

Robust Polymeric Membranes for the Separation of Petrochemicals using Pervaporation

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1. Introduction

Utilization of membranes offers the promise of extraordinary energy savings if successfully applied to hydrocarbon-hydrocarbon and other organic separations. Membranes are bound to enter into refining and petrochemical operations involving liquid separations once appropriate materials and modules are developed. Hybrid processes such as utilizing membrane modules to break azeotropes formed during distillation are particularly attractive because they offer less process complexity and reduced capital investment[1,2]. Such an approach is now accepted in the case of dehydration of ethanol as evidenced by the successful GFT process. Additionally, membranes are now available that can be used to reduce sulfur content in gasoline as evidenced by the introduction of the Sbrane™ process by the W.R. Grace company[3]. While presently limited in commercial application, these emerging success stories present an optimistic view for the future of membrane-based separations of organic liquids in demanding environments.

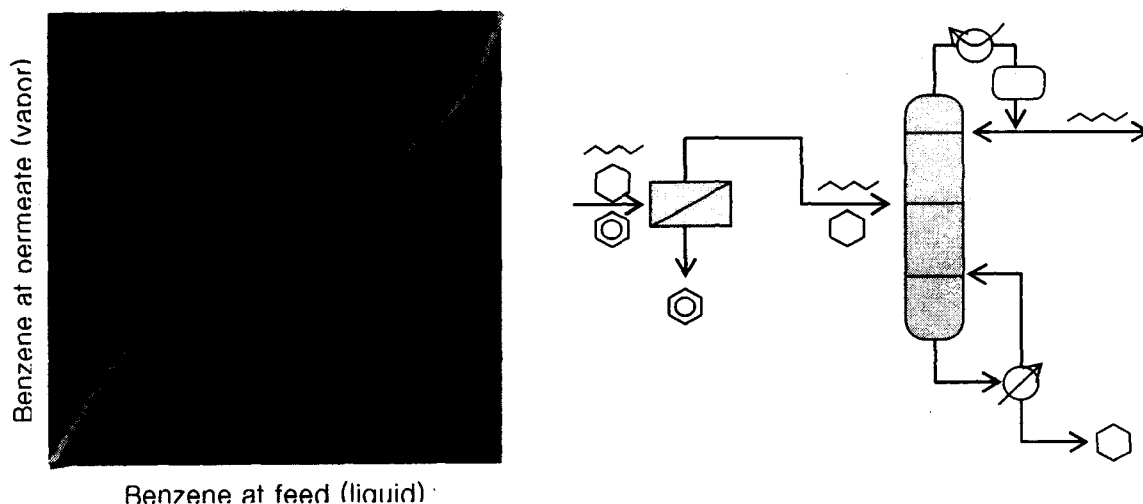


Fig. 1. Vapor-liquid equilibrium curve for benzene and cyclohexane mixtures and illustrated hybrid separation system for benzene and cyclohexane combined with pervaporation

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Benzene-cyclohexane separation is of interest for many reasons. Cyclohexane is physically very similar to benzene as demonstrated by the property comparison shown in Table I. As a result of the very close boiling points (0.6 °C) and similar physical properties benzene and cyclohexane form an azeotrope and thus provide a good model for azeotrope breaking by pervaporation. In addition, the pair may be used to represent the separation of aromatics (benzene) from aliphatics (cyclohexane); a class of separations of technological importance.

Table I. Physical properties of benzene and cyclohexane

		Benzene	Cyclohexane
Freezing point(°C)		5.5	6.6
Boiling point(°C)		80.1	80.7
Density (g/cm ³)		0.8737	0.7786
Refractive Index, n _{25D}		1.498	1.426
Viscosity (cP)		0.65	0.98
Surface Tension (dyn/cm)		28.2	25.3
Molar volume (cm ³ /mol)		89.4	108.7
Collision diameter		0.526	0.606
Solubility Parameters (MPa) ^{1/2}	δ _t	18.5	16.8
	δ _D	18.4	16.8
	δ _p	0.0	0.0
	δ _h	2.0	0.2

2. Materials and Methods

Conceptually, many choices are available for rubbery blends. In this work, the membrane system chosen consisted of the ternary blend of styrene butadiene rubber (SBR) copolymer, acrylonitrile butadiene rubber (NBR) copolymer, and polyvinylchloride (PVC). This blend is known to have a wide range of miscibility; NBR and PVC are miscible in all proportions. Additionally, this blend system possesses excellent solvent and good heat resilience[5]. NBRs and SBR were provided by Nippon Zeon and have 41.5, 28, 18% acrylonitrile content and 23.5% styrene content, respectively. PVC homopolymer was purchased from Aldrich Chemical Company.

