

Predicting Solubility and Permeation Properties of Organic Solvents in Viton Glove Material Using Hansen's Solubility Parameters

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ABSTRACT: A model based on a combination of the solubility parameters of Hansen and the polymer solution theory of Flory–Rehner was used to predict the solubility and permeation properties of organic solvents in Viton polymeric glove material. To test the validity of the model, weight gain data were collected for 32 organic solvents versus Viton. Samples were exposed for periods of 2 to 12 weeks until each glove sample had achieved a stable, equilibrium weight. Using a nonlinear least-squares regression, the three-dimensional solubility parameter was determined for Viton to be as follows: dispersion = 15.38, polar = 10.49,

and hydrogen bonding = 2.47. Breakthrough times, lag times, and steady-state permeation rates for the solvents versus Viton were also determined and combined with results obtained from the literature. A high level of correlation was observed between the model and the properties evaluated. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 93: 2688–2698, 2004

Key words: permeation; solubility; chemical protective clothing; Viton

INTRODUCTION

One primary route of chemical exposure in the workplace is through the skin. The major locations of chemical contact are the hands and forearms, which are commonly exposed during routine industrial and laboratory operations.¹ Reducing contact with hazardous chemicals is the main function of polymeric chemical protective clothing (CPC), with the most common form of protective clothing being gloves. However, to date no single polymeric CPC material has been found to be impervious to permeation by all liquid chemicals.^{2–5}

Proper selection of chemical protective clothing is often a complex task that involves understanding the factors that influence permeation. Degradation ratings have typically been the sole means of CPC selection for use with chemicals.⁶ However, degradation only measures the degree of swelling, discoloration, or any change due to chemical contact. Subjective “good” or “excellent” ratings for chemical protection may not account for permeation (penetration of a chemical from one side of a material to the opposite) since permeation can occur without any visible signs of material degradation.

When selecting an appropriate CPC for a specific application, it is critical to understand the extent of polymer–solvent interaction for proper selection. Manufacturers' selection guides often provide this type of information along with breakthrough times and permeation rates. Unfortunately, data are often noncomparable and difficult to interpret and testing conditions are not always standardized or documented. Due to the large number of possible CPC–solvent combinations and associated costs/time required for measuring protective properties, testing is commonly limited to representative solvents. As previously reported, it is virtually impossible to test all known chemicals and chemical mixtures versus every available polymeric membrane.^{7,8} The development of a predictive method, to be used in association with the collection of solubility and permeation data, would be of great benefit. It could be used to identify likely candidates for protection from a given solvent, reducing the number of experiments required to determine which CPC performs optimally. To better understand the solvent–CPC interaction, one common approach is to model chemical permeation using solubility parameters.^{6,9–16} This is largely attributed to the availability of published solubility parameters for commonly used solvents and many CPC polymers.^{17–19}

To successfully predict and accurately determine the solubility parameters of a CPC often requires careful study and critical analysis of the selected approach.

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Previous studies have attempted to correlate differences with CPC polymer and solvent (i.e., like dissolves like) directly with experimental permeation data steady-state permeation rate (SSPR) and breakthrough time (BT).^{9,20} Zellers¹⁴ observed that these correlations were poor and predictions of BT and SSPR were not accurate. For example, the graphical estimation method for determining Hansen solubility parameters (HSP) commonly described in the literature^{10,17,21} is unreliable and likely responsible for inconsistencies in published values of three-dimensional solubility parameters (3-DSPs) for common CPC materials. It is not always practical to perform the necessary manipulations to implement the graphical method, as this requires a large number of immersion tests that must be performed to ensure coverage of as much HSP space as possible.²⁴ Other indirect methods such as group contribution²² (equation of state) have been applied for the determination of the HSP for CPC polymers,²³ which provide only a statistical estimate as to the overall solubility (cohesive energy). Little attention is given to quantitative estimates of solvent-polymer solubility. While the group additive approach may be useful for some qualitative guidance, experimental determination has proven more accurate.²⁴

In a follow-up publication, Zellers²⁵ describes two alternate approaches for determining HSP for commercially available glove materials. In one approach, the polymer's parameters were determined from a weighted average of the HSP for a range of organic solvents. In the second approach, the polymer's values were determined by nonlinear regression of the modified Flory-Rehner equation. Employing the regression method is preferred since it has proven to be more superior (minimum overall error), rigorous, and user accessible for the determination of the HSP. Additional terms such as individual weight factors and the apparent molar mass between crosslinks of the polymer can also be estimated.

It is the goal of this paper to describe a solubility-based model that can be used to predict the degree of protection that can be obtained for a representative set of organic solvents based on Hansen solubility, the polymer-solution theory of Flory and Rehner,²⁶ and an improved weight gain test. The predictive capabilities of the model do not rely on estimations of polymer molecular weight or the use of individual weighting factors for specific solvent-polymer combinations.

Viton was selected for this study mainly for ease of comparison to other published work and the availability of published permeation data for a large range of solvents. This cross-linked copolymer has been shown to have excellent chemical resistance to solvents and fuels, in addition to its excellent stability over a wide range of temperatures.

Viton's solubility parameters are determined from a nonlinear least-squares regression routine with the weighting factors constant. The HSP values are then used to estimate the solvent/Viton solubility parameter difference. Available Viton BT, SSPR, and lag time (t_l) data from the manufacturer selection guide²⁷ and the literature²⁸ are also combined with experimentally collected permeation values for further validation of the model. Pertinent theoretical background and the key defining elements of the model will be reviewed and we will discuss how solubility estimates of various solvent/Viton combinations can be applied to assist in final CPC selection.

THEORETICAL BACKGROUND AND MODEL DESCRIPTION

The Regular Solution Theory as described by Hildebrand and Scott²⁹ introduced the concept of the solubility parameter. The use of solubility parameters to predict solubility is extremely useful and can be applied to low-molecular-weight materials and polymers.

$$\delta = \left(\frac{E}{V} \right)^{1/2}, \quad (1)$$

where the solubility parameter δ is equal to the square root of cohesive energy density, or the square root of cohesive energy per unit volume V . One basic assumption of solubility parameter theory is that a correlation exists between the cohesive energy density of pure substances and their mutual solubility is assumed.

