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16. Abstract (Limit: 200 words) A series of investigations of solvent permeation through clothing designed to offer protection against contact with hazardous chemicals was conducted. Variables studied included solvent type, glove type, temperature, exposure profile, mixtures of solvents, and post exposure thermal decontamination. The highest level of permeation resistance to the photoresists and related formulations containing glycol ether derivatives either in neat form or in mixtures with other solvents was generally provided by butyl rubber gloves. Nitrile rubber gloves also provided a high level of protection, but increased temperature or repeated exposures compromised their barrier properties. Gloves composed of natural rubber or blends of natural rubber with other polymers were less effective against the neat solvents and photoresist formulations. Permeation of the glycol ether derivatives in the formulations was faster for most glove samples than had been predicted based on the permeation behavior of the pure glycol ethers. Use of thin surgical type gloves composed of natural rubber or polyvinyl-chloride beneath the chemically protective gloves increased the net permeation resistance marginally. Use of these gloves alone offered no effective permeation resistance. Even at temperatures as high as 50 degrees-C, butyl rubber gloves provided exceptionally good resistance to permeation. The decrease in permeation resistance was due to increases in the rates of diffusion rather than to increases in solubility.

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Glove Permeation by Semiconductor Processing Mixtures:
Predicted and Experimental Results

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Abstract

This report describes a series of investigations of solvent permeation through chemical protective clothing. The effects on permeation of a number of important variables were studied, including solvent type, glove type, temperature, exposure profile (intermittent vs. continuous), mixtures of solvents, and post-exposure thermal decontamination. These factors have been examined for gloves and solvents commonly used in semiconductor device processing facilities. In addition, preliminary studies on the use of three-dimensional solubility parameters in predictive models of permeation have been performed. The approach and initial results are presented.

Chapter 1 describes an investigation of the permeation of photoresist formulations containing ethylene glycol ether derivatives which are recognized reproductive toxicants. Chapter 2 involves a similar study of propylene glycol monomethylether acetate, which is being used as a less toxic replacement solvent for the ethylene glycol ether derivatives in newer photoresist formulations. Chapter 3 focuses on the temperature dependence of glove permeation by N-methylpyrrolidone (NMP), which is degreasing solvent often used at high temperatures. Experimental results are compared to those predicted from two different models - one developed (in part) in Chapter 4 of this report. Chapters 4 and 5 depart from the focus on semiconductor processing and extend beyond the original goals of the study. In Chapter 4, a new approach to using three-dimensional solubility parameters in the context of glove permeation is presented. In constrast to previous studies involving qualitative correlations between permeation parameters and the solubility parameters of CPC polymers and challenge solvents, this model provides a means for quantitative prediction of solvent-CPC solubilities. The model can account for the degree of cross-linking in the CPC polymer as well as the exposure temperature. Previously published immersion-test data for a range of solvents in Viton glove samples are used to demonstrate the approach. In Chapter 5, a subset of the solvents examined in Chapter 4 (i.e., those for which permeation test data were available) was studied further. Solubility estimates were combined with empirical estimates of the solvent diffusion coefficients in a Fickian diffusion model to predict the breakthrough times and steady-state permeation rates of the solvents. Detailed summaries of each chapter are given in the following paragraphs.

Chapter 1 describes the results of permeation tests of several glove materials challenged with semiconductor processing formulations containing glycol-ether derivatives. Commercial glove samples of nitrile rubber (Edmont), natural

rubber (Edmont and Baxter), butyl rubber (North), PVC (Baxter), a natural/neoprene/nitrile rubber blend (Pioneer), and a natural/neoprene rubber blend (Playtex) were tested according to the ASTM F739-85 permeation test method (open-loop configuration). The liquid formulations examined included a positive photoresist thinner containing 2-ethoxyethyl acetate (2-EEA), n-butyl acetate, and xylene; a positive photoresist containing 2-EEA, n-butyl acetate, xylene, polymer resins, and photoactive compounds; a negative photoresist containing 2-methoxyethanol (2-ME), xylene, and cyclized poly(isoprene); and pure 2-methoxyethyl acetate (2-MEA) which is the solvent used in a commercial electron-beam resist.

With the exception of the negative photoresist, butyl rubber provided the highest level of protection against the solvent mixtures tested, with no breakthrough being observed after four hours of continuous exposure at 25°C. Nitrile rubber provided the highest level of protection against the negative photoresist, and reasonably good protection against initial exposure to the other solvent mixtures. Gloves consisting of natural rubber or natural rubber blends provided less protection against the mixtures than either nitrile or butyl rubber.

For most of the glove samples, permeation of the glycol-ether derivatives contained in the mixtures was faster than that predicted from the permeation of the pure solvents. Increasing the exposure temperature from 25 to 37°C did not significantly affect the performance of the butyl rubber glove. For the other gloves, however, exposures at 37°C resulted in decreases of 25-75% in breakthrough times and increases of 80-457% in steady-state permeation rates relative to values obtained at 25°C.

Repeated exposure of nitrile rubber samples resulted in shorter breakthrough times for all mixture components. In fact, exposure for as little as one-half of the nominal breakthrough time followed by air drying overnight resulted in measurable quantities of one or more of the component solvents at the inner surface of the gloves at the beginning of the next exposure. This effect was not observed with the butyl rubber samples. With the exception of the negative photoresist, heating previously exposed nitrile rubber samples at 70°C for 20 hr prior to re-testing reduced or eliminated the effects of residual solvents, permitting re-use of the gloves.

The use of thin PVC or natural rubber gloves adjacent to the nitrile gloves provided moderate increases in permeation resistance. Addition of 10% acetone to the positive photoresist resulted in shorter breakthrough times and faster permeation rates for all components through the nitrile rubber.

In Chapter 2 the permeation behavior of propylene glycol monomethyl ether acetate (PGMEA) is described. PGMEA has been introduced as a replacement solvent for ethylene glycol ethers and ether acetates in photoresist formulations used in semiconductor processing. While PGMEA does not exhibit the adverse reproductive health effects found with the structurally related ethylene-glycol derivatives, it is still readily absorbed through the skin and proper protection against dermal absorption is warranted. This paper describes the results of permeation tests of several glove materials commonly used in semiconductor fabrication facilities when challenged with PGMEA. Glove samples were tested at 25 and 37°C according to the ASTM F739-85 permeation test method. The effects of repeated exposure and post-exposure thermal decontamination on permeation resistance were also examined for one type of glove.

Of the gloves tested, those composed of butyl rubber (North B-161) afforded the highest level of protection against PGMEA, with no breakthrough being observed after more than four hours of continuous exposure at 25°C. Nitrile rubber gloves (Edmont Nytek) also provided good protection against initial exposure (breakthrough time > 2.4 hr at 25°C). Gloves composed of natural rubber (Edmont Puretek) or blends of natural rubber with other polymers (Pioneer Trionic, Playtex 827) provided significantly less protection (breakthrough times < 22 min at 25°C). Increasing the exposure temperature from 25 to 37°C did not affect the performance of the butyl rubber gloves. For the other gloves, however, decreases in breakthrough times (BT) by factors of 2-3 and increases in steady-state permeation rates (SSPR) by factors of 2-4 were observed.

Repeated exposure of nitrile rubber samples indicated that the PGMEA is retained in, and diffuses through, the gloves long after exposure has ceased. Following an initial exposure for about one-half of the nominal breakthrough time and air drying overnight at room temperature, vapors of PGMEA at concentrations greater than the breakthrough-time detection limit were detected permeating through glove samples. Much higher SSPR values were measured for the previously exposed samples as well. Heating previously exposed nitrile rubber samples at 70 or 100°C for 24 hr prior to re-testing failed to restore the initial permeation resistance.

Chapter 3 presents experimental and predicted results of the effects of temperature on the permeation of N-methylpyrrolidone (NMP) through butyl and natural rubber gloves. NMP is a polar organic solvent that is readily absorbed through the skin. Among its range of industrial applications, NMP is used in "die-coat" and high-temperature degreasing operations in the microelectronics industry.

This investigation was designed to characterize the temperature dependence of NMP permeation through several glove materials commonly used in microelectronics fabrication facilities. One type of butyl rubber glove (North B-161), two types of natural rubber gloves (Edmont Puretek and Ansell Pacific White) and a natural rubber/nitrile/neoprene blend glove (Pioneer Trionic) were tested at four temperatures from 25-50°C using the ASTM permeation test method. Results were compared to those based on recently developed predictive models of permeation.

The butyl rubber glove showed no breakthrough after four hours of exposure at any of the temperatures. Measured breakthrough times (BT) and steady-state permeation rates (SSPR) for the other gloves exhibited Arrhenius temperature dependences, with BT values decreasing by factors of 7-10 and SSPR values increasing by factors of 4-6 over the temperature range studied. The Ansell gloves showed consistently shorter BT and higher SSPR values than the Pioneer and Edmont gloves. Extrapolation to 70 and 93°C, the temperatures at which degreasing is often performed, yielded BT values of <2min and <0.5 min, respectively, for all three gloves. Following an initial exposure at 25°C and air drying overnight, low levels of NMP vapor were detected permeating through the gloves (except butyl rubber) but there were no significant changes in the SSPR values.

A comparison of experimentally determined activation energies indicates that the observed temperature effects are attributable mainly to increases in the solvent diffusion coefficient, D, rather than equilibrium solubility, S. Predicted values of S, calculated using a recently developed model based on solubility parameters, were within 3-25% of immersion-test values for the natural rubber gloves over the entire temperature range examined. Predicted values of D, obtained from correlations with the solvent kinematic viscosity, were within 13-33% of experimentally derived values. Combining predicted values of D and S in a Fickian diffusion model gave predicted values of BT that were, with one exception, within 60% of experimental values (all predicted BT values were within 13 minutes of experimental BT values). Predicted SSPR values were within 49% (typically within 18%) of experimental values. An alternative model based on empirical correlations of Arrhenius parameters provided useful but generally less accurate predictions of BT and SSPR at elevated temperatures.

Chapter 4 concerns the prediction of solvent-CPC solublities using solubility parameters. Solvent permeation through chemical protective clothing (CPC) is dependent on the solubility and diffusion coefficient of the solvent in the CPC material. Predicting the rate of permeation for a given solvent/CPC pair requires accurate estimates of both of these variable. In Chapter 4, a model based on three dimensional (3-D) solubility parameters is presented for the quantitative prediction of solvent/CPC solubilities. Published immersion-test solubility values for 39 solvents in Viton^R are used to demonstrate the implementation of the model. The effects of polymer cross-linking and exposure temperature can be addressed with this model. An adjustable weighting factor is used to account for the varying types and strengths of solubility interactions between the solvents and the polymer. Assuming an arbitrarily low degree of cross-linking in the Viton, predicted solubilities were within a factor of 2 of experimental values for 34 of the 39 solvents (and were within a factor of 3 for all solvents). The exceptions were solvents such as aliphatic alcohols whose solubilites were quite low. Linear regression of experimental vs. predicted solubilities (excluding one outlier) yielded a slope of 0.941 and a regression coefficient (r^2) of 0.968. The theoretical basis for the model and the effect of temperature of solubility estimates are described.

In Chapter 5, solubility values estimated with this model are used with estimated diffusion coefficient values to predict the breakthough times and steady-state permeation rates of a subset of these solvents in Viton^R. Analyses are still being completed from this phase of the study. Thus, results are considered preliminary. Account was taken of the change in the value of the diffusion coefficient over the course of the permeation test by evaluating diffusion coefficient values at breakthrough and at steady-state. Linear regressions of the logarithms of these D values versus the logarithms of the solvent molecular weights were then used to establish a means for "predicting" D. The adequacy of using molecular weight as a predictor of D was found to be satisfactory for most, but not all, solvents. Predicted BTs were within a factor of five of experimental values for 14 of the 15 solvents for which detection limits were reported (most were within a factor of three). Predicted SSPRs were within a factor of five of experimental values for 11 of the 18 solvents. Errors are attributable mainly to the use of molecular weight as the predictor of D. Alternative methods of predicting D are being explored.

List of Significant Findings

1. Butyl rubber gloves generally provided the highest level of permeation resistance to the photoresists and related formulations containing ethylene or propylene glycol ether derivatives either in neat form or in mixtures with other solvents. An exception to this was found in the case of a negative photoresist which contained a large percentage of xylene for which butyl rubber was an ineffective barrier. With the exception of the negative photoresist, the butyl rubber gloves maintained their barrier effectiveness at elevated temperatures and under repeated-exposure conditions.

2. Nitrile rubber gloves also provided a high level of permeation resistance against the photoresist formulations investigated. However, increased temperature and/or repeated exposure of these gloves seriously compromised their barrier properties. For the formulations containing ethylene glycol ether derivatives, thermal decontamination was effective at restoring the permeation resistance of the nitrile gloves. For propylene glycol monomethyl ether acetate, however, thermal decontamination was unsuccessful.

3. Gloves composed of natural rubber or blends of natural rubber with other polymers were less effective permeation barriers to the neat solvents and photoresist formulations examined.

4. For most of the glove samples, permeation of the glycol ether derivatives in the formulations was faster than that predicted based on the permeation behavior of the pure glycol ethers. The magnitude of this effect varied with the type of glove and the mixture components and relative concentrations.

5. Use of thin surgical-type gloves composed of natural rubber or PVC beneath chemically protective gloves (e.g., nitrile) increased the net permeation resistance marginally. Use of surgical-type gloves alone provided no effective permeation resistance.

6. Butyl rubber gloves provided exceptionally good resistance to permeation of N-methylpyrrolidone (NMP) even at temperatures as high as 50C. Natural rubber gloves provided fairly good protection at room temperature, but their permeation resistance was seriously degraded as temperature was increased.

7. The decrease in permeation resistance was found to be due to increases in the rates of diffusion rather than to

increases in solubility. This result is in agreement with data reported by other researchers for other solvent-CPC pairs and is probably generally applicable to solvent-CPC permeation.

8. The breakthrough times and steady-state permeation rates of NMP through the natural rubber gloves investigated were accurately predicted using recently developed models of equilibrium solubility and diffusion coefficients under the assumption of Fickian diffusion.

9. A new method for using three-dimensional solubility parameters was developed that permits accurate prediction of equilibrium solvent-CPC solubilities. The method is based on equations derived from polymer solution theory that permit account to be taken of the degree of crosslinking in the CPC polymer as well as the temperature of exposure.

10. Solubility estimates calculated using the above method were combined with values of diffusion coefficients empirically estimated from the solvent molecular weights in a Fickian diffusion model to predict values of the breakthrough times (BT) and steady-state permeation rates (SSPR) of solvents through Viton CPC samples. Predicted BT and SSPRs were typically within a factor of five of experimental values. Improvements in methods for estimating diffusion coefficients are needed to increase the overall accuracy of the model in predicting permeation parameters.

List of Publications Resulting from the Project

1. Edward T. Zellers, Huiqiong Ke, David Smigiel, Robert Sulewski, Samuel J. Patrash, and Mingwei Han and Guo Zheng Zhang: "Glove Permeation by Semiconductor Processing Mixtures Containing Glycol-Ether Derivatives," Am. Ind. Hyg. Assoc. J. (in press).

2. Edward T. Zellers and Robert Sulewski: "Glove Permeation by Propylene Glycol Monomethyl Ether Acetate (PGMEA) - A Photoresist Solvent Used in Semiconductor Device Processing," J. Appl. Occup. and Environ. Hyg., (in review, submitted August, 1991).

3. Edward T. Zellers and Robert Sulewski: "Temperature Dependence of N-Methylpyrrolidone Permeation Through Butyl and Natural Rubber Gloves: Predicted vs. Experimental Results", J. Appl. Occup. and Environ. Hyg., (in preparation).

4. Edward T. Zellers: " Using Solubility Parameters to Predict Equilibrium Solvent Solubilites in Protective Clothing," Am. Ind. Hyg. Assoc. J. (in revision)

5. Edward T. Zellers: "Predicting Solvent Permeation Through Viton Gloves," Am. Ind. Hyg. Assoc. J. (in revision).

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Chapter 1

Glove Permeation by Semiconductor Processing Mixtures Containing Glycol-Ether Derivatives

Introduction

The production of semiconductor devices involves a series of chemical and physical processes performed on a single-crystalline wafer of silicon or some other semiconducting substrate. The fabrication of these miniaturized devices is performed in so-called "clean rooms" that employ filtered supply-air and high ventilation rates to minimize the levels of particulates which might settle on the wafer and interfere with the formation of the circuitry. While each type of device requires a different series of processing steps, virtually all devices are made using various iterations of six unit processes: oxidation, microlithographic patterning, etching, junction formation, layer deposition, and metallization. Detailed reviews of the hazards associated with each of these processes have been published elsewhere.[1-5]

Considerable interest has been raised recently about the risks of adverse reproductive health effects associated with working in the semiconductor industry. Results from one study suggested an increase in spontaneous abortions among production workers in a major U.S. semiconductor manufacturing plant.[6] However, the findings from that study were considered inconclusive due to the small size of the study population and the failure to identify any specific etiologic agents that might be responsible for the observed health effects. A number of other studies have since been initiated to examine in more detail the risks of reproductive and other health effects in the semiconductor industry.[7-8]

Relatively little is known about specific reproductive hazards in semiconductor manufacturing;[9] although certain chemicals have been linked with teratogenic effects in test animals, most notably the glycol ethers and their derivatives which are used as solvents in microlithographic resist formulations.[10,11] Recognition of the toxicity of the glycol ethers has led several resist manufacturers to develop formulations containing less toxic solvents,[12,13] but the use of glycol-ether based resists is still quite prevalent.

The limited industrial hygiene data available for this industry suggest that 8-hr time-weighted-average exposures to vapors of the most common processing solvents are typically less than 10% of recommended standards.[14] However, the potential for exposure via dermal absorption has not been examined in detail. For large-scale semiconductor manufacturing many of the processing steps are automated which reduces the likelihood of chronic dermal exposure, but routine maintenance of equipment and restocking chemical source vessels still give rise to the potential for periodic employee exposure. In smaller production facilities, as well as academic and industrial research laboratories, smaller quantities of materials are used but most operations are performed manually. Thus, the potential for contact with the process chemicals remains high.

Statistics compiled by the Occupational Health System of the Semiconductor Industry Association indicate that contact with chemicals accounted for over 20% of all OSHA-recordable injuries and illnesses in the industry from 1982-1986, and dermatoses accounted for 45% of all OSHA-recordable illnesses among semiconductor workers over the same period.[15] Similarly, data from the Bureau of Labor Statistics Annual Reports show that "skin disorders and diseases" accounted for 28% and 41% of all illnesses in the semiconductor industry for 1984 and 1985, respectively.[16]

While many of the reports of chemical contact and dermatoses undoubtedly involved acid splashes, the relatively high number of such incidents raises the question of whether dermal absorption may represent a significant exposure route for systemic toxicants. In the case of the glycol-ether derivatives, this exposure route may be particularly important because they are readily absorbed through the intact skin.[11]

The selection of gloves for protection against dermal exposure to glycol-ether derivatives used in semiconductor processing is complicated by the use of mixtures of solvents in many of the formulations. Several reports have described the permeation of gloves by solvent mixtures,[17-19] and it has been shown that the permeation of solvents in mixtures can be significantly accelerated relative to that of the individual component solvents.[19]

Modest increases in temperature can also lead to significant increases in glove permeability.[20,21] In addition, solvents can be retained in the glove after an initial exposure and slowly permeate to the inner surface during periods of non-use.[22,23] Predictive models of permeation based on the physicochemical properties of the solvents and glove materials are being developed,[24-25] but have yet to provide any generally applicable selection rules. Thus, the confident selection of a glove material requires empirical testing by the end-user for the particular mixture involved.

In this paper the permeation behavior of several common glove materials challenged with semiconductor processing mixtures containing glycol-ether derivatives is described. Comparisons are made between the permeation of the solvents in the mixtures and the individual solvents comprising the mixtures. The effects of temperature from 25 to 37°C are also determined for most of the glove/mixture pairs. Results of repeated exposure of the butyl and nitrile rubber gloves to the mixtures are presented, as well as the use of thermal decontamination to remove residual solvents in the nitrile rubber gloves. The effects of glove thickness and additional glove layers (natural rubber or PVC) on the permeation of the nitrile rubber gloves by the mixtures are also evaluated.

Glove-Use Practices

In conjunction with this study, a survey was conducted of a number of semiconductor processing facilities to assess current glove-use practices.[26] In some facilities a single glove type was used for all chemicals. More typically, two types of gloves were used - one type for acids and bases, and one type for organic solvents. In a few facilities up to three types of gloves were used with specific recommendations made for each type of liquid for which protection was desired. For acids and bases, the most common type of glove used was natural rubber. For organic solvents, various glove materials were used but nitrile rubber was by far the most common. Most of the users surveyed indicated that gloves were re-used for up to five days before being replaced.

The use of thin surgical-type gloves is mandatory in most clean rooms in order to prevent contamination of the wafers by the oils and salts on the hands of the workers. While these gloves are not designed to serve as liquid or gaseous chemical barriers, the survey revealed a few cases where these gloves are used alone when handling chemicals. In most cases, these thin gloves are worn beneath more impervious gloves for protection against chemical exposure.

The need to minimize particulate generation within semiconductor production facilities precludes the use of flock-lined gloves. A number of manufacturers now offer gloves that have been specially treated and packaged to minimize particulate generation. It was found that these types of gloves are used extensively in the industry. The Edmont Nytek and Puretek, Pioneer Trionic, and Baxter gloves included in this study are examples of such treated gloves.

In addition to considerations of current glove-use practices in the industry, the choice of glove materials for this study was also based on information found in glove selection guides [21,27-30] and material safety data sheets for the solvents investigated.

EXPERIMENTAL MATERIALS AND METHODS

Table I lists the brands, models, polymer components, and mean thicknesses of the gloves tested. Individual solvents were of reagent grade or higher purity and were used without further purification (Aldrich, Milwaukee, WI). Table II presents the compositions of the liquid formulations tested, which included a positive photoresist thinner (Microposit Thinner Type A, Shipley, Co., Newton, MA), a positive photoresist (Microposit Photoresist S1400-17, Shipley, Co., Newton, MA), and a negative photoresist (Negative Photoresist 747, KTI Chemicals, Inc., Sunnyvale, CA). 2-methoxyethyl acetate (2-MEA), the solvent component of an electron-beam resist, was used in pure form in lieu of using the resist material itself. Additional tests were performed on a mixture of the positive photoresist and acetone to simulate operations where acetone is used to remove photoresist residues from wafers and processing equipment.

Permeation testing was performed according to the ASTM F739-85 method.[31] A 5.08-cm (2-in) diameter test cell (Pesce Lab Sales, Inc., Kennett Square, PA) was used in an open-loop configuration with dry N_2 gas being passed through the collection side of the cell at 500 cm^3/min. All downstream components of the system were constructed of Teflon^R or stainless steel to avoid adsorptive losses. The test cell was immersed in a constant-temperature water bath controlled to +/-0.5°C. The cell and a flask containing the challenge liquid were placed in the water bath for several minutes prior to testing to allow all system components to come to thermal equilibrium. The liquid was then transferred to the test cell either by syringe or by cannula (under a positive pressure of air). The temperature of the N_2 gas stream was also regulated to +/- 1.5°C with a heating mantle prior to passing it through the test cell. The N_2 temperature was monitored with a thermocouple placed just upstream from the cell. For the resist formulations, all manipulations were performed under yellow lights to avoid light-induced changes in the photoactive components of these formulations. All test mixtures were stirred with a glass rod connected to a mechanical stirrer.

Test samples cut from the gauntlet region of each glove were clamped into the cell and tightened to a constant pressure of 20 in-lb with a torque wrench. Mean sample thicknesses were determined from measurements with a micrometer at five random locations on the sample. Intersample thickness variations were less than 0.00254 cm (1 mil) for a given glove type. For the Edmont Nytek glove, tests were performed on gloves from each of two lots which differed in mean thickness (see Table I).

The gas downstream from the test cell was sampled periodically with a 5-mL gas-tight syringe and analyzed with a gas chromatograph (Model 2860, Varian Associates, Palo Alto, CA) equipped with a packed column (2-ft stainless-steel, 1/8-inch o.d., packed with 1% SP-1000 on 60/80 mesh Carbopack B, Supelco, Inc., Bellefonte, PA) and a flame-ionization detector. Peak areas were measured with an electronic integrator (Model 3390A, Hewlett Packard, Palo Alto, CA). Instrument calibrations were performed daily using test atmospheres of the analytes diluted in air in 100-L Tedlar^R bags (SKC, Inc., Eighty-four, PA). Wall adsorption losses were examined and found to be negligible for all solvents.

Steady-state permeation rates (PR, $\mu g/cm^2/min$) were calculated by averaging five measurements obtained after the downstream solvent concentration showed no further increase with time. Breakthrough times (BT, min) were defined as the times required for the downstream vapor concentration to reach 10 mg/m^3, which corresponds to a permeation rate of 0.25 $\mu g/cm^2/min$ for this test system. This concentration corresponds to injected masses that were well above the limits of detection for all of the vapors tested. For exposures at 37°C, the appropriate temperature correction was applied to the air concentrations of the injected samples.

For repeated exposures, samples were exposed initially, carefully removed from the test cell and patted dry to remove visible liquid, and then allowed to air dry in an exhaust hood having a face velocity of 27-30 m/min (90-100 ft/min). Thermal decontamination tests were performed by suspending exposed gloves in a vented oven maintained at 70°C. All manipulations of unexposed glove samples were performed wearing surgical gloves. All chemicals and pre-exposed gloves were handled with chemical protective gloves made of butyl or nitrile rubber.

RESULTS AND DISCUSSION

Pure Solvents vs. Mixtures

Table III presents the breakthrough times and steady-state permeation rates measured at 25°C for the individual solvents. For neat 2-EEA, 2-ME, and 2-MEA butyl rubber provided the best protection with no breakthrough being observed after four hours of exposure. For n-butyl acetate, again, butyl rubber showed the longest breakthrough time and the lowest permeation rate. For xylene, nitrile rubber showed the highest permeation resistance. The results obtained here are in qualitative agreement with those published by the glove manufacturers[27-30] and other sources of permeation data for these solvents.[11,21] Note that for both n-butyl acetate and xylene shorter breakthrough times and higher permeation rates were observed for all glove samples relative to the glycol-ether derivatives. Based on previous studies of solvent mixtures,[17-19] it was suspected that the presence of these solvents in the mixtures might compromise the resistance of the gloves to the glycol-ether derivatives.

The breakthrough times and steady-state permeation rates of the solvents in each of the mixtures measured at 25°C are presented in Table IV. Comparisons of the values for the component solvents in the photoresist thinner with those for the individual solvents (Table III) show that the xylene and n-butyl acetate permeated much more slowly in the mixture, consistent (qualitatively) with their low concentrations. For the 2-EEA in the mixture, however, the breakthrough times for all of the glove materials except butyl rubber were less than or equal to those of the neat 2-EEA (see Figure 1a), even though this solvent comprised only 82% by weight (80% by volume) of the mixture. In addition, the permeation rates for 2-EEA in the mixture for these four glove materials were greater than or equal to those for the neat 2-EEA (see Figure 1b) (note: the difference in the 2-EEA permeation rates for the nitrile glove was negligible).

Also presented in Figures 1 a and b are the breakthrough times and permeation rates, respectively, of the 2-EEA in the positive photoresist. In this case, the breakthrough times for 2-EEA in the mixture were virtually the same as those for neat 2-EEA for all of the gloves, and the permeation rates were about the same or lower for the mixture than for the neat 2-EEA. The improvements in permeation resistance relative to the resist thinner can be attributed to a combination of lower solvent concentrations and the presence of the polymer resin and photoactive compound which comprise 17% of the mixture. The resin used in this formulation is a phenol-formaldehyde polymer and the photoactive compound is a salt of a substituted diazo naphthalene sulfonic acid. Given the large molecular sizes of these components and the ionic nature of the photoactive compound, neither would be expected to permeate the gloves to a significant extent.

