

# Prediction of Pervaporation Performance Using Solubility Parameter Calculation

John R. Dorgan\* and Sang Yong Nam\*\*†

\*Chemical Engineering Department, Colorado School of Mines, Golden, Colorado 80401 USA

\*\*Department of Polymer Science and Engineering, Engineering Research Institute, Gyeongsang National University, Jinju 660-701, Korea

(Received November 27, 2003, Accepted December 9, 2003)

**Abstract:** A Prediction of pervaporation performance was studied by solubility parameter calculation approach for the benzene/cyclohexane mixture system using rubbery blend membrane with various solubility parameters. The solubility parameter of the rubbery blend membranes were controlled with different blend ratio of the poly(acrylonitrile-co-butadiene), poly(styrene-co-butadiene) and poly(vinyl chloride). Screening of blend formulations was accomplished by simple swelling tests. When the content of NBR is increased, the swelling of both benzene and cyclohexane are decreased. However, the ratio of benzene swelling to swelling by cyclohexane (the swelling selectivity) increases. The same is true for blends in which the PVC content is increased. Adoption of a solubility parameter calculation provides an *a priori* methodology for seeking the best blend formulation.

**Keywords:** *pervaporation, solubility parameter, benzene, cyclohexane*

## 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.

A common difficulty in utilizing membranes to separate organic liquids is that many common polymeric materials cannot withstand long-term exposure to organic liquids at the moderately high temperatures that are desirable. Excessive swelling of the polymers by organic liquids can produce selectivity losses. In extreme conditions, the membrane material may simply dissolve. If glassy polymers are used for separating liquids, a finite solubility of the organic will plasticize the polymer and lead to both selectivity and mechanical property losses. The need for *robust* membrane materials that are capable of withstanding exposure to the organic liquids has been identified as one of the primary obstacles in achieving organic separations utilizing membrane materials[4].

† Author for all correspondences  
(e-mail : walden@gsnu.ac.kr)

**Table 1.** 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 <sup>3</sup> )	0.8737	0.7786	
Refractive Index, n <sub>D</sub> <sup>25</sup>	1.498	1.426	
Viscosity (cP)	0.65	0.98	
Surface Tension (dyn/cm)	28.2	25.3	
Molar volume (cm <sup>3</sup> /mol)	89.4	108.7	
Collision diameter	0.526	0.606	
Solubility Parameters (MPa) <sup>1/2</sup>	$\delta_t$	18.5	16.8
	$\delta_D$	18.4	16.8
	$\delta_p$	0.0	0.0
	$\delta_h$	2.0	0.2

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 paper, these ideas are applied to the benzene-cyclohexane system.

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 1. 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.

## 2. Materials and Methods

### 2.1. Materials

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.

NBR, SBR and PVC were dissolved in cyclohexanone to prepare a polymer blend solution of known composition. Prepared blend samples are designated numerically as parts NBR, SBR, PVC. For example, 712 represents the blend containing 70wt% NBR, 10 wt% SBR and 20 wt% PVC. Crosslinking agents and when necessary, activator and accelerator, were added into the solution. The solution was cast onto glass plate and dried in a fume hood for approximately 1 day (16-24 h). This cast membrane film was crosslinked under vacuum in an oven at 130°C for 80 min.

### 2.1. Methods

Screening of blend formulations was accomplished by simple swelling tests. Prepared membrane samples were massed and subsequently submerged into solvent in sealed Erlenmeyer flasks with agitation provided by a shaker table for 1 day at 25°C. Upon removal, the samples were blotted dry using a Kimwipe paper towel and immediately massed. The swelling ratio (SR) of was calculated with following equation,

$$\text{Swelling Ratio} = \frac{W_d - W_s}{W_d} \times 100 \quad (1)$$

where  $W_d$  and  $W_s$  are the weight of dry and swollen samples, respectively.

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 cm<sup>2</sup>. 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( $\alpha$ ) and permeation rate are defined in the usual manner as follows in Equations 1 and 2.

$$\alpha = \frac{W_{p, Benzene} / W_{p, cyclohexane}}{W_{F, Benzene} / W_{F, cyclohexane}} \quad (2)$$

$$\text{Permeation Rate} = Q = \frac{q \times L}{A \times t} \quad (3)$$

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 ( $\mu\text{m}$ ), membrane area (m<sup>2</sup>) and operating time (in hours), respectively.

