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Organic-Organic Separation by Pervaporation. II. Separation of Methanol from Tame by an α-Alumina Supported Nay-Zeolite Membrane

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Abstract: Government legislation and an increased awareness of environmental issues with the general public have motivated chemical industries to look to more environmentally friendly production methods. The separation of organic-organic components to produce chemicals of a higher purity remains a problem in industry, because these type of chemicals usually form azeotropes in mixtures which are expensive to separate by traditional methods such as distillation. Most often the component to be separated is present in small amount, making the separation by distillation either impossible or very expensive. Membrane processes have proven to be very effective for the removal of low-concentration chemicals from mixtures, but application is always limited by the availability of a membrane that can both accomplish the separation and is stable under adverse conditions of high concentrations and varying flow rates. In this study, the application of a supported NaY-zeolite membrane for the separation of methanol from tert-amyl methyl ether is investigated with regard to varying feed concentration, feed temperature, and a change in membrane orientation. It is shown that this membrane can be successfully applied to the separation of an organic-organic mixture with a relative high flux and excellent selectivity toward methanol.

Keywords: Organic, Pervaporation, NaY membrane, TAME

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BACKGROUND

Pervaporation is a membrane-based separation process that utilizes the relative affinity of one of the components in a mixture for the membrane to preferentially separate that component from the mixture. In the last decade, many polymeric membranes have been applied to the separation of alcohol from alcohol-tertiary ether mixtures (1–5). The biggest disadvantage in using polymeric membranes for such separations is the swelling of the membrane at high concentrations of the permeating components and mechanical degradation at high temperatures and pressures. Ceramic membranes are considered to be chemically more stable since swelling cannot occur and zeolites have proven their mechanical integrity in catalytic processes that are usually carried out at high temperatures and high pressures. In recent years, there has been wide interest in the separation of organic-organic mixtures by ceramic membranes. There is a wide variety of literature available on the separation of organic-organic mixtures by gas permeation through silicalite and MFI-type membranes (6–13). Van de Graaf (6) investigated the gas separation of methane, ethane, propane, and n-butane and showed that the flux through an MFI-type membrane is dependent on both the diffusive and adsorption properties of the permeation components. This was characterized by a maximum in the surface flux for all the components that were studied. Funke et al. (9) investigated a wide selection of cyclic, branched, and linear hydrocarbon mixtures for separation by gas permeation and showed that n-alkanes can be separated easily from branched and cyclic alkanes by gas permeation through silicalite membranes. It was suggested that the n-alkanes block the pores to such an extent that the branched and cyclic alkanes cannot enter the pores and hence cannot permeate through the membrane. A later study also indicated that the permeance of the different pure hydrocarbons increased with an increase in temperature while the selectivity either showed a maximum or slightly decreased with an increase in the operating temperature. The same phenomenon was also observed by Van de Graaf et al. (14) and is attributed to a change in separation mechanism from adsorption-controlled to mobility-controlled. The separation of two molecules always depends on both the adsorption properties and the mobility of the two components. At lower temperatures, the molecule that adsorbs preferentially permeates preferentially, but as the temperature increases the amount adsorbed decreases and the effect of adsorption on the separation also decreases. At the same time, the mobility of both molecules increases, and according to Einstein's theory the movement of the smaller molecule will be faster and it should thus permeate preferentially. This is exactly what was found by the studies mentioned earlier.

The work by Van den Broeke et al. (10) also showed a maximum in permeance with an increase in temperature for methane. An almost linear relationship between flux and feed pressure was observed for methane and carbon dioxide. It was also shown that the orientation of the membrane toward the feed has a significant influence on the value of the flux. The orientation where the support is facing the feed always gives the higher flux (6). The latter can be explained by the difference in concentration gradient over the membrane layer for the two cases. If the support is facing the feed, the change in concentration over the support layer is negligible (11), but there is a significant change in concentration over the zeolite layer. If the zeolite layer is facing the feed, there is a significant change in concentration in both the zeolite layer and the support layer. For this latter case, the resistance to permeation is larger than when the support is facing the feed, and thus the overall flux should be lower.

Keizer at al. (12) was the first to observe the different separation mechanisms that influence the separation of different organic mixtures. The authors classified six separation regimes. In regime I, both permeating species are independent of any adsorption phenomena and separation is the result of difference in mobility alone taking into account surface transfer limitation due to entrance statistics. In regime II one component is independent of adsorption while the other is strongly adsorbed on the external surface as well as inside the zeolite pores, and separation is limited by interaction between the molecules. In regime III, both species are strongly adsorbed inside the zeolite pores but only one of the components is strongly adsorbed on the external surface of the zeolite membrane. For this regime, one molecule can easily block the pore mouth for the other molecule and, depending on which molecule adsorbs on the external surface, separation can be accomplished. In regimes IV to VI one component cannot enter the zeolitic pores while both components adsorb on the external surface. For these cases pore-mouth blocking can occur and have a significant influence on the permeance of the preferentially permeating component. If pore-mouth blocking is not significant, size exclusion plays an important role in the separation mechanism. The study by Coronas et al. (14) showed the same trends as the previously discussed investigations as well as a decrease in selectivity with time for membranes manufactured by different preparation techniques. The authors showed that the permeance and selectivity of hexane isomers are very much dependent on the method by which the membrane was manufactured. This would explain the wide variation in flux and selectivity data published for the same type of membrane.