Hansen expanded this concept in an effort to account for both polar and hydrogen bonding interactions in solvent-polymer systems: use of a three-dimensional solubility parameter (HSP) such that the total solubility parameter (cohesive energy in $\text{MPa}^{1/2}$) is separated into three separate parameters and takes into account the dispersion, polar, and hydrogen bonding effects of the solvent or solute³⁰

$$\delta_T^2 = \delta_D^2 + \delta_P^2 + \delta_H^2 \quad (2)$$

The Hansen HSP model is easily visualized and plotted in three-dimensional space. Thus, for a particular solute, the resulting point in three-dimensional space represents the solubility of the solute and a spherical shape surrounds the point and defines a "radius of interaction" for that solute. The equation that calculates differences in solubility parameters between two materials is

$$A = [a(D_P - D_S)^2 + b[(P_P - P_S)^2 + (H_P - H_S)^2]], \quad (3)$$

where the Euclidian between the solubility parameters of polymer and solvent is the variable A , the partial HSP represents D , dispersion, P , polarity/dipole-dipole, and H , hydrogen bonding contributions; and subscripts p and s are polymer and solvent, respectively. Assigning HSP to polymers is commonly based on correlations established from weight gain testing with solvents whose values are published.^{17–19}

Commonly, a spherical “volume” of solubility is formed when the dispersion parameter difference weighted by a factor of $a = 4$ and the polarity and hydrogen-bonding terms are left unweighted with $b = 1$.⁹ The empirical weight factors are used to ensure that all three terms are of similar weight in the model. This is needed because the dispersive values occur over a smaller range compared to the other two terms. Several authors have reported better correlations for polymer–solvent solubility using weight values of $a = 1$ and $b = 0.25$.^{7,15,21} Applying Eq. (3), b values less than unity will reduce the weight placed on δ_p and δ_h between solvent and polymer making the total difference smaller, which leads to higher solubility estimates. However, values of b less than unity have been rationalized as adjustments for the influence of polar materials inducing dipoles in nonpolar materials, thus resulting in an increase in interactions.

Another method that has been reported for determining a and b is to individually weight each chemical to obtain the overall solubility interaction between different solvents.¹⁴ In the current study, several different values of a and b were evaluated with the model for solubility estimates, with the best results obtained when the weighting factors were set at $a = 1$ and $b = 0.25$.

Many studies define the A term from eq. (3) as an independent, semiquantitative index of relative solubility.^{9,13,14} Attempts were made to develop relationships between A and the permeation terms BT and SSPR. It was reasoned that as A increases, solubility is expected to decrease between solvent and CPC, which thereby decreases permeation. However, the corresponding correlations often did not agree and predictions of BT and SSPR were largely unsuccessful.^{20,31}

Estimating a polymer’s 3-DSP values by incorporating Flory–Rehner polymer solution theory and subsequently applying nonlinear regression has proven to be a practical approach. Based on this method, accurate estimates of solubility are also possible when reliable 3-DSP values of the polymer are determined. Swelling equilibrium is approached when the chemical potential of the solvent inside the swollen polymer becomes equal to that of the outside phase, as originally described by the Flory–Rehner model.²⁶ Assuming that a network swells isotropically by liquid absorption, a modified version of the original Flory–Rehner equation describes equilibrium swelling:

$$\ln(1 - \phi_p) + \phi_p + \chi\phi_p^2 + \frac{V_M\rho_P}{M_c}\left(\phi_p^{1/3} - \frac{\phi_p}{2}\right) = 0, \quad (4)$$

where ϕ_p is the volume fraction of the polymer in the swollen mass, which is determined from a weight gain test. V_m is the molar volume (cm^3/mol) of the solvent, ρ is the density of the polymer, and M_c (density/number of moles per chain, g/mol) is the apparent molecular weight between crosslinks of the polymer. The polymer–liquid interaction, χ , is also known as the Flory interaction parameter.

To evaluate the swelling behavior of Viton at equilibrium the volume of the final term in Eq. (4) was found to be insignificant for a polyethylene–hexane–benzene system as Huang and Rhim³² reported, i.e., the molecular weight of the polymer becomes extremely large. The equation simplifies to

$$\ln(1 - \phi_p) + \phi_p + \chi\phi_p^2 = 0. \quad (5)$$

The combined theory of Flory–Huggins and Hildebrand–Scatchard provides a satisfactory approximation for the interpretation of most polymer–solvent data.³³ The Flory parameter, χ , can be defined in terms of Hildebrand solubility as

$$\chi_{12} = \chi_s + \chi_H = \chi_s + \frac{V_1(\delta_1 - \delta_2)}{RT}, \quad (6)$$

where χ_s is the entropic term (Flory combinatorial entropy correction factor β) and χ_H is the enthalpic term of the interaction parameter. Combining both Eqs. (3) and (6) leads to

$$\chi_{12} = \chi_s + \chi_H = \chi_s + \frac{V_M}{RT}A. \quad (7)$$

The value of A can be determined from Eq. (3) and is introduced to account for additional interactions, polar and hydrogen bonding effects progressing from the nonpolar Hildebrand solubility parameter when calculating χ_{12} . χ_s is a constant that is often set between 0.3 and 0.4,^{34,35} however, values from 0 to 2.5 have been used.¹⁷ A value of 0.34 for χ_s was previously reported for polymer–liquid systems^{19,36} as an average correction and was the value used in this study.

The Flory interaction parameter for a solvent–polymer combination can be related to mutual solubility by modifying the Flory–Rehner equation as

$$\left[\frac{V_M}{RT}A + \chi_s\right]\phi_p^2 = -[\ln(1 - \phi_p) + \phi_p]. \quad (8)$$

A minimum error solution for the Hansen D , P , and H values for the polymer Viton was determined from the

