

# Three-Dimensional Solubility Parameters and Chemical Protective Clothing Permeation. II. Modeling Diffusion Coefficients, Breakthrough Times, and Steady-State Permeation Rates of Organic Solvents in Viton® Gloves

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## SYNOPSIS

Three-dimensional (3-D) solubility parameters are used in separate models of the solubility,  $S$ , and diffusion coefficient,  $D$ , of organic solvents in polymers. Modeled values of these variables are then combined in Fickian diffusion equations to estimate solvent breakthrough times (BT) and steady-state permeation rates (SSPR). Published data on the permeation of 18 solvents through commercial Viton® glove samples are used to test the accuracy of the approach. Estimates of  $S$  are determined based on the model described in the preceding article. Of several empirical correlations investigated to model  $D$ , best results are achieved using the product of the solvent molar volume,  $V_1$ , and either the weighted solvent-Viton 3-D solubility parameter difference,  $A_w$ , or the Flory interaction parameter,  $\chi$ , also calculated from 3-D solubility parameters. To account for the change in the value of  $D$  over the course of the permeation test,  $D$  values are evaluated at breakthrough and steady state. Modeled BT values within a factor of three of experimental values (typically within a factor of two) are obtained for the 15 solvents for which analytical detection limits were reported. Modeled SSPR values within a factor of six of experimental values (typically within a factor of four) are obtained for the 15 solvents with valid SSPR measurements. © 1993 John Wiley & Sons, Inc.

## INTRODUCTION

In the preceding article, a model was described for estimating the equilibrium solubilities of solvents in polymers as a function of the solvent and polymer three-dimensional (3-D) solubility parameters.<sup>1</sup> In an extension of that work, this article examines several empirical correlations for estimating solvent diffusion coefficients,  $D$ . Values of  $S$  and  $D$  are then combined in Fickian diffusion equations to estimate the breakthrough time (BT) and steady-state permeation rate (SSPR) for a given solvent. The approach is developed and evaluated using previously published data on the permeation of 18 solvents through samples of commercial Viton® gloves. Em-

phasis is placed on the potential to use the model for the selection of chemical protective clothing (CPC) for industrial applications.

## THEORETICAL BACKGROUND

The permeation of solvents through CPC polymers can be described by Fick's laws of diffusion.<sup>2,3</sup> According to Fick's First Law, the rate of diffusional mass transfer of a solvent through a polymer membrane is described by

$$J = -Ddc/dx \quad (1)$$

where  $J$  is the flux ( $\mu\text{g}/\text{cm}^2/\text{min}$ );  $D$ , the solvent diffusion coefficient ( $\text{cm}^2/\text{min}$ ); and  $c$ , the solvent concentration ( $\mu\text{g}/\text{cm}^3$ ) at some point  $x$  (cm) in the polymer sample. For the case where the permeating solvent contacts one surface of the polymer sample

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and is continuously removed from the opposite surface, the flux at steady state,  $J_{SS}$  (or SSPR), is

$$J_{SS} = \text{SSPR} = DS/L \quad (2)$$

where  $S$  is the equilibrium solubility ( $\mu\text{g}/\text{cm}^3$ ), and  $L$ , the thickness of the polymer sample (cm). It is assumed in eq. (2) that the concentration of the solvent in the exposed surface layer of the sample reaches the equilibrium solubility value instantaneously.

Prior to steady state, account must be taken of the change in the solvent concentration gradient within the polymer over time,  $t$ . In this regime, the flux at a given time,  $J_t$ , is, from Fick's Second Law,<sup>2</sup>

$$J_t = DS/L \left\{ 1 + 2 \sum_{n=1}^{\infty} (-1)^n \times \exp[-(n\pi)^2(Dt/L^2)] \right\} \quad (3)$$

and the mass of solvent that has permeated a unit area of polymer at a given time,  $M_t$ , is

$$M_t = SL \left\{ Dt/L^2 - \frac{1}{6} - 2 \sum_{n=1}^{\infty} (-1)^n / (n\pi)^2 \times \exp[-(n\pi)^2 Dt/L^2] \right\} \quad (4)$$

If analytical detection limits are used to define values of  $J_t$  or  $M_t$ , then  $t$  in eqs. (3) and (4) is the breakthrough time, which is typically the most important criterion used in the selection of CPC materials. To use eqs. (2)–(4) for predicting the BT and SSPR of a given solvent/polymer pair, values of  $D$  and  $S$  are required. Alternatively, where permeation data and immersion test data are available, experimental values of BT, SSPR, and  $S$  can be used in eqs. (2)–(4) to determine  $D$ .

Key assumptions inherent in these equations are that  $D$  and  $L$  are constant, but these may change over the course of a permeation test. Swelling of the CPC sample by the solvent will lead to a gradual increase of  $L$ . For solvents that swell the polymer only slightly, the change of  $L$  will be negligible. For strong swelling agents, however, it may be more important. Immersion tests can be used to estimate the degree of swelling, but thickness changes measured after the entire sample has come to equilibrium, which can take several days to achieve for most thicknesses of CPC materials, will be larger than those observed after a few hours, typical of the time to reach a steady-state permeation rate for more soluble solvents.<sup>4,5</sup> Ideally, the sample thickness should be measured continuously over the course of a permeation test, but, in practice, the change of  $L$  is often ignored.

