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Pervaporation of Binary and Ternary Mixtures of Water with Methanol and/or Ethanol

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ABSTRACT

This article explores water, methanol, and ethanol transport through hydrophilic membranes, by measuring the flux and separation factor in pervaporation as a function of the feed composition for binary water/methanol and water/ethanol mixtures. Additionally, the influence of adding a third component to the feed is examined. Because the solution-diffusion model is considered to be the basic reference model for the description of transport through pervaporation membranes, it was used for

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understanding differences in transport characteristics. It was found that the feed composition has a large influence on flux and selectivity of all components. The results show that for a given feed concentration, the permeability is different for binary and ternary mixtures. Permeability thus depends also on the other feed components and their concentration, which contradicts the assumptions of the solution-diffusion model. The deviations from the ideal are explained qualitatively, and may be attributed to the swelling behavior of the membrane, and to differences in size and polarity of the components. Because of the low polarity (and the larger size) of ethanol, ethanol permeation is only possible in the presence of enough water. Furthermore, it was observed for both alcohols that the water–methanol or water–ethanol separation factor in the ternary mixtures was (much) higher than in the binary mixtures, indicating that the presence of a second alcohol in the feed decreases the permeation of both alcohols.

Key Words: Pervaporation; Non-idealities; Ternary mixtures; Methanol; Ethanol.

INTRODUCTION

Pervaporation is a membrane process in which a liquid mixture is separated by selective permeation of one (or more) component(s) from the feed mixture, thereby undergoing a phase change from liquid to vapor. In the case of water/organic separation, selective permeation of water occurs from a mixture with (an) organic compound(s) (hydrophilic membranes) or selective permeation of (an) organic compound(s) from an aqueous mixture (hydrophobic membranes).

Pervaporation proves useful in a number of separations, the most frequent application being the dewatering of organic solvents. The first commercial pervaporation plant was used to dehydrate ethanol to circumvent problems with the water–ethanol azeotrope when using distillation. A similar application is the production of anhydrous isopropyl alcohol (IPA).[1] Another category of applications is the removal of organic compounds from aqueous streams, e.g., the removal of volatile organic compounds (VOCs) in wastewater treatment[2–5] and aroma recovery in the food industry.[6,7] New applications focus on the separation of organic–organic mixtures, and more generally, on separations that are difficult to achieve with distillation (e.g., separations of products with only a small difference in volatility). An additional advantage of pervaporation is the use of moderate temperatures and pressures, which may be important in the pharmaceutical or food industry.

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Pervaporation may also be used as part of a hybrid system in combination with distillation, with a chemical reactor or with extraction.[8] In the case of the combination with distillation, the permeate can be fed back directly to the distillation tower, since it is a two-phase system, thus eliminating the need for permeate condensation, which reduces the cost of the installation. In combination with a reactor, pervaporation is used to continuously remove one of the reaction products, to shift the equilibrium reaction to higher yields. In most cases, the removed product is water, in an esterification reaction,[9] but removal of methanol has also been applied.[8]

There is still a need for accurate and reliable (predictive) modeling of the permeation process. The most commonly applied model for the permeation process is the solution-diffusion model, which considers three consecutive steps: sorption of the molecules onto the surface of, or into the membrane, diffusion of the molecules through the membrane, and finally, desorption at the permeate side.[10]

To understand transport through (hydrophilic) pervaporation membranes, this article investigates the pervaporation behavior of different binary and ternary mixtures of water with methanol and/or ethanol. The observed transport behavior is compared with the ideal behavior derived from the solution-diffusion model, and deviations are explained qualitatively.

THEORETICAL BACKGROUND

In the literature, the pervaporation and transport behavior of pure components and binary mixtures through specific membranes is extensively described. The most basic model[11] is described in more detail in the next paragraph. This model does not take in account commonly encountered phenomena, like flux coupling and the effect of swelling on the permeability, and thus leads to a constant permeability.

