

New Pervaporation Membrane for Petroleum Separation

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ABSTRACT

Hydrocarbon-hydrocarbon separations are one of the most important processes in petroleum refining. Distillation process has been used for separating hydrocarbons, but this conventional process is very energy consuming. Pervaporation separation through polymeric membranes is an emerging process alternative to distillation because of energy savings, compact system installation, reduced capital investment, and other performance attributes. In hydrocarbon separations, polymeric membranes are easily swollen by hydrocarbons and can lose mechanical strength. Chemically robust membranes are needed for the separation of hydrocarbons.

In this study, the blend membrane was applied to separate benzene and cyclohexane. This is a model system for aliphatic and aromatic separation. Cyclohexane is also physically very similar to benzene and as a result of the very closing boiling points (0.6°C), benzene and cyclohexane form an azeotrope. Thus the system provides a good model for azeotrope breaking by pervaporation. The semi-quantitative thermodynamic model predicts that the calculated selectivity increases with increasing Hydrin contents in the blend membranes. Pervaporation experiments utilizing various operating temperatures and feed concentrations with different blend membranes are compared with the result from semi-quantitative thermodynamic calculations.

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 SbraneTM 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.

The approach taken in the present research and development project is to use physical *blends of rubbery materials that are crosslinked*. Blending allows for control of the solubility selectivity of the membrane while chemical crosslinking provides sufficient robustness to meet technical requirements. It must be appreciated that the use of rubbery polymers inherently implies that separation selectivity will be primarily based on differences in solubility as opposed to differences in diffusivity. This premise is based on the fact that for the rubbery systems under consideration, the swelling is very large so that molecular mobility

is very high. The concept associated with the present novel membranes is that by blending together different components considerable control over the solubility selectivity may be achieved. Furthermore, semi-quantitative thermodynamic modelling may be used as a guide for formulating blends for specific separations. In this study, these ideas are applied to the benzene-cyclohexane system.

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.

THEORY

The theoretical approach taken rests on the transport mechanism of pervaporation following the solution-diffusion mechanism.⁶ The relevant quantitative relationship is given by Equation (1).

$$J_i = \frac{D_i}{L} (c_{i0,m} - c_{iL,m}) = \frac{D_i K_i^{gas}}{L} (p_{i0} - p_{iL}) = \frac{P_i}{L} (p_{i0} - p_{iL}) \quad (1)$$

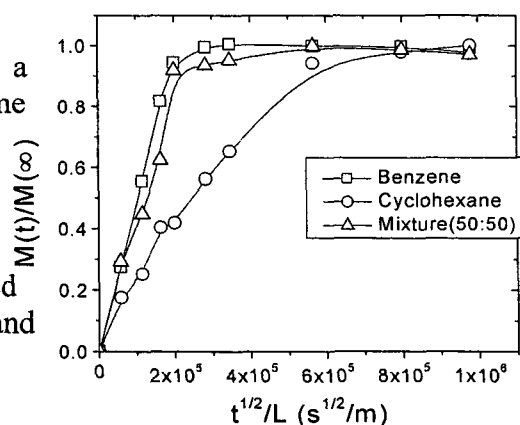
In Equation (1), J_i represents the flux of species i , D is diffusivity, L is the thickness of the membrane, and $c_{i0,m}$ represents the concentration of the species internal to the membrane at position 0 whereas $c_{iL,m}$ represents the concentration internal to the membrane at position L . The K_i^{gas} is a gas phase sorption coefficient that allows reference to the concentrations external to the membrane via the partial pressures on either side of the membrane, p_{i0} and p_{iL} . Finally in Equation (4), the gas permeability coefficient, P_i , is defined as the product of D_i and K_i^{gas} . For complete thermodynamic generality, it should be remembered that the concentration internal to the membrane is related to the concentration external to the membrane by the quality of chemical potentials (μ),

$$\mu_{i,m} = \mu_i \quad (2)$$

Equation (2) is the rigorous basis for the form presented in Equation (1). Equation (1) reveals the basic physics exploited by the present approach. Namely, blending is performed in order to maximize the difference in the product of $D_i K_i$ or in the case of solubility selectivity being dominant, directly in the values for $c_{i0,m}$. A fuller discussion of the quantitative methodology used to accomplish this goal is described below.

RESULTS

Swelling kinetics are of interest for many reasons; a simple experiment is used to both determine the time needed to equilibrate the rubber and to determine diffusion coefficients for the pure solvents. Kinetics of mass uptake for benzene, cyclohexane, and a 50:50 weight mixture of the two are presented in Figure 1 for a 712 blend. Equilibrium swelling is achieved within 4 hours. Diffusion coefficients for benzene and



cyclohexane in the blend are $1.12 \times 10^{-12} \text{ m}^2/\text{sec}$ and $1.92 \times 10^{-13} \text{ m}^2/\text{sec}$, respectively. Published diffusion coefficient data for benzene in natural rubber is $1 \times 10^{-11} \text{ m}^2/\text{sec}$ while the value for benzene in PVC is $3 \times 10^{-17} \text{ m}^2/\text{sec}$.⁷ Accordingly, the values determined are within reasonable bounds.