Literature on the separation by pervaporation through membranes other than MFI or silicalite has been preciously few (16–18). Kita et al. (17, 18) studied the separation properties of NaY and NaA membranes grown hydrothermally on the surface of a porous alumina substrate. The NaY membrane showed high methanol selectivity (>6000) in pervaporation of benzene and MTBE. The flux increased with methanol concentration in the feed up to approximately 20 mole% methanol after which it reached a constant value irrespective of the feed composition. Selectivity remained high for the entire range of feed compositions. Separation was said to occur by preferential adsorption and it was suggested that the constant value reached by the flux was caused by saturation of the membrane. As soon as the membrane is saturated with liquid, the effect of adsorption becomes negligible and separation is accomplished by the difference in mobility for the components. The selectivity and flux both increased with temperature. The total flux decreased and the selectivity increased with an increase in ethanol concentration in the feed in the study by Kondo et al. (16). The flux increased with temperature while the selectivity remained almost constant. The authors also showed some influence of the alumina content of the support on the separation properties of the membrane. In this study, the influence of different process parameters such as feed temperature, feed concentration, and membrane orientation on the pervaporation performance of a NaY-zeolite membrane will be investigated.

EXPERIMENTAL

Materials

Experimental NaY-zeolite membranes consisting of a NaY-zeolite layer grown hydrothermally on the outside of a porous, tubular α-alumina supports layer were obtained with permission from Mitsui Shipbuilding Company© (Japan). A SEM image of the NaY-zeolite membrane is shown in Fig. 1. The thickness of the zeolite layer and the α-Al_2O_3 support are 57.4 ± 5.1 μm and 3 ± 0.05 mm, respectively.

The scanning electron microscope (SEM) images and Energy Dispersive X-Ray (EDAX) analyses of the two layers of the NaY-zeolite membrane are given in Fig. 2 and 3 and Tables 1 and 2.

NaY-zeolite crystals were obtained from Aldrich Chemical Company, Inc. High-purity liquid chromatography (HPLC) grade methanol (MeOH) (99.8%) and HPLC grade tertiary amyl methyl ether (TAME) (97.6%) were purchased from Aldrich Chemical Company, Inc. All chemicals were used

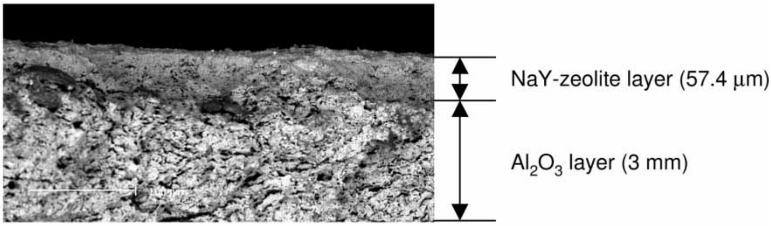

Figure 1. SEM image of a side view of a tubular NaY-zeolite membrane on an α-alumina support.

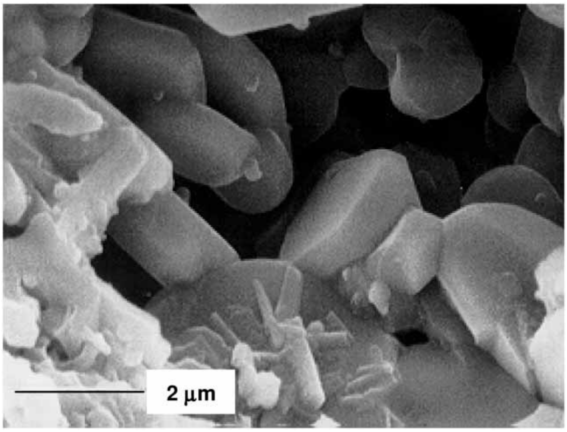

***Figure 2*.** SEM image of the silicon (Si)-rich layer (Na Y-zeolite).

without further purification. All analyses were done with a calibrated gas chromatograph (HP series 6985 fitted with a flame-ionization detector and a carbowax capillary column).

