Desalination and Water Treatment
www.deswater.com

1944-3994 / 1944-3986 © 2011 Desalination Publications. All rights reserved.
doi: 10.5004/dwt.2011.1626

25 (2011) 297–309
January

Crosslinked sodium alginate and sodium alginate-clinoptilolite (natural zeolite) composite membranes for pervaporation separation of dimethylformamide-water mixtures: A comparative study

Suat Kahya[a], Oya Şanlı[b]*, Erdem Çamurlu[c]

[a]*Aksaray Üniversitesi, Güzelyurt Meslek Yüksek Okulu, Gıda Teknolojisi, 68000, Aksaray, Turkey*
[b]*Gazi Üniversitesi, Fen Edebiyat Fakültesi, Kimya Bölümü, 06500, Ankara, Turkey*
Tel. +90 (312) 2126030/1007; Fax +90 (312) 2122279; email: osanli@gazi.edu.tr
[c]*Akdeniz Üniversitesi, Mühendislik Fak., Makine Müh. Bölümü, 07058, Antalya, Turkey*

Received 9 November 2009; Accepted in revised form 9 May 2010

ABSTRACT

Pervaporation performance of crosslinked composite membranes of clinoptilolite (Clt) and sodium alginate (NaAlg) has been studied for the separation of dimethylformamide (DMF)/water mixtures. The effects of feed composition (0–100 wt. %) and operating temperature (20–50°C) on the permeation rates and the separation factors were investigated. The observed flux values of composite membranes were much higher whereas the selectivities were lower than the plain NaAlg membranes. The highest permeation rate of 2.3 kg/m^2h and selectivity of 23 was exhibited by the composite membranes depending on the operating conditions and Clt loading. In addition sorption–diffusion properties of the composite membranes were investigated at the operating temperatures and the feed compositions. It was found that the sorption selectivity was dominant factor for the separating of DMF/water mixtures for both types of membranes. The membranes were characterized by Fourier transform infrared spectrometry (FTIR), differential scanning calorimetry (DSC), thermal gravimetric analysis (TGA) and scanning electron microscopy (SEM).

Keywords: Pervaporation; Separation techniques; Crosslinking; Zeolites

1. Introduction

Pervaporation (PV) separation, a widely accepted membrane-based technique, has been used in liquid–liquid separation through the permselective membranes. 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. Mass transport through the membrane occurs by the solution–diffusion principles [1,2] and the process takes place in three steps: sorption of liquid at the upstream side of the membrane surface, diffusion of liquids through the membrane, and desorption of the sorbed molecules in vapor form at downstream side of the membrane. PV is an important technology for the separation of organic compounds. PV is most often used for dehydration of organic solvents and the separation of binary mixtures [3–7].

Zeolites are hyratized natural and synthetic alumosilicates of spatial net structure made from $[SiO_4]^{4-}$ and $[AlO_4]^{4-}$ tetrahedrons joined by common oxygen atoms (Fig. 1). $[SiO_4]^{4-}$ and $[AlO_4]^{4-}$ tetrahedrons within the zeolite structure make two- and three-dimensional secondary units, which are combined and make a three-dimensional net structure that is characteristic for zeolites. The zeolite

---

* Corresponding author.

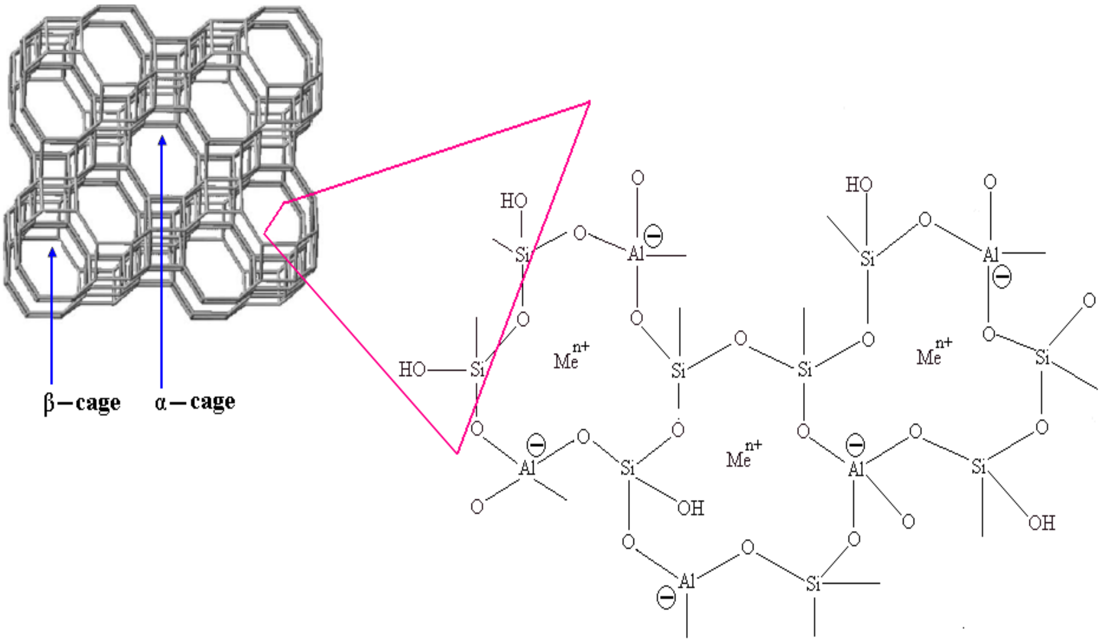

Fig. 1. Skeleton of zeolite.

structure is interlinked by channels of a certain shape and size, different from other alumosilicates and other crystalline materials. The shape and size of hollows and channels are constant and precisely defined as structural parameters of a certain zeolite type [8–11]. In their structure, some Si atoms are substituted by Al atoms, resulting in a negatively charged structure that originates from the difference between the $[SiO_4]^{4-}$ and $[AlO_4]^{4-}$ tetrahedral [12].

The zeolite group contains more than 40 naturally occurring species [13]. But only those containing chabazite, clinoptilolite, erionite, ferrierite, phillipsite, mordenite and analcime are available in sufficient quantity and purity to be considered as utilizable natural resources [14]. Clinoptilolite is a zeolite of the heulandite group being the most abundant in nature. It is very stable towards dehydration, and thermally stable up to 700°C in air [15]. The chemical composition of clinoptilolite is characterized by significant variations in the Si/Al ratio as well as in the composition of the exchangeable cations. The Si/Al (y/x ratio) ratio changes between 4 and 5.5, and low-silica members are enriched with calcium, whereas high-silica clinoptilolites are enriched with potassium, sodium, and magnesium [13].

The use of natural zeolites for environmental remediation (organic compounds and heavy-metal ions) is well established. Also, natural zeolites have been found to be helpful in the control of malodors (e.g., hydrogen sulphide and and ammonia) emanating from confined livestock-rearing areas, kennels, pet shops, zoos and pet-litter trays. Their high surface area, and therefore, their high adsorption capacity, as well as their ion-exchange properties make them very useful in these fields [16–18].

The use of low performance natural polymer like sodium alginate (NaAlg) in PV has some drawbacks due to its lower flux rates and separation factors (selectivity) [8,9]. 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 filters such as zeolites, 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 [19–23]. Chen et al. [24] studied the pervaporation separation of hydrophilic zeolite-filled chitosan membranes for organic-water systems. Kariduraganavar et al. [25] reported that both flux and selectivity could improve incorporating different amounts of suitable hydrophilic zeolite into NaAlg membranes for the separation of water–isopropanol mixtures.

