

Pervaporation of alcohol–toluene mixtures through polymer blend membranes of poly(acrylic acid) and poly(vinyl alcohol)

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Abstract

Homogeneous membranes were prepared by blending poly(acrylic acid) with poly(vinyl alcohol). These blend membranes were evaluated for the selective separation of alcohols from toluene by pervaporation. The flux and selectivity of the membranes were determined both as a function of the blend composition and of the feed mixture composition. The results showed that a polymer blending method could be very useful to develop new membranes with improved permselectivity. The pervaporation properties could be optimized by adjusting the blend composition. All the blend membranes tested showed a decrease in flux with increasing poly(vinyl alcohol) content for both methanol–toluene and ethanol–toluene liquid mixtures. The alcohols permeated preferentially through all tested blend membranes, and the selectivity values increased with increasing poly(vinyl alcohol) content. The pervaporation characteristics of the blend membranes were also strongly influenced by the feed mixture composition. The fluxes increased exponentially with increasing alcohol concentration in the feed mixtures, whereas the selectivities decreased for both liquid mixtures.

Key words: Pervaporation; Organic/organic separation; Poly(acrylic acid); Poly(vinyl alcohol); Polymer blend

1. Introduction

At the very early stage of pervaporation research it was recognized that this process possesses a high potential for the separation of organic liquid mixtures [1–4]. Since then much research has been carried out and reported [5,6]. Despite these studies no large-scale application for the organic–organic mixture separation in the chemical industry can be found so far. This is mainly due to the lack of good membranes for specific applications.

Three approaches are often followed to de-

velop ‘tailor-made’ materials: (a) synthesis of new polymers, (b) modification of existing polymers, and (c) polymer blending. The synthesis of new polymers or copolymers is the first way to prepare ‘tailor-made’ materials. Based on the knowledge of permeation and separation mechanism, specific membrane materials can be designed and synthesized for a given separation problem. For the pervaporation of organic liquid mixtures, many new polymers and copolymers were synthesized and tested [7–10]. These polymers generally showed an improved permselectivity when they contained specific groups which could preferentially interact with one component of a liquid mixture. In recent years new po-

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lymerization techniques such as radiation grafting and plasma grafting are also studied for the development of pervaporation membranes [11–13]. The modification of polymers can be done through a chemical reaction, a radiation or plasma treatment, or a combination of these methods. In this way specific groups are introduced to the polymer bulk [2,14] or only to the surface of polymer membranes [15]. A third method is the blending of existing polymers to produce materials with new properties. This approach has been tested for the development of membrane materials for the pervaporation of liquid mixtures, and promising results were observed [16–20].

The objective of material study is to develop membranes with both a high flux and a high selectivity. However, in most cases a so-called ‘trade-off’ trend can be found. This means that as the flux increases, then the selectivity decreases, or vice versa. For this reason membrane development is often characterized by an optimization procedure: the performance of membranes has to be adjusted for a given separation problem in order to achieve an optimal performance. For this purpose a polymer blend can offer a convenient tool. The aim of polymer blending is normally to create a new polymeric material that combines the properties of two (or more) homopolymers. In a homogeneous blend made of two polymers, the component polymers are mixed on a molecular level. In this case, the properties of the blend is generally in between those of two component polymers being related to the composition of the blend. This means that the physical and mechanical properties as well as the permeation properties of the blend can be influenced by changing the blend composition.

The main objective of this work is to develop new polymer membranes for the selective separation of alcohols from aromatic hydrocarbons by pervaporation. For this purpose a polymer blend concept was applied; in this study a blend of poly(acrylic acid) and poly(vinyl alcohol). The pervaporation property of this blend was evaluated for ethanol–toluene and methanol–toluene liquid mixtures.

2. Experimental

2.1. Materials

Poly(acrylic acid) (PAA) ($M_w=250,000$ g/mol) and poly(vinyl alcohol) (PVA) (96% hydrolyzed, $M_w=85,000$ – $146,000$ g/mol) were purchased from Aldrich Chemical Co. Methyl alcohol, ethyl alcohol, toluene, and isooctane (analytical grade) were obtained from Merck Co. They were used without any further purification. Water was demineralized before use.

2.2. Membrane preparation

Polymer blending was performed by a solution method. Both component polymers, PAA and PVA, were separately dissolved in water. The two solutions were mixed together in various proportions to obtain the desired polymer solutions. Homogeneous membranes were prepared by casting the polymer solution on a Perspex plate with a casting knife. The solvent, water, was slowly removed by evaporation in a flowing nitrogen gas stream at room temperature. The thickness of the resulting membranes was in the range of 15 to 60 μm .

2.3. Glass transition temperature measurements

The glass transition temperature of PAA, PVA, and blends of these two polymers was measured calorimetrically with a Perkin–Elmer Differential Scanning Calorimeter (DSC 4). The sample size ranged from 10 to 20 mg. DSC curves were recorded at a constant heating rate of 10 K/min. The temperatures at the midpoint of the heat capacity transition in the DSC curves were taken as the glass transition temperatures.

