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Separation of dimethylformamide/water mixtures through sodium alginate and sodium alginate/clinoptilolite composite membranes by vapor permeation with and without feed-membrane temperature difference

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ABSTRACT

The characteristics of permeation and separation of dimethylformamide (DMF)/water mixtures through crosslinked sodium alginate (NaAlg) and NaAlg/clinoptilolite (Clt) composite membranes were investigated by vapor permeation (VP) and vapor permeation with temperature-difference (TDVP) techniques. The effects of Clt content of the membrane, feed composition, permeation temperature, and membrane surrounding temperature on the permeation rates and the separation factors were studied. Permeation rates in VP and TDVP were found 0.03–0.41 kg/m^2 h and 0.10–0.45 kg/m^2 h, respectively. Separation factors were increased up to a certain content of zeolite (%15) than decreased, and higher separation factor was obtained in TDVP method (68.80) as compared to VP. Activation energy of permeation in VP was calculated to be 2.794 kcal/mol for 20 wt.% DMF solution.

Keywords: Zeolite; Sodium alginate; Vapor permeation; Dimethylformamide

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1. Introduction

In the last two decades, membrane separation technologies have drawn the attention of researchers in the separation field because of their better performance compared with the conventional separation processes. Pervaporation is one of the rapidly developing membrane separation processes and offers the advantages in the separation of close-boiling point mixtures, azeotropes and thermally sensitive compounds [1]. Recently, pervaporation has gained interest in the chemical industry as an effective and energy-efficient process, to carry out separations that are difficult to achieve by conventional means [2]. This technology has better separation capacity and energy efficiency which could lead to 40–60% energy savings [3–7].

Vapor permeation (VP) and vapor permeation with temperature-difference (TDVP) were proposed by Uragami et al. [8,9]. In these processes (Fig. 1(a) and (b)), feed in vapor form is fed into the unit containing the membrane. Since in the VP, the feed solution is not in direct contact with the membrane material and only the feed vapor contacts with the membrane. Some disadvantages, such as swelling or shrinking of the membrane, which causes a decrease in selectivity,

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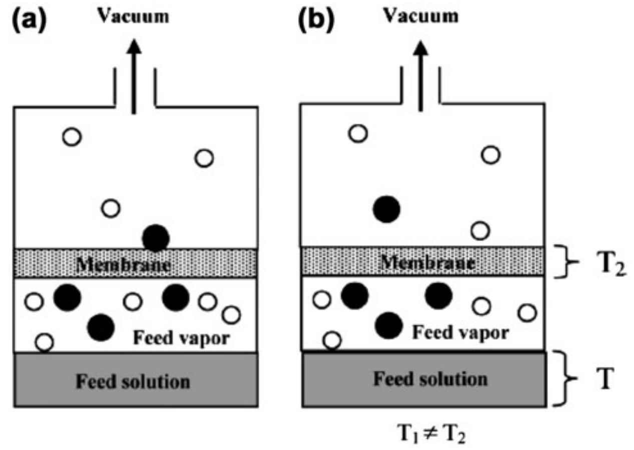

Fig. 1. Principal schemes of (a) the VP and (b) the TDVP cells.

have been prevented [10–12]. This more effective VP method that establishes a temperature difference between the feed solution and membrane surroundings is called as temperature difference-controlled evapomeation method (TDVP) [13,14].

Zeolites are highly crystalline inorganic structures having uniform molecular size pores and are used in a variety of separation problems. Because of the small pore size, the diffusion rates of some molecules with different sizes and adsorption strengths inside the crystals differ by orders of magnitude. Zeolites have been used as fillers to develop polymeric membranes to take advantage of the adsorption and diffusion differences to separate liquid mixtures [15]. The zeolite group contains more than 40 naturally occurring species [16]. Clinoptilolite (Clt) is a zeolite of the heulandite group being the most abundant in nature. It is very stable toward dehydration and thermally stable up to 700°C in air [17]. The chemical composition of Clt is characterized by significant variations in the Si/Al ratio as well as in the composition of the exchangeable cations [16].

Alginic acid that is highly hydrophilic polymer used in biotechnology, pharmaceutical, and cosmetic industries. Although alginic acid has limited solubility 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 [18,19]. The use of low-performance natural polymer like sodium alginate (NaAlg) in separation processes has some drawbacks due to its lower flux rates and separation factors [20,21]. For this reason, attempts have should be made for the modification of NaAlg.

