



Project Summary

Development and Assessment of Methods for Estimating Protective Clothing Performance

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Methods were developed for estimating the ability of protective clothing polymers to act as a barrier to chemical transport. The methods were developed for use by the U.S. Environmental Protection Agency (EPA), Office of Toxic Substances (OTS) to assess the ability of protective clothing to reduce chemical exposure risks as required in Premanufacture Notification (PMN) reviews. Two methods were focused on:

1. Development of a mathematical model based on Fickian diffusion theory. The model emphasizes prediction of cumulative permeation and is based on refinements of existing theoretical approaches for estimating two critical parameters; the solubility, S , and the diffusion coefficient, D . Permeation model predictions were compared to well-documented permeation data from the literature. The model's range of applicability and its limitations are described.
2. Critical review of the applicability and reliability of test methods for measuring permeation resistance, degradation resistance, liquid immersion weight change, and chemical sorption/desorption of protective clothing materials.

Efforts were initiated to develop an integrated system that will enable accurate and efficient evaluation of protective clothing requirements and recommendations. Specific accomp-

lishments include: computerization of the permeation estimation model, development of a hierarchy that ranks chemical resistance tests according to their ability to generate data needed to assess PMN clothing requirements, and recommendations for improving existing test methods.

This Project Summary was developed by EPA's Water Engineering Research Laboratory, Cincinnati, OH, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

Section 5 of the Toxic Substances Control Act (Public Law 94-469) requires prospective manufacturers to submit PMN's, which are reviewed by OTS prior to manufacture or import of new chemicals. OTS is permitted only 90 days to review each of the approximately 1,800 PMN's submitted annually. While many substances are not subjected to all aspects of the review process, those that are judged potentially toxic require detailed assessments of the potential for their environmental release and human exposure during manufacture, processing, and end use. If concerns are raised to warrant regulation; engineering controls, work practice restrictions, or protective clothing and equipment are investigated as a means to reduce exposure risks.

The submitter of the PMN often recommends protective clothing as the means to limit dermal exposures. Occasionally, the type of clothing is specified; more often it is not. In either case, OTS must

have means of assessing the exposure reduction provided by protective clothing. Two options are available to OTS for estimating the adequacy of protective clothing: (1) OTS can request that PMN submitters test the clothing materials and submit the resultant data, or (2) OTS can estimate clothing performance using available information and predictive models. Because of the volume of PMN's and the limited time permitted for each review, the development of a reliable model is desirable. If a model is to be used, it must estimate exposure protection using only the limited chemical property data available for PMN substances. If testing is to be specified, OTS must have an awareness of relevant test methods and the limitations of the data that are produced.

The overall assessment of protective clothing requirements must consider the potential health effects of the PMN substance, the probable exposure conditions, and the effectiveness of clothing in limiting exposures. This study focused on predicting the barrier effectiveness of clothing materials. Figure 1 provides an overview of the recommended system for

judging clothing effectiveness. Clothing performance depends directly on the exposure scenario, and the major factors that define the scenario are highlighted. Three general methods for assessing clothing performance were pursued—one to develop Fick's law predictive models, a second based on the analysis of existing performance test data, and a third involving the identification of appropriate chemical resistance test methods.

Predictive Models

Permeation theory was used to estimate chemical permeation through clothing materials under continuous exposure to pure substances. The model development effort focused on predicting the cumulative mass-permeated as a function of time and not solely a breakthrough time. OTS needs more than a single breakthrough time to judge whether clothing performance will be acceptable. OTS requires estimates of the time at which the cumulative amount permeated reaches a limit of unacceptable human risk. The time when this toxicity limit is reached may be well

beyond the time when breakthrough is detected.

Fickian diffusion behavior was assumed and the classic mathematical relationships were used for the estimation of the rate, J , and cumulative amount, Q , of chemical that permeates a polymer film at any time following the initiation of the exposure. These relationships require two key parameters: the diffusion coefficient, D , and the solubility S .

