

PERVAPORATION SEPARATION OF ETHANOL-WATER MIXTURES BY ZEOLITE-FILLED POLYMERIC MEMBRANES

ATILLA EVCIN, OSMAN TUTKUN*

*University of Afyon Kocatepe, Department of Materials Science and Engineering, 03200, Afyon, Turkey***University of Sakarya, Department of Chemistry, 54100 Adapazari, Turkey*

E-mail: evcin@aku.edu.tr

Submitted April 14, 2009; accepted July 10, 2009

Keywords: Pervaporation, PDMS, Zeolite-filled, Alcohol/water mixtures, VOCs

The incorporation of zeolites into rubbery polymers has been shown experimentally to enhance both the permeability and selectivity in pervaporative separation of organic compounds from water. Pervaporation is a promising membrane technique for separation of volatile organic compounds (VOCs) /water mixtures. Polydimethylsiloxane (PDMS) is widely used in different areas as an elastomer or a sealant. In this study, homogeneous PDMS membranes and mixed membranes were prepared by solution casting technique by introducing hydrophilic or hydrophobic zeolites into the polymer matrix. The prepared membranes were tested in a laboratory scale pervaporation experimental set-up. The effects of experimental parameters such as the type and composition of zeolites on permeation flux and separation factors were investigated. When tested on ethanol/water mixtures, the zeolite-filled membrane of hydrophobic origin was found to give much higher selectivity for ethanol compared to that of hydrophilic nature such as the 3A type.

INTRODUCTION

Pervaporation has a great potential for separations where the more conventional techniques, such as distillation, are not possible to be realized or too expensive. This includes the separation of azeotropes, of mixtures of components with only a slight difference in volatility, and of components that are pressure or temperature sensitive. These separations occur in the (petro) chemical and as well as the food industry and in waste water treatment [1-4]. For dehydration purposes, hydrophilic membranes are used. Up to now, mostly polymeric membranes have been used on an industrial scale. The active layer of the polymeric membranes consists in most cases of polyvinyl alcohol (PVA), although other materials are also reported, such as polyacrylonitrile (PAN), polyetherimide (PEI). Since earliest attempts to combine zeolites with variety of organic polymers, there have been problems concerning adhesion at the zeolite-polymer interface, but the use of polysiloxanes has made it possible to solve these problems [5-6]. Zeolites have unique properties that are very attractive features for a large number of industrial applications. In particular, the acid sites due to the presence of aluminium, the high specific surface and the well-defined pore dimensions have imposed them as selective catalyst materials. The crystalline nature of zeolites offers the opportunity to obtain membranes with a regular 3D network of micropores at the molecular scale and they are therefore able of separating mixtures of substances on the basis

of differences in the molecular size and shape [7], such as, for example, isomers [8], compounds with similar molecular weight and also azeotropic mixtures [9]. The advantage of using a zeolite membrane is that it can potentially separate molecules in a continuous way. For example, modules of hydrophilic zeolite A (LTA) membranes were recently commercialised for alcohol dehydration by pervaporation [10]. The advantage of using a zeolite membrane is that it can potentially separate molecules in a continuous way. Hennepe et al. [11] studied the pervaporation of aqueous ethanol solutions through silicone membranes filled with the hydrophilic (3A, 4A, 5A and 13X), as well as hydrophobic zeolite (silicalite) and established that the flux and selectivity of used membranes can be considerably influenced by the introduction of hydrophobic zeolite.

EXPERIMENTAL

Materials

Two zeolites are studied. The hydrophilic zeolites 3A was purchased from Fluka and had an average crystal size of 2.5 μm . The pore diameter is 0.42 nm and the Si to Al ratio is 1. The hydrophobic zeolite silicalite-1 was supplied by Union Carbide and had an average pore dimension of 0.54 nm in one direction and the ratio of Si to Al was infinite. The zeolites were activated by heat treatment to remove residual contaminants or in the case of silicalite-1, to remove the template compound.

Silicalite-1 was activated at 600 °C and zeolite 3 A at 400 °C for 6 and 4 hours respectively and they were kept in a desiccator at room temperature. A bicomponent room temperature vulcanization (RTV) system was used to obtain membranes based on polysiloxanes matrices: RTV-664A and RTV-664B (General Electric Corp., USA), being used as provided. Component A consisted of polydimethyl siloxanes endcapped with vinyl groups and component B consisted of polysiloxanes which contained a few silylhydro groups per molecule so that it acted as a cross-linker, and platinum which acted as a catalyst for the hydrosilylation reaction [6].

