Desalination and Water Treatment
www.deswater.com

51 (2013) 637–643
January

1944-3994/1944-3986 © 2013 Desalination Publications. All rights reserved
doi: 10.1080/19443994.2012.714582

Taylor & Francis
Taylor & Francis Group

Pervaporation of ethanol/water mixtures by zeolite filled sodium alginate membrane

Filiz Ugur Nigiz*, Nilufer Durmaz Hilmioglu

Department of Chemical Engineering, University of Kocaeli, 41380 Kocaeli, Turkey
Tel. +90 (262) 3033525; email: filiz.ugur@kocaeli.edu.tr

Received 27 February 2012; Accepted 18 July 2012

ABSTRACT

For a few decades, pervaporation (PV) has been considered as an energy saving, environmentally friendly and cost effective separation technique which separates close boiling point, azeotropic and thermally sensitive components. It is clearly well known that the PV has significant advantages in azeotropic mixtures separation where distillation needs an entrain solvent which must be removed in the following steps. The most important part of PV is the selection of the appropriate membrane. The inadequate selectivity and low flux values limited the expansion of this process. It is always assumed that efficient pervaporation means a membrane with good permeability and selectivity. In this work, sodium alginate (NaAlg) was used as the membrane material. Pristine NaAlg and zeolite 4A filled NaAlg mixed matrix membranes (MMMs) have been prepared by solution casting evaporation and cross-linking method. Phosphoric acid (PA) was used as the cross-linking agent. The morphologies of the membranes were studied using scanning electron microscopy (SEM), Thermogravimetric analysis (TGA) and Fourier transform infrared spectrophotometer (FTIR). Pervaporation performance of all membranes have been tested for dehydration of aqueous ethanol feed mixtures at 25˚C. The effects of zeolite loading and feed composition have been investigated. With the adding of zeolite to the polymer, flux values increased. However, selectivity values decrease unexpectedly because of the interfacial voids which were formed between zeolite and the polymer. With increasing water content in the feed mixture, flux increased but selectivity decreased as expected.

Keywords: Pervaporation; Sodium alginate; Zeolite 4A

1. Introduction

Pervaporation is an energy intensive membrane technology which has great potential to separate close boiling point, azeotropic and thermally sensitive compounds [1–3]. For several years, it has been promising to be an alternative cost effective system for the treatment of volatile organic compounds. It is well known that over 200 plants established for alcohol dehydration processes [2–6]. PV is available in the following areas; dehydration of organic solvents (acid, esters, alcohols), removal of dilute organic components from aqueous stream (aroma recovery, VOC recovery, biofuel separation) and organic–organic mixture separation [1,7–9]. In PV, the driving force is the concentration gradient which is maintained by

---

*Corresponding author.

Presented at the International Conference on Desalination for the Environment, Clean Water and Energy, European Desalination Society, 23–26 April 2012, Barcelona, Spain

vacuum or purge gases [10,11]. Vacuum PV which is called as standard PV has been shown in Fig. 1.

A vacuum PV system (Fig. 1) simply consists of a feed tank, membrane cell, vacuum and feed pump and cold traps. The mixture which will be separated is kept at a desired temperature. It is circulated to the membrane cell and contacts with non-porous membrane at the upstream side of it. One of the compounds is preferentially removed from the mixture due to the affinity of the membrane. The compound which is selected by the membrane diffuses through the membrane. The diffusion character of the membrane depends on the concentration gradient and diffusion rates difference between components. Vacuum pressure which is provided by the pump, maintains the driving force. The downstream pressure which is held below the saturation pressure of the selected compound leads to a phase change during the transport. The vapor phase which is called as the permeate is obtained as the liquid phase into the traps. The retentate is recycled to the feed tank.

The pervaporation efficiency is not only based on the operational variables (temperature, pressure, etc.) but also depends on the membrane selectivity and productivity. The physicochemical structure of the membrane is directly related to the performance of PV. It is controlled by the physical structure of the membrane, polarity and physicochemical properties of the mixture, component-membrane and component-component interaction, membrane affinity, and the hydrogen bonding ability [1,12].