TABLE I
Three-Dimensional Solubility Parameters and Physical Constants

Solvent	3-DSP values ¹⁸ (MPa) ^{1/2}			V_m (cm ³ /mol)	M_w (g/mol)	Weight gain ^a
	D	P	H			
1,2-Dichloroethane	19.0	7.4	4.1	79.4	98.96	11.64
1,4-Dioxane	19.0	1.8	7.4	85.7	88.11	78.75
1-Butanol	16.0	5.7	15.8	91.5	74.12	2.71
2-Butanone	16.0	9.0	5.1	90.1	72.11	331.15
2-Propanol	15.8	6.1	16.4	76.8	60.10	2.70
Acetonitrile	15.3	18.0	6.1	52.6	41.05	46.26
Acrylonitrile	16.0	12.8	6.8	67.1	53.06	61.69
Benzaldehyde	19.4	7.4	5.3	101.5	106.12	22.16
Benzene	18.4	0.0	2.0	89.4	78.11	11.73
Carbon tetrachloride	17.8	0.0	0.6	97.1	153.82	15.79
Chloroform	17.8	3.1	5.7	80.7	119.38	20.69
Cyclohexane	16.8	0.0	0.2	108.7	84.16	3.06
Diethyl ether	14.5	2.9	5.1	104.8	74.12	27.87
Dimethyl sulfoxide	18.4	16.4	10.2	71.3	78.13	53.96
Dimethylformamide	17.4	13.7	11.3	77.0	73.09	115.2
Ethanol	15.8	8.8	19.4	58.5	46.07	3.16
Ethyl acetate	15.8	5.3	7.2	98.5	88.10	294.93
Furfuraldehyde	18.6	14.9	5.1	83.2	96.09	20.69
Isooctane	14.1	0.0	0.0	166.1	114.23	1.50
Methylene chloride	18.2	6.3	6.1	63.9	84.93	23.02
<i>n</i> -Butyl acetate	15.8	3.7	6.3	132.5	116.16	157.11
<i>n</i> -Pentane	14.5	0.0	0.0	116.2	72.15	3.43
<i>o</i> -Xylene	17.8	1.0	3.1	121.2	106.16	10.67
Pyridine	19.0	8.8	5.9	80.9	79.10	48.67
Toluene	18.0	1.4	2.0	106.8	92.14	11.43
Trichloroethylene	18.0	3.1	5.3	90.2	131.40	14.97
Acetone	15.5	10.4	7.0	74.0	58.0	<i>degrade</i>
Carbon disulfide	20.5	0.0	0.6	60.0	76.14	<i>degrade</i>
Cyclohexanone	17.8	6.3	5.1	104.0	98.14	<i>degrade</i>
Diethylamine	14.9	2.3	6.1	103.2	73.14	<i>degrade</i>
Ethanolamine	17.0	15.5	21.2	59.8	61.08	<i>degrade</i>
Tetrahydrofuran	16.8	5.7	8.0	81.7	72.11	<i>degrade</i>

^a Weight gain, $W_s/W_v \times 100$, where W_s = weight of solvent in the sample, W_v = weight of outgassed Viton.

final form of the working equation. A solubility-based model was developed to determine 3-DSP values based on simple weight gain testing. Although the model does not “predict” permeation terms, excellent correlation between $\chi\phi_P^2$, a measure of solubility, and permeation rates and breakthrough times is observed, which is significantly improved from previous solubility-based models.

EXPERIMENTAL

Viton raw material is manufactured and licensed by Dupont-Dow Elastomers. There are three major classes of the elastomer: A, B, and F. Model F-091Viton gloves (The North Company, Charleston, SC) are manufactured from Viton B³⁷, a fluoroelastomer terpolymer of vinylidene (VF₂), hexafluoropropylene (HFP), and tetrafluoroethylene (TFE) with a fluorine content of 68%. The exact composition of the monomers is proprietary and information regarding the percentage of crystallinity, crosslinker used, or filler was not made available.³⁸ Samples used for this study

were either rejects or seconds donated by the manufacturer but were identical to commercially available Viton gloves.

Table I lists the 32 solvents used in this study; it also includes solvent solubility parameters, molar volumes, and molecular weights, which are necessary physical constants for modeling and were obtained from standard reference sources.^{17,18,28,39} To obtain reasonable precision and accuracy estimating the 3-DSP values, 27 solvents are typically recommended, assuming that the solvents represent a wide range of structures and functionalities.²⁵ The model incorporates a total of 26 solvents to estimate the 3-DSP values for Viton. All weight gain tests were performed in triplicate. The mean was used in the model after being adjusted for weight loss. Each individual sample for permeation testing was measured prior to exposure and breakthrough time data were thickness normalized to compensate for sample-to-sample thickness variations. The density of Viton was determined by displacement as specified by ASTM D792-91. Based on an average of three measurements, the value used

for all calculations was 1.89 g/cm^3 at $25 \pm 2^\circ\text{C}$, which is in close agreement to a previously reported value of 1.86 g/cm^3 at 25°C .¹⁴ All solvents were ACS reagent grade and were obtained from Fisher Scientific Co./Acros Chemical (Pittsburgh, PA) or Aldrich Chemical Co. (Milwaukee, WI).

Evaluation of weight gain

Rectangular, 0.5-g sections of sample were cut from either the cuff or the palm portion of the glove that had been inspected to ensure that there were no pinholes, cuts, or other defects. Samples were then dried and weighed and the thickness was measured at four different locations with a micrometer. The average thickness was determined to be 0.36 mm. Each sample was completely immersed in 30 mL of solvent in a sealed screw-tight container, which was maintained at a constant temperature of $25 \pm 2^\circ\text{C}$. At weekly intervals the samples were quickly removed, and excess solvent was wiped off and further dried by rolling over with a glass rod set between two Kimwipes, weighed, and then returned to the solvent. As reported by other investigators, the time involved for this procedure averaged ~ 30 s; therefore, no significant errors in weight uptake data of samples were introduced.⁴⁰ Collection of weight gain data continued until equilibrium weight was observed, typically 2–12 weeks depending on the solvent. To ensure that a stable equilibrium weight was reached, additional weight measurements were taken at 1- to 2-day intervals. Since there was the potential for sample loss due to handling, the initial weight was used only as a reference point for monitoring weight and to confirm that equilibrium had been achieved.

Acetone, tetrahydrofuran, cyclohexanone, diethylamine, ethanolamine, and carbon disulfide exposed samples were found to cause samples to swell to such a degree that it was impossible to obtain an accurate weight measurement. These solvents were excluded from further evaluation. All other exposures were performed in triplicate and the relative standard deviation for the replicates was between 5 and 10%.

Weight loss

It has been shown that additives can be extracted from an elastomeric material during exposure to a chemical, resulting in a decrease in sample mass.⁴¹ Losses are also possible as a result of the handling required when taking the weight of exposed samples. To make certain that accurate final weight gain values were reported, postexposure sample weights were obtained.