The solution-diffusion model starts with Fick's Law:

$$J_i = \frac{-D_i(x) \cdot C_i(x)}{RT} \nabla \mu_i(x) \tag{1}$$

with

$$\mu_i(x) = \mu_{i,\text{ref}} + RT \ln a_i(x) + \int_{p_\text{ref}}^{p(x)} v_i \, dp - \int_{T_\text{ref}}^{T(x)} S_i \, dT \tag{2}$$

For one-dimensional isothermal permeation, and for a constant pressure in the membrane equal to the feed pressure, and assuming chemical equilibrium at the membrane interphases:

$$\mu_{i_\mathrm{f}}{}^{1} = \mu_{i_\mathrm{f}}{}^{\mathrm{m}} \qquad \mu_{i_\mathrm{p}}{}^{1} = \mu_{i_\mathrm{p}}{}^{\mathrm{m}} \tag{3}$$

and

$$C_{i_\mathrm{f}}{}^{\mathrm{m}} = \frac{\gamma_{i_\mathrm{f}}{}^{1}}{\gamma_{i_\mathrm{f}}{}^{\mathrm{m}}} C_{i_\mathrm{f}}{}^{1} \tag{4}$$

$$C_{i_\mathrm{p}}{}^{\mathrm{m}} = \frac{\gamma_{i_\mathrm{p}}{}^{1}}{\gamma_{i_\mathrm{p}}{}^{\mathrm{m}}} C_{i_\mathrm{p}}{}^{1} \exp\left[\frac{-v_i(p_\mathrm{f}{}^{1} - p_\mathrm{p}{}^{1})}{RT}\right] \tag{5}$$

Substituting Eqs. (4) and (5) into Eq. (1), and assuming the exponential term in Eq. (5) is approximately 1, finally gives:

$$J_i = \frac{P_i}{1} C_{i_\mathrm{f}}{}^{1}\left(1 - \frac{p_{i_\mathrm{p}}{}^{1}}{p_{i_\mathrm{f}}{}^{1}}\right) \tag{6}$$

However, various assumptions are made to come to this equation: the pressure in the membrane is constant and equal to the feed pressure; concentrations in the permeate are small; the diffusion coefficient, activity coefficient, and partial molar volume are independent of concentration; the concentration of the penetrants in the membrane is low; sorption equilibrium exists at the membrane interphases; and the partial molar volume of the components in the membrane is equal to that in the feed. This equation is thus only valid when small quantities permeate through the membrane, and when concentrations within the membrane do not change significantly.

When the permeate pressure is negligible, the model leads to a simple expression for the separation factor:

$$\left.\begin{aligned} J_i &= C_i^{\mathrm{p}} \rho_{\mathrm{tot}} J_{\mathrm{tot}} = \frac{P_i}{l} C_i^{\mathrm{f}} \\ J_j &= C_j^{\mathrm{p}} \rho_{\mathrm{tot}} J_{\mathrm{tot}} = \frac{P_j}{l} C_j^{\mathrm{f}} \end{aligned}\right\} \Rightarrow \frac{C_i^{\mathrm{p}}/C_j^{\mathrm{p}}}{C_i^{\mathrm{f}}/C_j^{\mathrm{f}}} = \alpha = \frac{P_i}{P_j} \tag{7}$$

However, when comparing this model with experiments where interactions between the different feed components are important, a varying permeability with concentration is observed. Thus, attempts were made to incorporate flux coupling into the solution-diffusion model. One way to do this is by assuming a varying permeability with feed composition. Rautenbach and Albrecht[12] explicitly considered the permeation as a combination of sorption and diffusion, and described the influence of both processes separately. Feed component interactions are taken into account in the sorption coefficient, and flux coupling in the diffusion coefficient. Comparison between experiments and model showed good agreement when limited to low permeate pressures.

Other researchers tried to model sorption and diffusion separately.[13] It was also suggested to include formation of dimers or of other associations between different feed components. Specifically for the separation of water–ethanol mixtures, formation of a water–ethanol dimer was reported.[14] Membrane interactions can be taken into account, by introducing an extra convective flux, due to such imperfections.[15] Bausa and Marquardt[16] rejected the homogeneity of the membrane. The membrane is supposed to consist of two phases: an embedded phase (the polymer and sorbed water molecules) and a dissolved phase (water and ethanol molecules). Mulder[17] describes the effect of swelling on the membrane performance: with increasing swelling, all feed components can permeate more easily, thereby increasing total flux, but decreasing the separation factor. Other researchers rejected the solution-diffusion mechanism, and described the transport with a pore flow model,[18] a combination of both,[19,20] or treated the process as a black box, using parameters with only empirical meaning[13,15]

These models were in most cases tested for one- or two-component streams. Ternary mixtures were rarely considered, as the addition of a third component to the feed increases the number of possible interactions, thereby complicating the modeling. This lack of experimental observations results in a limited understanding of transport characteristics when mixtures are used and is, therefore, an impediment for successful modeling and application of pervaporation.

