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Project Summary

Refinement of a Model to Predict the Chemical Permeation of Protective Clothing Materials

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A prototype of a predictive model for estimating chemical permeation through protective clothing materials was refined and tested. The model applies Fickian diffusion theory and predicts permeation rates and cumulative permeation as a function of time for five materials: butyl rubber, low density polyethylene (LDPE), natural rubber, neoprene, and nitrile rubber. The model provides two approaches to estimate the solubility, one using a group contribution approach (UNIFAP S) and the second using an equation of state approach (EOS S). The model provides one approach to estimate the diffusion coefficient (CORR D). Refinement of the model was investigated through a preliminary analysis of the concentration dependence of the diffusion coefficient. A finite difference technique was developed and, for 50% of the cases analyzed, the permeation-time behavior could be described more accurately assuming concentration dependence. No correlation, however, was identified to apply this finding in a predictive mode. Correlations developed previously to estimate constant D values (CORR D) were refined using a larger data set. The accuracy and limitations of the refined model were evaluated by comparing model predictions with literature data. Overall, the accuracy of the model is fair; for 200 data sets representing a range of chemical types, 70%-80% of the predicted permeation rates were within an order of magnitude of the measured values. The UNIFAP S/CORR D approach was more accurate than the EOS S/CORR D approach, however the former could not be applied in many cases because UNIFAP parameters are not available for all functional groups.

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Introduction

Section 5 of the Toxic Substances Control Act requires prospective manufacturers to submit Premanufacture Notifications (PMNs), which are reviewed by the EPA's Office of Toxic Substances (OTS), before manufacturing or importing new chemicals. A primary objective of the review is to assess the potential risks to human health that could result from dermal or inhalation exposures during the manufacture, processing, or end use of the PMN substance. In those cases in which the PMN submitter recommends protective clothing as a way to minimize dermal exposures, OTS needs a rapid and well-substantiated method to assess the ability of protective clothing to act as a barrier to the PMN chemical.

The EPA's Office of Research and Development, in support of OTS, has explored approaches to develop predictive models and test methods for estimating the barrier properties of protective clothing materials. Chemical permeation of clothing materials has been the focus because it is an important mechanism by which chemicals can cross through protective clothing. Previous reports prepared under this ongoing effort

describe a prototype of a predictive model for estimating permeation resistance and guidelines for specifying and interpreting results from chemical resistance tests. This project report summarizes recent efforts to refine and test the prototype model.

The following criteria were specified by OTS to guide model development. The model should:

- be easy to use,
- apply to a wide range of chemical and protective clothing materials,
- apply to new chemicals not used to develop the model,
- not require data other than those typically supplied in PMN submissions,
- predict the cumulative mass of chemical that permeates the clothing material as a function of time, and
- enable prediction of breakthrough times at specified permeation rates or cumulative amounts permeated.

Accuracy requirements were not specifically defined.

The prototype model uses diffusion theory and Fick's law to estimate neat chemical permeation as a function of time through five clothing materials: butyl rubber, LDPE, natural rubber, neoprene, and nitrile rubber. The Fick's law approach was selected because it was judged to provide the best opportunity to satisfy the above criteria. While other methods (e.g., statistical correlation methods) may demonstrate better accuracy in some cases, such methods often cannot predict permeation behavior as a function of time and lack sufficient theoretical basis for extrapolation to new chemicals. The prototype model estimates two parameters: the solubility (S) and the diffusion coefficient (D) of the chemical in the protective clothing material. Two approaches to estimate S are provided, one using a group contribution approach (UNIFAP S) and the second using an equation of state approach (EOS S). The prototype provides one approach to estimate D (CORR D). The prototype model was coded in FORTRAN, runs on a personal computer, is easy to use, requires minimal data inputs, and predicts permeation behavior as a function of time including breakthrough times. This report summarizes the results of a study to refine the prototype model and document its accuracy and limitations.

Refinement and Testing of Predictive Model

Our previous validation of the prototype model was limited by the availability of reliable data. Consequently, the priorities of this effort were (1) to identify additional permeation data available for model development and testing, (2) to refine the procedure to estimate D, and (3) to test the refined permeation estimation model to document its accuracy and limitations.