Five generic polymers were emphasized: butyl rubber, natural rubber, Neoprene,* nitrile rubber, and low density polyethylene (LDPE). This report summarizes the progress to date; refinements to the permeation estimation model are continuing.

Solubility Estimation

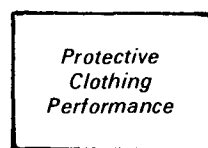
There are no well tested, purely theoretical approaches that provide accurate predictions of S for the systems of interest. A theoretical equation of state (EOS) approach shows promise although the technique requires further refinement. Three group contribution approaches were investigated and the Oishi and Prausnitz approach was determined the most accurate and broadly applicable. Empirical correlations with the functional groups of the solute molecule were also explored.

Theoretical Approach—Kumar Equation of State

A statistical mechanics-based lattice model EOS was recently used with success by Kumar et al. to model the phase behavior of supercritical fluids containing polymer molecules. A simplified form of the Kumar EOS was used here to estimate chemical/polymer solubilities at room temperature and pressure. S was predicted using this approach for natural rubber, butyl rubber and Neoprene. In general, the predictions are accurate to an order of magnitude but tend to underestimate values reported in the literature. An important advantage is that this approach requires only three pure component properties of the solute to estimate S : the molecular weight, vapor pressure, and liquid density at room temperature.

Exposure Scenario

- Physical state of chemical
 - Liquid, solid, gas
 - Neat
 - Mixture
- Temperature
- Duration
- Type of work
- Type of clothing



(1)

(2)

(3)

Predictive Models

- Permeation mechanisms
 - Fick's law
 - Solubility (S)
 - Equation of state
 - Group contributions
 - Statistical correlations
 - Diffusion Coefficient (D)
 - Empirical correlations
 - Concentration dependence
- Particulate penetration

Testing

- Chemical Resistance
 - Permeation
 - Degradation
 - Penetration
- Physical Properties
 - Abrasion
 - Cut
 - Torsional modulus
 - Tear
 - Tensile
 - Thickness
 - Puncture
- Particulate penetration

Data Bases

- Permeation
 - EPA "Guidelines"
 - NIOSH
 - CPCbase
 - GlovES
- S Values
- D Values
- Physical Properties
 - Must be developed

Figure 1. Schematic representation of an integrated system for judging the suitability of protective clothing recommendations.

*Mention of trade names or commercial product does not constitute endorsement or recommendation for use.

Group Contribution Approaches

Group contribution approaches require only that the generic structure of the solute and polymer be known. Most methods proposed in the literature stem from an activity coefficient correlation method called UNIQUAC (universal quasi-chemical activity coefficients). In this approach, γ , the activity coefficient, is expressed as a sum of γ_i and includes terms for combinatorial, residual, and free volume contributions.

Solubilities were predicted using three group contribution approaches and compared with measured values for butyl rubber, LDPE, natural butyl rubber, Neoprene, and nitrile rubber, when applicable. Table 1 presents results for

natural rubber in which predictions by the Oishi and Prausnitz, the Holten-Andersen, and the Ilyas and Doherty techniques are compared with solubility data. The UNIFAP (UNIQUAC functional group activity coefficients to polymer systems) approach by Oishi and Prausnitz and the Holten-Andersen approach are both very accurate for a wide range of chemicals; the predictions are accurate within an order of magnitude and many are within a factor of two (i.e., two times higher or half the measured value). Predictions are less accurate using the Ilyas and Doherty method and can only be made for a more limited set of chemicals. Results for butyl rubber, LDPE, Neoprene, and nitrile rubber are provided in the report.