EXPERIMENTAL

Instrumentation

All pervaporation experiments were carried out with a laboratory test cell (lab test cell unit, Sulzer Chemtech, Neunkirchen, Germany). The feed was heated in a 3-L stainless steel container and kept at constant temperature by a temperature control unit. A centrifugal pump circulated the feed. The membrane module contained a circular flat sheet membrane with a diameter of 6″ (152.4 mm). A more detailed description of the pervaporation module is given by Dotremont et al.[21] The permeate was collected in a glass container cooled in a Dewar flask containing liquid nitrogen. The vacuum was maintained by a two-stage vacuum pump. After 30–90 min (depending on the flux), a valve between the permeate side of the membrane and the glass container was closed, and the container was replaced by an empty one, after which the valve was reopened.

Membrane

All experiments were conducted with PERVAP 2201 membranes (Sulzer Chemtech). These membranes are hydrophilic polymeric membranes consisting of a polyvinylalcohol (PVA) active layer and a support of polyacrylonitrile (PAN). They can be used up to temperatures of 100°C. The major chemical constraints are: maximum 90% water, 50% organic acids, and 1% mineral acids in the feed.

Permeate and Feed Analysis

Permeate flux was determined gravimetrically by weighing the glass container before and after permeate collection. The balance used has a weighing capacity of 180 g, with an accuracy of 10^{-4} g. Methanol and ethanol were determined in the permeate and retentate by gas chromatography (GC) using a HP 5890 Series II gas chromatograph (column: J & W Scientific, DB1 30 m*0.53 ID, THK film 5.0 μm; FID detector, Delaware, USA) and a Shimadzu GC-14A gas chromatograph (column 80/120 Carbopack B/3% SP–1500, FID detector, Tokio, Japan) using IPA as internal standard. During the analysis, the column was held at a constant temperature of 140°C, while the injector and the detector were maintained at 200°C. The water concentration of permeate and retentate was calculated from the methanol and ethanol concentration as the amount needed to add up to 100%. Each sample was measured three times.

Experiments

Five series of experiments were carried out: binary mixtures methanol–water (M/0/W), binary mixtures ethanol–water (0/E/W), ternary mixtures prepared with 5 vol% water (apparent vol%, see further for explanation) and variable ethanol and methanol fractions (M/E/5), ternary mixtures prepared with 10 vol% water (apparent vol%) and variable ethanol and methanol fractions (M/E/10), and ternary mixtures prepared with 20 vol% water (apparent vol%) and variable ethanol and methanol fractions (M/E/20). The apparent volume fractions may be different from the actual vol% in the resulting mixture because of volume effects on mixing. The methanol and ethanol concentrations in the feed mixtures were measured with GC, and these results were then used to calculate activities with UNIFAC using the freeware program VLECalc.[22] Figure 1 gives the calculated activity constants for the binary mixtures as a function of vol% water in the liquid mixture. All

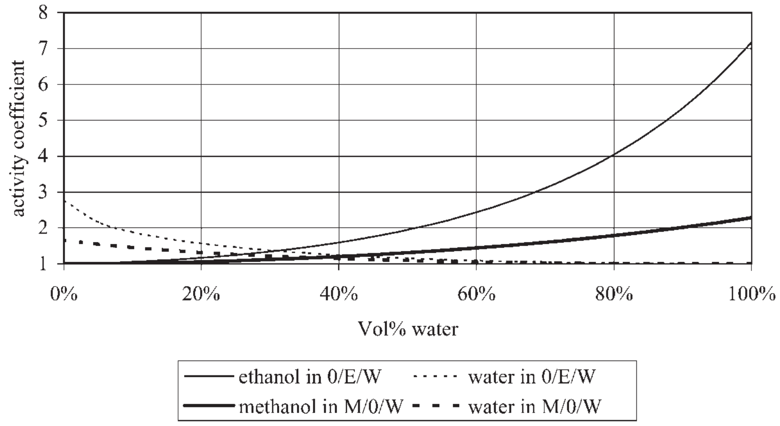

Figure 1. Activity coefficients as a function of vol% water in the liquid for the binary methanol–water mixtures and the binary ethanol–water mixtures.

series covered the whole concentration range with the restriction that the membrane was not used at water concentrations above 90 wt%.

