

Permeation of Mixtures of Organic Liquids through Polymeric Membranes: Role of Liquid–Liquid Interactions

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ABSTRACT: The permeation of pure organic liquids and mixtures of organic liquids through commercial butyl, neoprene, and nitrile membranes was studied using dynamic material deformation (swelling) and permeation techniques. The derived parameters, the breakthrough time (t_{BT}), steady-state permeation rate (SSPR), and initial swelling rate (SR), show deviations from additivity for the mixtures, based on the parameters of the pure liquids on a mol fraction basis. In the majority of cases for the three membranes examined, the deviations are independent of the nature of the membranes, and the signs of the deviations for t_{BT} are opposite to those for SSPR or SR, provided that the membranes are not degraded by one of the solvents. An approach that considers only solvent–solvent interactions based on the enthalpy of mixing was used to predict deviations for mixtures. For mixtures where the enthalpy of mixing is large and exothermic, the permeation of the mixture is less than expected, while for systems where the enthalpy of mixing is large and endothermic, the permeation is larger than expected. A simple semiempirical model predicts the sign and

magnitude of the permeation of 73% of the system–permeation property combinations investigated, which show significant deviations from ideality. It is interesting to note that the wrong predictions are for systems where the predictions are positive, that is, for SSPR and SR rates with endothermic systems and for t_{BT} with exothermic systems. The exceptions also seem to be for systems that correspond to materials having a high resistance to one of the solvents and a very low resistance to the other solvent. Examples of ternary–mixture permeation data are also given and show that, even if two of the pure components do not permeate through a membrane, the membrane will offer little protection if the third component shows a high affinity for the membrane and if the enthalpies of mixing of this component with the other liquids are endothermic. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 195–215, 2002

Key words: chemical permeation; mixed solvents; protective material; enthalpy of mixing

INTRODUCTION

The chemical resistance of polymeric materials used in protective clothing is usually evaluated with permeation tests that allow breakthrough times, permeation rates, and diffusion coefficients to be determined.^{1–3} Various models have been proposed to explain and predict the observed trends. Some assume that the mass transport of a substance through a polymeric barrier can be described by the Fickian diffusion theory, while others use the solubility concept, which assumes that the higher the solubility of the chemical in the material the lower its chemical resistance will be.^{4–6}

The situation is more complex for mixed solvents, since it is well known that the resistance of protective gloves to mixtures of organic solvents is often different from the permeation expected on the basis of the

properties of the two pure liquids.^{7–17} An extreme example of this is pervaporation,^{18–20} which is the phenomenon by which solvent mixtures can be separated by preferential diffusion of one of the components in a membrane. The general permeation of liquid mixtures is still not well understood and there is no generally accepted model to explain and predict all the observed trends. The objectives of the present study were, therefore, to reexamine the permeation of mixtures of solvents into commercial polymeric membranes, to develop rapid methods of investigating the permeation of mixtures, to better understand the origin of the large deviations from the additivity rule, and to develop a simple model capable of predicting these deviations. For this purpose, complementary techniques (ASTM F739, gravimetric and volumetric permeation tests, and dynamic swelling) were used to generate data on the chemical resistance of typical glove materials to a large number of pure and mixed solvents.

As a predictive tool for commercial systems, simple models are desired in terms of readily available parameters. The concept of solubility parameters has been reasonably successful in this respect.^{1–3} Perme-

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TABLE I
Origin and Purity of Solvents

Solvents	Abbreviation	Origin*	Purity
Acetone	AC	J.T. Baker	ACS reagent 99.8+%
Chloroform	CHCl ₃	MAT Laboratory	HPLC
<i>p</i> -Dioxane	<i>p</i> DIOX	American Chemicals	Spectra grade
Dimethyl sulfoxide	DMSO	MAT Laboratory	HPLC
Heptane	HEPT	Caledon	Distilled in glass
Hexane	HEX	MAT Laboratory	HPLC
Diisopropyl ether	IPE	Aldrich	Anhydrous 99%
2-Propanol	2PrOH	J.T. Baker	ACS reagent
Tetrachloromethane	CCl ₄	American Chemicals	Spectra grade
Tetrahydrofuran	THF	Sigma-Aldrich	HPLC 99.9+% inhibitor free
Toluene	TOL	MAT Laboratory	HPLC

*Suppliers from Montreal, Canada.

ation will be rapid if the solubility parameters of a solvent are close to those of the membrane and slow if they are quite different. Since the affinity of pure liquids for a membrane is related to the solubility parameters of the liquids and since these solubility parameters are related to the enthalpy of vaporization of the liquids, nonideality should be related, at least partially, to the excess enthalpies of the solvent mixture. As a starting point for our choice of systems, we therefore compared the literature data on the permeation of mixtures of solvents⁷⁻¹⁷ with the enthalpies of mixing of liquids. The great majority of systems published show deviations from additivity in the direction of enhanced permeation of the mixture relative to the behavior expected from the two pure liquids. However, to our surprise, nearly all these systems had endothermic enthalpies of mixing. Our choice of systems for the present investigation was therefore largely influenced by the enthalpies of mixing of solvents. Mixtures were chosen which had large and small endothermic and exothermic enthalpies of mixing.

EXPERIMENTAL

Glove materials

Commercially available glove materials were chosen for this study: butyl glove Model 878, 0.78 mm thick, from Best (Coaticook, Quebec, Canada); nitrile glove Model 37-145, 0.40 mm thick, from Ansell-Edmont (Coshocton, OH); and neoprene glove Model 29-870, 0.48 mm thick, from Ansell-Edmont. Also, neoprene from Fairprene (Fairfield, CT), 0.41 and 1.5 mm thick, was used for this study.

Solvents

The purity and origin of the solvents are summarized in Table I. The mixed solvents were prepared by mass and their compositions expressed as mol fractions.

Permeation tests

Permeation tests are the most common methods used to evaluate the chemical resistance of protective materials. In this study, the standard ASTM F739 permeation test²¹ and gravimetric permeation test²² were used.

For the ASTM F739 test method, the experimental setup consists of

- A permeation cell corresponding to the ASTM F739 standard cell. Alternatively, a smaller cell, easier to handle, based on the one described by Bromwich,²³ was used.
- A pneumatic valve controlled by a microprocessor with a 50- μ L injection system for the periodic sampling of the collector chamber of the permeation cell.¹⁷

The permeation products in the standard ASTM F739 test method were analyzed with a GC Hewlett-Packard Model 5890 using an FID ionization detector. Separation of the CHCl₃-THF mixture was obtained with a packed column 10% SP-2100 on an 80/100 Supelcoport 6 foot 1/8-in. o.d.. The temperature of the oven was 80°C. The CHCl₃-IPE mixture was separated with a packed glass column 0.1% SP-1000 on a Carbowax C 20 cm, and the AC-HEX mixture, on a glass column of 2-mm i.d., 25 cm in length, with a Carbowax B, XE-60/1% H₃PO₄.

The gas collector is air circulating, at a rate of 250 mL min⁻¹, in the ASTM permeation cell's collector chamber. With the Bromwich permeation cell, the flow rate was set at 80 mL/min. The sampling of the chamber varied from 30 s to 10 min depending on the mixtures. All experiments were performed at room temperature, which was maintained at 22.5 \pm 0.5°C.

For the gravimetric tests, a previously described conical permeation cell was used. Alternatively, a smaller cell was used. This cell is identical to the one used for volumetric tests, but in which the entrance for

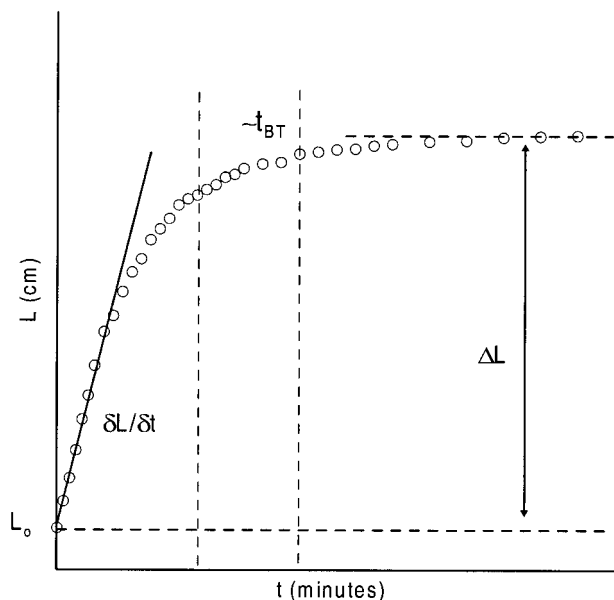


Figure 1 Typical change in length of a strip over time in the presence of liquid.

a Gilmont syringe was closed. A Sartorius balance, Model L420-S, with 1-mg sensitivity was used, and an acquisition system completed the setup.

It is well known that permeation tests that are based on the analysis of the chemical vapors that permeate the membrane and then evaporate are difficult to use with solvents of low volatility. In this study, alternative test methods by which the resistance of protective materials to chemicals of low volatility can be characterized were also used:

- A volumetric test method,²⁴ which consists of a permeation cell that allows the changes in volume of a liquid chemical in contact with the external part of a material to be followed as a function of time when the chemical diffuses through it;
- A dynamic swelling or elongation technique previously described²⁴ in which the change in length of a piece of polymeric membrane immersed in the chemical liquid is followed over time in a specially designed cell.

The breakthrough times were generally obtained from the ASTM F739 test and the gravimetric test methods, while the permeation rates were obtained from the gravimetric and volumetric test methods.

Diffusion coefficients for a pure solvent-polymer system, or mean diffusion coefficients for solvent mixtures-polymer systems, can be obtained from the half-life time of the material deformation using the dynamic swelling test.²⁵ An example of a swelling experiment is given in Figure 1.

As the liquid penetrates the membrane, the membrane swells and this can be followed over time by the

lengthening of a strip of polymeric material. Information on the solvent's solubility in the material can also be obtained from the maximum change in length. The incremental change in the length of the material strip, $\Delta L/L$, the initial swelling rate, $(\partial L/\partial t)/L$ and called SR in this article, and the variation in the mean diffusion coefficient D with the solvent composition are illustrated in Figure 2 for mixtures of THF and CHCl_3 in butyl. This figure shows that similar trends were observed for the three types of representations for material swelling. Since we are primarily interested in the present study for explaining and predicting the trends in deviation from additivity of the properties related to permeation, all swelling data will be reported in terms of SR.

