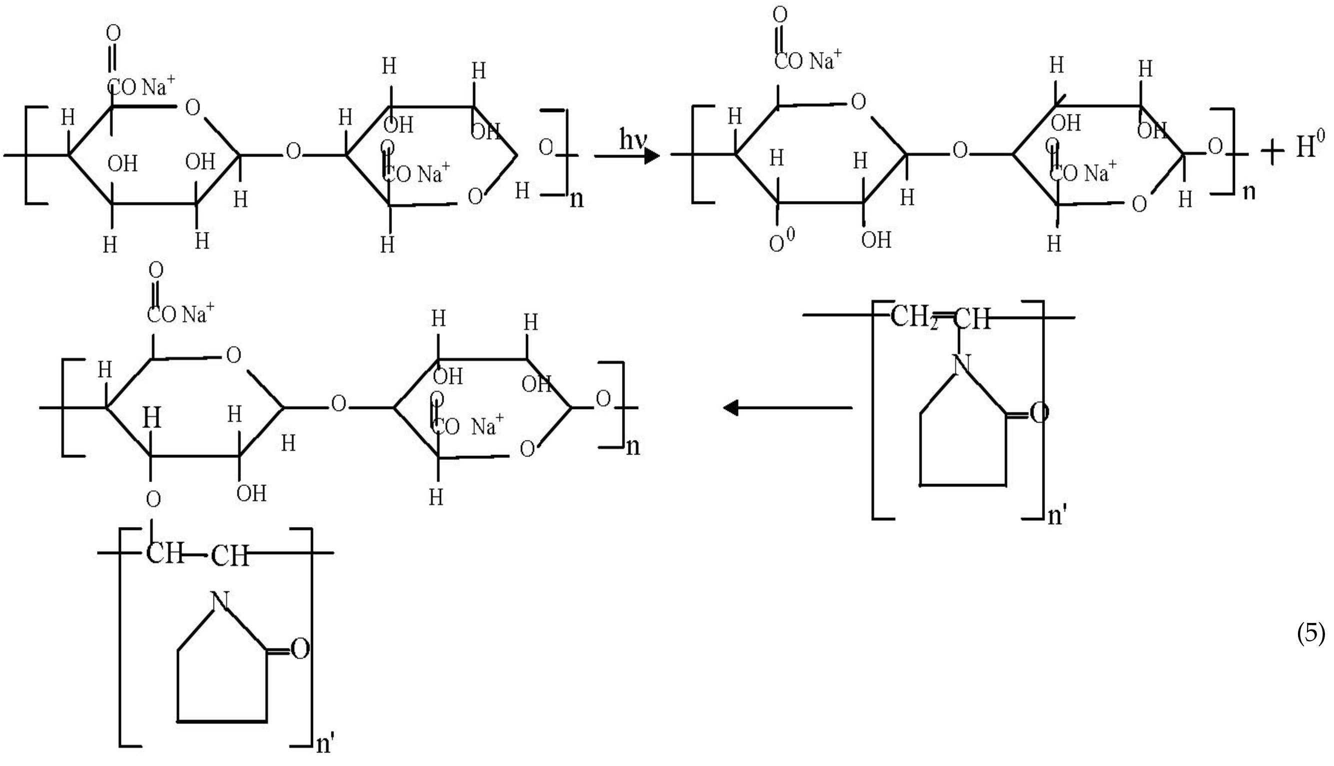
where *W* is the mass of permeate (kg), *A* is the membrane surface area (m^2), and *t* is the experiment time (h).

3. Results and discussion

3.1. Characterization of the NaAlg-g-NVP copolymer

The postulated reaction mechanism between NaAlg and NVP is given in Eq. (5). The grafted membranes (NaAlg-g-NVP) were characterized by infrared spectroscopy, thermal analysis and scanning electron microscopy.

Composition of the NaAlg-g-NVP copolymer was determined by elemental analysis (Table 1). The copolymer was found to contain 33% NVP by weight. The FTIR spectra of the copolymer are presented in Fig. 3. In the FTIR spectrum of NaAlg the peak at 3000–3500 cm^{-1} area presents the stretching vibration of the -OH band. In the FTIR spectrum of NaAlg-g-NVP these stretching vibrations appear as a wider band. The peaks at 1625 cm^{-1} in the spectrum of NaAlg is due to the stretching bands of C-O-O. The spectrum of PVP appears as a strong absorption band at 1640 cm^{-1} due to the presence of the C=C-N group. In the FTIR spectrum of NaAlg-g-NVP, these bands are seen together. The spectra of PVP, NaAlg and NaAlg-g-NVP appear as stretching bands of the C-H group at 2964 cm^{-1}, 2946 cm^{-1} and 2955 cm^{-1}, respectively.



