

Pervaporation of 50 wt % Ethanol–Water Mixtures with Poly(1-trimethylsilyl-1-propyne) Membranes at High Temperatures

Cristina López-Dehesa, José A. González-Marcos, Juan R. González-Velasco

Departamento de Ingeniería Química, Facultad de Ciencia y Tecnología, Universidad del País Vasco/ Euskal Herriko Unibertsitatea, Apartado 644, E-48080 Bilbao, Spain

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ABSTRACT: Poly(1-trimethylsilyl-1-propyne) (PTMSP) membranes have been used to separate ethanol–water mixtures by pervaporation. This polyacetylene is known to present high affinity toward ethanol, showing high selectivity and ethanol permeation flux. The performance of this polymer in the separation of alcohol–water solutions has been evaluated over long periods (572 h) at a high temperature (75°C) to examine the deterioration of the transport properties in the separation of 50 wt % ethanol–water solutions. Although PTMSP membranes present good characteristics for the separation of gases and liquid mixtures, their organic selectivity decrease with the operating time because of the relaxation processes of the poly-

meric chains, which affect the free volume of the polymer, the deterioration being more evident for concentrated solutions. The effects of the operation temperature on the characteristic parameters of pervaporation have also been studied to establish how this variable affects the performance of PTMSP membranes. The selectivity increases slightly with the operation temperature, but the effect of the temperature on the separation factor decreases as membranes are degraded with the operation time. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 103: 2843–2848, 2007

Key words: ageing; degradation; membranes; polyacetylenes

INTRODUCTION

Membrane technology is considered one of the most effective and energy-saving separation processes. The pervaporation technique has not yet been put to practical use because of the delay in the development of membranes with high selectivity and flux with the operation time. In recent years, there has been increasing interest in the use of the pervaporation technique for the separation of organic liquid mixtures. There is one area of application in which pervaporation can play an important role: the continuous removal of biosolvents with inhibitory effects on the production rate, such as ethanol and acetone from fermentation broths.^{1–4}

Poly(1-trimethylsilyl-1-propyne) (PTMSP) is known to show good performance in the separation of diluted ethanol–water solutions.^{5–9} Because this polymer presents high affinity for ethanol, the pervaporation of 50 wt % ethanol–water mixtures at high tem-

peratures has been studied with this polymer to determine the possibility of using it in the recovery of ethanol from concentrated solutions.

The stability and degradation of PTMSP membranes have been tested over long periods during the pervaporation of 50 wt % ethanol–water solutions at a high temperature (75°C) with polymeric films of different thicknesses. The characteristic parameters of pervaporation systems, that is, the separation factor and permeation flux, decrease with the operation time. On the other hand, the operation temperature affects the selectivity and permeation flux; nevertheless, its effect decreases as membranes are degraded with the operation time.

EXPERIMENTAL

Materials

1-Trimethylsilyl-1-propyne (TMSP; 99%) and TaCl₅ (99.9%) were purchased from Aldrich (Madrid, Spain), toluene (analytical-grade) and methanol (analytical-grade) were purchased from Panreac (Barcelona, Spain), and ethanol (analytical-grade) was purchased from Merck (Madrid, Spain). TaCl₅ was used as received, with care being taken not to allow decomposition from exposure to moisture and/or air. TMSP and toluene were distilled in the presence of calcium hydride under nitrogen before use.

Correspondence to: J. R. González-Velasco (iqpgovej@lg.ehu.es).

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TABLE I
Characteristics of the Membranes Used for the
Pervaporation of 50 wt % Ethanol–Water Solutions

Membrane	M7	M10	M29	M40
Temperature (°C)	75	50	75	75
Membrane thickness (μm)	52	59	78	61

Polymerization procedure

PTMSP was synthesized with a method previously described¹⁰ that was adapted from Masuda et al.'s method.^{11,12} The polymerization of PTMSP was carried out under dry nitrogen at 80°C for 24 h. The catalyst, TaCl₅, was dissolved in toluene, and the monomer was added to this solution. The reaction mixture was poured into a large amount of methanol, in which the catalyst was deactivated. The polymer was purified by the solution–precipitation method with a toluene–methanol system and was dried to a constant weight.