The present study indicated that the simplest technique for rapidly evaluating the chemical resistance of a material is the dynamic swelling experiment, which is independent of solvent volatility. A comparison of the data of SR for pure and mixed solvents immediately gives a good indication of solvent diffusion into the membrane and, consequently, the material's chemical resistance.

RESULTS

Components of the binary solvent systems investigated were systematically selected in order to have a wide variety of enthalpy of mixing values. Most of the systems used CHCl_3 as solvent 1, and THF, IPE, AC, or HEPT, as solvent 2.

Three parameters were used to characterize the diffusion of solvents through membranes: the breakthrough time t_{BT} , the steady-state permeation rate (SSPR), and the initial swelling rate (SR). For most of the solvent mixtures investigated, no attempt was made to obtain information on the permeation properties of the individual solvents.

The breakthrough times t_{BT} refer to the time at which the permeating chemical is first detected. When t_{BT} was more than 8 h, it was arbitrarily given the value 480 min, and SR and SSPR were assumed to be zero. The parameters derived for all the mixtures investigated are summarized in the Appendix. The mean diffusion coefficients derived from the permeation rates, swelling experiments, and solubilities are also given in the Appendix.

The commercial membranes used for this study often contain additives, were not always uniform in thickness, and presented stresses in some cases. Such factors may affect one property more than another. For example, for materials containing additives that are soluble in the solvent, the lengthening of the strip in the dynamic swelling test reaches a maximum and the excess solvent becomes slightly colored. Fortunately, the values and trends for the three parameters, t_{BT} , SR, and SSPR, for mixtures used in this study were

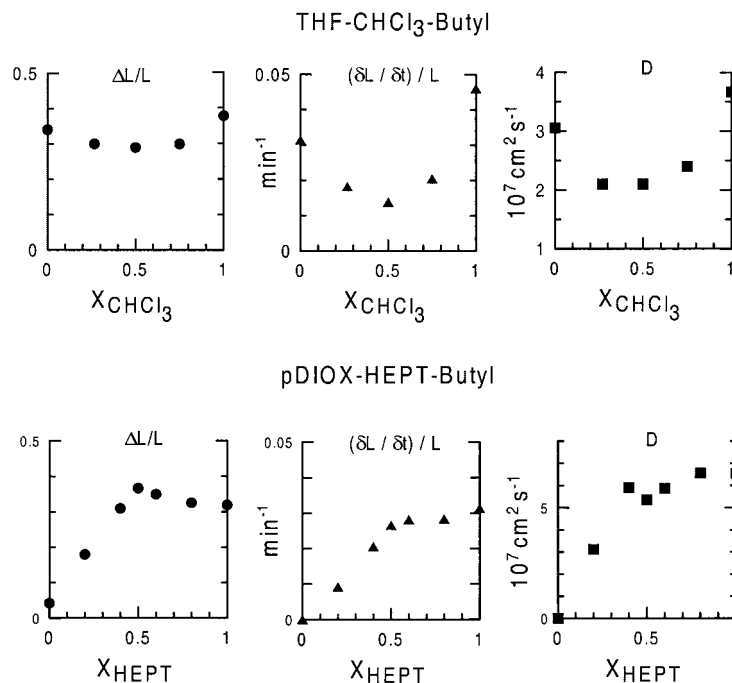


Figure 2 Comparison of the diffusion coefficients of a mixture of THF and CHCl_3 through a butyl membrane with the relative change in total length of a butyl strip and with the relative rate of change in length of the strip.

generally not significantly affected by the presence of such additives.

DISCUSSION

The data obtained with the different techniques for the mixtures were compared with the expected behavior assuming additivity of the parameters of the pure liquids on a mol fraction scale. The trends in the parameters based on different techniques are illustrated in Figure 3 for the CHCl_3 -THF mixture in neoprene membranes of different thicknesses and in Figure 4 for the same system in nitrile and butyl membranes. In some cases, depending on the technique used, differences in the experimental values of the parameters are observed, but the trends for the mixed solvents are generally similar. While the trends are all well defined with CHCl_3 -THF, with other systems, the deviations are small and no definite trends can be observed. When the deviations from additivity of the mixed solvent are significant, three general observations hold for most of the systems examined:

1. The sign of the deviation from additivity is the same for SSPR and SR and opposite that for t_{BT} .
2. The deviations from additivity are largely independent of the nature of the membrane in the case of the three polymeric materials investigated.
3. For mixtures that show large exothermic enthalpies of mixing, an increasing barrier protection

of the polymeric material is observed, while for systems that have large endothermic enthalpies of mixing, there is a decreasing barrier protection.

The similarity in the trends for SSPR and SR is expected since both properties are closely related to solvent diffusion in the membrane. Consequently, if solvent diffusion is faster, t_{BT} should be shorter. The other two rules suggest that solvent-solvent interactions are playing a leading role in the deviations from additivity; here, it is necessary to point out that the solvent-membrane interactions are considered in the present approach since the experimental data for the pure solvents are used. However, there are exceptions to these rules, as will be shown later, indicating that effects other than solvent-solvent interactions are also involved in the deviation from additivity of the parameters.

Thermodynamic model for mixtures

A large exothermic excess enthalpy is indicative of the formation of complexes, and such complexes would be expected to diffuse more slowly through a membrane. On the other hand, an endothermic enthalpy of mixing is associated with an effective repulsion between the two solvents. Therefore, a possible approach for predicting the permeation of mixtures would be to correct the permeation parameters, which are related to solvent-membrane affinity, for attractive

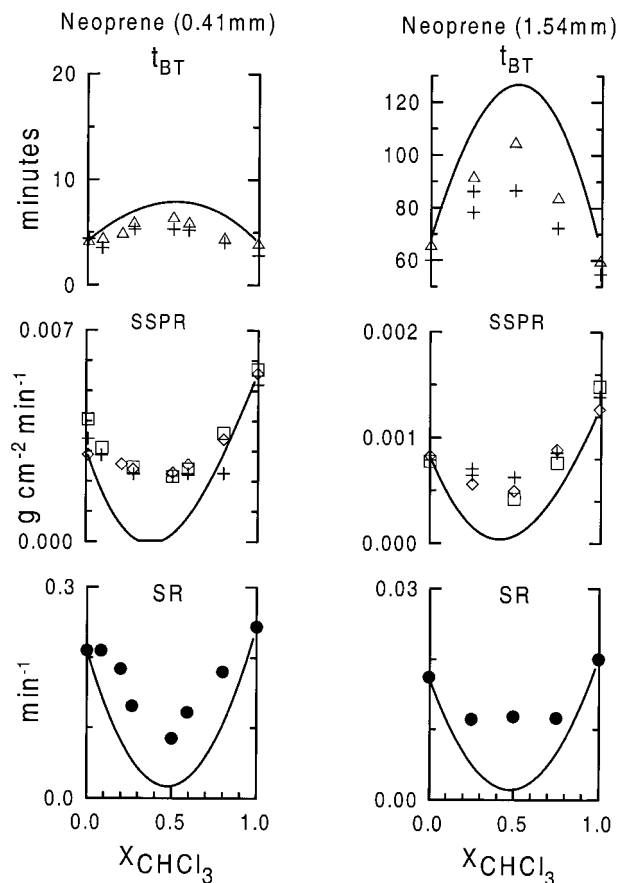
CHCl₃-THF

Figure 3 Comparison of t_{BT} , SSPR, and SR for mixtures of THF and CHCl₃ in neoprene of different thicknesses: (Δ , \diamond) gravimetric technique; (+) ASTM F 739; (\square) volumetric technique; (\bullet) SR.

and repulsive interactions between the two solvents. Vahdat⁹ developed a model for the solubility of liquid mixtures in polymeric membranes in terms of solvent-membrane and solvent-solvent interactions, using Flory-Huggins thermodynamics. Since our objective was to evaluate the role of solvent-solvent interactions and to develop a simple model in terms of readily available parameters, we assumed that the solvent-membrane interactions were additive in a mixture. In view of the studies of Vahdat, this assumption is probably less valid in cases where the permeation of one of the liquids is much less than that of the other.

For an ideal system, the property Y of the mixture is given by the Y property of the components:

$$Y = X_1 Y_1 + (1 - X_1) Y_2 \quad (1)$$

Such equations can be written for t_{BT} , SSPR, SR, D , or any other parameter such as solubility, which characterize solvent-membrane affinity. All these parameters are essentially equilibrium properties and, as

such, should be related to the free energy of the solvent in the membrane. The simplest way of accounting for solvent-solvent interactions is to correct these parameters for the nonideal free energies of each solvent, or $RT \ln \gamma_i$, where γ_i is the activity coefficient of solvent 1 or 2. Since SSPR and SR measure the affinity between the solvent and the membrane, while t_{BT} is inversely proportional to this affinity, the sign of the correction will depend on the property examined. The correction to eq. (1) for nonideal systems can be written for t_{BT} as

$$t_{BT} = X_1 t_{BT,1} (1 - \ln \gamma_1) + (1 - X_1) t_{BT,2} (1 - \ln \gamma_2) \quad (2)$$

For the two other properties, the correction for nonideality must be added instead of subtracted.

It is now necessary to find a very simple way of estimating this nonideal free energy in terms of available parameters. The activity coefficient of component 1 of a binary mixture is related to the excess free energy G^E by²⁶

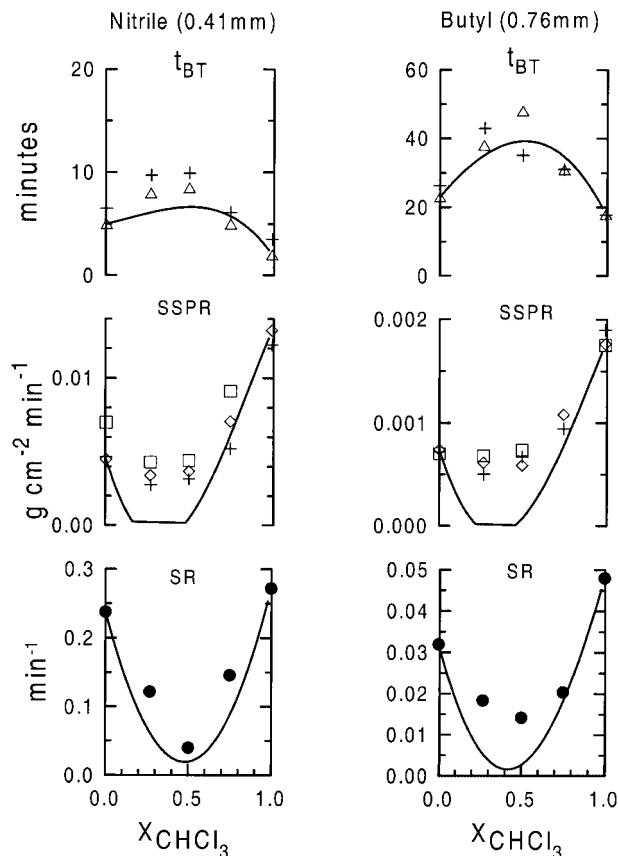
CHCl₃-THF

Figure 4 Comparison of t_{BT} , SSPR, and SR for mixtures of THF and CHCl₃ in nitrile and butyl membranes. Symbols are the same as in Figure 3.