The Oishi and Prausnitz method is the recommended approach. It can be used to estimate S for the five polymers emphasized here. In some cases, the Holten-Andersen approach is more accurate but its applicability is more limited. At present, the Holten-Andersen approach can treat natural rubber, butyl rubber, LDPE, and solutes from chemical classes including ketones, alcohols, esters, ethers, simple chlorinated compounds, and most hydrocarbons. The Ilyas and Doherty approach is more limited and demonstrates only marginal accuracy. For cases in which the UNIFAP technique cannot be applied, the Kumar EOS approach is recommended although the approach is generally less accurate. Chemical functional groups that cannot be treated by the UNIFAP method include nitriles, tertiary amines, phosphorous containing compounds, and compounds containing fluorine.

Table 1. Solubility Predictions for Natural Rubber/Solute Systems Using Group Contribution Approaches

| Chemical Name | Average* | Estimated S (g/cm)** | | |
|--------------------------|------------|------------------------|-----------|----------|
| | S (g/cm) | UNIFAP | Holt-And§ | Ily-Doh† |
| Acetic Acid | 0.078 | 0.062 | na | 0.002 |
| Acetic Anhydride | 0.039 | 0.012 | 0.009 | 0.009 |
| Acetone | 0.095 | 0.10 | 0.13 | 0.090 |
| Benzene | 3.2 | 1.6 | 1.7 | 6.5 |
| Benzyl Alcohol | 0.15 | 0.028 | 0.019 | na |
| Butylamine | 1.4 | 0.76 | na | 0.33 |
| Carbon Tetrachloride | 8.3 | 7.3 | 2.4 | na |
| Cyclohexane | 2.8 | 4.1 | 0.93 | 5.8 |
| Cyclohexanone | 2.4 | 2.4 | 0.62 | 9.8 |
| Dimethylaminopropylamine | 1.1 | 0.74 | na | na |
| Dimethylethanolamine | 0.17 | 0.020 | na | 0.010 |
| Dimethylformamide | 0.039 | 0.052 | na | na |
| Ethanol | 0.007 | 0.019 | 0.019 | 6.2 |
| Ethyl Acetate | 0.43 | 0.34 | 0.75 | 0.52 |
| 2-Ethyl-1-Butanol | 0.42 | 0.11 | 0.068 | 0.007 |
| Ethylene Dichloride | 2.1 | 0.21 | 2.9 | na |
| Ethylenediamine | 0.087 | 0.038 | na | 6.5 |
| n-Heptane | 1.6 | 3.5 | 2.0 | 4.5 |
| n-Hexane | 1.3 | 3.4 | 1.8 | 4.5 |
| Isopropyl Alcohol | 0.040 | 0.048 | 0.035 | 0.014 |
| Methanol | 0.002 | 0.008 | 0.008 | 5.7 |
| Methyl Acrylate | 0.52 | 0.15 | 0.14 | na |
| Methyl Chloroform | 4.5 | 4.4 | 5.0 | na |
| Methyl Ethyl Ketone | 0.46 | 0.18 | 0.24 | 0.14 |
| Methyl Isobutyl Ketone | 1.2 | 1.1 | 0.55 | 0.26 |
| Methyl Methacrylate | 1.1 | 0.28 | 0.37 | 0.27 |
| n-Pentanol | 0.12 | 0.088 | 0.085 | 0.17 |
| t-Pentanol | 0.39 | 0.082 | 0.085 | 0.028 |
| n-Propanol | 0.088 | 0.047 | 0.036 | 0.015 |
| n-Propyl Acetate | 1.3 | 0.40 | 0.22 | 1.4 |
| Tetrachloroethylene | 7.0 | 4.2 | na | na |
| Tetralin | 4.4 | 4.6 | 1.6 | 3.8 |
| Toluene | 3.5 | 3.7 | 1.2 | 1.4 |
| Trichloroethylene | 7.5 | 4.8 | na | na |
| o-Xylene | 3.8 | 5.0 | 0.79 | 1.5 |

*Experimental solubility data are average values for that chemical in natural rubber in the temperature range from 20° to 30°C.

** (na) indicates that the required group interaction parameters are not available for this solute/polymer system.

§Holten-Anderson approach.