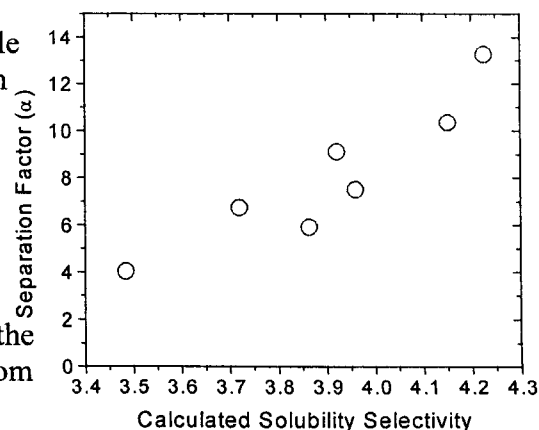
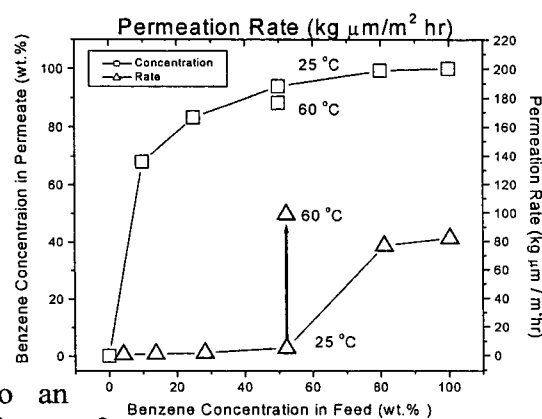
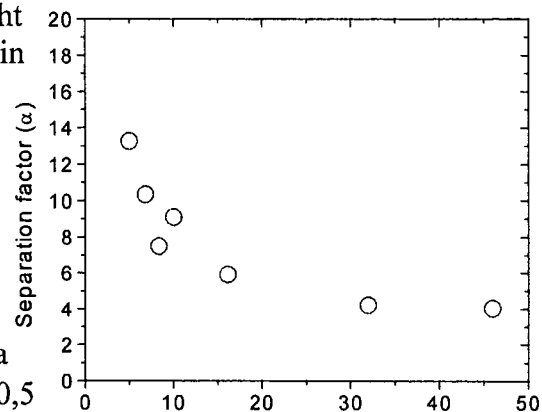
Pervaporation results for a 50:50 by weight mixture of benzene and cyclohexane are exhibited in Figure 2. In this figure, the selectivity factor, α , defined by Equation 2 is plotted against the permeation rate. A typical tradeoff curve is found with fluxes increasing as selectivity decreases. It should 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 $10 \mu\text{m}$ permselective layer could produce between 0,5 and 5,0 $\text{kg}/\text{m}^2\text{hr}$ at 25°C .

The material with the highest selectivity in Figure 3 is blend 316. Therefore this blended material was investigated across different compositions of the benzene cyclohexane feed mixture; results are presented in Figure 3. Figure 3 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 $98.9 \text{ kg } \mu\text{m} / \text{m}^2 \text{ hr}$). 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 ($\text{kg} / \text{m}^2 \text{ hr}$) utilizing a $10 \mu\text{m}$ 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.

A *predictive* approach to the formulation of blended membranes may be pursued through the utilization of group contribution methods. In particular, the UNIFAQ-FV model of Oishi and Prausnitz has been adopted to describe solubility of benzene and cyclohexane in the present blends.⁹ This procedure is only briefly described here but a more exhaustive description is forthcoming.¹⁰

A much more satisfactory description is possible utilizing the UNIFAQ-FV model as evidenced in Figure 4. In this case, the equilibrium solubilities of benzene and cyclohexane were calculated using the UNIFAQ-FV model. That is, the rigorous phase equilibrium problem has been solved for $c_{i,o}$ for both benzene and cyclohexane. This is an iterative calculation as the equilibrium concentration of benzene is affected by the concentration of cyclohexane and vice versa. From



the equilibrium concentrations, solubility selectivity may be calculated. The correlation between measured membrane performance and calculated selectivity is very good.

A few comments on the significance of Figure 4 are warranted. First, it should be considered a great success in the sense that the calculation does provide a rigorous means of screening blend formulations in an *a priori* fashion. There exists a well-posed optimization problem for any separation of organic liquids in which it is desired to maximize solubility differences. Utilizing a group contribution method, solubility selectivities may be calculated as the blend formulation is changed. Figure 4 demonstrates that such a calculation does in fact reveal the optimal formulation of the blend. At a minimum, the approach can distinguish, in an *a priori* fashion, promising blend formulations in a quantitative way and thus reduce the number of needed experiments during membrane development.

CONCLUSIONS

Membranes are entering into the demanding field of hydrocarbon separations as evidenced by the recent commercialization of pervaporation systems. The wide scale deployment of such systems holds the promise of tremendous energy savings and considerable associated environmental benefits. A limitation associated with greater usage is the lack of sufficiently robust membranes with acceptable mechanical and chemical properties. Additionally, the design of membrane materials from an *a priori* perspective for arbitrary separations remains an elusive goal of the membrane technical community.

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 group contribution thermodynamic model 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 / m² 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.

REFERENCES

1. Rautenbach, R.; Albrecht, R. *Journal of Membrane Science* **1985**, *25*, 25-54.
2. Stephan, W.; Nobel, R.D.; Koval, C.A. *Journal of Membrane Science* **1995**, *99*, 259.
3. White, L.S.; Lesemann, M. *Petroleum Chem. Div. Preprints, ACS* **2002**, *47*, 45-47.
4. Baker, Richard W. *Membrane Technology and Applications*; McGraw Hill: New York, 2000.
5. Hofmann, Werner *Rubber Technology Handbook*; Hanser: Munich, 1980.
6. Wijmans, J.G.; Baker, R.W. *Journal of Membrane Science* **1995**, *107*, 1.
7. Sperling, L.H. *Introduction to Physical Polymer Science*; 3rd ed.; John Wiley and Sons: New York, 2001.
8. Hansen, C.M. *Hansen Solubility Parameters: A User's Handbook*; CRC Press: Boca Raton FL, 2000.
9. Oishi, T.; Prausnitz, J. *Ind. Eng. Chem. Process Des. Dev.* **1978**, *17*, 333-339.