For systems of organic solvents and polymers,  $D$  may show a strong positive concentration dependence.<sup>5</sup> Thus, values of  $D$  determined at steady state may be larger than those determined at some earlier point in the permeation process. The concentration dependence of  $D$  arises from the plasticizing effect of the solvent where an increase in the mobility of polymer segments is caused by the solvent molecules initially diffusing through the polymer.<sup>5,6</sup>

Since theoretical approaches to predicting concentration-dependent  $D$  values<sup>5,7,8</sup> require parameters not readily available for most solvents and polymers, empirical correlations are often the most viable means of estimating  $D$ .<sup>9</sup> Several approaches have focused on correlating  $D$  with indices of molecular size and shape. Goydan et al. explored the relationship between experimentally determined  $D$  values for a number of solvent/CPC combination polymers and several solvent parameters such as the acentric factor, molecular connectivity, surface-to-volume ratio, and molecular weight.<sup>10</sup> Of these, the best correlations were found between the logarithm of the solvent molecular weight and the logarithm of  $D$ ; however, fairly large errors were found for a number of solvents. Others have reported correlations between  $D$  and the solvent molar volume,<sup>11</sup> viscosity,<sup>12</sup> and kinematic viscosity.<sup>13,14</sup>

The following relationship has been found for certain solvent-polymer mixtures to describe the dependence of  $D$  on the solvent concentration<sup>6</sup>:

$$D = D_0 e^{\gamma c} \quad (5)$$

where  $D_0$  is the diffusion coefficient at zero solvent concentration and  $\gamma$  has been referred to as a plasticizing coefficient that serves to weight the influence that a given concentration of a given solvent has on  $D$ .

Of particular interest here is the report by Kokes and Long<sup>15</sup> on the permeation of various solvent vapors through poly(vinyl acetate). Relationships of the form given in eq. (5) were found to hold, and  $\gamma$  was linearly related to the Flory interaction parameter,  $\chi$  which, in turn, was determined for each solvent from equilibrium sorption data. As described in the preceding article<sup>1</sup> and below,  $\chi$  can be estimated using 3-D solubility parameters. A primary goal of the present study was to determine if correlations between  $D$  and  $\chi$  could be found for solvents permeating through Viton<sup>®</sup> gloves.

## EXPERIMENTAL

Table I lists the solvents examined along with several relevant physical properties evaluated at the

Table I Physical Constants and Permeation Test Results<sup>a</sup>

| Solvent              | MW<br>(g/mol) | $V_1$<br>(cm <sup>3</sup> /mol) | $\eta$<br>(cP) | $\eta_k$<br>(cm <sup>2</sup> /s $\times 10^2$ ) | $A_w^2$<br>(J/cm <sup>3</sup> ) | $\chi$ |
|----------------------|---------------|---------------------------------|----------------|---|---------------------------------|--------|
| Methylene chloride   | 84.93         | 64.15                           | 0.433          | 0.327   | 47.6                            | 1.25   |
| Chloroform           | 119.38        | 80.16                           | 0.564          | 0.379   | 34.0                            | 1.12   |
| Carbon tetrachloride | 153.82        | 96.80                           | 0.931          | 0.586   | 42.3                            | 1.66   |
| 1,2-Dichloroethane   | 98.96         | 78.95                           | 0.836          | 0.667   | 49.9                            | 1.62   |
| Methylchloroform     | 133.41        | 99.70                           | 0.843          | 0.630   | 33.5                            | 1.37   |
| Trichloroethylene    | 131.40        | 90.25                           | 0.550          | 0.378   | 34.6                            | 1.26   |
| Perchloroethylene    | 165.83        | 102.71                          | 0.846          | 0.524   | 43.4                            | 1.80   |
| Acetone              | 58.08         | 74.11                           | 0.307          | 0.388   | 7.37                            | 0.22   |
| 3-Pentanone          | 86.13         | 106.44                          | 0.445          | 0.547   | 3.08                            | 0.13   |
| 1-Propanol           | 60.10         | 75.13                           | 1.898          | 2.36  | 72.1                            | 2.18   |
| 2-Ethoxyethanol      | 90.12         | 96.93                           | —              | —   | 29.4                            | 1.17   |
| Furfural             | 96.09         | 82.84                           | 0.150          | 1.29  | 40.1                            | 1.35   |
| Tetrahydrofuran      | 72.11         | 81.20                           | 0.550          | 0.619   | 6.11                            | 0.20   |
| Dioxane              | 88.11         | 85.70                           | 0.120          | 1.16  | 21.4                            | 0.74   |
| Nitrobenzene         | 123.11        | 102.53                          | 0.198          | 1.65  | 40.7                            | 1.70   |
| 2-Nitropropane       | 89.09         | 90.73                           | —              | —   | 8.55                            | 0.31   |
| Toluene              | 92.14         | 106.85                          | 0.552          | 0.637   | 31.4                            | 1.36   |
| Carbon disulfide     | 76.14         | 60.40                           | 0.363          | 0.288   | 87.2                            | 2.15   |