Dimethylformamide (DMF) is an important industrial chemical. Recovery of DMF is essential from acrylic fibre production plants, pharmaceutical plants, polyurethane based synthetic leather and elastic yarn production plants etc. From these plants DMF is released into air and a water scrubber is used for emission recovery, 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]. Some research groups have focused on the membrane development for the separation of dimethylformamide-water mixtures at different feed concentrations [27–29]. Shah and co-workers [27] prepared hydrophilic zeolite NaA membranes for the PV of alcohol water and 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. Solak and Şanlı [28] studied separation characteristics of DMF/water mixtures through alginate membranes by pervaporation, vapor permeation and vapor permeation with temperature difference methods. They have found that increase in the operating temperature in pervaporation and vapour permeation method increased the permeation rate whereas decreased the separation factor. Solak and Şanlı [29] have also found that the increase in the operating temperature increased the permeation rate whereas decreased the separation factor by using sodium alginate-g-n-vinyl-2-pyrrolidone membranes with pervaporation method.

Although there are some studies on the separation of DMF/water mixtures, there is only one study that uses pure NaA (4A) membrane which is a tailor made sodium zeolite. There is no study which utilizes natural zeolite for the pervaporation of polymeric membrane to separate DMF/water mixtures in the literature. In this mean this study is pioneer. Addition of zeolite to the polymeric material may increase the hydrophilic nature the polymeric membrane as well as precise micropore structure of the zeolite cage helps in a partial molecular sieving of molecules.

In the present study, NaAlg-Clt composite membranes were prepared in different ratios and crosslinked with glutaraldehyde. These membranes were used in pervaporation separation of DMF/water mixtures and the separation performance of the membranes as a function of temperature, feed composition and composite ratios was studied and compared with that of pure NaAlg membranes. A schematic representation of the crosslinking and the electrostatic interaction between NaAlg and Clt is given in Fig. 2.

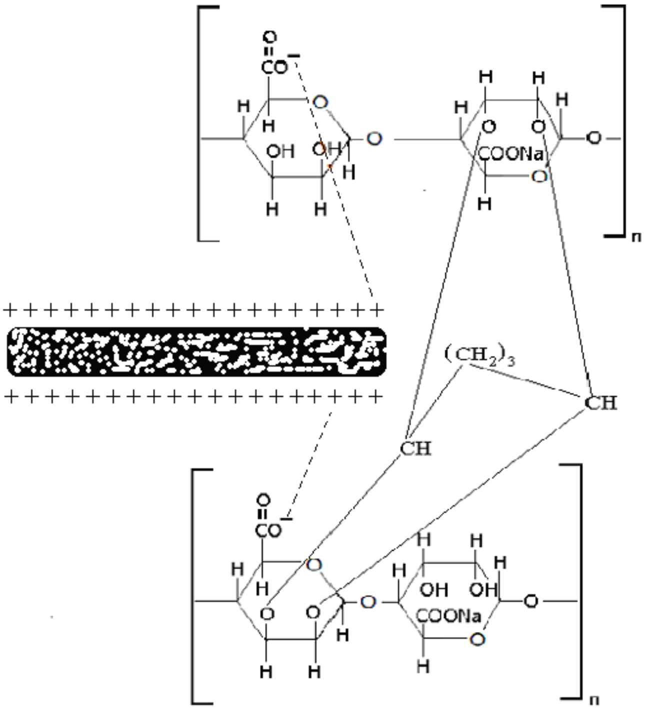

Fig. 2. Schematic representation of the crosslinking and the electrostatic interaction between NaAlg and Clt.

2. Experimental

2.1. Materials

NaAlg was provided from Sigma with medium viscosity. Gluteraldehyde (GA) solution, DMF and hydrochloride acid (HCl) were supplied by Merck. Clinoptilolite was provided from Etibank A.Ş. (Bigadiç-Balıkesir-Turkey). The samples were grinded by ball mill and sieved to ≈38 μm.

2.2. Preparation of zeolite-filled NaAlg and pure NaAlg membranes

NaAlg (2 g) was dissolved in 100 mL of water with continuous stirrrig. Then clinoptilolite particles were weighed separately in different amounts and dispersed in 20 mL water, mixed for 30 min, and then added to NaAlg solution (freshly prepared) for stirring overnight and casted onto rimmed round glass plates. Dried membranes were peeled off from the plates and crosslinked with GA (2.5 vol. %) and HCl (3 vol. %). After keeping the membranes in crosslinking mixture for 24 h, membranes were 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 wt. % and the resulting membranes were designated as M-1, M-2, M-3 and M-4, respectively. The pure crosslinked NaAlg membrane was also prepared in the same manner without clinoptilolite particles. Membrane thicknesses were measured by a micrometer screw gauge.

2.3. Infrared analysis

Infrared spectra of NaAlg-Clt composite membranes were measured with Mattson 1000 Fourier Transfer Infrared Spectroscopy (FTIR).

2.4. DSC analysis

The thermal analysis was carried out with differential scanning calorimeters (DSC, General V4.1C Dupont 2000). Measurements were performed over the temperature range of 25–400°C at the heating rate of 10°C/min.

2.5. TG analysis

Thermal stability of the membranes was measured using a Schimadzu TG/DTA (Japan) analyzer in the temperature range from 25 to 400°C, heated at the rate of 10°C/min and flushed with nitrogen gas, at a flow rate of 20 mL/min.

2.6. SEM analysis

SEM pictures were taken using scanning electron microscopy (SEM, JEOL JSM-5600).

2.7. Swelling degree measurements

NaAlg–Clt composite membranes were immersed in different concentrations of DMF 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 using Eq. (1) [29]:

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

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

2.8. 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 20°C to 50°C by using NaAlg–Clt composite membranes. The membrane surface area was 16.5 cm^2 and pressure was kept at 0.5 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 analyzed with Atago DD-5 type digital refractometer using a calibration curve.

The membrane performance was expressed by separation factor (α) and permeation rate (J) [Eqs. (2) and (3)]. The separation factor was defined as follows [29]:

$$\alpha_{\mathrm{sep.W/DMF}} = \frac{P_{\mathrm{W}} / P_{\mathrm{DMF}}}{F_{\mathrm{W}} / F_{\mathrm{DMF}}} \tag{2}$$

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

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

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

2.9. Sorption measurements

The composite and pure NaAlg membranes were immersed into different concentrations of DMF solutions for 48 h at 40°C. To remove the excess solvent, the membranes were blotted between the tissue paper, then placed into an empty pervaporation cell; the sorbed mixture was collected in the traps. The composition of the collected mixture was determined by Atago DD-5 type digital refractometer [30].

The sorption selectivity was calculated using Eq. (4) [29]:

$$\text{Sorption selectivity } \left(\alpha_{\mathrm{sorp.W/DMF}}\right) = \frac{Y_{\mathrm{W}} / Y_{\mathrm{DMF}}}{X_{\mathrm{W}} / X_{\mathrm{DMF}}} \tag{4}$$

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.

The diffusion selectivity can be calculated from the separation factor and the sorption selectivity by Eq. (5) as follows [29]:

$$\text{Diffusion selectivity } \left(\alpha_{\mathrm{dif.W/DMF}}\right) = \frac{\alpha_{\mathrm{sep.W/DMF}}}{\alpha_{\mathrm{sorp.W/DMF}}} \tag{5}$$

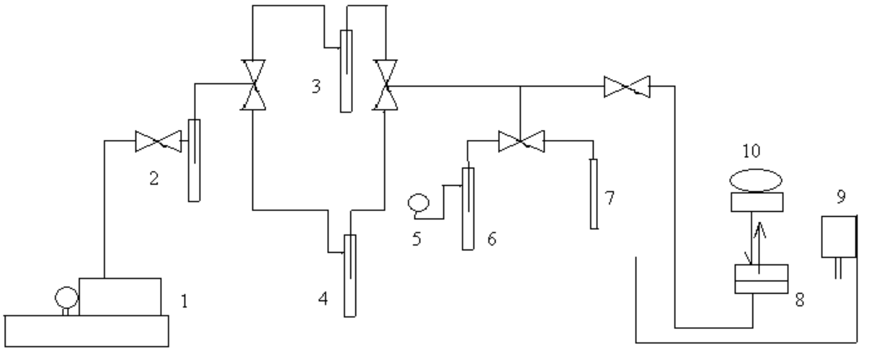

Fig. 3. Schematic diagram of the pervaporation apparatus: (1) vacuum pump, (2–4, 6) permeation traps; (5) McLeod manometer; (7) vent; (8) permeation cell; (9) constant temperature water bath; (10) peristaltic pump; (11) temperature indicator.