### 3. 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 (4).

$$J_i = \frac{D_i}{L} (c_{i0,m} - c_{iL,m}) = \frac{D_i K_i^{gas}}{L} (p_{i0} - p_{iL}) \quad (4)$$

$$= \frac{P_i}{L} (p_{i0} - p_{iL})$$

In Equation (4),  $J_i$  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 equality of chemical potentials ( $\mu$ ),

$$\mu_{i,m} = \mu_i \quad (5)$$

Equation (5) is the rigorous basis for the form presented in Equation (4). Equation (4) 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.

### 4. Results and Discussion

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 h. Diffusion coefficients for benzene and cyclohexane in the blend are  $1.12 \times 10^{-12}$  m<sup>2</sup>/sec and  $1.92 \times 10^{-13}$  m<sup>2</sup>/sec, respectively. Published diffusion coefficient data for benzene in natural rubber is  $1 \times 10^{-11}$  m<sup>2</sup>/sec while the value for benzene in PVC is 3

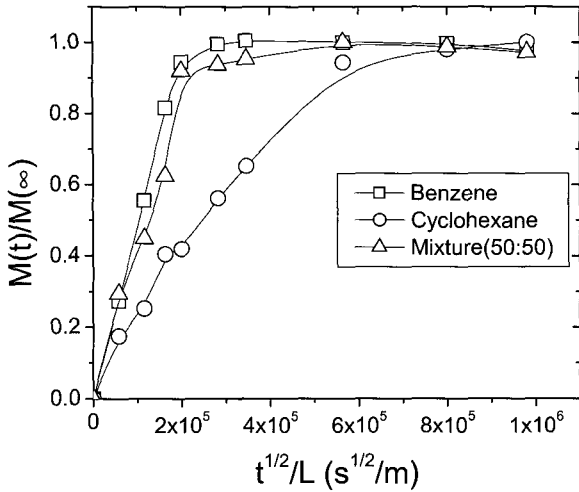


Fig. 1. Mass uptake of components in blend 712.

$\times 10^{-17} \text{ m}^2/\text{sec}$ [7]. Accordingly, the values determined are within reasonable bounds.

Knowing that the blends are equilibrated, a systematic investigation of the relationship between swelling and blend composition can be undertaken. Figure 2 shows the results of swelling tests performed as the NBR content and, separately, the PVC content were changed in two series of blends. When the content of NBR is increased, the swelling of both benzene and cyclohexane are decreased. However, the ratio of benzene swelling to swelling by cyclohexane (the swelling selectivity) increases. The same is true for blends in which the PVC content is increased. These results are easily rationalized by realizing that NBR and PVC are polar

in nature and thus preferentially solubilize benzene to cyclohexane.

The results of Figure 2 may be empirically described by utilizing the concept of the solubility parameter. This physical quantity is described for a low molecular weight compound according to Equation 6.

$$\delta = \left( \frac{E_{coh}}{V} \right)^{1/2} = \left( \frac{\Delta H_{VAP} - RT}{V} \right)^{1/2} \quad (6)$$

Here,  $\delta$  is the solubility parameter,  $E_{coh}$  is the cohesive energy,  $V$  is volume,  $\Delta H_{VAP}$  is the enthalpy of evaporation,  $R$  is the gas constant, and  $T$  is temperature. For polymers, the solubility parameter can be defined as equal to the value of the solvent that produces the maximum degree of swelling in a crosslinked version.

Solubility parameter values for the polymers used in this study are readily available and are often split into dispersion ( $\delta_d$ ), polar ( $\delta_p$ ) and hydrogen bonding ( $\delta_h$ ) components[8]. In the present study, it is convenient to define a parameter,  $d_a$ , according to Equation 7.

$$\delta_a^2 = \delta_p^2 + \delta_h^2 \quad (7)$$

In addition, a simple blending rule for solubility parameters of the blends in the form of Equation 8 is also utilized,