There have been some attempts to improve membrane performance by adding zeolite to natural polymers, such as NaAlg, chitosan, and cellulose. Bhat and Aminabhavi have attempted the modification of NaAlg by dispersing nano- or micron-sized inorganic fillers such as zeolite, clays, or mesoporous materials, which have shown a pronounced increase in membrane performance due to decrease in polymeric segmental motions as a result of interaction of the added particles within the polymer matrix [22–25].

Dimethylformamide (DMF) is an important chemical in industry. It is released into air from acrylic fiber, elastic yarn, synthetic leather and pharmaceutical production plants and a water scrubber is used for the emission, as DMF is highly soluble in water. Its separation from water is essential as DMF is carcinogenic to human beings as well as for other animals [26–28]. Recently, our research groups have focused on the membrane development for the separation of DMF–water mixtures at different feed concentrations, temperatures and techniques [29–33].

As a continuation of the studies on the separation of DMF/water mixtures in the present study, we have prepared zeolite-filled NaAlg membranes in different ratios and crosslinked with glutaraldehyde (GA). These membranes were used in VP and TDVP separation of DMF/water mixtures, and the separation performance of the membranes as a function of temperature, feed composition, and composite composition studied and compared with that of pure NaAlg membranes.

2. Experimental outline

2.1. Materials

NaAlg was provided from Sigma with medium viscosity. GA solution, DMF and hydrochloride acid (HCl) were supplied by Merck. Clt was provided from Etibank A.Ş. (Bigadiç-Balıkesir-Turkey) (Table 1) [34].

Table 1
Characteristic of Clt samples used in this study

Cations	Cilnoptilolite (used in this study)	
	meq/g	%eq./eq.
Ca^{2+}	1.48	53
Na^{+}	0.03	1
K^{+}	0.66	24
Mg^{2+}	0.63	22
Si/Al	5.17	

The samples were grinded by ball mill and sieved to ≈38 μm.

2.2. Preparation of zeolite-filled membranes

NaAlg (2 g) was dissolved in 100 mL of distilled water with continuous stirring. Certain amount of zeolite (Clt) particles were weighted separately and dispersed in 20 mL water, stirred for 30 min and then added to prepared NaAlg solution with further stirring for overnight and casted onto rimmed round glass plate and solvent was evaporated at 60°C to form membrane. Dried membrane was peeled off from the plate and crosslinked with GA (2.5% v/v) and HCl (3% v/v). After keeping the membrane in crosslinking mixtures for 24 h, it was removed, washed repeatedly with deionized water and dried in an oven at 60°C. The amount of zeolite in the polymer was varied as 5, 10, 15, and 20 mass%, and the resulting membranes were designated as M-5, M-10, M-15, and M-20, respectively. Thicknesses of dry zeolite containing membranes measured by a micrometer screw gauge were around 60 ± 10 μm.

2.3. Experimental procedures

The VP and TDVP experiments were carried out in the same way as the PV experiments [33]. In VP method, the mixture of DMF 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). In TDVP method, while the temperature of the feed solution was kept constant at 40°C, the temperature of the membrane surrounding was changed (0–50°C) by a cold medium in a permeation cell of a jacket type. Similar to PV method, composition of the permeate that was collected after steady-state conditions attained analyzed with Atago DD-5 type digital refractometer in VP and TDVP methods.

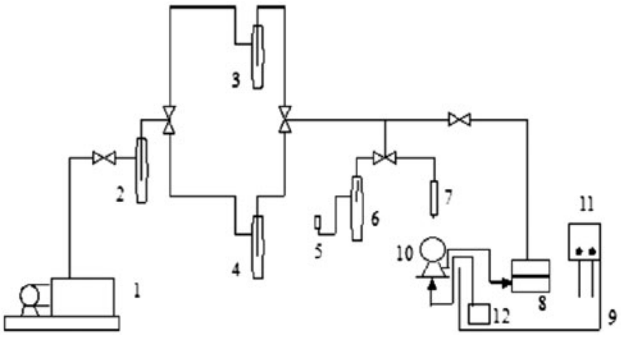

Fig. 2. Schematic diagram of the pervaporation apparatus: (1) vacuum pump, (2–4, 6) permeation traps; (5) Mc Leod manometer; (7) vent; (8) permeation cell; (9) constant temperature water bath; (10) peristaltic pump; and (11) temperature indicator.