A common practice in many research and production facilities is to use acetone to manually clean equipment contaminated with residual positive photoresist. To investigate the effects of small amounts of acetone on the permeation resistance of nitrile and butyl gloves, additional tests were performed at 25°C with a mixture of the positive photoresist and acetone (10% by volume). For the nitrile samples, decreases of approximately 30% in the breakthrough times and increases of 40% (2-EEA), 62% (n-butyl acetate), and 78% (xylene) in the permeation rates were observed relative to values for the positive photoresist alone. Acetone had an average breakthrough time of 81 ±1 min and an average permeation rate of 106 ±6 $\mu g/cm^2/min$ in the mixture. While the breakthrough times for all solvents were still greater than one hour, the decrease in protection due to this small amount of acetone is of some concern. Actual clean-up operations might involve much higher relative concentrations of acetone whichmight cause further reductions in permeation resistance to the photoresist solvents. No breakthrough was observed for the butyl rubber samples after four hours of exposure to this mixture.

For the negative photoresist, significant decreases in the breakthrough times of 2-ME were observed for the mixture relative to the neat solvent for all of the gloves, as shown in Figure 2a. This effect was most dramatic for the butyl rubber samples which showed no breakthrough after four hours of exposure to pure 2-ME, but had a breakthrough time of only 12 minutes for the 2-ME in the mixture (<6% by weight). In contrast to the behavior seen with the positive resist and the resist thinner, xylene apparently had a significant effect on the permeation resistance of the butyl glove to the negative resist. The nitrile rubber samples, which showed the greatest resistance to pure xylene, showed the least reduction in breakthrough time for the 2-ME in the negative resist. With the exception of nitrile rubber, the permeation rates for 2-ME in the mixture were greater than those for pure 2-ME for all of the gloves (see Figure 2b), although the permeation rates remained relatively low.

Comparison of the permeation of the solvent mixtures through the two nitrile rubber gloves (i.e., 0.043-cm samples vs. 0.036-cm samples) shows that the breakthrough times for the 0.036-cm samples were consistently lower, however, the thickness dependence of the breakthrough times varied with the type of solvent mixture. For the solvents in the photoresist thinner and the xylene in the negative photoresist, the ratios of breakthrough times were equal (within 9%) to the ratios of the squares of the glove thicknesses, whereas for the positive photoresist, the solvent breakthrough times varied directly with the thicknesses. For the 2-ME in the negative photoresist, the breakthrough times for the two gloves were virtually the same. For both solvents in the negative photoresist, considerably higher permeation rates were observed with the thinner nitrile rubber samples. In contrast, the steady-state permeation rates all other mixture solvents were nearly independent of glove thickness.

To put these results into perspective, it is useful to consider them briefly in the context of permeation theory. The permeation of organic solvents through polymeric glove materials is governed by the solubility and diffusion of the solvent in the glove.[21,32] In the ideal case, Fick's laws of diffusion are obeyed, the diffusion coefficient is constant, and the solubility of the solvent in the polymer is proportional to the solvent concentration in the challenge mixture. Under these conditions the steady-state permeation rate of a solvent in a mixture should be directly proportional to its concentration. The relationship between the breakthrough time and the solution concentration is more complex, but the breakthrough time should also decrease as the solvent concentration decreases. For a given solvent/glove pair, the steady-state permeation rate should vary inversely with the thickness of the glove sample. The theoretical variation in breakthrough time with thickness is approximately equal to the ratios of the squares of the thicknesses, as has been observed experimentally.[33]

The fact that the permeation rates of the glycol-ether derivatives were higher than expected and the breakthrough times lower than expected for most of the gloves challenged with the mixtures indicates that the other solvents (i.e., n-butyl acetate, xylene and acetone) were facilitating the diffusion of glycol-ethers through the gloves, most likely by swelling the glove polymers and increasing the effective diffusion coefficients and/or solubilities of the other solvents in the gloves. The exceptionally good resistance of the butyl rubber to the positive resist and resist thinner indicates that this effect was not significant where the other solvents were present in relatively small quantities. In contrast, the results for the butyl-rubber/negative-resist combination show that a high percentage of the rapidly permeating xylene had a pronounced effect on the permeation of 2-ME. The reason for the differences in the thickness dependence of the breakthrough times is not known but may be the result of varying degrees of glove swelling or to the presence of the polymeric resins in the resists. A more detailed examination of these results in light of empirical and theoretical models of permeation is currently underway.

Temperature Effects

Most of the processes involving potential contact with resist formulations are performed at room temperature. Thus, the relevant temperature range over which to examine the gloves is between room temperature (i.e., 25°C) and body temperature (i.e., 37°C). To determine whether significant changes in permeation would occur over this modest temperature range, permeation tests were repeated at 37°C.

Table V presents the ratios of the breakthrough times and permeation rates observed at 37 and 25°C (i.e., 37°C/25°C) for several of the glove/solvent pairs. With the exception of butyl rubber challenged with pure 2-MEA, a decrease in permeation resistance was observed for all of the solvents at the higher temperature. Focusing on the glycol-ether derivatives, the breakthrough times decreased by as much as 73% (Trionic/2-EEA) and permeation rates increased by as much as 300% (nitrile/2-ME) between 25 and 37°C.

The temperature effect was least significant for the butyl rubber. In the case of the photoresist thinner, breakthrough of the 2-EEA through the butyl rubber samples was observed after about four hours, but the steady-state permeation rate (4.2 µg/cm2/min) remained quite low. It is interesting to note that pure 2-EEA did not breakthrough the butyl rubber material at 37°C (data not shown). Thus, the other solvents apparently did affect the permeation of 2-EEA in the photoresist and photoresist thinner through butyl rubber, but the effect is of little practical significance.

Considered in terms of the absolute change in temperature (i.e., 310°K/298°K = 1.04, or a 4% increase) the effects on the permeation values for most of the gloves are quite large, and reflect the positive exponential (i.e., Arrhenius) temperature dependence of the permeation process. Vahdat et al. reported similar temperature effects for toluene and trichloroethane permeation through commercial glove samples.[34] Since the temperature of a glove while being worn is likely to be somewhere in the range of 25 to 37°C, the permeation rates and breakthrough times to be expected in practice (under similar exposure conditions) would be between the values reported here.

Double Glove Layers

As mentioned previously, workers in semiconductor clean rooms typically wear thin surgical-type gloves made of natural rubber or PVC beneath thicker chemically protective gloves. To determine whether these gloves provided any additional protection against dermal exposure, experiments were performed with the photoresist thinner using samples of such thin gloves placed behind samples of the nitrile rubber gloves.

Table VI shows the effects on the permeation of the photoresist thinner of combining nitrile samples with the Baxter PVC or natural rubber (NR) samples. From the ratios of the permeation parameters with and without the added layers it is seen that these gloves do provide a modest increase in permeation resistance, with the effect most significant for 2-EEA. The nitrile/PVC combination provides slightly greater protection than the nitrile/NR combination. Exposure of the PVC or NR samples alone at 37°C resulted in breakthrough almost immediately and, in the case of the PVC, disintegration of the sample. Clearly, these gloves should not be used alone when working with these chemicals.

Repeated Exposure and Thermal Decontamination

A series of experiments was then performed to determine the effects of repeated exposure of the nitrile and butyl rubber gloves to the solvent mixtures. Table VII presents the results for the 0.043-cm nitrile rubber gloves re-challenged with the photoresist thinner at 25°C. The mean breakthrough times and steady-state permeation rates for 'normal exposures' of previously unexposed gloves (i.e., continuous exposures performed until steady-state permeation was achieved) are included for reference (from Table IV). Re-exposure of nitrile samples following air drying overnight resulted in much lower breakthrough times for all solvents (Trial 2, Table VII). In fact, measurable levels of all solvents were observed in the initial background air samples taken before filling the test cell with solvent for the re-exposure. The largest reduction in breakthrough time occurred for the 2-EEA. The consistency of the steady-state permeation rates indicates, however, that the structural integrity of the glove was not measurably affected. For Trial 3, an initially exposed glove sample was allowed to air dry for five days before re-exposure. Here again, levels of n-butyl acetate and 2-EEA were detected in the initial background samples, and significant decreases in the breakthrough times for all of the solvents were still observed. The increase in permeation rate for 2-EEA suggests that some degradation of the glove may also have occurred, although the permeation rates for the other solvents did not change appreciably.

For Trial 4 in Table VII, a fresh nitrile rubber sample was exposed for about one-half of the time required for breakthrough of all of the solvents (i.e., 50 min) and allowed to air dry overnight. Again, measurable levels of the solvents were found in the background air samples the next day upon replacing the sample in the test cell, indicating that the solvents continued to diffuse through the glove after exposure had ceased.

Several reports have shown that protective clothing containing residual amounts of organic solvents can be decontaminated by moderate heating.[22,23] Based on the results from one of these studies,[23] a temperature of 70°C was selected for decontamination treatment. Pretreatment of a nitrile sample at 70°C overnight showed no indications of physical degradation. Exposure of this sample to the photoresist thinner resulted in slightly longer breakthrough times and lower permeation rates than observed for untreated samples (see Trial 5, Table VII), but the changes were minor. Exposure of a fresh nitrile rubber sample to the photoresist thinner for 50 min followed by treatment at 70°C overnight and re-testing (Trial 6, Table VII) gave breakthrough times for all of the solvents that were within 5% of the values observed for the previously unexposed samples.

Results of similar tests performed on the 0.036-cm nitrile rubber samples are shown in Table VIII. As with the thicker nitrile gloves, the steady-state permeation rates were unaffected by repeated exposure, but retention of the solvents was evident from the shorter breakthrough times. Re-exposure following an initial normal exposure again resulted in measurable levels of the solvents in the background samples the next day. For the longer drying period (Trial 3, Table VIII) or the shorter exposure period (Trial 4, Table VIII) reductions in the breakthrough times were still observed, but residual solvent levels were not detected in the initial background samples.

In contrast to the thicker nitrile rubber gloves, thermal treatment of the thinner samples following a normal exposure or an exposure for one-half of the nominal breakthrough times resulted in only partial recovery the permeation resistance (Trials 6 and 7, Table VIII). Subsequent breakthrough time values ranged from 86-90% of the initial values. The reason for the lack of a full recovery for the thinner samples is not clear. However, from a practical standpoint, the thermal treatment was effective enough to afford good protection upon re-use of the gloves.

Similar series' of experiments performed on the butyl rubber material showed no evidence of persistent permeation and no degradation in the level of protection afforded upon re-exposure to the photoresist thinner.

Table IX presents the results of repeated exposure of the 0.036-cm nitrile rubber gloves to the positive photoresist. Here again there is evidence for retention of the solvents in the glove samples. The decreases in breakthrough times upon re-exposure following a normal exposure and air drying overnight were generally greater than those observed for the photoresist thinner under similar conditions. Traces of all of the solvents were observed in the background samples prior to re-exposure. For an initial exposure of 45 min followed by air drying overnight, only 2-EEA was observed in the background samples the next day. Permeation rates were slightly higher for the re-exposed samples, as well, although the increases are not considered significant.

Thermal treatment improved the permeation resistance but recovery of the initial values was not achieved. Breakthrough times after thermal treatment ranged from 62-80% of the initial values and permeation rates remained slightly elevated. One explanation for the lack of recovery in the permeation resistance is that the resin in the photoresist inhibits offgassing of the residual solvents by forming a thin film at the glove surface (note: the glove samples were noticeably stained after exposure to the resist). Upon re-exposure this film could then redissolve in the resist solvents to allow normal permeation to proceed. In any case, even with only partial recovery of the permeation resistance, re-use of the gloves following thermal decontamination would afford reasonably good protection.

Results of repeated exposure of the nitrile rubber samples (0.036-cm and 0.043-cm) to the negative photoresist are presented in Table X. For both glove thicknesses, exposure for about one-half of the breakthrough times followed by air drying overnight and re-exposure resulted in reductions in the breakthrough times and, for the 0.043-cm sample, rather large increases in the steady-state permeation rates of 2-ME and xylene. Re-exposure of the 0.036-cm samples following an initial normal exposure also resulted in increased permeation rates. In this case, levels of xylene in the background samples taken before re-exposure were already above 10 mg/m^3. These data indicate significant retention of the solvents as well as irreversible changes in the structure of the glove upon exposure to the negative photoresist. Attempts to restore the permeation resistance of the 0.036-cm samples by thermal treatment were unsuccessful (see Trials 6 and 7, Table X).

For pure 2-MEA, the results of repeated exposure of the nitrile glove were similar to those for the photoresist thinner. Initial exposure for about about one-half of the breakthrough time followed by air drying overnight and re-exposure resulted in measurable quantities of 2-MEA in the background samples before the next exposure (Table XI). While there was a large decrease in the breakthrough time, the permeation rate was not affected. Treatment of the exposed glove overnight at 70°C restored the original permeation resistance to the 2-MEA. Butyl rubber samples showed no evidence of persistent permeation for the pure 2-MEA after repeated exposures for four hours.

SUMMARY AND CONCLUSIONS

The results presented here should serve as a basis for improving glove use practices in semiconductor processing facilities where formulations containing glycol-ether derivatives are used. Coupled with information on prevalent work practices, these results should also aid in ongoing efforts to assess chemical exposures (past or present) in the semiconductor industry and, in turn, to establish meaningful risk estimates for adverse health effects.

Of the gloves tested in this study, the North Model B-161 butyl rubber glove provided the best protection against the pure glycol-ether derivatives, the photoresist thinner, and the positive photoresist. Breakthrough times for these solvents and formulations were all greater than four hours, and there was no evidence of persistent permeation or significant temperature effects from 25-37°C. The resistance of the butyl rubber gloves to the negative photoresist was much lower, with breakthrough times of 12 min being observed for the component solvents, 2-ME and xylene.

While butyl rubber gloves are generally more expensive than the other types of gloves investigated, the ability to re-use them safely tends to offset the initial cost. It is unfortunate that these gloves are not suitable for clean-room environments: according to the manufacturer, adhesion problems necessitate the use of powder during glove packaging. Still, these gloves would be useful for emergency spill response, or for handling microlithographic solvent formulations in service areas where higher particulate levels could be tolerated.

The Edmont Nytek nitrile rubber gloves provided moderately good resistance to the pure glycol-ether derivatives and the processing mixtures for continuous exposures. In the case of the negative photoresist, the Nytek gloves provided better protection than the butyl rubber gloves. For the photoresist thinner tested, the use of thin natural rubber or PVC glove layers beneath the nitrile gloves further improved their permeation resistance. The Edmont Puretek (natural rubber), Pioneer Trionic (natural/nitrile/neoprene rubber blend), and Playtex Model 827 (natural/neoprene rubber blend) gloves showed significantly lower levels of protection than the nitrile and butyl rubber gloves against all of the solvent mixtures.

The permeation resistance of the Nytek gloves, however, decreased markedly from 25-37°C. The presence of small amounts of acetone also reduced the permeation resistance of these gloves to the solvents in the positive photoresist. In addition, solvents persisted in the gloves for up to several days following exposure. For all of the formulations tested, breakthrough times were significantly shorter for previously exposed gloves allowed to air dry overnight, even after relatively short initial exposures. For the negative photoresist, repeated exposure also resulted in increased steady-state permeation rates. These results are of particular concern in light of the fact that gloves are typically re-used at many semiconductor facilities.

Heating exposed nitrile gloves at 70°C overnight restored or nearly restored the permeation resistance of the Nytek gloves against all formulations except the negative photoresist. This procedure could be used to recycle previously exposed gloves to prolong their service life. Vented ovens, such as those used for pre-baking coated wafers might be adapted for this purpose in clean rooms. If thermal decontamination is not feasible, then nitrile gloves should be discarded where exposure to the glove has occurred or is suspected.

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TABLE I
Brand, Model, Polymer Component(s), and Mean Thickness of Each Glove Tested

Brand/Model	Composition	Thickness (cm)
Edmont Nytek (49-155)	nitrile	0.036, 0.043[A]
Edmont Puretek (30-139)	natural rubber	0.051
Pioneer Trionic	natural rubber/ neoprene/nitrile blend	0.046
Playtex (827)	natural rubber/ neoprene blend	0.038
North (B-161)	butyl rubber	0.038
Baxter (G7-224)	natural rubber	0.018
Baxter (G7-238)	PVC	0.018

[A] Each mean thickness represents a different lot of nitrile gloves.

TABLE II
Compositions of Liquid Formulations[A]

Formulation	Component Solvent	Weight Fraction(%)
Positive Photoresist Thinner	2-ethoxyethyl acetate (2-EEA)	82
	xylene	9
	n-butyl acetate	9
Positive Photoresist	2-ethoxyethyl acetate (2-EEA)	68
	xylene	7.5
	n-butyl acetate	7.5
	resins/photoactive compounds	17
Negative Photoresist	2-methoxy ethanol (2-ME)	<6
	xylene	80-92
	cyclized poly(isoprene)	5-15

[A] Based on material safety data sheets provided by the manufacturers.

TABLE III
Breakthrough Times (BT) and Steady-State Permeation Rates (PR) of Individual Solvents at 25°C[A]

Solvent	Glove	n	BT (min)	PR (μg/cm^2/min)
xylene	Playtex	2	3(0)	1031(96)
	Nat Rub	3	4(0)	886(99)
	Trionic	3	2(1)	837(156)
	Nitrile[B]	**3**	**62(6)**	**196(24)**
	Butyl	2	9(0)	760(42)
n-butyl acetate	Playtex	2	7(1)	679(3)
	Nat Rub	3	7(1)	844(78)
	Trionic	3	5(0)	789(20)
	Nitrile[B]	3	69(5)	239(17)
	Butyl	**2**	**82(0)**	**62(1)**
2-EEA	Playtex	3	14(1)	128(20)
	Nat Rub	3	14(2)	85(10)
	Trionic	3	13(3)	88(18)
	Nitrile[B]	3	112(5)	118(24)
	Butyl	**2**	**>240**	**ND[C]**
2-ME	Playtex	2	48(0)	12(1)
	Nat Rub	2	43(1)	4(1)
	Trionic	2	27(2)	6(1)
	Nitrile[B]	2	126(8)	88(7)
	Butyl	**2**	**>240**	**ND**
2-MEA	Nitrile[D]	2	42(1)	250(2)
	Butyl	**2**	**>240**	**ND**

[A] Numbers in parentheses are standard deviations.
[B] Thickness = 0.043 cm. [C] ND = none detected. [D] Thickness = 0.036 cm.

TABLE IV
Breakthrough Times (BT) and Steady-State Permeation Rates (PR) of the Solvents in the Mixtures at 25°C[A]

Solvent(wt%)	Glove	n	BT (min)	PR(µg/cm^2/min)
Photoresist Thinner				
xylene (9%)	Playtex	2	15(0)	37(1)
	Nat Rub	3	13(1)	37(2)
	Trionic	2	9(0)	44(1)
	Nitrile[B]	3	106(5)	22(1)
	Nitrile[C]	5	79(3)	23(1)
	Butyl	**1**	**>300**	**ND**[D]
n-butyl acetate (9%)	Playtex	2	14(0)	46(1)
	Nat Rub	3	12(1)	42(2)
	Trionic	2	8(0)	51(0)
	Nitrile[B]	3	103(5)	30(1)
	Nitrile[C]	5	74(3)	34(2)
	Butyl	**1**	**>300**	**ND**
2-EEA (82%)	Playtex	2	14(1)	135(0)
	Nat Rub	3	11(2)	128(10)
	Trionic	2	8(0)	154(1)
	Nitrile[B]	3	96(4)	116(6)
	Nitrile[C]	5	64(5)	118(8)
	Butyl	**1**	**>300**	**ND**
Positive Photoresist				
xylene (7.5%)	Playtex	2	16(3)	32(5)
	Nat Rub	2	17(0)	25(4)
	Trionic	2	15(1)	30(1)
	Nitrile[B]	2	129(1)	9(1)
	Nitrile[C]	3	107(7)	10(2)
	Butyl	**1**	**>240**	**ND**
n-butyl acetate (7.5%)	Playtex	2	13(0)	38(8)
	Nat Rub	2	16(0)	29(5)
	Trionic	2	14(1)	43(18)
	Nitrile[B]	2	120(3)	16(1)
	Nitrile[C]	3	98(5)	16(2)
	Butyl	**1**	**>240**	**ND**
2-EEA (68%)	Playtex	2	12(0)	101(21)
	Nat Rub	2	14(0)	78(12)
	Trionic	2	14(1)	90(7)
	Nitrile[B]	2	114(4)	70(2)
	Nitrile[C]	3	89(3)	68(6)
	Butyl	**1**	**>240**	**ND**

TABLE IV (cont.)

Solvent(%)	Glove	n	BT (min)	PR($\mu g/cm^2/min$)
Negative Photoresist				
xylene (80-92%)	Playtex	2	4(1)	569(40)
	Nat Rub	2	6(0)	669(57)
	Trionic	2	4(0)	604(33)
	Nitrile[B]	**2**	**66(7)**	**60(4)**
	Nitrile[C]	3	49(2)	82(8)
	Butyl	2	12(0)	554(35)
2-ME (<6%)	Playtex	2	5(1)	38(0)
	Nat Rub	2	6(0)	41(9)
	Trionic	2	4(0)	39(1)
	Nitrile[B]	**2**	**77(9)**	**6(0)**
	Nitrile[C]	3	72(4)	12(2)
	Butyl	2	12(0)	26(5)

[A] Numbers in parentheses are standard deviations.
[B] Thickness = 0.043 cm. [C] Thickness = 0.036 cm. [D] ND = none detected.

TABLE V
Ratios of Breakthrough Times (BT) and Steady-State Permeation Rates (PR) at 37°C and 25°C for the Mixtures and Neat 2-MEA

Solvent	Glove	n[A]	BT(37°C)/BT(25°C)	PR(37°C)/PR(25°C)
Photoresist Thinner				
xylene	Nat Rub	3	0.55	1.76
	Trionic	3	0.30	1.59
	Nitrile[B]	3	0.51	1.64
	Butyl[C]	2	278/>240	1.2/ND[D]
n-butyl acetate	Nat Rub	3	0.50	1.69
	Trionic	3	0.30	1.47
	Nitrile	3	0.50	1.70
	Butyl	2	266/>240	1.2/ND
2-EEA	Nat Rub	3	0.31	2.16
	Trionic	3	0.27	1.81
	Nitrile	3	0.51	2.16
	Butyl	2	235/>240	4.2/ND
Positive Photoresist				
xylene	Nitrile	2	0.58	1.89
	Butyl	2	296/>240	0.5/ND
n-butyl acetate	Nitrile	2	0.59	1.75
	Butyl	2	284/>240	0.6/ND
2-EEA	Nitrile	2	0.58	1.85
	Butyl	2	246/>240	1.6/ND
Negative Photoresist				
xylene	Nitrile	2	0.64	5.57
	Butyl	2	0.68	1.53
2-ME	Nitrile	2	0.66	4.00
	Butyl	2	0.75	1.44
Pure 2-MEA				
2-MEA	Nitrile	2	0.64	1.84
	Butyl	2	>240/>240	ND/ND

[A] n is the number trials performed at 37°C. [B] Thickness = 0.043 cm for all nitrile samples. [C] For the butyl rubber samples actual values of breakthrough time (min) and steady-state permeation rate (μg/cm^2/min) are presented for those tests where the ratios could not be determined. [D] ND = none detected.

TABLE VI
Breakthrough Times (BT, min) and Steady-State Permeation Rates (PR, μg/cm^2/min) of the Photoresist Thinner Through Nitrile Rubber With and Without Additional Layers of PVC or Natural Rubber (NR) Glove Samples at 37°C

		xylene		n-butyl acetate		2-EEA	
Trial/Sample	n	BT	PR	BT	PR	BT	PR
1 nitrile	3	54(2)	36(5)	52(1)	51(2)	49(2)	251(5)
2 NR	2	<2	105(1)	<2	140(1)	<2	321(3)
3 nitrile/NR (double layer)	2	65(3)	32(2)	61(1)	40(1)	60(1)	179(9)
Ratio 3/1		**1.20**	**0.92**	**1.17**	**0.80**	**1.22**	**0.71**
4 PVC[A]	1	----	----	----	----	----	----
5 nitrile/PVC (double layer)	2	75(3)	31(0)	72(3)	41(0)	69(2)	183(6)
Ratio 5/1		**1.39**	**0.86**	**1.38**	**0.80**	**1.41**	**0.73**

[A] This sample disintegrated within a few minutes of exposure.

TABLE VII
Repeated Exposure and Thermal Decontamination of 0.043-cm Nitrile Rubber Samples Challenged with Photoresist Thinner[A]

		xylene		n-butyl acetate		2-EEA	
Trial/Conditions	n	BT	PR	BT	PR	BT	PR
1 normal exposure	3	106(5)	22(1)	103(5)	30(1)	96(4)	116(6)
2 normal exposure, air-dry 20 hr, re-exposure	2	33(9)[B]	19(3)	50(12)[B]	27(1)	4(0)[B]	110(7)
Ratio 2/1		**0.31**	**0.86**	**0.49**	**0.90**	**0.04**	**0.95**
3 normal exposure, air-dry 5 days, re-exposure	1	82	24	79[B]	32	60[B]	140
Ratio 3/1		**0.74**	**1.14**	**0.73**	**1.07**	**0.59**	**1.24**
4 50-min exposure, air-dry 20 hr, re-exposure	2	60(7)[B]	23(1)	46(16)[B]	32(1)	8(3)[B]	115(9)
Ratio 4/1		**0.57**	**1.04**	**0.45**	**1.07**	**0.08**	**0.99**
5 70°C 20 hr, normal exposure	1	113	17	108	26	101	98
Ratio 5/1		**1.07**	**0.77**	**1.05**	**0.87**	**1.05**	**0.84**
6 50-min exposure, 70°C for 20hr, re-exposure	2	103(6)	18(1)	98(4)	29(0)	91(1)	109(1)
Ratio 6/1		**0.97**	**0.82**	**0.95**	**0.97**	**0.95**	**0.94**

[A] BT = breakthrough time in min, PR = steady-state permeation rate in µg/cm^2/min. [B] Low vapor concentrations (i.e., <10 mg/m^3) observed in background samples prior to re-exposure.

TABLE VIII
Repeated Exposure and Thermal Decontamination of 0.036-cm Nitrile Glove Samples Challenged with Photoresist Thinner[A]

Trial/Conditions	n	xylene BT	xylene PR	n-butyl acetate BT	n-butyl acetate PR	2-EEA BT	2-EEA PR
1 normal exposure	5	79(3)	23(1)	74(3)	34(2)	64(5)	118(8)
2 normal exposure, air dry 20 hr, re-exposure	1	35[B]	27	34[B]	32	4[B]	127
Ratio 2/1		**0.44**	**1.17**	**0.46**	**0.94**	**0.06**	**1.08**
3 normal exposure, air dry 5 days, re-exposure	1	56	20	53	30	46	121
Ratio 3/1		**0.71**	**0.87**	**0.72**	**0.88**	**0.72**	**1.02**
4 35-min exposure, air dry 20 hr, re-exposure	1	55	23	46	33	12	121
Ratio 4/1		**0.70**	**1.00**	**0.62**	**0.97**	**0.19**	**1.02**
5 70°C 20 hr, normal exposure	1	80	24	74	35	65	110
Ratio 5/1		**1.01**	**1.04**	**1.00**	**1.03**	**1.02**	**0.93**
6 35-min exposure, 70°C 20 hr, re-exposure	1	69	24	64	35	56	126
Ratio 6/1		**0.87**	**1.04**	**0.86**	**1.03**	**0.88**	**1.07**
7 normal exposure, 70°C 20 hr, re-exposure	1	68	25	65	36	60	129
Ratio 7/1		**0.86**	**1.09**	**0.88**	**1.06**	**0.94**	**1.09**

[A] BT = breakthrough time in min, PR = steady-state permeation rate in $\mu g/cm^2/min$. [B] Low vapor concentrations (i.e., <10 mg/m^3) observed in background samples prior to re-exposure.