(5)

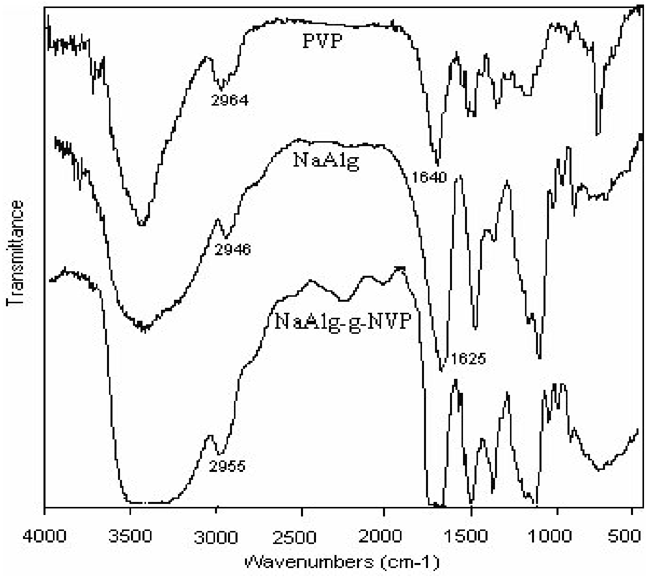


Fig. 3. IR spectra of PVP, NaAlg and NaAlg-g-NVP membranes.

Table 1
Elemental analysis of the NaAlg-g-NVP membrane

C%	55.70
H%	7.85
N%	9.32

The morphology of the membranes was observed using SEM with a (JEOL JSM-6400 [Fig. 4(a,b)]. It is seen from the SEM results that the ungrafted membrane surface (Fig. 4b) had a smoother appearance than the grafted one (Fig. 4a).

Thermal analysis was performed with a General V4.1C Dupont 2000 DSC. Results are illustrated in Fig. 5. The NaAlg polymer used in this study showed a T_g of 66 °C; however, this value for NaAlg-g-NVP has been found to be 68 °C. The increase in T_g could also be the evidence of the grafting reaction between NVP and NaAlg.

3.2. *Effect of the feed composition in VP*

The permeation performance of the NaAlg-g-NVP membrane in VP was investigated at 40 °C, and the results are shown in Fig. 6. As the amount of DMF in the feed vapor decreases, the membrane material becomes more swollen (Fig. 6), DMF molecules which have larger molecular size than that of water molecules [19] diffuse easily through the swollen membrane, and the permeation rate increases so the separation factor decreases.

3.3. *Effect of the operating temperature in VP*

The change of the permeation rate and separation

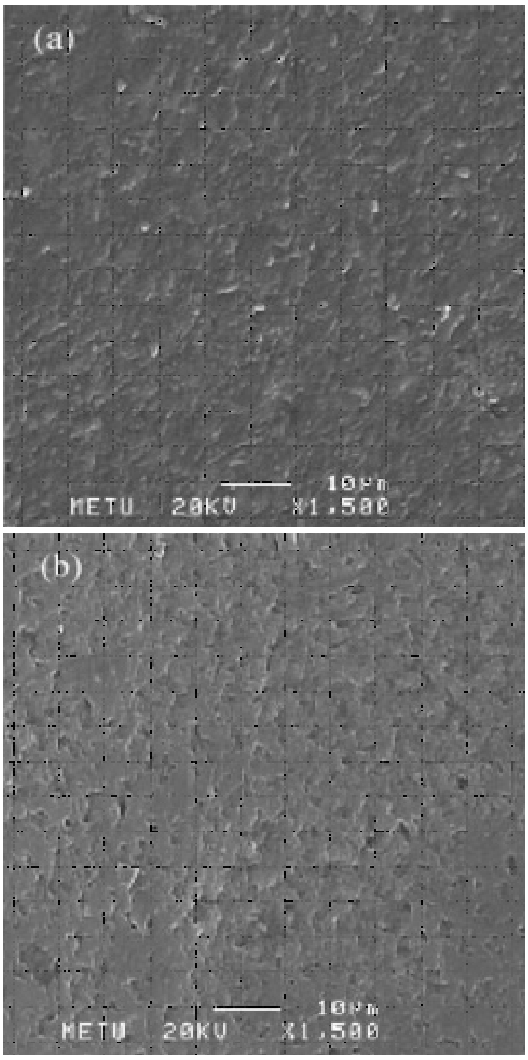


Fig. 4. Scanning electron microscopic picture of (a) ungrafted NaAlg membrane and (b) grafted NaAlg (NaAlg-g-NVP) membrane.

