Development of New Ionomer Blend Membranes, Their Characterization, and Their Application in the Perstractive Separation of Alkenes from Alkene–Alkane Mixtures. II. Electrical and Facilitated Transport Properties

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ABSTRACT: In this contribution, the synthesis and characterization of novel ion-exchange blend membranes which contain the SO_3Ag group for the application in the perstractive separation of alkene–alkane mixtures, where the Ag^+ ion serves as facilitated transport site for the alkene via formation of a pi complex with the alkene double bond, is presented. In this part of the article, the transport properties of the following blend membrane types are described: (1) acid–base blend membranes of ortho-sulfone-sulfonated polysulfone (PSU) with ortho-sulfone-diaminated PSU; (2) blend membranes of ortho-sulfone-sulfonated PSU with unmodified PSU; (3) blend membranes of ortho-sulfone-sulfone-sulfonated PSU with ortho-sulfone disilylated PSU. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 422–427, 1999

Key words: facilitated transport; alkene; SO_3Ag -containing polysulfone (PSU) blend membranes; blend of sulfonated and aminated PSU; blend of sulfonated and unmodified PSU

INTRODUCTION

The separations of hydrocarbons using membrane technology are low-cost alternatives to other separation technologies, such as distillation and extraction in terms of energy costs. However, low fluxes and bulk rather than precise separations have limited its application up to now.¹ The separation of olefin-paraffin mixtures has been achieved using mainly glassy polymers because alkene permeability through these polymers is

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Journal of Applied Polymer Science, Vol. 74, 422–427 (1999) © 1999 John Wiley & Sons, Inc. CCC 0021-8995/99/020422-06 known to be higher than that of the corresponding alkane.² Elastic polymers show similar permeabilities for alkenes and alkanes. The separation factors are generally low, in the order of 1.5–5; and as a result, transmembrane fluxes has been combined with reversible complexation reactions to increase membrane selectivity. The process is known as facilitated transport.

In the facilitated transport of olefins, metal ions (usually silver) confined to the membrane phase form reversible complexes with olefin molecules.³ The complexation enhances the olefin solubility in the membrane. The olefin–metal complex diffuses through the membrane due to a concentration gradient; and at the downstream side, the complexation is reversed. Paraffins are unable to form complexes with carrier ions and per-

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meate at a lower rate according to normal Fickanian diffusion. This results in olefin/paraffin separation.

Facilitated transport has been demonstrated for emulsion liquid membranes,⁴ liquid, flowing liquid, and supported liquid membranes.^{5,6} The disadvantage of these membranes is the loss of membrane solvent and carrier ions from the membrane phase due to shear forces and the hydrophobic nature of polymer supports. This problem can be overcome by using fixed-site facilitated transport membranes. Ion-exchange membranes are more hydrophilic and retain metal ions by electrostatic forces, resulting in increased stability for facilitated transport.³

Several studies have been reported on the development of stable ion-exchange membranes for facilitated transport.⁷⁻⁹ We previously reported the facilitated transport of olefins through newly developed sulfonated polysulfone (PSU) Udel® membranes.¹⁰ Good selectivity for olefin/paraffin separation was obtained, but low fluxes of the olefin through the membrane were observed. New membranes have been developed in an attempt to increase the fluxes through membranes by increasing the ion exchange capacity, increasing the polymer free volume, and reducing membrane thickness. The development and characterization of these blended membranes based on the chemically stable Polysulfone PSU Udel® has been reported.¹¹ In this article, the transport characteristics and separation of pentene-pentane mixtures using the different membranes are reported.

EXPERIMENTAL

Producing the new membranes required modification to the PSU Udel[®] polymer by sulfonation, amination, and silylation. Procedures are described in the literature.¹¹ The modified polymers were characterized by ¹H nuclear magnetic resonance (H¹-NMR), while newly produced membranes were characterized using Fourier transform infrared (FTIR) and electron microscopy, also described in the literature.¹¹

Ion exchange capacities were determined by converting the membranes to the Ag^+ -form, soaking the membranes in HNO₃, and measuring the Ag^+ content in solution by atomic absorption.