Separation via a non-porous membrane is mainly determined and explained by the solution-diffusion model [1,12,13]. Sorption depends on the hydrogen bonding interest of water in the active channels and the diffusion depends on structural parameters such as channel distribution and diameters. During the membrane separation process, the solvent which interacts inside changes the physical and chemical stability of the membrane material. It is important to the select an appropriate membrane in order to overcome stability problem and to increase membrane flux and selectivity [13].

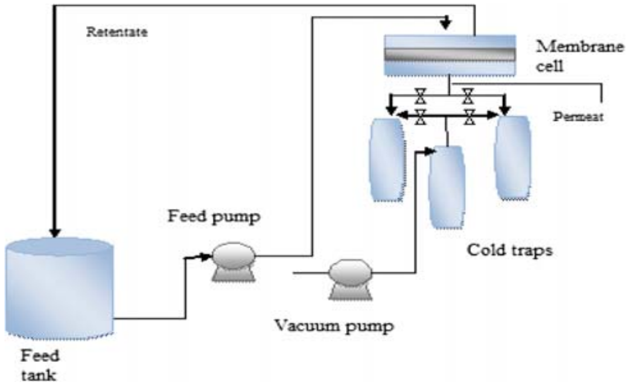


Fig. 1. A basic vacuum PV system.

In PV, polymers are often used as membrane materials due to the cheapness and modification ability. However, the organic chain structure could be easily destroyed by temperature or the chemical properties of the mixtures during the long term operation time [14,15]. Inorganic membranes are mechanically, thermally and chemically durable with respect to the polymeric material but these materials (zeolite, clay) are brittle thereby it is hard to product them as membrane form [12,15–17]. Inorganic filled polymeric membrane, (mixed matrix membrane, MMM) has been combined with the positive sides of polymeric and inorganic membranes. It has good thermal and chemical stability and mechanical strength and it is easy to operate them as a PV membrane [12,18].

Sodium alginate is a kind of polysaccharide which is found in brown seaweed. It consists of anionic and cationic organic groups hence it exhibits high affinity to water molecules. Recently NaAlg has been used as membrane material. Because of the high swelling character of NaAlg, especially in the case of alcohol dehydration process, it needs some modification such as cross-linking, blending, grafting and adding some inorganic filler [19–23].

In this study, pristine and 4A zeolite filled MMM have been prepared. All membranes have been cross-linked with phosphoric acid. Pervaporation experiments have been carried out at 25°C to separate water from aqueous alcohol feed mixtures. Effects of feed concentration and zeolite loading have been evaluated as a function of flux and selectivity. Membrane morphologies have been studied using scanning electron microscopy (SEM), thermal stabilities of the filled and unfilled membranes have been investigated using the thermogravimetric analysis (TGA) and the characteristic chemical bonds of cross-linked and uncross-linked membranes have been determined by the Fourier transform infrared spectrophotometer (FTIR).

2. Experimental

2.1. Materials

Sodium alginate, was purchased from Aldrich Chemicals, 99.5% purity ethanol, isopropanol and PA were purchased from Merck Chemicals. Deionized water was supplied from the laboratory.

2.2. Membrane preparation

For preparation of pristine and zeolite filled membranes following steps were applied: NaAlg (1.5 g) was dissolved in 40 ml water. The desired amount of zeolite (wt. 5, 7, 10% with respect to pure polymer weight) was added to polymer-water solution for the loaded membranes. All solutions were stirred for 24 h, poured onto glass petri dishes and dried at room temperature. After the membranes have formed, they were peeled off from glass petri dishes and cross-linked for 10 h in the water–isopropanol (20:80 vol.%) and PA (vol. 3% of mixture) bath. Cross-linking procedure was applied separately to all membranes. The cross-linked membranes were taken from the bath, washed with deionized water and then they were dried again for 1 h in vacuum oven at 40˚C to remove the solvent [21,24].