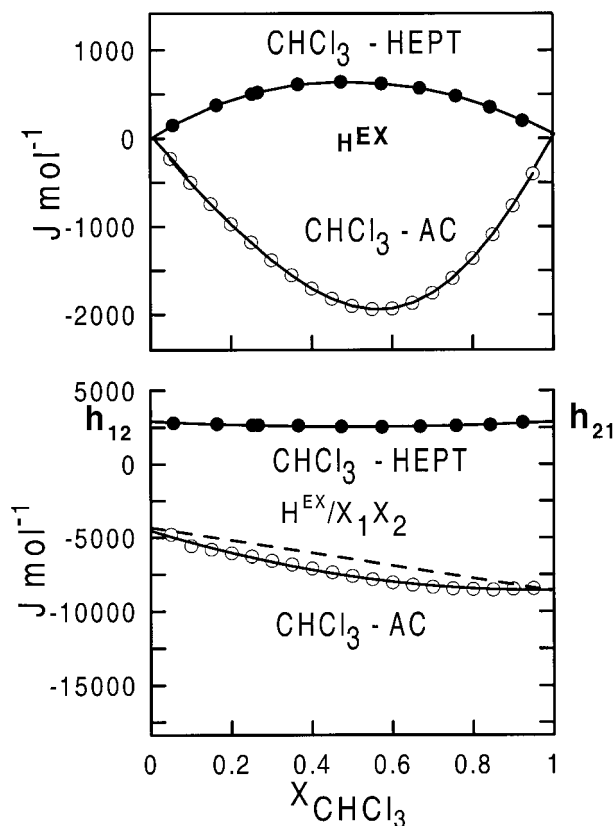


Figure 5 Enthalpies of mixing of liquid mixtures and determination of the partial molar excess enthalpies of both components. Data for CHCl_3 -HEPT²⁵ and CHCl_3 -AC²⁶ at 25°C were taken from the literature. CHCl_3 is component 1 in both cases.

$$RT \ln \gamma_1 = \partial(n_1 + n_2)G^E / \partial n_1 = G^E - X_2 \partial G^E / \partial X_2 \quad (3)$$

where n_i is the number of moles of each component.

Thermodynamic quantities of the mixing of organic solvents are best represented by a plot of Y^E/X_1X_2 against X_1 or X_2 .²⁷ This is illustrated in Figure 5 for enthalpies of mixing. The two parameters h_{12} and h_{21} can be obtained by extrapolation of H^E/X_1X_2 to $X_1 = 0$ and $X_2 = 0$ and are equal to the excess standard partial molar enthalpies:

$$h_{12} = H_1^0 - H_1^* \quad \text{and} \quad h_{21} = H_2^0 - H_2^* \quad (4)$$

where H_i^0 and H_i^* are the standard partial molar enthalpies of component i at infinite dilution and in the pure liquid form. Therefore, h_{12} stands for the difference in enthalpy of solute 1 at infinite dilution in solvent 2 and in the pure solvent 1, and h_{21} , for solute 2 in solvent 1. Since they are standard quantities, such parameters should show reasonably good group additivity. The χ parameter derived from the Flory-Huggins approach is related to an averaged value of h_{12} and h_{21} .

In terms of these parameters, the excess enthalpies of many liquid mixtures can be represented approximately by

$$H^E/X_1X_2 = h_{12} + X_1(h_{21} - h_{12}) \quad (5)$$

(See the dotted line in Fig. 5.) Notable exceptions are systems that self-associate in solution (alcohols in alkanes). It was assumed that eq. (5) holds for all the systems that were considered in the present investigation, and the parameters h_{12} and h_{21} for all the mixtures were calculated from published enthalpies of mixing data. They are given in Table II. If it is further assumed that $G^E \approx H^E$ (the excess entropy is neglected), then, from eq. (5), the activity coefficient of component 1 is given by

$$RT \ln \gamma_1 \approx X_2^2(2h_{21} - h_{12}) - 2X_2^3(h_{21} - h_{12}) \quad (6)$$

This equation can be further simplified when h_{12} and h_{21} do not differ by more than a factor of about 2. Then,

$$RT \ln \gamma_1 \approx X_2^2 g_{12} \approx X_2^2 h_{12} \quad (7)$$

Equation (3) for t_{BT} can then be written as

$$t_{\text{BT}} = X_1 t_{\text{BT},1} [1 - X_2^2/RT(2h_{21} - h_{12}) + 2X_2^3/RT \times (h_{21} - h_{12})] + X_2 t_{\text{BT},2} [1 - X_1^2/RT(2h_{12} - h_{21}) + 2X_1^3/RT(h_{12} - h_{21})] \quad (8)$$

The simpler relation is given by

$$t_{\text{BT}} = X_1 t_{\text{BT},1} (1 - X_2^2 h_{12}/RT) + X_2 t_{\text{BT},2} (1 - X_1^2 h_{21}/RT) \quad (9)$$

As stated earlier, for SSPR and SR, the correction terms for nonideality must be added.

This method of correcting for solvent-solvent interactions is equivalent but less rigorous than that of Vahdat.⁹ On the other hand, it is simpler in form and expressed in terms of readily available parameters.

Test of the model

Even though the model has a thermodynamic basis, it must be considered semiempirical in view of all the assumptions and approximations made. It should still be useful in evaluating the importance of solvent-solvent interactions in the permeation experiments. The trends generated by this model for the three permeation-related parameters are illustrated in Figure 6. Nonideality depends markedly on the sign and magnitude of h_{12} and h_{21} and on the magnitude and difference in the permeation parameters of both solvents.

TABLE II
Enthalpic Parameters and Summary of Agreement Between Model and Observed Trends

Mixed Solvents	Enthalpic Parameters			Neoprene			Nitrile			Butyl		
	h_{12} (J mol ⁻¹)	h_{21} (J mol ⁻¹)	Ref. ^a	t_{BT}	SSPR	SR	t_{BT}	SSPR	SR	t_{BT}	SSPR	SR
HEX-2PrOH	3870 ^b	20,000 ^b	a	Y	N	N	Y		Y	Y	N	N
DEC-AC	10,000	12,000	b				Y	N				
HEX-AC	7500	9000	c	Y	Y	Y	Y	N	N	Y	?	?
HEPT-AC	8060	8880	d	Y								
HEPT-pDIOX	10,000	8600	e	Y	Y	Y	Y	N	?	Y	Y	Y
AC-2PrOH	8206	7185	f	Y	?	?	Y	?	?			
HEPT-THF	4000	3300	g	Y	?	?	Y	N	N	Y	Y	Y
HEPT-CHCl ₃	3860	2860	h	Y	N	N	Y	N	N	Y	Y	Y
HEX-TOL	2680	1980	i	Y	Y		Y	N	N			
HEPT-TOL	2680 ^c	1980 ^c	j	Y	Y	Y						
HEPT-CCl ₄	1830	1160	k	Y	?	Y						
CCl ₄ -pDIOX	-930	-740	l	Y	Y	Y	Y	Y	Y	Y	Y	Y
CCl ₄ -THF	-3780	-2410	m	?	?	Y	N	Y	Y	Y	Y	Y
CHCl ₃ -AC	-4770	-8590	n	?	Y	Y	Y	Y	Y	?	Y	Y
CHCl ₃ -IPE	-9100	-8820	o	Y	Y	Y	N	Y	Y	Y	Y	Y
CHCl ₃ -THF 1.5 mm	-8530	-9720	p	Y	Y	Y	Y	Y	Y	Y	Y	Y
CHCl ₃ -THF 0.4 mm	-8530	-9720	q	Y	Y	Y	Y	Y	Y	Y	Y	Y
CHCl ₃ -DMSO	-5240	-14,860	r	N	Y	Y	N	Y	Y	?	Y	Y
CHCl ₃ -pDIOX	-4870 ^d	-10,307 ^d	s	?	Y	Y	?	Y	Y	N	Y	Y

^a Unless stated otherwise, all data are from the compilation by Maczynski and Bok²⁸: (a) Sakzak, (b) Messow, (c) Shafer, (d) Shen, (e) Inglese, (f) Nagata,²⁹ (g) Inglese, (h) Bissel,³⁰ (i) Lundberg, (j) Lundberg, (k) Grolier, (l) Murakami, (m) Dincer, (n) Becker, (o) Beath, (p) Dincer, (q) Dincer, (r) Fenby, (s) Van Ness.

^b Value of heptane-2PrOH.

^c Value of HEX-TOL.

^d $T = 30^\circ\text{C}$.

As can also be seen, the difference between the predictions with eqs. (8) and (9) are not very large, even when h_{12} and h_{21} differ by a factor of 2. The two equations also give identical predictions when the two permeation parameters are the same.

For a comparison with the experimental data, all systems given in the Appendix are summarized in Table II. The agreement (Y) or disagreement (N) be-

tween the predicted signs of the deviation are indicated in each case when there is no ambiguity. The cases where the deviation from additivity is not clear, considering the experimental uncertainty, the symbol "?" is given. The systems are placed in order of decreasing value of the enthalpic parameter h_{21} , and the systems that are shaded are those where the solubility of one of the components of the mixture in the mate-

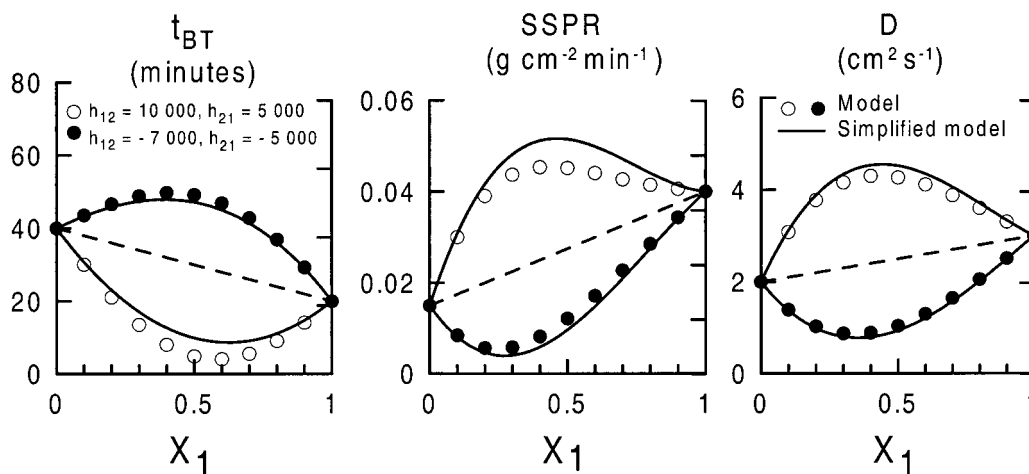


Figure 6 Application of the thermodynamic model in its complete and simplified form to permeation parameters of mixtures of liquids.

rial is quite low (very high t_{BT}), while the solubility of other one is high (very low t_{BT}).