2.4. Density measurements

The density of the membranes was measured with a buoyancy technique. A well-dried membrane sample was first weighed in air. Thereafter it was held in isooctane at 22.5°C and its weight was measured in that medium. The volume of the sample can be calculated from the weight dif-

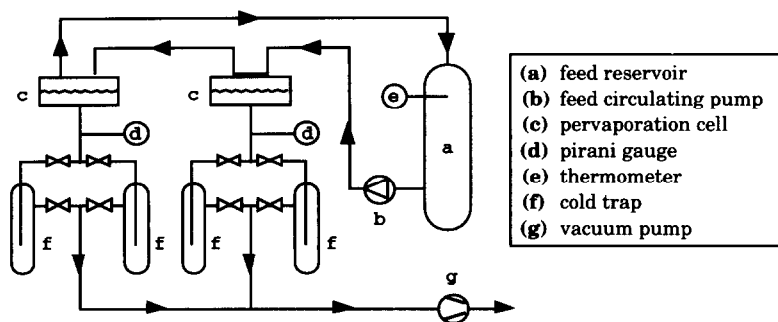


Fig. 1. Schematic representation of the pervaporation apparatus.

ference of both measurements; dividing it by the density of isooctane. From the weight in air and the volume, the density can be calculated.

2.5. Pervaporation experiments

The pervaporation experiments were performed using the apparatus shown in Fig. 1. Membranes which were immersed and swollen in the respective feed mixtures at room temperature were installed in the stainless steel pervaporation cells. The effective membrane area in each cell was 50 cm². The feed was circulated through the pervaporation cells from a feed reservoir kept at 30°C at a rate of ~1 l/min. The pressure at the downstream side was kept below 2 mmHg by a vacuum pump. The permeate was collected in cold traps cooled by liquid nitrogen. The composition of the collected permeate was determined by gas chromatography equipped with a thermal conductivity detector.

The pervaporation properties are characterized by the flux J and the selectivity α_p . Fluxes were determined by measuring the weight of liquid collected in the cold traps during a certain time at steady-state conditions. The fluxes of different membranes were normalized to a membrane thickness of 20 μm , assuming a proportionality between the flux and the reciprocal membrane thickness. The pervaporation selectivity α_p is defined by:

$$\alpha_p = (y_1/y_2)/(x_1/x_2) \quad (1)$$

where x and y represent the concentrations in the feed and in the permeate, respectively. Indices 1

and 2 refer to the more permeable component (methanol or ethanol in this study) and the less permeable one (toluene), respectively.

3. Results and discussion

3.1. Physical properties of the PAA–PVA blend

The properties of a polymer blend depends strongly on whether the blend is homogeneous or heterogeneous. Although it can be argued how to characterize homogeneity, the existence of only one glass transition temperature (T_g) is often a clear indication [21]. A miscible blend of two homopolymers shows a single T_g which is generally in between the T_g values of the individual polymers.

The polymer samples were carefully dried to remove completely the casting solvent, water. The presence of any solvent in a polymer sample can lower the measured T_g value due to a plasticizing effect. The samples were first dried by blowing dry nitrogen gas for 2–4 days at room temperature, and then dried for another day in a vacuum oven at room temperature.

The measured glass transition temperatures of PAA, PVA, and their blends are given in Fig. 2. The glass transition temperature decreases gradually from 129 to 84°C with an increase of the PVA content from 0 to 50 wt%. Over this composition range each blend shows only one T_g value, indicating that the blend is homogeneous. This was also confirmed by the transparency of the membranes.

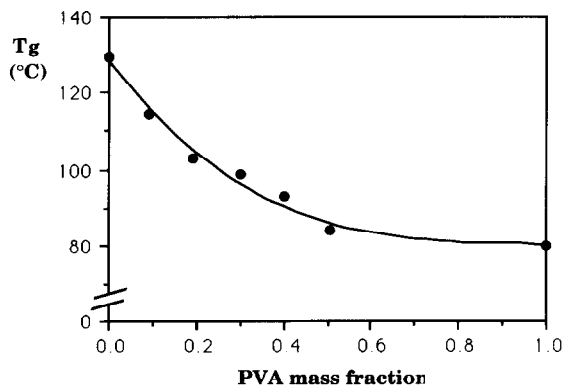


Fig. 2. Glass transition temperatures (T_g) of the PAA-PVA blend as a function of the blend composition.

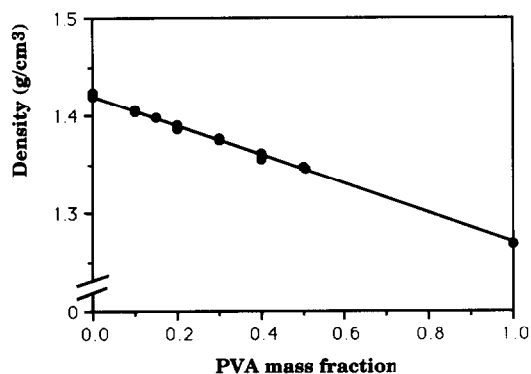


Fig. 3. Density of the PAA-PVA blend at 22.5°C, as a function of the blend composition: density of amorphous PVA = 1.27 g/cm³ [22].