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

$$\alpha_{\mathrm{sep}.W/\mathrm{DMF}} = \frac{P_W/P_{\mathrm{DMF}}}{F_W/F_{\mathrm{DMF}}} \tag{1}$$

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

$$J = \frac{W}{A\,t} \tag{2}$$

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

The separation index (SI) was calculated with the following equation:

$$\mathrm{SI} = J\alpha \tag{3}$$

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

2.4. Swelling degree measurements

NaAlg membranes were either immersed in different concentrations of DMF solutions or were exposed to vapor of DMF mixtures 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 Eq. (4) [31]:

$$\mathrm{SD} = \frac{(W_S - W_D)}{W_D} \times 100 \tag{4}$$

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

3. Results and discussion

3.1. Effects of feed composition on membrane swelling

The morphology of the NaAlg and NaAlg/Clt composite membranes was displayed (Fig. 3(a)–(d)) [33]. For SEM analysis, the dried membrane sputtered

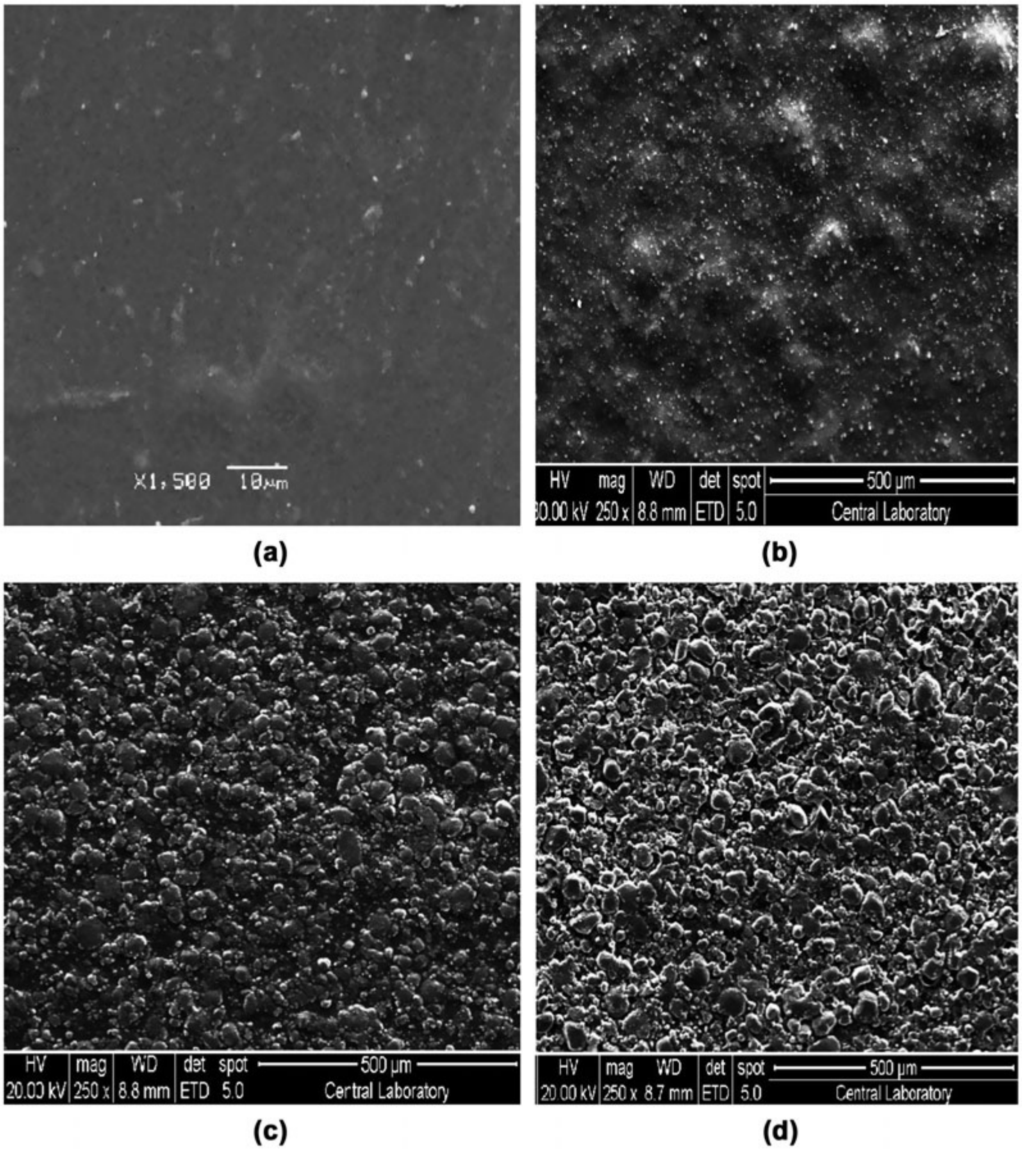

Fig. 3. Scanning electron microscopic picture of (a) pristine NaAlg membrane (b,c,d) NaAlg/Clt (5,10,15 wt.%, respectively) composite membrane (Ref. [33]).