Representative systems are presented graphically in Figures 7–11. Breakthrough times are shown in Figure 7 for two systems that show large exothermic and endothermic enthalpies of mixing. The model is applied to these parameters and gives the correct sign and magnitude for the CHCl_3 –THF with the neoprene system. However, in the case of AC–HEX with nitrile, the sign of the deviation is correctly predicted but a negative t_{BT} is actually predicted at high X_{AC} . Since this is physically impossible, the calculated curves were limited by the axis in all cases where negative values were generated. Another difficulty comes from the arbitrary assignment of a value of 480 for pure HEX and a value of zero for AC in nitrile. Finite values must be used to apply the model correctly.

A better way of testing the model would, therefore, be to use the solubility parameter approach for the pure liquids. In the Hansen model,¹ the difference in the solubility parameters of the liquids and the membranes is expressed as a parameter A . A small value for A indicates a good affinity between the membrane and the solvent, while a large value is indicative of low affinity. The application of the present model to these parameters shows, in Figure 7, a decreasing permeation at intermediate mixture concentrations (higher t_{BT}) for a system that has large exothermic enthalpies of mixing CHCl_3 –THF with neoprene and an increasing permeation for an AC–HEX system that shows a large endothermic enthalpy of mixing with nitrile.

The mixed solvent CHCl_3 –THF with neoprene 0.41 and 1.54 mm thick, represented in Figure 3, and with nitrile and butyl, represented in Figure 4, are good examples of systems where the predictions are nearly quantitative for the three parameters, t_{BT} , SSPR, and SR. All the permeation parameters for the two pure liquids have finite values with all the membranes.

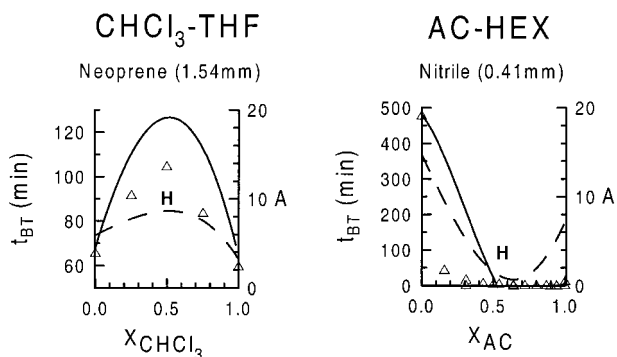


Figure 7 Application of the thermodynamic model to the breakthrough times of two systems: *(full line) the predictions based on the t_{BT} of the pure liquids and the enthalpic parameters; (dotted line) based on the Hansen parameters for the pure liquid and the enthalpic parameters for the deviations.

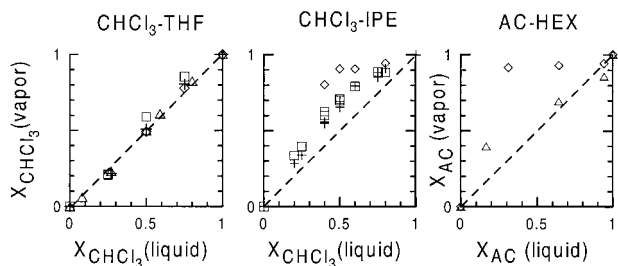


Figure 8 Comparison of the analysis of the permeating vapors with the liquid composition for CHCl_3 –THF and CHCl_3 –IPE through various membranes: (+) butyl 878; (Δ) neoprene Fairprene 0.40 mm; (\square) neoprene Fairprene 1.5 mm, (\diamond) nitrile Ansell–Edmont 37–145.

In Figure 8, the outgoing vapor compositions for three binary mixtures are represented, namely, CHCl_3 –THF, CHCl_3 –IPE, and AC–HEX with neoprene, nitrile, and butyl. In the case of the CHCl_3 –THF mixture, the enthalpy of mixing is quite exothermic and the composition of the outgoing vapors with the three materials indicates that both liquids diffuse at a similar rate, as expected from the strong attractive forces between the two liquids. This is a strong argument in favor of the leading role of solvent–solvent interactions on the chemical diffusion of chemical mixtures through membranes.

The CHCl_3 –IPE system in Figure 9 is another example where the enthalpy of mixing is large and exothermic. The agreement between the experimental and predicted trends is generally good for SSPR and SR for the three materials. In the case of t_{BT} , a good agreement exists with butyl, but is less satisfactory for neoprene where the observed excess value is much smaller than is the prediction, and the wrong deviation is predicted for t_{BT} in nitrile. The t_{BT} (in nitrile and butyl) was duplicated in the INRS and IRSST laboratories using the ASTM F739 test method, and the trends were confirmed. It can be pointed out here that the only case where the wrong t_{BT} deviation is predicted is with nitrile, which has a very low resistance to CHCl_3 and a very high resistance to IPE. An attempt was made to obtain the true t_{BT} value for pure IPE in nitrile, but there was still no passage of vapor after 1000 min. For the vapor composition of the permeating solvents, the CHCl_3 composition is richest with nitrile and slightly richer with neoprene and butyl than is the liquid composition, as shown in Figure 8. This unexpected behavior for systems having negative H^{EX} suggests, as mentioned previously, that effects other than solvent–solvent interactions may affect some of the excess properties.

The CHCl_3 –HEPT system in Figure 10 is an example where H^{EX} is endothermic but relatively small in magnitude (3–4 kJ mol^{-1}). The sign of the predictions are good in some cases and wrong in others (SSPR and SR in nitrile and in neoprene), but experiments confirm

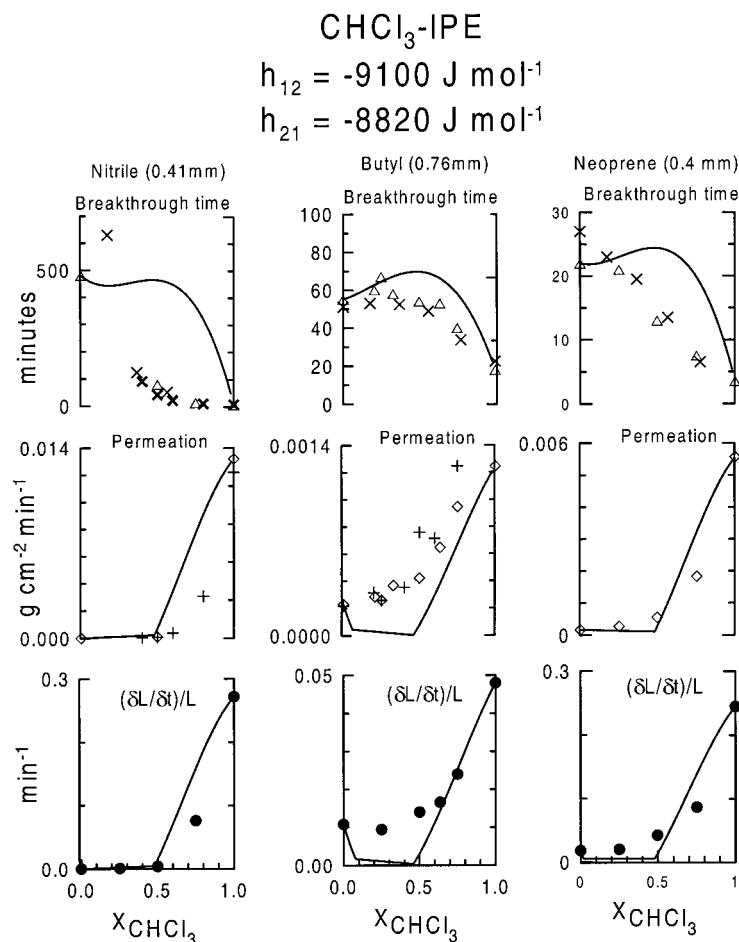


Figure 9 Comparison of t_{BT} , SSPR, and SR for mixtures of CHCl₃-IPE with the thermodynamic model: (Δ) elongation technique; (\times , $+$) ASTM F 739 test method; (\diamond) gravimetric technique.

the predictions that the deviations from additivity should be small. Here, again, specific effects might have influenced some parameters more than others. In addition, the model is less reliable in cases where h_{12} and h_{21} are relatively small since some of the approximations, such as the neglect of the nonideal excess entropy and the assumption that the solvent-polymer interactions are additive for both solvents, may be less valid.

The AC-HEX mixture (Fig. 11) is typical of systems that have large endothermic enthalpies of mixing. The predictions of t_{BT} are quite good for the three materials. However, the sign of the deviation for SSPR and SR with neoprene is predicted, but not the magnitude. In neoprene, the affinities of AC and HEX for the membrane are comparable and it is a typical case where the model predicts the deviation of the permeation parameters. In the case of nitrile, the wrong deviation is predicted for SSPR and SR and the deviation for butyl is not clearly defined. In nitrile and butyl, the affinity is completely different for both solvents: Acetone has a high solubility in nitrile and a low solubility in butyl, but hexane has a low solubility in nitrile and a high solubility in butyl.

AC-HEX is the kind of mixture in which the solvent 1-solvent 1 and solvent 2-solvent 2 interactions are greater than are the solvent 1-solvent 2 interactions, and the solvents have a tendency to unmix. Contrary to systems showing exothermic enthalpies of mixing, the analysis of the outgoing vapor of the mixture shows that AC permeates much faster in nitrile, while both liquids permeate at approximately the same rate in neoprene (Fig. 8). The HEX-AC in nitrile and butyl and CHCl₃-IPE in nitrile systems are typical examples of pervaporation. The present study suggests that the basic conditions for pervaporation to occur are that only one of the solvents has a strong affinity for the membrane and that the enthalpy of mixing of the liquid mixture be large and endothermic.