The degree of swelling (SW) was determined according to the following equation

$$SW = rac{m_{
m Wet} - m_{
m Dry}}{m_{
m dry}} imes 100 \ [\%]$$

where $m_{\rm wet}$ is the mass of the water swollen membrane, and $m_{\rm dry}$ is the mass of the membrane dried at 80°C under vacuum.

Protonic conductivity of the membranes composed of sulfonated and aminated PSU was determined via impedance spectroscopy (EIS) with an im6 setup from Zahner elektrik. The membrane impedance has been determined in 0.5N HCl. The impedance at which the phase angle between current and voltage was zero was taken as the ohmic resistance of the membrane.

Perstraction experiments were performed using a vertically arranged two-compartment cell, with a membrane separating the two compartments.¹² Peristaltic pumps supplied constant flow of the feed solution through the upper compartment and the sweep solution through the lower compartment. Pentene–pentane was used as feed mixture, and hexane was used as the sweep solution. Samples from the sweep solution were analyzed periodically on a 8610 SRI gas chromatograph. Fluxes were calculated from the slopes of concentration versus time plots and separation factors from the ratios of olefin to paraffin fluxes.

RESULTS AND DISCUSSION

It was shown that sulfonated $(PSU-SO_3H)$ and aminated polysulfone $(PSU-NH_2)$ blends formed stable membranes due to salt-forming reactions $(R-SO_3^-NH_3^+-R)$ and physical entanglement of the polymers.¹¹

Membranes produced from blends of nonmodified PSU and sulfonated polysulfone (PSU–SO₃H) were stable due to physical entanglement of polymers, but phase separation occurred within the membrane matrix.

Large free volume in the membranes was obtained by addition of bulky trimethylsilane groups [(CH₃)₃Si—] ortho to the sulfone bridges of polysulfone. This increased the hydrophobicity of the polymer. Blends with the hydrophilic sulfonated PSU resulted in unstable membranes consisting of two distinct layers. However, a singlelayer membrane with low PSU–Si(CH₃)₃ content and high swellability was produced. The sulfonated PSU, normally soluble in water, was stabilized by physical entanglement with the PSU– Si(CH₃)₃ polymers.

Membrane	IEC ^b (meq/g)	IEC After HCl Treatment (meq/g)	Thickness (µm)	Degree of Swelling (%)
Sulfonated/aminated (70/30) ^a	0.2	2.06	85	42.1
Sulfonated/aminated (80/20) ^a	0.2	2.29	90	63.3
Sulfonated/aminated (88/12) ^a	1.2	2.59	96	120.8
Sulfonated/aminated (93/7) ^a	0.3	2.91	100	306.3

Table I Characteristics of PSU-SO₃H-PSU-NH₂ Blended Membranes

 $^{\rm a}$ PSU–SO₃H having IEC of 2.6 meq/g and PSU–NH₂ with 1.67 amino groups per repeating unit.

^b Ion-exchange capacity in meq/g.

Swelling of the Ionomer Blends in Dependence of the Ion-Exchange Capacity

Shown in Table I is the characteristics of PSU– SO₃H/PSU–NH₂ blended membranes. Initial ion exchange capacities are low due to the interactions of the —SO₃H and —NH₂ groups. Treating the membrane with hydrochloric acid partially protonizes these groups, resulting in extremely high ion exchange capacities.

$$PSU-SO_{3}^{-}||||H^{+}|||H_{2}N-PSU + HCl \rightarrow$$
$$PSU-SO_{3}H + [Cl^{-+}H_{3}N-PSU] \quad (1)$$

The degree of swelling increases exponentially with an increase in the ion exchange capacity of the blended membranes (Fig. 1). This is to be expected because the hydrophilic nature of the membrane is enhanced by the high content of sulfonate groups in the membrane matrix. The polar $\rm NH_3^+$ -groups also contribute to larger amounts of water absorbed into the membranes.

Table II shows the characteristics of PSU/ PSU–SO₃H blends. Although the degree of swell-



Figure 1 Swelling of the $PSU-SO_3H$ — $PSU-NH_2$ acid-base blends in dependence of their ion-exchange capability (IEC).

ing is higher for membranes with higher ion exchange capacity, the trend is not as profound as in the case of the $PSU-SO_3H/PSU-NH_2$ blends. This is because only sulfonate groups contribute to the hydrophilicity of the polymer blends.