|                      | $T$<br>(°C) | $L$<br>(cm) | $BT_E$<br>(min) | $SSPR_E$<br>( $\mu\text{g}/\text{cm}^2/\text{min}$ ) | $J_t$<br>( $\mu\text{g}/\text{cm}^2/\text{min}$ ) | $M_t$<br>( $\mu\text{g}/\text{cm}^2$ ) |
|----------------------|-------------|-------------|-----------------|--|---|--|
| Methylene chloride   | 23          | 0.023       | 60              | 43.9   | 0.0965  |  |
| Chloroform           | 20          | 0.036       | 572             | 2.76   |   | 5.73                                   |
| Carbon tetrachloride | 20          | 0.042       | 5355            | 0.030  |   | 0.176                                  |
| 1,2-Dichloroethane   | 20          | 0.023       | 414             | 4.86   | 0.0238  |  |
| Methylchloroform     | 20          | 0.036       | 1450            | 3.06   |   | 6.42                                   |
| Trichloroethylene    | 25          | 0.023       | 445             | 1.44   | 0.00813   |  |
| Perchloroethylene    | 25          | 0.038       | 2580            | 0.022  |   | 1.95                                   |
| Acetone              | 25          | 0.028       | < 5             | 9810   | —   |  |
| 3-Pentanone          | 25          | 0.030       | < 8             | 3300   | —   |  |
| 1-Propanol           | 25          | 0.033       | 1220            | 0.040  | 0.00542   |  |
| 2-Ethoxyethanol      | 20          | 0.036       | 385             | 8.28   |   | 4.33                                   |
| Furfural             | 23          | 0.023       | 216             | 88.8   | 0.0155  |  |
| Tetrahydrofuran      | 20          | 0.036       | < 5             | 6680   | —   |  |
| Dioxane              | 25          | 0.023       | 23              | 161  | 0.00252   |  |
| Nitrobenzene         | 21          | 0.037       | 1320            | 0.635  |   | 0.553                                  |
| 2-Nitropropane       | 25          | 0.023       | 21              | 156  | 0.0298  |  |
| Toluene              | 25          | 0.037       | 810             | 0.415  |   | 1.17                                   |
| Carbon disulfide     | 22          | 0.036       | 400             | 0.222  |   | 0.088                                  |

<sup>a</sup> — indicates data not available. Weighting factors ( $a$ ,  $b$ ) used for calculating  $A_w$  can be found in Ref. 1. Subscript  $E$  indicates experimentally determined values.

temperatures at which permeation tests were performed. The molar volume and viscosity,  $\eta$ , of each solvent were obtained from standard references<sup>16-19</sup> and the kinematic viscosity,  $\eta_k$ , was calculated by dividing  $\eta$  by the solvent density.

Also presented in Table I are the results of solvent permeation tests of North Viton<sup>®</sup> gloves originally reported by Perkins et al.<sup>20</sup> A portion of that data was collected by the authors of that report and the remainder was collected by the Radian Corp. under

contract with the glove manufacturer.<sup>21</sup> In either case, permeation tests were performed using 5.08 cm (2 in.) diameter test cells at (nominally) constant temperatures ranging from 20 to 25°C.<sup>22,23</sup>

Data from Perkins et al. were collected in either open-loop or closed-loop systems using gas chromatographic or infrared vapor analysis, respectively. Table I reflects several corrections in the originally reported data made by the same authors.<sup>22</sup> For acetone, 2-pentanone, and tetrahydrofuran (THF),

where breakthrough occurred very rapidly, detection limits were not determined and the breakthrough times listed in Table I are approximate upper limits. Data from the glove manufacturer were collected in an open-loop system using gas chromatographic analysis.<sup>23</sup> Flow rates, collection-loop volumes, and analytical detection limits were obtained upon inquiry of the investigators.

On reviewing the data for 2-nitropropane and furfural, it was found that, at the stated flow rates through the collection side of the test cell, the air concentrations calculated from the reported  $SSPR_E$  values exceeded the saturation vapor concentrations of these solvents by factors of 2 and 11, respectively, indicating an error in the reported  $SSPR_E$  values for these solvents. Therefore, these  $SSPR_E$  values were excluded from further consideration. The  $BT_E$  values, however, were retained.

Experimental  $S$  values for the solvents,  $S_E$ , were measured at 20 and 25°C by 5 day immersion tests as described previously.<sup>1</sup> Where necessary,  $S_E$  values at temperatures between 20 and 25°C were estimated by linear interpolation.

Modeled solubilities were determined as described in the preceding paper.<sup>1</sup> Briefly, this involved first calculating the weighted difference between the solvent and polymer 3-D solubility parameters,  $A_w$ , using the following equation:

$$A_w = \delta_1 - \delta_2 = [a(\delta_{d1} - \delta_{d2})^2 + b(\delta_{p1} - \delta_{p2})^2 + b(\delta_{h1} - \delta_{h2})^2]^{1/2} \quad (6)$$

where  $\delta_1$  and  $\delta_2$  [(J/cm<sup>3</sup>)<sup>1/2</sup>] are the solubility parameters for the solvent and polymer, respectively; the subscripts  $d$ ,  $p$ , and  $h$  designate the dispersion, dipolar, and hydrogen-bonding components of the 3-D solubility parameters; and  $a$  and  $b$  are empirical weighting factors determined for the chemical class or subgroup to which a given solvent belonged. Methylene chloride, acetone, and carbon tetrachloride were exceptional solvents, requiring individual weighting factors for the determination of  $A_w$ . Solubility parameters were corrected for temperature where necessary.<sup>1</sup>

This value of  $A_w$  was then used to calculate the Flory interaction parameter,  $\chi$ , at the permeation test temperature by

$$\chi = V_1 A_w^2 / (RT) \quad (7)$$

where  $V_1$  is the solvent molar volume (cm<sup>3</sup>/mol);  $R$ , the gas constant (J/mol K); and  $T$ , the temperature (K). The following expression was then

used to determine the volume fraction of the solvent in the polymer,  $\phi_1$ :

$$\chi = -2\nu V_1 (\phi_2^{-5/3} - \frac{1}{2}\phi_2^{-1}) - (\ln \phi_1)\phi_2^{-2} - \phi_2^{-1} \quad (8)$$

where  $\nu$  is the polymer cross-link density (mol/cm<sup>-3</sup> or cm<sup>-3</sup>) and  $\phi_2$  is the polymer volume fraction (1 -  $\phi_1$ ). A value of  $\nu = 10^{-4}$  cm<sup>-3</sup> was assumed based on previous analyses.<sup>1</sup> Multiplying the volume ratio,  $\phi_1/\phi_2$ , by the solvent density gave the modeled solubility value, which is designated as  $S_{Mw}$  to indicate that it is based on weighted solubility parameter differences.