†Ilyas and Doherty approach.

Diffusion Coefficient Estimation

Models to estimate D for solute/polymer matrix systems are much less advanced than solubility estimation procedures. There are no broadly applicable theoretical models to estimate D in concentrated polymer solutions. At present, a useful approach is an empirical correlation of experimental diffusion coefficients with physical properties of the solute molecule.

Theoretical Approach—Theoretical approaches to diffusion coefficient prediction generally involved application of free volume theory. Although these models provide a good qualitative representation of variations in D with temperature and solute concentration, they are difficult to apply and require physical property data that are not generally available. Consequently, these approaches are not suitable for PMN review evaluations where simplicity and broad applicability are essential requirements.

Empirical Approach—Because of the limitations of theoretical approaches, the project focused on correlating diffusion coefficient data with properties of the solute. The goal was a simple, broadly applicable technique that requires only the physical property data typically available in a PMN. Published diffusion coefficients were obtained by literature review. Additional values were calculated from permeation versus time data reported in the literature.

Correlations of measured D values with properties representative of solute size and shape were investigated. These

properties include molecular weight, molecular connectivity, surface/volume ratios, and the acentric factor. The best correlations were with molecular weight, although, for the polymers with less extensive data sets, the correlations are not well defined.

In Figure 2, D 's are plotted for organic liquids and gases in natural rubber versus the molecular weight of the solute. In general, the data show a consistent trend with molecular weight. For the straight-chain hydrocarbons and other approximately linear molecules, the D values decrease approximately linearly by two orders of magnitude as the molecular weight increases from 10 to 1,000 on the log-log scale. However, the values for branched or cyclic molecules lie above the general trend.

The development of correlations requires a sufficiently large set of D values. Few diffusion coefficient values were found for butyl rubber, Neoprene, and nitrile rubber, (less than 10 in each case), and the degree of confidence in

the correlation equations is less for these polymers. In general, the approach is not accurate for cyclic molecules. Analysis of additional permeation data sets continues and should enable significant improvements to the preliminary correlations presented here.

Prediction of Permeation Behavior

A permeation estimation model prototype was developed based on the above estimation techniques. The model was coded in FORTRAN and designed to run on personal computers at OTS. The permeation model uses Fick's law with the assumption of a constant diffusion coefficient. The overall accuracy of the model is determined by the accuracy to which D and S can be predicted and the applicability of simple Fick's law equations to describe the permeation behavior.

Permeation data from the literature were used to judge the accuracy of the model in predicting the full permeation

curve. Four sources of good quality, well documented data were used. In total, the data set for model validation include data for approximately 2 to 7 solutes for each of the five polymers of interest. Predictions were generated using the computer model; two approaches were used when applicable—one using the molecular weight correlation for D and UNIFAP for S and a second using the molecular weight correlation for D and Kumar EOS for S .

The permeation data and the model predictions are summarized in terms of breakthrough time and steady-state permeation rate estimates; graphs comparing the model predictions with the data over the entire permeation curve are provided in the report for each of the 28 polymer/solute combinations evaluated. Values of the breakthrough time were calculated at a given minimum detected flux or minimum detected amount permeated. The results for natural rubber are summarized in Table 2. Figure 3 compares the model predictions with