3. Results and discussion

3.1. Characterization of membranes

Crosslinked membranes were scanned with FTIR (Fig. 4). In the FTIR spectrum of pristine NaAlg, the peak at 3000–3500 cm^{-1} area presents the stretching vibration of O–H band. NaAlg–Clt composite membranes, the characteristic broad band appearing at about 3400 cm^{-1} corresponds to O–H stretching vibration of NaAlg backbone. The sharp peaks observed around 1720 and 1100 cm^{-1} corresponds, respectively, to the asymmetric and symmetric stretching of the carboxyl group of NaAlg. A peak around 1050–1100 cm^{-1} corresponds to the C–O stretching of NaAlg and also for Si–O bonds in clinoptilolites. A peak appearing between 600 and 800 cm^{-1} corresponds to the Al–O stretching vibrations of the clinoptilolite. The spectrum of plain NaAlg and NaAlg-Clt composite membranes was in accordance with literature report [31] and the data confirmed the presence of clinoptilolite in a zeolite-filled membrane.

The thermal analysis was carried out with differential scanning calorimeter and the results are shown in Fig. 5. The crosslinked NaAlg polymer membrane used in this study shown a Tg of 85°C, however, this value for NaAlg in the composite membrane has been found to increase with clinoptilolite loading. Increase in Tg may be attributed to the decrease in the free volume with crosslinking NaAlg and clinoptilolite loading.

Thermal degradation of the crosslinked pristine NaAlg and crosslinked NaAlg–Clt composite membrane and pristine Clt was examined by TGA. The results displayed in Fig. 6 show that for the crosslinked pristine NaAlg, one weight loss stage around 180–235°C was seen. On the other hand, the crosslinked NaAlg–Clt and pure clt exhibited weight loss stage around 205–250°C. Thus, an increase in thermal stability of NaAlg–Clt composite membranes can be stated. Similar result was stated in literature [32].

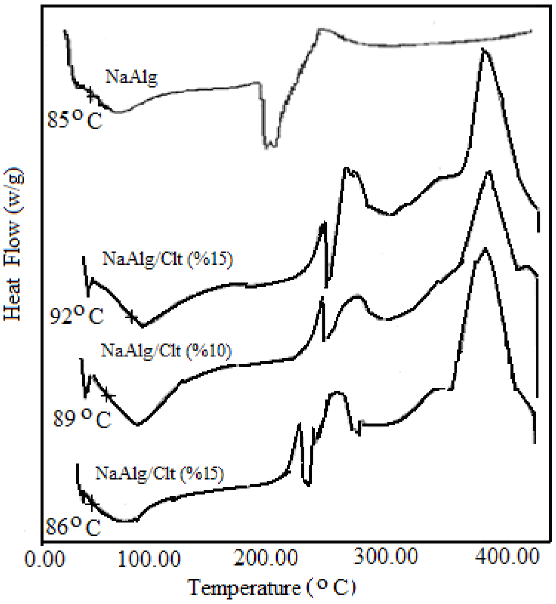

Fig. 5. Differantial scanning calorimeter (DSC) curves of pristine NaAlg and NaAlg/Clt (5, 10, 15 wt. %) composite membranes.

The morphology of the NaAlg and NaAlg-Clt composite membranes was observed using scanning electron microscopy (Figs. 7a–d). It is seen from the SEM results that the NaAlg membrane surface has a smoother apperance than the composite membranes for the same magnification. SEM pictures indicate almost uniform distribution of Clt particles in the composite medium with increasing Clt loading.

3.2. Effect of membrane thickness

Membranes with varying thicknesses (20–120 μm) were prepared from the pure NaAlg solution by a cast-

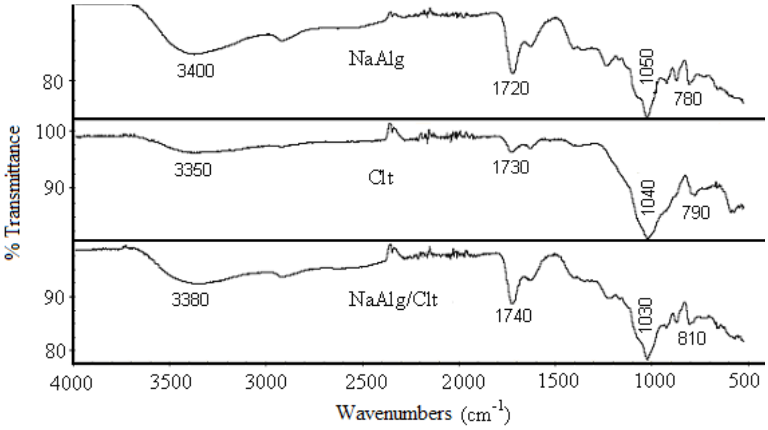

Fig. 4. FTIR spectra of NaAlg/Clt, NaAlg membranes and Clt.

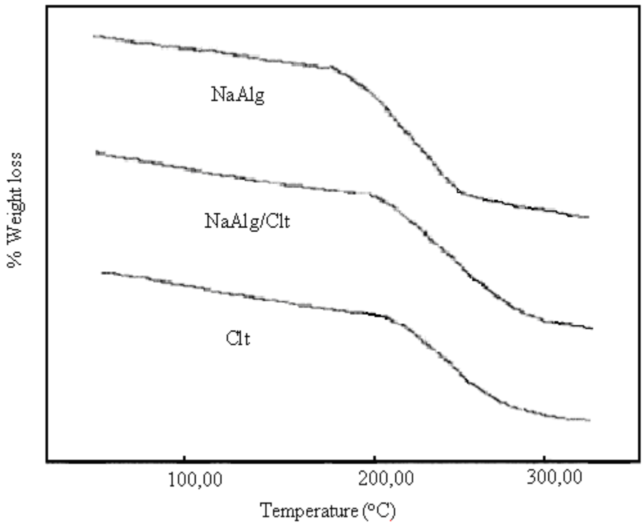

Fig. 6. Thermal gravimetry (TGA) curves of pristine NaAlg, NaAlg/Clt composite membranes and pristine Clt.

ing method. The separation factor and permeation rate as a function of membrane thickness were studied for the separation 20 wt. % DMF mixture at 40°C, and the results are presented in Fig. 8. As it is seen from the figure that the permeation rate decreases with membrane thickness whereas the separation factor increases.

Membranes of 60 μm thickness were preferred in the rest of the study for performing repetitive results (acceptable flux and separation factor) which could stand vacuum and be used at least seven times. Fig. 9 shows a linear relationship between the total permeation rate and the reciprocal of the membrane thickness as is predicted by the solution–diffusion model (Fickian behavior).