TABLE IX
Repeated Exposure and Thermal Decontamination of 0.036-cm
Nitrile Glove Samples Challenged with Positive Photoresist

		xylene		n-butyl acetate		2-EEA	
Trial/Conditions	n	BT	PR	BT	PR	BT	PR
1 normal exposure	3	107(7)	10(2)	98(5)	16(2)	89(3)	68(6)
2 normal exposure, air dry 20 hr, re-exposure	1	21[B]	11	18[B]	18	4[B]	71
Ratio 2/1		**0.20**	**1.10**	**0.18**	**1.12**	**0.04**	**1.04**
3 45-min exposure, air dry 20 hr, re-exposure	1	61	16	58	20	43[B]	76
Ratio 3/1		**0.57**	**1.60**	**0.59**	**1.25**	**0.48**	**1.12**
4 normal exposure, 70°C 20 hr, re-exposure	1	67	14	64	19	55	72
Ratio 4/1		**0.63**	**1.40**	**0.65**	**1.19**	**0.62**	**1.06**
5 45-min exposure, 70°C 20 hr, re-exposure	1	80	13	74	19	71	85
Ratio 5/1		**0.75**	**1.30**	**0.76**	**1.19**	**0.80**	**1.25**

[A] BT = breakthrough time in min, PR = steady-state permeation rate in $\mu g/cm^2/min$. [B] Low vapor concentrations (i.e., <10 mg/m^3) observed in background samples prior to re-exposure.

TABLE X
Repeated Exposure and Thermal Decontamination of Nitrile Rubber Samples Challenged with Negative Photoresist[A]

		2-ME		xylene	
Trial/Conditions	n	BT	PR	BT	PR
1 normal exposure (0.043-cm sample)	2	77(9)	6(0)	66(7)	60(4)
2 40-min exposure, air-dry 20 hr, re-exposure (0.043-cm sample)	1	68	10	50[B]	109
Ratio 2/1		**0.88**	**1.67**	**0.76**	**1.82**
3 normal exposure (0.036-cm sample)	3	72(4)	12(2)	49(2)	82(8)
4 30-min exposure, air dry 20 hr, re-exposure (0.036-cm sample)	1	43	10	20[B]	76
Ratio 4/3		**0.60**	**0.83**	**0.41**	**0.93**
5 normal exposure, air dry 20 hr, re-exposure (0.036-cm sample)	2	24(6)	22(4)	---[C]	208(39)
Ratio 5/3		**0.33**	**1.83**		**2.54**
6 30-min exposure, 70°C 20 hr and re-exposure (0.036-cm sample)	2	44(8)	26(13)	35(5)	182(64)
Ratio 6/3		**0.61**	**2.17**	**0.71**	**2.22**
7 normal exposure, 70°C 20 hr, re-exposure (0.036-cm sample)	2	36(6)	26(2)	32(0)[B]	220(22)
Ratio 7/3		**0.50**	**2.17**	**0.65**	**2.68**

[A] BT = breakthrough time in min, PR = steady-state permeation rate in μg/cm^2/min. [B] Low vapor concentrations (i.e., <10 mg/m^3) observed in background samples prior to re-exposure. [C] Background vapor concentration was >10 mg/m^3 prior to re-exposure.

TABLE XI
Repeated Exposure and Thermal Decontamination of 0.036-cm Nitrile Rubber Samples Challenged with Neat 2-MEA[A]

Trial/Conditions	n	2-MEA BT	 PR
1 normal exposure	2	42(1)	250(2)
2 25-min exposure, air-dry 20 hr, re-exposure	1	4[B]	256
Ratio 2/1		**0.10**	**1.02**
3 25-min exposure, 70°C 20 hr, re-exposure	1	40	252
Ratio 3/1		**0.95**	**1.01**

[A] BT = breakthrough time in min, PR = steady-state permeation rate in µg/cm^2/min. [B] Low vapor concentrations (i.e., <10 mg/m^3) observed in background samples prior to re-exposure.

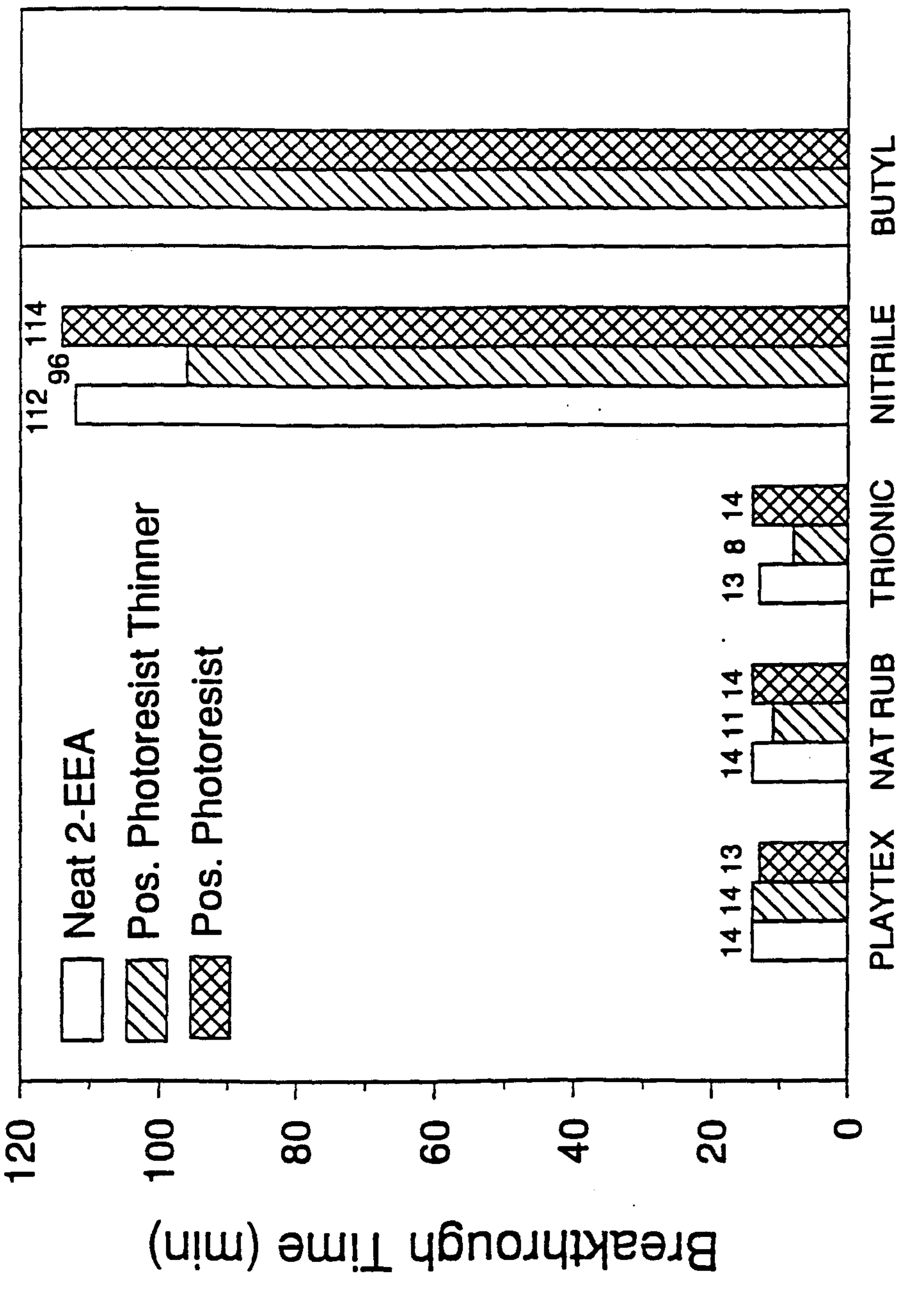
Breakthrough Time (min)
120
100
80
60
40
20
0
Neat 2-EEA
Pos. Photoresist Thinner
Pos. Photoresist
14 14 13
14 11 14
13 8 14
112
96
114
PLAYTEX
NAT RUB
TRIONIC
NITRILE
BUTYL

Figure 1a

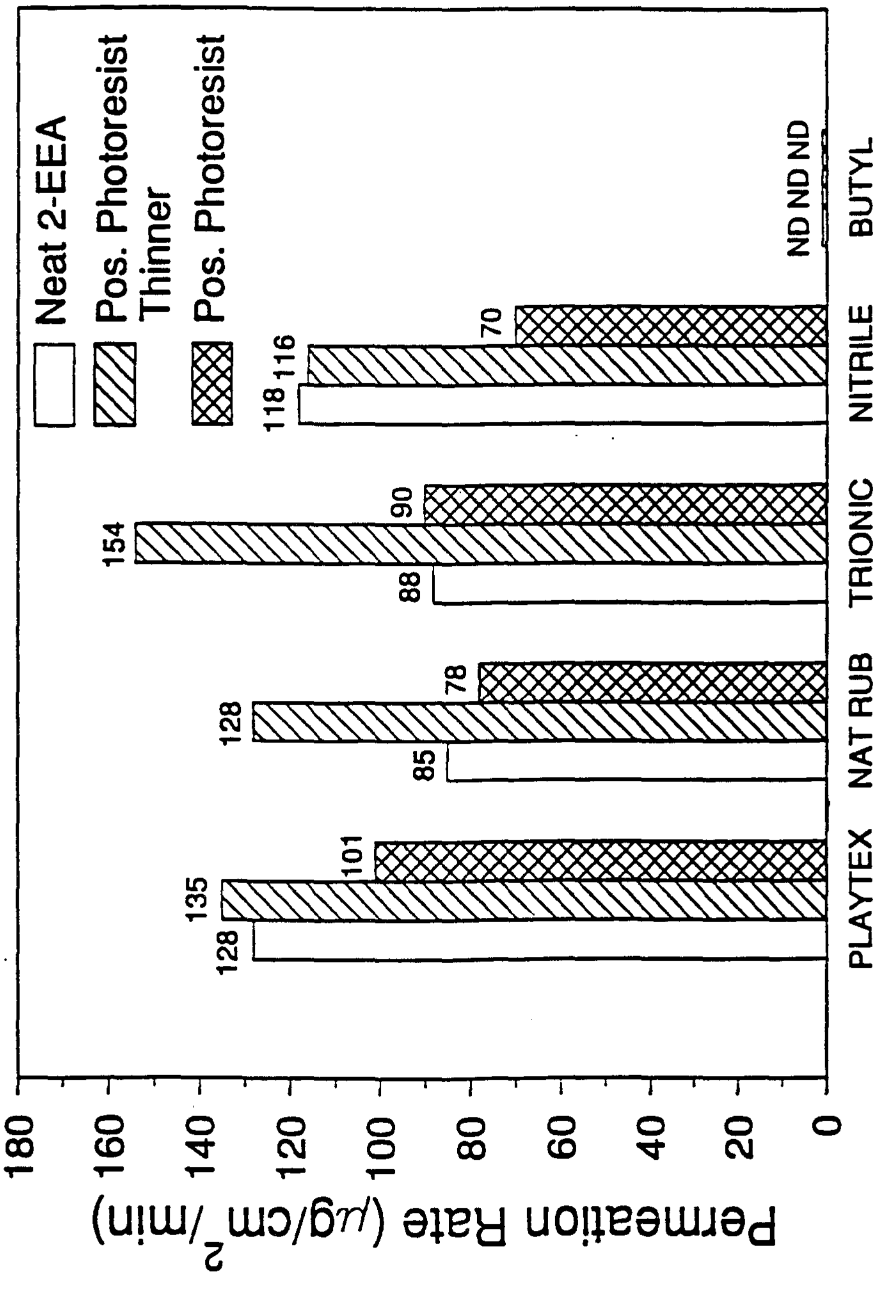
Neat 2-EEA
Pos. Photoresist Thinner
Pos. Photoresist
Permeation Rate (µg/cm^2/min)
180
160
140
120
100
80
60
40
20
0
PLAYTEX
NAT RUB
TRIONIC
NITRILE
BUTYL
128
135
101
85
128
78
88
154
90
118
116
70
ND ND ND

Figure 1b

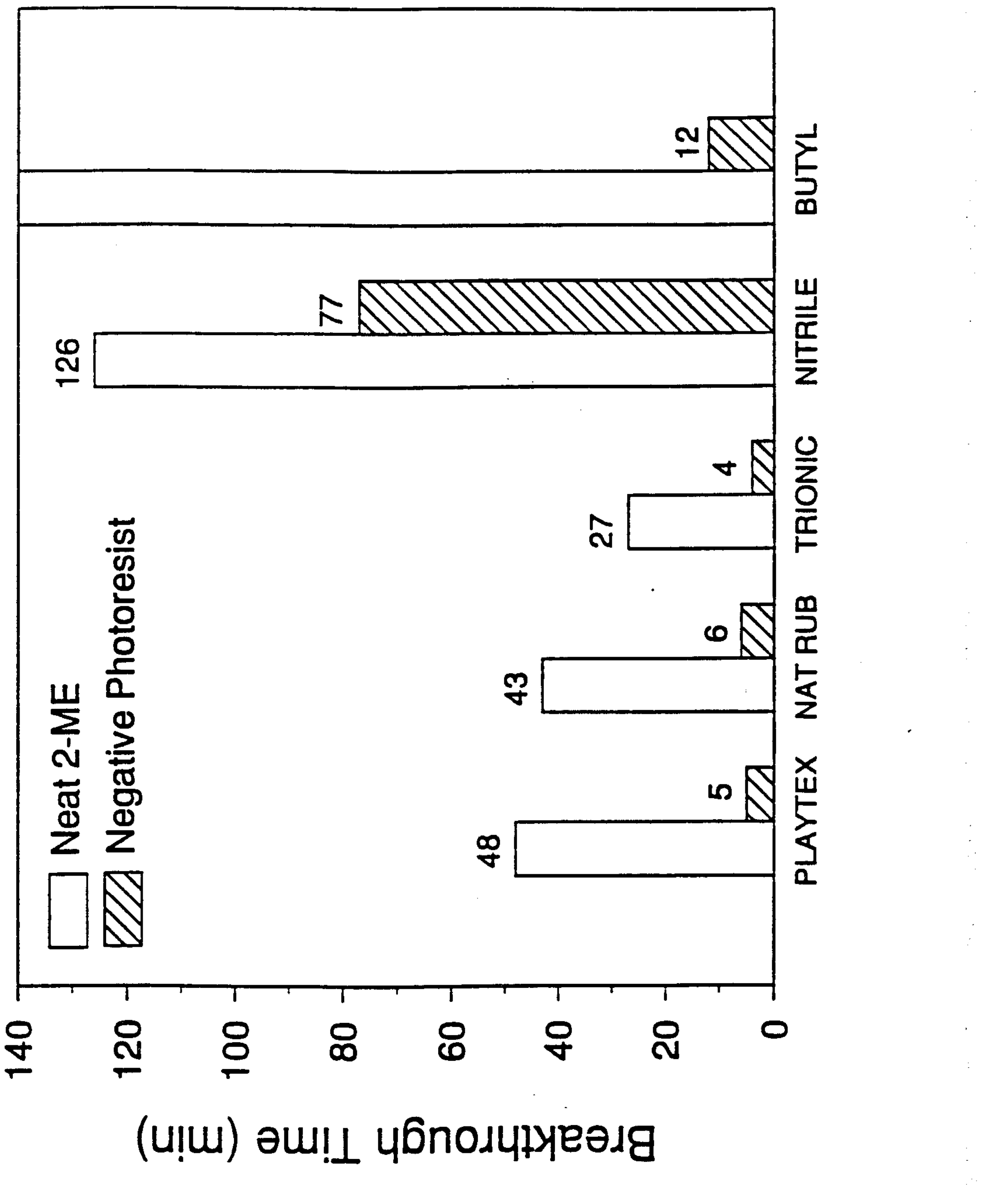
Breakthrough Time (min)
140
120
100
80
60
40
20
0
Neat 2-ME
Negative Photoresist
48
5
43
6
27
4
126
77
12
PLAYTEX
NAT RUB
TRIONIC
NITRILE
BUTYL

Figure 2a

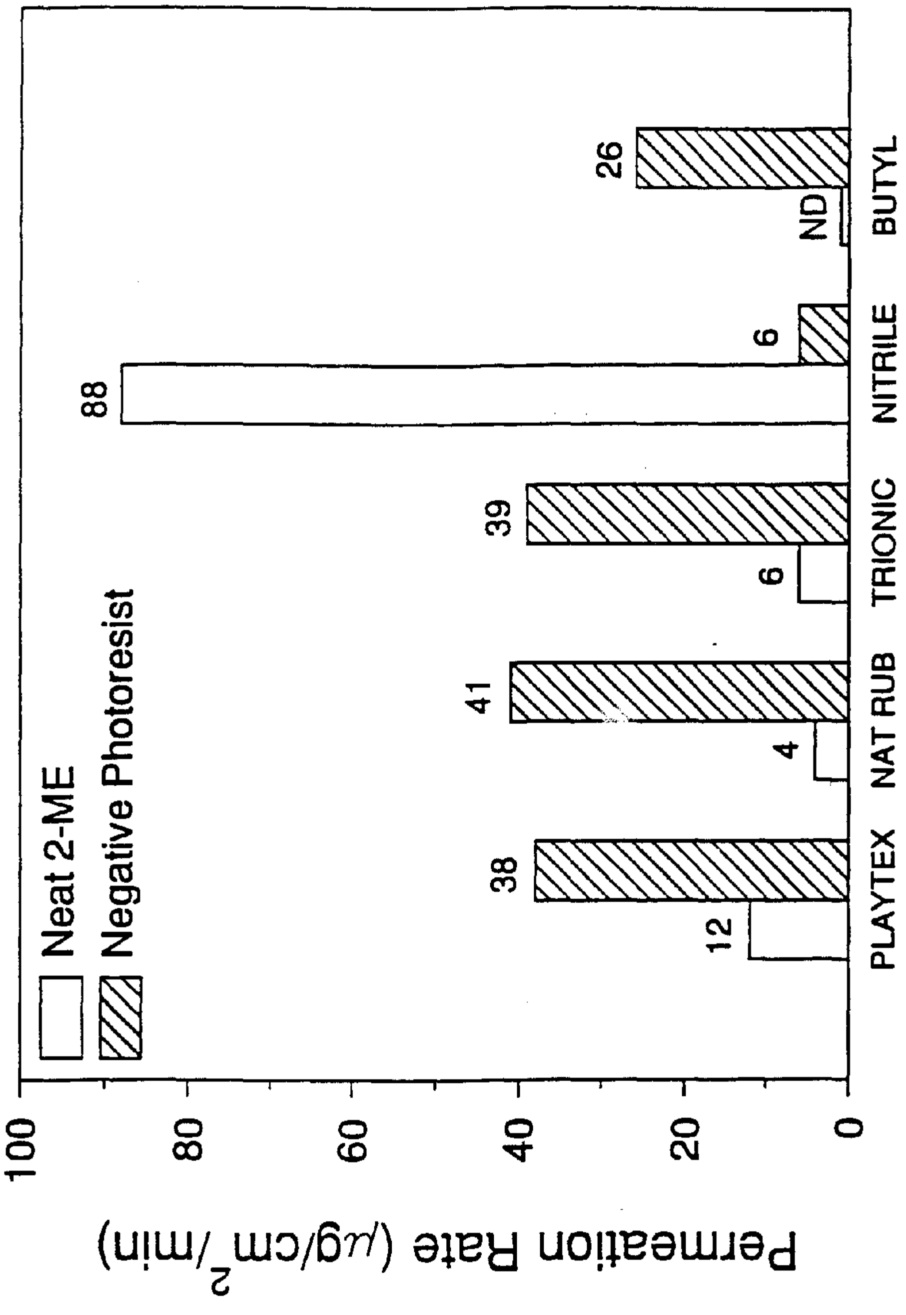
Permeation Rate (μg/cm²/min)
0
20
40
60
80
100
▢ Neat 2-ME
▨ Negative Photoresist
PLAYTEX
12
38
NAT RUB
4
41
TRIONIC
6
39
NITRILE
88
6
BUTYL
ND
26

Figure 2b

Chapter 2

Glove Permeation by Propylene Glycol Monomethyl Ether Acetate (PGMEA) - A Photoresist Solvent Used in Semiconductor Device Processing

Introduction

The production of semiconductor devices involves a series of processing steps performed on a wafer of silicon or some other semiconducting material.(1) One of the key steps is the microlithographic patterning of circuitry on the surface of the wafer. For most commercial devices this entails solvent-casting a thin film of a light-sensitive photoresist onto the wafer followed by UV exposure through a mask that has transparent and opaque regions which define the circuit pattern. A developer solution is used to remove the exposed (or unexposed) photoresist leaving a positive (or negative) image of the pattern. Additional processing (e.g., etching, dopant deposition/diffusion, and metallization) is then performed on the exposed surface to create the desired circuit elements. In most cases, these steps must be repeated many times using a series of different mask patterns to produce the final product.

Ethylene glycol ethers and their ester derivatives, often referred to by their Union-Carbide tradenames Cellosolves^R, historically have been the most common solvents used in positive photoresist formulations. Evidence of adverse reproductive effects in male and female animals exposed to these solvents(2,3) has prompted photoresist manufacturers to replace them with less toxic solvents.(4,5) Among the solvents that have emerged as useful replacements are derivatives of the propylene glycol ethers, such as PGMEA.

Commercial sources of PGMEA consist primarily of the so-called alpha isomer, 1-methoxy-2-propyl acetate. Limited animal toxicity testing of the analogous compound, 1-methoxy-2-propanol, indicates no significant adverse reproductive health effects.(4) The difference in toxicity between the ethylene-glycol derivatives and the propylene-glycol derivatives is attributed to differences in their metabolic pathways.(2,4) The former compounds are metabolized to the corresponding alkoxyacetic acids, which are thought to be the proximate teratogens. For the alpha-isomers of the latter compounds this metabolic route is blocked and the initial product of metabolism, propylene glycol, enters the Krebs cycle and is converted to carbon dioxide.

One feature that PGMEA shares with its ethylene-glycol predecessors is the ability to readily penetrate the intact skin. Thus, while PGMEA apparently exhibits a low level of toxicity, good industrial hygiene practice dictates the use of proper procedures to avoid dermal contact.

With respect to the potential for contact with processing solvents, available statistics indicate that dermatoses and other skin disorders attributable to chemical exposures have historically accounted for a significant fraction of all injuries and illnesses in the semiconductor industry.(6,7) While the use of automated equipment tends to minimize direct contact with processing chemicals in most large-scale manufacturing facilities, routine maintenance and solvent transfer operations can give rise to periodic exposures. Additionally, in research laboratories, it is more common to find processing being performed manually.

Responding to the need for chemical protection in the specialized environments of semiconductor production facilities (i.e., clean rooms), several glove manufacturers have developed low-particulate chemically protective gloves. A recent survey of glove-use practices in this industry indicated that these types of gloves are used extensively.(8) The survey also revealed that the most common types of gloves used for protection against organic solvents were composed of nitrile rubber, although various other glove materials were also used. Most of the respondents indicated that gloves were used for up to several days before being replaced.

In a previous report from our laboratory, the permeation behavior of several glove materials challenged with semiconductor processing mixtures containing ethylene glycol-ether derivatives was described.(9) Among the results from that study, it was found that increasing the temperature from 25 to 37°C caused marked decreases in permeation resistance of most of the gloves. In addition, previously exposed gloves were found to retain the glycol-ether derivatives for up to several days following exposure, serving as a potential source of exposure to these solvents upon subsequent re-use. In light of these results and the limited amount of published information on the permeation behavior of PGMEA, we investigated the permeation of PGMEA through various gloves commonly used in semiconductor fabrication facilities.

Experimental Material and Methods

Table I lists the model, polymer component(s), and range of measured thicknesses of each type of glove tested. All gloves were used as received. PGMEA (99%, Aldrich, Milwaukee, WI) consisted of a mixture of alpha and beta isomers that could not be resolved under the gas chromatographic conditions used in this study.

Permeation tests were performed according to the American Society for Testing Materials (ASTM) F739-85 method,(10) using a 5.1-cm (2-in) diameter test cell (Pesce Lab Sales, Inc., Kennett Square, PA) in an open-loop configuration with N_2 gas as the collection medium. The N_2 flow rate was maintained at 0.5 L/min for all experiments. Components downstream from the test cell were constructed of Teflon^R or stainless steel. A thermostatted water bath controlled the cell temperature to +/-0.5°C. The test cell and the flask in which the PGMEA was stored were thermally equilibrated in the water bath prior to testing. The PGMEA was then transferred to the challenge side of the cell by cannula under a positive pressure of air. The temperature of the N_2 gas stream was also regulated to +/- 1.5°C by heating a coiled section of the upstream tubing with a heating mantle prior to passing it through the test cell. The N_2 temperature was monitored with a thermocouple inserted in-line just upstream from the cell.

Test samples cut from the gauntlet region of each glove were clamped into the cell and tightened to a constant pressure of 30 in-lb with a torque wrench. Sample thicknesses were determined by averaging micrometer measurements at five locations across the sample.

The gas downstream from the test cell was sampled periodically with a 5-mL gas-tight syringe and analyzed with a gas chromatograph (Model 3700, Varian Associates, Palo Alto, CA) equipped with a packed column (2-ft stainless-steel, 1/8-inch o.d., packed with 1% SP-1000 on 60/80 mesh Carbopack B, Supelco, Inc., Bellefonte, PA) and a flame-ionization detector. The output from the detector was monitored with a standard strip-chart recorder and peak heights were used to quantify signal intensities. Instrument calibrations were performed daily using test atmospheres of PGMEA diluted in air in 100-L Tedlar^R bags (SKC, Inc., Eighty-four, PA).

Steady-state permeation rates (SSPR) were calculated by averaging five measurements obtained after the downstream solvent concentration showed no further increase with time. The breakthrough time (BT) was defined as the time required for the downstream vapor concentration to reach 4 mg/m^3, which corresponds to a permeation rate of 0.1 $\mu g/cm^2/min$ for this test system. This concentration corresponds to an injected mass of 19 ng (for a 5-mL injection) which was well above the limit of detection for PGMEA (0.38 ng). Where necessary, BT values were interpolated from measurements collected just before and after the critical concentration was measured in the collected samples. For exposures at 37°C, the appropriate temperature correction was applied to the air concentrations of the injected samples. All permeation tests were performed in duplicate unless otherwise indicated.

For repeated exposures, samples were exposed initially, removed from the test cell and patted dry with a paper towel to remove visible liquid, and then allowed to air dry in an exhaust hood having a face velocity of 90-100 ft/min. Thermal decontamination was performed by placing exposed gloves in a vented oven at 70 or 100°C.

Results and Discussion

Table I shows the BT and SSPR values measured for each glove at 25°C. The butyl rubber gloves (North B-161) provided the highest level of resistance to PGMEA, with no breakthrough being observed over the 4-hr test period. Nitrile rubber gloves (Edmont Nytek) also provided excellent permeation resistance (BT = 147 min). Gloves composed of natural rubber (Edmont Puretek) and blends of natural rubber with other polymers (Pioneer Trionic and Playtex 827) provided much shorter breakthrough times. SSPR values were similar, and rather low, for all of the gloves exhibiting breakthrough, with values ranging from 55-81 $\mu g/cm^2/min$ (Table I).

At the conclusion of each permeation test qualitative assessments were made of the degree of deformation of the glove sample. With the exception of the North gloves, all of the gloves showed some degree of swelling which persisted after removal from the cell. Interestingly, while the Nytek gloves showed the highest permeation resistance of these gloves, they also showed the most deformation after exposure. For experiments involving repeated exposure of the Nytek gloves, recovery of the shapes samples was evident after standing in a fume hood overnight.

Thickness normalized BT and SSPR values are also presented in Table I (in brackets below the corresponding measured values). Thickness normalized BT values were calculated by dividing the measured BT values by the square of the thickness (L).(11) Thickness-normalized SSPR values were calculated by multiplying the observed SSPR values by L. This latter quantity (SSPR x L) is equivalent to the permeability coefficient, P.(12)

Comparison of the thickness-normalized BTs and SSPRs for the different gloves emphasizes that the Nytek gloves have inherently greater permeation resistance than the other materials for which breakthrough was detected. It is interesting to note that the Playtex gloves, which contain roughly equivalent proportions of neoprene and natural rubber (according to the manufacturer), provide about the same permeation resistance as the natural rubber Puretek gloves. On the basis of solubility considerations, one might have expected the more polar neoprene to improve the permeation resistance of this material. A similar argument might be made for the Trionic gloves. However, according to the manufacturer of this glove, the product consists primarily of natural rubber with only traces of the other polymers added. Thus, the similarity between permeation behavior of the Trionic and Puretek gloves is not surprising.