Experimental values of  $D$  were determined at breakthrough and at steady state using the immersion test  $S$  values listed in Table II together with the experimental  $BT_E$  and  $SSPR_E$  values listed in Table I. The experimental breakthrough diffusion coefficient,  $D_{BE}$ , was calculated via either eq. (3) or (4), for open-loop or closed-loop test systems, respectively, using reported  $M_t$  or  $J_t$  values at the limits of detection (Table I). Solutions to eqs. (3) and (4) were obtained using a simple computer program employing a standard bisection method. Experimental steady-state  $D$  values ( $D_{SE}$ ) were calculated from eq. (2) using the  $L$  values listed in Table I.

Simple linear regression was then employed to examine the relationships between several independent variables and the  $D_{BE}$  and  $D_{SE}$  values, with the correlation coefficient,  $r^2$ , being used to assess the goodness of fit. Finally, modeled diffusion coefficients ( $D_{BM}$  and  $D_{SM}$ , for breakthrough and steady-state  $D$  values, respectively) obtained from the regression equations providing the best correlations were combined with  $S_{Mw}$  values in eqs. (2)–(4) to determine the modeled permeation indices designated  $BT_M$  and  $SSPR_M$ .

## RESULTS AND DISCUSSION

Table II presents  $S_E$  and  $S_{Mw}$  values for each solvent at the temperatures at which permeation tests were performed, along with the  $S_{Mw} : S_E$  ratios. Consistent with the results presented in the preceding article,<sup>1</sup> most of the modeled values were within a factor of two of experimental values. A notable exception was 2-ethoxyethanol whose solubility was underestimated by a factor of about three. This was not unexpected, however, since this solvent exhibited anomalous solubility behavior due, apparently, to its capability for self-association through intermolecular hydrogen-bonding.<sup>1,24,25</sup>

A comparison of  $D_{BE}$  and  $D_{SE}$  values (Table II) shows that for five solvents  $D_{BE} > D_{SE}$ , in contrast to what would be expected for  $D$  with a positive concentration dependence. With the exception of toluene, where  $D_{BE}$  and  $D_{SE}$  were nearly equal, the relative order of the  $D$  values could not be accounted for by the increase of  $L$ , even if it is assumed that the increase of  $L$  is equal to the nominal volume increase determined from immersion tests. Decreases of  $D$  with increasing concentration have been reported,<sup>5</sup> but these cases involved solvents, such as methanol and water, capable of strong hydrogen-bonding interactions. Although this might explain the results for propanol, it cannot explain the results for the other solvents. Internal stresses in the CPC sample during the initial phases of permeation would lead to steeper concentration gradients than assumed in eqs. (3) and (4) and, consequently, higher  $D_{BE}$  values,<sup>26</sup> but it is not clear why only these solvents would be affected. A final possibility is experimental error. The five solvents for which  $D_{BE} > D_{SE}$  compose those with the longest BT and lowest SSPR values. Slight drifts in temperature over the course of the permeation tests could account for the decreases in  $D$  values, since  $D$  is known to be a sensitive function of temperature.<sup>14</sup>

Table III summarizes the results of attempts to model  $D_{BE}$  and  $D_{SE}$  using several different predictor variables. The first group of results is for correlations based on various indices of molecular size. In general, the correlations were quite poor. For the molecular weight (MW) correlation with  $D_{SE}$ , however, visual inspection of the regression plot revealed propanol and carbon disulfide to be outliers, with their  $D$  values being greatly overestimated. Omitting these solvents gave an  $r^2$  of 0.797. These solvents were also among those for which  $D_{BE}$  was poorly estimated with this predictor variable. As with 2-ethoxyethanol, propanol will tend to self-associate. Thus, the effective  $D$  would be smaller than expected based on the molecular weight of a discrete propanol molecule. The reason for the poor correlation for carbon disulfide is not clear (note:  $D_{SE}$  for 2-ethoxyethanol was also overestimated from the MW correlation, but to a lesser extent than for propanol).

The next group of  $r^2$  values presented in Table III was obtained from correlations with  $\phi_1$ ,  $S_E$ ,  $\chi$ , and  $A_w$  individually and in various combinations. Correlations with  $\phi_1$  and  $S_E$  were reasonably good, improving markedly in the former case upon removal of methylene chloride ( $r^2$  increased to 0.762 and 0.862 for  $D_{BE}$  and  $D_{SE}$  correlations, respectively). Correlations based on  $\chi$ ,  $A_w$ , and  $A_w^2$  were rather poor for  $D_{BE}$ , though somewhat better for  $D_{SE}$ . Using

combinations of these predictor variables did not improve upon the correlations obtained using the individual variables.

The last group of results in Table III involved correlations where a measure of solvent size ( $V_1$  or MW) was combined either with  $\phi_1$  or with one of the variables determined from the weighted solvent-CPC solubility parameter difference. As a group, these correlations were generally better than the others examined. The quantities  $A_w V_1$  and  $\chi V_1$  provided the best overall results, although  $\chi MW$  also gave good correlations. It is interesting to note the improvement in the strength of the correlations when these predictor variables are combined vs. when they are used separately (e.g., for  $D_{BE}$  the correlation coefficients with  $\chi$  and  $V_1$  were 0.004 and 0.181, respectively, compared to 0.834 for  $\chi V_1$ ).

If one considers  $A_w$  and  $\chi$  as measures of solvent interaction or plasticization strength, the physical interpretation of these results is straightforward. As expected, the diffusion coefficient generally decreases with increasing solvent size; however, this effect is modulated by the degree of plasticization caused by the solvent. Recall that  $A_w$  and  $\chi$  decrease with increasing interaction strength. Thus, for solvents of similar MW or  $V_1$ , those interacting more strongly with the polymer will have larger values of  $D$ .