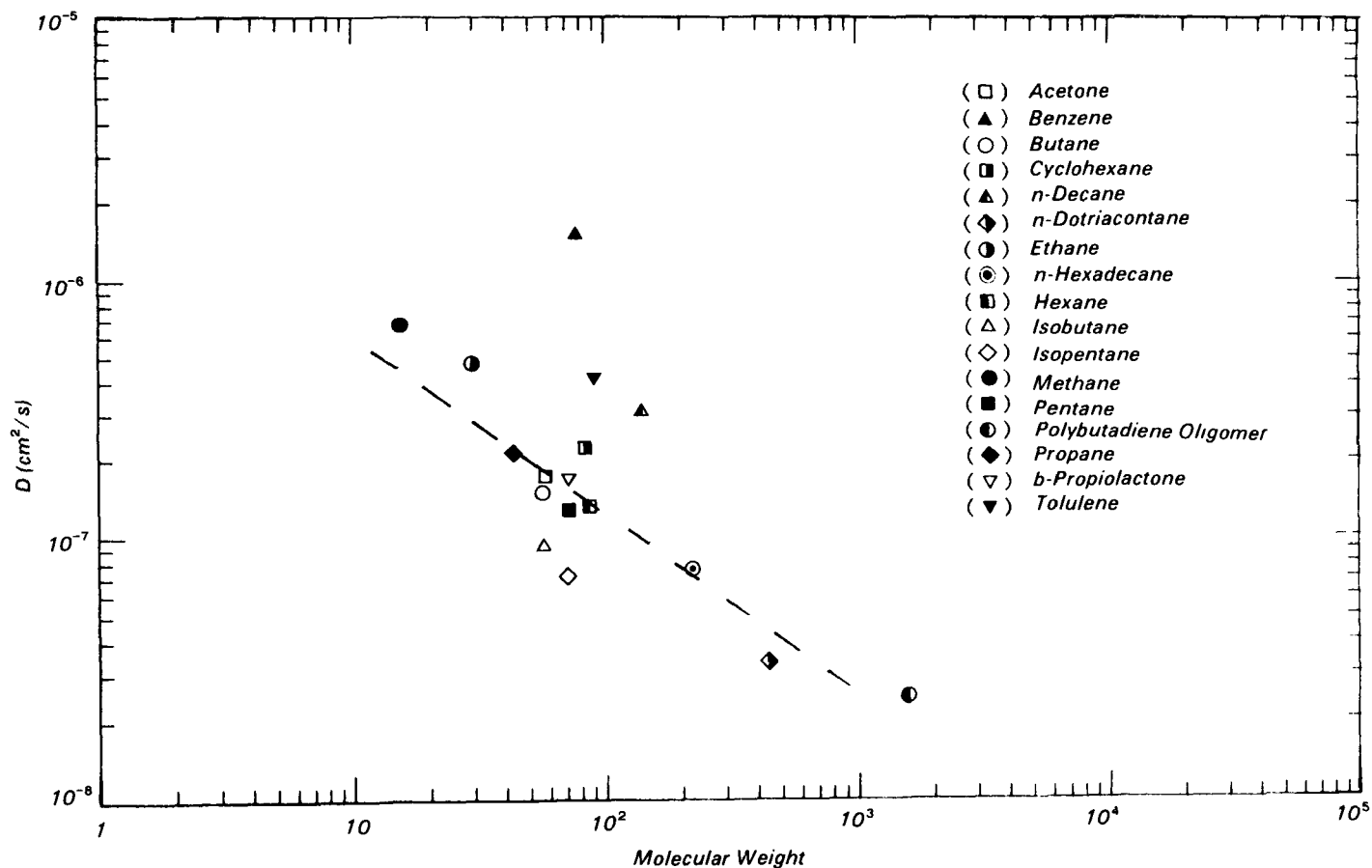


Figure 2. Correlation of diffusion coefficients with solute molecular weight for solute/natural rubber systems.

Table 2. Comparison of Permeation Data with Permeation Model Predictions for Natural Rubber

| | Thickness (cm) | Breakthrough Time | | Steady State Permeation Rate ($\mu\text{g}/\text{cm}^2\text{-min}$) | | |
|-----------------------|-------------------|-------------------|--|--|----------|------------|
| | | Measured (min) | Basis* ($\mu\text{g}/\text{cm}^2\text{-min}$) | Predicted** (min) | Measured | Predicted |
| Natural Rubber | | | | | | |
| Acetone | 0.06 | 17 | 0.76 | 8 20 | 34 | 34 2 |
| Cyclohexane | 0.06 | 19 | 1.8 | 8 13 | 525 | 959 59 |
| Isopropanol | 0.06 | 5340 | 1.0 | 11 115 | 1.0 | 16 1 |
| b-Propiolactone | 0.03 | 25 | 19.7§ | — 7 | 3.6 | — 22 |
| Toluene | 0.06 | 10 | 109.7 | 21 77 | 782 | 792 126 |

*These values are the permeation rate detected at breakthrough and were used as the basis for predicting breakthrough times.