Table I also presents the BT and SSPR values obtained at 37°C along with the ratios of these values to those obtained at 25°C. These temperatures were chosen because most operations involving potential exposure to positive photoresists are performed at room temperature. Thus, the glove temperature is likely to be between room temperature and body temperature.

With the exception of the North gloves, significant decreases in permeation resistance were observed at the higher temperature. BT values (and thickness-normalized BT values) decreased by factors of 2-3, with slightly larger effects observed for the Trionic and Playtex gloves than for the Nytek and Puretek gloves. SSPR values increased by factors of 2.6-4.0 (2.5-4.3 for thickness normalized values). The influence of temperature on the SSPRs was greater than that on BT values in all cases. The largest effect on the SSPR was seen for the Nytek gloves. This result, together with the low SSPR observed at the lower temperature, is consistent with a higher activation energy for permeation.(13)

The rather large influence of temperature on the BT and SSPR values seen in this study is characteristic of the Arrhenius (i.e., positive exponential) temperature dependence of the permeation process. In this case, a change in absolute temperature of only four percent caused changes in these permeation parameters of 100-300%. The magnitudes of the temperature effects observed here are similar to those reported for other solvent/glove combinations.(13,14) These results point out the limitations of using data collected at 25°C as the basis for selecting gloves for use in hot work environments. Even for normal temperature working conditions, heat from the body may be sufficient to reduce the permeation resistance significantly. This also emphasizes the need for careful temperature control during permeation testing.

Following these initial tests, a series of experiments was performed to determine the effects of repeated exposure of the Nytek and North gloves to PGMEA. Given the relatively low resistance of the other gloves, they were not included in this second series.

The North samples continued to show excellent permeation resistance, with no evidence of solvent breakthrough following a 4-hr exposure, air-drying overnight at room temperature and a 4-hr re-exposure. Table II presents the BT and SSPR values for Nytek glove samples for an initial exposure of 1.3 hr (i.e., slightly greater than one-half the nominal BT value) followed by one of several post-exposure treatments and then re-exposure. The mean BT and SSPR values for previously unexposed samples are also presented in Table II for comparison.

The first post-exposure treatment examined was air-drying in a fume hood at room temperature (~23°C). Replacement of the test samples in the cell following this treatment resulted in concentrations of PGMEA in the collected samples, prior to filling the challenge side of the test cell with solvent, that were already above the breakthrough-time detection limit. This result demonstrates that the PGMEA continues to permeate through the glove during periods of non-use. The SSPR values upon re-exposure were about three times higher than those observed for the previously unexposed gloves, suggesting some alteration of the glove structure caused by the PGMEA (e.g., extraction of non-polymer glove components, or non-reversible swelling of the polymer network).

It has been shown for solvents which penetrate the outer surface of a glove that thermal treatment is more effective for removal of residual solvents than surface cleaning with solvents or detergents.(15,16) Our initial attempts at thermal decontamination involved heating the previously exposed samples at 70°C. In this case, there was some recovery in the BT values, but SSPR values were still elevated relative to those obtained for previously unexposed gloves (Table II). Raising the post-exposure treatment temperature to 100°C resulted in BT values that were still only 75% of the expected value. SSPR values were even higher than those observed following the 70°C treatment. Apparently, elevated temperatures promote whatever degradation process is occurring in the glove.

The results obtained here can be compared to those obtained for the same glove materials in our previous study involving ethylene glycol monoethyl ether acetate (EGMEA) which is an isomer of PGMEA.(9) The relative order of permeation resistance exhibited by the gloves was the same for both solvents. That is, the North B-161 butyl rubber gloves provided the highest resistance followed by the Edmont Nytek nitrile gloves and then the gloves containing natural rubber. For a given glove type, EGMEA consistently had shorter BT values and higher SSPR values than PGMEA. This is consistent with the smaller diffusion coefficient expected for the PGMEA as a result of the greater degree of branching in this isomer.(12) The permeation of EGMEA at 37°C was not examined for the neat solvent, but rather as a mixture (82%) with xylene (9%) and n-butyl acetate (9%) in a photoresist thinner formulation. Still, the decreases in BT values for the EGMEA at the higher temperature were similar to those observed for PGMEA. Increases in the SSPR values with temperature were somewhat smaller for the EGMEA than for the PGMEA.

As with the PGMEA, EGMEA was found to persist in the Nytek gloves following initial exposure and air-drying. For the EGMEA (in the mixture), however, it was possible to decontaminate the gloves by treatment at 70°C. Upon re-exposure to EGMEA, the BT and SSPR values of the thermally decontaminated gloves were virtually the same as those of the previously unexposed gloves. Considering that both the vapor pressure and evaporation rate of PGMEA are higher than those of EGMEA,(4) the difference in the thermal decontamination results is curious. Apparently the larger diffusion coefficient of the EGMEA coupled, perhaps, with the presence of the other solvents (which did enhance the permeation of the EGMEA) predominated in effecting evaporation of the EGMEA from the samples. The elevated SSPRs observed for PGMEA in the thermally treated previously exposed gloves, however, cannot be explained.

Finally, there remains the question of whether the results obtained for neat PGMEA are representative of those expected for photoresist formulations containing PGMEA. The non-solvent components of the positive photoresists are present in concentrations ranging from about 15-35% by weight and consist of polymeric resins and photoactive compounds designed to promote dissolution upon exposure to UV radiation.(17) These components are high-molecular-weight and/or ionic compounds that would not be expected to permeate through the gloves studied here.

Referring again to the results for EGMEA, it was found that the presence of the resins and photoactive components served to reduce the EGMEA permeation slightly. Given the similarities in the permeation of EGMEA and PGMEA (for initial exposure, at any rate) a similar reduction in the permeation of PGMEA in photoresist formulations, relative to the neat solvent, seems likely.

Summary and Conclusions

Of the gloves tested in this study, the North Model B-161 butyl rubber gloves provided the best protection against PGMEA. The breakthrough time was greater than four hours, and there was no evidence of persistent permeation or significant temperature effects from 25-37°C. While these gloves are not suitable for clean-room environments because of the need to apply powder to the gloves during packaging (to reduce the inherent tack of the butyl rubber), these gloves would be useful for emergency spill response or for handling microlithographic solvent formulations in service areas outside of the clean room.

The Edmont Nytek nitrile rubber gloves also provided good resistance to PGMEA under continuous exposure conditions. While the permeation resistance of the Nytek gloves decreased significantly from 25-37°C, the BT observed at the higher temperature (83 min) is long enough to provide adequate protection for many work situations. The Edmont Puretek (natural rubber), Pioneer Trionic (natural/nitrile/neoprene rubber blend), and Playtex Model 827 (natural/neoprene rubber blend) gloves showed significantly lower levels of protection against all of the solvent mixtures than the nitrile and butyl rubber gloves. BT values were all less than 22 minutes at 25°C and were less than 10 minutes at 37°C. These gloves may provide protection against incidental contact but should not be used for any length of time following exposure.

Of some concern is the persistent permeation of the PGMEA through the Edmont Nytek gloves after a relatively short initial exposure, and evidence (i.e., significantly higher SSPR values) of a change in the structure of the glove as a result of the initial exposure. Heating previously exposed Nytek gloves at 70 or 100°C overnight led to only partial recovery of BT values (75% of expected) and still higher SSPR values. Thus, thermally reconditioned Nytek gloves should be used for only limited periods following an initial exposure. Repeated thermal reconditioning cannot be recommended at this point.

With respect to the relative permeation resistance of the gloves investigated, the results observed for PGMEA are similar to those observed for its isomer ethylene glycol monoethyl ether acetate (EGMEA) in a previous study.(9) The effects of temperature on permeation were also similar for the two solvents. However, thermal decontamination of previously exposed gloves, which was successful for EGMEA, was not successful for PGMEA even though PGMEA is more volatile. The persistence of PGMEA in the gloves may be attributable to its smaller diffusion coefficient relative to EGMEA. The marked increase in SSPR values for gloves previously exposed to PGMEA, which was not seen in the case of EGMEA, warrants further investigation.

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Table I. Permeation Test Results^{A}

Glove Material	Polymer Components	Thickness (cm)	BT$_{25^\circ C}$ (min)	BT$_{37^\circ C}$ (min)	Ratio BT$_{37^\circ C}$/BT$_{25^\circ C}$	SSPR$_{25^\circ C}$ (μg/cm^2/min)	SSPR$_{37^\circ C}$ (μg/cm^2/min)	Ratio SSPR$_{37^\circ C}$/SSPR$_{25^\circ C}$
North (B-161)	butyl rubber	0.040	>250	>300	----	---	---	---
Edmont Nytek (49-155)	nitrile rubber	0.041-0.045	147(1) [87]	83(2) [40]	0.56 [0.46]	55(3) [2.3]	221(22) [9.9]	4.0 [4.3]
Pioneer Trionic	natural/nitrile/neoprene blend	0.047-0.048	16(2) [7]	6(0) [3]	0.38 [0.43]	61(0) [2.9]	221(11) [10.4]	3.6 [3.6]
Playtex (827)	natural/neoprene blend	0.039-0.042	19(3) [11]	6(0) [4]	0.32 [0.36]	81(7) [3.4]	256(4) [10.0]	3.2 [2.9]
Edmont Puretek (30-139)	natural rubber	0.051-0.053	22(1) [8]	10(0) [4]	0.45 [0.50]	58(0) [3.1]	151(1) [7.7]	2.6 [2.5]

A Numbers in parentheses are standard deviations. Numbers in brackets represent thickness normalized BT (BT/L^2, min/cm^2 x 10^3) and SSPR (SSPR x L, μg/cm/min) values at 25°C.

Table II. Permeation Resistance of Pre-Exposed Nytek Gloves

Exposure and Treatment Conditions[A]	BT (min)	SSPR (μg/cm2/min)
No Pre-exposure	147(1)	55(3)
Pre-exposed (1.3 hr), dried 23°C (24 hr)	0(-)	165(3)
Pre-exposed (1.3 hr), dried 70°C (24 hr)	74(9)	182(11)
Pre-exposed (1.3 hr), dried 100°C (24 hr)[B]	106(-)	200(--)

[A] All exposures were performed at 25°C. Numbers in parentheses are standard deviations.

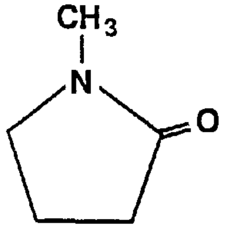
[B] Only one trial was performed under these conditions.

Chapter 3

Temperature Dependence of N-Methylpyrrolidone Permeation Through Butyl and Natural Rubber Gloves: Predicted vs. Experimental Results

Introduction

N-methylpyrrolidone (NMP), also referred to by the tradename M-Pyrol, is a dipolar aprotic solvent having the following structure:



It is used industrially as a selective extraction solvent for aromatic and other conjugated unsaturated hydrocarbons, and as a formulating solvent for paints, paint strippers, plastics, cleaners, and pesticides [1]. NMP is also used widely in the microelectronics industry as a photoresist stripper, degreasing agent, and solvent for phenolic "die-coat" resins for encapsulating finished device packages [2].

The low vapor pressure of NMP (0.342 mm Hg @25°C) [1] limits the saturated vapor concentration to about 450 ppm at room temperature, although hydrolysis in air at relative humidities of 40-60% can reduce maximum NMP concentrations to approximately 130 ppm [3]. This, in turn, reduces the potential inhalation hazard of NMP. However, NMP is readily absorbed through the skin and repeated or prolonged skin contact with the liquid can cause severe dermatitis [4].

Acute effects of NMP vapor exposure include headache and irritation of the eyes and respiratory tract [2]. Animal toxicity testing indicates that NMP is not mutagenic or carcinogenic, but there is evidence for teratogenicity at high doses [5]. Subchronic exposures to aerosol/vapor mixtures caused respiratory, hematologic and hematopoetic effects in rats [6] but vapor exposures to similar concentrations did not cause these effects. Aerosol size and relative humidity levels appear to influence the toxicity. It has been suggested that dermal absorption may be partly responsible for observed differences in effects between aerosol and vapor exposures [5].

The EPA has recently proposed a test rule and additional toxicity testing for NMP in anticipation of its use in commercial paint strippers [7,8]. While there are currently no established limits for occupational NMP exposure in the US [9, 10, 11], several European countries have adopted eight-hour time-weighted-average (8-hr TWA) limits of 100 ppm [12]. GAF Chemicals Corporation, one of the major US manufacturers of NMP, recommends a limit 100 ppm (8-hr TWA) [2] and the DuPont Company, a major user of NMP, recommends a limit of 25 ppm [3].

In a recent study of exposures to NMP vapors in microelectronics production facilities, symptoms of eye irritation and headache were observed at relatively low vapor concentrations (0.72-15 ppm) [2]. Based on these results, the authors of that study recommended a maximum exposure limit of 0.1 ppm. A "skin" designation was also recommended in recognition of the dermal absorption potential of NMP, although the importance of this exposure route was not investigated.

The use of chemical protective clothing (CPC) is required in most microelectronics facilities, in part, because of the extensive use of organic solvents, mineral acids and bases in standard production processes. Yet, contact with chemicals has historically ranked highly as a cause of injury and illness in this industry [13]. Published glove permeation data indicate that butyl rubber and natural rubber gloves provide reasonably good resistance to NMP permeation at room temperature [14-16] but data at higher temperatures are not available. These factors, coupled with the high dermal absorption potential and use of NMP at elevated temperatures prompted this investigation.

The gloves selected for testing included one butyl rubber glove (North B-161) and three other gloves composed of either natural rubber (Edmont Puretek, Ansell Pacific White) or a blend of natural rubber with small percentages of nitrile and neoprene rubbers (Pioneer Trionic) (note: since this glove is composed predominantly of natural rubber we will for convenience refer to it as a natural rubber glove throughout this report). The latter three gloves were selected because they are specially designed/packaged to minimize particulate generation and are marketed specifically for use in microelectronic production facilities (so-called "clean rooms"). Butyl rubber gloves are not generally used in such facilities because they are treated with talc as an adhesion inhibitor during packaging. However, the expectation of good permeation resistance warranted their inclusion in the study.

Use of three natural rubber gloves permitted an assessment of the variation in performance between glove manufacturers. Practical limitations allowed testing only up to 50°C, however extrapolation to 70 and 93°C, typical of degreasing bath temperatures [2, 25], was possible. The relative importance of diffusional and solubility effects on the temperature dependence of permeation was also examined. Comparisons were also made between experimental values of permeation parameters and those predicted from recently developed models.

Theoretical Considerations

The importance of temperature effects on the permeation of solvents through polymers and polymeric chemically protective clothing (CPC) has been recognized for some time (17-19), but very few systemmatic studies have been performed on commercial CPC materials (20-22). Invariably, permeation rates increase with increasing temperature, resulting in shorter breakthrough times (BT) and higher steady-state permeation rates (SSPR). The extent to which these permeation parameters are affected by temperature is a function of the composition of the solvent and the CPC material.

The following expression, which assumes Fickian diffusion, describes the theoretical temperature dependence of solvent permeation through a polymer (or CPC material):

$$P = J_{SS}L = DS = P_o e^{-E_p/RT} \tag{1}$$

where P is the steady-state permeability coefficient (g/cm-s), J_{SS} is the steady-state flux (g/cm^2-s, equivalent to the SSPR), L is the polymer thickness (cm), D is the steady-state diffusion coefficient of the solvent in the polymer (cm^2/s), S is the equilibrium solubility of the solvent in the polymer (g/cm^3), P_o is an entropic constant that is independent of temperature (g/cm-s), E_p is the activation energy of permeation (Kcal/mole), R is the gas constant (1.987×10^{-3} Kcal/mole-°K), and T is the absolute temperature (°K) [17]. Plotting ln P versus 1/T (an Arrhenius plot) at several temperatures should yield a straight with a slope equal to $-E_p/R$.

The temperature dependence of P arises from the combined effects of temperature on D and S. It is possible, therefore, to rewrite the Arrhenius relationship of Equation 1 in terms of these two temperature dependent quantities:

$$P = (D_o e^{-E_D/RT})(S_o e^{-\Delta H_S/RT}) \tag{2}$$

where E_D is the diffusion activation energy, ΔH_S is the heat (enthalpy) of solution and D_o and S_o are constants. By evaluating P and S at different temperatures one can obtain values of E_p and ΔH_S, from which E_D can be obtained (since $E_p = E_D + \Delta H_S$). Alternatively, E_D can be determined directly from Arrhenius plots of D, where D at a given temperature is obtained from experimental P and S values using Equation 1. Comparing ΔH_S to E_D can then reveal the relative importance of diffusional and solubility effects to the temperature dependence of the overall permeation process.

Prior to steady state, the theoretical expression for the flux or permeability coefficient at a given elapsed time, t, for an open-loop system is (from Fick's Laws) [23]

$$P_t = J_tL = DS[1 + 2\Sigma\ (-1)^n \exp[-(n\pi)^2(Dt/L^2)]] \qquad (3)$$

Provided that values of D and S are known, the breakthrough time can be determined by setting J_t equal to the permeation-rate detection limit and solving for t. This expression shows that the variation of the BT with temperature is more complex than that of the SSPR. However, it has been found experimentally that the temperature dependence of BT can be described by an Arrhenius equation of the following form:

$$BT = B_o e^{E_B/RT} \qquad (4)$$

where B_o is a constant and E_B is the (nominal) activation energy for breakthrough (Kcal/mole) [20]. Thickness normalized BT values ($BT_N = BT/L^2$) can also be used in the above expression for comparing values obtained from different glove materials.

Equations 1 and 4 can be used to predict the changes in the SSPR and BT with temperature. That is, once E_P, P_o, E_B, and B_o are defined, the SSPR and BT values at higher temperatures can be determined by extrapolation, provided the temperature range is not too broad [17].

Predictive Models of D and S

The approach described above for estimating SSPR and BT at different temperatures requires values of the Arrhenius parameters which, in turn, requires measurement of SSPR and BT at several temperatures. It is desirable to be able to predict the variation of BT and SSPR with temperatures without having to actually perform permeation tests at different temperatures.

Perkins and You recently examined the temperature dependence of permeation for a number of solvent-CPC combinations [22]. From their results they derived empirical linear relationships between the permeation coefficient and thickness-normalized breakthrough time measured at 25°C (P_{25} and BT_{N-25}, respectively) and the corresponding activation energies, E_P and E_B. Additional equations relating the activation energies to the pre-exponential factors, P_o and B_o, were also derived. These equations are given below:

$$\ln P_{25} = -0.079E_P + 7 \qquad (r^2 = 0.884) \qquad (5a)$$

$$\ln P_o = 0.33E_p + 6.8 \qquad (r^2 = 0.990) \qquad (5b)$$

$$\ln (BT_{N-25}) = 0.08E_B + 1.84 \qquad (r^2 = 0.846) \qquad (5c)$$

$$\ln B_o = -0.33E_B + 2.2 \qquad (r^2 = 0.990) \qquad (5d)$$

Thus, according to this model measurements of P and BT at 25°C can be used to determine the variables needed in Equations 1 and 4 for determining P and BT values at higher temperatures. While the accuracy of this approach has not been assessed, the regression r^2 values in Equations 5a and 5c suggest that at least approximate estimates should be obtainable (note: this model is referred to as Model A below).

An alternative approach to predicting the temperature dependence of permeation involves estimating D and S separately and then combining these values in Equations 1 and 3 to obtain estimates of BT and SSPR. In Chapter 4 we describe a method for predicting the equilibrium solubility of solvents in CPC-polymers using three-dimensional (3-D) solubility parameters [24]. In that method, the solubility parameters of the solvent and polymer are used to derive a value for the dimensionless Flory-Huggins interaction parameter, χ, using the following expression:

$$\chi = \chi_S + \chi_H = \chi_S + V_1(\delta_1-\delta_2)^2/(RT) \qquad (6)$$

where χ_S is an entropic correction term, χ_H is the enthalpic contribution to χ, V_1 is the solvent molar volume, δ_1 and δ_2 are the 3-D solubility parameters of the solvent and polymer, respectively, R is the gas constant and T is the absolute temperature. If it is assumed that the CPC polymer is not crosslinked, χ_S takes on a value of 0.5. For the crosslinked case, which is most relevant in the case of CPC polymers, $\chi_S = 0$.

The solubility parameter difference in Equation 6 is calculated by the following equation:

$$\delta_1-\delta_2 = [(\delta_{d1} - \delta_{d2})^2 + b(\delta_{p1} - \delta_{p2})^2 + b(\delta_{h1} - \delta_{h2})^2]^{1/2} \qquad (7)$$

where the subscripts 1 and 2 refer to the solvent and polymer, respectively, and δ_d, δ_p and δ_h are the 3-D solubility parameters corresponding to dispersion, dipolarity and hydrogen-bonding interactions, respectively. A value of b = 0.25 has been recommended by Hansen [25] to properly weight the dipolar and hydrogen-bonding terms (note, however, that this value will change with the polymer and the solvent, as shown in Chapter 4).

The value of χ predicted from the solubility parameters is then used to calculate the equilibrium volume fraction of solvent in the CPC polymer using the following expression (assuming a lightly cross-linked polymer):

$$\chi = -(2KV_1/RT)(\phi_2^{-5/3} - 1/2\phi_2) - (\ln \phi_1)/\phi_2^2 - 1/\phi_2 \qquad (8)$$

where K is related to the crosslink density, ϕ_1 is the equilibrium solvent volume fraction and ϕ_2 is the equilibrium polymer volume fraction (note: $\phi_2 = 1-\phi_1$). Multiplying ϕ_1/ϕ_2 by the solvent density gives the equilibrium solubility (S) in grams of solvent per cubic centimeter of polymer. Equations 6-8 can be used to predict S at any temperature. The change in the solubility parameter values with temperature can be estimated using the thermal expansion coefficients of the solvent and polymer and the equations described in Chapter 4 and reference

26.

Theoretical models of solvent diffusion coefficients in polymers have been reported by a number of researchers [17]. Those based on so-called free-volume theories are among the most recent to emerge [27,28]. Unfortunately, the application of these theoretical approaches to the determination of D requires estimation of parameters not readily available for many solvent-CPC systems. Models of D based on empirical correlations with readily measurable parameters represent a more practical, though less rigorous, alternative.

The kinetic theory described by Dullien [29] and the free-volume theories described by Paul [27] and Vrentas and Duda [28], suggest the following approximate relationship to describe the change of the solvent diffusion coefficient (D) with temperature:

$$D_{(T1)}/D_{(T2)} \approx \eta_{k(T2)}/\eta_{k(T1)} \qquad (9)$$

where T1 and T2 refer to two different temperatures, and η_k is the kinematic viscosity (dynamic viscosity/density) in units of cm^2/s. Thus, the change of D with temperature can be related to the change of viscosity. Use of this relationship was reported by Vahdat [21] who found excellent correlations between log D and log η_k for three solvents in each of two CPC polymers over the temperature range of 25-65°C. Southern and Thomas also reported strong correlations between viscosity and D for various solvents permeating through natural rubber at 25°C [30]. In that study the relationship between D and η was linear for η values below about 100 centipoise which includes the values for most organic solvents.

Combining predicted values of D and S into equations 1 and 4 allows predictions of BT and SSPR at any temperature.

Experimental Materials and Methods

Table I lists the model, polymer component(s), and mean thickness of each type of glove tested. NMP (99%, Aldrich, Milwaukee, WI) and the glove materials were used as received.

Permeation tests were performed according to the American Society for Testing Materials (ASTM) F739-85 method [30a], using a 5.1-cm (2-in) diameter test cell (Pesce Lab Sales, Inc., Kennett Square, PA) in an open-loop configuration with N_2 gas as the collection medium. The N_2 flow rate was maintained at a constant value between 500 and 3000 cm^3/min for all experiments (see below). Components downstream from the test cell were constructed of Teflon^R or stainless steel. A thermostatted water bath controlled the cell temperature to +/-0.5°C. The test cell and flask in which the NMP was stored were thermally equilibrated in the water bath prior to testing. The NMP was then transferred to the challenge side of the cell by cannula under a positive pressure of air. The temperature of the N_2 gas stream was also regulated to +/- 1.5°C by heating a coiled section of the upstream tubing with a heating mantle prior to passing it through the test cell. The N_2 temperature was monitored with a thermocouple inserted in-line just upstream from the cell. The downstream tubing and gas-tight sampling syringe were also heated to prevent condensation of NMP vapor from the sample stream.

Test samples cut from the gauntlet region of each glove were clamped into the cell and tightened to a constant pressure of 20 in-lb with a torque wrench. Sample thicknesses were determined before testing by averaging micrometer measurements at five locations across the sample.

The gas downstream from the test cell was sampled periodically with a 5-mL gas-tight syringe and analyzed with a gas chromatograph (Model 3700, Varian Associates, Palo Alto, CA) equipped with a glass-lined flash injector, a packed column (2-ft glass, 1/4-inch o.d., packed with 4% Carbowax 20M and 0.8% KOH on 60/80 mesh Carbopack B, Supelco, Inc., Bellefonte, PA) and a flame-ionization detector. The output from the detector was monitored with a standard strip-chart recorder and peak heights were used to quantify signal intensities. Instrument calibrations were performed daily using solutions of NMP in CS_2 that spanned the range of injected NMP masses encountered during permeation testing. For the higher temperature experiments, the gas-tight sampling syringe was pre-heated between injections to avoid condensation of the NMP on the interior surfaces of the syringe. Experimental temperatures were limited to 50°C because of practical difficulties in handling the syringe above this temperature.

Mean SSPR values were calculated from five measurements obtained after the downstream solvent concentration showed no further increase with time. The breakthrough time was defined as the time required to reach a permeation rate of 0.10 $\mu g/cm^2/min$. This permeation rate corresponds to downstream vapor concentrations of 4.0 and 0.7 mg/m^3 for the N_2 flow rates of 500 and 3000 cm^3/min, respectively, used in this study. These concentrations yielded injected masses that were well above the limits of detection for NMP. Where necessary, BT values were interpolated from measurements directly before and after the defined breakthrough-time permeation rate. Appropriate corrections were applied to the air concentrations of injected samples collected at different temperatures. All tests were performed in duplicate unless otherwise indicated.

To examine the effects of repeated exposures, samples were exposed initially until steady-state permeation was achieved, carefully removed from the test cell and patted dry to remove visible liquid, and allowed to air dry overnight (~24 hr) in an exhaust hood having a face velocity of 27-30 m/min (90-100 ft/min). Samples were then re-mounted in the test cell and the N_2 stream was sampled for residual solvent vapor emanating from the glove. The challenge chamber was then filled with NMP and the test was performed in the usual manner.

Equilibrium solubility measurements were obtained by placing small (~5 cm^2) pre-weighed samples of each glove material in vials of NMP and allowing the samples to stand in an oven for several hours at each of the temperatures used for permeation testing. For each test temperature, an unexposed glove sample was also heated and weighed along with the exposed samples to account for any non-solvent-induced weight changes. Weight changes of the exposed samples were then adjusted accordingly. Samples were weighed at 2-hr intervals until no change in weight was observed. For the Ansell glove samples, a reduction in weight was observed after two hr at all test temperatures, indicating that some component was being extracted from the glove. As a result, S values were based on the 2-hr weight change.

For predicting permeation parameters with Model A, experimental BT and SSPR values measured at 25°C were used to calculate the corresponding P and BT_{N-25} values which were inserted into Equations 5a and c to obtain values of E_P and E_B. Since these equations are sensitive to the units used for these quantities, units of ug-mm/cm^2-s were used for P and units of min/mm^2 were used for BT_N). Equations 5b and d were then used to obtain P_o and B_o. From these predicted Arrhenius parameters, predicted SSPR and BT values were calculated using Equations 1 and 4.