Membrane preparation

A zeolite-filled PDMS membranes were obtained from 60 % isooctane solution of mixture of precursors: RTV-664A and RTV-664B (10:1 (w/w)), and various quantities of desired zeolites (10, 20, 30, 40, 50 and 60 wt.% in a siloxane-zeolite mixture), according the general experimental procedure reported elsewhere [11, 12]. Homogeneous mixtures were placed on a clean and smooth glass plate using a doctor's blade and casting solution was allowed to be evaporated at 70°C in an oven for 12 hours and cooling to room temperature, the obtained elastomer material was immersed in a water-ethanol bath and removed from the glass base. The elastomer films of desired thicknesses, such as ranged from 80 to 150 µm, were obtained by the adjustment of gap in the blade.

Pervaporation measurements

The experiments were carried out in a laboratory batch apparatus. The pervaporation apparatus, as shown Figure 1, was composed of a glass cell (a) in which the polymeric membrane was placed on a gauzed stainless steel metal support (e), and had cold traps (j) to condense the permeate, a mixer (b), vigorous stirring of the bulk mixture to avoid polarisation effects on the outside of the membrane. The cell was kept at constant temperature of 20 ±1°C by a variac controlled heating tape (c). The pressure at the permeate side was maintained below 1 mbar using a high vacuum pump (k) (Vacubrand, Germany). Four hours were mixed and then samples were taken in known periods of time. The samples were collected in the traps, which are immersed in liquid nitrogen, running periodically. The samples were analyzed by measuring refractive indexes of ethanol-water mixtures using an Abbe refractometer.

The permeation flux of water or ethanol (J_i , [kg/m² h]) was calculated from Equation (1) [11] :

$$J_i = \frac{W_i}{At} \left(\frac{d}{100} \right) \quad (1)$$

where W_i is the permeate mass (kg), d the membrane thickness (µm), A the effective membrane area (m²), and t the duration of pervaporation (h). As can be seen from Equation (1), the flux are normalized to a membrane thickness of 100 µm.

The membrane thickness ranged from 50 to 70 µm.

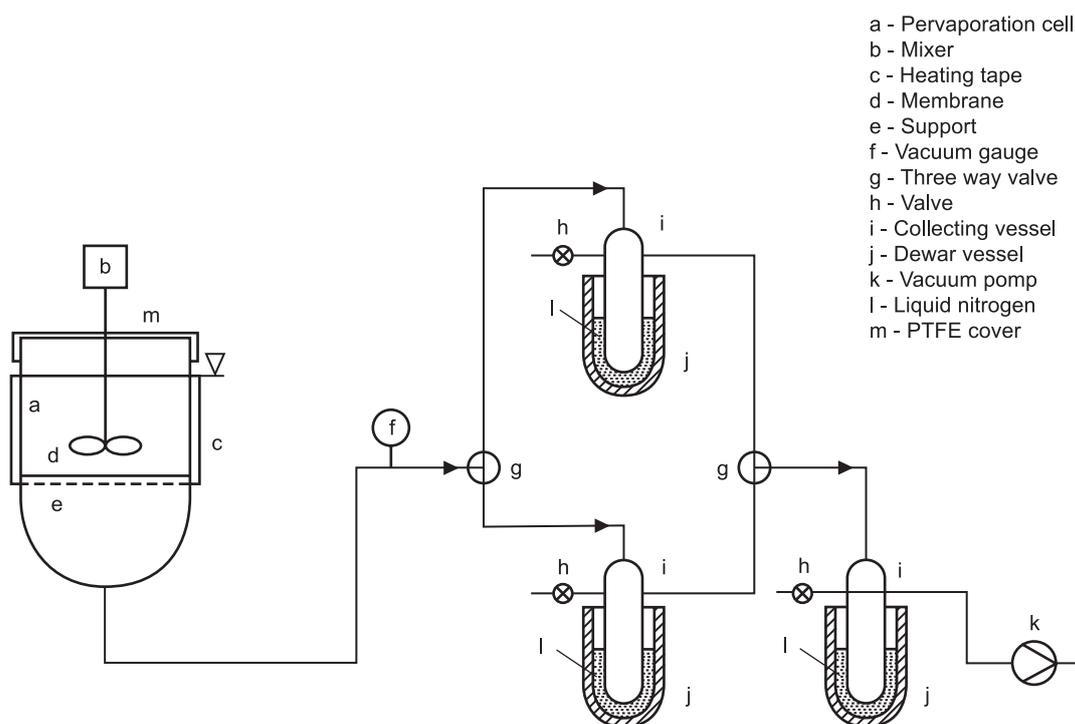


Figure 1. Pervaporation apparatus.