Based on the data in Table III, the choice of modeling  $D$  values with  $A_w V_1$  or  $\chi V_1$  was arbitrary. Both provided similar levels of accuracy. However, in a related study involving different solvent-polymer combinations, it was found that the temperature dependence of  $D$  could be modeled more accurately using correlations based on  $\chi V_1$  rather than  $A_w V_1$ .<sup>14</sup> Therefore,  $\chi V_1$  was selected as the predictor variable for  $D_{BM}$  and  $D_{SM}$  here.

Figure 1 (a) and (b) illustrate the strength of the correlations between  $\chi V_1$  and  $\ln D_{BE}$  and  $\ln D_{SE}$ , respectively. In Table II,  $D_{BM}$  and  $D_{SM}$  values calculated from the appropriate regression equations are listed along with the corresponding experimental values and the modeled-to-experimental ratios. In all cases,  $D_{BM}$  is within a factor of three of  $D_{BE}$  and, in most cases, is within a factor of two.  $D_{SM}$  values are less accurate, falling within only a factor of four of  $D_{SE}$ .

$D_{SM}$  is the least accurate for nitrobenzene. However, it is suspected that this is due to experimental error. Permeation tests were performed using a Miran 1A infrared analyzer, which is calibrated by injecting the liquid solvent into a closed-loop system. As described by Samimi,<sup>27</sup> solvents with low vapor pressures may not vaporize completely during such

**Table II** Experimental and Modeled Values of  $D$ ,  $S$ ,  $BT$ , and  $SSPR^a$ 

| Solvent              | $S_E$<br>(g/cm <sup>3</sup> ) | $S_{Mw}$<br>(g/cm <sup>3</sup> ) | $S_{Mw}/S_E$ | $D_{BE}$<br>(cm <sup>2</sup> /s × 10 <sup>9</sup> ) | $D_{BM}$<br>(cm <sup>2</sup> /s × 10 <sup>9</sup> ) | $D_{BM}/D_{BE}$ |
|----------------------|-------------------------------|----------------------------------|--------------|---|---|-----------------|
| Methylene chloride   | 0.345                         | 0.333                            | 0.96         | 6.36  | 4.75  | 0.75            |
| Chloroform           | 0.375                         | 0.492                            | 1.31         | 2.03  | 3.71  | 1.82            |
| Carbon tetrachloride | 0.134                         | 0.192                            | 1.43         | 0.21  | 0.59  | 2.68            |
| 1,2-Dichloroethane   | 0.231                         | 0.164                            | 0.71         | 1.08  | 1.40  | 1.30            |
| Methylchloroform     | 0.321                         | 0.266                            | 0.83         | 0.84  | 1.12  | 1.33            |
| Trichloroethylene    | 0.302                         | 0.359                            | 1.19         | 0.81  | 2.01  | 2.47            |
| Perchloroethylene    | 0.162                         | 0.160                            | 0.99         | 0.43  | 0.32  | 0.75            |
| Acetone              | 4.27                          | 4.79                             | 1.12         | —   | —   | —               |
| 3-Pentanone          | 4.46                          | 4.56                             | 1.02         | —   | —   | —               |
| 1-Propanol           | 0.026                         | 0.046                            | 1.77         | 1.02  | 0.56  | 0.55            |
| 2-Ethoxyethanol      | 0.866                         | 0.272                            | 0.31         | 2.54  | 2.02  | 0.80            |
| Furfural             | 0.384                         | 0.239                            | 0.62         | 1.60  | 2.10  | 1.31            |
| Tetrahydrofuran      | 5.10                          | 5.21                             | 1.02         | —   | —   | —               |
| Dioxane              | 1.35                          | 1.28                             | 0.94         | 13.1  | 7.34  | 0.71            |
| Nitrobenzene         | 0.299                         | 0.136                            | 0.45         | 0.68  | 0.41  | 0.61            |
| Nitropropane         | 2.81                          | 4.38                             | 1.56         | 25.1  | 18.0  | 0.72            |
| Toluene              | 0.208                         | 0.176                            | 0.85         | 1.29  | 0.92  | 0.71            |
| Carbon disulfide     | 0.104                         | 0.078                            | 0.75         | 1.93  | 1.33  | 0.69            |

|                      | $D_{SE}$<br>(cm <sup>2</sup> /s × 10 <sup>9</sup> ) | $D_{SM}$<br>(cm <sup>2</sup> /s × 10 <sup>9</sup> ) | $D_{SM}/D_{SE}$ |
|----------------------|---|---|-----------------|
| Methylene chloride   | 48.4  | 21.7  | 0.45            |
| Chloroform           | 4.42  | 14.1  | 3.20            |
| Carbon tetrachloride | 0.16  | 0.60  | 3.85            |
| 1,2-Dichloroethane   | 8.06  | 2.63  | 0.33            |
| Methylchloroform     | 5.72  | 1.78  | 0.31            |
| Trichloroethylene    | 1.83  | 4.92  | 2.69            |
| Perchloroethylene    | 0.09  | 0.21  | 2.44            |
| Acetone              | 1072  | 369   | 0.34            |
| 3-Pentanone          | 37  | 407   | 1.10            |
| 1-Propanol           | 0.88  | 0.54  | 0.62            |
| 2-Ethoxyethanol      | 5.74  | 4.97  | 0.87            |
| Furfural             | —   | 5.33  | —               |
| Tetrahydrofuran      | 785   | 364   | 0.46            |
| Dioxane              | 45.6  | 45.7  | 1.00            |
| Nitrobenzene         | 1.29  | 0.32  | 0.25            |
| Nitropropane         | —   | 215   | —               |
| Toluene              | 1.26  | 1.28  | 1.01            |
| Carbon disulfide     | 1.28  | 2.41  | 1.88            |