After samples had reached equilibrium weight, a desorption or weight loss experiment was performed to evaluate the extent of extraction. This was accomplished by placing each sample in a clean, preweighed

glass container and transferring it to an oven set at 40°C . At regular intervals, each sample was removed, cooled to room temperature, weighed, and placed back into the oven. It was found that most samples exhibited a weight loss of $<5\%$, although in a few cases the losses were as high as 20%. The mass of solvent absorbed by each sample was then determined as the difference between the equilibrium exposure weight and the postexposure weight.

Permeation testing

Permeation data were collected for different solvent-Viton combinations using a previously described testing procedure, a modification of the widely used and accepted ASTM F739–96 for testing of chemical protective clothing.^{42,43} The method incorporates modifications that were recommended by several authors in that both temperature and flow are controlled.^{44,45} The method makes use of open loop testing to ensure that there is complete solvent contact during the entire exposure period. A maximum response is obtained, any extracted materials are flushed from the system, and membrane swelling will not prevent solvent contact.

The cell and all fittings were constructed of 316 stainless steel. Each cell half had a 0.65-cm-diameter opening, resulting in a 0.33-cm^2 exposure area. In addition, the large cell diameter (7.9 cm) and thickness (3 cm) made the cell more resistant to temperature fluctuations during exposure. A controlled flow of solvent would enter the top half of the cell, after which it would be collected. The collecting medium entered the lower half of the cell, contacted the exposed inner surface of the membrane, and exited the cell, where it then entered a sampling valve and a gas sampling loop. Each experiment was conducted at a relative humidity of $50 \pm 5\%$ and a temperature of $22 \pm 1^\circ\text{C}$. A flow rate of 1.0 and 7.0 mL/min was used for the solvent and collecting medium, He, respectively.

The analytical equipment consisted of a Hewlett-Packard (Palo Alto, CA) 5980 Series II gas chromatograph (GC) equipped with a flame ionization detector (FID) and high-temperature, 10 port, two-position GC sampling valve. The valve was used to direct permeant effluent through one of two flow paths. Initially, the effluent is directed from the cell, through a 0.25-mL sampling loop, and then to the FID detector for continuous monitoring of permeant concentrations. In the alternate position, cell effluent is diverted to a charcoal trap and the contents of the sampling loop are passed to a capillary column and then FID detection. This mode was used to quantify the amount of permeant at any point during an exposure, compared to standards assayed prior to each exposure study. System control, data collection, and flow monitoring were accomplished using a Hewlett-Packard

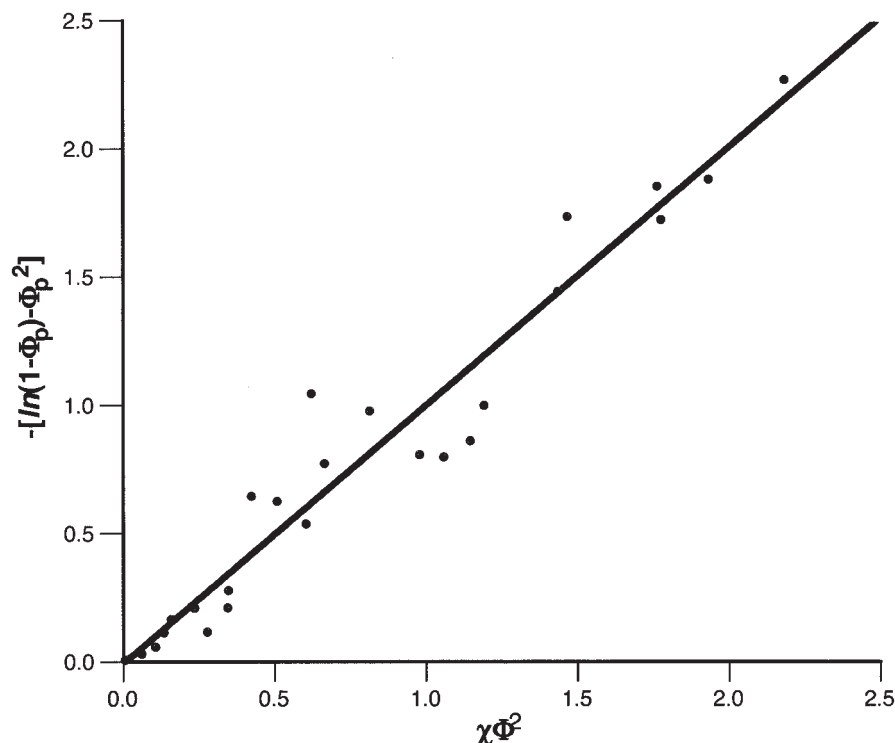


Figure 1 Nonlinear least-squares regression fit of model. $r^2 = 0.975$.

5895A Pascal GC ChemStation and GC software. During data acquisition, the FID signal and flow rate were monitored and stored. Each solvent–Viton combination was tested at a constant temperature of 25°C, in triplicate. The analytical response is different for each solvent tested and included in the results is a comparison of the first observed BT based on instrument response, breakthrough time normalized at 0.1 $\mu\text{g}/\text{cm}^2/\text{min}$. All breakthrough time values were also corrected for system dead time of 0.133 min.

Data analysis

The Hansen solubility parameters D , P , and H for North Viton glove material were determined from a nonlinear least-squares regression fit of Eq. (8), where the A term is defined in Eq. (3). Polymer volume fractions, ϕ_p , were determined using the experimentally obtained weight gains and polymer density. Solvent related values, such as density and 3-DSP values, were obtained from the literature. A commercially available interactive data analysis program, Data Desk 6.0 (Data Description, Ithaca, NY), was used for the best fit of Viton's 3-DSP. Once the D , P , and H values for Viton were determined, the relationship between $\chi\phi_p^2$ from Eq. (8) for Viton and breakthrough time, permeation rate, and lag time was evaluated.

RESULTS AND DISCUSSION

Figure 1 represents the fit obtained for Eq. (8) using the data obtained from the 26 solvents included in this

study. The three-dimensional solubility parameters were found to be the dispersion parameter (D), 15.38 ± 0.78 ; the polar parameter (P), 10.49 ± 0.68 ; and the hydrogen bonding parameter (H), 2.47 ± 1.01 , with units in $\text{MPa}^{1/2}$. Values are reported along with their 95% confidence limits and a correlation (r^2) of 0.975 was observed. These results are comparable to those reported by Perkins⁹ (D , 17.0; P , 10.6; H , 6.1), Barton¹⁷ (D , 15.3; P , 10.2; H , 5.3) and Hansen¹⁹ (D , 15.6; P , 9.6; H , 7.8).