Anomalous trends

Table II summarizes the agreement between the predicted and observed deviations: agreement in 99 cases, disagreement in 21, and no clear trend in 16 cases. In no cases are the predictions wrong for all three properties. Any model based on either the solubility or

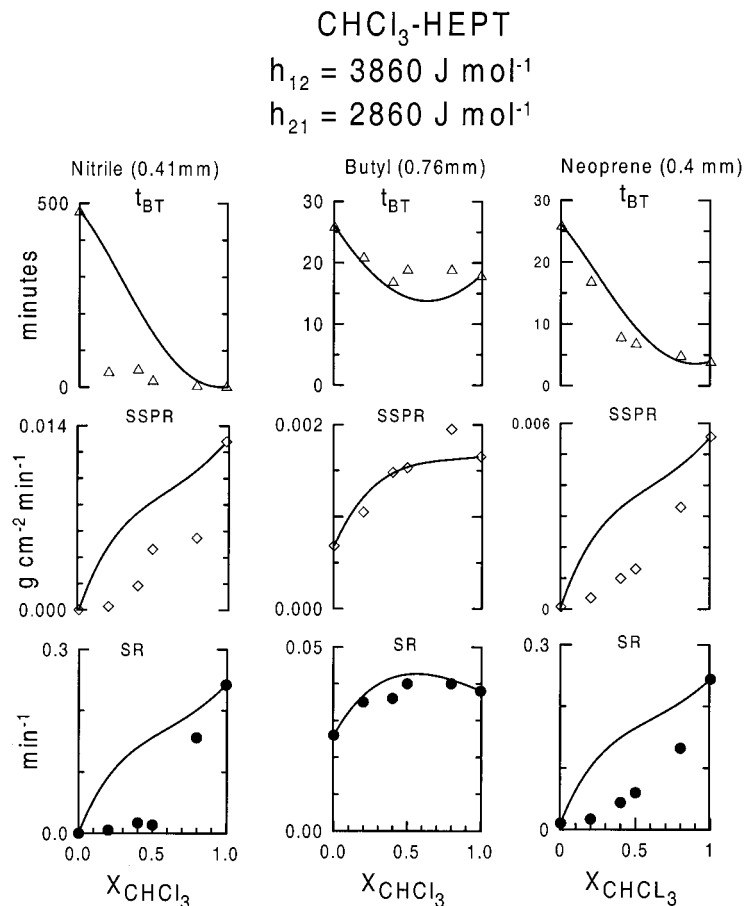


Figure 10 Comparison of t_{BT} , SSPR, and SR for mixtures of CHCl₃-HEPT with the thermodynamic model.

diffusion of the solvents will always predict that the deviation for t_{BT} should be of opposite sign to SSPR and SR. With some of the systems, the affinity of one solvent for the membrane is very high while for the other it is very low, and the sign of the deviations is the same for t_{BT} , SR, and SSPR, which is unexpected. The permeation of such systems was studied by Vahdat et al.⁸ and they suggested that the solubility of the solvent of low permeation is drastically enhanced by the presence of the other solvent, while the solubility of the solvent of high permeation is only slightly decreased. They attributed these observed trends to the plasticizing effect of the liquids and to the elasticity limit of the crosslinked polymeric membranes, which can only accommodate a certain volume of the total solvent. However, examination of Table II shows that this is not always true.

The disagreement between the predicted and observed trends is in systems where the material has a high resistance to one of the solvents and very low resistance to the other one. Furthermore, the deviation from the model is always for systems where the predictions are positive, that is, for SSPR and SR rates with endothermic systems and for t_{BT} with exothermic systems. There is no correlation of the exceptions with

the mixing volumes since, for the mixtures considered in this study, the sign of all the volumes of mixing were the same as those of the enthalpies of mixing. Therefore, the model correctly predicts the observed trends in the majority of the systems studied. This demonstrates the important role of solvent interactions. Deviation from the model's prediction is probably related to material degradation by one of the solvents of the mixture.

Ternary systems

Industrial solvents often contain more than two components. In such cases, the question that arises is: What happens to the protection when the glove is known to be resistant to most components but not all? Such behavior was tested for one ternary system (HEX-AC-2PrOH) with nitrile, butyl, and neoprene membranes. These three solvents are the main components of a commercial cleaner for brakes. In the case of butyl and nitrile, the membrane offers excellent protection to two of the solvents but not to the third one. Figure 12 represents the breakthrough times of the 1:1:1 HEX-AC-2PrOH mixture with the butyl system. The base of the prism represents the composition

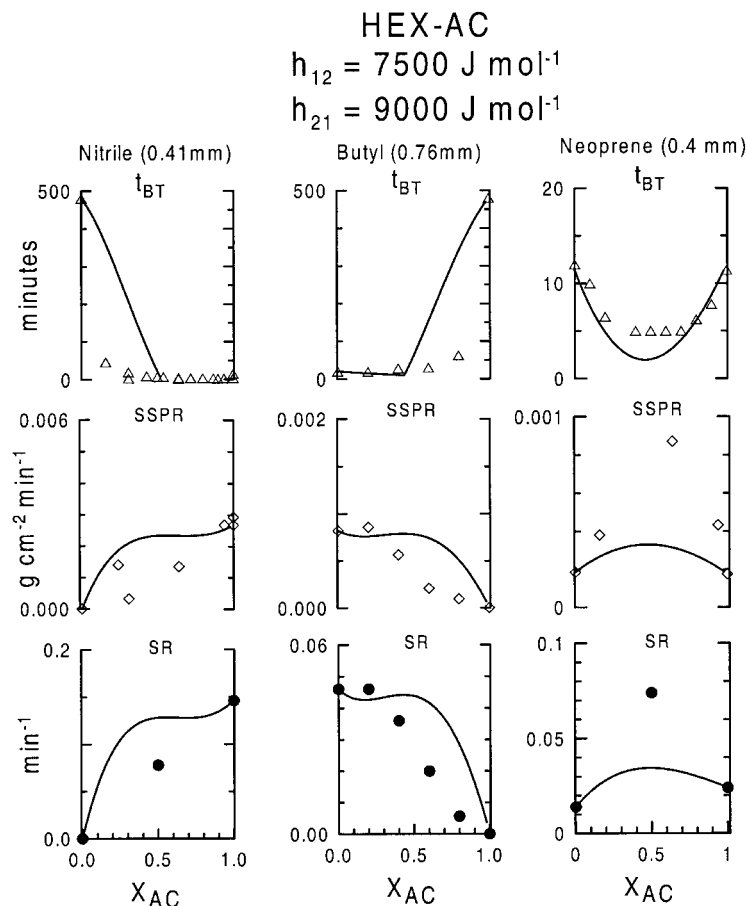


Figure 11 Comparison of t_{BT} , SSPR, and SR for mixtures of AC-HEX with the thermodynamic model.

of the binary or ternary mixtures, and the round point at the center is the 1:1:1 solvent mixture. The simulated breakthrough times for the binary systems are represented on the wall of the prism, and the breakthrough time experimentally obtained with the ternary solvent mixture is represented at the center of the figure. This figure demonstrates that even if butyl is resistant to the AC-2PrOH binary mixture the ternary mixture will permeate more rapidly than expected due to the presence of HEX. The same was observed for a nitrile membrane. This implies that, for multi-component mixtures, it is sufficient that one of the components have an affinity for the membrane and the membrane will offer little protection to the mixture if the enthalpies of mixing of this component with the others are endothermic.

CONCLUSIONS

The aim of the present project was to study the chemical resistance of commercial protective membranes to mixed solvents. All the techniques used gave comparable results, but the swelling experiment, based on the elongation of a polymeric strip over time, is probably the simplest way of estimating the resistance of

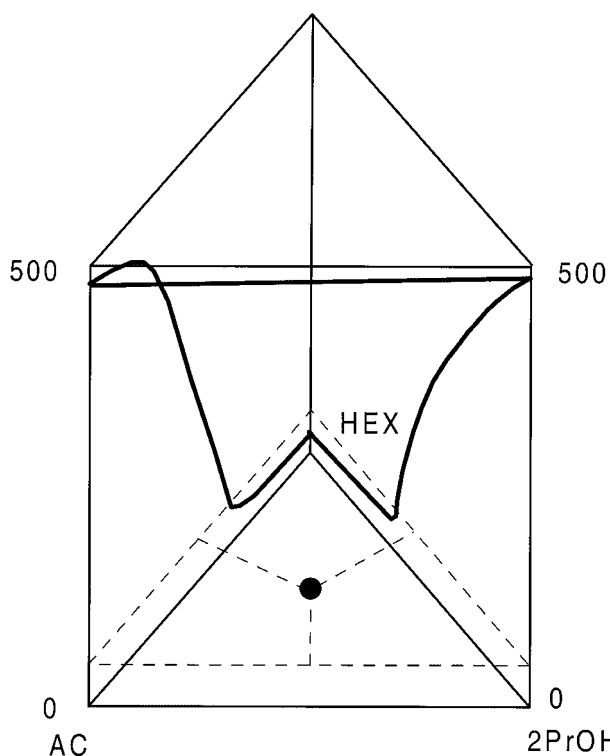


Figure 12 Breakthrough times of the ternary mixture AC-HEX-2PrOH through a butyl membrane.

various membranes to pure solvents or solvent mixtures.

For most systems examined, the observed deviations from additivity for the mixtures, based on the data for the pure solvents on a mol fraction scale, follow three simple rules: (1) The observed trends for t_{BT} are opposite those for SSPR and SR, showing that all these properties are related to the diffusion in the membrane, (2) the sign of the deviation from additivity of the thermodynamic parameters of the pure liquids in the mixture is independent of the nature of the three membranes, provided that the membranes are not degraded by one of the solvents, and (3) the sign and magnitude of the trends are largely related to the enthalpy of mixing of the liquids. The results of this study suggest that solvent-solvent interactions play a leading role in the deviations from additivity in chemical mixtures.

Based on the above observations, a simple semiempirical thermodynamic model was developed to predict the influence of solvent-solvent interactions using permeation parameters for the pure liquids and standard enthalpic parameters for the mixtures. Considering the large uncertainty that is often observed with the determination of permeation parameters of commercial protective membranes, the model generally correctly predicts the sign and even the magnitude of the deviation for most systems when the enthalpic parameters are large. With systems where the enthalpic parameters are small, the model correctly predicts that little deviation from additivity should be observed. However, for systems where one of the solvents of the mixture has a high solubility into the material and the other a very low solubility, the model systematically predicts the wrong deviation for t_{BT} for mixtures where the enthalpy of mixing is endothermic and for SSPR and SR when the enthalpy of mixing is endothermic. The present model predicts positive deviation for these systems. While the model can be improved if necessary, this is not justified at the present time in view of the uncertainty in the origin of

the disagreement and in the determination of the actual parameters characterizing the chemical resistance of membranes to mixed solvents.