Different results concerning the effect of membrane thickness were reported in the literature [4,33]. Işıklan and Şanlı [33] studied the separation characteristics of acetic acid–water mixtures by pervaporation using PVA membranes modified with malic acid. They have reported that as the membrane thickness increases the permeation

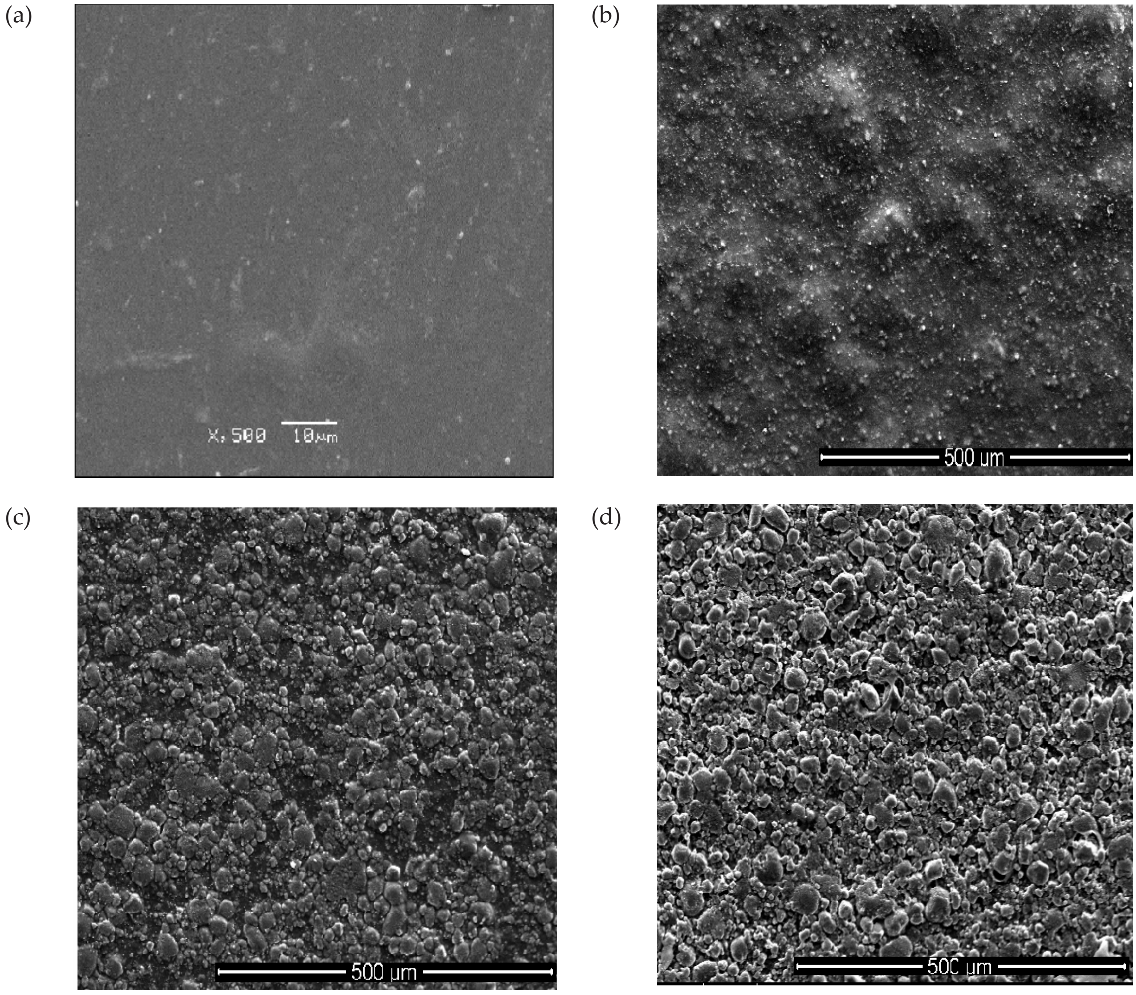

Fig. 7. Scanning electron microscopic picture of (a) pristine NaAlg membrane (b,c,d) NaAlg/Clt (5, 10, 15 wt.-%, respectively) composite membrane.

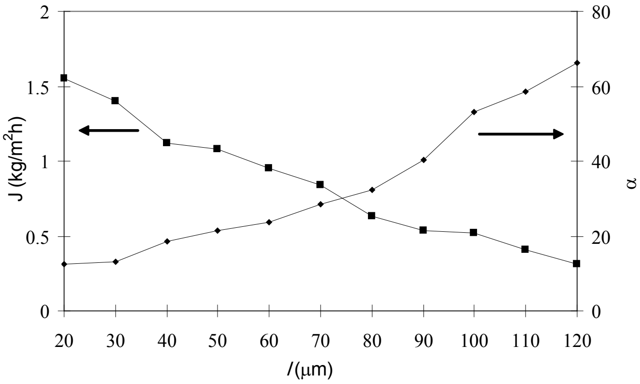

Fig. 8. Effect of membrane thickness on the permeation rate and the separation factor for pristine NaAlg membrane.

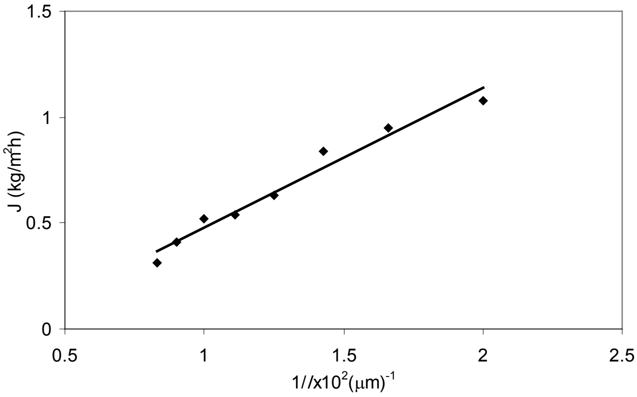

Fig. 9. Permeation rate as a function of the reciprocal of the membrane thickness for pristine NaAlg.

rate decreases whereas the separation factor stays almost constant below a membrane thickness of 70 μm and then increases sharply between 70 and 100 μm membrane thickness.

3.3. *Effects of feed composition on membrane swelling*

Fig. 10 shows the swelling behavior of pristine and NaAlg–Clt composite membranes as a function of feed mixture composition at 40°C. It was observed that the degree of swelling decreased with increasing feed DMF concentrations up to a certain percent and then increased for all the Clt containing membranes whereas they decreased steadily as the feed concentration increased for pristine NaAlg membrane. This unexpected tendency (except for pure NaAlg membrane) may not only be due to the decrease in the free volume available in the membrane matrix with Clt loading but also due to the cluster formation of water molecules at high concentrations of water in the feed. 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 dipol moment (3.85 D) so that strong attractive interactions between Clt and DMF are expected which also contributes to membrane swelling. Kariduraganavar et al. [34] studied pervaporation separation of water–acetic acid mixtures through PVA–silicone based hybrid membranes and found similar results.

Swelling tendencies of composite membranes are displayed in Fig. 11 as a function of filler loading. An increase in Clt content first results in an increase in the swelling degree since Clt has hydrophilic nature leading to the stronger interaction with water molecules. However, after 15 wt. % loading swelling decreases due to the decrease in the free volume available in the membrane matrix. Different results were observed in the literature [35,36]. 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 increasing 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.

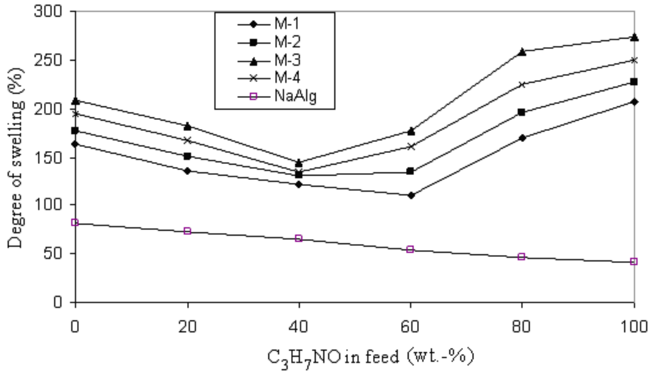

Fig. 10. Change in the swelling degree with feed composition.