For Model B, predicted values of S were determined from Equations 6-8 using the values for the 3-D solubility parameters listed in Table I. The values used for NMP were $\delta_d = 8.8$, $\delta_p = 6.0$, $\delta_h = 3.5$ $(cal/cm^3)^{1/2}$ [31]. The 3-D solubility parameters used for the Edmont, Pioneer and North gloves were those published by Perkins et al. [32,33]. The values used for the Ansell glove are the same as those used for Pioneer since values for the former were not available. Predicting S at temperatures above 25°C was performed using published values of the NMP molar volume and density at different temperatures [1]. Solubility parameter values were adjusted using thermal expansion coefficients, α, according to the methods described in Chapter 4 and reference 26. An average value of $\alpha = 9.65 \times 10-4$ $°K^{-1}$ was used for NMP based on calculations over the range of 25-50°C. For natural rubber, a value of $\alpha = 6.6 \times 10^{-4}$ $°K^{-1}$ was used based on data collected for lightly crosslinked (vulcanized) samples [34,35]. For butyl rubber, a α value of 4.6×10^{-4} $°K^{-1}$ was used based on data collected for a crosslinked polyisobutylene filled with carbon black (33% by wt.) [34] (note: according to the manufacturer, the North butyl rubber glove contains 26% carbon black filler). Kinematic viscosity values were determined from published values of dynamic viscosity and density at different temperatures [1].

Results and Discussion

N_2 Flow Rate Effects

The low vapor pressure of NMP required that the N_2 collection stream and sampling syringe be heated for tests performed above room temperature in order to avoid condensation of the NMP. The possibility that permeating NMP might condense on the inner surface of the glove samples rather than completely evaporating in the collection side of the cell was also recognized and investigated.

Initial permeation tests were performed with the Edmont and Pioneer gloves at N_2 flow rates of 500 cm^3/min, and no evidence of condensation on the inner surface of the samples was observed by visual inspection. However, for the Ansell glove small droplets of amber liquid were observed at the end of initial experiments at each of the four challenge temperatures.

To determine whether these droplets consisted of condensed NMP or only some non-volatile component being leached from the glove during permeation, experiments with the Ansell glove were repeated at different flow rates and the resultant BT and SSPR values were compared. Tests were performed at 25°C at N_2 flow rates of 500, 1500, and 3000 cm^3/min (note: pressure readings within the collection side of the cell over this range of flow rates remained below 3" H_2O, confirming that pressure changes at the higher flow rates were negligible). Results for the lowest and highest flow rates are shown in Figures 1 a and b.

Increasing the flow rate to 1500 cm^3/min did not significantly affect the measured BT values but caused a dramatic increase in the measured SSPR values. In addition, no residual droplets were observed on the glove sample following exposure. Increasing the flow rate to 3000 cm^3/min did not change the measured BT or SSPR values relative to those at 1500 cm^3/min. All permeation tests for the Ansell glove were then repeated at 3000 cm^3/min. Similar tests of flow rate effects were performed for the Pioneer glove, but there was no effect on the measured permeation parameters. Tests on the Edmont glove were deemed unnecessary since it had the lowest SSPR values of the three gloves and showed no signs of NMP condensation at any temperature.

It is interesting to note that even at the lower flow rates the SSPR values for the Ansell glove increased monotonically with increasing temperature. In fact, the data could be described well by an Arrhenius equation but the activation energy, which provides an index of the temperature dependence of the SSPR, was much lower than that measured at 3000 cm^3/min.

Experimental Permeation Parameters

Table II presents the results of permeation tests at each temperature for all four of the gloves. Permeation through the butyl rubber glove was not detected at any temperature. For the remaining three gloves the permeation resistance decreased significantly as the temperature was increased. Results for the Edmont and Pioneer gloves were very similar whereas the Ansell glove showed consistently shorter BT values and higher SSPR values. Changes in the BT and SSPR values with temperature, however, were of the same order for all of the natural rubber gloves, with BT values decreasing by factors of 7-10 and SSPR values increasing by factor of 5-6 on going from 25 to 50°C.

Results of repeated exposure to NMP at 25°C are presented in Table II below the corresponding values for the initial exposure. The butyl rubber glove continued to provide excellent resistance with no breakthrough being observed. For the other three gloves residual NMP was measured in the background samples prior to re-exposure in all cases. For the Edmont glove, these levels exceeded the breakthrough criterion concentration, while for the Pioneer and Ansell gloves the levels were slightly below this concentration. All three gloves behaved similarly, though, in that the residual concentration remained relatively constant for the period prior to the sharp increase typically associated with breakthrough. The similarity between the SSPR values for the first and second exposures indicate that the integrity of the gloves is not affected by prolonged contact with the NMP.

Figures 2 a and b show Arrhenius plots of BT_N (i.e., BT/L^2) and P for each of the natural rubber gloves. Linear regression correlation coefficients (r^2) were >0.99 in all cases. The corresponding activation energies and pre-exponential constants were determined from the slopes and intercepts of the regression lines, respectively. These values are listed in Table III and will be discussed further below. With these values it is possible to determine BT and SSPR values at higher temperatures by extrapolation. As discussed above, degreasing operations involving NMP are typically performed in the range of 70-93°C (note: the NMP flash point is about 96-98°C). The BT values for the natural rubber gloves determined at 70 and 93°C were <2min and <0.5 min, respectively (Table II) representing reductions by factors of >26 (70°C) and >100 (93°C) relative to values at 25°C. SSPR values increased by factors of >15 (70°C) and >47 (90°C) relative to those at 25°C.

Table IV shows the results of immersion tests at each temperature. In all three cases, increasing temperature led to increased solubility. For the natural rubber samples S values at 50°C were only 1.2-1.4 times those at 25°C. For the butyl rubber samples S increased by a factor of 2.5 between 25 and 50°C. Arrhenius plots of these data (Figure 3) yielded the ΔH_s values listed in Table III.

Experimental values of D were calculated from Equation 1 using the measured values of SSPR and S. These values are presented in Table IV. The Edmont and Pioneer values are quite similar and are slightly lower than the Ansell values. These results are consistent with the evidence that there is some extractable (i.e., NMP-soluble) material in the Ansell glove in which the NMP would have a higher D value or which, upon extraction by the NMP, would render the glove more permeable.

Examination of the quantities listed in Table III can provide insight into the fundamental mechanisms of the permeation process. The similarity in E_P values for the Edmont and Pioneer gloves reflects the similarity in their SSPR values. The lower E_p value for the Ansell gloves is consistent with the higher SSPR values and with the fact that the increase in SSPR with temperature is smaller than that for either the Edmont or Pioneer gloves (i.e., the relative increase in SSPR is smaller for the Ansell glove). The difference in E_{BT} values for the gloves is not very large but the more rapid decline in BT with increasing temperature for the Ansell glove is consistent with its slightly higher E_{BT} value.

Comparison of E_P, ΔH_S and E_D shows that for all of the gloves the value of E_P is dominated by diffusional effects consistent with the experimental results showing a much larger increase for D than for S as the temperature increases. Finally, a comparison of E_p and E_{BT} values shows that the breakthrough time is a more sensitive function of temperature than is the steady-state permeation rate. The relative values of activation parameters observed here are similar to those reported by Vahdat and Bush based on similar analyses of other solvent/glove combinations [20].

Predicted vs Experimental Results

The first model examined was that of Perkins and You [22], referred to here as Model A. The predicted values of BT and SSPR are listed in Table II beneath the corresponding experimental values at each temperature. The errors in BT values range from 37-160% and steadily increase with increasing temperature. From a practical standpoint, however, the estimates are reasonably accurate, perhaps as a result of the BT values being so low. The SSPR values are also overpredicted in all cases with this model (40-105%) and, again, increase steadily with temperature.

As the first step in predicting BTs and SSPRs with Model B, predicted values of S were calculated using Equations 6-8. These values are listed in Table IV below the experimental S values for each glove. The values of the key variables used in calculating S at each temperature are listed in Table V. S values predicted at 25°C are quite accurate for the Edmont and Pioneer gloves and somewhat less accurate for the Ansell glove. At higher temperatures, the error increases in all cases. A comparison of the ratios of higher temperature S values to those at 25°C show that the variation in the predicted S values with temepraturе is about 10-20 percent lower than actually observed. However, the range of error even at the higher temperatures, -3 to -25%, is still quite low. For the butyl rubber glove, values of S were consistently overpredicted even after accounting for the percentage of carbon black in the gloves. Given the very low S value the practical implications of this error are probably minor. One contributing factor to this error is may be a constrictive effect associated with the carbon black that acts like an increase in cross-linking. Such an effect was observed for natural rubber filled with carbon balck in studies of toluene sorption [36]. Experimental values may also be low due to insufficient time allowed for true equilibrium to be obtained. The change in predicted S values with temperature for the butyl rubber samples is smaller than actually observed, consistent with the results for the natural rubber samples.

Plots of log η_k versus log D_s are shown in Figure 4 along with the equations and correlation coefficients (r^2) obtained from linear regression. The high r^2 values indicate that the model accurately predicts D. Comparing the resultant predicted D values with experimental D values yielded errors of only 0.4-8% (Table IV) (note: similar correlations were obtained using viscosity rather than kinematic viscosity). The plot for the Ansell gloves is displaced from those of the Edmont and Pioneer gloves due to the higher Absell D values. In practice, it would not usually be feasible to determine such inter-glove differences. Therefore, a single regression equation for all three gloves was generated by combining the data. The resulting equation and r^2 value are shown in Figure 4 below the individual regression equations. Not surprisingly, the r^2 value is lower thanthat for the individual regressions. Predicted values of D from this equation, however, differed from the experimental D values by only 13-33%. This level of error is still adequate for estimating D in most cases. The high correlation of D with the kinematic viscosity found here for NMP in natural rubber is similar to those found for other solvents in other polymers by Vahdat [21], providing support for the generality of the model.

Inserting the predicted values of D and S into Equations 1 and 3 yielded the series of predicted BT and SSPR values shown in Table II under the heading Model B. The predicted BT values were typically within 57% of experimental values (the exception being the Edmont glove at 50°C which gave an error of 100%). In terms of absolute error, however, all predicted values wee within 13 min of the actual BT values. Errors in predicted SSPR values ranged from 0-18% for the Pioneer and Edmont gloves and from -39 to -49% for the Ansell gloves. The accuracy of predicted values for the Edmont gloves is remarkable. The consistent underprediction for the Ansell gloves, again, may be due to the extractable material in the glove which would tend to accelerate the experimental SSPRs. Figures 5-7 provide a graphical comparison of the two predictive models and indicate that with the exception of the Ansell gloves at 37 and 44°C, Model B provided more accurate predictions than Model A. However, both models provide an adequate degree of accuracy for most practical applications.

Conclusions

As shown from these results, temperature effects on the BT and SSPR can be significant even over relatively small temperature ranges. While the effects of temperature on the natural rubber gloves were similar, the Ansell gloves consistently provided lower permeation resistance, apparently due to the presence in the glove of some extractable material. While thermal discomfort reduces the likelihood of sustained contact with NMP above 70°C, these results indicate that even incidental contact, such as a splash, at elevated temperatures can lead to rapid permeation and potential dermal irritation or absorption. The butyl rubber gloves provided excellent protection under all test conditions suggesting that these gloves be used for protection from NMP in all cases where particulate contamination can be tolerated. Use of natural rubber gloves may be adequate provided that they are changed if any exposure occurs.

Initial exposure of the natural rubber gloves to NMP results in residual contamination at the inner surface following air drying overnight, but no evidence of degradation of the glove material was observed. Extending the drying period beyong 24 hr or applying mild heat would likely remove residual NMP and permit re-use of the gloves.

Arrhenius plots of data revealsed that the increase in permeation with increasing temperature is largely due to increases in the diffusion rate of NMP rather than solubility. This result appears to be general [20] and stresses the need for accurate measures of D in attempting to predict the effects of temperature on permeation.

Of the two predictive models examined here Model B based on solubility parameters, solvent viscosity and Ficks Laws, provided consistently better estimates of the change in BT and SSPR with temperature than the model of Perkins and You [22] based on activation parameters. However, both provided useful levels of accuracy. The latter model is simpler but requires permeation testing to determine the permeability coefficient and breakthrough time at 25°C. The former model can predict BT and SSPR values at all temperatures but is somewhat more complex and requires values for the solubility parameters and viscosity of the solvent at different temperatures. In addition, the relationship between D and η_k must be determined. At the same time, viscosity and density data at different temperatures are available for a wide range of organic solvents [37], and a previous report applying similar analyses to different solvent-CPC combinations [22] suggests that for a given CPC material the equations derived for one solvent should be applicable to all solvents. While these results need to be validated for a wider range of solvent-CPC combinations, the potential for broad application appears promising.

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TABLE I
Brand, Model, Polymer Composition, Mean Thickness (L) and 3-D Solubility Parameters of Gloves Tested

			Solubility Parameters $(cal/cm^3)^{1/2}$		
Brand/Model	Composition	L (cm)	δd	δp	δh
Edmont Puretek (30-139)	natural rubber	0.051	9.4	1.0	1.0[A]
Pioneer Trionic	natural rubber/ neoprene/nitrile blend	0.046	9.2	1.6	1.2[A]
Ansell Pacific White (LP-050)	natural rubber	0.041	9.2	1.6	1.2[B]
North (B-161)	butyl rubber	0.039	8.6	0	0[C]

A reference 32.
B 3-D solubility parameters assumed to be the same as the Pioneer values.
C reference 33.

Table II

Experimental and Predicted Breakthrough Times (BT) and Steady-State Permeation Rates (SSPR) of NMP at Different Temperatures[A]

Breakthrough time (BT, min)

	Edmont	Pioneer	Ansell	North
25°C				
experimental				
1st exposure	57(3)[C]	42(1)[C]	47(-)[C]	>240[C]
2nd exposure	<1(0)	41(0)	35(-)	>240
predicted (Model A)	--	--	--	---
error				
predicted (Model B)	70	55	43	----
error	23%	31%	-9%	
37°C				
experimental	20(0)	17(1)	16(-)	>240
predicted (Model A)	31	23	24	
error	55%	37%	50%	
predicted (Model B)	29	22	18	----
error	45%	29%	13%	
44°C				
experimental	12(1)	9(2)	7(-)	----
predicted (model A)	21	16	16	
error	75%	78%	130%	
predicted (model B)	18	14	11	----
error	50%	55%	57%	
50°C				
experimental	6(0)	6(0)	5(-)	>240
predicted (Model A)	15	12	13	
error	150%	100%	160%	
predicted (Model B)	12	9	7	----
error	100%	50%	40%	

70°C[B]				
extrapolated	1.4	1.6	1.0	----
93°C[B]				
extrapolated	0.3	0.4	0.2	----

Steady-State Permeation Rate (SSPR, μg/cm^2/min)

25°C				
experimental				
1st exposure	6(0)[C]	7(0)[C]	18(-)[C]	----[C]
repeat exposure	6(0)	7(0)	14(-)	----
predicted (Model A)	--	--	--	
error				
predicted (Model B)	7	8	10	
error	17%	14%	-44%	
37°C				
experimental	16(1)	17(0)	40(-)	----
predicted (model A)	24	27	56	
error	50%	59%	40%	
predicted (Model B)	16	20	22	
error	0%	18%	-45%	
44°C				
experimental	25(1)	27(2)	68(-)	----
predicted (Model A)	45	51	96	
error	80%	89%	41%	
predicted (model B)	25	31	35	
error	0%	15%	-49%	
50°C				
experimental	37(0)	44(4)	84(-)	----
predicted (model A)	76	85	149	
error	105%	94%	78%	
predicted (model B)	37	45	51	
error	0%	2%	-39%	

70°C[B]				
extrapolated	140	139	274	----
93°C[B]				
extrapolated	526	476	851	----

[A] numbers in parentheses are standard deviations. BT and SSPR values for the Ansell gloves were based on single determinations.

[B] extrapolated from lower temperatures using Equations 1 and 4 and data from Table III.

[C] results of re-exposure following air-drying overnight.

[D] using D values obtained from group regression.

Table IV

Experimental and Predicted Solubility and Diffusion Coefficient Values

Solubility (S, g/cm^3)

	Edmont	Pioneer	Ansell	North
25°C				
experimental	0.229	0.262	0.330	0.028
predicted	0.221	0.247	0.247	0.067[A]
% error	-3%	-6%	-25%	139%
37°C				
experimental	0.279	0.290	0.349	0.046
predicted	0.243	0.271	0.271	0.076[A]
% error	-13%	-7%	-22%	65%
44°C				
experimental	0.304	0.321	0.365	-----
predicted	0.253	0.283	0.283	0.081[A]
% error	-17%	-12%	-22%	-----
50°C				
experimental	0.320	0.341	0.390	0.070
predicted	0.267	0.298	0.298	0.087[A]
% error	-17%	-13%	-24%	24%

Diffusion Coefficient (D, cm^2/s x 10^8)

	Edmont	Pioneer	Ansell	North
25°C				
experimental	2.17	2.11	3.66	----
predicted[B]	2.22	2.07	3.71	
error	2%	-2%	2%	
predicted[C]	2.62	2.62	2.62	
error	21%	24%	-28%	
37°C				
experimental	4.92	4.39	7.79	----
predicted[B]	4.69	4.44	7.76	
error	-5%	1%	-0.4%	
predicted[C]	5.54	5.54	5.54	
error	13%	26%	-29%	
44°C				
experimental	6.98	6.33	12.5	----
predicted[B]	7.09	6.76	11.5	
error	2%	1%	-8%	
predicted[C]	8.36	8.36	8.36	

error	20%	32%	-33%	
<u>50°C</u>				
experimental	9.83	10.1	15.0	----
predicted[B]	9.96	9.55	16.0	
error	1%	-5%	7%	
predicted[C]	11.7	11.7	11.7	
error	20%	16%	-22%	

A predicted S values wighted by 0.85 to account for carbon black in glove.
B based on individual regression equations.
C based on group regression equation.

Table III

Activation Energies and Heats of Solution for NMP in Natural Rubber Gloves[A]

	Edmont	Pioneer	Ansell
E_p	14.10	13.54	12.06
E_{BT}	16.35	15.80	17.51
ΔH_s	2.61	2.03	1.21
E_D	11.49	11.51	10.85

[A] all values are in Kcal/mole.

TABLE V

Temperature Dependent Parameters Used in Predictive Models of Solubility and Diffusion Coefficients

	V_1 (cm^3/mole)	$(\delta_1-\delta_2)^2$ (cal/cm^3)	χ (Eq. 6)	η (g/cm-s)	density (g/cm^3)	η_k (cm^2/s)
25°C	96.6	8.17(E)	1.33(E)	5.31	1.026	5.14
		7.81(P)	1.27(P)			
		7.81(A)	1.27(A)			
		12.1(N)	1.97(N)			
37°C	97.7	8.07(E)	1.28(E)	3.87	1.015	3.82
		7.72(P)	1.22(P)			
		7.72(A)	1.22(A)			
		11.8(N)	1.88(N)			
44°C	98.5	8.02(E)	1.25(E)	3.26	1.007	3.24
		7.67(P)	1.20(P)			
		7.67(A)	1.20(A)			
		11.7(N)	1.83(N)			
50°C	98.8	7.97(E)	1.23(E)	2.84	1.003	2.83
		7.63(P)	1.17(P)			
		7.63(A)	1.17(A)			
		11.6(N)	1.78(N)			

E=Edmont; P=Pioneer; A=Ansell; N=North

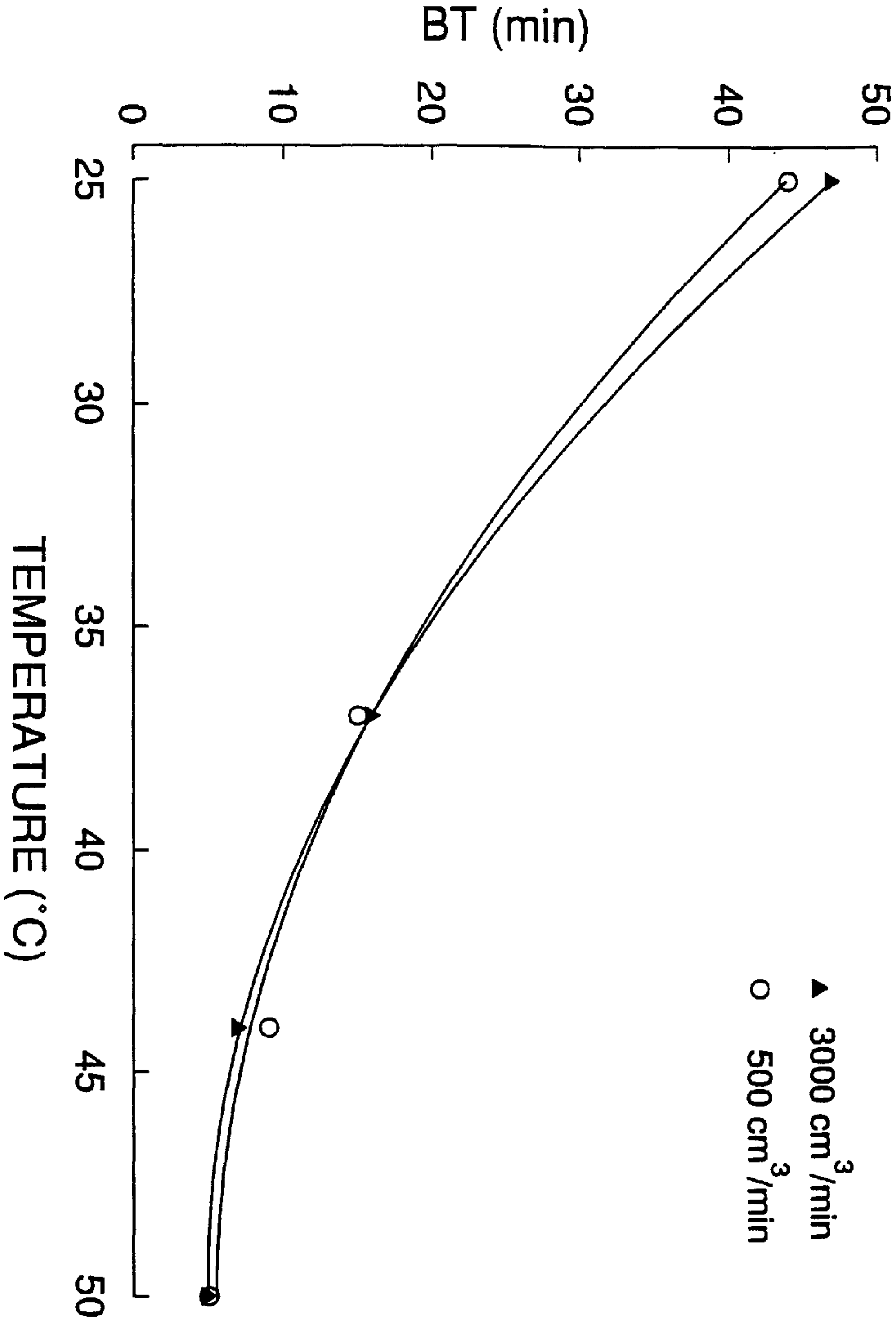
BT (min)
0
10
20
30
40
50
25
30
35
40
45
50
TEMPERATURE (°C)
▲ 3000 cm³/min
○ 500 cm³/min

Figure 1a

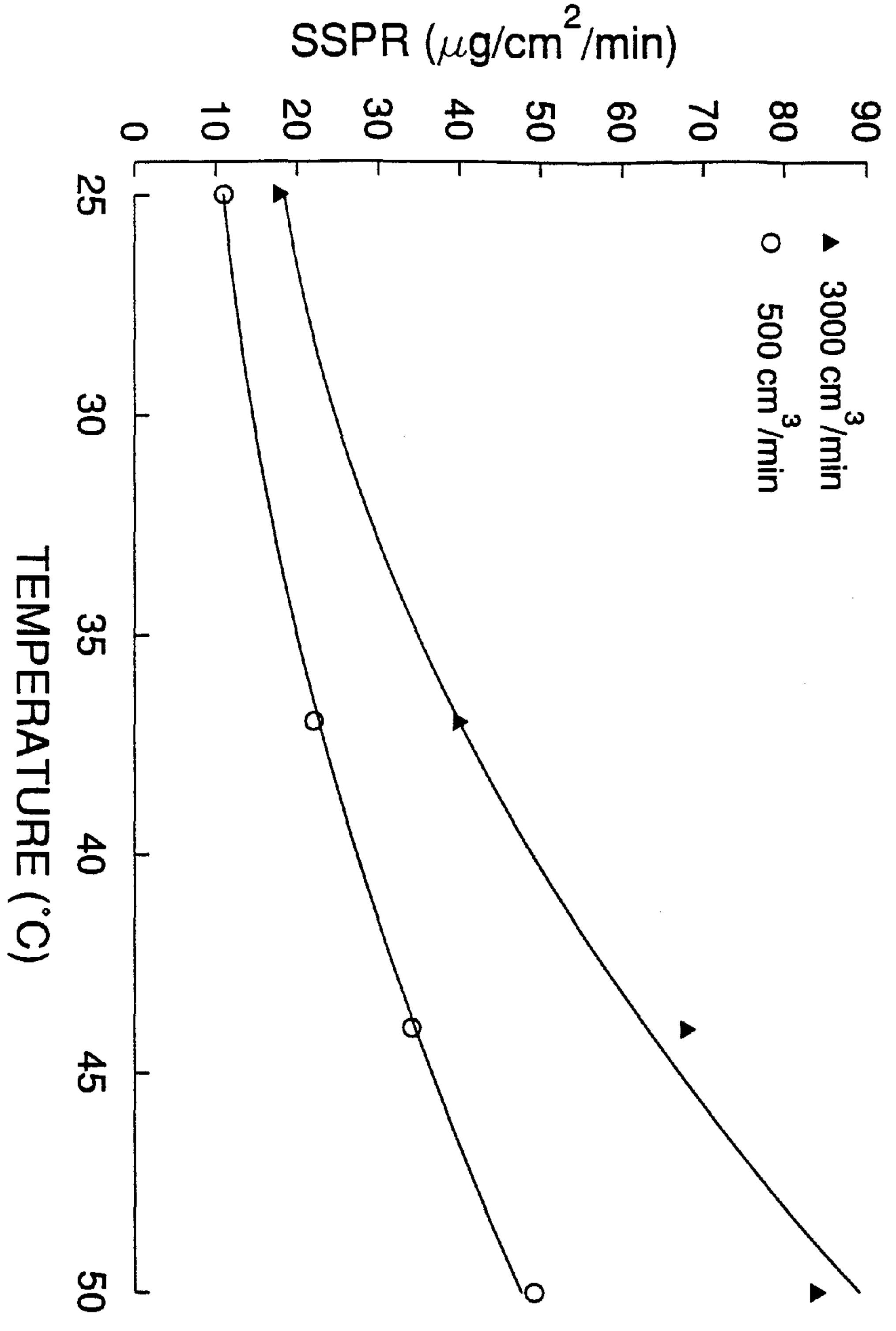
SSPR (μg/cm²/min)
0
10
20
30
40
50
60
70
80
90
25
30
35
40
45
50
TEMPERATURE (°C)
▲ 3000 cm³/min
○ 500 cm³/min