The separation factor of ethanol to water $\alpha_{E/W}$ was determined from Equation (2):

$$\alpha_{E/W} = \frac{(X_E / X_w)_{permeate}}{(X_E / X_w)_{feed}} \quad (2)$$

where X_E and X_w are the mass fractions of ethanol and water, respectively, in permeate and feed.

RESULTS AND DISCUSSION

The pervaporation experiments were performed with a feed mixtures of 5 wt.% of what in a mixture with water and membranes prepared from pure polymer (PDMS) and from the polymer filled with particles of the zeolites 3A and silicalite-1 at 50°C unless otherwise stated.

Effect of zeolite 3A content on fluxes and separation factors

The component fluxes as well as the overall fluxes through the membranes were calculated from Eqn. (1) and they are shown in Figure 2 for the zeolite 3A. It can be seen from Figure 2 that the incorporation of 3A into the polymer leads to an increase of 265 % in water flux when the zeolite content in the membrane ranged from 0 to 60 wt.%. On the other hand the ethanol flux remains to be almost constant and thus the overall flux also increases. The incorporation of the zeolite 3A of hydrophilic nature into the membrane modifies the membrane properties and thus the water flux is preferably sorbed and hence causes an increase in water flux while the ethanol flux remains almost constant.

The separation factors of ethanol to water for ethanol-water mixture was calculated from Equation (2) and is shown in Figure 3 for the zeolite 3A. For similar reason the selectivity of ethanol to water decreases as the zeolite content increases from 0 to 60 wt.%.

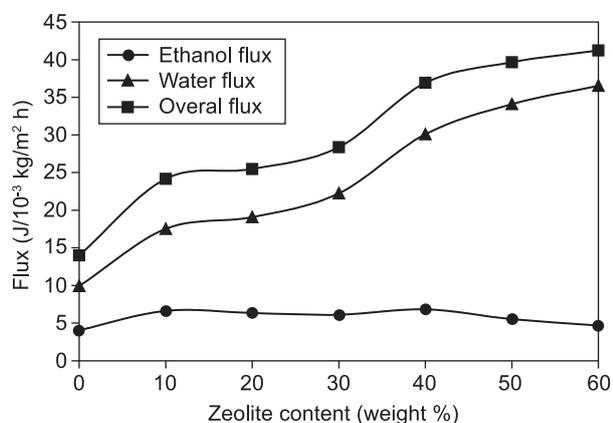


Figure 2. Effect of zeolite content (3A) in the membrane on permeation fluxes (Feed mixture: 5 % w/w ethanol; temperature: 50 °C).

Effect of zeolite silicalite content on fluxes and separation factors

It can be observed from Figure 4 that when silicalite-1 of hydrophobic nature is incorporated into the membrane from 0 to 60 wt.% it results in an increase of about 250 % in the ethanol flux while the water flux remains to be almost constant and overall flux also increases. This is due to the relatively more hydrophobic nature of silicalite-1 compared to 3A. Figure 5 confirms the results of Hennepe et al. [11] that both the ethanol and overall fluxes and separation factors are enhanced with increasing silicalite type of zeolite,

CONCLUSIONS

From the pervaporation experiments carried out for ethanol-water mixtures at 50°C using zeolite-filled, hydrophilic 3A and hydrophobic silicalite-1, membranes the following conclusions can be drawn:

1. An increase of zeolite content (3A) in the membrane results in an increase in the water and overall fluxes, while a decrease in separation factors. On the other hand the ethanol flux remains to be almost constant.
2. An increase in the zeolite content (silicalite-1) in the membrane results in an increase in the ethanol and overall fluxes while a decrease in the water flux.
3. The type of zeolite used and its physicochemical characteristics, predominantly the degree of hydrophobicity strongly influences the pervaporation properties of the membrane. Hydrophobic silicalite-filled membranes provide higher selectivity than the hydrophilic zeolites, 3A. It is also found that the hydrophobic zeolites ensures higher fluxes than those of the hydrophilic nature.