The density of the blends was measured to determine the presence of crystallites. Since PVA is a semi-crystalline polymer, it may aggregate into small crystalline domains. The measured density values are plotted against the PVA content (see Fig. 3). This figure shows that all measured densities are lying on a straight line connecting the densities of pure PAA and amorphous PVA. From this figure it appears that in the composition range of 10 to 50 wt% PVA there is no or a negligible crystalline fraction in the blends.

3.2. Pervaporation characteristics of the PAA-PVA blend

The separation of alcohol-toluene mixtures through PAA-PVA blend membranes was eval-

uated to investigate the polymer blend concept in developing membrane materials. Since this study was focussed on the selective removal of alcohols from organic mixtures, PAA was selected as a polymer material based on its high affinity for alcohols. PAA is highly swollen or even soluble in the low molecular weight aliphatic alcohols such as methanol and ethanol. In addition, PAA can preferentially interact with alcohols through hydrogen bond formation. To improve both mechanical stability and permselectivity towards alcohol-toluene liquid mixtures, PAA has been blended with PVA which is hardly swollen in alcohols. No degradation or change in properties for the blends has been observed during the tested period up to three weeks. The thermal stability of the blends have been tested up to a temperature of 50°C and this has been described elsewhere [27].

PVA is reported to be very selective for alcohols over hydrocarbons [23]. The blend membranes were preswollen in the feed prior to the pervaporation experiment. The preswelling occurs in a mixture with a higher alcohol concentration than the actual pervaporation experiment and this results in a higher flux. This phenomenon has been described in more detail elsewhere [27]. The pervaporation characteristics of the PAA-PVA blend membranes for the ethanol-toluene and the methanol-toluene liquid mixtures are presented in Figs. 4 and 5, respectively. In these figures the flux and the selectivity are given as a function of the PVA concentration in the blend. The fluxes of different membranes are normalized to a membrane thickness of 20 μm since it is very difficult to make every membrane exact 20 μm thick, and the selectivity is calculated according to Eq. (1). Within the range of membrane thickness (15 to 60 μm) the proportionality between fluxes and reciprocal membrane thickness has been confirmed experimentally.

It can be observed, as expected, that the transport properties of the PAA-PVA blends depend strongly on the PAA/PVA ratio in the blend. The pervaporation flux decreases gradually for all feed mixtures with different compositions as the PVA content in the blends increases from 10 to 40

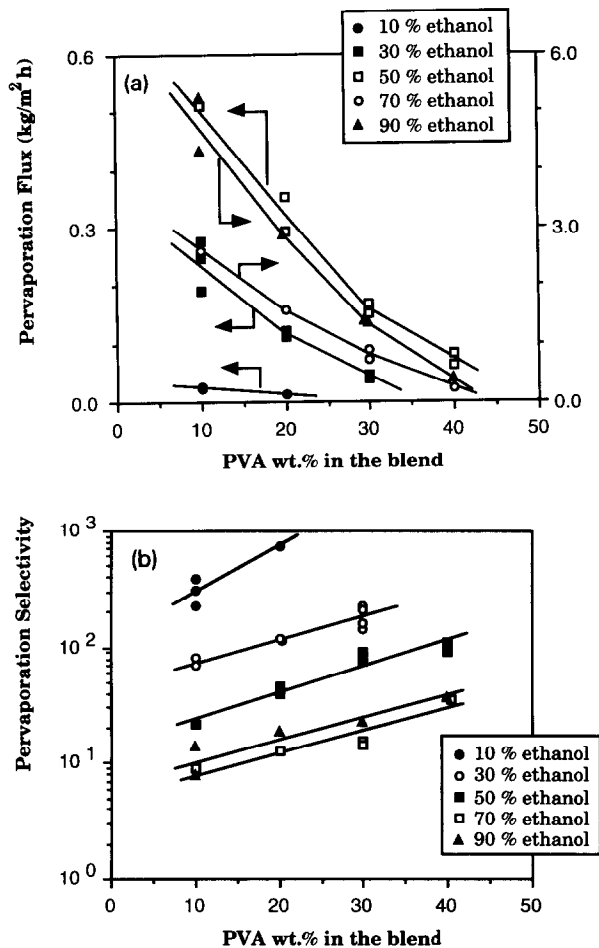


Fig. 4. Pervaporation characteristics of PAA-PVA blend membranes for ethanol-toluene liquid mixtures, as a function of the blend composition. Note the different scale on the ordinates in (a).

wt%. These figures show that by controlling the PVA amount in the blend a great variety of fluxes can be obtained for any feed mixture. In the case of a feed mixture of ethanol-toluene (1/1 by wt), for example, a flux decline from 0.51 to 0.07 $\text{kg/m}^2 \text{h}$, about one order of magnitude, can be observed as the PVA content increases from 10 to 40 wt%. The reason for this behavior is probably the reduced swelling of the blend membranes. PAA is soluble in ethanol, whilst PVA is very little swollen in ethanol [24]. Therefore the higher the PVA content is, the less the membrane is