Measurement of the molecular weight

The molecular weight of the samples was determined with gel permeation chromatography (Water 510 pump, Waters 410 differential refractometer, and Waters Styragel HR 5E column, Barcelona, Spain). Tetrahydrofuran was used as the solvent, and standard polystyrenes were used for calibrating the molecular weight.

Membrane preparation

The membranes were fabricated through the casting of polymer–toluene solutions (1.5–2.0 wt %) into a Petri dish, and the solvent was allowed to evaporate at room temperature until a constant weight. The fabricated membranes were transparent and yellowish and appeared to be uniform and dense. The membrane thickness was determined through the direct measurement of its weight, with a reported density value of 0.75 g/cm³,^{13–17} and with scanning electron microscopy (6400, JEOL, Tokyo, Japan).

Pervaporation experiments

The pervaporation apparatus was presented in a previous publication.¹⁸ The effective area of the membrane was 14 cm², and the permeate pressure was kept at about 2 mmHg by a rotary vacuum pump. The ethanol contents in the feed, in the permeate, and in the retentate were analyzed by refractive-index measurements with a calibration curve (RX-5000 refractometer, Atago, Tokyo, Japan).

The performance of the PTMSP membranes in pervaporation was evaluated with the permeation flux and the separation factor. The total permeation flux

$[F \text{ (g m}^{-2} \text{ h}^{-1})]$ was calculated with the following expression:

$$F = q/(A \times t) \quad (1)$$

where q is the collected amount of the permeate (g), A is the area of the membrane (m²), and t is the sampling time (h).

With the composition of the permeated fraction, individual fluxes could be calculated. The separation factor ($\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$) was defined as follows:

$$\alpha_{\text{H}_2\text{O}}^{\text{EtOH}} = [Y/(1 - Y)]/[X/(1 - X)] \quad (2)$$

where X is the weight fraction of ethanol in the feed solution (wt %) and Y is the weight fraction of ethanol in the permeate (wt %).

RESULTS AND DISCUSSION

Stability and degradation

The stability of the PTMSP membranes has been evaluated with membranes of a molecular weight of 1.6×10^6 g/mol and different thicknesses during the pervaporation of 50 wt % ethanol–water solutions at 75 and 50°C for different periods. The characteristics of the membranes used in the pervaporation runs are summarized in Table I. Polymers of the same molecular weight were selected to obtain membranes so that we would not need to consider this variable in the study of the stability of the polymer in the pervaporation process.

Separation factor

The variation of the separation factor with the operation time for the membranes used for the pervaporation of 50 wt % ethanol–water solutions is presented in Figure 1.

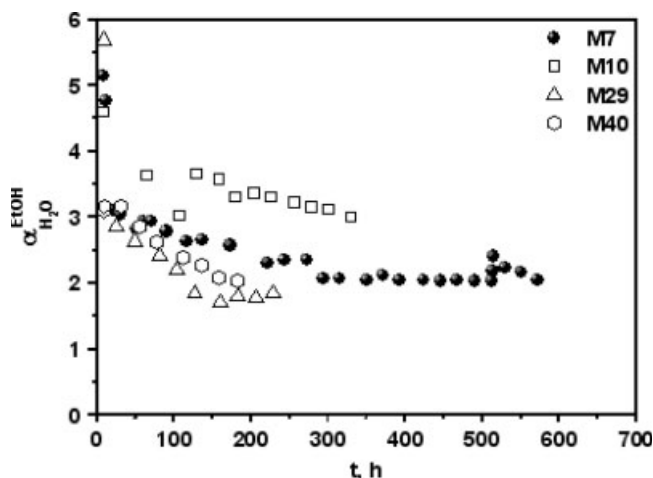


Figure 1 Variation of the separation factor ($\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$) with the operation time (t) at 75 and 50°C for 50 wt % ethanol–water solutions.

Although M7, M29, and M40 were obtained from the same polymer (the same molecular weight), for the same operation time, they present different values of the separation factor. The separation factor increases with the membrane thickness up to 50–60 μm approximately, and for thicker membranes, it remains constant.¹⁹ Although M40 is thicker than M7, it presents an initial value of the separation factor lower than that of M7. This is because with membrane M40, the variation of the transport properties with the operation temperature was studied before the variation with the operation time. Therefore, the initial free volume of the polymeric membrane was slightly modified, and the initial value of the separation factor was not as high as expected. On the other hand, the deterioration due to the temperature study was almost nil, and the experimental data obtained in the study of time were valid because M40 shows the same tendency as that obtained with fresh membranes.