Permeation model refinement and testing were performed through the analysis of an additional, large set of permeation data that had been generated for the National Toxicology Program (NTP) by the Radian Corporation. The data set includes permeation data for approximately 50 chemicals per material for butyl rubber, natural rubber, neoprene, and nitrile rubber. Permeation-time curves were made available to us for a total of approximately 40 of the 200 chemical/material combinations. For the remainder of the data set, only undefined breakthrough times and steady-state permeation rate values were available. Model refinements focused on improving procedures to estimate values for the diffusion coefficient. No revision was made to either of the solubility estimation techniques. The D refinement effort was twofold: (I) to undertake a preliminary investigation of the importance of the concentration dependence of D to accurately predict permeation behavior as a function of time, and (2) to explore approaches for improving the estimation of constant D values using the NTP data set.

Concentration Dependent Diffusion Coefficients

The investigation of concentration dependent diffusion coefficients was exploratory and used numerical methods to calculate permeation-time profiles for general cases of concentration dependent behavior. Two general cases were studied, D as a linear function and as an exponential function of concentration, in addition to the constant D case.

A finite difference numerical technique was developed and used to calculate a parametric series of permeation-time profiles for these functions. The permeation-time profiles were plotted on a dimensionless scale so that their characteristic curve shape could be compared. In general, concentration dependent diffusion coefficients reduce the initial rate of permeation (i.e., increase the breakthrough time) and produce a sharper increase, at later times, to the steady-state rate compared with the constant D case. The parametric profile curves were then used to analyze for the presence of concentration dependent behavior for 31 chemical/polymer combinations. Overall, 50% of the chemical/polymer combinations tested show some concentration dependent D behavior. Because no correlation was identified to apply this finding in a predictive mode, however, the permeation estimation model will continue to be based on the assumption of a constant D.

Estimation of Constant Diffusion Coefficients

As an extension of our previous efforts, we again investigated correlations of the constant D values calculated from the available permeation data set with characteristics representative of the permeant size and shape. These properties included molecular weight, molecular connectivity, surface/volume ratios, and the acentric factor. As found previously, the best correlation was with molecular weight. Correlations with other properties were less accurate and imposed additional estimation requirements on the user. Revised correlation equations were established for butyl rubber, natural rubber, neoprene, and nitrile rubbers.

Permeation Model Testing

The refined permeation estimation model was tested by comparing the model predictions with permeation data from the NTP data set. For solubility estimation, both the Oishi and Prausnitz UNIFAP group contribution technique (UNIFAP S) and the Kumar equation of state technique (EOS S) were used. For D estimation, the revised equations for estimating constant D values from the permeant molecular weight were used (CORR D).

Model predictions using the UNIFAP S/ CORR D approach require input of the following properties for the permeant of interest:

- Molecular weight, g/mol,
- Liquid density, g/cm^3, and
- Chemical structure, defined according to a specified set of functional group designations.

Model predictions using the EOS S/ CORK D approach require input of the following permeant properties:

- Molecular weight, g/mol,
- Liquid density, g/cm^3, and
- Vapor pressure, mm Hg.

Both approaches require the user to select the protective clothing material of interest and input the material thickness.

For each approach, the permeation rate and the cumulative mass permeated as a function of time were predicted. From these curves, breakthrough times and steady-state permeation rates are calculated. Breakthrough times were estimated on the basis of the first reported rate or cumulative amount permeated. The permeation data subset with values reported as a function of time, 36 chemical/material combinations, was used to judge the accuracy of the models in predicting the full permeation-time curve. Because of the limited permeation-time data

set available, a second validation effort was undertaken using the remainder of the NTP data for which only undefined breakthrough times and steady-state rate values were reported, approximately 200 chemical/material combinations. Since steady-state permeation rates are independent of test conditions, these values are useful for model validation purposes.

Prediction Accuracy

The model predictions by both approaches were compared with the measured data to assess the prediction accuracy. Accuracy was judged by calculating a percent error for each predicted value:

Percent error (%) = [(Predicted value-Measured value)/Measured value] * 100

Overall, the accuracy of the model is fair for predicting the permeation of organic chemicals through butyl rubber, natural rubber, neoprene, and nitrile rubber. The model prediction results are summarized in Tables 1 and 2 in terms of the number of predictions that fall within specific (although arbitrary) accuracy ranges defined using the percent error values. Table 1 summarizes the results for the prediction of steady-state permeation rates and Table 2 summarizes the results for breakthrough time prediction. The results are organized by modeling approach (UNIFAP S/CORR D versus EOS S/CORR D) and by polymer type.