Figure 1b

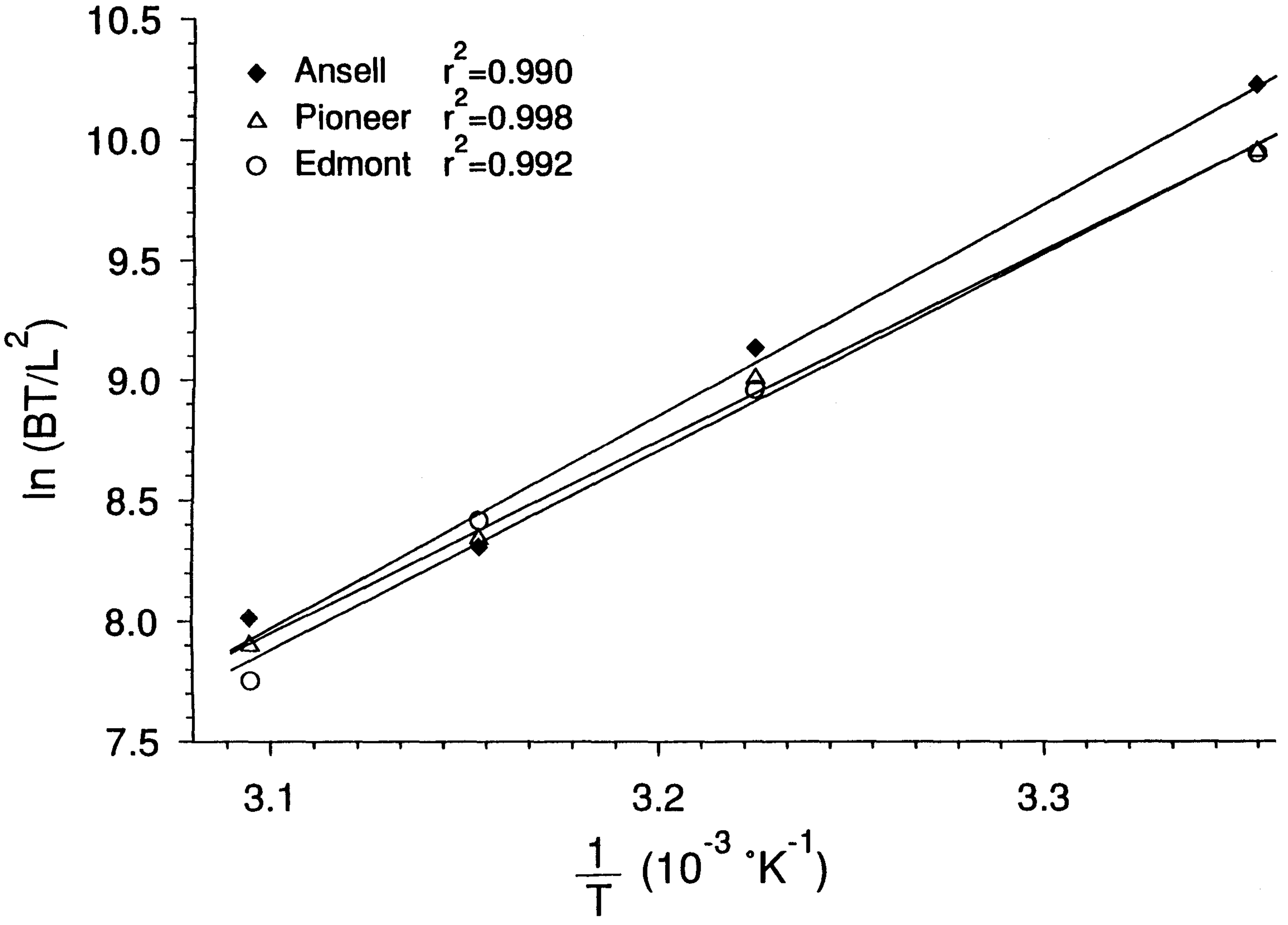
10.5
10.0
9.5
9.0
8.5
8.0
7.5
ln (BT/L^2)
3.1
3.2
3.3
$\frac{1}{T}$ (10^{-3} °K^{-1})
◆ Ansell r^2=0.990
△ Pioneer r^2=0.998
○ Edmont r^2=0.992

Figure 2a

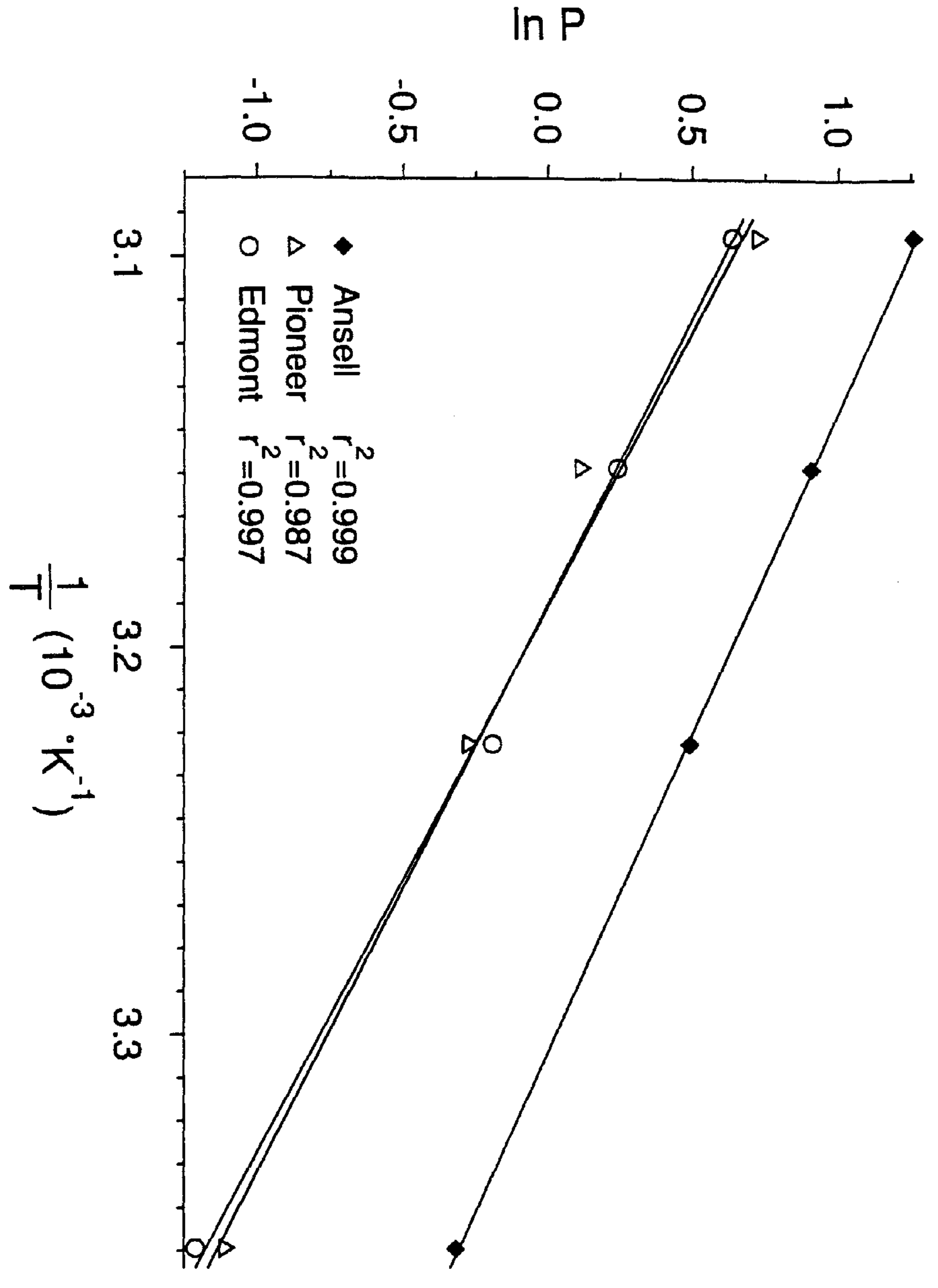
ln P
1.0
0.5
0.0
-0.5
-1.0
◆ Ansell r^2=0.999
△ Pioneer r^2=0.987
○ Edmont r^2=0.997
3.1
3.2
3.3
$\frac{1}{T}$ (10^{-3} °K^{-1})

Figure 2b

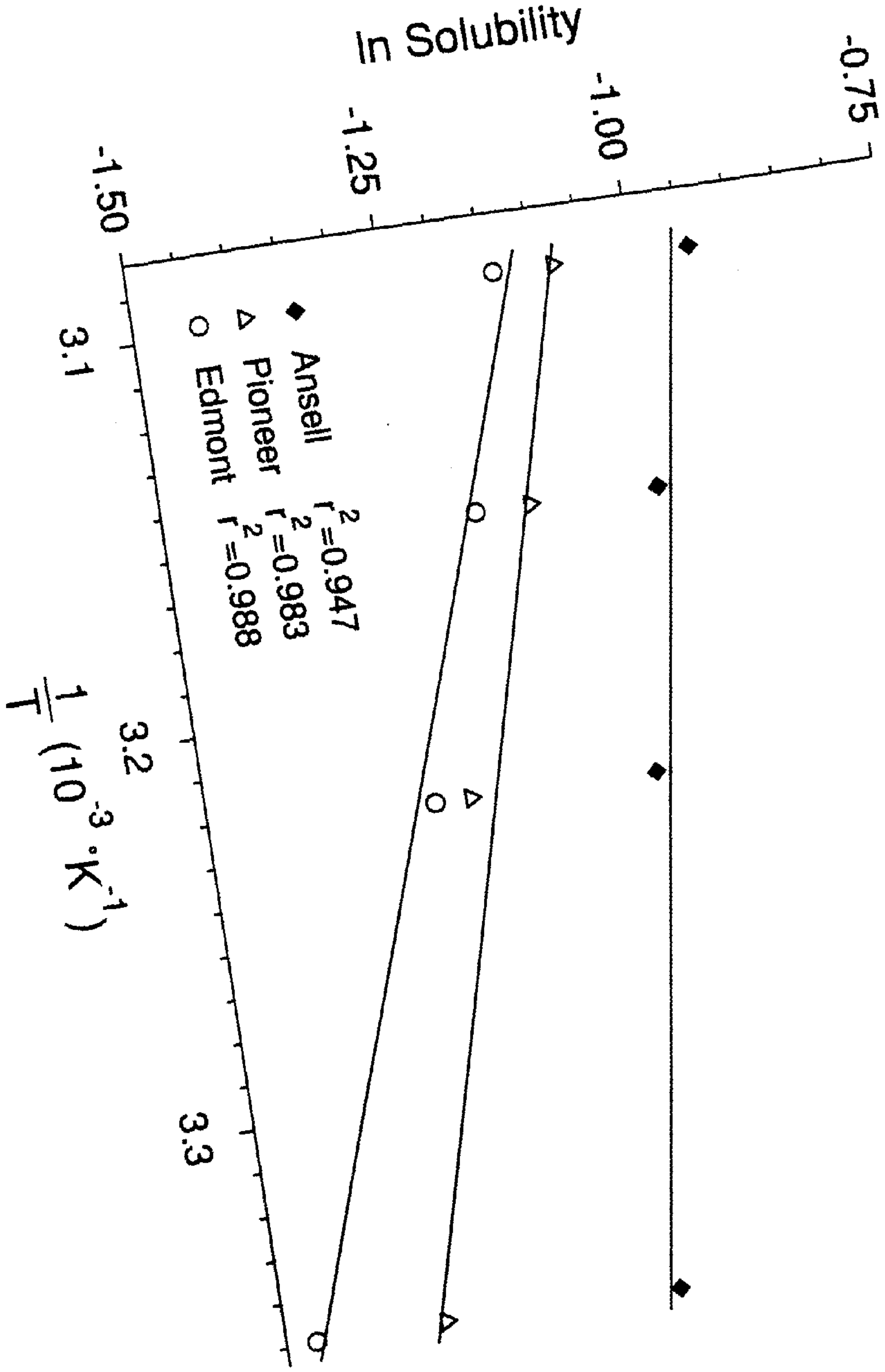
ln Solubility
-0.75
-1.00
-1.25
-1.50
3.1
3.2
3.3
1/T (10^-3 °K^-1)
◆ Ansell r²=0.947
△ Pioneer r²=0.983
○ Edmont r²=0.988

Figure 3

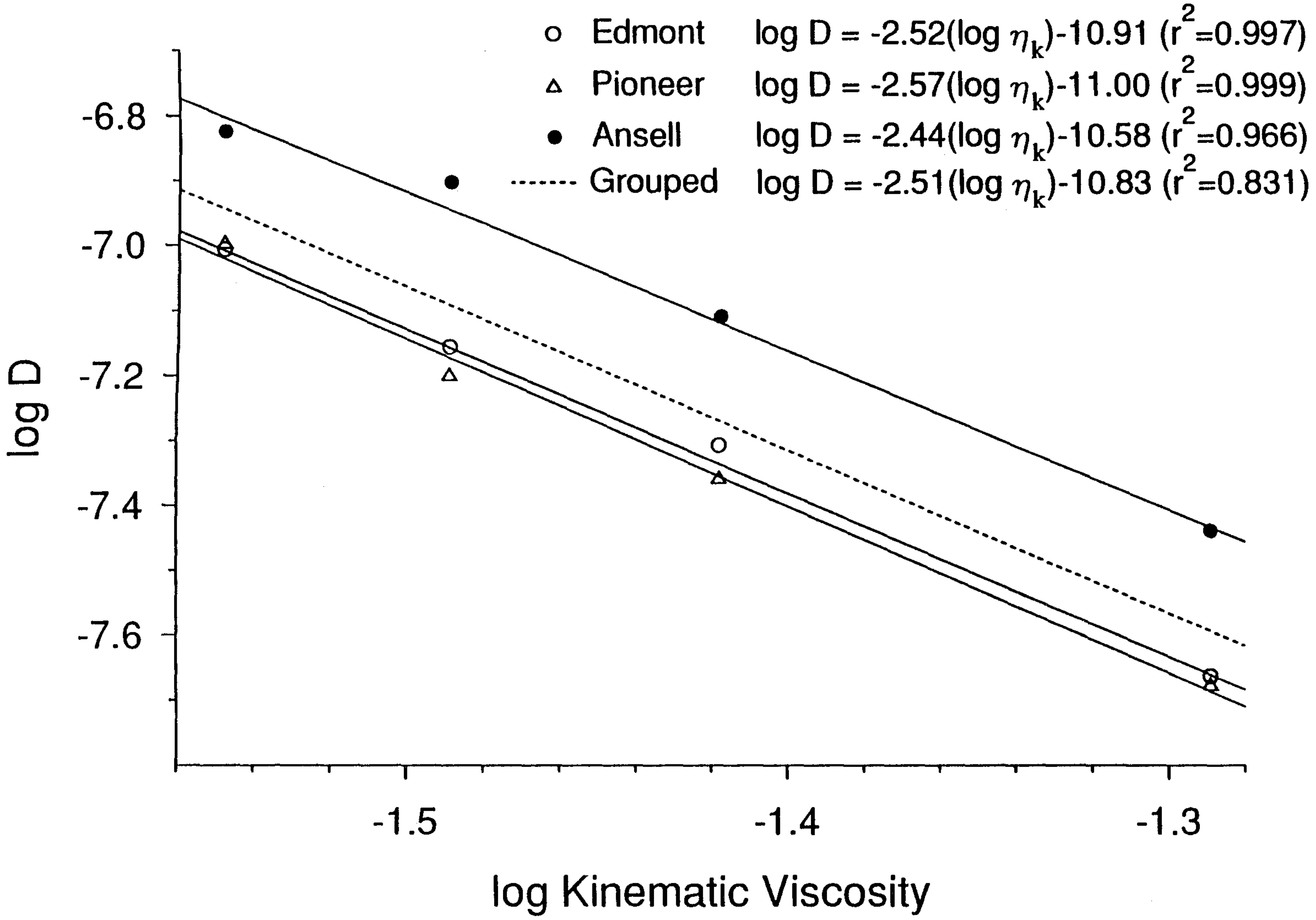
○ Edmont log D = -2.52(log η_k)-10.91 (r^2=0.997)
△ Pioneer log D = -2.57(log η_k)-11.00 (r^2=0.999)
● Ansell log D = -2.44(log η_k)-10.58 (r^2=0.966)
------ Grouped log D = -2.51(log η_k)-10.83 (r^2=0.831)
log D
-6.8
-7.0
-7.2
-7.4
-7.6
-1.5
-1.4
-1.3
log Kinematic Viscosity

Figure 4

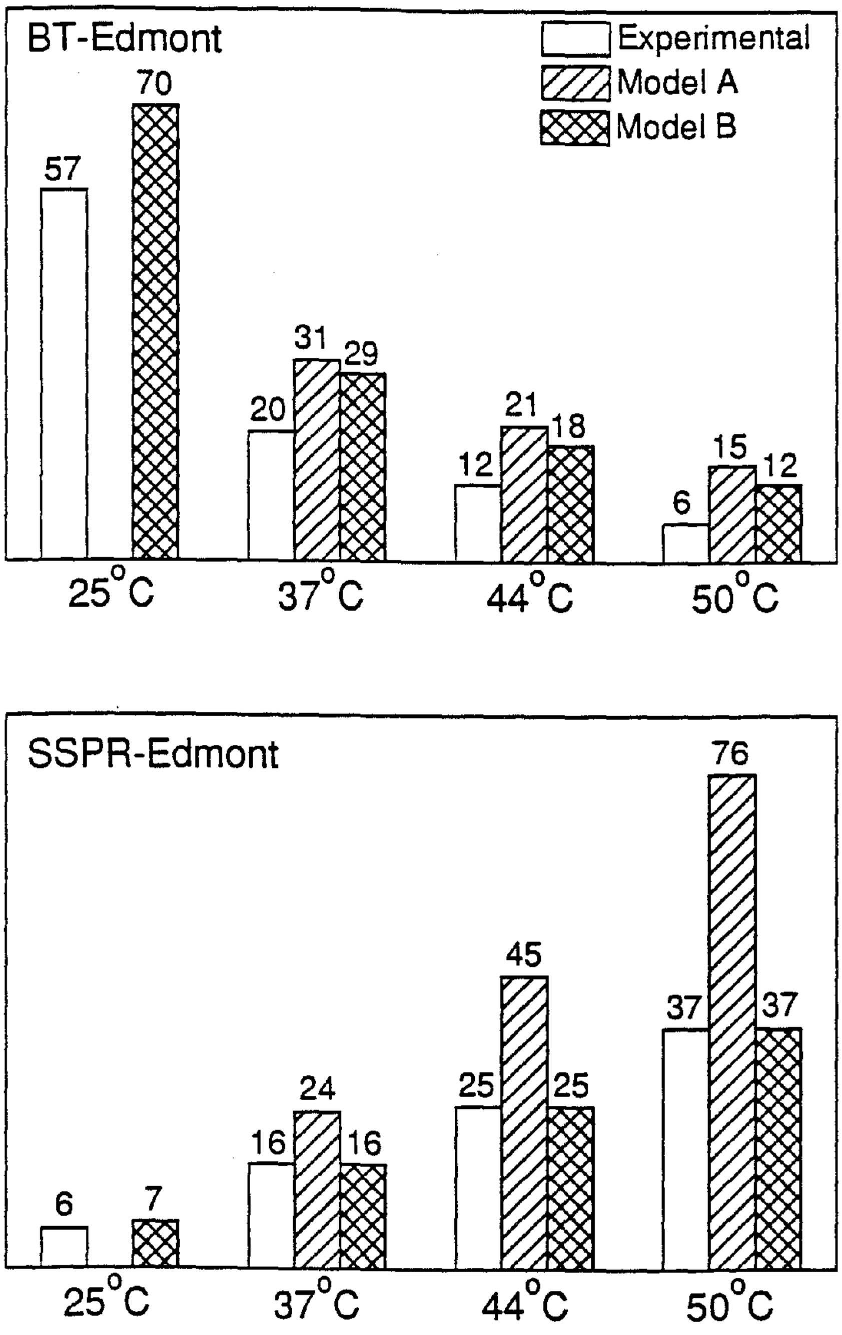
BT-Edmont
Experimental
Model A
Model B
57
70
20
31
29
12
21
18
6
15
12
25°C
37°C
44°C
50°C
SSPR-Edmont
6
7
16
24
16
25
45
25
37
76
37
25°C
37°C
44°C
50°C

Figure 5

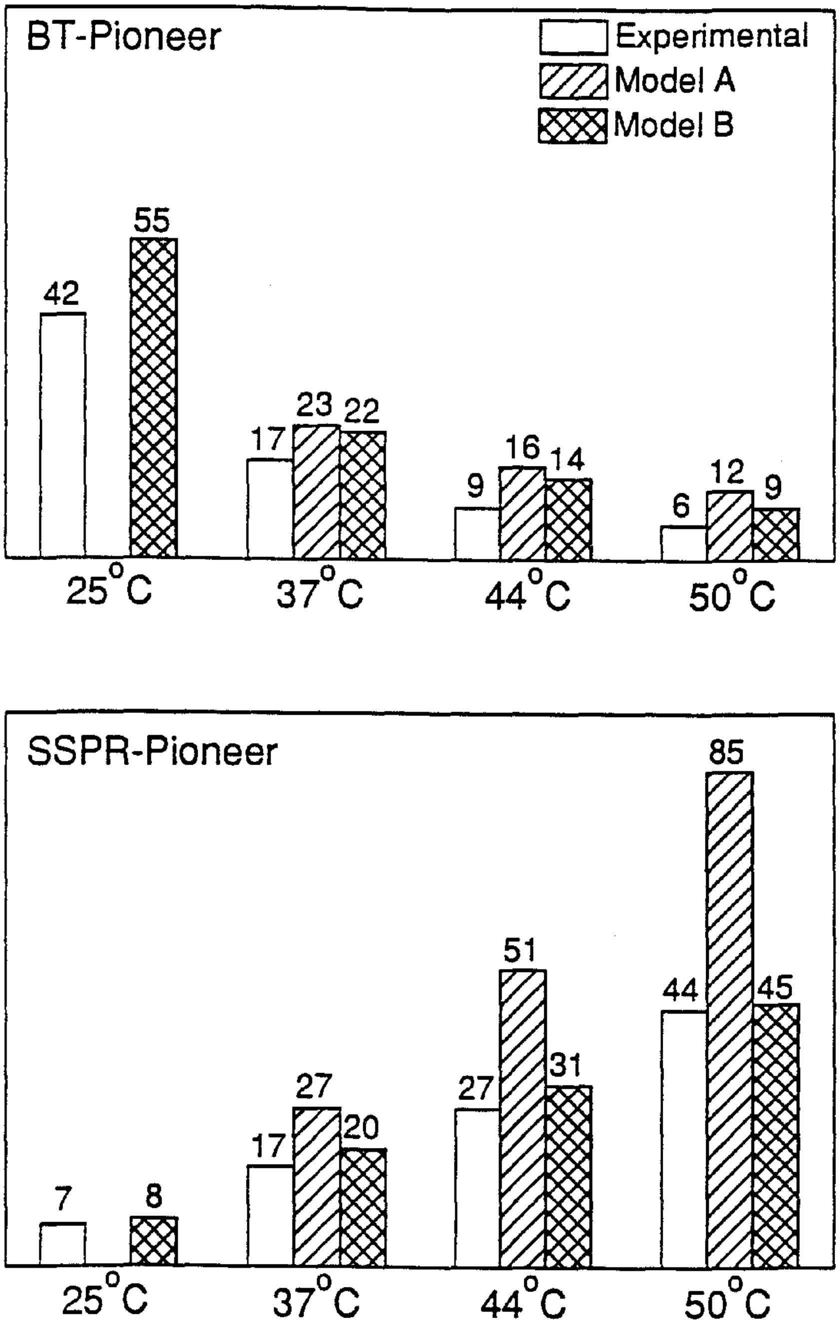
BT-Pioneer
Experimental
Model A
Model B
42
55
17
23
22
9
16
14
6
12
9
25°C
37°C
44°C
50°C
SSPR-Pioneer
7
8
17
27
20
27
51
31
44
85
45
25°C
37°C
44°C
50°C

Figure 6

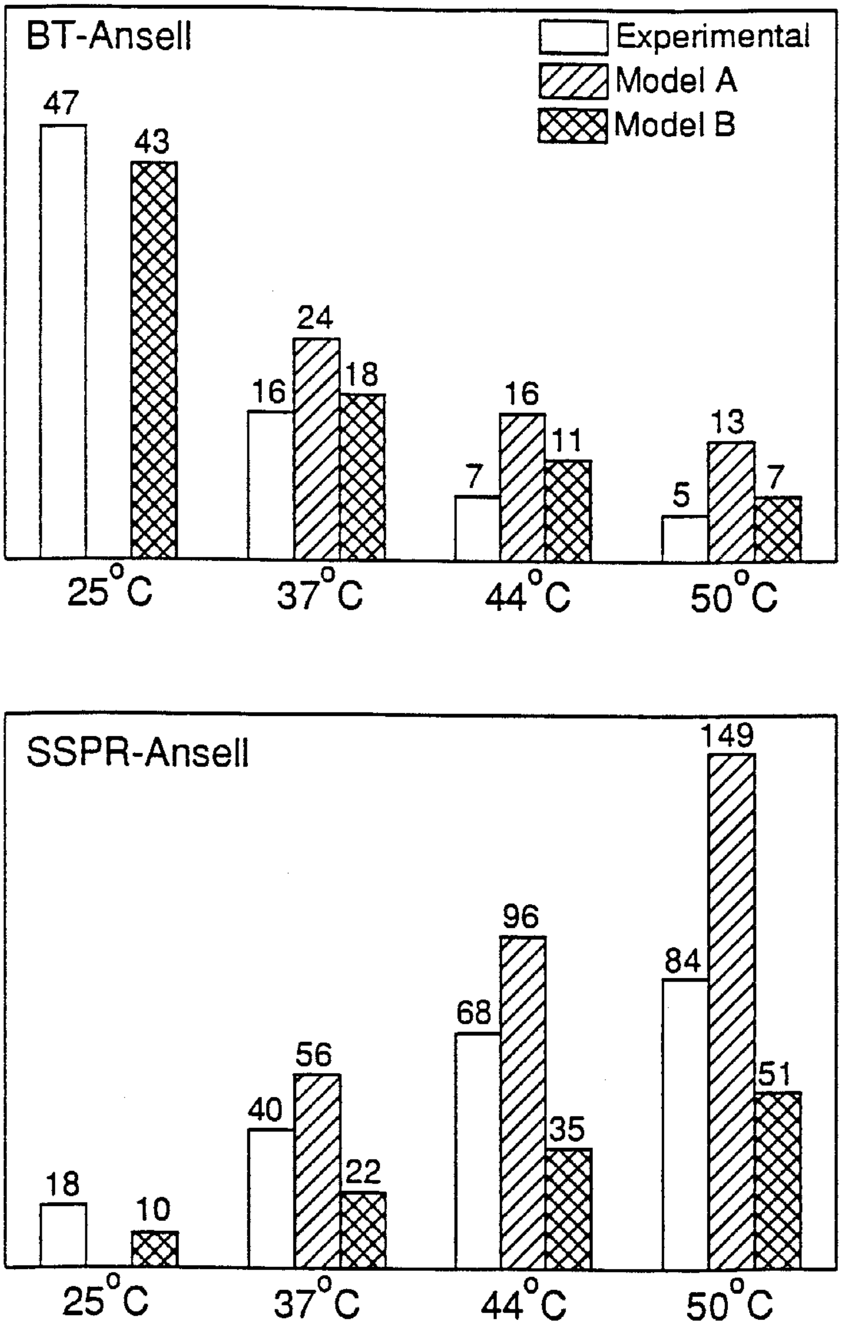
BT-Ansell
Experimental
Model A
Model B
47
43
24
16
18
16
7
11
13
5
7
25°C
37°C
44°C
50°C
SSPR-Ansell
149
96
84
68
56
40
51
35
22
18
10
25°C
37°C
44°C
50°C

Figure 7

Chapter 4

The Use of Solubility Parameters to Predict Equilibrium Solvent Solubilities in Chemical Protective Clothing

INTRODUCTION

The most widely accepted models of solvent permeation through polymeric CPC materials are based on Fick's laws of diffusion,[1,2] where the rate of permeation is viewed as a combined function of the solubility, S, and rate of diffusion of the solvent in the CPC sample. The latter quantity is usually expressed in terms of the diffusion coefficient, D. Attempts to predict permeation behavior therefore usually focus on establishing correlations between measurable physical or chemical properties of the solvent and CPC-polymer and the parameters S and D.