Previous reports have attempted to establish a relationship with some component of their model and solubility, steady state permeation rates, and breakthrough. These include using the A term given in Eq. (3), A^2 , the Flory interaction parameter χ , or the Flory–Rehner relationship^{9,14,24,25,31}. $\chi\phi_p^2$ was expected to provide good correlation with the natural logarithm of either solubility and SSPR because it is a measure of the residual free energy of mixing for the solvent.^{18,48}

$$\Delta G_s^R = RT\chi\phi_p^2, \quad (9)$$

This assumption was tested by evaluating the correlation between $\chi\phi_p^2$ and the experimentally determined solubility values obtained from the weight gain study. Unlike earlier work, molar solubility (mmol/cm^3) rather than mass solubility was used. Figure 2 shows the fit, where a correlation, r^2 , of -0.956 was observed. The high degree of correlation showed that $\chi\phi_p^2$ would be a good predictor of solubility and possibly permeation properties. This compares favorably

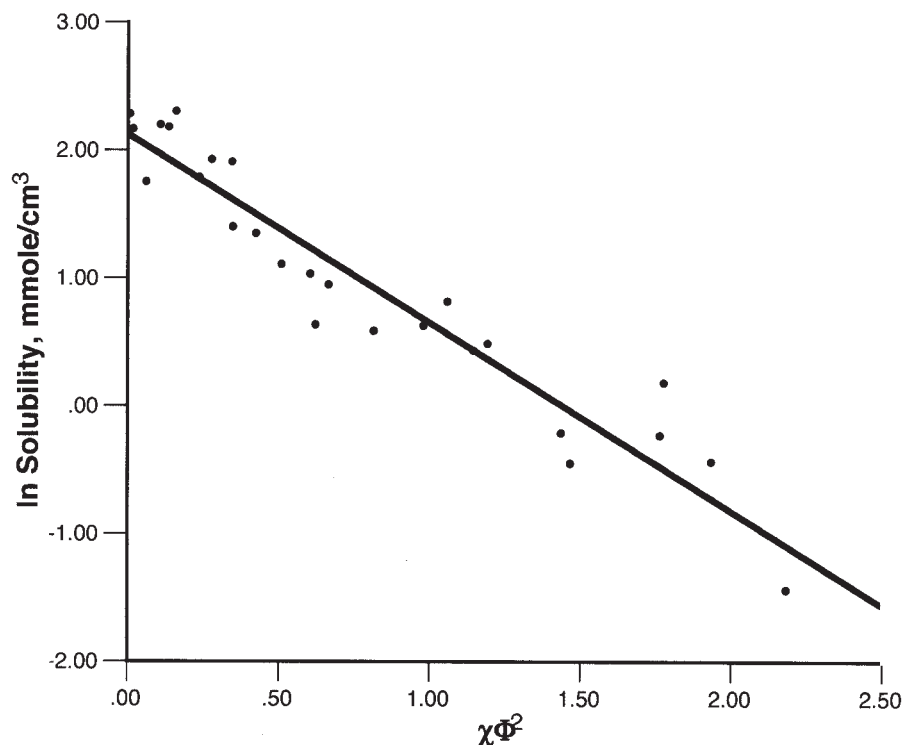


Figure 2 Relationship between $\chi\phi^2$ and the natural logarithm of molar solubility. $r^2 = -0.956$.

with the results reported by Zellers¹⁴, who obtained a correlation of 0.516 for the solubility of 40 solvents in Viton. By individually weighting of the data, they were able to improve this ($r^2 = 0.959$).

Permeation data obtained from various sources, including Forsberg²⁸ and Zellers,¹⁴ were combined with data from this study to test the applicability of the model (shown in Table II). The units used for perme-

TABLE II
Summary of Permeation Results for Viton

Solvent	Thickness, mm		Breakthrough time, min		Steady-state permeation rate, mg/m ² /s		Lag time, min	
	current study	previous work ^A	current study	previous work	current study	previous work	current study	previous work ^B
Acetonitrile	0.41	0.26	13.8	6	195	126.3	25.6	
Acrylonitrile	0.34	0.40	5.5		335.6	176	12.0	
Benzaldehyde	0.47	0.25	385.6	594	1.35	4.0	457.5	
Benzene	0.41	0.23	323.5	354	0.103	0.017	544.6	
2-Butanone	0.37	0.24	3.6		818.3	1092	5.6	
Butyl acetate	0.38		7.5		108.6		9.4	
Carbon tetrachloride		0.42		5355		0.0035		7830
Chloroform	0.39	0.36	413.7	570	0.415	0.467	661.5	677
1,2-Dichloroethane	0.39	0.23	462.1	415	1.64	0.817	683.6	
Dimethylformamide	0.46	0.26	9.5	7	123.8	275	14.6	
Dimethylsulfoxide	0.44		104.5		5.15		133.8	
1,4-Dioxane	0.40	0.23	64.5	23	48.8	26.67	85.2	
Ethyl acetate	0.37	0.26	3.0	3	2059.4	750	7.0	
Ethyl ether	0.42	0.28	21.9	12	32.58	21.5	29.1	
Furfural	0.34	0.27	138.3	216	6.65	14.8	199.3	
Methylene chloride	0.40	0.23	38.4	60	11.57	7.33	55.7	116
Toluene		0.37		810		0.069		
Trichloroethylene	0.39	0.23	334.5	444	0.336	0.233	609.7	

^a Previous work: Forsberg (values listed in italics);²⁸ Zellers;³¹ Perkins (values listed in bold).²⁰