Pervaporation experiments were carried out with laboratory scale equipment consisting of a Millipore membrane holder having an effective membrane area in contact with the feed liquid of 13,8 cm². The feed liquid was continuously circulated from and returned to a 3 L reservoir. Downstream pressure was maintained below 5 torr, typically at about 2 torr. After an equilibration period of at least 6 hours, permeate was collected at constant time intervals by means of freezing in a liquid nitrogen cooled cold finger. Analysis of feed and

permeation stream compositions was performed by Gas Chromatography – Mass Spectrometry (Agilent GC-MASS G2570A) and checked by simple refractive index measurements. The separation factor(α) and permeation rate are defined in the usual manner as follows in Equations 1 and 2.

$$\alpha = \frac{w_{P,Benzene} / w_{P,cyclohexane}}{w_{F,Benzene} / w_{F,cyclohexane}} \quad (1) \quad \text{Permeation Rate} = Q = \frac{q \times L}{A \times t} \quad (2)$$

Here $w_{P,i}$ is the weight fraction of component i in permeate and $w_{F,i}$ is that in the feed. Q is the normalized flux or permeation rate where q , L , A and t represent the mass of collected permeate (g), membrane thickness (μm), membrane area (m^2) and operating time (in hours), respectively.

3. Results and Discussion

Pervaporation results for a 50:50 by weight mixture of benzene and cyclohexane are exhibited in Figure 2 (a). In this figure, the selectivity factor, α , defined by Equation 1 is plotted against the permeation rate defined by Equation 2. A typical tradeoff curve is found with fluxes increasing as selectivity decreases. It should be remembered that in this plot each point represents a different blend composition having a distinct performance. Attention should also be focused on the high permeation rates. In principle, a 10 μm permselective layer could produce between 0,5 and 5,0 $\text{kg}/\text{m}^2\text{hr}$ at 25°C.

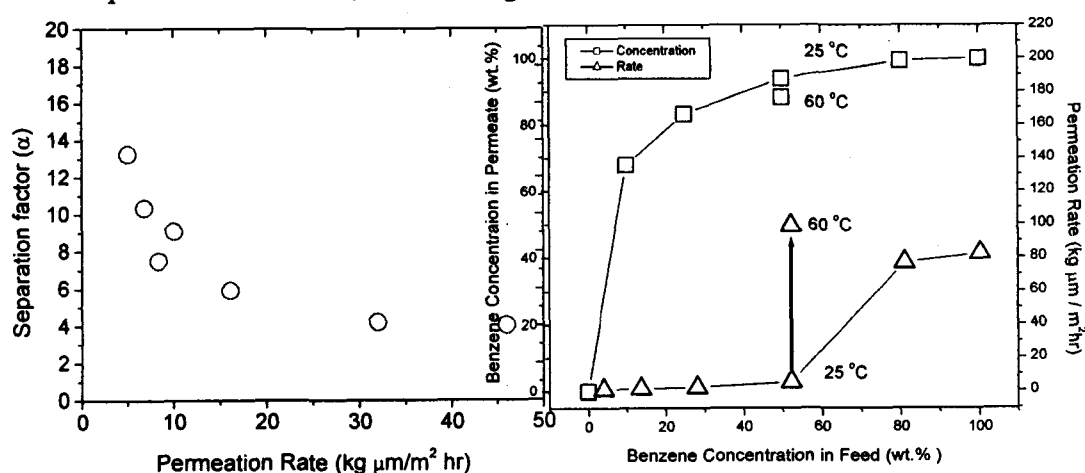


Fig 2. Pervaporation performances of benzene/cyclohexane mixtures through rubbery blend membranes (a) Pervaporation selectivities for a series of rubbery blend membranes, (b) Pervaporation results for optimised (316) formulation

The material with the highest selectivity in Figure 2 (a) is blend 316. Therefore this blended material was investigated across different compositions of the benzene cyclohexane feed mixture; results are presented in Figure 2 (b). Figure 2 (b) also presents one data set for

the 316 blend separating a 50:50 mixture at a temperature of 60 °C. Increasing the temperature from 25 to 60 °C results in a relatively small decrease in permeate concentration (from 93.9 to 88.3 wt.%) but to an enormous increase in permeation rate of nearly a factor of twenty (from 5.0 to 98.9 kg $\mu\text{m} / \text{m}^2 \text{ hr}$). From a practical perspective this means that the azeotropic composition in the benzene-cyclohexane system can be enriched to greater than 85 wt.% at a productivity of nearly 10 (kg / $\text{m}^2 \text{ hr}$) utilizing a 10 μm permselective layer of the optimised blend. To the authors' knowledge, this is the highest fluxing material able to achieve this level of separation reported to date.

4. Conclusions

In this study, a novel approach is undertaken that consists of using blends of rubber polymers that are crosslinked in order to obtain sufficient mechanical and chemical robustness. The utilization of blended materials allows for a wide range of chemical functionality within the blend that can be exploited in order to produce the best possible solubility selectivity. Adoption of a solubility parameter calculation provides an *a priori* methodology for seeking the best blend formulation. While quantitative agreement with experiment is not achieved, the modeling does predict the best blend formulation and as such serves the needed role of providing a rational methodology for *designing* blend membranes for specific purposes. The ideas put forth in this ongoing work have been demonstrated on the model system of benzene and cyclohexane. This system is of industrial interest in itself and also serves as a good model for both azeotrope breaking and aliphatic-aromatic separations. The optimized blend is capable of enriching a 50 wt.% mixture to 88.3 wt.% at a permeation rate of nearly 10 (kg / $\text{m}^2 \text{ hr}$) utilizing a 10 μm permselective layer when operated at 60 °C. This performance is among the best ever reported for the benzene-cyclohexane system.

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