with gold in vacuum before viewing under an electron microscope (JEOL JSM-5600). From the SEM results, the NaAlg membrane surface had a smoother appearance than the zeolite-filled membranes for the same magnification and smoothness of the membrane decreased as the zeolite content increased. Fig. 4 shows the swelling behavior of NaAlg membranes as a function of feed mixture composition both in liquid and in vapor at 40˚C. It was observed that degree of swelling did not changed considerably in vapor comparing to in the liquid, so the effect of Clt content is followed in liquid. As it is reflected Fig. 5 that swelling decreased up to a certain DMF concentration and then increased for all the Clt containing membranes

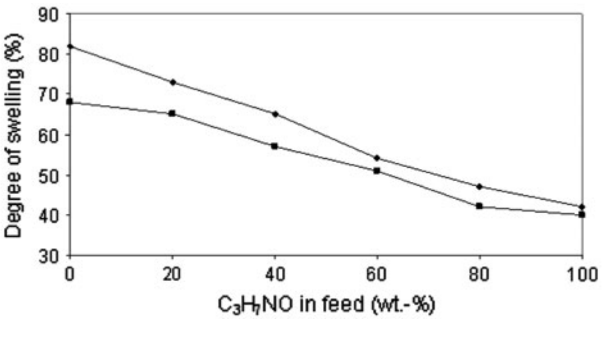

Fig. 4. Change in the swelling degree with the feed composition. (◆: NaAlg in liquid; ■: NaAlg in vapour).

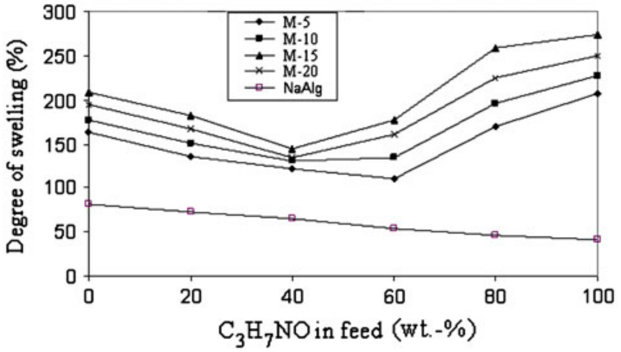

Fig. 5. Variation of degree of swelling with different wt.% of Clt for 20 wt.% of DMF in the feed.

whereas decreased steadily as the feed concentration increased for pristine NaAlg membrane [33]. The pronounced increase in the membrane swelling at high DMF concentrations may be attributed to the interaction of DMF molecules with the Clt matrix. DMF has a very large dipole moment (3.85 D) so that strong attractive interactions between Clt and DMF are expected which also contribute to membrane swelling. Kariduraganavar et al [35], studied pervaporation separation of water/acetic acid mixtures through PVA-silicone based hybrid membranes and found similar results.