The membrane produced from 10/90 w/w % PSU–Si(CH₃)₃ and PSU–SO₃H had an ion exchange capacity of 2.53 meq/g and a degree of swelling of 126%. Comparing this with the 10/90 w/w % PSU/PSU–SO₃H blended membrane clearly shows the effect of the bulky trimethylsilane group on the free volume of the polymers.

Ionic Conductivity of PSU–SO₃H—PSU–NH₂ Blend Membranes in Dependence of IEC

In Figure 2, the dependence of specific H^+ resistance of PSU–SO₃H/PSU–NH₂ blend membranes in dependence of their IEC is shown. It can be seen that the electric membrane resistances are very low, making these membranes interesting candidates as polymeric proton conductors in applications like electrodialysis and fuel cells.

To investigate whether there is a correlation between pentene fluxes through the silver-exchanged PSU–SO₃H/PSU–NH₂ blend membranes and the specific H^+ resistances of the membranes,

Table II	Characteristics of PSU–PSU-SO ₃ H
Blends	

Membrane (PSU—PSU–SO ₃ H)	Thickness (µm)	IEC (meq/g)	Swelling (%)
70/30	65	0.38	13.47
50/50	60	1.20	52.99
30/70	70	1.99	38.98
20/80	50	2.16	53.76
10/90	80	2.44	63.4



Figure 2 Dependence of specific H^+ resistance of the of PSU-SO₃H—PSU-NH₂ blend membranes from the ion-exchange capacity (IEC).

the pentene fluxes were depicted versus the specific H^+ resistances (Fig. 3).

From Figure 3, it can be seen that there is no direct correlation between pentene fluxes and proton conductivity, which means that the transport mechanisms and transport paths of pentene through the silver-exchanged membranes are different from those of protons through the membranes, confirming the findings already mentioned in the literature.¹⁰

Pentene and Pentane Permeability and Pentene– Pentane Permselectivity in Dependence of the Ion-Exchange Capacity of the Different Investigated Blends

Pentene fluxes through blended membranes showed a strong dependence on the ion-exchange capacities of the membranes because higher amounts of silver are retained in the membrane matrix. As a result, the selectivity for pentene– pentane separation also increases. In Figure 4, the dependence of pentene fluxes and pentene–



Figure 3 Pentene fluxes fluxes through the silverexchanged $PSU-SO_3H$ — $PSU-NH_2$ blend membranes versus their specific H^+ resistances.



Figure 4 Fluxes for pentene and separation factors for pentene-pentane mixtures as a function of ion-exchange capacities of sulfonate-aminated PSU blends.

pentane separation factors on the ion-exchange capacities of $PSU-NH_2$ and $PSU-SO_3H$ blended membranes are shown.

The results for the separation of pentene–pentane mixtures using different blended membranes are shown in Table III. The pentene flux of 2.65×10^{-8} mol cm⁻² s⁻¹ for a sulfonated/aminated PSU blended membrane with an ion-exchange capacity of nearly 3 meq/g is one of the highest obtained for PSU membranes.¹⁰

In Figure 5, the fluxes through blends of PSU/ PSU–SO₃H and separation factors for pentene– pentane mixtures are shown as a function of the ion-exchange capacities of the membranes. Fluxes of pentene showed a dependence on the silver content in the membranes. Low transport of pentane through the membranes made accurate flux measurements difficult. Fluxes were determined to be in the order of 1×10^{-11} mol cm⁻² s⁻¹, resulting in separation factors in excess of 200. The membrane with a 10/90% ratio of PSU/ PSU–SO₃H showed the best results with a pentene flux of 4.42×10^{-9} mol cm⁻² s⁻¹ and a separation factor of 286 (Table III).