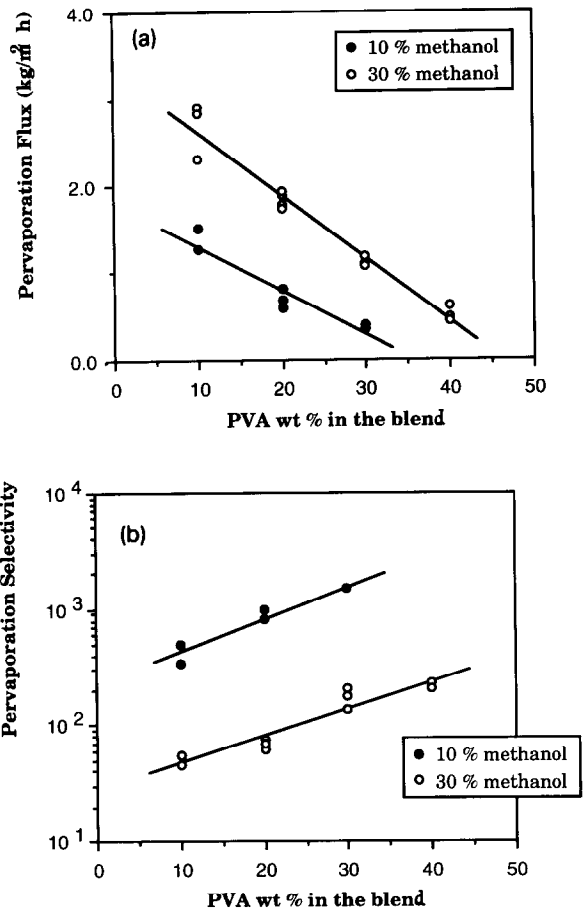


Fig. 5. Pervaporation characteristics of PAA-PVA blend membranes for methanol-toluene liquid mixtures, as a function of the blend composition.

swollen. This decreasing sorption ability results in a decreasing penetrant concentration in the membrane, and consequently results in a decreasing permeation rate.

The increasing content of PVA in the membrane has a favorable effect on the selectivity. All membranes are selective to methanol and ethanol, and the selectivity increases with increasing PVA content in the blend.

The total flux J can be divided into the component flux of alcohol, J_{alcohol} , and that of toluene, J_{toluene} , by using the permeate composition data:

$$J_{\text{alcohol}} = J \times y_{\text{alcohol}} \quad (2)$$

$$J_{\text{toluene}} = J \times y_{\text{toluene}} \quad (3)$$

where y_{alcohol} and y_{toluene} are the concentrations of alcohol and toluene in the permeate, respectively. As an example, the component fluxes of an ethanol–toluene (1/1 by wt) mixture calculated from these equations are given in Fig. 6 as a function of the blend composition. This figure clearly indicates that for this system the increase in selectivity is attributed to a more rapid decrease in the toluene component flux compared to ethanol with increasing PVA content. For all other mixtures the same trend is observed.

3.3. Influence of the feed composition

The permeation of molecules through a non-porous polymer membrane is generally described by a solution–diffusion mechanism in a sequence of three steps: sorption, diffusion, and evaporation. According to this model the permselective properties of pervaporation membranes are determined by solubility and diffusivity of the permeating components in the membrane. Because generally both sorption and diffusion phenomena are dependent on the composition of the liquid mixture, also the permeation characteristics of membranes are usually strongly influenced by the feed composition.

The effect of the feed composition on the flux

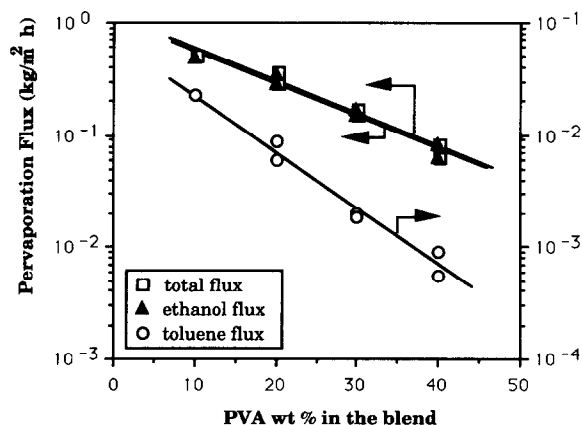


Fig. 6. Total and component fluxes of an ethanol–toluene (1/1 by wt) mixture through PAA–PVA blend membranes, as a function of the blend composition.

and selectivity was investigated over the whole mixture concentration range for ethanol–toluene mixtures. Fig. 7 represents the effect of the feed composition on the pervaporation fluxes. Although low fluxes are obtained when the ethanol content in the feed is low, the fluxes increase strongly for all blend membranes as the ethanol concentration increases. For instance, in the case of a blend membrane containing 10 wt% PVA the flux for the ethanol–toluene liquid mixture increases exponentially from 0.025 to 4.8 kg/m² h, i.e., more than two orders of magnitude, as the ethanol concentration increases from 10 to 90 wt%. For all the other blends the same trend is observed, which indicates a strong interaction between the membrane and the feed mixture components.