ADSORPTION EXPERIMENTS

Liquid phase adsorption experiments were carried out to determine the maximum saturation capacities of pure methanol and pure TAME. A known weight of pure Na Y-zeolite crystals was stirred in a flask while one of the

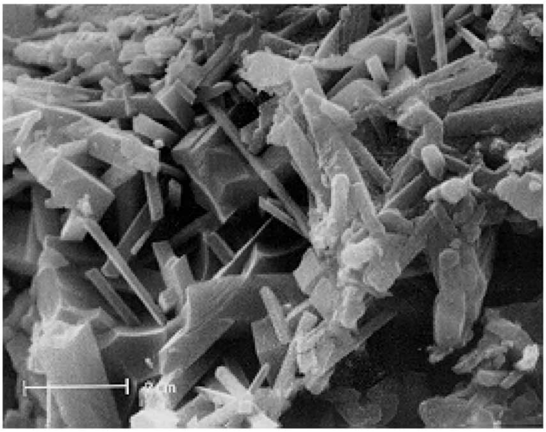

***Figure 3*.** SEM image of the aluminium (Al)-rich support.

Table 1. EDAX analyses of silicon-rich layer (Na Y-zeolite)

Element	Wt%
Oxygen (O)	45.6 ± 3.8
Sodium (Na)	2.1 ± .06
Aluminium (Al)	20.5 ± 5.4
Silicon (Si)	22.9 ± 4.5
Magnesium (Mg)	0.4 ± .01
Calcium (Ca)	3.4 ± .01

pure components was added from a burette. The mixture of liquid and dry zeolite was stirred continuously and the pure component liquid added until the mixture in the flask coagulated. Coagulation of the dry crystals indicated that the crystals no longer adsorbed any of the liquid and the excess liquid caused the crystals to coagulate or stick together, indicating that the crystals were saturated with liquid and that the saturation capacity of the crystals for the liquid had been reached. The saturation capacity could then be calculated as the weight of liquid added per the weight of dry zeolite crystals.

The occupancy of liquid methanol and TAME inside NaY-zeolite crystals was evaluated by binary liquid adsorption analogous to the method described in detail by Kärger and Ruthven (19). The method involves the suspension of a known mass of zeolite crystals in a liquid mixture of methanol and TAME of a known composition. The suspension is left for 2 days to allow enough time for the liquid mixture to be adsorbed into the crystals until equilibrium has been reached. The crystals are then removed from the liquid mixture by centrifugal force. The crystals are then washed with one of the components of the mixtures (methanol or TAME) to replace the mixture that had adsorbed onto the crystals. If the crystals containing the adsorbed binary phase were washed with methanol, the methanol would de-adsorb the amount of TAME

Table 2. EDAX analyses of aluminium-rich support

Element	Wt%
Oxygen (O)	42.9 ± 0.4
Sodium (Na)	0.00
Aluminium (Al)	40.6
Silicon (Si)	15.2 ± 0.09
Magnesium (Mg)	0.5 ± 0.1
Calcium (Ca)	0.4 ± 0.09

that had adsorbed and thus the amount of TAME that had adsorbed could be measured. If the crystals containing the adsorbed binary phase were washed with TAME, the amount of methanol that had adsorbed could be measured. The desorbed phase was analyzed by gas chromatography to determine the amount of each component that had adsorbed into the Na Y-crystals. This data was used to calculate the occupancy of each component of the mixture in the crystals. In all adsorption experiments, samples were taken after 24 and 48 h and a maximum deviation of 3.2% in the mass adsorbed was found, indicating that equilibrium was indeed reached and that the data presented in this study is equilibrium adsorption data. Van de Graaf (6) showed that the correlation between the adsorption of a mixture into zeolite crystals and the behavior of the same mixture in a zeolite membrane is not always comparable. It does however give a good approximation of the behavior of the two components in the presence of each other.

PERVAPORATION EXPERIMENTS

The pervaporation experiments were performed using a tubular membrane (with a diameter of 9 mm and length of 9.3 mm) module with an effective transport area of $2.62 \cdot 10^{-4}\,m^2$ in a standard pervaporation apparatus (see Fig. 4).

The feed solution was maintained at the desired temperature via a water bath with a circulator and fed to the membrane cell with a magnetic pump (flow rate $= 0.3\,m^3\,hr^{-1}$). The permeate side of the cell was kept at a constant pressure of 1 kPa with a vacuum pump, and the vapor from the permeate side was collected in cold traps with liquid nitrogen. The total permeation flux was determined by measuring the weight collected in the cold traps over a certain period of time at steady-state conditions. The composition of the collected fluid in the cold traps was analyzed by gas chromatography, from which the selectivity was

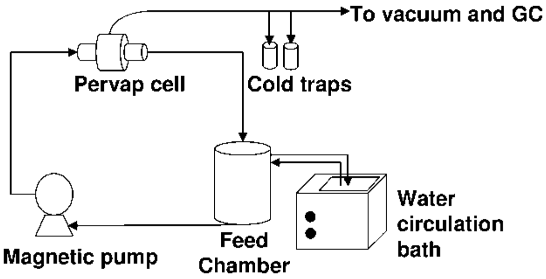

Figure 4. Schematic diagram of standard experimental pervaporation setup.

calculated. The total experimental error for all pervaporation experiments was below 3%. The 95% confidence limits for all fitted parameters are reported in the table or text where they are presented.