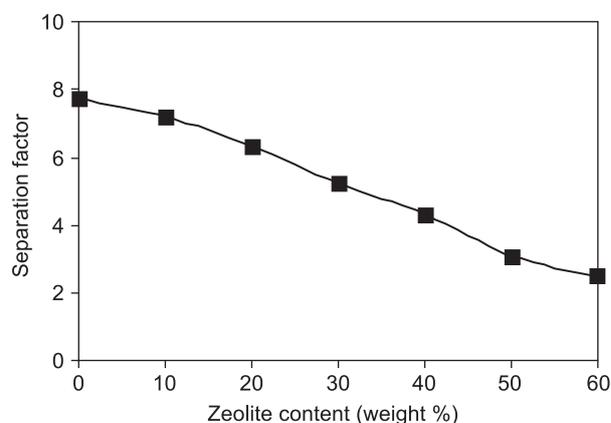


Figure 3. Effect of zeolite content (3A) in the membrane on separation factors (Feed mixture: 5 wt.% ethanol; temperature 50 °C).

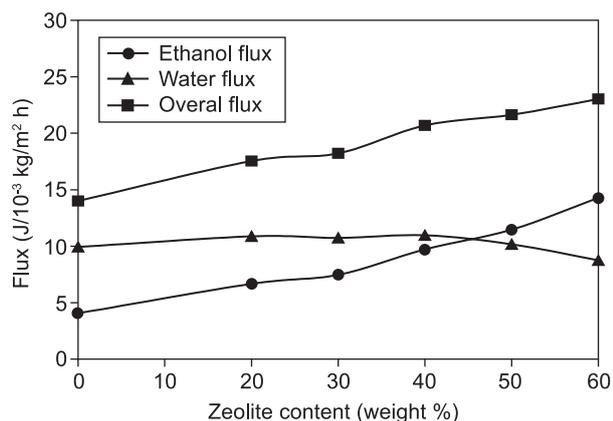


Figure 4. Effect of zeolite content in the silicalite-filled membrane on permeation fluxes (experimental conditions are given same as above).

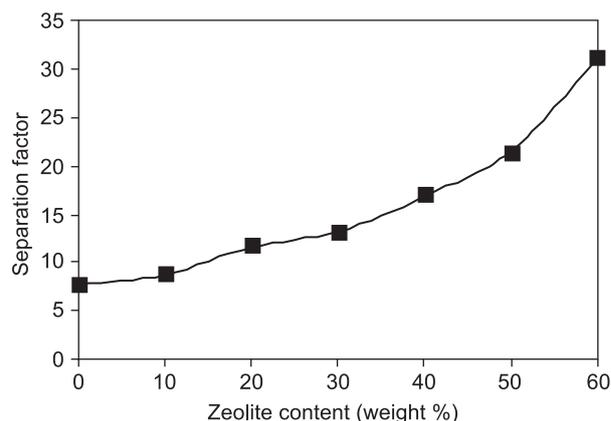


Figure 5. Effect of zeolite content in the silicalite-filled membrane on separation factors (experimental conditions are given same as above).

References

- Garcia Villaluenga J. P., Tabe-Mohammadi A.: *J. Memb. Science* *169*, 159 (2000).
- Lipnizki F., Field R. W., Ten P. K.: *J. Memb. Science* *153*, 183 (1999).
- Sampranpiboon P., Jiraratananon R., Uttapa D., Feng X., Huang R. Y. M.: *J. Memb. Science* *174*, 55 (2000).
- Kujawski W.: *Polish J. Env. Studies* *9*, 13 (2000).
- Vankelecom I. F. J., Scheppers E., Heus R., Uytterhoeven J. B.: *J. Phys. Chem.* *98*, 12 (1994).
- Adnadjovic B., Jovanovic J., Gajinov S.: *J. Memb. Science* *136*, 173 (1997).
- Caro J., Noack M., Kolsch P., Schafer R.: *Microporous Mesoporous Mater.* *38*, 3 (2000).
- Nair S., Lai Z., Nikolakis V., Xomeritakis G., Bonilla G., Tsapatsis M.: *Microporous Mesoporous Mater.* *48*, 219 (2001).
- Coronas J., Santamaria J.: *Sep. Purif. Methods* *28*, 127 (1999).
- Morigami Y., Kondo M., Abe J., Kita H., Okamoto K.: *Sep. Purif. Technol.* *25*, 251 (2001).
- Te Hennepe H. J. C., Bargeman D., Mulder M. H. V., Smolders C. A. in: *Permeation through zeolite filled silicone rubber membranes, Characterization of Porous Solids*, pp. 411–420, Ed. K. Unger, Elsevier, Amsterdam 1988.
- Evcin A.: *Preparation of zeolite-filled polydimethyl siloxane membranes for separation of alcohol-water mixture by pervaporation*, PhD Thesis, Sakarya University, Adapazari, Turkiye 2003.