$$\delta_{a, Blend} = \sum_i \psi_i \delta_{a, i} \quad (8)$$

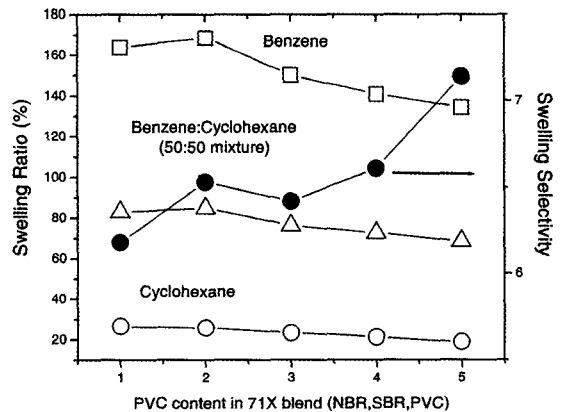
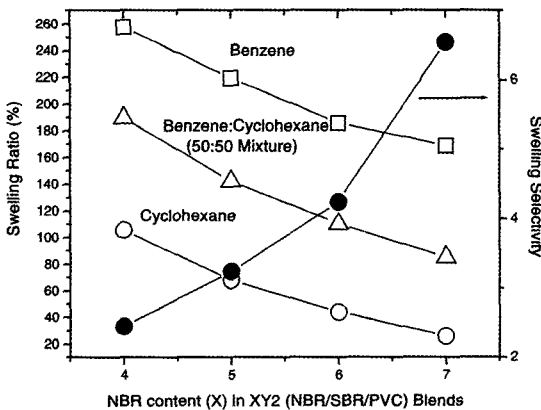


Fig. 2. Effects of blend composition on equilibrium swelling.

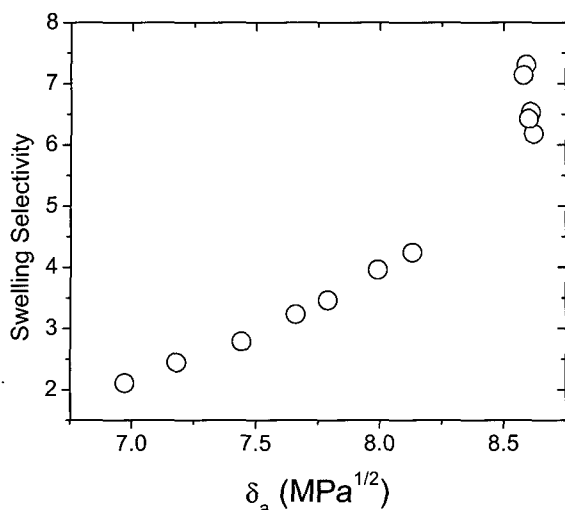


Fig. 3. Selectivity versus polar components of the solubility parameter.

where  $\varphi_i$  represents the volume fraction of species  $i$ . Figure 3 presents the measured swelling selectivities as a function of the calculated polar component solubility parameter for several different blends. From this figure, it can be seen that a reasonably quantitative relationship between solubility selectivity and the polarity of the polymer blend does exist. This establishes a design heuristic for the separation of benzene and cyclohexane, namely, the blend should be made as polar as possible.

Careful inspection of Figure 3 reveals that the solubility parameter approach is limited in utility. Several blends have  $\delta_a$  values around 8.6 MPa<sup>1/2</sup> but significantly different swelling selectivities. Accordingly, while solubility parameters are an easy way to screen blend materials they do not provide a rigorous, quantitative predictive capability.

Pervaporation results for a 50:50 by weight mixture of benzene and cyclohexane are exhibited in Figure 4. In this figure, the selectivity factor,  $\alpha$ , defined by Equation 2 is plotted against the permeation rate defined by Equation 3. 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 mm

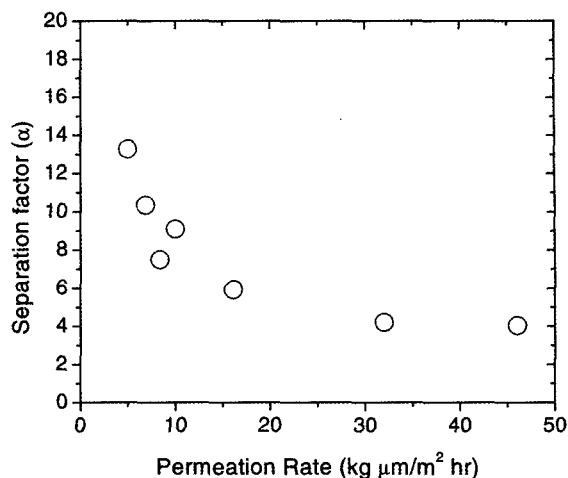


Fig. 4. Pervaporation selectivities for a series of rubbery blend membranes.

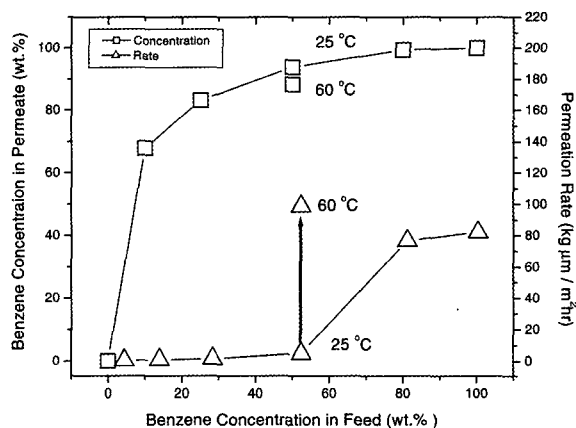


Fig. 5. Pervaporation results for optimised (316) formulation.

permeative layer could produce between 0.5 and 5.0 kg/m<sup>2</sup>·hr at 25°C.