Swelling tendencies of composite membranes are given in Fig. 5 as a function of filler loading. An increase in Clt content first results in an increase in swelling degree, since Clt has hydrophilic nature (Si/Al = 5.12) leading to the stronger interaction with water molecules and free volume increases due to zeolite loading. However, after 15 wt.% loading, swelling decreases due to nonuniform and brittle membranes. Veerapur et al [36], studied PVA-zeolite T mixed matrix composite membranes for PV separation of water + 1,4-dioxane mixtures. They found that the degree of swelling increases with increased loadings of zeolite T particles. These data indicate that water molecules sorbed preferentially and then diffuse more easily through the mixed matrix membranes than with the plain PVA membrane because of the availability of pores created by the zeolite particles.

3.2. *Effect of the feed vapor composition in VP*

The performance of NaAlg/Clt composite membrane for DMF mixture by VP is shown in Figs. 6 and 7. The permeation rate increased with increasing water concentration in the feed vapor. The transport mechanism on VP through polymeric membranes can be described by solution-diffusion model. Since the molecular size of water (0.26 nm) is smaller than DMF (0.55 nm) molecules. They can be selectively incorporated into the hydrophilic membrane and predominantly diffused. As a result, permeation rate increases with the increase in the water content of the feed vapor. In VP method, high permeation rates, but very small separation factors, were obtained by using NaAlg/Clt composite membranes than plain NaAlg membranes. Lai et al. [37] used vinyl acetate grafted nylon-4 membrane in PV and VP processes and observed that with the increase in the water concentration in the feed, the permeation rate increased, but the separation factor decreased.

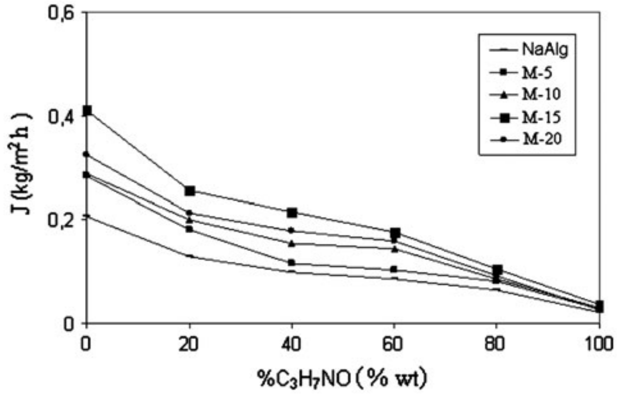

Fig. 6. Variation of flux with feed vapor concentration for pristine NaAlg and NaAlg/Clt membranes in. VP. The permeation conditions; ℓ: 60 μm, *t*: 40°C, *P*: 0.5 mbar.

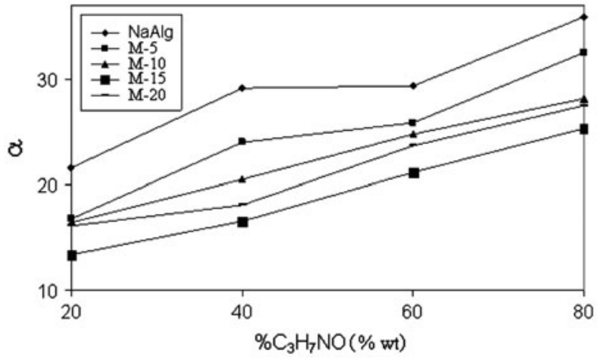

Fig. 7. Variation of selectivity with feed vapor concentration for pristine NaAlg and NaAlg/Clt membranes in VP. The permeation conditions; ℓ: 60 μm, *t*: 40°C, *P*: 0.5 mbar.

3.3. *Effect of operating temperature in VP*

Effect of operating temperature on the permeation rate and the separation factor was studied using NaAlg/Clt membranes for 20 wt.% DMF solution, and

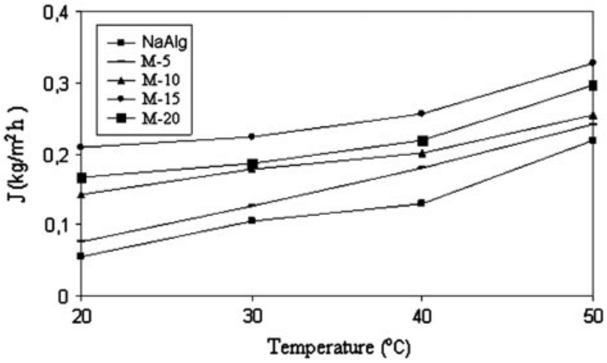

Fig. 8. Effect of temperature on flux in VP. The permeation conditions; DMF: 20 wt .%, ℓ: 60 µm, P: 0.5 mbar.