2.3. Pervaporation procedure

Experiments were carried out at room temperature. At downstream side vacuum was applied and the pressure was measured as 40 mbar. Membrane cell is made from PTFE (Teflon) that has 28 cm^2 effective membrane area and the volume capacity of cell is 500 ml. The ethanol–water mixture was fed into the cell continuously. The permeated mixture was condensed in liquid nitrogen traps. Two traps were operated, one of them was replaced with another after 1 h and the sample was taken from the operated ones. The permeate mixture was measured and the samples were analyzed using a Refractometer (Krüss) in order to obtain the refractive index of the binary mixtures [25]. The compositions of the permeate samples were determined by the refractive index.

The flux (J) was calculated from the weight of the permeate (W_p), the effective area of membrane (A) and the experiment time period (t) as seen in Eq. (1).

$$J = W_p / A \cdot t \tag{1}$$

The water selectivity (α) values of the samples were calculated in following equation:

$$\alpha = (P_w/P_e)/(F_w/F_e) \tag{2}$$

P_w and F_w are the weight % of water in the permeate and the feed, respectively. P_e and F_e are the weight % of ethanol in the permeate and feed mixtures, respectively [26,27].

2.3. Membrane characterization

2.3.1. Scanning electron microscope (SEM)

SEM of the membranes was taken with a JEOL JSM-6,335 F “field emission scanning electron” microscope. The membrane samples were broken in liquid nitrogen and their surface was covered with gold.

2.3.2. Thermogravimetric analysis (TGA)

The thermal stability of the membranes was determined by using Perkin–Elmer PYRIS 1 TGA. The samples were heated, under nitrogen atmosphere, up to 150˚C and kept at this temperature for half an hour to the remove moisture completely. The samples were cooled down to 80˚C and then re-heated up to 900˚C with a heating rate of 10˚C/min.

2.3.3. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra were recorded for membranes and heteropoly acid salt using Perkin–Elmer Pyris 1 FTIR spectrophotometer. Membrane samples were prepared by making KBr pellets.

3. Results and discussion

3.1. SEM studies

Fig. 2a and b shows the SEM micrograph of 10 wt.% zeolite filled NaAlg membrane. Interfacial voids between the polymer and zeolite are clearly seen in figures.

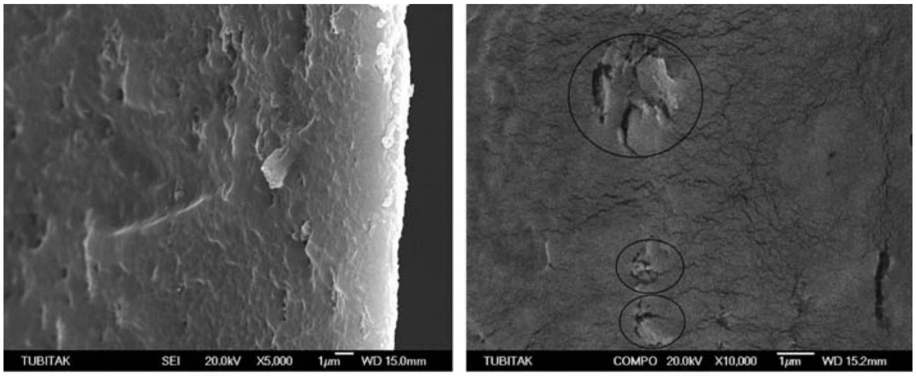
3.2. TGA studies

The TGA curves of pristine and loaded NaAlg membranes are shown in Fig. 3. It is seen that the weight loss occurs above 180˚C for all membranes. M curve shows that the pristine membrane has a second decomposition point around 440˚C.

Fig. 3 indicates that the incorporation of 4A zeolite into the NaAlg membrane improves the thermal stability since no decomposition occurs in the curves of M5, M7, M10. According to this observation, it is clearly predicted that the use of 4A filled NaAlg membranes is applicable at high temperatures in PV experiments.

3.3. FTIR studies

The FTIR spectra of the cross-linked and uncross-linked NaAlg membrane have been shown in Fig. 4.



(a) (b)

Fig. 2. SEM micrograph 10 wt.% zeolite filled NaAlg membranes: (a) X5.000 and (b) X10.000.