|                      | $BT_M$<br>(min) | $BT_M/BT_E$ | $SSPR_M$<br>(μg/cm <sup>2</sup> /min) | $SSPR_M/SSPR_E$ |
|----------------------|-----------------|-------------|---------------------------------------|-----------------|
| Methylene chloride   | 84              | 1.40        | 23.0                                  | 0.53            |
| Chloroform           | 300             | 0.52        | 13.7                                  | 4.97            |
| Carbon tetrachloride | 1914            | 0.36        | 0.16                                  | 5.26            |
| 1,2-Dichloroethane   | 327             | 0.79        | 1.19                                  | 0.25            |
| Methylchloroform     | 1129            | 0.78        | 0.81                                  | 0.27            |
| Trichloroethylene    | 151             | 0.34        | 5.08                                  | 3.52            |
| Perchloroethylene    | 3484            | 1.35        | 0.05                                  | 2.14            |
| Acetone              | —               | —           | 5590                                  | 0.57            |
| 3-Pentanone          | —               | —           | 5506                                  | 1.67            |
| 1-Propanol           | 2247            | 1.84        | 0.04                                  | 1.05            |

**Table II** (Continued)

|                  | BT <sub>M</sub><br>(min) | BT <sub>M</sub> /BT <sub>E</sub> | SSPR <sub>M</sub><br>(μg/cm <sup>2</sup> /min) | SSPR <sub>M</sub> /SSPR <sub>E</sub> |
|------------------|--------------------------|----------------------------------|--|--------------------------------------|
| 2-Ethoxyethanol  | 579                      | 1.50                             | 2.64   | 0.32                                 |
| Furfural         | 170                      | 0.79                             | —  | —                                    |
| Tetrahydrofuran  | —                        | —                                | 4655   | 0.70                                 |
| Dioxane          | 34                       | 1.47                             | 195  | 1.21                                 |
| Nitrobenzene     | 2404                     | 1.82                             | 0.07   | 0.10 <sup>b</sup>                    |
| 2-Nitropropane   | 29                       | 1.37                             | —  | —                                    |
| Toluene          | 1165                     | 1.44                             | 0.36   | 0.86                                 |
| Carbon disulfide | 602                      | <u>1.51</u>                      | 0.33   | <u>1.48</u>                          |
|                  |                          | $r_g = 1.02$                     |  | $r_g = 1.05$                         |
|                  |                          | $s_g = 1.72$                     |  | $s_g = 2.62$                         |
|                  |                          | CI <sub>0.95</sub> = 0.77–1.34   |  | CI <sub>0.95</sub> = 0.64–1.71       |
|                  |                          | PI <sub>0.95</sub> = 0.26–3.90   |  | PI <sub>0.95</sub> = 0.10–11.4       |

<sup>a</sup>  $r_g$  = geometric mean ratio;  $s_g$  = geometric standard deviation; CI<sub>0.95</sub> = 95% confidence interval; PI<sub>0.95</sub> = 95% prediction interval determined from  $\exp[r_1 \pm t_{0.95} s_1 (1 + 1/n^{1/2})]$ , where  $r_1$  and  $s_1$  are the mean and standard deviation of the log-transformed ratios, respectively.

<sup>b</sup> Omitted from calculations of summary statistics (see text).

calibration procedures. For isophorone, which has a vapor pressure of 0.43 mmHg, errors in concentration as large as -46% were observed. Since ni-

**Table III** Correlations of  $\ln D_{BE}$  and  $\ln D_{SE}$  with Several Predictor Variables<sup>a</sup>

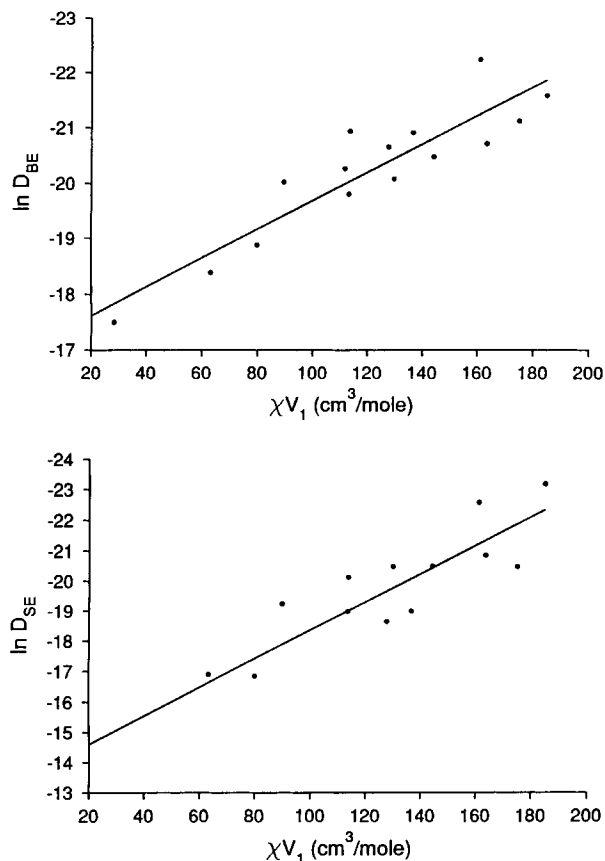
| Independent Variable | $r^2$        |              |
|----------------------|--------------|--------------|
|                      | $\ln D_{BE}$ | $\ln D_{SE}$ |
| $\ln MW$             | 0.284        | 0.405        |
| $\ln \eta$           | 0.047        | 0.227        |
| $\ln \eta_k$         | 0.004        | 0.030        |
| $\ln V_1$            | 0.116        | 0.065        |
| $V_1$                | 0.181        | 0.074        |
| $\phi_1$             | 0.664        | 0.789        |
| $S_E$                | 0.638        | 0.730        |
| $\chi$               | 0.004        | 0.765        |
| $A_w$                | 0.254        | 0.576        |
| $A_w^2$              | 0.152        | 0.449        |
| $\phi_1 A_w$         | 0.536        | 0.516        |
| $\phi_1 A_w^2$       | 0.264        | 0.028        |
| $\phi_1 \chi$        | 0.134        | 0.003        |
| $\phi_1 MW$          | 0.524        | 0.648        |
| $\phi_1 V_1$         | 0.561        | 0.679        |
| $A_w MW$             | 0.726        | 0.793        |
| $A_w^2 MW$           | 0.638        | 0.790        |
| $\chi MW$            | 0.805        | 0.848        |
| $A_w^2 V_1$          | 0.532        | 0.769        |
| $A_w V_1$            | 0.838        | 0.897        |
| $\chi V_1$           | 0.834        | 0.901        |