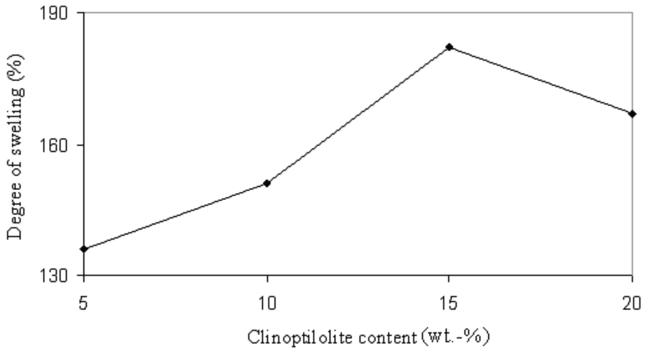

Fig. 11. Variation of degree of swelling with different wt. % of Clt for 20 wt. % of DMF in the feed.

3.4. Effects of feed composition on pervaporation properties

Fig. 12 shows the effect of feed composition on the total permeation flux for all the membranes at 40°C. It is observed that the total permeation flux decreased almost linearly with the increasing amount of DMF in the feed for all the membranes. As the water concentration decreased the amorphous regions of the polymer got less swollen and polymer chain segments became less mobile thus increasing the energy required for diffusive transport through the membrane for the pristine NaAlg membranes. Addition of Clt to the membrane matrix improves the flux of the membranes. Clt loading into the membrane facilitates the permeation of both water and DMF since the average pore size of the Clt (1.75 nm) [37] is higher than the kinetic diameter of both DMF (0.55 nm) and water (0.26 nm) [38] thus increasing the flux compared to pristine NaAlg membranes. However, the improvement on separation is not observed for Clt-filled membranes because of the large pore size of the zeolite as is reflected from Fig. 13. DMF is small enough to enter to the pores of zeolite but diffuses slowly due to the interaction with the zeolite matrix so that water transport is hindered leading to low selectivity. Similar results were found in the literature [31, 34–36]. Naidu et al. [31] studied zeolite-filled NaAlg and PVA-polyaniline semi-IPN network membranes for PV separation of water–acetonitrile mixture and found that the permeation flux decreased for all the membranes with increasing the amount of acetonitrile concentration in the feEffect of Clt content on the pervaporation properties can also be seen from Figs. 12 and 13. As it is reflected from Fig. 12, permeation rate increases with Clt loading up to 15 wt. % and then decreases. Clt used in this study has Si/Al ratio of 5.0 which is not a high ratio indicating hydrophilic nature and have high affinity toward water (Table 1) [37]. Clt has a pore size as stated previously, that is larger than the kinetic diameter of both water and DMF, so both water and DMF molecules can pass through the pores of zeolite leading to the increase in flux as Clt loading increases. There is also an interaction between DMF and Clt due to cations present in the zeolite structure which hinders the passage of DMF molecules. This is also supported by the swelling results (Fig. 13). The decrease of the permeation rate after 15 wt. % loading may also be attributed to the ''leaks'' around the clinoptilolite during PV when zeolite loading is high.

Gao et al. [39] investigated the effect of zeolite content on PVA membrane performance for the separation of various alcohol solutions. They observed that the flux rose with increasing KA zeolite content, whereas the separation factor was maintained upon addition of zeolite until 11% and then decreased. They concluded that this phenomenon might have been resulted from ''leaks'' around the zeolite during PV when the zeolite load was high.

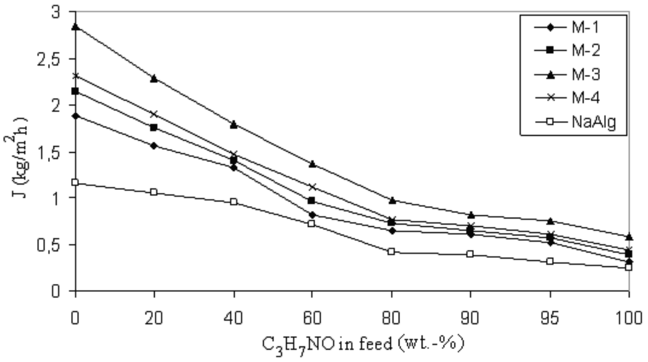

Fig. 12. Variation of pervaporation flux with feed concentration for pristine NaAlg and NaAlg/Clt membranes. The permeation conditions: *ℓ* 60 μm, *t* 40°C, *P* 0.5 mbar.

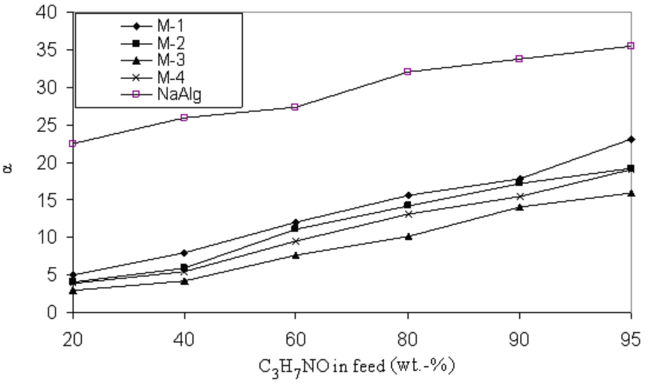

Fig. 13. Variation of selectivity with feed concentration for pristine NaAlg and NaAlg/Clt membranes. The permeation conditions: *ℓ* 60 mm, *t* 40°C, *P* 0.5 mbar.

Table 1
Characteristics of clinoptilolite 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	

Fig. 14a,b shows the relationship between the sorption selectivity and the diffusion selectivity of plain NaAlg and NaAlg–Clt (M-3) membranes at different DMF concentrations. The sorption selectivity and the diffusion selectivity increased with increasing DMF concentration in the feed solution. A possible reason for this could be the fact that DMF being highly polar strongly sorbs on the ionic sites so the sorption increases as the DMF concentration

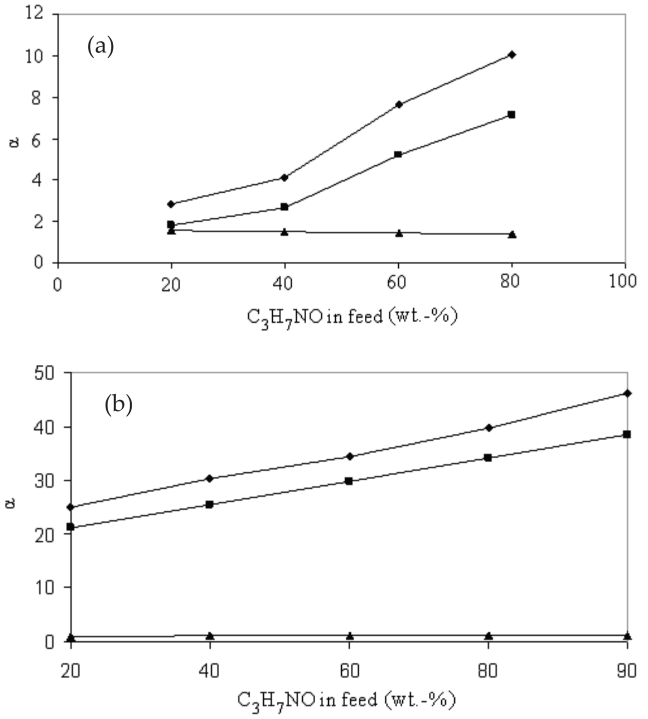

Fig. 14. (a) Relationship between the selectivities at different feed compositions for M-3 membrane. (b) Relationship between the selectivities at different feed compositions for plain NaAlg membrane. ◆ separation selectivity, ■ sorption selectivity, ▲ diffusion selectivity.

is increased. As seen from the figures, sorption is the predominant factor for the permeation irrespective of the type of the membrane.

Toti et al. [40] prepared NaAlg 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.

Transport of molecules in PV has been explained by the solution–diffusion model [41]. Diffusion happens as a result of concentration gradient. For this reason, it is important to estimate the diffusion coefficient, D_i of solvent molecules to understand the transport mechanism. Using Eq. (6)] [42], from the PV results D_i has been calculated.

$$J_i = \frac{D_i}{\delta} C_i \tag{6}$$

where D_i is presumed to be constant across the effective membrane thickness (δ), C_i the concentration of water or DMF in the feed after the process, J_i the permeation flux of water or DMF. The values of Di at 40°C are given in Table 2.