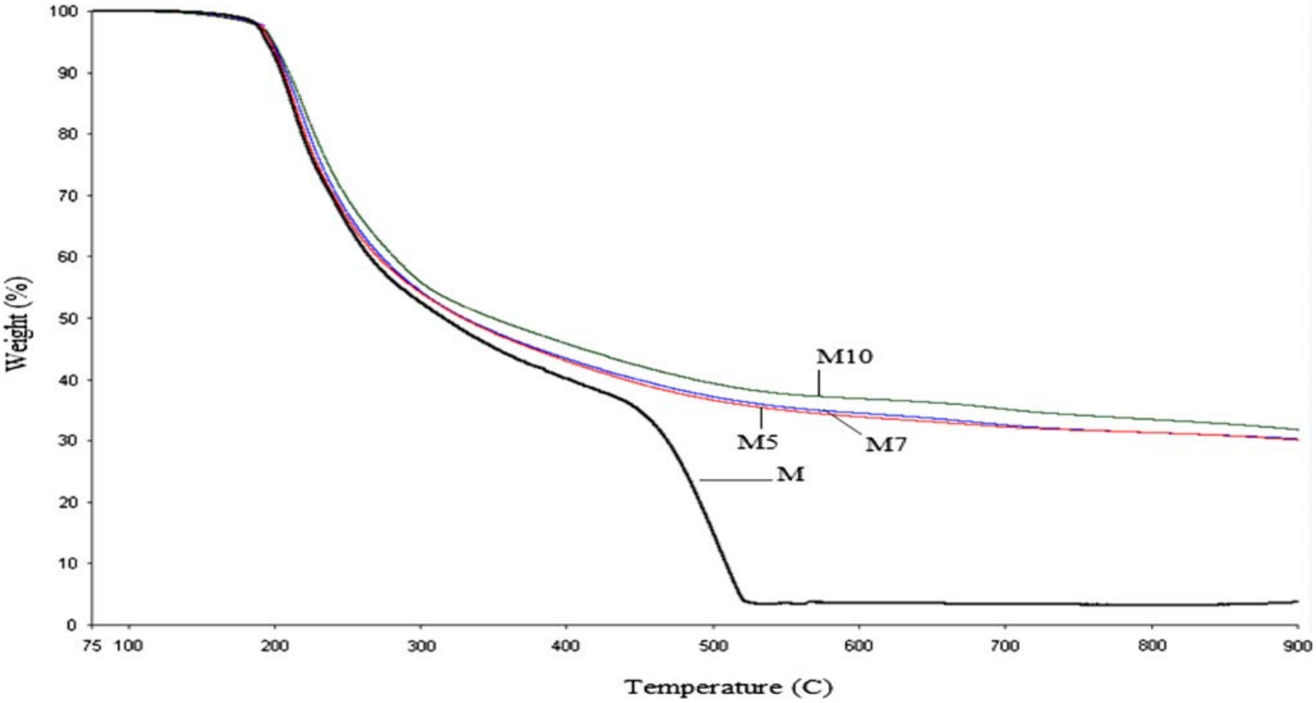


Fig. 3. TGA curves of membranes (M: Pristine, M5: 5 wt.% 4A, M7: 7 wt.% 4A, M10: 10 wt.% 4A filled NaAlg).

Characteristic peaks of the hydroxyl group in NaAlg were seen around 3,450–3,430 cm^{-1}. The prominent peaks observed around 1,600–1,650 and 1,400–1,420 cm^{-1} correspond to asymmetric and symmetric stretching of carboxyl groups of NaAlg.

The peaks which were observed around 1,720 cm^{-1} may be assigned to new –OC–O–P bonds which had been formed between hydroxyl groups of PA and acetate groups of NaAlg [21].

3.4. Pervaporation results

3.4.1. Effect of feed concentration

Figs. 5 and 6 show the effect of water concentration on flux and selectivity.