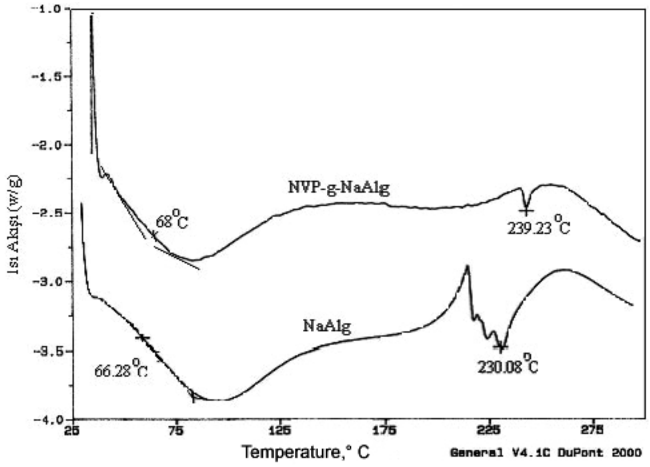


Fig. 5. Differential scanning calorimeter curves of Na-Alg-g-NVP and NaAlg membranes.

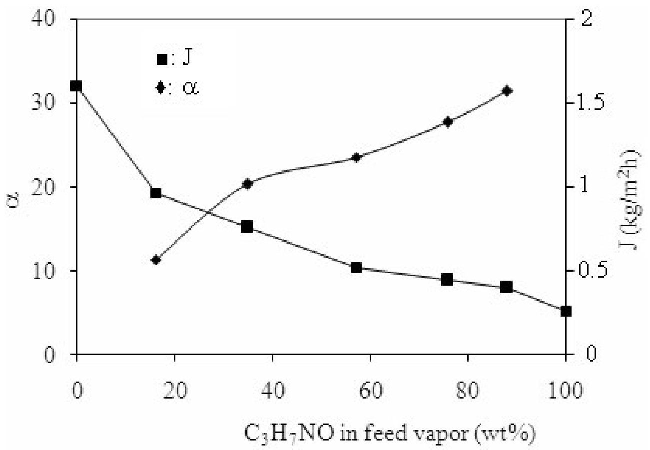


Fig. 6. Effect of the feed composition in VP. Permeation conditions; membrane thickness: 70 µm, operating temperature: 40 °C, pressure: 0.6 mbar.

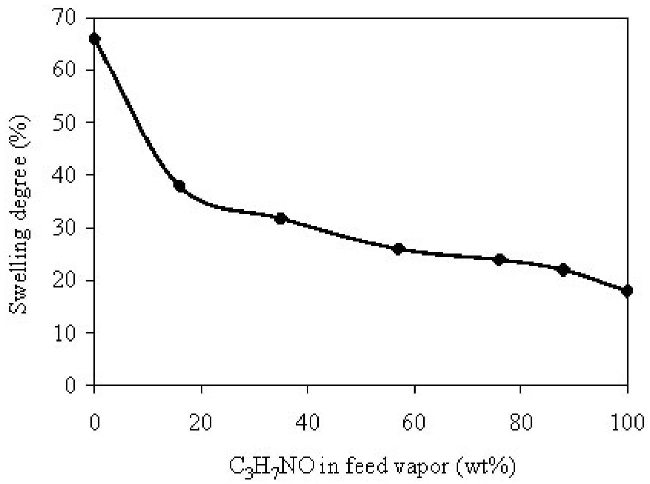


Fig. 7. Change in the swelling degree with the feed composition in VP.