3.5. *Effect of temperature on membrane performances*

The effect of operating temperature on pervaporation performances for 20 wt. % of DMF in the feed was studied and the results are given in Figs. 15 and 16. It was observed that the permeation rate was found to increase from 20 to 50°C, whereas the separation factor decreased. As the temperature increases, the frequency and the amplitude of chain jumping increase so the free volume becomes larger, both DMF and water molecules pass through the membrane, resulting in increased total permeation rate and decreased separation factor. However, at lower temperature, only water molecules can transport through the membrane matrices.

The temperature dependence of the permeation rates fittes with the Arrhenius type equation [Eq. (7)] [28]:

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

where A_p is permeation rate constant, E_p is activation energy for permeation.

Fig. 17 shows that the permeation rate is inversely proportional to the absolute temperature, indicating that experimental results agree well with the Arrhenius equation. The activation energies of DMF and water permeating through the pristine NaAlg membrane and zeolite-filled NaAlg membrane (M-3) were calculated to be 6.750 and 4.290 kcal/mol, respectively. The solubility of dimethylformamide in the membrane was smaller than in water, leading to larger heat of solution (ΔH_s) and dimethylformamide having larger permeating molecule size can have higher diffusion activation energy (E_D) than in the case of water. If activation energy is positive, the permeation flux increases with increasing temperature.

Table 2
Diffusion coefficients of water and DMF calculated from Eq. (6) at 40°C

Mass % of water	$D_W \times 10^{13}$ (m^2s^{-1})					$D_{DMF} \times 10^{13}$ (m^2s^{-1})				
	NaAlg	M-1	M-2	M-3	M-4	NaAlg	M-1	M-2	M-3	M-4
20	0.78	1.21	1.33	1.71	1.38	0.10	0.14	0.15	0.22	0.20
40	1.83	2.13	2.53	3.50	2.89	0.11	0.15	0.17	0.24	0.22
60	3.84	5.36	5.75	7.22	5.92	0.13	0.18	0.21	0.29	0.26
80	8.70	12.74	14.25	18.6	15.42	0.17	0.24	0.28	0.37	0.33

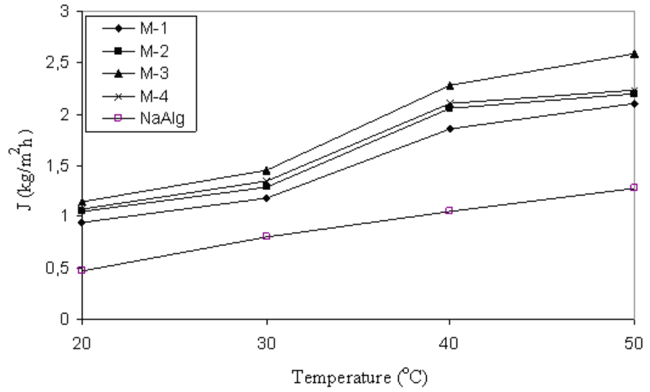

Fig. 15. Effect of temperature on pervaporation flux. The permeation conditions: DMF 20 wt %, *l* 60 μm, *P* 0.5 mbar.

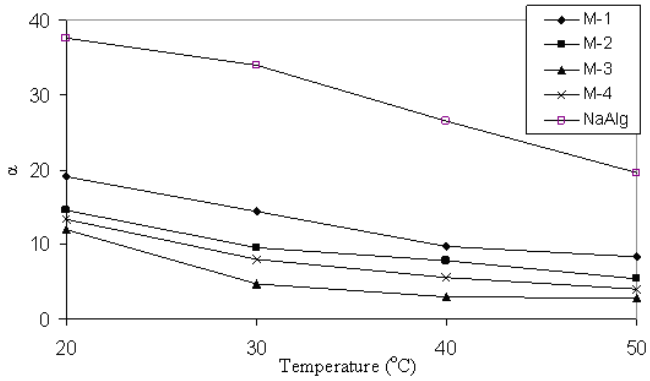

Fig. 16. Effect of temperature on selectivity. The permeation conditions: DMF 20 wt. %, *l* 60 μm, *P* 0.5 mbar.

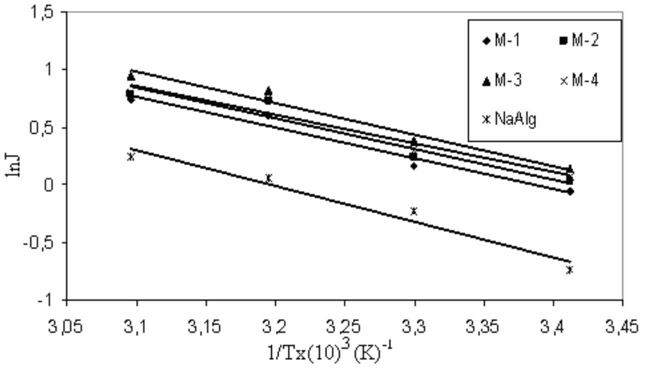

Fig. 17. Variation of ln *J* with temperature for different membranes at 20 wt. % of DMF in the feed. (◆ M-1; ■ M-2; ▲ M-3; x M-4, * NaAlg).

All these result in an increase of driving force due to the increase in temperature. In the same manner, mass transport due to diffusion was calculated using the Arrhenius type equation [Eq. (8)] [42]:

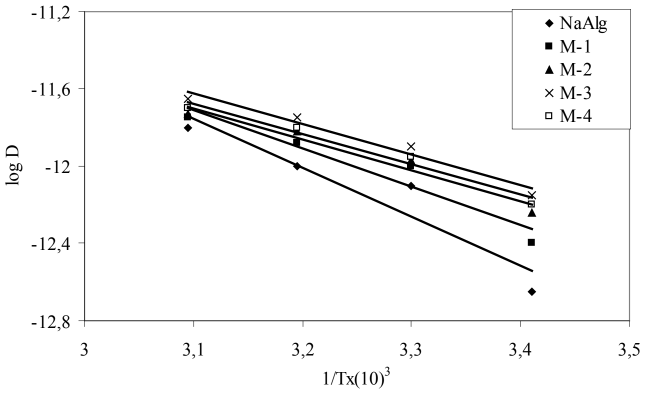

Fig. 18. Variation of log D with temperature for different membranes at 20 wt. % of DMF in the feed. (■ M-1; ▲ M-2; x M-3; □ M-4, ◆ NaAlg).

$$D_i = D_{i0} \exp\left(-E_D / RT\right) \tag{8}$$

Here E_D is the activation energy for diffusion, *i* stands for water or DMF components of the mixture. Arrhenius plot of log *D* vs. 1/*T* × 10^3 is given in Fig. 18 for the temperature dependency of diffusion. Linear behaviour was observed, suggesting that diffusivity follows the Arrhenius trend. The activation energies for diffusion were estimated from the Arrhenius plots, and the values obtained are presented in Table 3. It is noticed that the pristine NaAlg membrane exhibits higher E_p and E_D values compared to those of Clt–filled membranes (M-1 to M-4). This suggests that both permeating and diffusing molecules require more energy for transport through the pristine membrane since it has dense nature.

Using the E_p and E_D values, the heat of sorption was calculated using Eq. (9):

$$\Delta H_s = E_p - E_D \tag{9}$$

The calculated ΔH_s values, E_p and E_D are given in Table 4. The ΔH_s values give extra information about the transport of molecules through the polymer matrix. In this study, the ΔH_s values taken were positive for all the membranes, giving an endothermic contribution.

It can be seen that the activation energies for pure NaAlg membrane are higher than those of the composite NaAlg membranes for all the feed mixtures. For this reason, more energy is required for molecules to transport across the membrane at similar conditions. The smaller activation energy values observed for the NaAlg-Clt composite membrane may suggest that the energy barrier has decreased and that the feed mixtures can more readily transport. Similar results were found in the literature [35,36].