**All predictions used the molecular weight correlation for D. Predictions using UNIFAP for S are reported on the first line followed by predictions using the Kumar EOS S on the second line. (—) indicates that predictions were not possible.

§This value is the cumulative mass permeated, in units of $\mu\text{g}/\text{cm}^2$, detected at breakthrough.

experimental data for natural rubber/acetone. In most cases, the permeation predictions using a constant D are accurate within factors of 2 to 5 and are often well within the range of experimental values reported in the literature.

Test Methods and Test Data Interpretation

For instances when the predictive models do not apply or clothing performance data for the chemical of interest do not exist, OTS may need to request protective clothing performance data to facilitate a thorough review. This is often the case for mixtures. Thus, it is very important to have well defined test methods and data reporting requirements. Chemical resistance and physical property test methods were reviewed relative to OTS needs, with the emphasis on chemical resistance testing.

Chemical Resistance

Chemical resistance test methods were compared on the basis of the types of results obtained, their approximate cost, the relative skill level required to perform them, and their inherent limitations. Based on this comparison, a testing hierarchy was developed, as discussed below.

Permeation Tests—In a permeation test, the chemical of interest is placed on one side of the clothing material and

the other side is monitored for the appearance of the chemical. From the results, the total amount (mass) of chemical permeating a known surface area of the clothing at any given time can be calculated. The cumulative permeation (mass/area) or the corresponding permeation rate (mass/area/time) can be used along with the estimated frequency, duration, and exposed body surface area to estimate dermal exposures for specific workplace activities.

Although the test is straightforward and a standard method (ASTM F739) exists for its performance, variable results can be obtained under different testing conditions for the same chemical/clothing material. Consequently, in describing or interpreting the results of a permeation test, there is a certain, minimum amount of information required. This information includes the breakthrough time, the steady state permeation rate, the clothing material thickness and surface area, the analytical sensitivity, the collection medium flow rate (open-loop systems) or volume (closed-loop systems), and temperature.

Immersion Tests—In an immersion test, the clothing material is exposed on one or both sides of the chemical of interest for some period of time. The change in weight or in other physical characteristics is measured. In tests in which the weight is accurately monitored

as a function of time, D and S of the chemical in the material can be calculated. Such tests are referred to as sorption/desorption tests and may be performed using either liquid or vapor exposures.

In addition to weight, other physical characteristics of the clothing material can be used to assess the overall resistance to a chemical or solution of chemicals. These characteristics include dimensions, puncture resistance, tear resistance, elongation resistance, strength, and so forth. Such tests are referred to as degradation tests since significant detrimental changes in the clothing due to the chemical are of interest.

Testing Hierarchy

Both the chemical resistance and the physical properties of the clothing material must be considered in judging its acceptability. While the physical property requirements are specific to the particular application, chemical resistance is a more general concept. Therefore, a test hierarchy was proposed for assessing chemical resistance only (Table 3). The testing hierarchy ranks chemical resistance tests according to their ability to generate data that can be used directly to estimate the effectiveness of the clothing material in reducing exposure risks.

Physical Characteristics

In combination with chemical resistance, protective clothing must possess certain physical characteristics. These characteristics can be classified under three headings: physical properties of the base materials and components of construction, type and quality of construction, and human factors. Physical property test procedures to measure these characteristics were reviewed; however, the applicability and limitations of these procedures have not been established relative to clothing requirements. The present state of the art is such that the ideal set of physical characteristics for any particular application may be difficult to define and quantify. Efforts in this regard should be pursued.