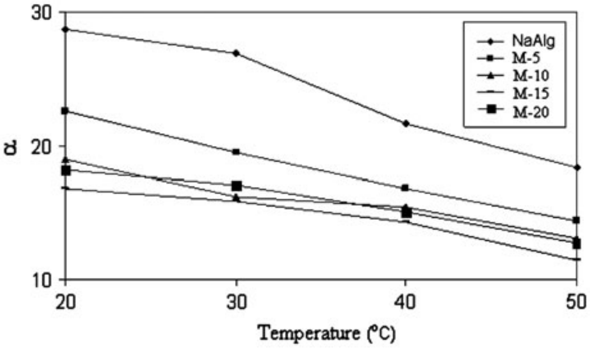

Fig. 9. Effect of temperature on selectivity in VP. The permeation conditions; DMF: 20 wt.%, ℓ: 60 µm, P: 0.5 mbar.

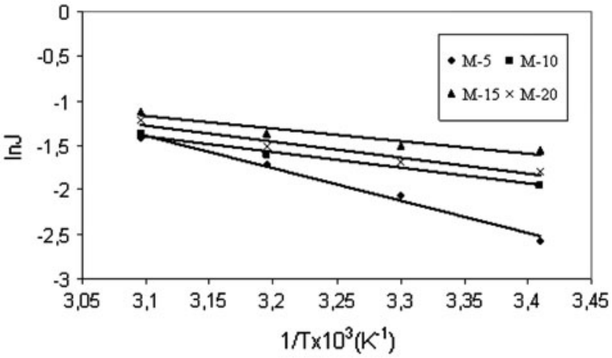

Fig. 10. In VP method, variation of ln J with temperature for different membranes at 20 wt.% of DMF in the feed. (: M-5; ■: M-10; ▲: M-15; ×: M-20).

the results were shown in Figs. 8 and 9. The permeation rate increased as the operating temperature increased, whereas the separation factors decreased as expected. In VP method by using NaAlg/Clt composite membranes, greater permeation rates (0.07–0.32 kg/m^2 h) were determined, whereas the separation factors (12–23) were lower than plain NaAlg membranes at 20–50˚C.

Kondolot Solak and Şanlı [29] have investigated the effect of permeation temperature on the permeation rate and the separation factor in VP of DMF solution. They have reported that when the temperature increased (20–50˚C) flux increased in PV and VP methods.

The activation energies of permeation in VP were calculated to be as 2.794 and 5.662 kcal/mol (Fig. 10), respectively, for zeolite-filled NaAlg membrane and pure NaAlg membrane. In VP, Arrhenius parameters were calculated, and results were given in Table 2.

3.4. Effect of the feed composition in TDVP

The effect of the feed composition on the permeation rate and the separation factor in TDVP was studied and results were given in Figs. 11 and 12. In this study, the temperature of the membrane surrounding was kept constant at 40˚C as the feed temperature 15˚C. We obtained parallel results in TDVP as in VP. When DMF and water that had been vaporized from the mixture come in contact with the membrane, DMF vapor aggregates easier than the water vapor since the freezing point of DMF is smaller than that of water (−61 and 0˚C, respectively). This aggregation of DMF molecules is responsible for permselectivity for water through NaAlg/Clt compos-

Table 2
Arrhenius parameters for permeation, diffusion, and heat of sorption in VP

Parameter (kcal/mol)	NaAlg	M-1	M-2	M-3	M-4
E_p	5.66	4.15	3.82	2.79	3.26
E_D	4.81	3.03	2.45	1.05	1.73
ΔHs	0.85	1.12	1.37	1.74	1.53

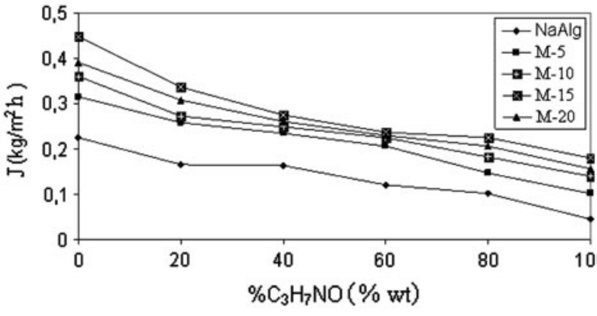

Fig. 11. Change of permeation rate with the feed vapor composition in TDVP. The permeation conditions; temperature of membrane surroundings: 15°C, P: 0.5 mbar, temperature of feed solution (t): 40°C.