A feed temperature of 60°C was used in all experiments and a permeate pressure of 10 mbar. When the temperature reached a steady value (approximately after 1 hr), permeate collection started, and for every considered mixture, four permeate samples were collected. The feed flow velocity was 2 L/min, resulting in a Reynolds number of approximately 100 (calculated in the same way as Dotremont et al.[21]). Effects of concentration polarization were neglected, because this study aimed at the observation of trends, rather than a precise calculation of fluxes with the models previously mentioned. Although concentrations may shift somewhat due to concentration polarization, the trend of the observed flux as a function of activity is independent of concentration polarization.

RESULTS AND DISCUSSION

Deviations from the ideal solution-diffusion model [Eq. (6)] may be caused by interactions between the different components in the feed. The occurrence of these interactions can be seen in Fig. 1, and is also known to exist from the vapor–liquid equilibrium diagram of the binary systems ethanol–water and methanol–water (ethanol–water even shows an azeotrope at atmospheric pressure).

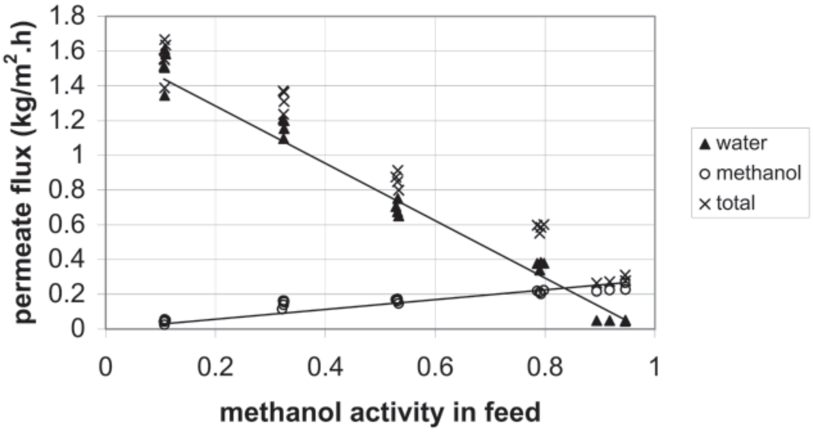

Figure 2. Partial and total permeate fluxes as a function of methanol activity in the feed for binary M/0/W mixtures.

Binary Mixtures

In a first step, the binary mixtures are studied in detail. For the binary mixture M/0/W, partial fluxes as a function of methanol activity are given in Fig. 2. The partial methanol flux increases linearly as a function of methanol activity, the partial water flux decreases linearly. As a consequence, also a linear correlation exists between methanol activity in the feed and total flux. These observations are in line with the model of Lee,[11] implying no interactions between methanol and water during permeation.

In Fig. 3, the water-methanol separation factor is shown as a function of the methanol activity in the feed. For methanol activities under 0.8, the separation factor is in agreement with expectations:[17] the separation factor increases with increasing methanol activity, i.e. decreasing activity for the preferentially permeating component, water. However, for activities above 0.8, the separation factor drops again to a low value. At such high methanol content in the feed, there is a competition between water and methanol for the available sorption sites. Although methanol is a larger and less polar molecule than water, it sorbs significantly into the membrane at very high concentrations, until finally the excess of methanol favors the permeation of methanol.

The permeation of the binary 0/E/W mixtures shows a very different behavior. The partial methanol flux (in the M/0/W mixture, ○ in Fig. 2) increases with increasing methanol activity, whereas the partial ethanol flux (in the 0/E/W mixture, ◇ in Fig. 4) decreases with increasing ethanol

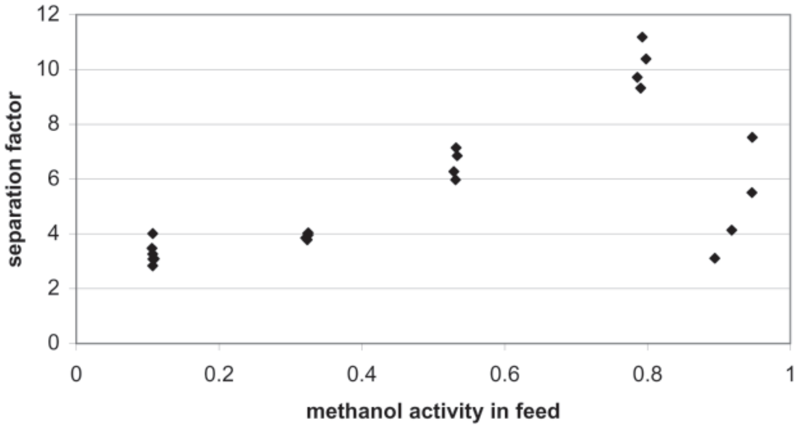

Figure 3. Water–methanol separation factor as a function of methanol activity in the feed for the binary M/0/W mixture.