As seen in Fig. 5, flux increases with increasing water concentration in the feed mixture. Carboxyl groups of NaAlg make strong hydrogen bond with water therefore the nature of NaAlg allows the water

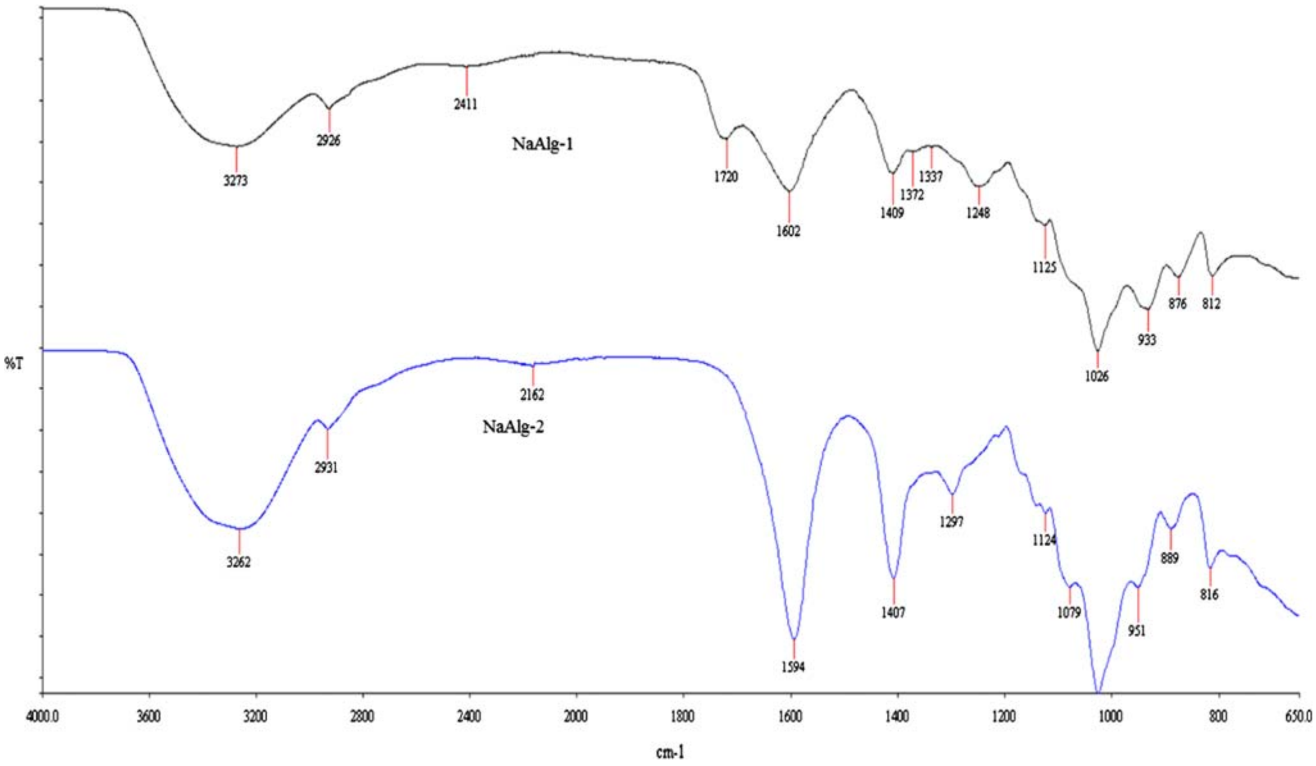


Fig. 4. FTIR spectra of cross-linked (NaAlg-1) and uncross-linked (NaAlg-2) membranes.

transport through the membrane. However this ability gives a high swelling character to the membrane. Separation via the PV particularly depends on the difference in the diffusion rates between the components. For the molecular level separation, the kinetic diameters of components are important. Water molecules have smaller diameter than ethanol molecules hence the diffusion rates of water are higher than that of the ethanol molecule into a non-porous polymeric material. Swollen channels of the polymer prevent this selective diffusion character of the membrane and allow the transportation of ethanol molecules through the membrane easily. Therefore selectivity of the