Fig. 8 shows the ethanol concentration in the permeate as a function of the feed composition together with the vapor–liquid equilibrium curve of the ethanol–toluene mixtures at 30°C for comparison. The vapor–liquid equilibrium data were calculated from the Wilson equation with parameters obtained from the literature [25]. For all blends tested the ethanol concentration in the permeate was higher than 95 wt%. This is much higher than the ethanol concentration in the vapor which is in equilibrium with the liquid. Furthermore, the separation problem of the azeotrope could easily be overcome.

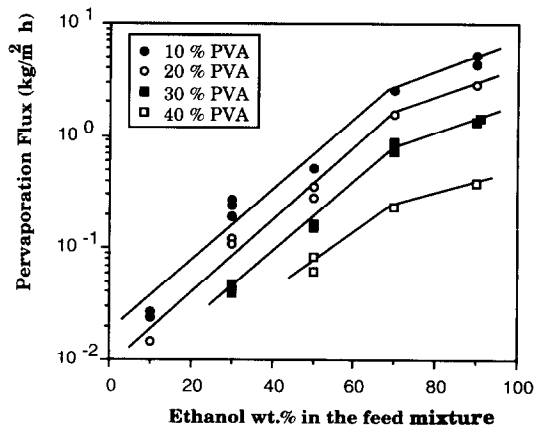


Fig. 7. Influence of the feed composition on the pervaporation flux of ethanol–toluene mixtures through various PAA–PVA blend membranes.

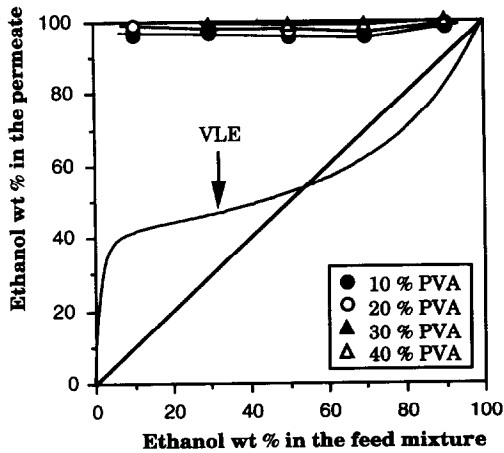


Fig. 8. Permeate composition in the pervaporation of ethanol-toluene mixtures through various PAA-PVA blend membranes, as a function of the feed composition. The vapor-liquid equilibrium curve is also given.

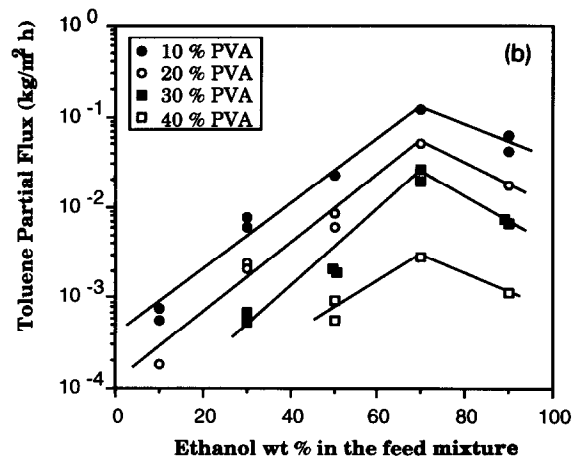
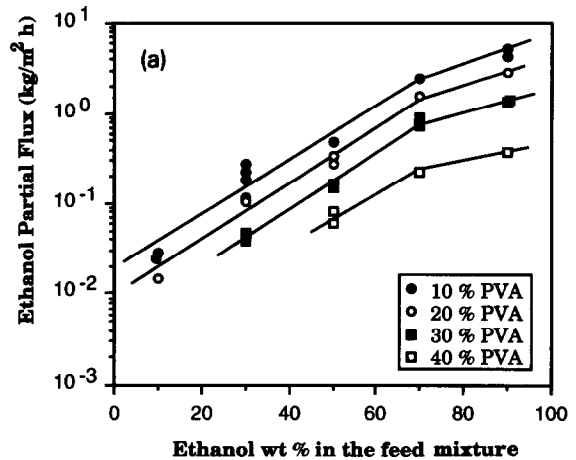


Fig. 10. Component fluxes of ethanol (a) and toluene (b) through various PAA-PVA blend membranes as a function of the ethanol concentration in ethanol-toluene liquid mixtures.

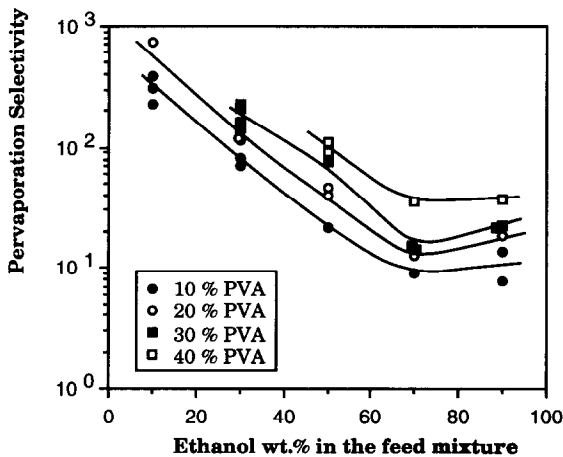


Fig. 9. Influence of the feed composition on the pervaporation selectivity of ethanol-toluene mixtures through various PAA-PVA blend membranes.