Recent work by Goydan et al. represents the most comprehensive effort to develop predictive CPC-permeation models for industrial hygiene applications.[3-5] In their approach, solvent/CPC solubility values are predicted using a molecular group-contribution (MGC) method which is based on the cumulative interactions of the functional groups of the CPC polymer with those of the permeating solvent. While the computations are somewhat involved, this approach has yielded fairly accurate estimates of solubility (often within a factor of 2 of experimentally determined values) for a wide range of solvents in common CPC polymers such as natural rubber, butyl rubber and low-density polyethylene. However, estimates for more polar polymers such as nitrile were somewhat less accurate. The approach is also limited by the fact that group-contribution parameters are currently available for only certain functional groups and polymers. In addition, the influence of temperature and CPC manufacturing variables (e.g., polymer crosslinking, fillers, etc) are not easily addressed. While group-contribution parameters are apparently known for the relevant carbon-fluorine functional groups in Viton^{R},[3] the MGC approach has not been successfully applied to solvent permeation through this material.

Other approaches to predicting the permeation of solvents through CPC materials have focused on empirical correlations between solubility and permeation resistance. Several investigations have shown that CPC materials that absorb large amounts of solvent upon immersion generally exhibit shorter breakthrough times and/or higher steady-state permeation rates.[6-8] However, the correlations observed have not permitted quantitative predictions of BT and SSPR. An obvious shortcoming is that the use of solubility alone fails to account for the kinetics of the permeation process (i.e., diffusion rate). This approach also suffers from the need for experimental determination of solvent uptake on a case-by-case basis.

Solvent/CPC permeation can also be modelled using solubility parameters. The solubility parameter of a substance (e.g., a solvent or polymer) is a relative index of intermolecular interaction energy.[9] The three-dimensional solubility parameter partitions this interaction energy into

three components corresponding to dispersion, dipolarity, and hydrogen-bonding. In general, substances with similar solubility parameters will be mutually soluble. Use of solubility parameter differences as a semi-quantitative measure of solvent-polymer compatibilities has been applied with some success to the formulation of inks, coatings, resins, lubricants, etc.[10-13] This concept has also been used to correlate the permeation of solvents and solvent mixtures through CPC materials.[14-19]

One potential advantage of using solubility parameters to predict permeation behavior is that solubility parameter values for a large number of solvents and polymers are available.[10,11] Thus, predictions can be made without experimental testing. Solubility parameters for materials without published values can be derived experimentally by established methods.[16,21] By measuring solubility parameters of actual CPC samples (rather than their pure polymer components alone), account can be taken of changes in product formulations that might affect permeation. It is also possible to predict the variation in solubility parameter values with temperature, and to determine solubility parameters for solvent mixtures.[9] Thus, a number of important factors affecting permeation can be addressed using the solubility parameter approach.

Several reports have shown that the difference in solubility parameters between a solvent or solvent mixture and a CPC polymer is inversely related to the permeation resistance of the CPC material.[14-19] However, these correlations have been semi-quatitative, at best, and there has yet to be established any rigorous basis for the use of solubility parameters in the context of accepted permeation theory.

In this chapter, equations relating the solubility parameters of a solvent and CPC polymer to the equilibrium solubility are derived from the Flory-Huggins polymer solution theory.[22] An expression based on the Flory-Rehner equation is then presented which accounts for the effect of polymer crosslinking on solubility.[23] The means for using these equations to estimate equilibrium solvent/CPC solubilities based on three-dimensional solubility parameters is then described. Also presented are equations describing how the solubility parameter values change with temperature. Published results of immersion testing of Viton[R] with 39 organic solvents are used to determine adjustable weighting factors. A subset of 15 solvents is used to demonstrate how to account for temperature with this approach and to show that temperature is predicted to have a relatively minor effect on solubility between 25 and 37C. The entire data set is then used to assess the accuracy of the model.

THEORETICAL BACKGROUND AND MODEL DEVELOPMENT

The first step in the permeation of a solvent through a CPC polymer is dissolution of the solvent in the surface of the CPC sample. Since this is equivalent to mixing of the two pure components, it can be described by the thermodynamic relationship,

$$\Delta G_m = \Delta H_m - T\Delta S_m \qquad (1)$$

where G_m is the Gibbs free energy of mixing, H_m is the heat (enthalpy) of mixing, T is the absolute temperature, and S_m is the entropy of mixing. In order for mixing to occur spontaneously, ΔG_m must be negative, implying that ΔH_m must be small relative to $T\Delta S_m$.

For an ideal solution ΔH_m is zero. However, for real solutions ΔH_m is typically positive, and its magnitude is a function of the intermolecular interaction energies of the mixture components. The theory of regular solutions was developed to account for this feature of solvent mixtures, and the simple solubility parameter, δ_S, was adopted to quantify ΔH_m for different mixtures.[25,26]

For a low-molecular-weight solvent, δ_S is defined as the square root of the molar energy of vaporization per unit volume. Values of δ_S for volatile solvents can be determined by measuring the heat of vaporization calorimetrically or by calculating the heat of vaporization from vapor pressure data.[27,28] For polymers, δ_S values can be derived from the molar attraction constants (analogous to group-contribution parameters)[29] of the constituent functional groups or estimated by immersion in a series of solvents of known δ_S values.[9] In the latter case, the polymer is assigned the δ_S value of the solvent(s) in which it most readily dissolves (or in which it shows the greatest degree of swelling for the case of cross-linked or cured polymers).

The solubility parameters of two mixture components, 1 and 2, can be related to the partial molar enthalpy of component 1, ΔH_{m1}, by the following expression where component 1 is assumed to be the "solute" present in low concentration and component 2 is assumed to be the "solvent" present in excess:

$$\Delta H_{m1} = V_1(\delta_1 - \delta_2)^2 \qquad (2)$$

where ϕ_2 is the volume fraction of 2, V_1 is the molar volume of 1, and it is assumed that no change occurs in the total volume upon mixing (i.e., the volume of the mixture is equal to the sum of the volumes of the two pure components).[26] Thus, similar values of δ will lead to a small ΔH_{m1}, which favors mixing since ΔG_m becomes more negative.

For mixtures of solvents of similar size and shape, regular solution theory states that entropy changes follow ideal behavior. For mixtures of solvents with polymers, there are additional considerations associated with the fact that the polymers consist of long chains of molecules that may be connected into networks via cross-linking. In general, the entropy changes accompanying dissolution of polymers are lower than those observed for low-molecular-weight species. The Flory-Huggins theory of polymer solutions accounts for these entropy changes using a three-dimensional lattice to model the configurations of a polymer in a solvent.[22] An expression can be derived from this theory for the partial molar free energy of mixing (ΔG_{m1}) of a low-molecular-weight solvent (component 1) with an infinite-molecular-weight polymer (component 2):

$$\Delta G_{m1} = RT \ln a_1 = RT(\ln \phi_1 + \phi_2 + \chi\phi_2^2) \qquad (3)$$

where a_1 is the activity of the solvent, ϕ_1 and ϕ_2 are the volume fractions of the solvent and polymer, respectively, and χ is a dimensionless interaction parameter. To a first approximation, the first two terms on the right-hand side of Equation 8 describe the combinatorial entropy of mixing, and the third term describes the enthalpy due to exchange interactions occuring upon mixing.

For a pure solvent in equilibrium with a solvent-polymer mixture (i.e., where $\ln a_1 = 0$), Equation 3 leads to the following expression for χ in terms of the volume fraction of the polymer (or the solvent since $\phi_1 = 1-\phi_2$) :

$$\chi = -\ln(1-\phi_2)/\phi_2^2 - 1/\phi_2 \tag{4}$$

In this expression it is assumed that the solvent partitions into the polymer but the polymer does not partition into the solvent.

For any value of χ, there will be a unique value of ϕ_2 (or ϕ_1) which can then be expressed in more conventional units of solubility (e.g., g/cm^3). Thus, if χ is known for a given solvent/polymer pair, the equilibrium solvent solubility can be obtained. For the condition of unit activity, χ approaches 0.5 as ϕ_2 approaches zero (i.e., in the limit of infinitely dilute polymer).

Cross-linked Polymers

Equation 4 was derived under the assumption that the polymer was amorphous and consisted of linear chains. For cross-linked polymers the expression must be modified to account for the elastic stiffness of the cross-linked network relative to the linear polymer. The free energy change of the solvent-polymer system can be expressed as the sum of the contributions from mixing and elasticity:[32,33]

$$\Delta G = \Delta G_M + \Delta G_{el} \tag{5}$$

where ΔG_{el} represents the contribution of elastic effects of the cross-linked polymer network to the total free energy change. This term can be derived from the theory of rubber-like elasticity[23] and expressed as

$$\Delta G_{el} = 2V_1K(\phi_2^{1/3} - \phi_2/2) \tag{6}$$

where K is a constant derived from stress-strain measurements at low degrees of elongation.[33-35]

At equilibrium $\Delta G_m = \Delta G_{el}$ or

$$-RT(\ln \phi_1 + \phi_2 + \chi\phi_2^2) = 2V_1K(\phi_2^{1/3} - \phi_2/2) \tag{7}$$

Solving for χ gives

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

where ν = K/RT is the average density of cross-links in the polymer. It is assumed in Equation 8 that there are four segments at each point of cross-linking and that the volume fraction of polymer is unity during the cross-linking process.[35]

As with Equation 4, a given value of χ will yield unique values of ϕ_1 and ϕ_2 which can be used to calculate the solubility (in g/cm^3) of the solvent in the polymer.

Relating δ to χ

The interaction parameter is related to the solubility parameters of the mixture components by

$$\chi = \chi_S + \chi_H = \chi_S + V_1(\delta_1 - \delta_2)^2/(RT) \qquad (9)$$

where χ_S is an "entropic" correction factor that accounts for disparities between χ and χ_H (where simple δ values are used). Disparities have been attributed to nonrandom mixing effects arising from specific chemical interactions between the mixture components.[30] An accurate characterization of these effects could not be achieved within the scope of the Flory-Huggins theory. Thus, while the enthalpic term (χ_H) can be calculated from solubility parameters, the entropic correction term (χ_S) must be approximated or determined experimentally (e.g., from immersion testing).

It should be noted that for many polymer solutions the Flory-Huggins theory provides only approximate predictions of solubility. Deviations stem largely from violations of the assumption of zero excess volume change upon mixing, and the consequent effects on the entropy and enthalpy changes[31] (note: the assumption of no excess volume change does not mean that polymer swelling does not occur but rather that the total volume of the mixture is equal to the sum of the volumes of the two components). In addition, χ can change with polymer concentration. In studies of polymer-solvent phase equilibria, errors due to these factors are generally small for moderate-to-high polymer concentrations, but can be large in the dilute-polymer region.[31] For systems of interest here, where a solvent permeates through an intact polymer membrane, the polymer concentrations remain high and errors from these factors should be small.

Three-Dimensional Solubility Parameters

Another limitation to this theory concerns the dependence on simple solubility parameters to estimate the mixing enthalpy. The use of simple solubility parameters assumes that interactions occurring between mixture components are governed solely by dispersive intermolecular forces, i.e., van der Waals forces.[26] Equation 9 is strictly applicable, therefore, only to mixtures of non-polar molecules. To expand the solubility parameter concept, several researchers have explored ways of partitioning the solubility parameter to account for additional specific interactions between molecules.[9,27] This has led to the development of the three-dimensional (3-D) solubility parameter[11-13] where a solvent or polymer is assigned solubility parameters that correspond (approximately) to each of three interaction forces: dispersion, dipole-dipole, and hydrogen-bonding (or charge transfer). The total 3-D solubility parameter, δt, is represented as the sum of these solubility parameters:

$$\delta_t = \delta_d + \delta_p + \delta_h \qquad (10)$$

where subscripts d, p, and h represent dispersion, polar (i.e., dipole-dipole), and hydrogen bonding forces, respectively. Differences in solubility parameters between two materials are then calculated as:

$$\delta_1 - \delta_2 = [a(\delta_{d1}-\delta_{d2})^2 + b(\delta_{p1}-\delta_{p2})^2 + b(\delta_{h1}-\delta_{h2})^2]^{1/2} \quad (11)$$

where a and b are correction factors used to weight the dispersion, polarity and hydrogen-bonding terms.[36] Assignment of 3-D solubility parameter values is typically based on correlations established from solubility testing.[11,16,21] As a result, both enthalpic and entropic contributions to the solubility interaction are incorporated into the 3-D values. In the context of the Flory-Huggins theory, the use of 3-D solubility parameters rather than simple solubility parameters to estimate χ_H should eliminate or reduce the magnitude of the χ_S term.

A comment about the weighting factors, a and b, in Equation 11 is appropriate at this point since their importance has been largely overlooked in previous approaches to using solubility parameters in the context of permeation studies. In several studies a value of a=4 has been invoked in order to render the "solubility zone" around a given polymer more spherical. But the use of such weighting (correction), as emphasized by Hansen and Beerbower,[36] is necessary to obtain proper solubility correlations. From the derivations presented by Weimer and Prausnitz[37] the b factor is seen to account for with the induction of polarity or hydrogen-bonding interactions in non-polar materials by more polar or hydrogen-bonded materials. In effect, b, which is generally less than or equal to one, reduces the weight placed on large differences in δ_p and δ_h between two materials, rendering the total difference smaller and leading to higher predicted solubilities. Values of b for a few types of polymers and solvents are listed in reference 36 according to chemical class. It is clear from this that such weighting factors will vary depending on the structures of the interacting solvents and polymers.

Temperature Effects

Inspection of Equations 8 and 9 shows that solubility estimates will be affected by temperature. In addition to the direct temperature effect, the molar volume of the solvent (V_1)and the solubility parameters of the solvent and polymer will change with temperature as well. The change in V_1 with temperature parallels the change in density (since they are related by the molecular weight. Values of solvent molar volumes and densities at different temperatures can be found in standard references for many solvents.[38]

Changes in solubility parameter values with temperature are also based on volume changes expressed in terms of the volume thermal expansion coefficient, α, defined by

$$\alpha = 1/V(dV/dT) \quad (12)$$

for solvents and by

$$\alpha = 1/\rho(dv/dT) \quad (13)$$

for polymers, where ρ is the polymer density and v is the polymer specific volume. The relationships between the thermal expansion coefficients and the solubility parameters are given in Equations 14-16 below:[36]

$$d\delta_d/dT = -1.25\alpha\delta_d \tag{14}$$

$$d\delta_p/dT = -\delta_p\alpha/2 \tag{15}$$

$$d\delta_h/dT = -\delta_h(1.22 \times 10^{-3} + \alpha/2) \tag{16}$$

As shown by these equations, the solubility parameters will decrease with increasing temperature. The effect on the solubility parameter difference between a solvent and polymer will depend on their respective α values. Since these are generally of the same order of magnitude, the overall effect of temperature usually is not very large. This is supported by experimental data indicating in general a rather small effect of temperature on the equilibrium solubility of solvents in polymers[39]. The data on NMP in natural rubber presented in Chapter 3 indicates that the above approach may, however, slightly underestimate the effect of temperature on solubility.

The method of calculating S depends on whether the polymer is assumed to be cross-linked or uncross-linked. In all cases, Equation 9 is used to determine a value of χ which is then used to calculate ϕ_1 from Equation 4 (uncross-linked case) or Equation 8 (cross-linked case). Multiplication of ϕ_1 by the solvent density gives S in grams of solvent per cm^3 of solvent-swollen polymer.

The value of χ_S used in Equation 9 also depends on whether simple or 3-D solubility parameters are used and on whether a cross-linked or uncross-linked polymer is assumed. While the actual value of χ_S will be different for each solvent, it is necessary for the purpose of prediction to assign a specific (fixed) value to this term. For the uncross-linked polymer cases, χ is constrained to a minimum value of 0.5. Accordingly, when using 3-D solubility parameters to estimate χ a value of $\chi_S = 0.5$ is adopted, since values of $\chi_H = 0$ are possible. For the cross-linked polymer cases there is no such limiting value of χ, and a value of $\chi_S = 0$ is adopted. Recall that the 3-D solubility parameter difference is assumed to account implicitly for specific chemical interactions between the solvent and CPC, thereby obviating the need to empirically estimate χ_S. Where simple solubility parameters are used it is necessary to estimate χ_S from immersion-test data. Given the previously stated shortcomings of using simple solubility parameters, they will not be dealt with in this model. Rather we will focus exclusively on the cross-linked polymer case using 3-D solubility parameters.

Predicted values of χ are determined using Equation 9. Predicted values of ϕ_1 are then determined by iterative solution of Equations 8, from which values of S are calculated as described above. Arranging the solvents by chemical class can then permit selection of the weighting factor values so as to optimize agreement with experimental solubilities.

MODEL EVALUATION FOR VITON^R

Table I lists the solvents used to develop and evaluate the predictive method. Viton^R is a registered trademark of the DuPont Company referring to a copolymer of vinylidene fluoride and hexafluoropropylene. Immersion test weight gains for samples cut from North Viton gloves were obtained from the report of Perkins and Tippit[15] based on the work of Holcomb.[16] The 3-D solubility parameters for the solvents were obtained from reference 22. The 3-D solubility parameters used for the Viton were $\delta_D = 17.0$, $\delta_P = 10.6$, and $\delta_H = 6.1$ $(J/cm^3)^{1/2}$ as determined by Perkins and Tippit.[15]

Experimental solubility values were calculated from published immersion-test weight changes measured at 37°C, assuming a polymer density of $(1.86\ g/cm^3)$.[40] The changes in the molar volumes of the solvents with temperature were obtained for a subset of 15 solvents from the literature.[38] These values were used to calculate the volume thermal expansion coefficients according to Equation 12. An α value of 9×10^{-4} $°K^{-1}$ was used for Viton based on values of structurally similar fluorinated polymers.

Estimates of Viton^R cross-linking at high levels of elongation using stress-strain data obtained from the glove manufacturer yielded unrealistically high values for the cross-link density (i.e., $\nu > 10^{-2}$ cm^{-3}). In retrospect this was to be expected because the elastic limit is generally exceeded for polymers at high levels of strain, and the relationship between cross-link density and stress-strain behavior is valid only below the elastic limit.[35] Therefore, a value of $\nu = 1.2 \times 10^{-4}$ cm^{-3}, typical of lightly-cross-linked polymers, was assumed.[33,41]

The solubility parameter difference between Viton and each solvent was calculated using Equation 11 and solubility parameter values found in the literature without correcting for temperature. This value was then used in Equation 9 to determine the uncorrected predicted χ value from which the volume fraction was obtained using Equation 8. Unweighted i.e., (uncorrected) values of S were then determined using the solvent densities at 25C (298K). Corrected values of S were determined as described above. Note that this approach is, in a sense, flawed, because predicted S values are being calulated at 25C and then corrected based on experimental values at 37C. While the accuracies of the predicted S values are not in question, the weighting factors may actually be slightly different than given below. At the time of writing this report, the proper temperature corrections could not be performed on all of the solvents. To demonstrate that the error in the correction factors is rather small, however, predicted S values at both 37 and 25C were calculated for a subset of 15 solvents (see below).

RESULTS AND DISCUSSION

Figure 1 shows plots of χ versus ϕ_1 for uncross-linked (upper curve) and cross-linked (lower curves, $\nu = 5 \times 10^{-4}$ and $V_1 = 60$ and $106\ cm^3/mole$) polymers using Equations 4 and 8, respectively. This range of V_1 includes that of the subset of 15 solvents used in this study and many common organic solvents. For higher values of χ, it is seen that cross-linking has little effect on the predicted volume fraction, but for lower χ values the predictions from the two equations depart significantly. The lower curves illustrate the dependence of the solubility estimates on the solvent molar volume and the finite limit on the solubility. A finite limit for ϕ_1 is consistent with cross-linking since cross-linked polymers cannot fully dissolve without breaking covalent bonds. The shape of the curve and the maximum ϕ_1 predicted by Equation 8 also will depend on the cross-link density, with lower degrees of cross-linking leading to higher ϕ_1 values. For example, for $\nu = 10^{-5}$, the limiting value of ϕ_1 increases from 0.843 to 0.974 (for V_1=60 cm^3/mole). As the degree of cross-linking is reduced further, Equations 4 and 8 predict very similar ϕ_1 values over the entire range of χ.

Table II presents the experimental solubility values (S_E), predicted solubility values (S_{Pu} and S_{Pc} for uncorrected and corrected cases, respectively), and the ratios of predicted-to-experimental values. The uncorrected values were in many cases reasonably close to experimental values (e.g., within a factor of 2). However, in several cases there were large errors. Most of the uncorrected values underestimated the experimental values (e.g., the aromatic and aliphatic hydrocarbons and aliphatic alcohols), although in a few cases the opposite was found. In the former cases, the low estimates were assumed to arise from the large differences in the polarity and hydrogen-bonding terms of the solubility parameters, which were subsequently weighted so as to reduce their influence on the toal solubility parameter difference. For the cases where uncorrected S values were greater than experimental S values, the dispersion weighting factor (a) was increased so as to increase the total solubility parameter difference. While these corrections may seem arbitrary, they are perfectly reasonable since the importance of each of the three solubility parameter interactions would be expected to change from solvent to solvent.

In most cases, the use of one set of values of the weighting factors (a,b) resulted in fairly accurate predicted S values for all members of a chemical class. An exception this is found for the chlorinated solvents. The number of chlorine substituents and their relative positions apparently affect their solubility properties strongly.

Figure 2 presents a plot of predicted (corrected) vs. experimental solubilities, along with the coefficients obtained from linear regression. The solid line in Figure 2 is the line of perfect correlation (i.e., slope = 1). The actual slope of regression line is very close to 1, the intercept is close to zero and the r^2 value reflects the high correlation. The geometric mean of the ratios of predicted-to-experimental solubilities (r_g) was 1.08 indicating a slight tendency toward overestimation, on average. The geometric standard deviation of the ratios was 1.5 indicating a low degree of dispersion in the distribution of predicted values (i.e., reasonably high precision).

Table II presents data related to the effect of temperature on the predicted S_{Pc} values. Values for each solvent were calculated at 298°K and at 310°K. As shown, the predicted effect of temperature is not very large, amounting to less than 20% of the lower temperature value in all cases. This is consistent with experimental data reported for other polymer solvent combinations, where the effects of temperature on solubility values were quite small.[39,40] The fact that permeation rates are often strongly affected by temperature is thought to be due to the effects on the diffusion rate rather than equilibrium solubility. In a few cases, such as the ketones, the solubility is predicted to decrease with increasing temperature. This has also been observed experimentally.[39]

SUMMARY AND CONCLUSIONS

A theoretical framework for using solubility parameters to predict equilibrium solvent/CPC solubilities has been presented. This approach represents a departure from previous attempts to correlate solubility parameter differences directly with permeation rates and breakthrough times. With the current approach, separate estimates of the solvent diffusion coefficient are needed in order to predict breakthough times and permeation rates (see Chapter 5). However, the current approach is consistent with established theories of polymer solubility and permeation. The ability to account for temperature and CPC-polymer cross-linking adds to the generality of the model. However, further testing is needed to demonstrate its general utility.

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TABLE 1

Experimental and Predicted Equilibrium Solubilities of Solvents in Viton Using Uncorrected and Corrected Solubility Parameter Differences

Solvent	S_E	uncorr. S_{Pu}	ratio S_{Pu}/S_E	corr. S_{Pc}	ratio S_{Pc}/S_E
<u>Ketones</u>				(a=1, b=0.25)	
acetone	0.652	0.667	1.02	0.687	1.05
2-butanone	0.679	0.675	0.99	0.688	1.01
4-methyl-2-pentanone	0.693	0.129	0.19	0.555	0.81
3-pentanone	0.703	0.534	0.76	0.668	0.95
cyclohexanone	0.753	0.375	0.50	0.764	1.01
<u>Amides</u>				(a=1, b=0.35)	
formamide	0.025	<0.001	0.02	0.054	2.16
dimethly formamide	0.747	0.225	0.30	0.731	0.98
N-methyl pyrrolidone	0.904	0.851	0.94	0.873	0.97
2-pyrrolidone	0.491	0.045	0.09	0.361	0.74
<u>Alcohols</u>				(a=1, b=0.50)	
methanol	0.099	0.004	0.04	0.041	0.41
propanol	0.02	0.006	0.30	0.043	2.15
butanol	0.023	<0.001	<0.01	0.042	1.83
octanol	0.028	<0.001	<0.01	0.022	0.79
ethylene glycol	0.0019	<0.001	<0.05	0.005	2.63
<u>Ether-Alcohols</u>				(a=1, b=0.37)	
2-ethoxyethanol	0.272	0.035	0.13	0.265	0.97
2-butoxyethanol	0.103	-----	----	0.139	1.35
<u>Sulfur Compounds</u>					
				(a=1, b=0.60)	
carbon disulfide	0.057	0.013	0.23	0.053	0.93
				(a=1, b=0.50)	
dimethyl sulfoxide	0.481	0.149	0.31	0.502	1.04
<u>Aliphatic Hydrocarbons</u>				(a=1, b=0.20)	
hexane	0.043	<0.0001	<0.01	0.056	1.32
heptane	0.037	<0.0001	<0.01	0.037	1.03
iso-octane	0.033	<0.0001	<0.01	0.026	0.61
<u>Aromatic Hydrocarbons</u>				(a=1, b=0.28)	
benzene	0.131	0.003	0.02	0.197	1.50
toluene	0.123	0.005	0.04	0.166	1.35

xylene	0.119	0.001	<0.01	0.083	0.70
Esters				(a=1, b=0.35)	
ethyl acetate	0.745	0.188	0.25	0.646	0.87
ethylene carbonate	0.126	0.017	0.13	0.239	1.90
2-ethoxyethyl acetate	0.281	0.019	0.07	0.238	0.85
Nitriles				(a=1, b=0.65)	
acetonitrile	0.305	0.165	0.54	0.341	1.12
acrylonitrile	0.349	0.156	0.45	0.336	0.96
Aldehydes				(a=5, b=1)	
furfuraldehyde	0.246	0.609	2.48	0.304	1.24
benzaldehyde	0.161	0.556	3.45	0.118	0.73
Ethers				(a=1, b=0.22)	
dioxane	0.508	0.025	0.05	0.504	0.99
tetrahydrofuran	-----	0.317	----	0.743	----
Nitro Compounds				(a=3, b=1)	
nitropropane	0.770	0.825	1.07	0.798	1.04
nitrobenzene	0.180	0.653	3.63	0.173	0.96
Chlorinated Hydrocarbons					
				(a=6, b=1)	
methylene chloride	0.233	0.947	4.07	0.699	2.99
1,2 dichloroethane	0.192	0.312	1.62	0.113	0.59
perchloroethylene	----	-----	----	0.097	----
				(a=1, b=0.65)	
chloroform	0.234	0.133	0.57	0.307	1.31
1,1,1-trichloroethane	0.236	0.071	0.30	0.185	0.78
trichloroethylene	-----	-----	----	0.237	----
				(a=1, b=0.28)	
carbon tetrachloride	0.188	0.002	0.01	0.190	1.01

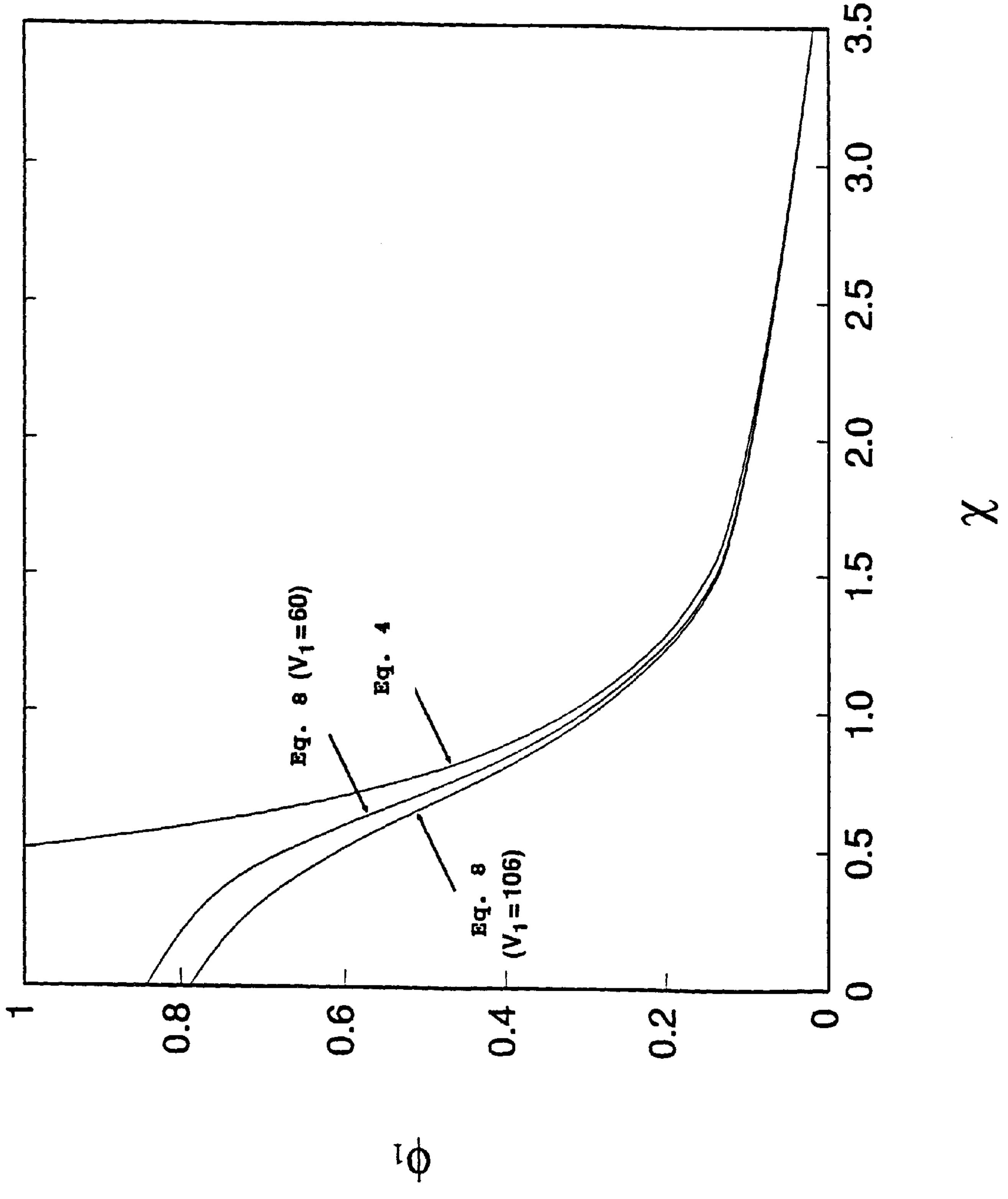
A S_E = experimental solubility values. S_{Pc} = predicted solubility values obtained using the correction factors (a,b) shown for each functional group. S_{Pu} = predicted solubility values calculated without correction factors (uncorrected).