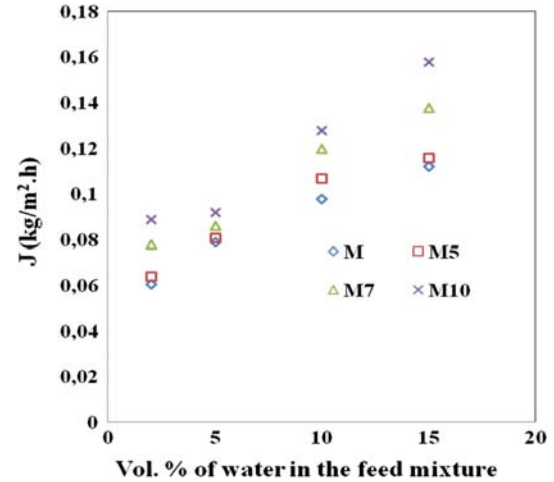


Fig. 5. Effect of water content on flux (M: Pristine, M5: 5 wt.% 4A, M7: 7 wt.% 4A, M10: 10 wt.% 4A filled NaAlg).

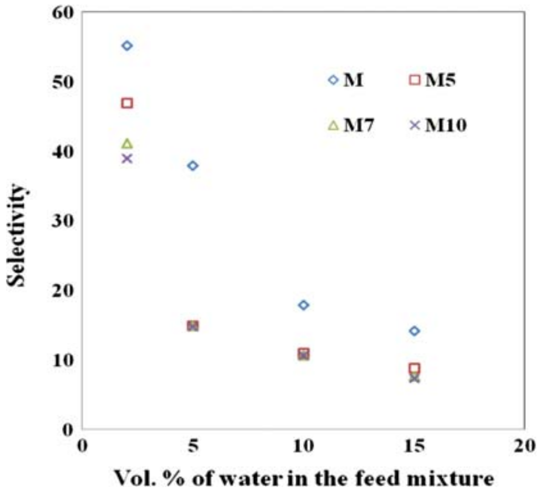


Fig. 6. Effect of water content on selectivity (M: Pristine, M5: 5 wt.% 4A, M7: 7 wt.% 4A, M10: 10 wt.% 4A filled NaAlg).

membrane decreases with increasing water content in the feed mixture as seen in Fig. 6 [25,26].

3.4.2. Effect of zeolite loading

Fig. 7 shows the flux values which were affected positively by the zeolite filling due to the hydrophilic nature of 4A. Na form of hydrophilic zeolite has strong water retention capability. Herewith this capacity, flux values increased with increasing amounts of zeolites [16,21,22].

It was mostly seen in literature that incorporation of zeolite into the polymer matrix improved the selectivity values. Contrary to the literature survey, in this study, selectivity values were negatively affected by the zeolite loading as seen in Fig. 8. The reason for this case would be explained with the inorganic–organic interfacial adhesion problem. Particularly, during the evaporation of zeolite–polymer solution a huge stress would occur between the contact areas of the polymer–zeolite and non-selective voids would be formed [28–31]. In this study, interfacial voids were clearly seen in cross-sectional SEM micrograph as seen in Fig. 2a and b.

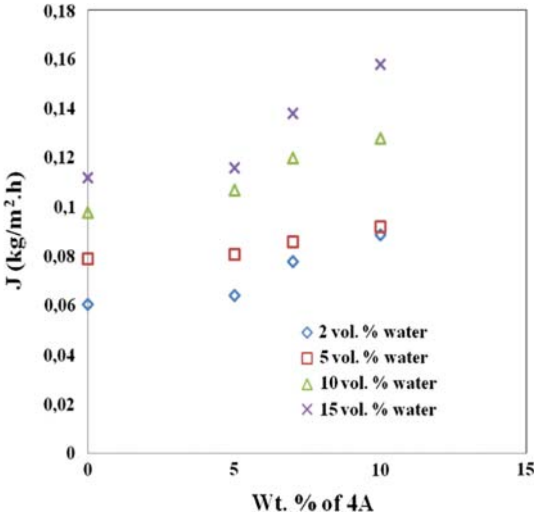


Fig. 7. Effect of zeolite loading on flux.