<sup>a</sup>  $r^2$  was determined from simple linear regression.

trobenzene has a saturation vapor pressure < 1 mmHg (probably < 0.4 mmHg) at the permeation test temperature,<sup>28</sup> it is likely that the reported SSPR<sub>E</sub> value is overestimated. Consequently, the  $D_{SE}$  calculated from this SSPR<sub>E</sub> value would also be overestimated. Given the likelihood of this error, the SSPR<sub>E</sub> for nitrobenzene is viewed with skepticism. BT and  $D_{BE}$  values would also be affected, but the rapid change of concentration typically observed in the vicinity of the BT would tend to reduce the importance of this error.

The modeled values of  $S$  and  $D$  from Table II were then used to calculate BT<sub>M</sub> and SSPR<sub>M</sub>. As shown in Table II, BT<sub>M</sub> was within a factor of three of BT<sub>E</sub> (in most cases, within a factor of two) for all 15 solvents for which detection limits were available. Note that the nitrobenzene BT<sub>M</sub> was slightly overestimated, consistent with the calibration error mentioned above. Figure 2(a) shows the correlation of BT<sub>M</sub> and BT<sub>E</sub> (log scales were used because of the wide range of values).

The geometric mean of the BT<sub>M</sub> : BT<sub>E</sub> ratios (Table II) indicates a slight tendency toward overestimation. From the estimated prediction interval, BT<sub>M</sub> values within a factor of four of BT<sub>E</sub> would be expected 95% of the time. In terms of practical application to the problem of glove selection, this level of accuracy would be of most value in extreme cases; i.e., for solvents with BT values of a few minutes, the modeled values would be sufficiently accurate to indicate that a glove should not be used. Similarly, for modeled BT values greater than a few hours, there is sufficient accuracy to judge such gloves suit-



**Figure 1** Plot of  $\chi V_1$  vs. (a)  $\ln D_{BE}$  and (b)  $\ln D_{SE}$ . Values of  $r^2$  were determined from linear regression.

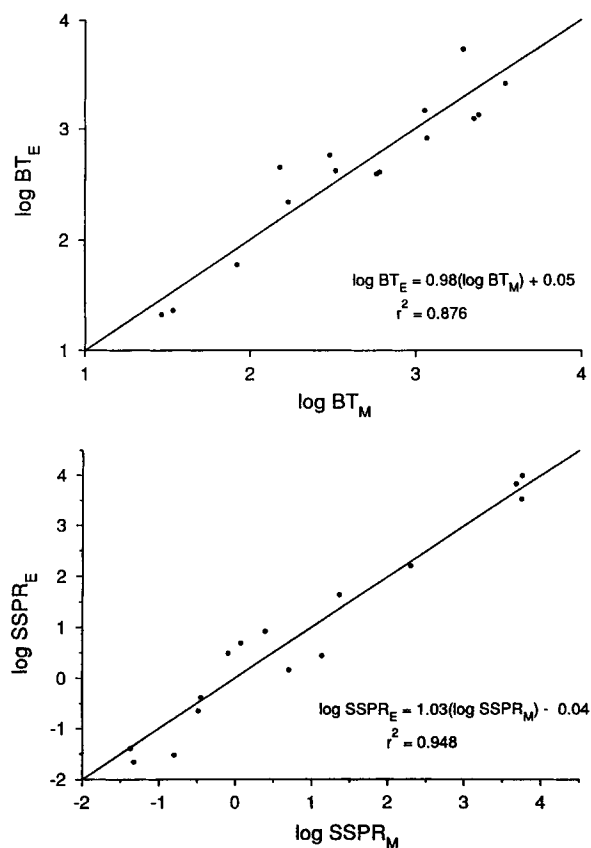
able for most workplace applications. For intermediate modeled values of BT, the decision would be less clear. Of course, if a significance level less than 95% could be tolerated, the useful range of BT predictions would improve correspondingly.

SSPR<sub>M</sub> values are generally less accurate than the BT<sub>M</sub> values, falling within a factor of six of the corresponding SSPR<sub>E</sub> values, though typically within a factor of four (excluding nitrobenzene). Figure 2(b) shows the correlation of SSPR<sub>M</sub> and SSPR<sub>E</sub>. The geometric mean SSPR<sub>M</sub>: SSPR<sub>E</sub> ratio (Table II) also indicates a slight tendency toward overestimation with the model. The higher variability in the SSPR<sub>M</sub> data leads to a much larger prediction interval: At the 95% significance level, SSPR<sub>M</sub> values within only a factor of 10 or 11 of experimental values are expected. Here, again, for extreme cases, this would provide useful information, but for intermediate SSPR<sub>M</sub> values, there would be considerably less confidence in decisions based on the modeled data.