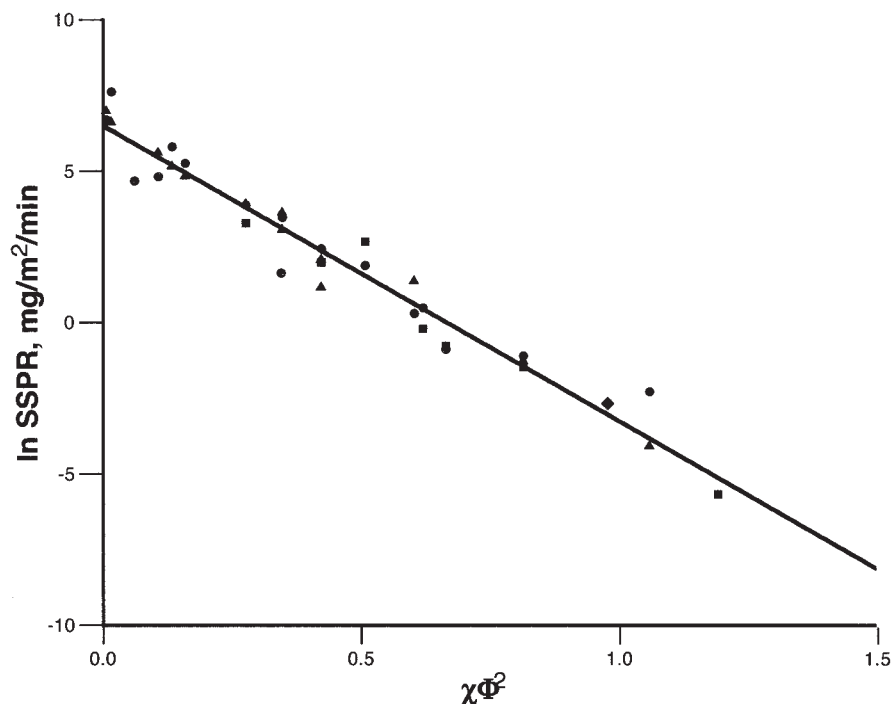


Figure 3 Linear regression fit $\chi\phi^2$ and the natural logarithm of steady-state permeation rate. $r^2 = -0.979$. ●, current study; ◆, North²⁷; ■, Zellers¹⁴; ▲, Forsberg²⁸.

ation rate data were in milligrams per square meter per second, as reported in the manufacturer's selection guide.²⁷ Figure 3 shows the relationship between \ln SSPR and $\chi\phi^2$, where an r^2 of -0.979 was obtained. This is a significant improvement over earlier work where attempts to model \ln SSPR with a solubility term resulted in r^2 of 0.699 and 0.516 .³¹ In the latter study, the authors were able to obtain improved results ($r^2 = 0.985$) using individual weights for each data point. Benzene was found to have a permeation rate that was much greater than that previously reported. It was also an outlier when evaluating the relationship between $\chi\phi^2$ and either breakthrough or lag times. In a study by Goydan et al., the authors demonstrated that benzene was a significant outlier when determining diffusion coefficients for solute/natural rubber systems.⁴⁷ For these reasons, it was excluded when evaluating the relationship between $\chi\phi^2$ and the permeation properties investigated. Since permeation rates are related to solubility, using molar permeation rates (nSSPR) would be expected to provide an improved fit. However, no significant change in the quality ($r^2 = -0.973$) was observed. Possible reasons for this include the logarithmic nature of the fit and the relatively small molecular weight range.

The relationship between $\chi\phi^2$ and both BT and t_1 were investigated. Although there is no theoretical basis for a relationship, previous authors found some degree of correlation between their models and BT.^{9,14,31} Hansen rationalized that it is possible to cor-

relate barrier properties if the solvent molecules are of similar molecular weight and shape. He also reports that when evaluating Viton, molecules should fall within a molecular weight range of 72.6 – 148.9 amu.¹⁹ Of the 33 BT values included in the fit, only 5 measurements fell outside this range, 1 of which was just 3% above the recommended maximum. Figure 4 shows the relationship between \ln BT and $\chi\phi^2$ using data collected in this study and values that had been previously reported. Breakthrough time as defined by ASTM F739–99 was used, where it is the point at which the permeation rate reaches $0.1 \mu\text{g}/\text{cm}^2/\text{min}$. This was done to account for variations in detector response factors for each chemical. A correlation of 0.951 was obtained. Thickness normalized values (BT/L) were also evaluated but no significant change in the quality of the fit was observed ($r^2 = 0.952$). The correlation compares favorably with results reported by Perkins⁹, who obtained a correlation of 0.65 , Zellers,³¹ where an r^2 of 0.876 was observed if samples were individually weighted, and Hansen²⁰, where an r^2 of 0.896 was given when the molecular weight range of the solvents was limited.

Figure 5 represents the plot of $\chi\phi^2$ versus $\ln t_1$ (lag time) where an r^2 of 0.960 was obtained. Values for lag time are not readily available in the literature; however, it is an important variable to consider as it can be used to calculate the diffusion coefficient of a solvent/membrane system. Lag times are found by extrapolation of the linear portion of a cumulative permeation

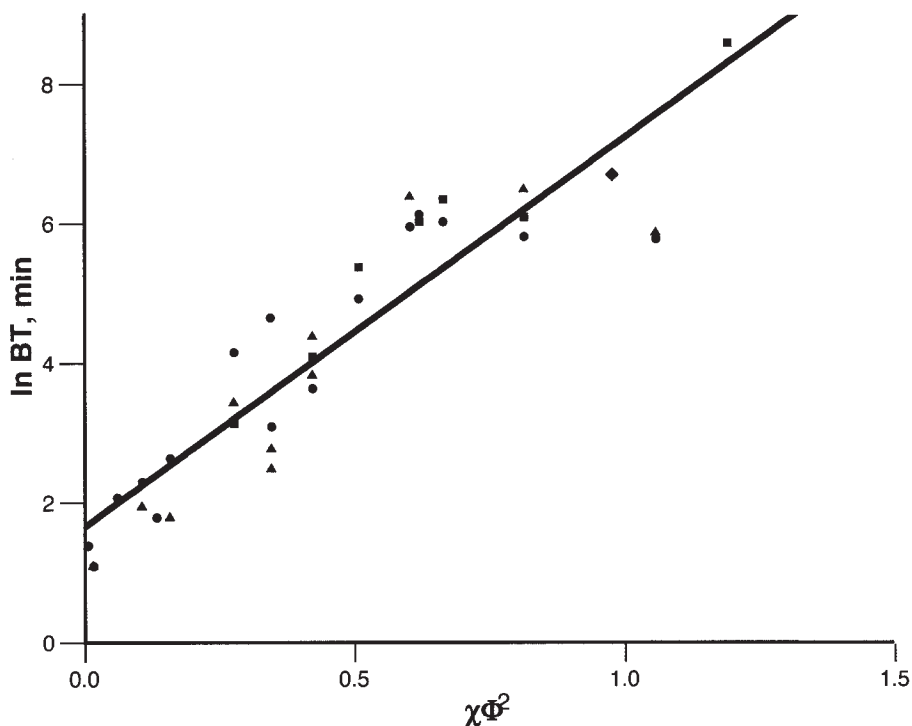


Figure 4 Linear regression fit of $\chi\phi^2$ and the natural logarithm of breakthrough time. $r^2 = 0.951$. ●, current study; ◆, North²⁷; ■, Zellers¹⁴; ▲, Forsberg²⁸.