RESULTS AND DISCUSSION

Adsorption Characteristics of Pure Components

The saturation capacity for pure methanol and for pure TAME was found to be 0.55 ± 0.02 g methanol.g zeolite^{-1} and 0.057 ± 0.02 g TAME.g zeolite^{-1}, respectively. This corresponds to an adsorption concentration of 17.2 mol methanol.kg zeolite^{-1} for methanol and 5.6 mol TAME.kg zeolite^{-1} for TAME. The maximum saturation capacity was assumed to be constant for the temperature range used in this study.

Adsorption Characteristics for Methanol-Tame Mixtures Onto Nay-Zeolite Crystals

The extended Langmuir adsorption isotherm for binary mixtures was fitted to the binary adsorption data to obtain the adsorption constants K_{MEOH} and K_{TAME}. The general form of the extended Langmuir adsorption isotherm is given in Eq. (1), and the extended Langmuir adsorption istoherm for methanol as used in this study is given in Eq (2).

$$\theta_i = \frac{K_i C_i}{1 + \sum_{j=1}^{n} K_j C_j} \tag{1}$$

$$\theta_{MEOH} = \frac{K_{MEOH} C_{MEOH}}{1 + K_{MEOH} C_{MEOH} + K_{TAME} C_{TAME}} \tag{2}$$

where C_{MEOH} and C_{TAME} are the concentrations in the adsorbed phase with units of kg component. kg zeolite^{-1}.

The constants for the extended Langmuir adsorption isotherm obtained from the binary liquid adsorption experiments with 95% confidence limits are given in Table 3.

The saturation capacity for methanol and TAME was assumed to have an equal and constant value of 17.2 mol liquid.kg zeolite^{-1} over the temperature range used in this study. The binary adsorption isotherms for methanol at the different temperatures and methanol feed concentrations are presented in Fig. 5.

From Fig. 5 it can be seen that the amount of methanol adsorbed increases with an increase in methanol concentration and with an increase

Table 3. Extended Langmuir adsorption parameters for methanol and TAME for binary adsorption of methanol and TAME onto NaY-zeolite crystals

T (K)	K_{MEOH} ($m^3.mol^{-1}$)	K_{TAME} ($m^3.mol^{-1}$)
299	$2.7 \cdot 10^{-2} \pm 2 \cdot 10^{-3}$	$3.9 \cdot 10^{-4} \pm 2 \cdot 10^{-5}$
309	$1.3 \cdot 10^{-2} \pm 4 \cdot 10^{-4}$	$4.6 \cdot 10^{-4} \pm 1 \times 10^{-5}$
320	$2.3 \cdot 10^{-2} \pm 8 \cdot 10^{-3}$	$4.5 \cdot 10^{-4} \pm 1 \cdot 10^{-8}$
330	$2.0 \cdot 10^{-2} \pm 1 \cdot 10^{-3}$	$5.0 \cdot 10^{-4} \pm 2 \cdot 10^{-5}$

in temperature. The binary adsorption isotherms for TAME at different temperatures and TAME feed concentrations are presented in Fig. 6.

Pervaporation Characteristics of Pure Components

The influence of feed temperature on the pervaporation rate of the pure components was investigated by varying the feed temperature and measuring the total flux through the membrane. The experiments were carried out with two different orientations of the membrane, i.e., with the feed on the support layer and with the feed on the active zeolite layer. The total experimental error in measuring the flux was less than 3%. According to Feng and Huang (20) the apparent activation energy for the separation process can be calculated with an Arrhenius type exponential relation of permeation flux to temperature

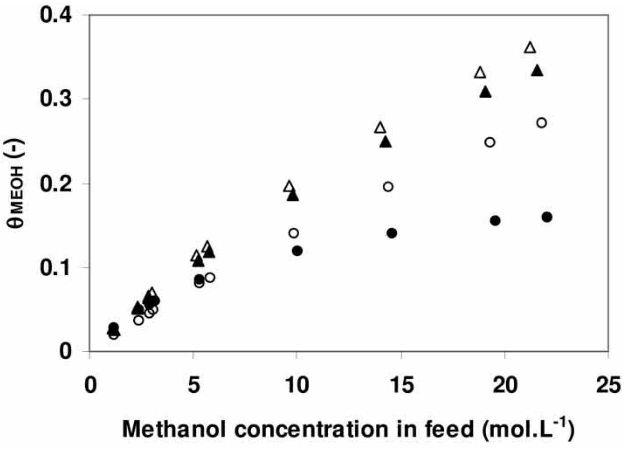

Figure 5. Binary adsorption isotherms for methanol at different temperatures and methanol feed concentrations (●: 299 K, ○: 309 K, ▲: 320 K, △: 330 K).