The individual  $S_{Mw}$ ,  $D_{BM}$ , and  $D_{SM}$  values were examined to determine if the accuracy of modeled BT and SSPR values was merely a fortuitous com-

ination of high  $S$  and low  $D$  values or vice versa. With the possible exception of the propanol SSPR<sub>M</sub> value, this was clearly not the case. Invariably, the sign and magnitude of the error in BT<sub>M</sub> reflects that of  $D_{BM}$  rather than of  $S_{Mw}$ , which is consistent with fact that BT is a more sensitive function of  $D$  than of  $S$ .<sup>10</sup> SSPR<sub>M</sub> is affected equally by errors in  $S$  and  $D$  [see eq. (2)], and because  $S_{Mw}$  values were generally more accurate than  $D_{SM}$ , the errors in SSPR<sub>M</sub> also tend to reflect the errors in the latter variable. The advantage of using separate estimates of  $D$  is apparent from the fact that using  $D_{BM}$  rather than  $D_{SM}$  provided more accurate BT<sub>M</sub> estimates for all solvents except toluene and carbon disulfide (data not shown). The difference in accuracy for the two exceptional solvents, however, was not very large, as would have been predicted by the lack of a strongly concentration-dependent  $D$  value in either case (see Table II).

The approach taken here for estimating BT and SSPR is similar, in some respects, to that employed by Goydan et al. in their recent study of permeation models<sup>29</sup>: Both approaches involve individual esti-



**Figure 2** Log-log plot of modeled vs. experimental (a) BT and (b) SSPR values. Solid lines represent perfect correlation. Values of  $r^2$  were determined from linear regression.



mates of  $S$  and  $D$  that are combined in Fickian diffusion equations to estimate BT and SSPR. In their approach, however,  $S$  is modeled using either a molecular group-contribution (MGC) method or an equation-of-state method, with the former providing the most accurate results. Estimates of solubility typically within a factor of five (often within a factor of two) of experimentally determined values were reported for a range of solvents in several common CPC polymers.

The MGC method is somewhat limited by the fact that the required group-contribution parameters are currently available for only certain solvents and polymers. However, a similar criticism could be made of the solubility model used here with respect to the required 3-D solubility parameters. One advantage of the MGC method is that no experimental data are needed to estimate  $S$ , whereas in the model used here, empirical weighting factors are needed. However, variables such as temperature and CPC-polymer cross-linking, which are accounted for in the current model, have apparently not been incorporated into the MGC method. In addition, while group-contribution parameters are known for the relevant carbon-fluorine functional groups in Viton,<sup>30</sup> the MGC method has not been successfully applied to solvent permeation through this material.

As mentioned above (see Theoretical Background), Goydan et al. employed correlations with the solvent molecular weight to estimate  $D$ . Although this approach is simple and also requires no experimental data, it is very approximate. The correlations based on  $\chi V_1$  used here appear to be more accurate, but, again, require estimates of  $\chi$  that must be determined from the weighted 3-D solubility parameter difference for each solvent.

Overall, the accuracy of their model in predicting permeation parameters was only fair, with predicted BT and SSPR values for various solvents through four common CPC polymers (butyl rubber, nitrile rubber, natural rubber, and neoprene) falling within a factor of five of experimental values for only 17–75% of the solvent/polymer combinations tested.<sup>29</sup> Clearly, additional data are needed to assess the general applicability of the approach presented here, but the preliminary results just described demonstrate the potential for this approach to provide improved accuracy in modeling solvent-CPC BT and SSPR values.

## CONCLUDING REMARKS

A new approach to modeling solvent-CPC permeation using 3-D solubility parameters has been pre-

sented and evaluated for several solvents permeating through samples of Viton gloves. In contrast to previous approaches involving comparisons of solubility parameter differences directly with BT and SSPR values (see Ref. 1 and references therein), this approach employs solubility parameters to determine explicit values of the solubility and diffusion coefficient, which are then used in Fickian diffusion equations to estimate BT and SSPR values. Although somewhat more complex, the current approach has a more rigorous physical and theoretical basis. The ability to account for temperature and CPC-polymer cross-linking in estimating solubilities<sup>1</sup> is also an advantage of this approach.

Accurate models of the solvent diffusion coefficients evaluated at breakthrough and at steady state were developed based on empirical correlations of experimental  $D$  values with the product of the solvent molar volume,  $V_1$ , and either the Flory interaction parameter,  $\chi$ , or the weighted solvent-CPC solubility parameter difference,  $A_w$ . In a separate study, correlations based on  $\chi V_1$  were found to be more accurate than those based on  $A_w V_1$  in modeling the temperature dependence of  $D$ ,<sup>14</sup> suggesting that  $\chi V_1$  may be of more general utility in the context of solvent-CPC permeation.

Modeled BT values were typically within a factor a two of experimental values for the solvents examined here, and from the distribution of modeled values, a 95% prediction interval within a factor of four of experimental values was determined. This degree of accuracy should be adequate for making glove selections in many cases. While modeled SSPR values were less accurate than were modeled BT values, falling within a factor of six of experimental values, glove selections are often based principally on BT criteria and only secondarily on SSPR data.

Although the accuracy with which permeation indices can be modeled with the approach presented here has been demonstrated, the need to empirically determine the weighting factors used to calculate  $A_w$  and  $\chi$  limits its predictive capacity. However, the weighting factors are evidently related to the structures of the solvents and polymers under consideration<sup>1</sup> and it is expected that with further research a means of estimating their values based on known physical or chemical properties should be possible.

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