On the other hand, the separation factor decreases very quickly for a short operation time, and for operation times longer than 250 h, it decreases slightly. The decrease in the separation factor obtained for 50 wt % ethanol solutions is higher than that for diluted solutions.²⁰ The high ethanol content in the feed solution enhances the mobility of the polymeric chains, making the reorientation of the chains easier and causing a decrease in the size of the free-volume elements and higher deterioration of the transport properties. Figure 1 also shows that for the M10 membrane run at a lower temperature, the rate of the decrease in the ethanol selectivity with the operation time is less. Therefore, the experimental results suggest that a high operation temperature allows a higher mobility of polymeric chains, causing a higher reduction of the free-volume elements. The decrease in the size of the free-volume elements makes it difficult to transport ethanol molecules because they are higher in size than water molecules; therefore, the selectivity decreases with the operation time.

Permeation flux

The permeation flux is a measurement of the number of permeate molecules that cross the membrane per unit of time and unit of the membrane surface. Figure 2 shows the variation of the total permeation flux with the operation time for membranes at 75 and 50°C. For both operation temperatures, first the permeation flux decreases quickly, and for operation time longer than 250 h, it decreases slightly with the operation time. On the other hand, as seen for the separation factor, the deterioration of the transport properties at the low temperature (50°C) is lower than at the high temperature (75°C).

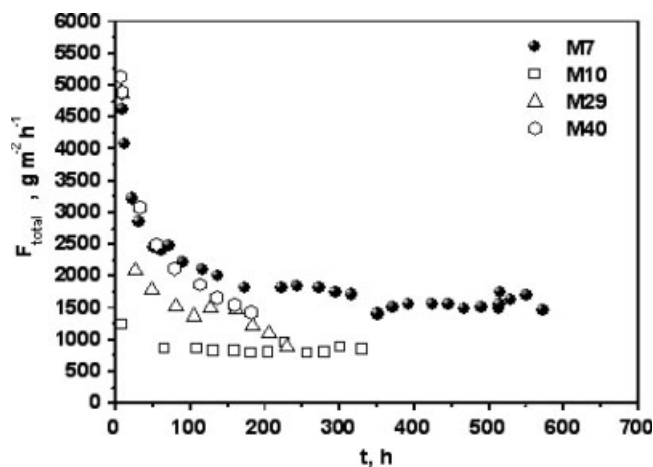


Figure 2 Variation of the total permeation flux (F_{total}) with the operation time (t).

Although it seems that the decrease in the separation factor with the operation time is higher than that observed for the flux, the reduction of the pervaporation parameters with the operation time is about 35% for both variables. The initial value of the separation factor for M10 is approximately 4.5, and it decreases up to 3, so the separation factor decreases 35% for the whole operation time. For the permeation flux, the initial value of the variable is $1200 \text{ g m}^2 \text{ h}^{-1}$ and approximately decreases to $800 \text{ g m}^2 \text{ h}^{-1}$, so the total permeation flux also decreases 33% (same order).

Effect of the temperature

The operation temperature is a variable that affects the performance of polymeric membranes in the pervaporation of liquid mixtures; therefore, the effect of this variable in the pervaporation of 50 wt % ethanol–water solutions has been evaluated.

Separation factor

The influence of the temperature on the separation factor is shown in Figure 3, in which the standard deviation of the separation factor is also presented.

For the M7 membrane, the effect of the temperature has been studied after stabilization for 572 h. For the M7 membrane, the separation factor remains constant with the operation temperature in the range of 50–75°C because the polymeric material has been degraded by the operation time. This tendency has also been observed for membranes used for the separation of 10 wt % ethanol–water solutions for long periods.²⁰

For the M29 and M40 membranes, the effect of the temperature has been studied after stabilization for 229 and 0 h (fresh membrane), respectively. Figure 3 shows that for the M29 and M40 membranes, the