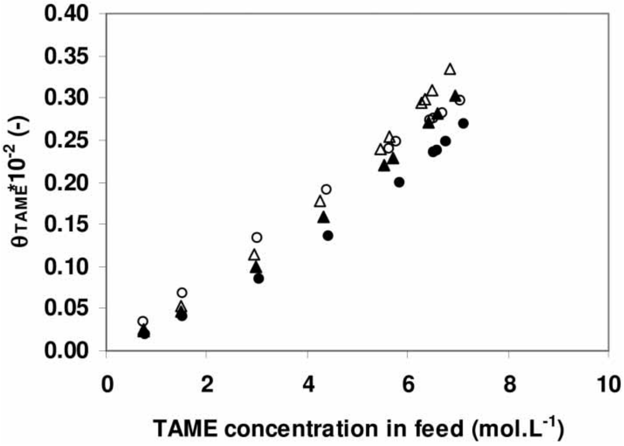

Figure 6. Binary adsorption isotherms for TAME at different temperatures and TAME feed concentrations (●: 299 K, ○: 309 K, ▲: 320 K, △: 330 K).

(see Eq. (3). The activation energy of the process can thus be obtained from a plot of the logarithm of the permeation flux against the inverse of temperature.

$$\ln J_i = \ln J_{i,0} - \frac{E_{process}}{RT} \quad (3)$$

The influence of feed temperature on the pure component fluxes for both orientations is shown in Figs. 7 and 8.

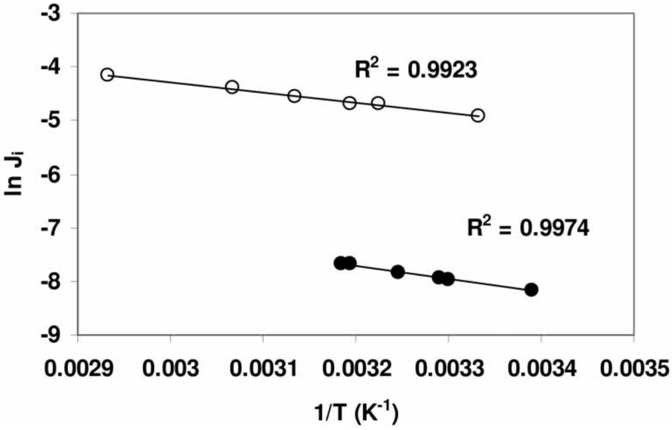

Figure 7. Influence of feed temperature on pure component fluxes for the orientation where the feed is on the support (○: Pure Methanol flux, ●: Pure TAME flux) The units of J_i is mol.m^{-2}.s^{-1}.

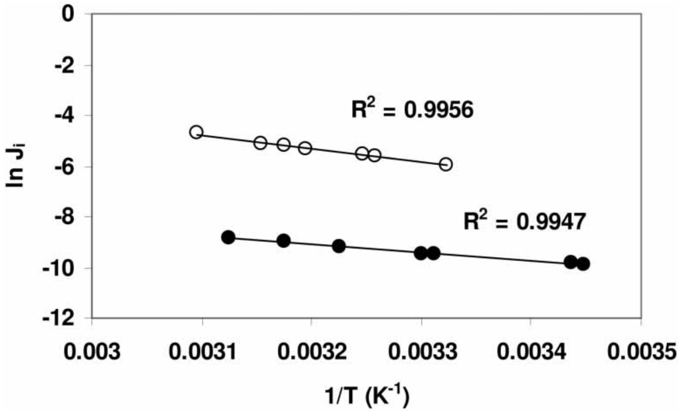

Figure 8. Influence of temperature on the pure methanol and pure TAME flux with the zeolite layer facing the feed (○: Pure methanol flux, ●: Pure TAME flux). The units for J_i is mol.m^{-2}.s^{-1}.

A straight line was fitted through the data in Figs. 7 and 8 to calculate the activation energy of pervaporation. The accuracy of the fit is given by the R^2 values [see Eq. (4)] which were 0.992 for the methanol data and 0.997 for the TAME data.

$$R^2 = 1 - \frac{\text{Sum of squares of differences}}{\text{Sum of squares}} = 1 - \frac{\sum(x-y)^2}{\sum(x^2+y^2)} \quad (4)$$

The calculated activation energies for pervaporation (E_{process}) with 95% confidence limits and comparative literature values for the activation energy of methanol, TAME and MTBE, are presented in Table 4.

It can be seen from Figs. 7 and 8 that the activation energy remains constant for the temperature range under consideration. Comparison between literature values for the activation energy and the values obtained in this study can at best only be relative. The activation energy for pervaporation depends not only on the mixture being separated but also on the membrane being used, since the activation energy for pervaporation is the sum of the activation energy for diffusion and the heat of sorption (polymers) or heat of adsorption (ceramics) (22). The difference in activation energy for pervaporation for methanol and TAME is very small (only 4 kJ.mol^{-1}).