One of the main limitations of the present model is the availability of the enthalpic parameters for liquid mixtures. These parameters could, in principle, be determined quite accurately from the enthalpies of a solution, combined with the enthalpies of dilution, if necessary. Unfortunately, such data are generally not available for organic mixtures and the excess standard partial molar enthalpies have to be calculated from the initial slopes of the enthalpies of mixing. With many mixtures, enthalpic measurements were not made at sufficiently low concentration for the extraction of reliable parameters. Furthermore, for many of the mixtures that are used in industry or that are potentially hazardous to health, enthalpies of mixing are not available. It would therefore be very useful if models could be developed to predict these enthalpic parameters from the group additivity of molecular parameters of both pure liquids. A similar model can also be developed using data for vapor-liquid equilibria to estimate the interaction parameters, but the above difficulties would again be present.

Systems with large endothermic enthalpies of mixing are especially troublesome since our present study shows that with such binary or ternary systems only one of the components has to have an affinity for the membrane for the latter to offer little protection to the mixture. This situation is generally encountered with mixtures of polar and nonpolar solvents. Many industrial solvents fall into this category. It is therefore a major problem to develop protective clothing for such mixtures based on single polymeric materials.

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APPENDIX
Permeation Parameters for Mixed Solvents

Solvent mixture	$\Delta L/L$ (cm)	SR (min ⁻¹)	t_{BT} (min)	SSPR gravimetric (g min ⁻¹ cm ⁻²)	SSPR volumetric (g min ⁻¹ cm ⁻²)	S (g/g)	S (g/cm ³)	D_S (10 ⁷ cm ² /s)	D_G (10 ⁷ cm ² /s)	D_V (10 ⁷ cm ² /s)	
Material: Neoprene											
THF-CHCl ₃	X CHCl ₃										
Fairprene 1.54 mm thick	0	0.51	0.0174	66	0.000826	0.000774	1.74	2.64	13.1	7.9	7.4
	0.2514	0.45	0.0114	92	0.000557		1.83	2.86	9.4	4.7	
	0.5020	0.44	0.0118	105	0.000493	0.000417	1.72	2.83	9.6	4.2	3.6
	0.7514	0.44	0.0116	84	0.000885	0.000761	1.38	2.25	10.6	6.60	5.88
								9.2			
	1	0.51	0.02	60	0.00127	0.00148	2.54	3.88	12.5	8.0	9.3
THF-CHCl ₃	X CHCl ₃										
Fairprene 0.41 mm thick	0	0.44	0.21	4.25	0.00318	0.00405	1.66	2.48	10.2	8.56	10.9
					0.00285				6.32	7.67	
	0.0831	0.466	0.21	4.5		0.00311	0.99	1.48	9.06		14.0
	0.1993	0.44	0.184	5	0.00257		2.16	3.23	8.2	5.25	
	0.2671	0.41	0.131	6	0.00240	0.00247	1.12	1.67	7.24	9.38	9.65
	0.5005	0.3	0.0848	6.5	0.00228	0.00216	1.65	2.46	4.98	6.25	5.92
	0.5914	0.38	0.122	6.0	0.00255	0.0024	1.11	1.65	6.59	10.2	9.60
	0.8003	0.44	0.180	4.5	0.00339	0.00360	2.06	3.07	10.5	8.10	8.60
								6.37			
	1	0.51	0.244	3.5	0.00557	0.0059	2.54	3.79	9.51	9.79	10.4
AC-CHCl ₃	X CHCl ₃										
	0	0.08	0.024	12	0.000185	0.000181	0.196	0.302	5.31	4.08	4.00
	0.2504	0.14	0.034	10	0.000523	0.000408	0.365	0.545	5.28	6.33	4.94
	0.4759	0.24	0.074	9	0.00106		0.657	0.981	5.39	7.20	
	0.7485	0.36	0.094	6	0.00247	0.00244	0.927	1.38	6.69	11.9	11.8
	1	0.51	0.244	3.5	0.00557	0.0059	2.54	3.79	9.51	9.79	10.4
DMSO-CHCl ₃	X CHCl ₃										
	0	0.05	0.00021	480	0		0.216	0.322	0.088		
	0.1402	0.03	0.00042	240	0.000080		0.266	0.397	0.35	1.40	3.34
	0.21985	0.058	0.00092	125	0.000137	0.000191	0.231	0.345	0.37	2.76	
	0.3041	0.062	0.0024	94	0.000034	0.000282	0.479	0.715	0.81	0.32	2.62
	0.4672	0.15	0.0194	38	0.000213		0.578	0.863	1.67	1.65	
	0.5487	0.164	0.0116	28	0.000247	0.000331	0.525	0.784	1.67	2.17	2.91
	0.7238	0.29	0.046	12	0.00143	0.00115	0.925	1.38	4.02	7.18	5.77
	1	0.5	0.244	3.5	0.00557	0.0059	2.54	3.79	9.51	9.79	10.4
IPE-CHCl ₃	X CHCl ₃										
	0	0.11	0.018	25	0.000168	0.000174	0.215	0.331	4.34	3.38	3.24
	0			27							
	0.1737			23							
	0.25	0.13	0.020	21	0.000273		0.315	0.470	3.8	3.85	
	0.3659			19.5							
	0.5006	0.184	0.042	13	0.000553	0.000494	0.553	0.826	4.75	4.43	3.96
	0.5641			13.5							
	0.6397				0.00128		0.890	1.33	5.3	6.33	
	0.7503	0.296	0.086	7.5	0.00183	0.00195	0.996	1.49	6.22	8.18	8.72
	0.7997			6.5							
	1	0.51	0.244	3.5	0.00557	0.0059	2.54	3.79	9.51	9.79	10.4
PDIOX-CHCl ₃	X CHCl ₃										
	0	0.39	0.028	20	0.00533		1.18	1.82	2.16	2.02	
	0.5	0.358	0.05	12.5	0.00119	0.00106	1.75	2.61	3.45	3.04	2.71
	1	0.5	0.244	4	0.00557	0.0057	2.54	3.79	9.51	9.79	10.0
HEPT-CHCl ₃	X CHCl ₃										
	0	0.07	0.0106	26	0.000078	0.000118	0.122	0.188	4.05	2.76	4.18
	0.2	0.12	0.0172	17	0.000366		0.280	0.418	4.29	6.42	

APPENDIX *Continued*

Solvent mixture	$\Delta L/L$ (cm)	SR (min ⁻¹)	t_{BT} (min)	SSPR		S (g/g)	S (g/cm ³)	D_s (10 ⁷ cm ² /s)	D_c (10 ⁷ cm ² /s)	D_v (10 ⁷ cm ² /s)
				gravimetric (g min ⁻¹ cm ⁻²)	volumetric (g min ⁻¹ cm ⁻²)					
	0.4	0.20	0.044	8	0.000997		0.458	0.684	5.79	10.4
	0.5	0.22	0.060	7	0.00130		0.751	1.12	8.66	8.89
	0.8	0.36	0.132	5	0.00329		1.51	2.26	8.15	9.97
	1	0.5	0.244	4	0.00557	0.0057	2.54	3.79	9.51	9.79
THF-CCl ₄	X CCl ₄									
	0	0.484	0.21	4	0.00320	0.00405	1.66	2.48	7.21	8.61
	0.20029	0.46	0.20	5	0.00318	0.00340	1.02	1.52	9.27	14.3
	0.45663	0.44	0.128	8	0.00261	0.00276			6.05	
	0.83359	0.368	0.072	12	0.00215	0.00200	1.77	2.64	4.01	5.41
	1	0.460	0.062	12	0.00178	0.00144	2.38	3.67	3.58	3.23
pDIOX-CCl ₄	X CCl ₄									
	0	0.39	0.028	20	0.00533		1.18	1.82	2.16	2.02
	0.469	0.355	0.046	15	0.00122		1.20	1.80	2.53	4.52
	1	0.460	0.062	12	0.00178	0.00144	2.38	3.67	3.58	3.23
HEPT-CCl ₄	X HEPT									
	0	0.460	0.062	12	0.00178	0.00144	2.38	3.67	3.58	3.23
	0.09969	0.3	0.08	14	0.00123	0.00109				
	0.1413	0.32	0.046	15	0.00119	0.00135	1.38	2.06	4.13	3.99
	0.39703	0.19	0.098	13	0.000626	0.000572	0.764	2.06	3.52	2.10
	0.7693	0.106	0.0154	23	0.000131	0.000105	0.239	0.357	3.19	2.50
	0.9	0.068	0.006	28	0.000086	0.000067	0.157	0.234	1.92	2.53
	1	0.07	0.0106	26	0.000078	0.000118	0.122	0.188	4.05	2.76
TOL-HEPT	X HEPT									
	0	0.37	0.112	6	0.00169	0.00163	1.50	2.24	7.2	5.28
	0.09435	0.35	0.122	7	0.00164	0.00184	1.19	1.77	8.48	6.45
	0.18727	0.33	0.118	7	0.00145	0.00192	1.04	1.55	8.04	6.42
	0.42037	0.23	0.054	8	0.000821	0.000851	0.704	1.05	5.61	5.14
	0.78537	0.104	0.022	17	0.000199	0.000142	0.198	0.296	5.12	4.62
	0.89201	0.080	0.0134	22	0.000100	0.000081	0.158	0.236	4.25	2.93
	1	0.07	0.0106	26	0.000078	0.000118	0.122	0.188	4.05	2.76
pDIOX-HEPT	X HEPT			1						
	0	0.39	0.028	20	0.00533		1.18	1.82	2.16	2.02
	0.06579	0.3	0.05	16	0.000660	0.000624	1.12	1.67	3.9	2.69
	0.14152	0.35	0.054	14	0.000813	0.000798	1.15	1.72	3.7	3.22
	0.5	0.22	0.05	11	0.000839	0.000787	0.94	1.40	3.43	4.02
	0.78391	0.18	0.046	15	0.000360	0.000230	0.406	0.606	5.52	4.11
	0.89602	0.104	0.024	21	0.000118	0.000127	0.197	0.294	6.10	2.76
	1	0.07	0.0106	26	0.000078	0.000118	0.122	0.188	4.05	2.76
AC-HEPT	X AC			1						
	0	0.07	0.0106	26	0.000078	0.000118	0.122	0.188	4.05	2.76
	0.5			8			0.417	0.623	6.93	
	0.6649						0.420	0.627	7.40	8.17
	1			13			0.192	0.287	5.31	4.30
THF-HEPT	X HEPT									
	0	0.484	0.21	4	0.00319	0.00405	1.66	2.48	7.21	8.58
	0.5	0.224	0.07	7.5	0.000796	0.000798	0.595	0.888	6.59	6.03
	1	0.07	0.0106	26	0.000078	0.000118	0.122	0.188	4.05	2.76
AC-2PrOH	X AC			1						
	0									
	0.5	0.052	0.005	35	0.000060		0.134	0.199	4.14	2.06
	1	0.08	0.024	12	0.000185	0.000181	0.196	0.293	5.31	4.21

