Modified Polysulfone Membranes. III. Pervaporation Separation of Benzene–Cyclohexane Mixtures through Carboxylated Polysulfone Membranes*

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ABSTRACT: Membranes prepared from carboxylated polysulfone permeated benzene preferentially from benzene–cyclohexane mixtures by pervaporation. Hydrophilic polysulfones containing carboxyl groups with degrees of substitution (DS) ranging from 0.46 to 1.90 groups per repeating unit were selected for this study. The membrane having a carboxyl group DS of 0.88 showed the best trade-off between flux and permselectivity. The permselectivity towards benzene was 234 at the weight fraction of benzene in feed of 0.1. From pervaporation and sorption experiments, it was evident that permselectivity toward benzene was due to solubility selectivity. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 407–412, 1999

Key words: membrane; pervaporation; permselectivity; polysulfone; benzene–cyclohexane

INTRODUCTION

Functionalized polymers are of general interest in many technology applications.[1] Customized polymers for reagents, catalysts, chromatography media, controlled release formulations, and so forth are examples of their applications. Advances in membrane technology are being made both in membrane formation processes and in membrane materials. Customized polymeric materials are useful to improve membrane performance. In general, functionalized polymers are prepared by polymerization of functional monomers or by modifying existing polymers. The modification approach adopted in the present study has the advantage of preparative convenience for introducing different amounts of carboxyl groups on the polysulfone chain in order to adjust the hydrophilicity of the parent polymer.

Polysulfone (PSf) has thermal stability combined with good mechanical strength and membrane-making qualities. It has a stable backbone onto which functional groups can be attached and is a good candidate material for specialty polymeric membranes. Methods for modifying PSf have been reported, which include lithiation,[2–9] sulfonation,[10–16] halomethylation reactions,[17–20] aminomethylation,[17,21,22] amination,[8,17,22,23] and halogenation.[17,24] Lithiation has been used to prepare carboxylated polysulfones that have been investigated in a variety of membrane separation processes, including ultrafiltration (UF),[9,25–28] nanofiltration and reverse osmosis (RO),[9,27,29,30] and chiral separation.[31] Lithiation has been used to introduce other functional groups for mem-

brane applications, including liquid separations,[32,33] gas separation,[9,34−37] pervaporation,[34,35,38,39] affinity separation,[40] and electromembrane processes.[41,42]

In the present article, we studied pervaporation of benzene–cyclohexane mixtures through carboxyl-modified PSf membranes. Separation or removal of benzene is one of the interesting and important subjects in connection with environmental issues.[43] The separation of benzene from cyclohexane is industrially relevant in connection with petroleum refining as well. Not a few articles have dealt with the pervaporation separation of benzene–cyclohexane mixtures.[44−46] From pervaporation results reported previously,[44−46] the increased membrane hydrophilicity introduced by the carboxyl group can be expected to have affinity towards benzene, the more polar component of the mixture. Based on this, the pervaporation performance of the present polymeric membranes was investigated by applying the benzene–cyclohexane mixture as a model mixture.

EXPERIMENTAL

Materials

A series of carboxylated polysulfones (PSf–COOH) were prepared by lithiation and carboxylation of commercial polysulfone Udel P-3500 (Amoco Performance Products, Inc.), as reported previously.[47] For the present membrane study, four modified polymers were prepared having DS of 0.46, 0.88, 1.62, and 1.90. The DS of each polymer was determined by nuclear magnetic resonance (NMR) techniques of methyl ester derivatives.

$$DS = x + y$$

Membranes

Membranes were prepared as follows: a 0.25 g of modified polysulfone was dissolved in a 5 cm^3 of tetrahydrofuran (THF). The THF solution thus prepared was poured onto a flat laboratory dish (7.0 cm diameter), and the solvent was allowed to evaporate at ambient temperature for 24 h. Sub-

sequently, the membrane was dried at 50°C for 2 h. The thickness of the membrane used in the present study were 33–57 μm.

Pervaporation

Permeation of benzene–cyclohexane mixtures were performed by the usual pervaporation technique using a glass apparatus and cell.[48] The upstream membrane area in contact with the liquid feed was 17.3 cm^2. The downstream pressure applied was close to 267 Pa (2.0 mmHg). Pervaporation experiments were carried out at a constant operating temperature of 50°C.

Separation analysis of the permeate mixture was carried out on a Shimadzu GC-8APT gas chromatograph equipped with a 3.0-m-long column packed with polyethyleneglycol 6000 (Shimalite TPA).

The separation factor, α, is defined as

$$\alpha = (Y_{benzene}/Y_{cyclohexane})/(X_{benzene}/X_{cyclohexane})$$

where Y's are the weight fractions of benzene or cyclohexane in the permeate and X's are those in feed, respectively.

Solubility Measurement

The solubility selectivity of the DS 0.88 PSf-COOH membrane was measured as described previously.[49] Solubility selectivity S_S is defined as

$$S_S = (Z_{benzene}/Z_{cyclohexane})/(X_{benzene}/X_{cyclohexane})$$

where Z's are the weight fractions of benzene or cyclohexane in the membrane and X's are those in solution, respectively.