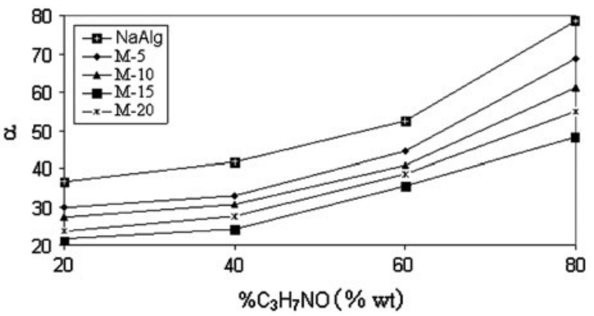

Fig. 12. Change of separation factor with the feed vapor composition in TDVP. The permeation conditions; temperature of membrane surroundings: 15°C, P: 0.5 mbar, temperature of feed solution (t): 40°C.

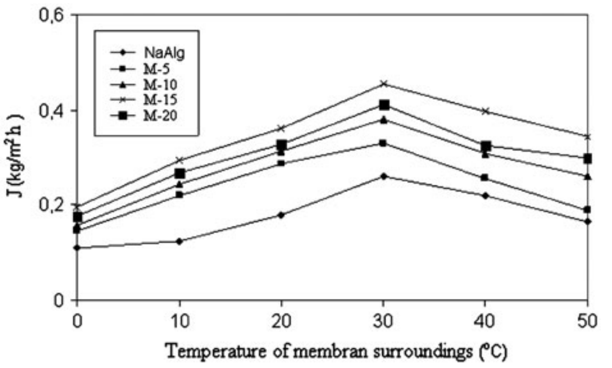

Fig. 13. Effect of membrane surroundings temperature on the permeation rate. The permeation conditions; λ: 60 µm, P: 0.5 mbar, temperature of feed solution (t): 40°C.

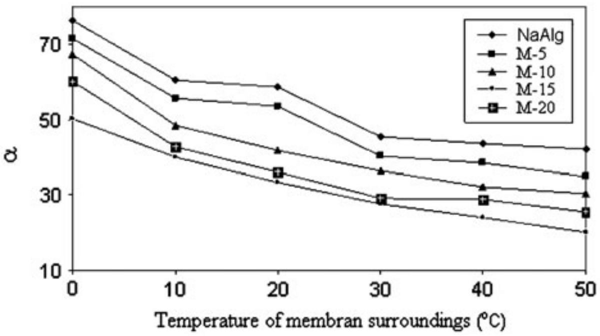

Fig. 14. Effect of membrane surroundings temperature on the separation factor. The permeation conditions; P: 0.5 mbar, temperature of feed solution (t): 40°C.

ite membranes. High permeation rates but small separation factors were obtained with NaAlg/Clt composite membranes than the plain NAAlg membranes in TDVP method.

Kondolot Solak and Şanlı [29] searched the separation of DMF/water mixtures through alginate membranes in VP and TDEV. The feed was an aqueous solution of 20 wt.% DMF, the temperature of the feed solution was kept constant at 40˚C, and the temperature of the membrane surroundings was changed to a temperature lower than the temperature of the feed solution. They observed that the permeation rate decreased but the separation factor toward water increased with the lowering of the temperature of the membrane surroundings. The decrease in the permeation rate was attributable to the decrease in the motion of the permeating molecules and polymer chains comprising the membrane with a reduction of the temperature of the membrane surroundings.

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

Figs. 13 and 14 reflect the effect of temperature of the membrane surroundings on the permeation rate and the separation factor in TDVP. The temperature of the membrane surrounding was changed in the range of 0–50˚C. The permeation rate increased, whereas the separation factor decreases with the increase in the temperature of the membrane surroundings. In TDVP method by using NaAlg/Clt composite membranes, higher permeation rates (0.1–0.45 kg/m^2 h) were determined, whereas the separation factors (28–72) were lower than plain NaAlg membranes at 20–50˚C.