activity. This is contradictory to the solution-diffusion model, where flux is proportional to the gradient in chemical potential, implying an increasing flux with increasing feed concentration. The explanation of the unexpected behavior can be found in the chemical nature of ethanol and of the membrane. Since the membrane is hydrophilic, it has a high affinity for polar molecules. At moderate and low water content, the partial ethanol fluxes are one order of

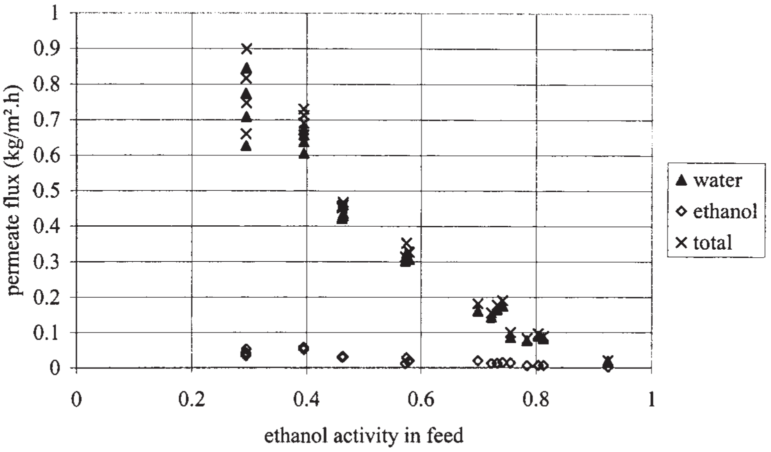

Figure 4. Partial and total permeate fluxes as a function of ethanol activity in the feed for binary 0/E/W mixtures.

magnitude smaller than those for methanol [partial ethanol flux for 0/E/W at water activity of 0.60 (ethanol activity of 0.73) is 0.013 kg/m^2 hr, partial methanol flux for M/0/W at water activity of 0.63 (methanol activity of 0.53) is 0.17 kg/m^2 hr]. It can thus be concluded that ethanol is not polar enough, or too large to be significantly sorbed into the membrane, in contrast to methanol. However, if sufficient water is present, permeation of ethanol is possible, presumably because the ethanol molecules can be shielded from the membrane by water molecules surrounding the polymer chains, as suggested by Bausa and Marquardt,[16] or surrounding the ethanol. The latter suggests a sort of association between water and ethanol molecules, forming a larger structure that is able to sorb and penetrate. One possible association is dimer-formation, as suggested by Radovanovic et al.[14] It was attempted to fit the experimental results to this theory (Fig. 5). The theory predicts a linear relationship between partial water flux divided by water activity in the feed and ethanol activity in the feed, with a positive slope. This was not confirmed by the experiments [although the linear correlation is good (R^2 equals 0.925), the slope is *negative*] and it can be concluded that the formed structure is not a dimer.

Figure 6 gives the separation factor as a function of the ethanol activity in the feed. At high ethanol activities (low water content), the separation factor is much higher than at low ethanol activities (high water content). This behavior confirms the observations of Mulder[21] (swelling increases when the feed concentration of the preferentially permeating component increases) and is

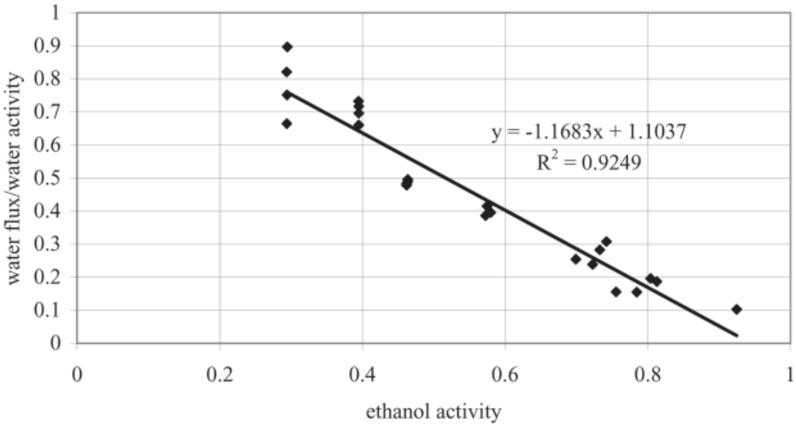

Figure 5. Testing of the hypothesis of dimer formation: partial water flux divided by water activity in the feed as a function of ethanol activity in the feed for the 0/E/W mixture.