TABLE II

Comparison of Predicted Solubilities at 25 and 37°C[A]

Solvent	S_{PC}(25°C)	S_{PC}(37°C)	ratio
acetone	0.687	0.669	0.97
3-pentanone	0.668	0.656	0.93
propanol	0.043	0.051	1.19
2-ethoxyethanol	0.265	0.294	1.11
carbon disulfide	0.053	0.061	1.15
toluene	0.166	0.179	1.08
furfural	0.304	0.363	1.19
dioxane	0.504	0.537	1.07
nitrobenzene	0.173	0.201	1.16
nitropropane	0.798	0.800	1.00
1,1,1-trichloroethane	0.185	0.199	1.08
1,2-dichloroethane	0.113	0.134	1.18
carbon tetrachloride	0.190	0.206	1.04
chloroform	0.307	0.331	1.08
methylene chloride	0.699	0.789	1.14

[A] S_{PC} is the equilibrium solubility predicted using correction the factors listed in Table I.



ϕ_1
1
0.8
0.6
0.4
0.2
0
0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
χ
Eq. 8 (V_1=60)
Eq. 4
Eq. 8 (V_1=106)

Figure 1

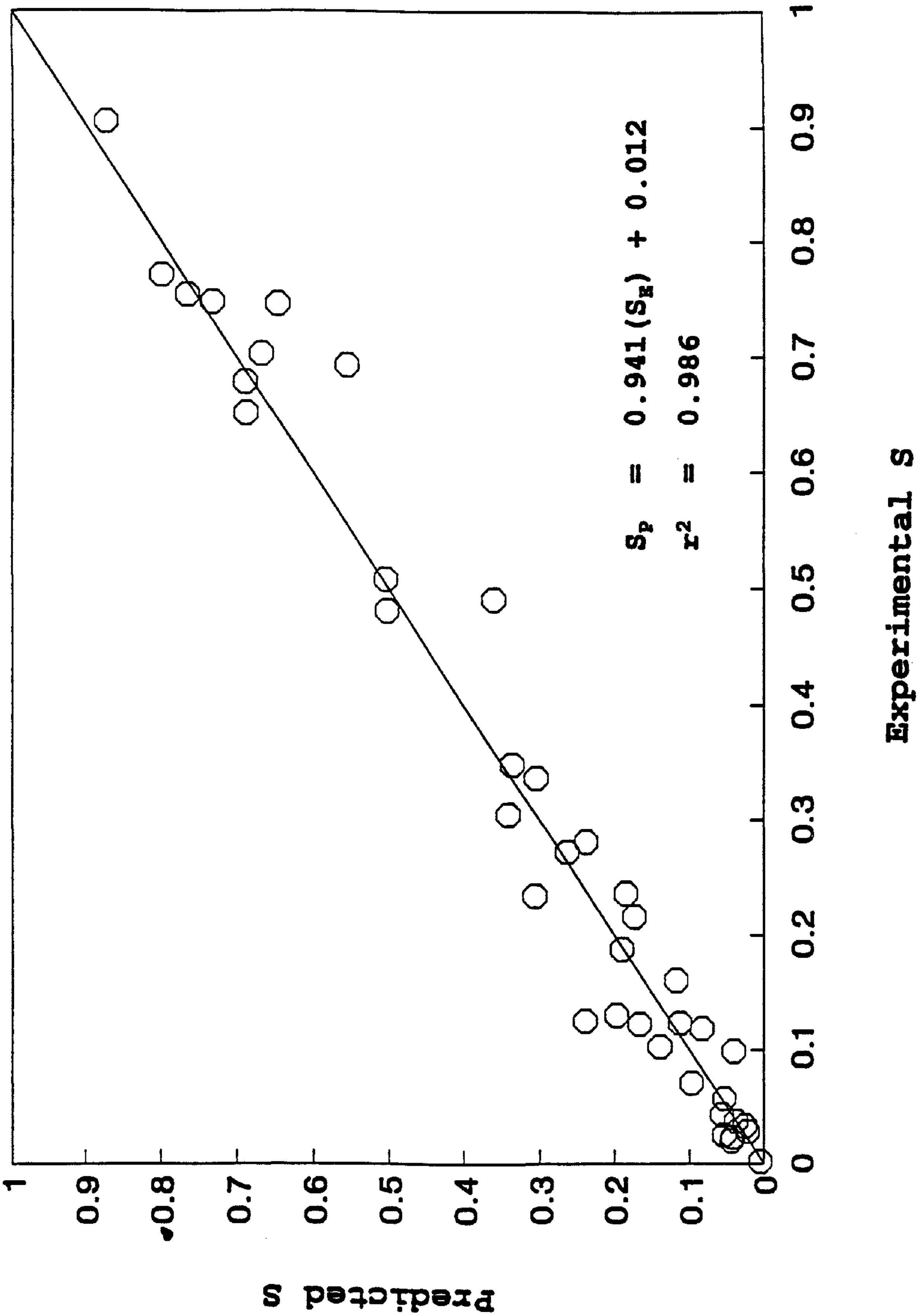

$S_P = 0.941(S_E) + 0.012$
$r^2 = 0.986$
Experimental S
Predicted S
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1

Figure 2

Chapter 5

Use of Predictive Models of Equilibrium Solubility and Diffusion Coefficients to Predict Solvent Permeation Through Chemical Protective Clothing

INTRODUCTION

The most widely accepted models for the permeation of solvents through polymers used in CPC products are based on Fick's laws of diffusion. Since detailed discussions of this topic exist elsewhere[1-3] only the salient features are discussed here.

The rate of diffusional mass transfer of a solvent through a polymer membrane is described by Fick's First Law:

$$J = -D\ dc/dx \tag{1}$$

where J (g/cm^2/min) is the flux, D (cm^2/min) is the solvent diffusion coefficient, c (g/cm^3) is the solvent concentration in the polymer sample, and x (cm) is the diffusion distance. For the case where the permeating solvent contacts one surface of the polymer sample and is continuously removed from the opposite surface, the flux at steady state, J_{ss} (or SSPR), is

$$J_{SS} = SSPR = DS/L \tag{2}$$

where S (g/cm^3) is the equilibrium solubility of the solvent in the polymer and L (cm) is the thickness of the sample.

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 can be estimated from Fick's Second Law as[1]

$$J_t = DS/L\ [1 + 2\Sigma\ (-1)^n \exp[-(n\pi)^2 (Dt/L^2)]] \tag{3}$$

The mass of solvent that has permeated a unit area of polymer at a given time is

$$M_t = SL\ [Dt/L^2 - 1/6 - 2\Sigma\ (-1)^n/(n\pi)^2 \exp[-(n\pi)^2 Dt/L^2]] \tag{4}$$

Determining SSPRs and BTs from Equations 2-4 requires estimates of D and S for a given solvent/CPC pair. Where permeation data are available D and S can be calculated from the permeation vs. time curve. For open-loop testing systems, this can be achieved by solving Equations 2 and 3 simultaneously to obtain an expression for D in terms of J and t (the S terms cancel out). In this case, values of J and t

measured at some point before steady-state are used with the value of J measured after steady-state has been reached. This value of D can then be substituted back into either Equation 2 or 3 to obtain a value of S.[1]

For closed-loop permeation test systems D can be estimated from the measured lag time, t_L, as

$$D_L = L^2/6t_L \tag{5}$$

where t_L is obtained from a plot of cumulative permeation versus time by extrapolating the steady-state permeation rate to the time axis (note: t_L can also be estimated by integration of the concentration vs. time plot from an open-loop test, but appreciable errors may result from the inability to detect the analyte in the early stages of permeation). This value of D can then be used with permeation and breakthrough time data to estimate S from Equations 2 or 4. Alternatively, S can be obtained directly from measurements of solvent uptake in immersion testing. This value of S can then be used in Equation 2 or 3 to obtain a value of D.

Assumptions in Equations 3-5 are that D, S, and L are constant. However, these values may change appreciably with time and/or solvent concentration, especially in cases where significant swelling of the CPC polymer occurs. For systems of organic solvents and polymers, D will often show a strong positive concentration dependence. Thus, values of D determined at steady-state may be larger than those determined at some earlier point in the permeation process. While several approaches describe the concentration dependence of D for specific polymer/solvent combinations,[4] they have been of limited use in predictive models because the nature of the concentration dependence of D is not usually known apriori. Thus, only 'average' values of D can be obtained.

Since theoretical approaches to predicting D require parameters not readily available for most solvents and polymers, empirical correlations are often the most useful means of estimating D. Goydan et al. have explored the relationship between experimentally determined D values for a number of solvent/CPC combinations polymers and several solvent parameters such as the acentric factor, molecular connectivity, molar volume, and molecular weight.[5] Of these, reasonably good correlations were found between the logarithm of the solvent molecular weight and the logarithm of D, with predicted values generally falling within a factor of five of experimental values. While this approach does not account for the known effects on D of specific solvent-polymer interactions, it is quite general and appears adequate for this application. Estimates of D for the solvents studied here have been obtained using similar correlations.

METHODS

It is assumed here that the permeation process is accurately described by Fick's laws. Thus, predicted values of BT and SSPR are obtained using Equations 2-4 for a given solvent/polymer pair. The method used for estimating D is based on empirical correlations of the solvent molecular weights with D values derived from permeation and immersion test results. To account for the effect of concentration, D values were determined at two different points in the permeation process: at breakthrough and at steady-state. This approach represents a modification of that recommended by Goydan et al.[5] Use of lag-time D values (D_L) was not adopted because some of the permeation tests were conducted in open-loop systems and because the concentration dependence of D cannot be accounted for with this approach.

Steady-state D values (D_S) were calculated by Equation 2 using immersion-test S values and experimental SSPR and L values. Breakthrough-time D values (D_B) were determined from Equations 3 or 4 using reported M_T or J_T values at the limits of detection along with S values from immersion testing. Solutions to Equations 3 and 4 can be obtained using a simple computer program employing a standard bisection method. The logarithms of the D values were then plotted versus the logarithms of the solvent molecular weights and predicted values of D_S and D_B were obtained by simple linear regression. These values were then used with predicted S values from Chapter 4 to obtain predicted BT and SSPR values.

Table I lists the solvents used to evaluate the model along with several relevant physical properties. Also presented in Table I are previously reported results of permeation testing of North Viton^R gloves challenged with the pure solvents. Permeation tests were performed using 5.08-cm (2-in) diameter test cells at constant temperatures ranging from 19-25°C. Table I reflects corrections made to the original data of Perkins et al.[6] made by the same authors.[7] Permeation data reported by Perkins et al. were collected with a closed-loop system having an internal volume of 5.95 L, an open-loop system with N_2 gas flow rates of 0.020-0.055 L/min through the collection chamber, or by gravimetric analysis.[7] For acetone, 2-pentanone and tetrahydrofuran (THF), where breakthrough occurred very rapidly, detection limits were not reported and the listed breakthrough times are approximate. Data reported by the manufacturer were collected in an open-loop system with N_2 flow rates ranging from 0.015-0.055 L/min.[8,9] Analytical detection limits (i.e., concentrations at which breakthrough was detected) were obtained upon inquiry of the investigators. Published Viton^R permeation test results for solvents not used in developing the model are also being compared to model predictions to evaluate the generality of the relationships established for this initial set of solvents. These will be reported at a later date.

RESULTS AND DISCUSSION

Ratios of predicted-to-experimental BT and SSPR values are shown in Table II. Since detection limits for acetone, 3-pentanone and tetrahydrofuran were not available their predicted BT values could not be determined. Of the remaining 15 solvents, BT values for 14 were within a factor of five of experimental values (most of the predictions were within a factor of two). The one exception was propanol. The geometric mean ratio (excluding propanol) was 1.12 indicating an average tendency toward overprediction. The geometric standard deviation of the ratios was 2.18 indicating a fairly high degree of dispersion in the distibution of values. Figure 1 shows a plot of the experimental (BT_E) vs predicted (BT_P) values (with values for propanol and perchloroethylene omitted). The line in Figure 1 is the line of perfect correlation (slope = 1). The linear regression correlation coefficient ($r^2 = 0.872$) shows only moderate correlation. Omitting the point in the upper right corner corresponding to carbon tetrachloride, which weights the regression disproportionately, yields an r^2 value of 0.695.

Predicted SSPR values were generally not as accurate as predicted BT values (Tables II). Only 11 of the 18 predicted SSPR values were within a factor of five of the experimental values. Consistent with the results for BT, SSPRs for propanol and carbon disulfied were the least accuarately predicted, owing to the poor correlation of molecular weight with D for these solvents. Propanol is known to form associated complexes that would increase its effective molecular weight and correspondingly reduce its diffusion coefficient. Perhaps a similar phenomenon occurs with carbon disulfide. SSPR predictions for pentanone and toluene were also very poor, which is less easily explained. Figure 2 shows a plot of experimental SSPR ($SSPR_E$) versus predicted SSPR ($SSPR_P$) for 14 of the 18 solvents (omitting values for the four solvents just mentioned). The line in the figure represents the line of perfect correlation. The regression coefficients show fairly good correlation (slope = 0.919, $r^2 = 0.903$). Use of other predictors of D are needed to improve the model predictions of BT and SSPR. Several of these are currently being investigated.

SUMMARY AND CONCLUSIONS

Estimated solubilities have been combined with estimated diffusion coefficients in a Fickian diffusion model to predict breakthrough times and steady-state permeation rates for 18 solvents in Viton. This approach to using solubility parameters for predicting permeation is consistent with established permeation theory and thus should be more generally applicable than empirical approaches to predicting permeation based only on solubility parameter differences. The ability to account for temperature and CPC-polymer cross-linking in estimating solubilities adds to the generality of the model.

The use of solvent molecular weight as the predictor of diffusion coefficients was satisfactory for some solvents, but highly inaccurate for others, particularly propanol and carbon disulfide. Other predictors of D are currently being investigated. It should be noted that, given that the permeation test data used for comparison to predicted values were collected from several different test systems, the amount of error attributable to the model alone cannot be determined. The results obtained here are comparable to or better than those reported for other solvent/CPC polymer systems using more complex models,[17] however it is clear that improvements are needed before this approach will find general application.

A key impediment to further development of this and other predictive permeation models is poor documentation of experimental conditions, most notably detection limits at breakthrough, in published permeation test data. Efforts to resolve this have been mounted by organizations such as the ASTM F23 Committee, but need to be adopted by other organizations involved in collecting such data. Proprietary restrictions on permeation test results and CPC formulation variables (e.g., polymer and additive composition and cross-link densities) also impede efforts such as this.

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TABLE I

Published Permeation Test Results for 18 Solvents through Viton

Solvent	L (cm)	BT (min)	SSPR (ug/cm^2/min)	J_{BT}* or M_{BT}^{A}
methylene chloride	0.037	79	20.28	10.3
chloroform	0.036	572	2.76	5.73
carbon tetrachloride	0.042	5355	0.021	0.132
1,2-dichloroethane	0.023	418	4.86	0.0238*
1,1,1-trichloroethane	0.036	1450	3.06	6.42
trichloroethylene	0.023	445	1.44	0.00813*
perchloroethylene	0.038	2580	0.0264	2.05
acetone	0.031	< 5	9810	----
3-pentanone	0.030	< 8	3300	----
1-propanol	0.033	1220	0.0384	0.00542*
2-ethoxyethanol	0.036	385	8.28	4.33
furfural	0.023	210	88.8	0.0155*
tetrahydrofuran	0.036	< 5	6678	----
dioxane	0.036	46	26.4	0.00935*
nitrobenzene	0.038	1320	0.648	0.586
nitropropane	0.023	17	156	0.00298*
toluene	0.038	810	0.264	1.17
carbon disulfide	0.036	281	0.222	0.0879

A M_{BT} = mass permeated at breakthrough in ug/cm^2 and J_{BT} = permeation rate at breakthrough ug/cm^2/min (values marked with an asterisk).
B ---- indicates data not available.

TABLE V

Comparison of Predicted and Experimental Breakthrough Times and Steady-State Permeation Rates

Solvent	BT_P	BT_P/BT_E	$SSPR_P$	$SSPR_P/SSPR_E$
methylene chloride	79	2.27	158	7.78
chloroform	1168	2.04	2.1	0.77
carbon tetrachloride	4278	0.80	0.079	3.76
1,2-dichloroethane	164	0.39	8.7	1.79
1,1,1-trichloroethane	2494	1.72	0.39	0.13
trichloroethylene	684	1.54	0.94	0.65
perchloroethylene	8913	3.45	0.020	0.77
acetone	----	----	10456	1.07
3-pentanone	----	----	169	0.05
1-propanol	10	0.008	433	>11296
2-ethoxyethanol	222	0.58	35	4.19
furfural	86	0.41	32	0.36
tetrahydrofuran	----	----	1008	0.15
dioxane	110	2.39	79	3.00
nitrobenzene	1129	0.86	0.84	1.30
nitropropane	38	2.23	185	1.19
toluene	244	0.30	17	63.9
carbon disulfide	60	0.21	41	184

BT_P = predicted breakthrough time (min).
BT_E = experimental breakthrough time (min) from Table I.
$SSPR_P$ = predicted steady-state permeation rate (ug/cm2/min).
$SSPR_E$ = experimental steady-state permeation rate (ug/cm2/min) from TableI.

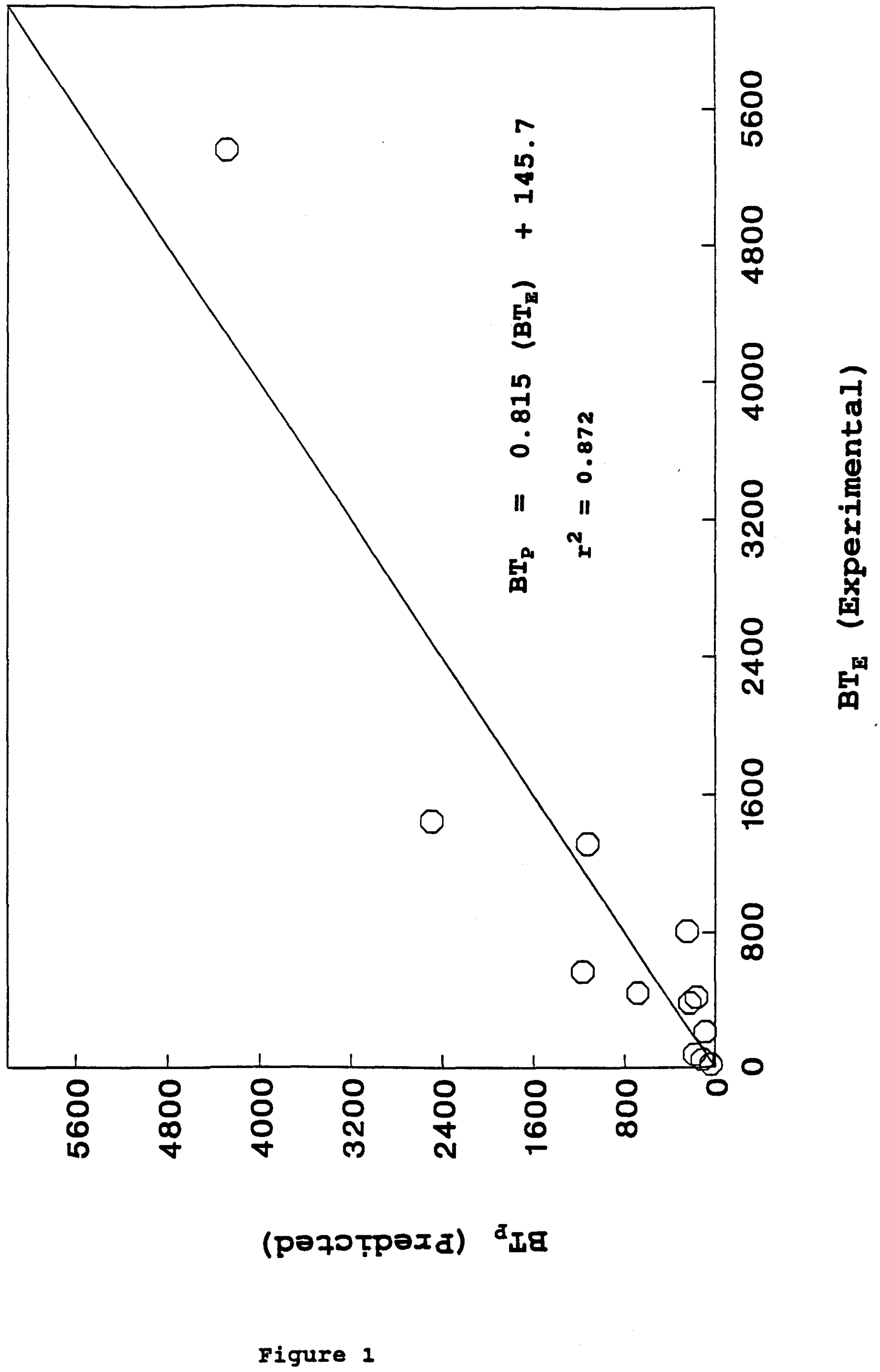
BT_P = 0.815 (BT_E) + 145.7
r^2 = 0.872
BT_E (Experimental)
BT_P (Predicted)
0
800
1600
2400
3200
4000
4800
5600

Figure 1

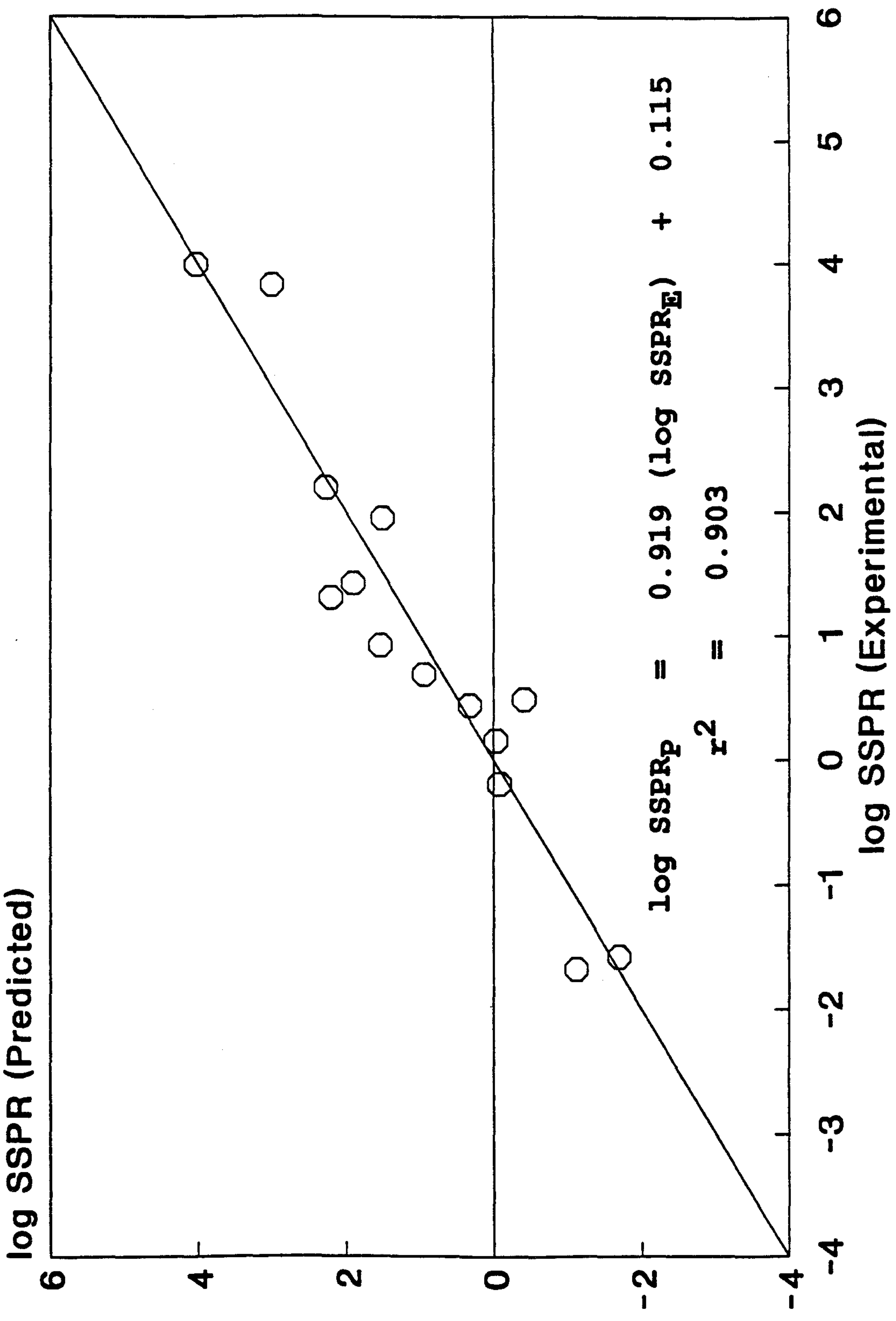
log SSPR (Predicted)
6
4
2
0
-2
-4
log SSPR (Experimental)
-4
-3
-2
-1
0
1
2
3
4
5
6
$\log SSPR_P = 0.919 (\log SSPR_E) + 0.115$
$r^2 = 0.903$

Figure 2