RESULTS AND DISCUSSION

Pervaporation

The benzene component in the benzene–cyclohexane mixture is a partial solvent for PSf and induces membrane instability by swelling. The solvent resistance and stability of the membrane to benzene is improved by incorporating carboxyl groups into the polymer chain. The resulting increased membrane hydrophilicity shows preferential affinity to benzene, the more polar solvent in the binary mixture. Figure 1 summarizes the effect of the carboxyl group content on the perva-

Figure 1 Effect of the DS on the pervaporation, separation factor (α), and flux (J) of benzene–cyclohexane mixture through PSf–COOH membranes [weight fraction of benzene in feed, ca. 0.5; operating temperature, 50°C; downstream pressure, ca. 267 Pa (2.0 mmHg)].

poration of the benzene–cyclohexane mixture, where the weight fraction of benzene in feed was 0.5. Membranes with DS of 0.46, 0.88, and 1.62 had permselectivity towards benzene, with permselectivity increasing to a maximum for DS 0.88. This initial increase in permselectivity up to a maximum is most likely related to improved benzene–membrane affinity due to the direct effects of introducing hydrophilicity. However, as the DS was increased to 1.62, there was a sharp decrease in permselectivity. This decreasing trend continued with a high DS for DS 1.90, where no benzene permselectivity occurred. Flux values lie in the range of approximately 4 to 6 g m^{-2} h^{-1} for all the membranes, except DS 1.90, which was negligible. A possible explanation for declining membrane pervaporation performance with increasing DS lies in the nature of the polymer repeating unit. In previous studies,[47] we determined the

relative ratios of mono-, di-, and unsubstituted repeating units for a series of polymer of different carboxyl group DS. In the DS range of 0.8–1.0, where the polymer solubility characteristics exhibit a marked change compared with PSf, the large majority of the repeating units are monosubstituted carboxyl repeating units, with a small percentage of di- and unsubstituted units. It is obvious that as the DS increases, the majority of repeating units are disubstituted. In the case of DS 1.90, the geometry of two carboxyl groups around the sulfone link would facilitate the formation of intramolecular hydrogen bonding as well as the likelihood of intermolecular hydrogen bond crosslinks. These combined effects may help to explain the observations of benzene permeation and permselectivity decline with increased DS above 0.88.

Of the four carboxylated membrane types investigated, DS 0.88 had the best performance combination of the highest benzene permselectivity and good permeation. This membrane alone was selected for subsequent experiments. Figure 2 shows the results of pervaporation of various benzene–cyclohexane mixtures through the DS 0.88 membrane, where the weight fractions of benzene permeate are plotted against those in feed ranging from 0.1 to 0.9. The vapor–liquid equilibrium curve for benzene–cyclohexane mixtures at 50°C[50] is also given in the figure. The separation factor was a maximum of 234 at the weight fraction of 0.1 and decreased with increasing benzene content in feed. At a weight fraction of benzene in feed of 0.9, there was no benzene permselectivity. The general trend of decreasing permselectivity with increasing benzene in the feed could be related to the swelling of this membrane. The permeation results indicate a gradual increase in benzene permeation flux as the weight fraction increases from 0.1 to 0.7. However, there is a dramatic permeation increase of orders of magnitude for benzene weight fraction of 0.9 accompanied by a loss of selectivity, indicating that the membrane is excessively swollen in this environment.

Sorption

The amounts of benzene and cyclohexane sorbed in the membrane with DS of 0.88 and the total amounts sorbed in the membrane are shown in Figure 3. As expected, the amounts of benzene sorbed in the membrane were far greater than those of cyclohexane and increased with the in-

Figure 2 Effect of feed composition on the pervaporation of benzene–cyclohexane mixtures through PSf–COOH (D.S. = 0.88) membranes [operating temperature, 50°C; downstream pressure, ca. 267 Pa (2.0 mmHg)].

creasing benzene content in the mixture. Cyclohexane accounted for only a small portion sorbed in the membrane for the full range of benzene weight fractions in the feed. From these data, solubility selectivities S_S were obtained. Obeying the solution–diffusion theory, diffusivity selectivity S_D is given by

$$S_D = \alpha/S_S(=D_{\text{benzene}}/D_{\text{cyclohexane}})$$

where D_{benzene} and $D_{\text{cyclohexane}}$ are the diffusion coefficients of benzene and cyclohexane, respectively.[51] The separation factor, solubility selectivity, and diffusivity selectivity for the membrane with DS of 0.88 are shown in Figure 4 as a function of weight fraction of benzene in feed. It was concluded that solubility selectivity towards benzene was the dominant factor contributing to the permselectivity of the membrane.

CONCLUSIONS

Four types of hydrophilic membranes containing carboxyl groups with DS of 0.46, 0.88, 1.62, and 1.90 were prepared. Membranes with DS below 1.0, particularly the one with a DS 0.88, showed the best benzene permselectivity results for a feed of 0.5 weight fraction of benzene in the benzene–cyclohexane mixture. The effect of a range of feed compositions from 0.1 to 0.9 weight fraction benzene on the pervaporation of benzene–cyclohexane mixtures was studied for the DS 0.88 membrane. At a feed weight fraction of 0.1, the membrane had a high benzene permselectivity of 234. As the benzene weight fraction increased up to 0.7, there was a steady decline in benzene permselectivity to approximately 10. Above this point,

Figure 3 Effect of benzene concentration in feed on the composition of solution sorbed in PSf–COOH (D.S. = 0.88) membrane.

Figure 4 Effect of feed composition on separation factor α, solubility selectivity S_S, and diffusivity selectivity S_D, of PSf–COOH (DS = 0.88) membrane at 50°C ($\bullet$, α; $\circleddash$, S_S; $\circ$, S_D).

there was a significant decrease in permselectivity and a dramatic increase in permeation due to excessive membrane swelling. Sorption studies indicated that solubility selectivity was the dominant factor contributing to benzene permselectivity of the membrane. In summary, the DS 0.88 membrane has useful benzene permselectivity properties for pervaporation of benzene–cyclohexane mixtures in which the weight fraction of benzene in feed is at a lower level.

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