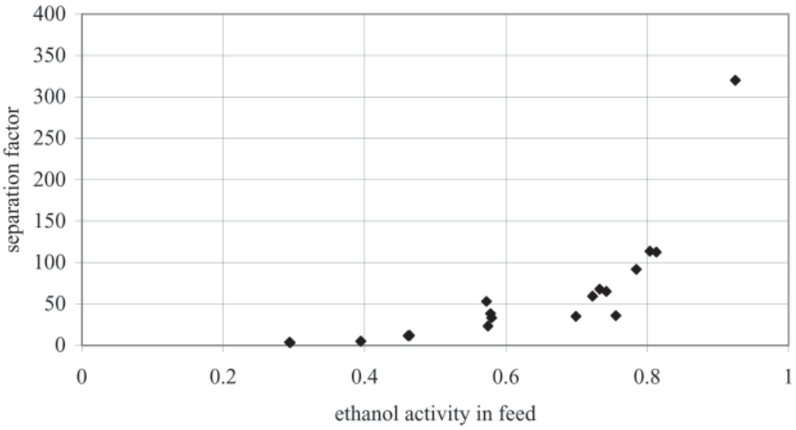

Figure 6. Ethanol separation factor as a function of ethanol activity in the feed for the binary 0/E/W mixture.

beneficial for the intended application of the membrane, being the dewatering of organic solvents. A negative point of the observed behavior is the low water flux at high ethanol activity.

Ethanol concentration in the permeate was between 5 and 8 vol%, without apparent trend. The assumption that ethanol permeation requires the presence of sufficient water is confirmed by the fact that the ethanol concentration in the permeate is relatively independent of the feed concentration, proving there is no competition for the sorption places of the membrane: for the binary 0/E/W, this means on average that transport of 1 molecule of ethanol requires permeation of 50 molecules of water.

The permeation behavior of ethanol also suggests that the membrane is not homogeneous (in contrast to the assumptions of the solution-diffusion model), confirming the theory of Bausa and Marquardt.[16] Permeation of ethanol is only possible if voids are present in the membrane (the free volume), filled with water, in which the ethanol can subsequently be dissolved. The more water in the feed, the more water is sorbed, resulting in swelling of the membrane and an increase in free volume, which enhances ethanol permeability.

Ternary Mixtures

In a next step, pervaporation with ternary mixtures was studied and compared to the pervaporation behavior of the binary mixtures. The effect of adding a third component to the feed is apparent when the partial water fluxes of the different mixtures are compared (Table 1): firstly, the partial water fluxes of the ternary mixtures are higher than or comparable to those of the binary water-ethanol mixtures with the same amount of water, but lower than those of the binary water-methanol mixtures. All ternary mixtures contained at least 5 vol% ethanol, which decreases water permeation and flux significantly.

Secondly, the competition between methanol and water at low water and high methanol activity can be seen: for M/E/5, the partial water flux decreases with increasing methanol fraction from 0.075 kg/m^2 hr to 0.04 kg/m^2 hr. However, for M/E/10 and M/E/20, the partial water flux is nearly stable, without a definite increasing or decreasing trend.

Adding a third component to the feed also leads to an interesting observation when the value of the water–methanol separation factor for the binary M/0/W mixture is compared with the values of the ternary mixtures (Table 2). At a methanol activity of 0.3 the separation factor for the binary mixture is 4 (see also Fig. 3), while for the ternary mixtures at approximately the same methanol activity, all values are higher than 25, meaning less methanol in the permeate relative to the amount of water. Again, the presence of ethanol in the feed lowers the tendency of methanol to sorb into the membrane. In the ternary mixtures considered here, there is at least 50 wt% ethanol, making the feed much less polar than the feed of the binary mixture. Therefore, methanol prefers staying in the feed rather than sorbing into the polar membrane. This can also be seen in Fig. 1: the activity coefficient for methanol increases at high water fractions, indicating strong repulsive interaction between water and methanol molecules.

When the ternary mixtures with increasing water content are compared, the separation factor for the ternary mixtures at an approximate methanol activity of 0.3 is 25 for the mixture with 5 vol% water, 30 for the mixture with 10 vol% water, and 45 for the mixture with 20 vol% water. As the water content increases, water sorption dominates more and more over methanol

Table 1. Numerical values of partial water flux (L/m^2 hr) as a function of water content for the different feed mixtures.