APPENDIX *Continued*

Solvent mixture	$\Delta L/L$ (cm)	SR (min^{-1})	t_{BT} (min)	SSPR gravimetric ($\text{g min}^{-1} \text{cm}^{-2}$)	SSPR volumetric ($\text{g min}^{-1} \text{cm}^{-2}$)	S (g/g)	S (g/cm^3)	D_s ($10^7 \text{cm}^2/\text{s}$)	D_G ($10^7 \text{cm}^2/\text{s}$)	D_V ($10^7 \text{cm}^2/\text{s}$)	
AC-HEX- 2PrOH	X AC										
	0.3333	0.11	0.0268	11	0.000356 0.000294	0.000256	0.276	0.412	6.13	6.05 5.00	4.24
2PrOH-HEX	X HEX										
	0			1							
	0.5	0.05	0.0058	26	0.000066	0.000043	0.128	0.191	2.18	2.36	1.54
	1.0	0.13	0.0090	16	0.000141		0.115	0.177	3.92	5.31	
HEX-AC	X AC										
	0	0.13	0.0090	16	0.000141		0.115	0.177	3.92	5.31	
	0.5	0.208	0.074				0.393	0.587	8.46		
	1	0.08	0.024	12	0.000185	0.000181	0.196	0.293	5.31	4.21	4.12
	0			10.1	0.000185						
	0.16			6.2	0.000381						
	0.64			3.4	0.000871						
	0.94			8.2	0.000433						
	1			12.3	0.000175		0.196	0.293	5.31	3.99	
	0			11.4							
	0.16			7.8							
	0.31			6.3							
	0.43			5.0							
	0.54			5.2							
	0.6			5							
	0.73			5							
	0.81			5.2							
	0.88			6.5							
	0.94			10.0							
	1			12.0							
Fairprene 0.8 mm thick	0	0.07	0.0048								
	0.08610	0.11	0.008								
	0.1659	0.14	0.0116								
	0.3091	0.18	0.018								
	0.6416	0.22	0.024								
	0.8774	0.14	0.013								
	0.9416	0.10	0.0084								
	0.9714	0.09	0.0072								
	1	0.07	0.0040	53							
Fairprene 1.7 mm thick	0			163	0.000057						
	0.16			121	0.000110						
	0.64			74	0.000306						
	0.94			107	0.000175						
	1.0			196	0.000053						
TOL-HEX	X HEX										
Fairprene 0.41 mm thick	0			4.8	0.001693		1.5	2.24		5.29	
	0.08			2.8	0.001643						
	0.43			4.0	0.001298						
	0.88			7.0	0.000335						
	1.0	0.13	0.0090	16	0.000141		0.115	0.177	3.92	5.31	
	0			4.4							
	0.08			3.8							
	0.18			3.7							
	0.26			3.5							
	0.36			3.8							
	0.43			4.3							
	0.56			5.3							
	0.66			6.2							
	0.77			7.5							
	0.88			8.0							
	1.0			11.4							

APPENDIX *Continued*

Solvent mixture	$\Delta L/L$ (cm)	SR (min^{-1})	t_{BT} (min)	SSPR gravimetric ($\text{g min}^{-1} \text{cm}^{-2}$)	SSPR volumetric ($\text{g min}^{-1} \text{cm}^{-2}$)	S (g/g)	S (g/cm^3)	D_s ($10^7 \text{cm}^2/\text{s}$)	D_c ($10^7 \text{cm}^2/\text{s}$)	D_v ($10^7 \text{cm}^2/\text{s}$)		
Material: Nitrile												
THF- CHCl_3	X CHCl_3											
Solvex 37-145												
0.40 mm	0	0.68	0.238	5	0.0045	0.007	3.05	3.20	3.81	6.56	9.84	
thick	0.2677	0.54	0.122	8.	0.00339	0.00444	1.67	1.76	2.62	8.62	11.3	
	0.5	0.532	0.04	8.5	0.00368	0.00512	1.98	2.08	1.81	8.33	11.6	
	0.75	0.62	0.146	5.	0.00706	0.00940	3.12	3.27	2.10	2.82	9.99	13.3
	1	0.86	0.272	2.5	0.0132	0.0216	4.34	4.55	4.32	13.5	22.1	
AC- CHCl_3	X CHCl_3											
	1	0.50	0.19	3.5	0.003338	0.003467	4.34	4.55	4.32	3.33	3.54	
	0.2504	0.53	0.238	5	0.00355	0.00513	1.19	1.25	4.11	12.5	18.1	
	0.4759	0.57	0.162	6	0.00415	0.00565			2.92			
	0.7485	0.71	0.204	5	0.00778	0.0105	3.63	3.81	3.65	9.85	13.3	
	1	0.85	0.272	3.5	0.0132	0.0216	4.34	4.55	4.32	13.5	22.1	
DMSO- CHCl_3	X CHCl_3											
	0	0.36	0.022	44		0.00153	1.44	1.51	0.55		4.90	
	0.1791	0.522	0.024	30		0.00468	2.14	2.25	0.67		9.93	
	0.4672	0.66	0.044	19	0.00242				1.02			
	0.4953	0.686	0.044	19	0.00210	0.00651	4.25	4.46	1.14	2.27	7.04	
	0.6043	0.686	0.034	13	0.00288	0.0112	2.67	2.80	1.43	4.99	19.4	
	0.7238	0.66	0.076	8	0.00552	0.0147	3.84	4.03	2.56	6.58	17.5	
	0.8548	0.81	0.174	5	0.00984	0.0293	3.48	3.65	3.15	12.8	38.0	
	1	0.85	0.272	2	0.0132	0.0216	4.34	4.55	4.32	13.5	22.1	
IPE- CHCl_3	X CHCl_3											
	0	0.054	0.00006	480	0		0.114	0.120	.0094			
	0.1737			630								
	0.25	0.082	0.00092	480								
	0.3659			128								
	0.5	0.198	0.0042	78	0.000098		0.821	0.861	0.22	0.512		
	0.5641			50								
	0.75	0.462	0.076	11		0.00249						
	1	0.85	0.272	2	0.0132	0.0216	4.34	4.55	4.32	13.5	22.1	
pDIOX- CHCl_3	X CHCl_3											
	0	0.66	0.028	28	0.000885		2.26	2.37	1.10	1.74		
	0.5	0.57	0.072	17.5	0.00215	0.00235	3.12	3.27	1.23	2.95	3.23	
	1	0.85	0.272	2	0.0132	0.0216	4.34	4.55	4.32	13.5	22.1	
CHCl_3 -HEPT	X CHCl_3											
	0	0	0	480	0	0						
	0.2	0.10	0.0052	44	0.00027		0.411	0.431	0.425	3.44		
	0.4	0.21	0.0172	51	0.00183		0.878	0.921	0.77	9.93		
	0.5	0.28	0.0136	20	0.00461		1.19	1.25	0.97	19.6		
	0.8	0.574	0.156	6	0.00547		2.58	2.71	3.51	10.1		
	1	0.84	0.242	3.5	0.0128	0.0057	4.34	4.55	4.32	13.1	58.4	
THF- CCl_4	X CCl_4											
	0	0.64	0.13	5	0.00452		3.05	3.20	3.81	6.59		
	0.5	0.46	0.022	22	0.000968				5.31			
	1	0.17	0.002	160	0.000027	0.00054	0.193	0.202	6.89	0.62	12.4	
pDIOX- CCl_4	X CCl_4											
	0	0.66	0.028	28	0.000885		2.26	2.37	1.1	1.80		
	0.469	0.35	0.0128	84G 48V	0.000314		2.28	2.39	0.76	0.65		
	1	0.17	0.00172	-160		0.000540	0.193	0.202	0.057	0.62	12.4	

APPENDIX *Continued*

Solvent mixture	$\Delta L/L$ (cm)	SR (min^{-1})	t_{BT} (min)	SSPR gravimetric ($\text{g min}^{-1} \text{cm}^{-2}$)	SSPR volumetric ($\text{g min}^{-1} \text{cm}^{-2}$)	S (g/g)	S (g/cm^3)	D_s ($10^7 \text{cm}^2/\text{s}$)	D_c ($10^7 \text{cm}^2/\text{s}$)	D_v ($10^7 \text{cm}^2/\text{s}$)
AC-2PrOH	X AC									
	0	0.04	0.000018	480						
	0.5	0.29	0.076	13	0.000688	0.000469	0.717	0.752	2.42	4.42
					0.000453	0.000361				2.91
	1	0.50	0.19	3.5	0.003338	0.003467	4.34	4.55	4.32	3.33
										3.54
AC-HEX- 2PrOH	X AC									
	0.3333	0.216	0.032	20	0.000349	0.000432	0.495	0.519	1.65	3.47
										3.61
2PrOH-HEX	X HEX									
	0	>0.04	0.000018	480						
	0.5	0.08	0.00014	480			0.170	0.178	0.019	
	1.0	0.03	0.000006	480						
AC-HEX	X AC									
	0	0.03	0.000006	480						
	0.24			23		0.000115				
	0.5	0.274	0.078	7						
	0.9			2.2						
	1	0.50	0.19	3.5	0.003338	0.003467	4.34	4.55	4.32	3.33
	0			480	0					3.54
	0.31			15.4	0.000316					
	0.64			3.2	0.001343					
	0.94			2.2	0.002658					
	1.0			3.2	0.002650					
	0			480						
	0.16			46						
	0.31			19.3						
	0.43			9.2						
	0.54			7.2						
	0.64			4.8						
	0.72			3.7						
	0.80			3.5						
	0.87			3.3						
	0.94			2.2						
	1.0			3.5						
Solvex 37-165 0.63 mm thick	0									
	0.7286	0.38	0.0092					4.49		
	0.8774	0.44	0.024					5.01		
	1	0.46	0.034							
AC-DEC	X AC									
Solvex 37-145 0.40 mm thick	0			480						
	0.2			72	0.000040					
	0.5			11	0.000699					
	1	0.50	0.19	3.5	0.003338	0.003467	4.34	4.55	4.32	3.33
										3.54
THF-HEPT	X HEPT									
	0	0.686	0.252	5.5	0.00521	0.000720	3.05	3.20	3.81	7.59
									5.31	1.05
	0.5	0.18	0.032	50	0.000095	0.000327	0.252	0.264	1.25	1.52
	1	0	0	480	0	0				5.22
pDIOX-HEPT	X HEPT									
	0	0.66	0.028	28	0.000885		2.26	2.37	1.1	1.74
	0.1999	0.37	0.024	32	0.000587	0.000803	1.38	1.45	0.838	1.94
	0.4	0.28	0.002	55	0.000229	0.000292	0.911	0.956	0.56	1.14
	0.5	0.23	0.01	58	0.000173	0.000213	0.669	0.702	0.65	1.02
	0.6	0.20	0.009	60	0.000099	0.000125	0.599	0.628	0.50	0.70
	0.8	0.12	0.003	480	0.0000076		0.35	0.367	0.13	0.098
	1	0	0	480	0	0.0				