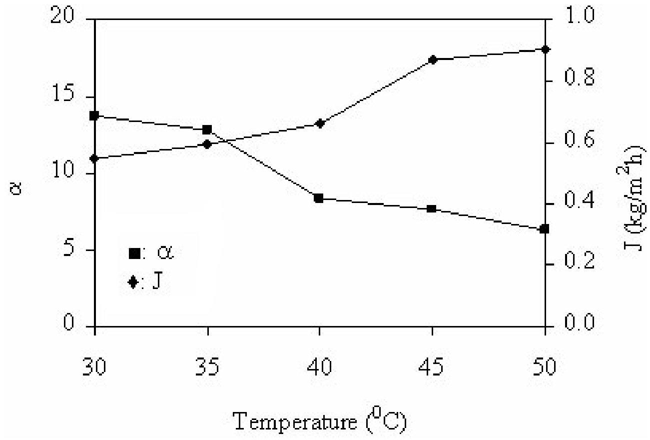


Fig. 8. Change in the permeation rate and the separation factor with the temperature in VP.

factor with the temperature in VP for 20 wt% DMF is shown in Fig. 8. The permeation rate increased as the operating temperature increased whereas the separation factors decreased. Similar results were reported in the studies of Fialova et al. [20], Sommer and Melin [21,22], Uragami and Shinomiya [23], Işıklan and Şanlı [18,24] and Asman and Şanlı [25].

In Fig. 9, the change of the permeation rate with the inverse of the temperature was shown. The activation energy was calculated as 2.11 kcal/mol.

3.4. *Effect of the membrane surrounding temperature in TDVP*

Fig. 10 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 theseparation factor decreases.

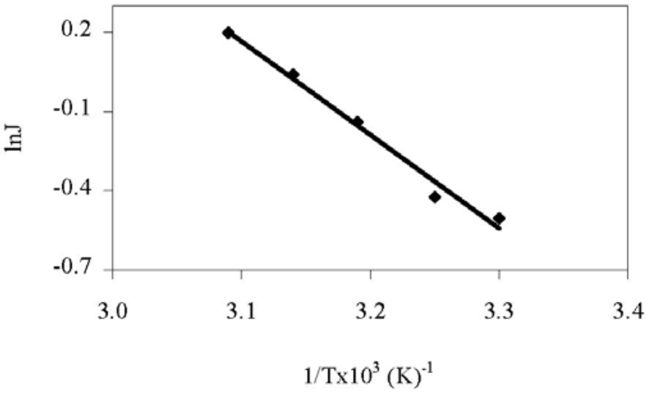


Fig. 9. Arrhenius plots of ln(dimethylformamide permeation rate) with 1/T for the NaAlg-g-NVP membrane in VP.

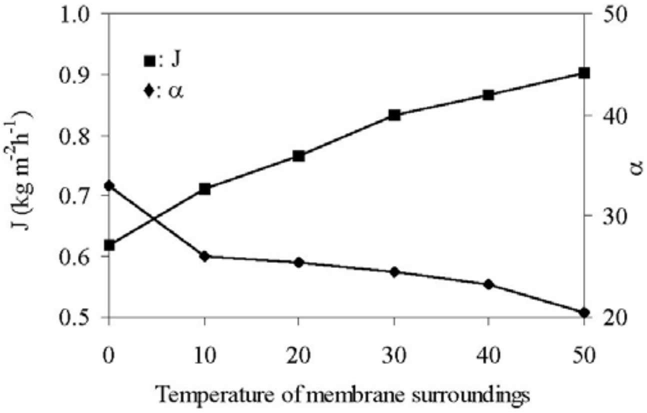


Fig. 10. Effect of temperature of the membrane surroundings on permeation rate and separation factor. Permeation conditions — membrane thickness: 70 µm, temperature of feed solution: 40 °C, pressure: 0.6 mbar.

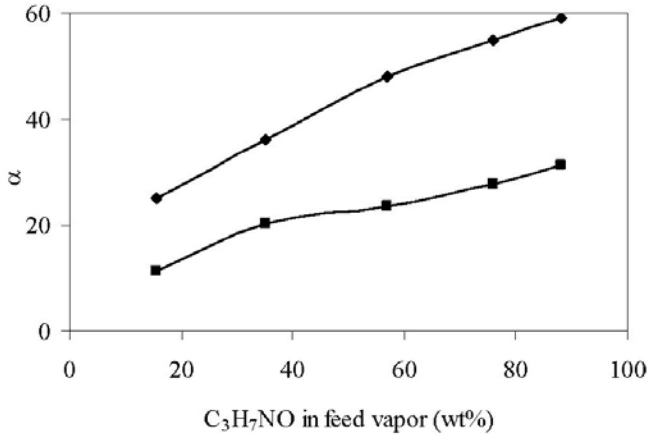


Fig. 11. Change in the separation factor in VP (■) and TDVP (◆) methods. Permeation conditions — membrane thickness: 70 µm, operating temperature: 40°C, pressure: 0.6 mbar, membrane surrounding temperature: 10°C.