	5 vol% water	10 vol% water	20 vol% water
M/0/W	0.06	0.2	0.45
0/E/W	0.04	0.0838	0.1728
M/E/5	0.075–0.04		
M/E/10		0.1–0.13	
M/E/20			0.15–0.18

Table 2. Comparison of the water–methanol separation factor for the different types of mixtures and the water–ethanol separation factor for the different types of mixtures.

Water activity in the feed		Water–methanol separation factor at methanol activity of 0.3	Water–ethanol separation factor at ethanol activity of 0.4–0.45
M/0/W	0.81	4	
0/E/W	0.90		12
M/E/5	0.18	25	
	0.15		50
M/E/10	0.32	30	
	0.33		60
M/E/20	0.54	45	
	0.61		120

sorption, decreasing methanol sorption and increasing the separation factor. So, with increasing water content, two effects have a conflicting influence: on the one hand, the increasing water content decreases methanol sorption, thereby increasing the separation factor; and on the other hand, the increasing water content increases the polarity of the feed, thereby increasing the methanol sorption into the membrane, and decreasing the separation factor. The latter effect dominates at high water content, leading to the low separation factor (4) for the binary mixture; the former dominates at low water content, leading to an increase of the separation factor from 25 to 45 when the water content increases from 5 to 20 vol%. A similar trend applies to the water–ethanol separation factor. At an ethanol activity of 0.46, the binary 0/E/W mixture shows an average separation factor of 12. The ternary mixtures on the other hand, show average separation factors of 50, 60, and 120 for M/E/5, M/E/10, and M/E/20, respectively at ethanol activities ranging from 0.37 to 0.43.

However, when the water–alcohol separation factor (this separation factor is calculated as a regular separation factor, but instead of using the methanol or ethanol concentration, the sum of both is used) is taken as a function of water activity in the feed for the five different mixtures (Fig. 7), the curves of the binary mixtures form the upper and lower sides of a triangle. The separation factors of the ternary mixtures fall in between these boundaries, with the separation factors being close to the binary methanol line for methanol-rich mixtures, and close to the binary ethanol line for ethanol-rich mixtures.

In Fig. 8, the permeate composition is given as a function of methanol activity in the feed. As stated earlier, when the water-to-methanol ratio

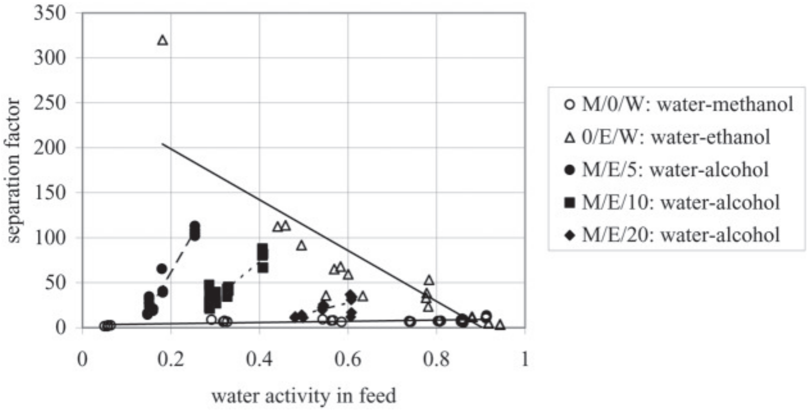

Figure 7. Water–alcohol separation factors as a function of water activity in the feed for the binary and ternary mixtures.

increases, the competition for sorption places decreases: for M/E/5 the water content increases from 50% to 90%, for M/E/10 from 70% to 95%, and for M/E/20 from 90% to 97%. In Fig. 9, the mass percentage water in the permeate is given as a function of the water activity in the feed. The curves of the ternary mixtures are located between the boundaries set by the binary mixtures, as was the case for the water–alcohol separation factor.