curve to where it intersects the time axis. The approach has been found to be suitable when applied to rubbery polymers.⁴⁹ Since the method used to monitor perme-

ation permitted continuous monitoring of effluent concentration, cumulative permeation curves were readily obtained. While lag time also has an established relation-

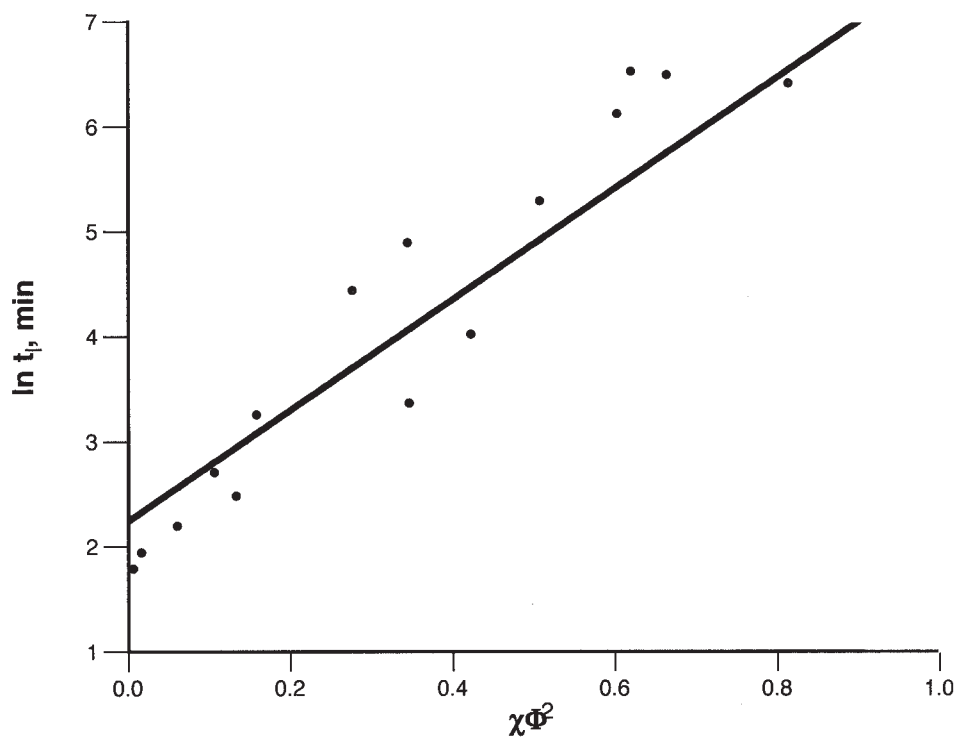


Figure 5 Linear regression fit of $\chi\phi^2$ and the natural logarithm of lag time, t_l . $r^2 = 0.960$.

ship with thickness, it was found that thickness normalization had no significant effect on the quality of the fit. The fact that the quality of neither the fits of $\chi\phi_P^2$ versus BT nor t_1 was improved by thickness normalization is likely due to the logarithmic fit and the small range of thicknesses evaluated (0.34–0.47 mm).

CONCLUSION

In this study, a nonlinear regression analysis method yielded a minimum error solution of Viton 3-D solubility parameters. The standard solubility and polymer solution theories of Hansen and Flory and Rehner formed the basis of the model. It was possible to show strong correlation between $\chi\phi_P^2$, a measure of the ΔG_{mixing} , and solubility. By using molar solubility, instead of the more commonly used mass values, a better quality fit was obtained. $\chi\phi_P^2$ also proved to be a good predictor of the permeation properties of SSPR, BT, and t_1 . This should allow for the prediction of permeation properties. Unlike earlier work, only a single set of weighting factors is required, resulting in a more robust model. The use of a single set of weighting factors should allow for the incorporation of additional glove materials into the model.

Improving the method of measuring sample weight gain was also critical to the development of the model. Standard weight gain testing time is on the average of 14 days. However, it was observed in this study that many samples continued gaining weight beyond 14 days and may require as long as 12 weeks. Because equilibrium swelling is supported by theory, steps such as collecting polymer weights for extended time ensure that equilibrium has been achieved. In addition, some of the original sample can be lost during solvent exposure or the handling required to monitor weight changes. Determining the glove material mass after exposure and outgassing of the solvent eliminated sample loss as potential sources of error.