3.6. Comparasion of the performance of the NaAlg based membranes

Results of the studies reported in the literature on the

Table 3
Diffusion coefficients of water and DMF calculated from Eq. (8) at different temperatures for 20 wt. % of DMF in the feed mixture

Temperature (°C)	$D_W \times 10^{13}$ (m^2s^{-1})					DDMF × 10^{13} (m^2s^{-1})				
	NaAlg	M-1	M-2	M-3	M-4	NaAlg	M-1	M-2	M-3	M-4
20	3.89	7.74	8.26	9.25	8.73	0.10	0.18	0.23	0.23	0.27
30	6.55	9.62	10.40	12.16	10.96	0.14	0.21	0.27	0.34	0.29
40	8.68	12.82	14.36	18.56	15.45	0.16	0.26	0.29	0.39	0.34
50	13.40	17.04	18.10	21.11	18.06	0.26	0.38	0.45	0.56	0.52

Table 4
Arrhenius parameters for permeation, diffusion and heat of sorption

Parameter (kcal/mol)	NaAlg	M-1	M-2	M-3	M-4
E_p	6.75	5.41	5.06	4.29	4.48
E_D	5.96	4.43	3.91	2.80	3.12
ΔH_s	0.79	0.98	1.15	1.49	1.36

PV performance of the NaAlg membranes are listed in Table 5 for comparison purposes. As is seen from the table, permeation rates of NaAlg–Clt membranes are higher than those of other NaAlg based membranes without sacrifying the selectivity so much. However selectivity of pure NaA (4A) zeolite membranes is higher than NaAlg-Clt membranes.

4. Conclusions

The following conclusions can be drawn from the study on the separation of DMF–water mixtures using plain NaAlg and NaAlg–Clt composite membranes crosslinked with gluteraldehyde.

1. As the clinoptilolite content increased the permeation rate increased up to 15 wt % clinoptilolite whereas the separation factor increased after 15 wt. % clinoptilolite loading.
2. Increase in the operating temperature in the PV method increased the permeation rate whereas it decreased the separation factor for all the membranes.
3. The permeation rate decreased whereas the separation factor increased as the DMF content of the feed increased for both pristine NaAlg and NaAlg-Clt composite membranes.
4. The diffusion selectivity and the sorption selectivity were studied and compared to pristine NaAlg and NaAlg-Clt composite membranes. It was found that the sorption selectivity was the dominant factor for both membranes.
5. The zeolite-incorporated membranes exhibited lower activation energy compared to that of a plain membrane, implying that the permeants require less energy during the process. Activation energy was found as 6.750 and 4.290 kcal/mol for plain NaAlg membrane and NaAlg–Clt composite membrane (M-3), respectively.

Acknowledgements

We are grateful to Gazi University Research Fund for the support of this study.

Symbols

A — Membrane surface area, m^2
A_p — Permeation rate constant, kg/m^2h

Table 5
Comparasion of the performance of the NaAlg-based membranes

Membrane	Feed composition (%) (w/w)	Temperature (°C)	Permeation rate J (kg/m^2h)	Separation factor α	Separation method	Reference
NaAlg(Pure)	0–100	30–50	0.264–1.417	13.3–31.3	PV	28
NaAlg-g-NVP	0–100	30–50	0.963–2.046	5.6–15.4	PV	29
NaAlg/PVP	0–100	30–50	0.960–1.810	5.5–27.0	PV	30
Zeolite 4A (Pure NaA)	30	60	1.6	330	PV	27
NaAlg/Clt (M-3)	0–100	20–50	0.580–2.839	2.86–15.93	PV	This study

C_i — Concentration of water or DMF in the feed after the process, wt%
D_i — Diffusion coefficient, m^2s^{-1}
E_D — Diffusion activation energy, kcal/mol
E_p — Activation energy for permeation, kcal/mol
F_{DMF} — Mass fractions of DMF in the feed, wt%
F_W — Mass fractions of water in the feed, wt%
ΔH_s — Heat of sorption, kcal/mol
J — Permeation rate, kg/m^2h
J_i — Permeation flux of water or DMF, kg/m^2h
ł — Membrane thickness, μm
P_{DMF} — Mass fractions of DMF in the permeate, wt. %
P_W — Mass fractions of water in the permeate, wt. %
R — Gas constant
SD — Swelling degree, %
T — Temperature, K
T — Time of experiment, h
W — Mass of permeate, kg
W_D — Mass of the dried membrane, g
W_s — Mass of the swollen membrane in the feed solution, g
X_{DMF} — Mass fractions of DMF in the DMF solution (feed), wt %
X_W — Mass fractions of water in the DMF solution (feed), wt %
Y_{DMF} — Mass fractions of DMF in the membrane, wt %
Y_W — Mass fractions of water in the membrane, wt %

Greek

α — Separation factor
$\alpha_{dif.}$ — Diffusion selectivity
α_{sorp} — Sorption selectivity
δ — Effective membrane thickness, μm

References

[1] J.G. Wijmans and R.W. Baker, The solution-diffusion model: A review, J. Membr. Sci., 107 (1995) 1–21.

[2] X. Feng and R.Y.M. Huang, Liquid separation by membrane pervaporation: a review, Indust. Eng. Chem. Res., 36 (1997) 1048–1066.

[3] K.L. Pandey, C. Saxena and V. Dubey, Modification of poly (vinyl alcohol) membranes for pervaporative separation of benzene/cyclohexane mixture, J. Membr. Sci., 227 (2003) 173–182.

[4] N. Alghezawi, O. Şanlı, L. Aras and G. Asman, Separation of acetic acid–water mixtures through acrylonitrile grafted poly(vinyl alcohol) membranes by pervaporation, Chem. Eng. Processessing, 44 (2005) 51–58.

[5] H. Benguergoura, T. Aouak and S. Moulay, Use of pervaporation technique to monitor the oxidation of primary alcohols: n-propanol and n-butanol, J. Membr. Sci., 229 (2004) 107–116.

[6] J. Lu, Q. Nguyen, J. Zhou and Z-H. Ping, Poly(vinyl alcohol)/poly(vinyl pyrrolidone) interpenetrating polymer network: Synthesis and pervaporation properties, J. Appl. Polym. Sci., 89 (2003) 2808–2814.

[7] T.M. Aminabhavi, B.V.K. Naidu, S. Sridhar and R. Rangarajan, Pervaporation separation of water-isopropanol mixtures using polymeric membranes: Modeling and simulation aspects, J. Appl. Polym. Sci., 95 (2005) 1143–1153.

[8] U.S. Toti and T.M. Aminabhavi, Different viscosity grade sodium alginate and modifed sodium alginate membranes in pervaporation separation of water-acetic acid and water-isopropanol mixtures, J. Membr. Sci., 228 (2004) 199–208.

[9] B.V.K. Naidu, K.S.V. Krishna Rao and T.M. Aminabhavi, Pervaporation separation of water + 1,4-dioxane and water + tetrahydrafuran mixtures using sodium alginate and its blend membranes with hydroxyethylcellulose — A comperative study, J. Membr. Sci., 260 (2005) 131–141.

[10] S.T. Wilson, B.M. Lok, C.A. Messina, T.R. Cannon and E.M. Flenigan, Aluminophosphate molecular sieves: a new class of microporous crystalline inorganic solids, J. Amer. Chem. Soc., 104 (1982) 1146–1147.

[11] T. Armbruster, A. Galarnau, F. Di Renzo, F. Faujula and J. Vedrine, eds., Clinoptilolite-Heulandite: Applications and Basic Research. Studies in surface science and catalysis, Zeolites and mesoporous materials at the dawn of the 21 st century, Elsevier, Amsterdam, 2001, pp. 13–27.

[12] M.W. Ackley and R.T. Yang, Adsorption characteristics of high-exchange clinoptilolites, Indust. Eng. Res., 30 (1991) 2523–2530.