Integrated System Development

The overall objective of this project is to improve OTS's capability to rapidly and effectively assess the adequacy of the protective clothing recommendations

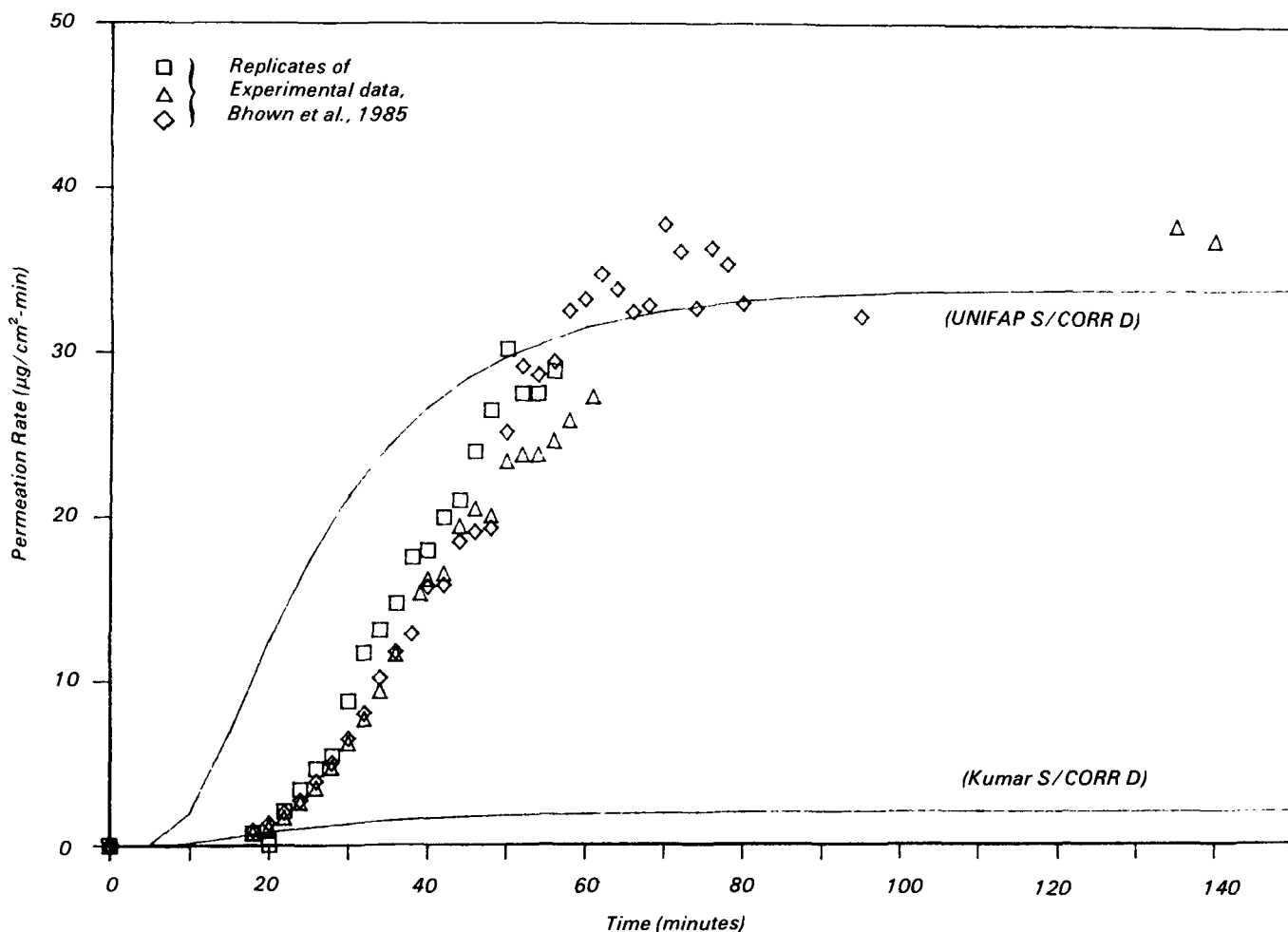


Figure 3. Comparison of model predictions for permeation flux as a function of time with experimental data for acetone/natural rubber.