The material with the highest selectivity in Figure 4 is blend 316. Therefore this blended material was investigated across different compositions of the benzene cyclohexane feed mixture; results are presented in Figure 5. Figure 5 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  $\mu\text{m}/\text{m}^2$  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/m<sup>2</sup> hr) utilizing a 10 mm 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

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 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/m<sup>2</sup> hr) utilizing a 10  $\mu$ m permselective layer when operated at 60°C. This performance is among the best ever reported for the benzene-cyclohexane system.

#### Nomenclature

$A$	[m <sup>2</sup> ] membrane area
$a$	[ $II$ ] activity
$c_{i0,m}$	[kg/m <sup>3</sup> ] concentration of $i$ at position 0
$c_{iL,m}$	[kg/m <sup>3</sup> ] concentration of species $i$ at position L.
$D_i$	[m <sup>2</sup> /s] diffusion coefficient of species $i$
$E_{coh}$	[MJ] cohesive energy
$J_i$	[kg/m <sup>2</sup> ·s] flux of species $i$
$K_i^{gas}$	[kg/m <sup>3</sup> ·Pa] gas phase sorption coefficient
$L$	[ $\mu$ m] membrane thickness
$p_{i0}$	[Pa] partial pressures of species $i$ in equilibrium with $c_{i0,m}$
$p_{iL}$	[Pa] partial pressures of species $i$ in equilibrium with $c_{i0,L}$
$P_i$	[(m <sup>2</sup> /s)(kg/m <sup>3</sup> ·Pa)] permeability of species $i$ ; the product of $D_i$ and $K_i^{gas}$ .
$q$	[kg] mass of permeate
$Q$	[kg m/m <sup>2</sup> ·hr.] permeation rate / normalized flux
$t$	[hr or s] time
$T$	[°C] temperature
$V$	[m <sup>3</sup> ] volume
$w_{P,i}$	[ $II$ ] weight fraction of component $i$ in permeate
$w_{F,i}$	[ $II$ ] weight fraction of component $i$ in feed.
$W_d / W_s$	[g] weight of dry sample / weight of swollen sample
$\alpha$	[ $II$ ] separation factor
$\Gamma_k$	[ $II$ ] group residual activity
$\Gamma_k^j$	[ $II$ ] group residual activity in a reference solution of pure $j$ .
$\delta$	[MPa <sup>1/2</sup> ] solubility parameter
$\varphi_i$	[ $II$ ] volume fraction of species $i$
$\mu$	[J/kgmol] chemical potential

$\tilde{v}$	[ <i>II</i> ] reduced volume fraction
$\nu_k^j$	[ <i>II</i> ] number of groups of type <i>k</i> in molecule <i>j</i>
$\Delta H_{VAP}$	[ <i>MJ</i> ] enthalpy of evaporation
$3c_1$	[ <i>II</i> ] number of external degrees of freedom per molecule

## References

1. R. Rautenbach and R. Albrecht, "The separation potential of pervaporation : Part 2. Process design and economics", *J. of Membr. Sci.*, **25**, 25-54 (1985).
2. W. Stephan, R. D. Nobel, and C. A. Koval, "Design methodology for a membrane/distillation column hybrid process", *J. of Membr. Sci.*, **99**, 259 (1995).
3. L. S. White and M. Lesemann, *Petroleum Chem. Div. Preprints, ACS* **2002**, **47**, 45-47 (2002).
4. Baker and W. Richard, *Membrane Technology and Applications*; McGraw Hill: New York, 2000.
5. Hofmann, Werner *Rubber Technology Handbook*; Hanser: Munich (1980).
6. J. G. Wijmans and R. W. Baker, "The solution-diffusion model: a review", *J. of Membr. Sci.*, **107**, 1-21 (1995).
7. L. H. Sperling, *Introduction to Physical Polymer Science*; 3rd ed.; John Wiley and Sons: New York, (2001).
8. C. M. Hansen, *Hansen Solubility Parameters: A User's Handbook*; CRC Press: Boca Raton, FL, (2000).
9. T. Oishi and Prausnitz, *J. Ind. Eng. Chem. Process Des. Dev.* **17**, 333-339 (1978).