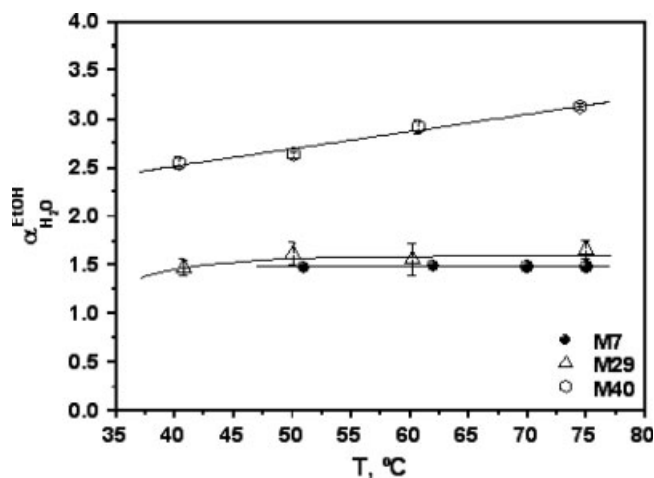


Figure 3 Effect of the operation temperature (T) on the separation factor ($\alpha_{\text{H}_2\text{O}}^{\text{EtOH}}$).

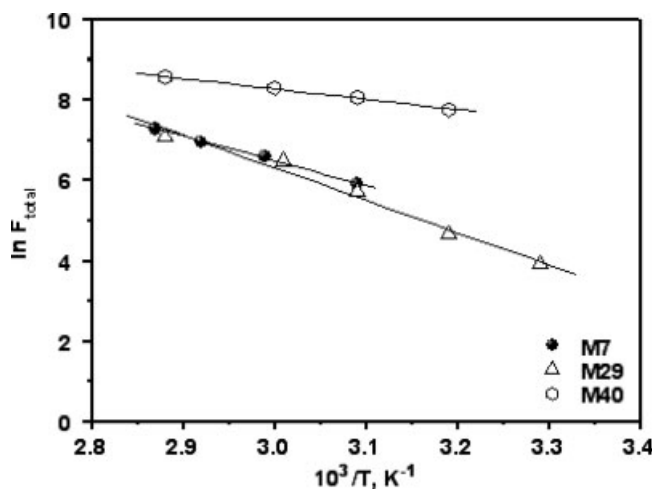


Figure 4 Effect of the temperature (T) on the permeation flux (F_{total}).

ethanol selectivity increases slightly with the operation temperature because the polymer is not completely degraded. Thus, the polymeric chains present higher mobility with the temperature, making more free volume available for the diffusion process. Because of the hydrophobic nature of the polymer, the ethanol selectivity increases with the operation temperature, and this is more evident for the fresh membrane.

Figure 1 shows that for the same operation time, the separation factor is lower for membranes studied at high temperatures. For the initial time (0 h), the value of the separation factor for the membrane run at 50°C (M10) is lower than that of the runs at 75°C (M7, M29, and M40; M40 presents a lower value because it is a fresh membrane). For the higher operation time, the separation factor of M7, M29, and M40 is lower than that of M10. Therefore, a higher operation temperature (75°C) causes a higher reduction of the transport properties.

Permeation flux

The temperature dependence of the permeation flux [F ($\text{g m}^{-2} \text{h}^{-1}$)] generally exhibits an Arrhenius-type relationship:

$$F = B \exp[E_P/(R \times T)] \quad (3)$$

where B is a pre-exponential factor ($\text{g m}^{-2} \text{h}^{-1}$), E_P is the apparent activation energy of permeation (cal/mol), R is the gas constant ($\text{cal mol}^{-1} \text{K}^{-1}$), and T is the operation temperature (K).

The effect of the temperature on the permeation flux is shown in Figure 4. For all the studied membranes, the permeation flux follows the Arrhenius law.

Membranes M7 and M29 present almost the same slope because they have worked for a long period, and molecules find it difficult to diffuse through the polymer. On the other hand, the M40 membrane presents a smaller slope because it is a fresh membrane and molecules can diffuse easily through the polymeric material. This tendency is related to the apparent activation energy of permeation. From the slope of Figure 4, the values of the apparent activation energy of permeation for the total flux are summarized in Table II. For all the membranes, ethanol flux and water flux present the same tendency with the operation temperature as that shown for the total flux. From the slope of the individual fluxes versus the operation time, the apparent activation energy of permeation for each component has been determined and is given in Table II.