The difference in activation energy observed for the two orientations in this study is probably due to the difference in phases present in the support layer for the two orientations. The phase in the support layer has a significant influence on the chemical potential difference across the membrane, resulting in a significant change in activation energy necessary for diffusion. When the

Table 4. Activation energy of pervaporation for methanol and tertiary ethers through different membranes

Membrane	Temperature range (K)	Weight % methanol	$E_{process}$ (kJ.mol^{-1})	Reference
Methanol				
PAA-PAN Blend	296–323	100	19	(20)
Cellulose triacetate	303–323	19.4	6.15	(3)
Cellulose triacetate	303–323	19.4	6.15	(3)
NaY/Al_2O_3	298–333	100	16 ± 0.7	This work (feed on support)
NaY/Al_2O_3	298–333	100	49 ± 1.5	This work (feed on zeolite)
MTBE				
PAA-PAN Blend	296–323	0	19	(20)
Cellulose triacetate	303–323	19.4	17.57	(3)
TAME				
NaY/Al_2O_3	298–333	0	20 ± 0.4	This work (feed on support)
NaY/Al_2O_3	298–333	0	28 ± 1.0	This work (feed on zeolite)

zeolite layer is facing the vacuum, the vacuum is right next to the zeolite (active membrane) layer, so that the pressure at the zeolite permeate surface is the true measured pressure. When a support layer is placed between the vacuum and the selective layer, the actual pressure at the zeolite permeate side is increased to such an extent that the true driving force across the zeolite layer is decreased significantly, resulting in a significant reduction in pure component flux.

The feed temperature has a positive effect on the flux of both methanol and TAME and the flux increases with an increase in feed temperature. The increase in flux with temperature can be explained by the increase in pressure drop (apparent driving force) across the composite membrane. The saturated vapor pressure on the feed side increases with an increase in feed temperature, while the permeate vacuum pressure remains constant. The pressure difference across the membrane is thus increased with temperature and an increase in the flux is observed (23). Besides the increased driving force with an increase in temperature, diffusivity is also increased if the activation energy of diffusion is positive. A maximum in the surface flux is usually observed for gas permeation and is the result of interplay between the diffusion and adsorption phenomena that governs separation by gas permeation. No maximum was observed for the temperature range under consideration in this study, which could point to a diffusion-controlled mechanism, as was observed by Nishiyama et al. (24).

Pervaporation Characteristics of Methanol and Tame Mixtures Influence of Feed Temperature

The influence of feed temperature on the total pervaporation flux and partial methanol and TAME flux is presented in Figs. 9, 10, and 11. The experimental error for binary experiments was below 3%. All fluxes were obtained with the feed on the support layer.

From Figs. 9, 10, and 11 it can be seen that flux shows a linear increase with an increase in temperature for the total pervaporation flux as well as the partial methanol flux. This could be the result of either an increase in mobility (diffusion) or an increase in adsorption. From the adsorption isotherms and the pure component data it is evident that although the mobility increases rapidly with temperature, the amount of methanol adsorbed does not increase very rapidly and there is very little difference between the amount adsorbed at 299 K and the amount adsorbed at 330 K. This could mean that although adsorption plays a role in the sense that only that which is adsorbed can diffuse, adsorption as a phenomenon does not play a significant role in the increase of the flux with temperature for methanol.

The TAME flux shows a maximum at 310 K. A maximum in partial flux was also observed by Van de Graaf (6) for binary gas permeation of methane and ethane. The maximum in the ethane flux was explained as interplay between the activated process of diffusion and the adsorbed phase concentration. Initially the flux increases purely due to the diffusion. At a certain temperature, the decrease in the adsorbed phase becomes significant enough that the flux starts to decrease. The increase in flux at 330 K is

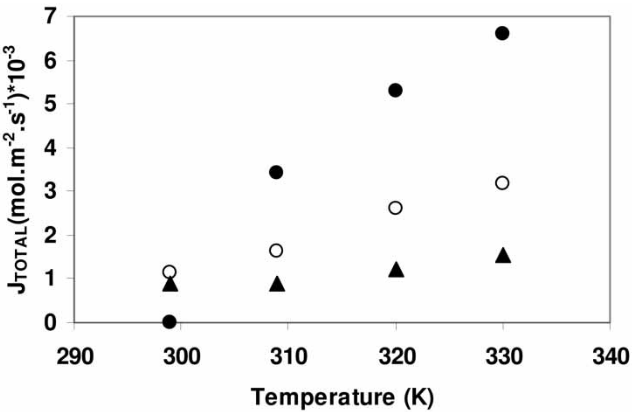

Figure 9. Influence of temperature on the total pervaporation flux (●: 14 mol% methanol, ▲: 32 mol% methanol, ○: 70 mol% methanol).