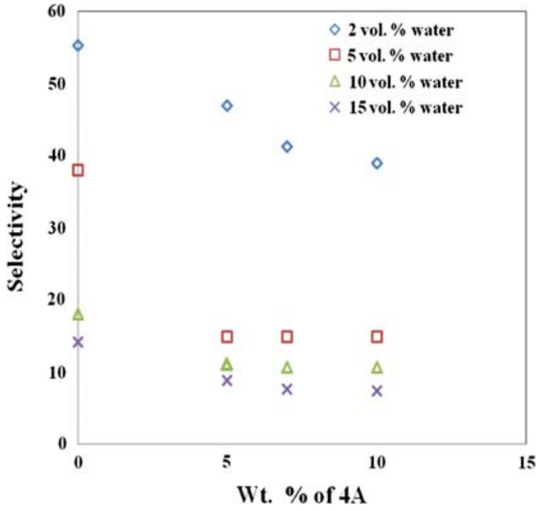


Fig. 8. Effect of zeolite loading on selectivity.

Additionally, the selectivity reduction may be explained by the effect of the ordering the cross-linking and zeolite filling procedures. This would happen because of the cross-linking procedure which was applied after zeolite loading. Activation of cross-linking reaction between the hydroxyl groups of PA and the acetate groups of NaAlg might be blocked by the zeolite particles. Hence the selectivity values decreased from 55 to 40 for pristine membrane near the azeotropic point of ethanol–water mixtures.

4. Conclusion

In this study, it was concluded that the increasing of water content in the feed mixture enchanced the flux values of all membranes. However, selectivity values decreased with increasing of water concentration. Addition of zeolite into the NaAlg matrix improved the flux values. Because of the interfacial voids formed, selectivity values were negatively affected. The pristine membrane gave better selectivity results but with the adding of zeolite the selectivity values decreased.

The present study clearly shows the availability of sodium alginate membranes in PV process. However it needs some improvements to increase the performance of the system. Pervaporation offers high efficiency, sensitivity, environmental friendly separation when it is compared to other processes. Production of the membrane which has high chemical, thermal and mechanical stability will carry more advanced level this technology.

References

[1] X. Feng, R.Y.M. Huang, Liquid separation by membrane pervaporation: A review, Ind. Eng. Chem. Res. 36 (1997) 1048–1066.
[2] K.V. Ramana, K. Ganesan, L. Singh, Pervaporation performance of a composite bacterial cellulose membrane: dehydration of binary aqueous–organic mixtures, World J. Microbiol. Biotechnol. 22 (2006) 547–552.
[3] C.S. Slater, Membrane technology for energy conservation in traditional and emerging engineering fields, IEEE 4 (1989) 1731–1736.
[4] M. Roza, E. Maus, Industrial experience with hybrid distillation–pervaporation or vapor permeation applications, IChemE (2006) 619–627.

[5] F. Lipnizki, R.W. Field, P.K. Ten, Pervaporation-based hybrid process: a review of process design, applications and economics, J. Membr. Sci. 153 (1999) 183–193.

[6] V.V. Hoof, L.V. Abeele, A. Buekenhoudt, C. Dotremont, R. Leysen, Economic comparison between azeotropic distillation and different hybrid systems combining distillation with pervaporation for the dehydration of isopropanol, Sep. Purif. Technol. 37 (2004) 33–49.

[7] Q. Li, P. Yu, T. Zhu, L. Zhang, Q. Li, Y. Luo, Pervaporation performance of crosslinked PVA and chitosan membranes for dehydration of caprolactam solution, Desalin. Water Treat. 16 (2010) 304–312.

[8] J. Xu, A. Ito, Removal of VOC from water by pervaporation with a hollow-fiber silicone rubber membrane module, Desalin. Water Treat. 17 (2010) 135–142.

[9] Y. Huang, J. Fu, Y. Zhou, X. Huang, X. Tang, Pervaporation performance of trifluoroethoxy substituting polyphosphazene membrane for different organic compounds aqueous solutions, Desalin. Water Treat. 24 (2010) 210–219.

[10] C. Brazinha, V.D. Alves, R.M.C. Viegas, J.G. Crespo, Aroma recovery by integration of sweeping gas pervaporation and liquid absorption in membrane contactors, Sep. Purif. Technol. 70 (2009) 103–111.