Uragami and Shinomiya [14] studied permeation and separation characteristics for aqueous alcoholic solutions through a modified silicone rubber membrane containing poly(propylene glycol) by VP method. They reported that when the temperature of membrane surroundings was kept constant and the temperature of aqueous ethanol solution was varied, the permeation rate and the permselectivity for ethanol are clearly influenced by the temperature. They observed that the permeation rate for 10 wt.% ethanol solution decreased due to the lowering the motions of polymer constituting the membrane and the activity of permeants.

The high separation factors obtained in TDVP method that can be attributed to temperature difference between the feed mixture and the membrane surrounding. When the DMF and water molecules are vaporized, these vaporized molecules come close to membrane surrounding kept at a lower temperature, the DMF molecules are liable to aggregated more than the water molecules. This aggregation of DMF is responsible for the increase in the separation factor of water. The changes in α, J, and SI with DMF concentration were given for VP and TDVP methods in Table 3 for NaAlg and M-15 membranes. From the table, it was seen that TDVP method is highly

Table 3
Separation performance of plain NaAlg and NaAlg/Clt (M-15) composite membranes in VP and TDVP methods

C_3H_7NO in the feed (wt.%)	VP						TDVP					
	NaAlg (Plain)			NaAlg-Clt (M-15)			NaAlg (Plain)			NaAlg-Clt (M-15)		
	α	J (kg/m^2)	SI	α	J (kg/m^2)	SI	α	J (kg/m^2)	SI	α	J (kg/m^2)	SI
20	21.6	0.13	2.80	13.3	0.26	3.46	36.5	0.16	5.84	21.6	0.34	7.26
40	29.2	0.10	2.92	16.6	0.22	3.65	41.6	0.16	6.65	24.2	0.28	6.68
60	29.4	0.08	2.35	21.2	0.18	3.81	52.4	0.12	6.28	35.4	0.24	8.43
80	35.9	0.06	2.15	25.3	0.11	2.78	78.6	0.10	7.86	48.2	0.23	10.85

effective technique than VP for the separation of DMF-water mixtures by using plain NaAlg and NaAlg/Clt composite membranes. As it is clearly seen from the table, NaAlg/Clt (M-15) composite membranes have very good separation ability than plain NaAlg membranes in VP and TDVP methods.

4. Conclusions

The following conclusions were obtained from the study on the separation of DMF–water mixtures using NaAlg/Clt membranes crosslinked with GA.

1. (1) Increase in the operating temperature increased the permeation rate whereas decreased the separation factor in VP and TDVP methods.
2. (2) Permeation rate decreased whereas separation factor increased as the DMF content of the feed increased in VP and TDVP methods used.
3. (3) As the Clt content increased permeation rate increased up to 15 wt.% Clt content then decreased.
4. (4) The zeolite-incorporated membranes exhibited lower activation energy compared with that of a plain membrane, suggesting that the permeants require less energy during the process. Activation energies for VP were found as 5.662 and 2.794 kcal/mol for plain NaAlg membrane and NaAlg-Clt composite membrane (M-15), respectively.
5. (5) Permeation rates in VP and TDVP were found 0.03–0.41 kg/m^2 h and 0.10–0.45 kg/m^2 h, respectively. The higher separation factor was obtained in TDVP method (68.80) as compared to VP.

Acknowledgement

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List of symbols

W_s — the mass of the swollen membrane in the feed solution
W_D — the mass of the dried membrane
SD — the swelling degree
α — separation factor
P_W — the mass fractions (wt.-%) of water in the permeate
P_{DMF} — the mass fractions (wt.-%) of DMF in the permeate
F_W — the mass fractions (wt.-%) of water in the feed
F_{DMF} — the mass fractions (wt.-%) of DMF in the feed
J — permeation rate
W — the mass of permeate (kg)
A — membrane surface area (m^2)
t — the time of experiment (h)
SI — separation factor
A_p — permeation rate constant
E_p — activation energy for permeation
ΔHs — heat of sorption
E_D — diffusion activation energy

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