APPENDIX *Continued*

Solvent mixture	$\Delta L/L$ (cm)	SR (min ⁻¹)	t_{BT} (min)	SSPR gravimetric (g min ⁻¹ cm ⁻²)	SSPR volumetric (g min ⁻¹ cm ⁻²)	S (g/g)	S (g/cm ³)	D_s (10 ⁷ cm ² /s)	D_c (10 ⁷ cm ² /s)	D_v (10 ⁷ cm ² /s)	
TOL-HEX	X HEX										
	0	0.35	0.032	14.8							
	0.09			20.5							
	0.18			28.0							
	0.26			41.0							
	0.36			51.0							
	1.0			480							
	0			14.3	0.000681	0.93	0.976	1.47	3.26		
	0.08			20.7	0.000388						
	0.36			32.6	0.000141						
	0.46			51.6	0.000103						
	1.0			480	0.0						
Solvex 37-165 0.60 mm thick	0	0.32	0.0066					1.50			
	0.0823	0.26	0.0042					1.25			
	0.1680	0.21	0.0032					1.67			
	0.2571	0.16	0.0024					1.15			
Material: Butyl											
THF-CHCl ₃	X CHCl ₃										
	0	0.34	0.032	23	0.000741	0.000702	1.21	1.36	6.02	6.78	5.91
	0.267	0.30	0.0184	38	0.000614	0.000682	1.32	1.49	4.27	4.92	5.46
	0.5	0.284	0.0142	48	0.000588	0.000737	1.40	1.58	4.23	4.66	5.84
									3.96		
	0.75	0.30	0.0204	31	0.00108		1.55	1.75	4.60	7.29	
	1	0.38	0.048	18	0.00194	0.00175	2.29	2.59	7.51	8.85	7.54
AC-CHCl ₃	X CHCl ₃										
	0			480	0		0.046	0.052			
	0.1727	0.02	0.00007	480		(0.000081)	0.103	0.117	0.29		
	0.3007			480							
	0.4759	0.066	0.00092	172	0.000023	0.000095	0.247	0.280	1.39	1.02	4.20
	0.5662	0.084	0.00248	127	0.000030	0.000193	0.364	0.412	2.09	0.87	5.57
	0.6606	0.116	0.0052	69	0.000200	0.000119	0.564	0.638	2.65	3.38	2.01
	1	0.376	0.044	15	0.00194	0.00175	2.29	2.59	7.51	8.85	7.98
DMSO-CHCl ₃	X CHCl ₃										
	0			480							
	0.3956			480							
	0.6043			480							
	0.6622	0.052	0.0024	290	0.0000063		0.198	0.224	0.81	0.30	
									0.55		
	0.7238	0.064	0.00102	145	0.000044	0.000108	0.388	0.439	1.17	1.15	2.83
	0.8548	0.16	0.0126	40	0.000461	0.000432	0.813	0.920	4.69	5.29	4.96
	1	0.38	0.048	18	0.00194	0.00175	2.29	2.59	7.51	8.85	7.98
IPE-CHCl ₃	X CHCl ₃										
	0	0.21	0.0108	45	0.000243	0.000202	0.575	0.649	3.77	3.99	3.47
	0			51.1							
	0.1772			53							
	0.25	0.216	0.0094	67	0.00025	0.000406	0.748	0.847	3.04	3.56	5.78
	0.3710			52.5							
	0.5	0.254	0.014	54	0.00043	0.000357	1.04	1.18	3.97	4.62	3.84
	0.5611			48.9							
	0.6355	0.30	0.0166	53	0.0007	0.000628	1.39	1.57	3.46	5.20	4.66
	0.75	0.344	0.024	40	0.00095		1.93	2.19	5.27	5.60	
	0.4450			33.8							
	1			22.6			2.29	2.59	7.51		
	1	0.38	0.048	18	0.00194	0.00175	2.29	2.59	7.51	8.85	7.98
PDIOX-CHCl ₃	X CHCl ₃										
	0	0.042	0.000008	480		0.0000089	0.234	0.265	0.28		0.19
	0.5	0.122	0.0036	150	0.000056	0.000056					
	1	0.38	0.048	18	0.00194	0.00175	2.291	2.593	7.51	8.85	7.98

APPENDIX *Continued*

Solvent mixture	$\Delta L/L$ (cm)	SR (min ⁻¹)	t_{BT} (min)	SSPR		S (g/g)	S (g/cm ³)	D_s (10 ⁷ cm ² /s)	D_G (10 ⁷ cm ² /s)	D_V (10 ⁷ cm ² /s)
				gravimetric (g min ⁻¹ cm ⁻²)	volumetric (g min ⁻¹ cm ⁻²)					
	0.30	0.296	0.0138							
	0.40	0.364	0.0155							
	0.50	0.392	0.0206							
	0.60	0.420	0.0202							
	0.70	0.440	0.025							
	0.80	0.462	0.0304							
	0.90	0.416	0.0268							
	1.0	0.432	0.0294							

Mol Fraction Composition for the Chloroform–Diisopropyl Ether Mixture
in the Challenge Liquid and the Permeating Vapor

Glove	Mol fraction X CHCl ₃ Liquid	Permeation rate				X CHCl ₃ Vapor
		Chloroform		Isopropyl ether		
		($\mu\text{g cm}^{-2} \text{min}^{-1}$)	($\mu\text{mol cm}^{-2} \text{min}^{-1}$)	($\mu\text{g cm}^{-2} \text{min}^{-1}$)	($\mu\text{mol cm}^{-2} \text{min}^{-1}$)	
Butyl 878	0			238	2.33	0.00
				215	2.10	0.00
	0.2	100	0.84	215	2.10	0.28
		93	0.78	200	1.96	0.28
	0.25	97	0.81	162	1.59	0.34
	0.4	211	1.77	143	1.40	0.56
	0.4	194	1.63	137	1.34	0.55
	0.5	309	2.59	139	1.36	0.66
		474	3.97	179	1.75	0.69
	0.5	492	4.12	187	1.83	0.69
	0.6	586	4.91	130	1.27	0.79
		502	4.21	122	1.19	0.78
	0.75	1360	11.39	203	1.99	0.85
0.75	1123	9.41	128	1.25	0.88	
0.8	1289	10.80	107	1.05	0.91	
	1175	9.84	99	0.97	0.91	
1	2277	19.07			1.00	
Neoprene 29–865	0			109	1.07	0.00
	0.2	72	0.60	122	1.19	0.34
	0.25	81	0.68	106	1.04	0.40
	0.4	247	2.07	126	1.23	0.63
	0.4	226	1.89	128	1.25	0.60
	0.5	322	2.70	118	1.15	0.70
	0.5	450	3.77	158	1.55	0.71
	0.6	724	6.06	163	1.60	0.79
	0.75	1510	12.65	165	1.61	0.89
	0.8	2338	19.58	262	2.56	0.88
1	4550	33.11			1.0	
Nitrile Ansell Edmont 37–145	0					
	0.2	0	0	0	0	0.00
	0.4	33	0.28	6.9	0.07	0.80
	0.5	69	0.58	6	0.059	0.91
	0.6	349	2.92	31	0.30	0.91
	0.8	2828	23.69	141	1.38	0.94
	1	2042	17.11			1

Mol Fraction Composition for the Chloroform–Tetrahydrofuran Mixture
in the Challenge Liquid and the Permeating Vapor

Glove	Mol fraction X CHCl ₃ Liquid	Permeation				X CHCl ₃ Vapor
		Chloroform		Tetrahydrofuran		
		($\mu\text{g cm}^{-2} \text{min}^{-1}$)	($\mu\text{mol cm}^{-2} \text{min}^{-1}$)	($\mu\text{g cm}^{-2} \text{min}^{-1}$)	($\mu\text{mol cm}^{-2} \text{min}^{-1}$)	
Butyl 878	0	0	0	719	9.97	0.00
	0.27	156	1.31	341	4.73	0.22
	0.5	426	3.57	247	3.43	0.51
	0.75	822	6.89	120	1.66	0.81
	1	1896	15.88			1.00

APPENDIX *Continued*

Glove	Mol fraction X CHCl ₃ Liquid	Permeation				X CHCl ₃ Vapor
		Chloroform		Tetrahydrofuran		
		$\mu\text{g cm}^{-2} \text{min}^{-1}$	$\mu\text{mol cm}^{-2} \text{min}^{-1}$	$\mu\text{g cm}^{-2} \text{min}^{-1}$	$\mu\text{mol cm}^{-2} \text{min}^{-1}$	
Neoprene						
Fairprene	0	0	0	3411	47.30	0.00
(0.40 mm)	0.08	276	2.31	2588	35.89	0.06
	0.27	744	6.23	1498	20.77	0.23
	0.5	1354	11.34	816	11.32	0.50
	0.59	1626	13.62	627	8.70	0.61
	0.8	2807	23.51	358	4.96	0.83
	1	5196	43.52			1.00
Nitrile						
Ansell	0	0	0.00	4652	64.51	0.00
Edmont	0.27	896	7.51	1851	25.67	0.23
37-145	0.5	1946	16.30	1206	16.72	0.49
	0.75	4458	37.34	764	10.59	0.78
	1	12,216	102.33			1.00
Neoprene						
Fairprene	0	0	0.00	786	10.90	0.00
(1.5 mm)	0.25	197	1.65	446	6.18	0.21
	0.25	212	1.78	494	6.85	0.21
	0.5	392	3.28	233	2.28	0.59
	0.75	748	6.27	109	1.07	0.85
	1	1386	11.61			1.00

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