As can be seen in Table II, the values of the apparent activation energy of permeation obtained for the membranes used for long periods (M7 and M29) are higher than those of the fresh membrane (M40). This suggests that when membranes are degraded because of the operation time, water and ethanol molecules require more energy for diffusing through the polymeric membrane because the polymer presents fewer and/or smaller free-volume elements; that is, the degraded polymer presents denser structures and chains with lower mobility, and this means high values of the apparent activation energy of permeation.²¹

TABLE II
Apparent Activation Energy of Permeation (kcal/mol)

Component	M7	M29	M40
Ethanol	12.5 ± 2.7	13.9 ± 6.6	5.4 ± 1.7
Water	12.5 ± 2.7	13.4 ± 7.9	4.0 ± 1.8
Total	12.5 ± 2.7	13.7 ± 7.1	5.0 ± 1.7

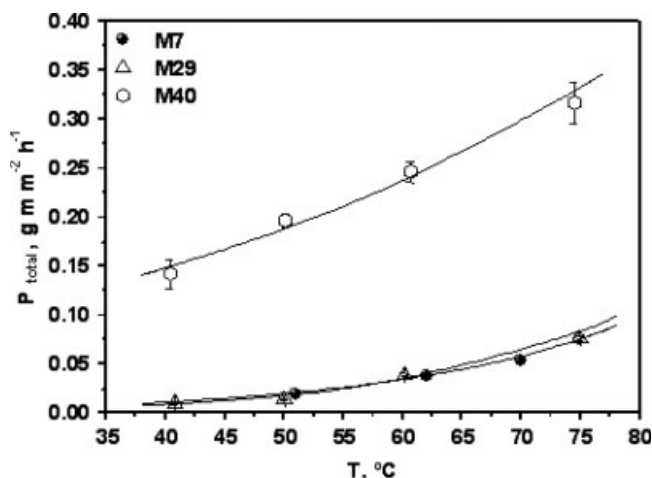


Figure 5 Variation of the total specific permeation rate (P_{total}) with the operation temperature (T).

According to some authors, the first effects of polymer degradation are an increase in the density and a degradation of the transport properties. Consolati et al.²² observed that because of aging, the polymer presented a higher density and the permeability decreased. They established that the reduction of the transport properties was due to a reorientation of polymeric chains with the reduction of the size and/or number of free-volume elements.^{23–25}

On the other hand, a thermal treatment causes a degradation similar to that obtained with physical aging.²² Experimentally, it has been observed that for polymers of the same thickness that have been thermally treated in a temperature range of 160–180 °C for 100 min, the N₂ adsorption capacity decreases with the temperature of the thermal treatment.²⁶ The difference in the adsorption of thermally treated polymers can be related to low permeation properties and a more stable performance in the pervaporation process.

The values of the apparent activation energy of permeation obtained for the 50 wt % ethanol–water solutions with membranes used for long periods of time are similar to those obtained for 10 wt % ethanol–water solutions.¹⁹ In principle, when the ethanol concentration in the feed solution increases, the polymeric material suffers from a swelling process, and polymeric chains become more flexible and present higher mobility; this makes it easier for the transport of molecules and reduces the energy for the diffusion process.²⁷

Specific permeation rate

The variation of the total specific permeation rate for the studied membranes is shown in Figure 5. For all the studied membranes, the variation of the water and

ethanol specific permeation rates is the same as that of the total specific permeation rate.

At a high temperature, permeating molecules can diffuse faster through the polymeric material because the frequency and jump amplitude of the polymeric chains make free-volume elements bigger. Therefore, when the operation temperature is high, the diffusion rate of individual and associate molecules is higher, increasing the total specific permeation rate.

CONCLUSIONS

A high operation temperature allows high values of the permeation flux to be obtained, as well as quick degradation of the transport properties in short periods.

The selectivity increases slightly with the operation time; nevertheless, the effect of this variable decreases with the operation time because of a relaxation process of the polymeric chains that reduces the number and/or size of the free-volume elements of the polymer.

Membranes used for long periods for the pervaporation of 50 wt % ethanol–water solutions present higher values of the apparent activation energy of permeation than fresh membranes because of the decrease in the size of the free-volume elements.

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