The selectivity values are presented in Fig. 9. The selectivity first decreases with increasing ethanol content up to 70 wt%, and then remains more or less constant. This seems to be related to the variation in the component flux of toluene. Fig. 10 represents the component fluxes of ethanol and toluene for the ethanol-toluene liquid mixtures. It is clearly seen from this figure that the component flux of ethanol for the blends

of various compositions follows practically the same trend and the same degree of variation as the total flux with increasing ethanol content in the feed mixture (compare Fig. 10a with Fig. 7). However, the toluene flux shows a different dependency (see Fig. 10b). These fluxes first increase exponentially as the ethanol concentration increases up to 70 wt%. However, as the ethanol concentration increases from 70 to 90 wt%, the toluene fluxes decrease. In the concentration range below 70 wt% ethanol, the slope of the increase in the toluene fluxes is steeper com-

pared to ethanol. This more rapid increase of the toluene fluxes causes a loss in selectivity. However, in the ethanol concentration range between 70 and 90 wt%, the ratio of component fluxes of ethanol and toluene is equal to the concentration ratio of ethanol and toluene in the feed mixture. Hence the selectivity remains constant.

The initial increase in the toluene component fluxes might be related to the swelling of the membranes. When a penetrant i diffuses through a membrane, the flux J_i is the product of the concentration C_i and the linear velocity v_i of the penetrant inside the membrane. The velocity is the product of mobility B_i and driving force. In the case of pervaporation, the driving force is a gradient in the chemical potential across the membrane, i.e., $-\mathrm{d}\mu_i/\mathrm{d}x$. Therefore the following relation expresses the flux in a pervaporation process [28]:

$$J_i = v_i C_i = -C_i B_i \mathrm{d}\mu_i/\mathrm{d}x \quad (4)$$

According to this relation the flux should decrease as the activity, i.e., the chemical potential, of a mixture component in the feed decreases because the activity in the permeate side is kept constant by a continuous evacuation. However, in the concentration range of ethanol between 10 and 70 wt%, the toluene permeability increases despite the decreasing activity. A possible explanation for this contradicting phenomenon might be the plasticization of the polymer matrix by the sorbed ethanol molecules. As liquid molecules are more sorbed into a polymer, then the polymer matrix becomes looser. Experimental evidence on sorption measurements are given elsewhere [26] showing an increase of sorption of ethanol–toluene liquid mixtures with increasing ethanol content in the mixtures. In a more swollen membrane the toluene molecules can permeate faster. At the same time, however, the driving force for the toluene permeation is continuously decreasing. These two opposing terms are compensating each other. Until an ethanol concentration up to 70 wt%, the effect of the plasticization of the polymer matrix seems to prevail over the decreasing driving force for the toluene permeation. Both effects should be of the same magnitude at around 70 wt% ethanol in the feed. At

higher ethanol concentrations the effect of the decreasing driving force might be predominant, which results in a decreasing toluene permeability.

3.4. Pervaporation of methanol–toluene mixtures

The pervaporation results for the methanol–toluene mixtures are given in Fig. 11. Here again the trend of the dependence of flux and selectivity on the feed composition is almost the same as that for the ethanol–toluene mixture. With in-

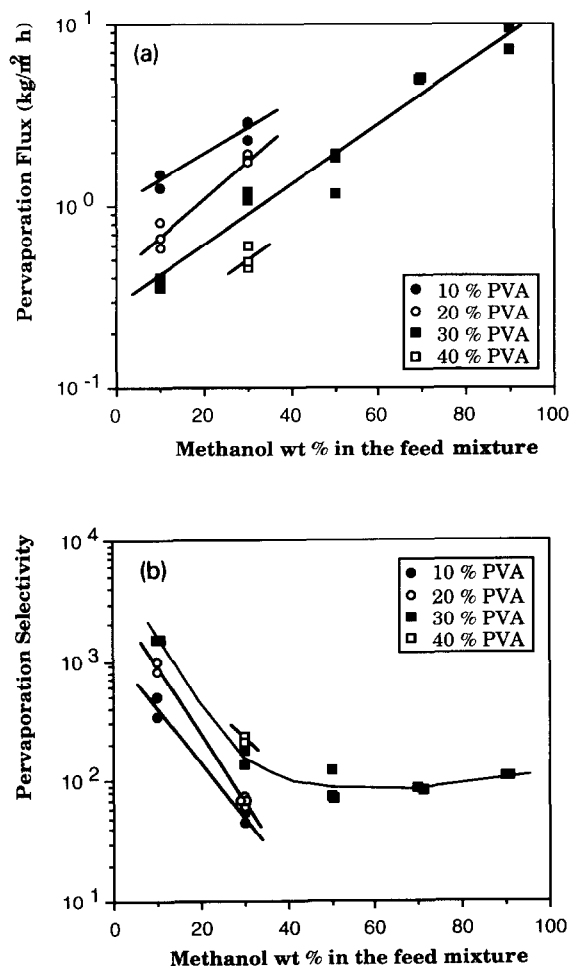


Fig. 11. Pervaporation flux and selectivity of methanol–toluene liquid mixtures through various PAA–PVA blend membranes, as a function of the feed composition.

creasing methanol concentration in the feed, the flux increases exponentially, while the selectivity first decreases and then remains constant.