[11] C. Vallieres, E. Favre, Vacuum versus sweeping gas operation for binary mixtures separation by dense membrane processes, J. Membr. Sci. 244 (2004) 17–23.

[12] P.D. Chapman, T. Oliveira, A.G. Livingston, K. Li, Membranes for the dehydration of solvents by pervaporation, J. Membr. Sci. 318 (2008) 5–37.

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

[14] S.L. Wee, C.T. Tye, S. Bhatia, Membrane separation process—Pervaporation through zeolite membrane, Sep. Purif. Technol. 63 (2008) 500–516.

[15] P. Shao, R.Y.M. Huang, Polymeric membrane pervaporation, J. Membr. Sci. 287 (2007) 162–179.

[16] T.C. Bowen, R.D. Noble, J.L. Falconer, Fundamentals and applications of pervaporation through zeolite membranes, J. Membr. Sci. 245 (2004) 1–33.

[17] J. Caro, M. Noack, Zeolite membranes—Recent developments and progress, Micropor. Mesopor. Mater. 115 (2008) 215–233.

[18] T.S. Chung, L.Y. Jiang, Y. Li, S. Kulprathipanja, Mixed matrix membranes (MMMs) comprising organic polymers with dispersed inorganic fillers for gas separation, Prog. Polym. Sci. 32 (2007) 483–507.

[19] S. Kahya, E.K. Solak, O. Şanlı, Sodium alginate/poly(vinyl alcohol) alloy membranes for the pervaporation, vapour permeation and vapour permeation with temperature difference separation of dimethylformamide/water mixtures: A comparative study, Vacuum 84 (2010) 1092–1102.

[20] S. Kalyani, B. Smitha, S. Sridhar, A. Krishnaiah, Blend membranes of sodium alginate and hydroxyethylcellulose for pervaporation-based enrichment of t-butyl alcohol, Carbohydr. Polym. 64 (2006) 425–432.

[21] S. Kalyani, B. Smitha, S. Sridhar, A. Krishnaiah, Pervaporation separation of ethanol–water mixtures through sodium alginate membranes, Desalination 229 (2008) 68–81.

[22] S.D. Bhat, T.M. Aminabhavi, Pervaporation separation using sodium alginate and its modified membranes—a review, Sep. Purif. Rev. 36 (2007) 203–229.

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

[24] S.D. Bhat, 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.

[25] H. Dogan, N.D. Hilmioglu, Chitosan coated zeolite filled regenerated cellulose membrane for dehydration of ethylene glycol/water mixtures by pervaporation, Desalination 258 (2010) 120–127.

[26] S.D. Bhat, B.V.K. Naidu, G.V. Shanbhag, S.B. Halligudi, M. Sairamand, T.M. Aminabhavi, Mesoporous molecular sieve (MCM-41)-filled sodium alginate hybrid nanocomposite membranes for pervaporation separation of water–isopropanol mixtures, Sep. Purif. Technol. 49 (2006) 56–63.

[27] Suzana Pereira Nunes, Klaus-Viktor Peinemann, Membrane Technology in the Chemical Industry, second ed., Wiley-VCH, Weinheim, 2006, pp. 171–184.

[28] C.K. Yeom, K.H. Lee, Characterization of sodium alginate and poly (vinyl alcohol) blend membranes in pervaporation separation, J. Appl. Polym. Sci. 67 (1998) 949–959.

[29] C.K. Yeom, K.H. Lee, Characterization of sodium alginate membrane crosslinked with glutaraldehyde in pervaporation separation, J. Appl. Polym. Sci. 67 (1998) 209–219.

[30] R. Mahajan, W.J. Koros, Factors controlling successful formation of mixed-matrix gas separation materials, Ind. Eng. Chem. Res. 39 (2000) 2692–2696.

[31] R. Mahajan, R. Burns, M. Schaeffer, W. Koros, Challenges in forming successful mixed matrix membranes with rigid polymeric materials, J. Appl. Polym. Sci. 86 (2002) 881–890.