References

- Williams, J. R. *Am Ind Hyg Assoc J* 1979, 40(10), 877.
- Mickelsen, R. L.; Roder, M. M.; Berardinelli, S. P. *Am Ind Hyg Assoc J* 1986, 47, 236.
- Sansone, E. B.; Tewari, Y. B. *Am Ind Hyg Assoc J* 1978, 39, 169.
- Perkins, J. L.; *Appl Ind Hyg* 1987, 2, 220.
- Dartmouth College, *Chem Health Saf* 1997, 4(6), 14.
- Mikatavage, M.; Que Hee, S. S.; Ayer, H. E. *Am Ind Hyg Assoc J* 1984, 45, 617.
- Brown A. S.; Philpot, E. F.; Segers, D. P.; Sides, G. D.; Spafford, R. B. Predicting the Effectiveness of Chem-Protective Clothing: Model and Test Development; EPA/600/S2-86/055, U. S. Environmental Protection Agency, Cincinnati, OH, 1986.
- Hansen, C. M.; Billing, C. B. Jr.; Bentz, A. P. In *Performance of Protective Clothing: Vol.4*, ASTM STP 1133; McBriarty, J. P.; Henry, N. W., Eds.; American Society for Testing and Materials: Philadelphia, 1992.
- Perkins, J. L.; Tippit, A. D. *Am Ind Hyg Assoc J* 1985; 46, 455.
- Ridge, M. C.; Perkins, J. L. Permeation of Solvent Mixtures through Protective Clothing Elastomers in Chem Protective Clothing Performance in Chem Emergency Response, Perkins, J. L.; Stull, J. O., Eds.; ASTM: Philadelphia, 1989.
- Spence, M. W. Paper presented at the American Industrial Hygiene Conference, San Francisco, CA, May 15–20, 1988.
- Vahdat, N. *Am Ind Hyg Assoc J* 1987, 48(2), 155.
- Henriksen, H. Selection of Materials for Safety Gloves. Polymer Membranes to Protect against Contact with Epoxy Products; Directorate of Labor Inspection, Copenhagen, 1982 (translated by NIOSH, Morgantown, WV).
- Zellers, E. T. *J Appl Polym Sci* 1993, 50, 513.
- Zellers, E. T.; Sulewski, R. *Am Ind Hyg Assoc J* 1993, 54, 465.
- Bentz, A. P.; Billing, C. B. Jr. Determination of Solubility Parameters of New Suit Materials. In *Performance of Protective Clothing: Second Symposium*, Mansdorf, S. Z.; Sager, R.; Nielsen, A. P., Eds.; Philadelphia: ASTM, 1988.
- Barton, A. F. M. *CRC Handbook of Solubility Parameters and Other Cohesion Parameters*, 2nd ed., CRC Press, Boca Rotan, FL 1991.
- Grulke E. A., *Polymer Handbook*, 3rd ed., Brandup, J.; Immerguy, E. H., Eds.; Wiley: New York, 1989.
- Hansen, C. M. *Hansen Solubility Parameters: A Users Handbook*; CRC Press: Boca Raton, FL, 2000.
- Perkins, J. L.; Ridge, M. C.; Holcombe, A. B.; Wang, M. K.; Nonidez, W. E. *Am Ind Hyg Assoc J* 1986, 47, 803.
- Hansen, C. M.; Beerbower, A. *Solubility Parameters in Kirkthmer Encyclopedia of Chem Technology*, 2nd ed.; Standen, A., Ed.; Wiley: New York, 1971.
- Van Krevelen, D. W., *Properties of Polymers: Their Correlation with Chem Structure. Their Estimation and Prediction from Additive Group Contributions*; Elsevier: Amsterdam, 1990.
- Remigy, J. C.; Nakache, E.; Brechot, P. D. *Ind Eng Chem Res* 1999, 38, 4470.
- Zellers, E. T.; Anna, D. H.; Sulewski, R.; Wei, X. *J Appl Polym Sci* 1996, 62, 2069.
- Zellers, E. T.; Anna, D. H.; Sulewski, R.; Wei, X. *J Appl Polym Sci* 1996, 62, 2081.
- Flory, P. J.; Rehner, J. Jr. *J Chem Phys* 1943, 11, 521.
- North Hand Protection, *Chem and Permeation Guide*, North Hand Protection Division of Siebe North, Inc., Charleston, SC, 1986.
- Forsberg, K.; Keith, L. H. *Chem Protective Clothing Permeation and Degradation Compendium*; Lewis/CRC Press: Boca Raton, FL, 1995.
- Hildebrand, J. H.; Prausnitz, J. M.; Scott, R. L. *Regular and Related Solutions*; Van Nostrand Reinhold: New York, 1970.
- Hansen, C. M. *J Paint Technol* 1967, 39(505), 104.
- Zellers, E. T.; Zhang, G. Z. *J Appl Polym Sci* 1993, 50, 531.
- Huang, R. Y. M.; Rhim, J. W. *J Appl Polym Sci* 1990, 41, 535.
- Aminabhavi, T. M.; Aithal, U. S.; Shukla, S. S. *JMS Rev Macromol Chem Phys C* 1988, 28(3&4), 421.
- Du, Y.; Xue, Y.; Frisch, H. L. In *Physical Properties of Polymers Handbook*; Mark, J. E., Ed.; American Institute of Physics: Woodbury, NY, 1996.
- Jacques, C. H. M.; Wyzgoski, M. G. *J Appl Polym Sci* 1979, 23, 1153.
- Blanks, R. F.; Prausnitz, J. M. *Ind Eng Chem Fund* 1964, 3(1), 1.
- Brown, J. Personal Communication; May 2000.
- Aminabhavi, T. M.; Phayde, H. T. S.; Ortego, J. D.; Stahl, W. M. *J Appl Polym Sci* 1997, 63, 1223.
- The Merck Index, Budavari, S., Ed.; Merck: Whitehouse Station, NJ, 1994.
- Amnibahvi, T. M., Harlapur, S. F.; Aralaguppi, M. J. *J Appl Polym Sci* 1997, 66, 717.
- Vahdat, N.; Sullivan, V. D. *J Appl Polym Sci*. 2001, 79, 1265.

42. American Society for Testing and Materials (ASTM), Standard Test Method for the Resistance of Protective Clothing Materials to Permeation by Liquids or Gases Under Conditions of Continuous Contact (ASTM Method F739-96); ASTM: Philadelphia, PA, 1996.
43. Jencen, D. A.; Hardy, J. K. *Am Ind Hyg Assoc J* 1988, 49(6), 293.
44. Zellers, E. T.; Sulewski, R.; Anna, D. H. *Am Ind Hyg Assoc J* 1998, 59, 547.
45. Bromwich, D. *Am Ind Hyg Assoc J* 1998, 59, 842.
46. Barton, A. F. M. *Pure Appl Chem* 1985, 57(7), 905.
47. Goydan, G.; Schwope, A. D.; Reid, R.; Krishnamurthy, S.; Wong, K. Approaches to Predicting the Cumulative Permeation of Chemicals Through Protective Clothing Polymers in Performance of Protective Clothing; Mansdorf, Sager, and Neilsen, Eds.; ASTM STP 989: Philadelphia, PA, 1988.
48. Barton, A. F. M. *CRC Handbook of Polymer-Liquid Interaction Parameters and Solubility Parameters*; CRC Press: Boca Raton, FL, 1991.
49. Naylor, T. de V. In *Comprehensive Polymer Science, The Synthesis, Characterization, Reactions and Applications of Polymers*; Allen, G.; Bevington, J. C., Eds.; Pergamon Press: Elmsford, NY, 1989.