[13] G.V. Thitsishvili, T.G. Andronikashvili, G.M. Kirov and L.D. Filizova, Natural Zeolites, Ellis Horwood, Chichester, UK, 1992.

[14] M.J. Zamzow, B.R. Eichbaum, K.R. Sandgren and D.E. Shanks, Removal of heavy metals and other cations from wastewater using zeolites, Separ. Sci. Technol., 25(13–15) (1990) 1555–1569.

[15] M. Çulfaz and M. Yağız, Ion exchange properties of natural clinoptilolite: lead-sodium and cadmium-sodium equilibria, Separ. Purif. Technol., 37(2) (2004) 93–105.

[16] M.E. Gonzales, J. Mattush, W. Einicke and R. Wennrich, Sorption of natural solids for arsenic removal, Chem. Eng. J., 81 (2001) 187–195.

[17] M. Rozic, S.C. Stefanovic, S. Kurajica, V. Vancina and E. Hodzic, Ammonium nitrogen removal from water by treatment with clays and zeolites, Wat. Res., 34(14) (2000) 3675–3681.

[18] R.S. Bauman, Applications of surfactant-modified zeolites to enviromental remediation, Micropor. Mesopor. Mater., 61 (2003) 43–56.

[19] S.D. Bhat and T.M. Aminabhavi, Novel sodium alginate composite membranes incorporated with SBA-15 molecular sieves for the pervaporation dehydration of aqueous mixtures of isopropanol and 1,4-dioxane at 30°C, Micropor. Mesopor. Mater., 91 (2006) 206–214.

[20] S.D. Bhat and T.M. Aminabhavi, Novel sodium alginate–Na^+ MMT hybrid composite membranes for pervaporation dehydration of isopropanol, 1,4-dioxane and tetrahydrafuran, Separ. Purif. Technol., 51 (2006) 85–94.

[21] S.G. Adoor, L.S. Manjeshwar, S.D. Bhat and T.M. Aminabhavi, Aluminum-rich zeolite beta incorporated sodium alginate mixed matrix membranes for pervaporation dehydration and esterification of ethanol and acetic acid, J. Membr. Sci., 318 (2008) 233–246.

[22] S.G. Adoor, B. Prathab, L.S. Manjeshwar and T.M. Aminabhavi, Mixed matrix membranes of sodium alginate and poly(vinyl alcohol) for pervaporation dehydration of isopropanol at different temperatures, Polymer, 48 (2007) 5417–5430.

[23] S.D. Bhat and T.M. Aminabhavi, Pervaporation-aided dehydration and esterification of acetic acid with ethanol using 4A zeolite-filled cross-linked sodium alginate-mixed matrix membranes, J. Appl. Polym. Sci., 113 (2009) 157–168.

[24] X. Chen, H. Yang, Z. Gu and Z. Shao, Preparation and characterization of H-Y zeolite-filled chitosan membranes for pervaporation separation, J. Appl. Polym. Sci., 79 (2001) 2101–2109.

[25] M.Y. Kariduraganavar, A.A. Kittur and S.S. Kulkarni, Development of novel pervaporation membranes for the separation of water–isopropanol mixtures using sodium alginate and zeolites, J. of Membrane Science, 238 (2004) 165-175.

[26] S. Das, A.K. Banthia and B. Adhikari, Pervaporation separation of DMF from water using a crosslinked polyurethane urea-PMMA IPN membrane, Desalination, 197 (2005) 106-116.

[27] D. Shah, K. Kissick, A. Ghorpade, R. Hannah and D. Bhattacha-

ryya, Pervaporation of alcohol–water and dimethylformamide-water mixtures using hydrophilic zeolite NaA membranes: Mechanisms and experimental results, J. Membr. Sci., 179 (2000) 185–205.

[28] E.K. Solak and O. Şanlı, Separation characteristics of dimethylformamide/water mixtures through alginate membranes by pervaporation, vapor permeation and vapor permeation with temperature difference methods, Separ. Sci. Technol., 41 (2006) 627–646.

[29] E.K. Solak and O. Şanlı, Separation characteristics of dimethylformamide/water mixtures using sodium alginate-g-N–vinyl-2-pyrrolidone membranes by pervaporation method, Chem. Eng. Proc., 47 (2008) 633–641.

[30] E.K. Solak, O. Şanlı, G. Asman and P. Çamurlu, Sorption, diffusion, and pervaporation characteristics of dimethylformamide/water mixtures using sodium alginate-poly(vinyl pyrrolidone) blend membranes, Vacuum, 82 (2008) 579–587.

[31] B.V.K. Naidu, S.D. Bhat, M. Sairam, A.C. Wali, D.P. Sawant, S.B. Halligudi, N.N. Mallikarjuna and T.M. Aminabhavi, Comparison of the pervaporation separation of a water-acetonitrile mixture with zeolite-filled-polyaniline semi-interpenetrating polymer network membranes, J. Appl. Polym. Sci., 96 (2005) 1968–1978.

[32] B.P. Mallikarjunagouda and T.M. Aminabhavi, Pervaporation separation of toluene/alcohol mixtures using silicalite zeolite embedded chitosan mixed matrix membranes, Separ. Purif. Technol., 62 (2008) 128–136.

[33] N. Işıklan and O. Şanlı, Separation characteristics of acetic acid–water mixtures by pervaporation using poly(vinyl alcohol) membranes with malic acid, Chem. Eng. Proc., 44 (2005) 1019–1027.

[34] M.Y. Kariduraganavar, S.S. Kulkarni and A.A. Kittur, Pervaporation separation of water-acetic acid mixtures through poly(vinyl alcohol)-silicone based hybrid membranes, J. Membr. Sci., 246 (2005) 83–93.

[35] R.S. Veerapur, M.B. Patil, K.B. Gudasi and T.M. Aminabhavi, Poly(vinyl alcohol)-zeolite T mixed matrix composite membranes for pervaporation separation of water + 1,4-dioxane mixtures, Separ. Purif. Technol., 58 (2008) 377–385.

[36] S.D. Bhat, N.N. Mallikarjuna and T.M. Aminabhavi, Microporous alumina-phosphat (AlPO4-5) molecular sieve-loaded novel sodium alginate composite membranes for pervaporation dehydration of aqueous-organic mixtures near their azeotropic compositions, J. Membr. Sci., 282 (2006) 473–483.

[37] K. Gedik and İ. İmamoğlu, Removal of cadmium from aqueous solutions using clinoptilolite: Influence of pretreatment and regeneration, J. Hazard. Mater., 155 (2008) 385–392.

[38] J.E. Elshof, C R. Abadal, J. Sekulic, S.R. Chowdhury and D.H.A. Blank, Transport mechanisms of water and organic solvents through microporous silica in the pervaporation of binary liquids, Micropor. Mesopor. Mater., 65 (2003) 197–208.

[39] Z. Gao, Y. Yue and W. Li, Application of zeolite-filled pervaporation membrane, Zeolites, 16 (1996) 70–74.

[40] U.S. Toti, M.Y. Kariduraganavar, K.S. Soppimath and T.M. Aminabhavi, Sorption, diffusion and pervaporation separation of water-acetic acid mixtures through the blend membranes of sodium alginate and guar gum-grafted-polyacrylamide, J. Appl. Polym. Sci., 83 (2002) 259–272.

[41] M.D. Kurkuri and T.M. Aminabhavi, Polyacrylonitrile-g-poly(vinyl alcohol) membranes for the pervaporation separation of dimethylformamide and water mixtures, J. Appl. Polym. Sci., 91 (2002) 4091–4097.

[42] S.S. Kulkarni, S.M. Tambe, A.A. Kittur and M.Y. Kariduraganavar, Preparation novel of composite membranes for the pervaporation separation of water-acetic acid mixtures, J. Membr. Sci., 285 (2006) 420–431.