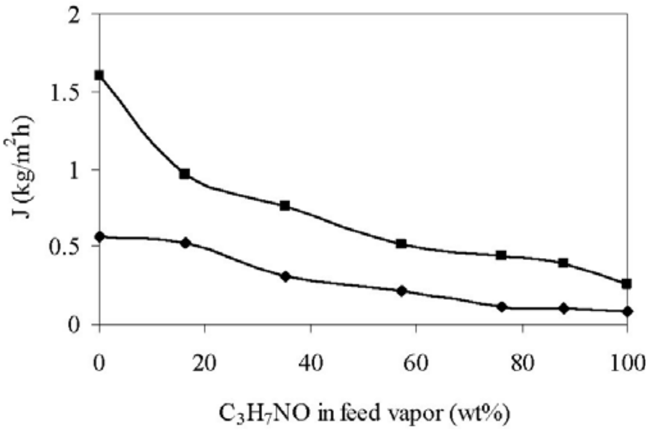


Fig. 12. Change in the permeation rate in VP (■) and TDVP (◆) methods. Permeation conditions — membrane thickness: 70 µm, operating temperature: 40°C, pressure: 0.6 mbar, membrane surrounding temperature: 10°C.

Table 2
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	13
PVA–g–Polyacrylamide (48%)	10–90	25–45	0.070–0.266	11.0–49.1	PV	13
PVA–g–Polyacrylamide (93%)	10–90	25–45	0.013–0.459	22.0–65.2	PV	13
PVA	10–90	25	0.016–0.200	11.0–28.5	PV	14
PAN–g–PVA (46%)	10–90	25	0.090–0.164	15.0–32.1	PV	14
PAN–g–PVA (93%)	10–90	25	0.018–0.108	23.0–36.7	PV	14
NaAlg	0–100	30–50	0.264–1.417	13.3–31.3	PV	6
NaAlg	0–100	30–50	0.181–1.195	17.3–45.2	VP	6
NaAlg	0–100	30–50	0.021–0.534	25.1–63.0	TDVP	6
NaAlg–g–NVP (33%)	0–100	30–50	0.871–2.046	5.6–15.4	PV	16
NaAlg–g–NVP (33%)	0–100	30–50	0.546–1.613	13.7–31.4	VP	This study
NaAlg–g–NVP (33%)	0–100	30–50	0.104–0.810	14.7–57.3	TDVP	This study

3.4. Comparison of the effect of the feed vapor composition in VP and TDVP

Figs. 11 and 12 show the comparison of the two methods. The highest separation factors obtained in the TDVP method may be attributed to the temperature difference between the feed mixture and the membrane surrounding. When the DMF and water molecules are vaporized, they come close to the surrounding membrane kept at a lower temperature, and the DMF molecules are likely to be aggregated more than the water molecules [the freezing point of DMF (−16°C) is lower than that of water (0°C)]. This aggregation of DMF is responsible for the increase of the water separation factor.

Results of the studies reported in the literature on the separation of DMF/water mixtures are listed in Table 2 for comparison purposes. As can be seen from the table, the best separation factor was obtained in the TDVP method compared to the PV and VP methods when NaAlg-g-NVP membranes were used in DMF separation. It was also found that performance of NaAlg-g-NVP membranes was better than the pure NaAlg membranes from the point of view of the permeation rate.

4. Conclusions

NaAlg-g-NVP membranes were prepared and used in the separation of acetic acid/water mixtures. It was shown experimentally that grafted NaAlg membranes could be used to separate DMF/water mixtures with acceptable permeation rates and separation factors. The effects of feed composition, permeation temperature and membrane surrounding temperature on the permeation rate and separation factor were investigated. An increase in the operating temperature in VP and TDVP methods increased the permeation rate but decreased the separation factor. Permeation rates decreased whereas the separation factor increased as the DMF content of the feed increased in both methods. The highest separation factor (57) was found in the TDVP method whereas the highest permeation rate (1.1 kg $m^{-2}h^{-1}$) was observed in the VP method.

Acknowledgements

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