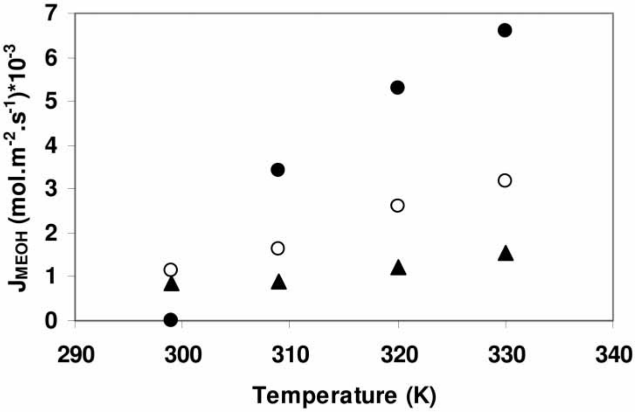

Figure 10. Influence of temperature on the partial methanol flux (●: 14 mol% methanol, ▲: 32 mol% methanol, ○: 70 mol% methanol).

not significant and falls within the experimental error of this study. The influence of temperature on the selectivity is shown in Fig. 12.

From Fig. 12 it can be seen that there is some variation in selectivity with temperature. At the lower methanol feed concentrations, the selectivity shows a minimum at 320 K while at the higher methanol feed concentrations the selectivity shows a maximum at 320 K. From a comparison between the partial component fluxes and the pure component fluxes it is clear that the pure component fluxes are much higher than the partial fluxes of the

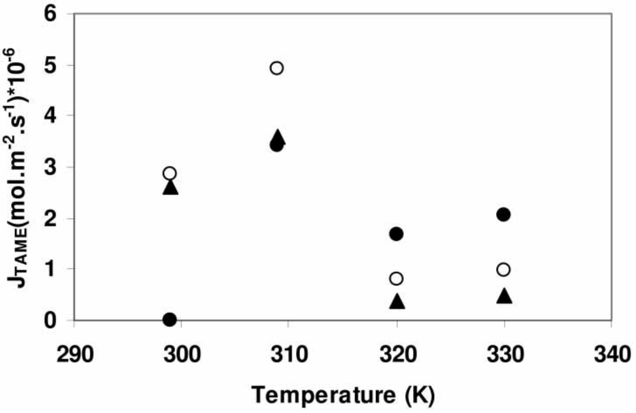

Figure 11. Influence of temperature on the partial TAME flux (●: 14 mol% methanol, ▲: 32 mol% methanol, ○: 70 mol% methanol).

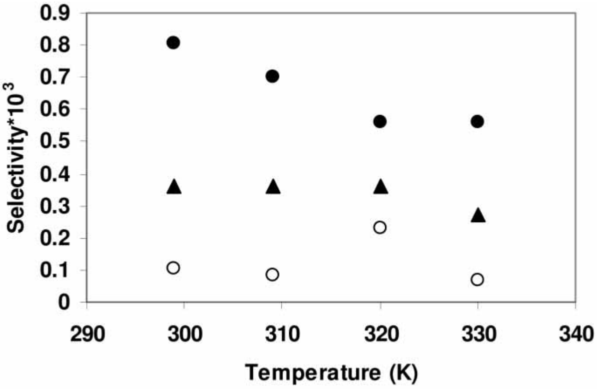

Figure 12. Influence of temperature on the selectivity of the membrane towards methanol (●: 26 mol% methanol, ▲: 48 mol% methanol, ○: 83 mol% methanol).

two components in the mixture, indicating that each molecule is influenced by the presence of the other in the mixture.

The pure TAME flux is almost 100 times larger than the partial TAME fluxes while the pure methanol flux is approximately 3 times larger than the partial methanol fluxes. This shows that the TAME molecules are more severely hindered by the presence of the methanol molecules than the methanol by the TAME molecules. At the lower methanol concentrations, the methanol flux is the most severely influenced by the presence of the TAME molecules, while at the higher methanol concentrations, the TAME flux is most severely influenced by the presence of the methanol molecules. At the lower methanol feed concentrations, the selectivity toward methanol would therefore be lower than at higher methanol concentrations and thus the difference in behavior of the selectivity toward methanol with changing feed concentration is explained.

Influence of Feed Composition

The influence of feed composition on the total pervaporation flux and the partial fluxes is shown in Figs. 13, 14, and 15.

From Figs. 13 and 14 it can be seen that both the total flux and the methanol flux increases steadily with an increase in methanol concentration in the feed. From the adsorption isotherms it can be seen that the amount of methanol that adsorbs increases with an increase in methanol concentration in the feed. The more methanol that adsorbs, the more methanol will permeate. While the partial methanol flux is increasing, the partial TAME flux is decreasing (see Fig. 14), due to the higher amount of methanol

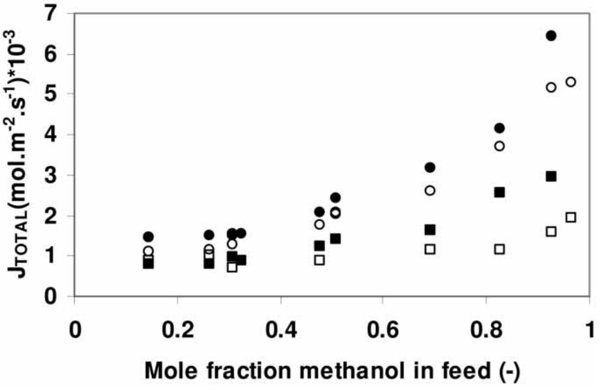

Figure 13. Influence of feed composition on the total pervaporation flux (●: 330 K, ○: 320 K, ■: 309 K □: 299 K).