Table 3. Test Data Priority for Estimating the Chemical Resistance of Protective Clothing Polymers

| Chemicals | Test Methods |
|----------------------------------|--|
| Single-Component Liquid/Gases | <ol style="list-style-type: none"> 1. ASTM Method F739 Permeation Test 2. Permeation Cup (if chemical has sufficient vapor pressure) 3. Weight change from liquid immersion. 4. D and S from vapor or liquid sorption/desorption test. |
| Multicomponent Solutions | <ol style="list-style-type: none"> 1. ASTM Method F739 Permeation Test |

provided in PMN submittals. This involves assessing the feasibility of developing a model, test methods, and test data interpretation guidelines to meet OTS needs for accuracy and efficiency. This assessment will serve as the basis for developing an integrated system for reviewing PMN protective clothing requirements based on both predictive model estimates and clothing performance data.

The current PMN review process was analyzed in detail with OTS. Based on this review, a permeation estimation computer model was developed and evaluated by OTS for incorporation into the standard review process. The computer model was designed for use on IBM personal computers. The model requires input of basic physical properties (i.e., molecular weight, liquid density, vapor pressure and/or the functional groups)

of the PMN substance. Permeation predictions are output in either tabular or graphic form. This computer model prototype represents one component of the overall system recommended for use in reviewing clothing recommendations. Existing databases of chemical resistance information were also reviewed. These were reviewed to assess the feasibility of using data for existing chemicals with structures and properties similar to those of a PMN substance to estimate clothing performance for a PMN substance.

Conclusions and Recommendations

A system for estimating clothing performance should consider the cumulative amount of chemicals that cross the protective clothing boundary. A theoretical model developed in this project was successful in estimating the cumulative permeation to within a factor of five. If

greater accuracy is required in PMN review, additional refinement of the models is necessary. Alternatively, OTS can estimate protective clothing performance on the basis of data for existing chemical analogues. Where there is no such chemical, the PMN chemical/clothing combination must be tested.

The recommended approaches to estimating permeation behavior as a function of time are those based on Fick's law. These require the estimation of the diffusion coefficient and the solubility of the chemical in the polymer. Techniques for estimating D and S were developed and used in a permeation model prototype based on Fick's law. In most cases, the permeation predictions were well within the range of experimental values reported for a specific permeant/polymer system. In other cases, the predictions were less consistent with the experimental data and this result may be because certain assumptions of the methodology were not valid. For example, the assumption of a constant diffusion coefficient is likely to be invalid for polymers that are swollen to a high degree by the permeant.

For PMN substances that are mixtures and those with no chemical analogues

for which there are permeation data, testing is required. Permeation testing is preferred and should be performed according to ASTM Method F739 or a similar procedure under well controlled and documented experimental conditions. Degradation and sorption/desorption test methods provide either fundamental parameters for use with predictive models or general indications of clothing performance. However, the results of these tests require interpretation by persons with some training in polymer permeation science.

To achieve the goal of developing an accurate and efficient method for judging the suitability of PMN protective clothing recommendations, OTS should continue its efforts to develop a three-part, integrated system. The system should incorporate (1) predictive models for estimating chemical resistance, (2) existing chemical resistance and physical property databases, and (3) the identification and specification of appropriate test methods.

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Michael D. Royer is the EPA Project Officer (see below).

The complete report, entitled "Development and Assessment of Methods for Estimating Protective Clothing Performance," (Order No. PB 88-133 657/AS; Cost: \$25.95, subject to change) will be available only from:

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