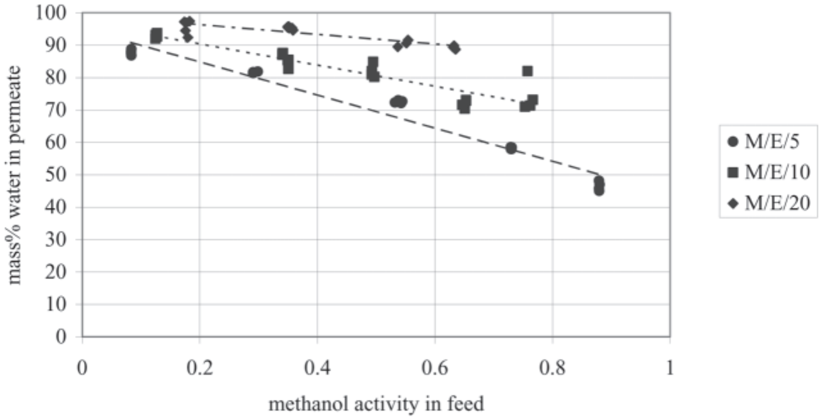

Figure 8. Permeate composition as a function of methanol activity in the feed for the ternary mixtures.

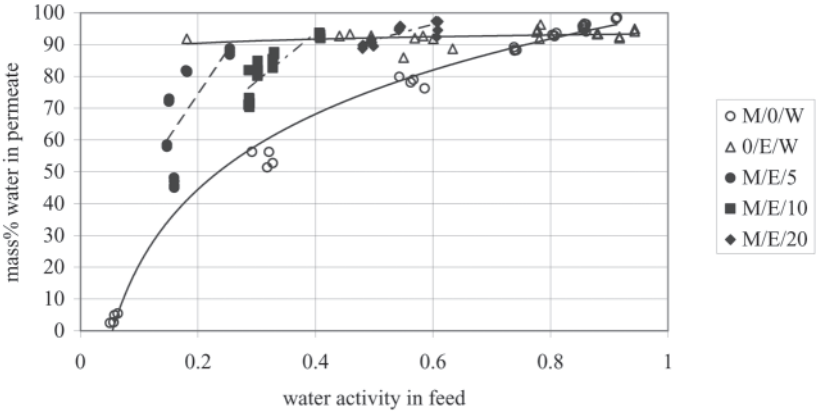

Figure 9. Permeate composition as a function of water activity in the feed for the binary and ternary mixtures.

CONCLUSION

From the experiments, it is clear that significant interactions occur between the feed components and the membrane, and between the different feed components. These interactions have a consequence on the pervaporation behavior of the different components, thus affecting flux and selectivity. The deviations from ideal, noncoupled permeation (as assumed by the solution-diffusion model) were explained qualitatively. At high methanol activities, methanol competes with water for the sorption sites of the membrane. Ethanol is unable to sorb into the membrane without sufficient water to shield the ethanol. When two alcohols are present in the feed, the water–methanol and the water–ethanol separation factor increases dramatically in comparison with the binary mixtures: the alcohol molecules have less tendency to sorb into the hydrophilic (and thus polar) membrane when the feed is less polar. It seems feasible to model quantitatively the water–alcohol separation factor and the permeate concentration as a function of water activity. In the future, water–IPA mixtures will be studied to test some of the hypotheses made here. Also, experiments with water–acetic acid mixtures will be carried out to test the importance of molecular weight vs. functional group.

SYMBOL LIST

$a_i(x)$ = activity of component i in a mixture, defined as partial pressure divided by the pure vapor pressure (−)

$C_i(x)$ = concentration of component i (kg/m^3)
C_i^{f}, C_i^{p} = concentration of component i in the feed and the permeate, respectively (kg/m^3)
$D_i(x)$ = diffusion coefficient for component i (m^2/s)
J_i, J_j = partial permeate flux of component i respectively component j (kg/m^2 sec)
J_{tot} = total permeate flux (kg/m^2 sec)
l = thickness of the active layer of the membrane (m)
$p(x)$, p_{ref} = pressure (Pa)
p_i = partial pressure of component i (Pa)
P_i = permeability of component i (m^2/sec)
R = universal gas constant (8.3145 J/K mol) (J/K mol)
S_i = partial entropy of component i (J/K mol)
T, $T(x)$, T_{ref} = temperature (K)
v_i = partial molar volume of component i (m^3/mol)

Greek Letters

α = separation factor between component i and j, with i being the preferentially permeating component (−)
γ_i = activity coefficient of component i (−)
ρ_{tot} = density of the (feed) mixture (kg/m^3)
$\mu_i(x)$, $\mu_{i,\mathrm{ref}}$ = chemical potential of component i (J/mol)

Subscripts

f = property in the feed or on the feed side of the membrane
p = property in the permeate or on the permeate side of the membrane

Superscripts

m = property in the membrane, at the membrane interphase
l = property in the liquid or vapor phase, at the membrane interphase

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