permeating. The TAME flux shows a weak maximum between 50 mol% and 70 mol% methanol at all the temperatures investigated in this study. The fact that the partial TAME flux increases with an increase in methanol concentration in the feed, and at a certain concentration starts to decrease, could point to more than one mechanism controlling the partial TAME flux. The partial TAME flux increases very slowly before the azeotrope concentration and thereafter drops very rapidly. This could indicate that up to the azeotropic concentration, the vapor-liquid equilibrium of the system is playing a role in determining the amount of each component that adsorbs, since the vapor phase composition would be different than the liquid phase composition. An increase in methanol feed concentration beyond that of the azeotropic mixture would result in an azeotropic composition for the vapor phase. If only diffusion

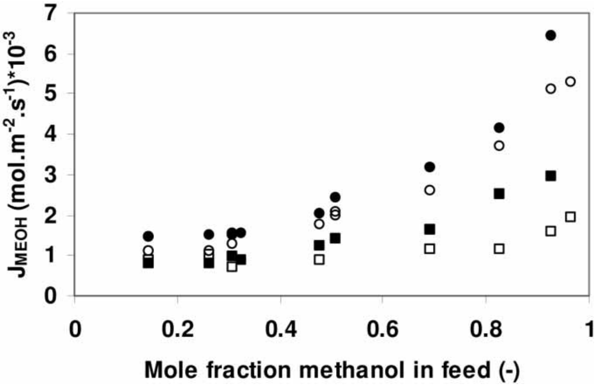

Figure 14. Influence of feed composition on the partial methanol flux (●: 330 K, ○: 320 K, ■: 309 K, □: 299 K).

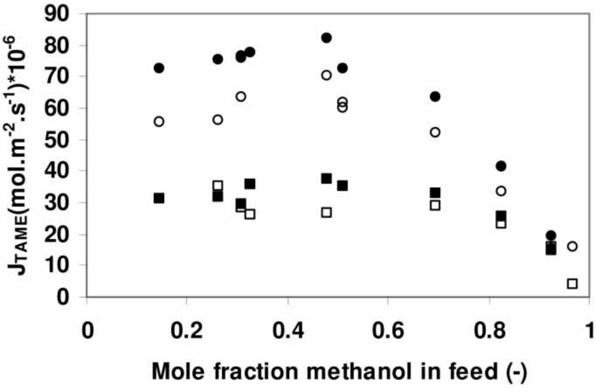

Figure 15. Influence of feed composition on the partial TAME flux (●: 330 K, ○: 320 K, ■: 309 K □: 299 K).

played a role in determining the magnitude of the flux, the partial methanol and TAME fluxes should stay constant after the azeotropic point, but instead they are increasing (methanol) and decreasing (TAME). It is generally assumed that the vapor-liquid equilibrium is at the feed side surface of the zeolite layer. The zeolite layer is made up of crystals grown onto the support and defects in the form of openings between the crystals are a common occurrence (24). It is therefore plausible that the real liquid-vapor equilibrium is not at the feed side surface of the zeolite layer but actually somewhere inside the zeolite layer. It is therefore postulated that after the azeotropic point, the composition at the permeate side is purely determined by the affinity of the membrane for one of the components, in this case, methanol. The higher the methanol concentration in the feed, the further inside the selective layer the vapor-liquid equilibrium interface will be. This effectively lowers the thickness of the selective layer where pervaporation is taking place and thus the flux of the preferentially permeating component is increased.

CONCLUSIONS

The experimental pure component and binary mixture pervaporation data were presented and discussed.

The extended Langmuir model was fitted to binary liquid adsorption data and the fitted parameters were used to calculate the surface coverage at the feed and permeate sides of the zeolite layer.

The pure component fluxes of both methanol and TAME for both orientations showed an almost linear relationship with temperature and the activation energy for the process for both orientations could be calculated with an Arrhenius type relation to temperature. It was found that the apparent activation energy for the pervaporation process almost doubled when the membrane orientation was reversed from the zeolite layer facing the vacuum to the zeolite layer facing the feed.

The total binary flux also increases linearly with temperature and exponentially with feed composition. The partial TAME flux is much lower than the partial methanol flux for both orientations. The membrane is highly selective toward methanol and the selectivity decreases with increase in methanol feed concentration. The selectivity increased or decreased with an increase in temperature, depending on the methanol feed concentration. The variation in selectivity with temperature could be explained by the influence of the methanol molecules on the partial TAME flux and the influence of the TAME molecules on the partial methanol flux. It was found that the partial TAME flux is more severely influence by the presence of the methanol molecules than the methanol partial flux is influenced by the presence of the TAME molecules.

The partial TAME flux showed a maximum at 310 K, which could be explained by the combined influence of diffusion and adsorption.

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