From the comparison of the pervaporation characteristics of a methanol–toluene versus an ethanol–toluene mixture, it is observed that in the case of methanol–toluene the fluxes are much higher, about one order of magnitude, than in the case of ethanol–toluene for the same feed composition. This might be due to a different degree of interaction. Methanol shows a stronger affinity for the blend of PAA and PVA than ethanol since methanol is more polar and has a higher ability of hydrogen bonding. This stronger interaction results in a higher sorption, and thereby in a higher permeation rate of the methanol mixture than the ethanol mixture (the experimental evidence for the higher sorption of the methanol mixture is given in ref. 26). In addition, the difference in molecular size favors the permeability of methanol as well. The molar volume of methanol is about two thirds of that of ethanol, which implies that methanol, the smaller molecule, will permeate faster through a membrane than ethanol. Another reason is the difference in the activities of methanol and ethanol in a mixture with toluene. For example, the activity of methanol in a methanol–toluene mixture at 10 wt% methanol is 0.76, while the ethanol activity in an ethanol–toluene mixture at the same concentration is 0.62. Such a difference in activity results in a difference in driving force, and consequently in a difference in the pervaporation flux.

Despite the higher flux with the methanol mixture, the selectivities for both mixtures at lower alcohol content are about equal. This may be explained in terms of coupling phenomena. The higher permeation of methanol seems to be compensated by a higher permeation of toluene with roughly the same factor.

4. Conclusions

Transparent homogeneous membranes could be prepared from a polymer blend of PAA with PVA. Their pervaporation properties were investigated by using methanol–toluene and

ethanol–toluene liquid mixtures. For both mixtures high fluxes and high selectivities were observed, which were strongly dependent on the blend composition. The flux decreased gradually as the PVA content in the blends increased, whereas the selectivity increased. It implies that such a polymer blend can offer a convenient way to optimize the separation characteristics of a membrane for a particular separation task. This means that the separation characteristics of a blend membrane can easily be adjusted by varying the blend composition.

It was also observed that the membrane performance was strongly influenced by the feed mixture composition. For both mixtures the flux increased exponentially, but the selectivity decreased with increasing alcohol concentration in the feed.

In the case of methanol–toluene mixtures the fluxes are much higher, about one order of magnitude, compared to ethanol–toluene mixtures for the same feed composition (% by weight). This is due to a stronger affinity of methanol for the PAA–PVA blends than ethanol. This stronger interaction results in a higher sorption, and thereby in a higher flux of the methanol mixtures. In addition, the difference in the molecular size between methanol and ethanol favors the permeability of the smaller methanol as well.

References

- [1] R.C. Binning, R.J. Lee, J.F. Jennings and E.C. Martin, Separation of liquid mixtures by permeation, *Ind. Eng. Chem.*, 53 (1961) 45–50.
- [2] E.C. Martin, R.C. Binning, L.M. Adams and R.J. Lee, Separation process, US Pat. 3,140,256 (1964).
- [3] J.W. Carter and B. Jagannadhaswamy, Separation of organic liquids by selective permeation through polymeric films, *Br. Chem. Eng.*, 9 (1964) 523–526.
- [4] J.M. Stuckey, Method of separating hydrocarbons, US Pat. 2,930,754 (1960); Method of separating hydrocarbons using ethyl cellulose permselective membrane, US Pat. 2,958,656 (1960); and Method of separating hydrocarbons using ethyl cellulose permselective membrane, US Pat. 3,043,891 (1962).
- [5] H.C. Park, Separation of Nonaqueous Organic Liquid Mixtures by Pervaporation, Internal report, University of Twente, Enschede, Netherlands, 1989.