Correlation of Pentene–Pentane Permselectivity with Swelling

The high degree of swelling of membranes with high ion-exchange capacities further contributes to exceptionally high pentene fluxes. Blending sulfonated PSU polymers with aminated polymers, and posttreating the membranes with HCl, resulted in the formation of microphases within the membrane matrix.¹¹ The microphases play an important role in the degree of swelling of the membranes. Larger volumes of water are impregnated into the membranes, and water plays a critical role in the separation process. Pentene

	Initial Fluxes	~	
Membrane	Pentene (/10 ⁻¹⁰)	Pentane (/10 ⁻¹¹)	Separation Factors
Sulfonated/aminated PSU (70/30)	6.88	4.81	14
Sulfonated/aminated PSU (80/20)	26.0	4.58	57
Sulfonated/aminated PSU (88/12)	128	5.22	245
Sulfonated/aminated PSU (93/7)	265	6.33	419
PSU—PSU–SO ₃ H (50/50)	4.72	0.472	100
$PSU - PSU - SO_3 H (30/70)$	33.2	1.2	280
PSU—PSU–SO ₃ H (20/80)	37.9	1.30	290
PSU—PSU–SO ₃ H (10/90)	44.2	1.54	286
PSU–Si(CH ₃) ₃ —PSU–SO ₃ H	382	—	~ 2000

Table III Fluxes and Separation Factors for PSU Blends

and pentane are sparingly soluble in water, but the presence of ionically bound and solvated silver ions increases the solubility of pentene in the aqueous phase of the membrane. As a result, the fluxes of pentene increases dramatically, and high factors for pentene–pentane separation are observed. From Figure 6, it can be seen that a nearly linear dependence exists between membrane swelling and pentene fluxes at the PSU– $SO_3H/PSU-NH_2$ blend membranes.

Only one membrane was made from PSU– Si(CH₃)₃ and PSU–SO₃H polymers. High pentene flux arises from the large free volume produced by the trimethylsilane groups attached to the polymer backbone. The high free volume is confirmed by the extremely high swellability of the membrane and by comparison of fluxes through the 10/90 w/w % ratios of PSU/PSU–SO₃H and PSU– Si(CH₃)₃/PSU–SO₃H blended membranes (Table III). The PSU–Si(CH₃)₃/PSU–SO₃H membrane showed the highest pentene flux of all membranes (3.8×10^{-8} mol cm⁻² s⁻¹). Pentane flux was low and difficult to measure, and separation factors in excess of 2000 were observed.

CONCLUSION

Olefin fluxes were enhanced by increasing the amount of silver impregnated into the membranes and increasing the free volume of the polymer. Higher silver content was possible by the higher ion-exchange capacities of $PSU-SO_3H/PSU-NH_2$ blended membranes, and larger polymer free volume was achieved in $PSU-Si(CH_3)_3/PSU-SO_3H$ blended membranes.

The blend of sulfonated and aminated PSU membrane showed extremely good efficiency. Pentene fluxes through the membranes were four times higher than those through commercial perfluorosulfonated ionomer (PSI) membranes¹² and 38 times higher than those through previously reported PSU membranes.¹⁰ Separation factors were 13 times higher than with the PSI membranes and 5 times higher than with the initial PSU membranes. Pentene flux through PSU–Si(CH₃)₃/PSU–SO₃H blended membranes was 55 times higher than through the first sulfonated



Figure 5 Fluxes for pentene as a function of ionexchange capacities of PSU–PSU–SO₃H blends.



Figure 6 Swelling versus pentene fluxes for the $PSU-SO_3H$ — $PSU-NH_2$ blend membranes.



Figure 7 Development of ion-exchange membranes for facilitated transport in terms of pentene fluxes: (1) PSU crosslinked via disproportionation; (2) PSU crosslinked via *s*-alkylation; (3) homogeneous sulfonated PSU; (4) homogeneous sulfonated PEEK; (5) sulfonated PSU–sulfonated PEEK blend; (6) PSU–PSU– SO₃H blend; (7) reinforced PSU; (8) PSU–SO₃H—PSU– NH₂ blend; (9) PSU–Si(CH₃)₃—PSU–SO₃H blend.

PSU membranes, while separation factors increased 30-fold. The pentene fluxes were 5–6 times higher than those through the commercial PSI membranes. Figure 7 shows the progress in the development of sulfonated PSU membranes in terms of pentene fluxes through the membranes.

It can be concluded that alternative membranes for fixed-site facilitated transport of olefins has been developed. These membranes feature exceptionally high olefin fluxes as well as extremely good separation factors for olefin-paraffin mixtures.

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