- [6] C. Herion, Zum Verhalten asymmetrischer Membranen in der Pervaporation, Ph.D. thesis, Rheinisch – Westfälischen Technischen Hochschule Aachen, Aachen, Germany, 1988, pp. 150–165.
- [7] K. Ishihara, K. Matsui, H. Fujii, H. Nishide and I. Shinohara, Separation of xylene isomers by pervaporation through a highly permselective polymer membrane having dinitrophenyl group, *Chem. Lett.*, (1985) 1663–1666.
- [8] F. Suzuki, K. Onozato, H. Yaegashi and T. Masuko, Pervaporation of organic solvents by poly[bis(2,2,2-trifluoroethoxy)phosphazene] membrane, *J. Appl. Polym. Sci.*, 34 (1987) 2197–2204.
- [9] G. Chen, F. Lu, B. Wu, Y. Shi, S. Zhang and C. Zhang, Pervaporation of organic liquid mixtures through polyphenylquinoxaline membranes, in R. Bakish (Ed.), *Proc. 3rd Int. Conf. Pervaporation Processes in the Chemical Industry*, Bakish Materials Corp., Englewood, NJ, 1988, pp. 188–193.
- [10] H. Ohst, K. Hildenbrand and R. Dhein, Polymer structure/properties – correlation of polyurethane PV-membranes for aromatic/aliphatic separation, in R. Bakish (Ed.), *Proc. 5th Int. Conf. Pervaporation Processes in the Chemical Industry*, Bakish Materials Corp., Englewood, NJ, 1991, pp. 7–21.
- [11] P. Aptel, J. Cuny, J. Jozefonwicz, G. Morel and J. Néel, Liquid transport through membranes prepared by grafting of polar monomers onto poly(tetrafluoroethylene) films. II. Some factors determining pervaporation rate and selectivity, *J. Appl. Polym. Sci.*, 18 (1974) 351–364.
- [12] P. Aptel, J. Cuny, J. Jozefonwicz, G. Morel and J. Néel, Liquid transport through membranes prepared by grafting of polar monomers onto poly(tetrafluoroethylene) films. I. Some fractionations of liquid mixtures by pervaporation, *J. Appl. Polym. Sci.*, 16 (1972) 1061–1076.
- [13] G. Ellinghorst, A. Niemöller, H. Scholz, M. Scholz and H. Steinhauser, Membranes for pervaporation by radiation grafting and curing and by plasma, in R. Bakish (Ed.), *Proc. 2nd Int. Conf. Pervaporation Processes in the Chemical Industry*, Bakish Materials Corp., Englewood, NJ, 1987, pp. 79–99.
- [14] E.C. Martin and J.T. Kelly, Organophosphorous-modified cellulose esters, *US Pat.* 2,981,730 (1961).
- [15] S. Yamada and T. Hamaya, Liquid permeation and separation by surface-modified polyethylene membranes, *J. Membrane Sci.*, 17 (1984) 125–138.
- [16] I. Cabasso, J. Jagur-Grodzinski and D. Vofsi, Polymeric alloys of polyphosphonate and acetyl cellulose. I. Sorption and diffusion of benzene and cyclohexane, *J. Appl. Polym. Sci.*, 18 (1974) 2117–2136; A study of permeation of organic solvents through polymeric membranes based on polymeric alloys of polyphosphonates and acetyl cellulose. II. Separation of benzene, cyclohexene, and cyclohexane, *ibid.*, 18 (1974) 2137–2147.
- [17] I. Cabasso, Organic liquid mixtures separation by permselective polymer membranes. 1. Selection and characteristics of dense isotropic membranes employed in the pervaporation process, *Ind. Eng. Chem. Prod. Res. Dev.*, 22 (1983) 313–319.
- [18] Q.T. Nguyen, Polymer blending concept for the preparation of permselective membranes (for pervaporation), in B. Sedlacek and J. Kahovec (Eds.), *Synthetic Polymeric Membranes*, Walter de Gruyter, Berlin, 1987, pp. 479–494.
- [19] Z. Yun, M.-Y. Huang and Y.-Y. Jiang, Gas permeability of hydrogen-bonding interpolymer complex and their metal-ion complex membranes, *Polym. Bull.*, 20 (1988) 277–284.
- [20] E. Ruckenstein and J.S. Park, The separation of water-ethanol mixtures by pervaporation through hydrophilic-hydrophobic composite membranes, *J. Appl. Polym. Sci.*, 40 (1990) 213–220.
- [21] F.E. Karasz Glass transitions and compatibility; phase behavior in copolymers containing blends, in D.J. Walsh, J.S. Higgins and A. Maconnachie (Eds.), *Polymer Blends and Mixtures*, NATO ASI Series, Martinus Nijhoff, Dordrecht, 1985, Chap. 2.
- [22] R.L. Miller, Crystallographic data for various polymers, in J. Brandrup and E.M. Immergut (Eds.), *Polymer Handbook*, 3rd ed., Wiley, New York, 1989, pp. VI/1–VI/208.
- [23] W.H. Schneider, Purification of anhydrous organic mixtures by pervaporation, in R. Bakish (Ed.), *Proc. 2nd Int. Conf. Pervaporation Processes in the Chemical Industry*, Bakish Materials Corp., Englewood, NJ, 1987, pp. 169–175.
- [24] J.W.F. Spitzen, E. Elsinghorst, M.H.V. Mulder and C.A. Smolders, Solution-diffusion aspects in the separation of ethanol/water mixtures with PVA membranes, *ibid.*, pp. 209–224.
- [25] J. Gmehling, U. Onken and J.R. Rarey-Nies, Vapor-Liquid Equilibrium Data Collection: Chemistry Data Series, Vol. 1, Part 2e, Dechema, Frankfurt/Main, Germany, 1988, p. 370.
- [26] H. Park, M.H.V. Mulder and C.A. Smolders, Sorption of alcohol-toluene mixtures in PAA-PVA blend membranes and its role on pervaporation, *J. Appl. Polym. Sci.*, accepted.
- [27] H. Park, N. Ramaker, M.H.V. Mulder and C.A. Smolders, Separation of MTBE-methanol mixtures by pervaporation, *Ind. Eng. Chem. Res.*, submitted.
- [28] P. Meares, The physical chemistry of transport and separation by membranes, in P. Meares (Ed.), *Membrane Separation Processes*, Elsevier, Amsterdam, 1976, p. 1.