The accuracy of the permeation model predictions was also analyzed using an analysis of variance (ANOVA) statistical technique. Only the steady-state permeation rate prediction results were analyzed. The analysis shows that the model is not sufficiently "accurate" in the traditional sense that rigorous statistical descriptions of accuracy are not meaningful. Consequently, our discussion of model accuracy involves only qualitative observations.

When applicable, the UNIFAP S/CORR D modeling approach was found to be more accurate than the EOS S/CORR D approach. As noted in Table 1, the UNIFAP S/CORR D approach was used to predict steady-state permeation rates for a total of 122 chemical/material combinations for the four clothing materials. There were, however, an additional 96 chemical/material combinations that could not be addressed because the required UNIFAP parameters are not available for several, common chemical functional groups. Seventy-five percent of these combinations involved neoprene or nitrile rubber.

For the cases in which the UNIFAP S/CORR D approach could be applied, the predicted values overall were within a factor of 5 (i.e., percent errors in the range from -80% to +400%) of the measured values for 64% of these combinations and within a factor of 10 (i.e., percent errors in the range from -90% to +900%) for 80% of the combinations. The predictions for natural rubber and nitrile rubber were somewhat more accurate than those for butyl rubber and neoprene. Also, the model tended to overestimate the steady-state permeation rates for neoprene and nitrile rubber.

Table 1. *Summary of Model Accuracy for Predicting Steady-State Permeation Rates*

			No. of Predictions in Accuracy Range						
	No. of Chemicals in Data Set	*No. of Chemicals Model Applied*	*<-90% (<factor of -10)*	*-90% to -80% (factor of -5 to -10)*	*-80% to 400% (factor of ± 5)*	*400% to 900% (factor of 5 to 10)*	*>900% (>factor of 10)*	*Predictions Within -80% to 400% Error (factor of ±5)*	*Predictions Within -90% to 900% Error (factor of ±10)*
UNIFAP S/CORR D									
Butyl Rubber	58	44	4	5	25	5	5	57%	80%
Natural Rubber	47	36	4	1	25	3	3	70%	81%
Neoprene	57	21	0	0	13	2	6	62%	71%
Nitrile Rubber	56	21	0	1	15	1	4	71%	81%
EOS S/CORR D									
Butyl Rubber	54	54	14	6	31	0	3	57%	69%
Natural Rubber	37	37	7	5	16	3	6	43%	65%
Neoprene	54	54	19	8	19	1	7	35%	52%
Nitrile Rubber	50	50	9	6	31	2	2	62%	78%

Table 2. *Summary of Model Accuracy for Predicting Breakthrough Times*

	No. of Predictions in Accuracy Range								
	No. of Chemicals in Data Set	No. of Chemicals Model Applied	<-90% (<factor of -10)	-90% to -80% (factor of -5 to -10)	-80% to 400% (factor of ± 5)	400% to 900% (factor of 5 to 10)	>900% (>factor of 10)	Predictions Within -80% to 400% Error (factor of ± 5)	Predictions Within -90% to 900% Error (factor of ± 10)
UNIFAP S/ CORR D									
Butyl Rubber	10	7	2	2	3	0	0	21%	71%
Natural Rubber	5	4	1	1	2	0	0	50%	75%
Neoprene	11	4	1	0	3	0	0	75%	75%
Nitrile Rubber	10	6	2	2	1	1	0	17%	67%
EOS S/ CORR D									
Butyl Rubber	10	10	2	3	4	1	0	40%	80%
Natural Rubber	5	5	1	1	3	0	0	60%	80%
Neoprene	11	11	2	0	5	1	3	45%	55%
Nitrile Rubber	10	10	2	1	3	2	2	30%	60%

Table 2 reports the results for the UNIFAP S/CORR D prediction of breakthrough times for the 21 of 36 chemical/material combinations that could be addressed using this approach. The predicted breakthrough times, used to judge model accuracy at early times, were within a factor of 5 of the measured values for only 43% of these combinations and within a factor of 10 for 71% of the combinations on average. In general the method underestimated the measured values.

In comparison, the EOS S/CORR D could be used to make predictions for all of the chemical/polymer combinations in the data set, however, the accuracy of this approach is only fair to poor. The predicted values for steady-state permeation rates were within a factor of 5 of the measured values for only 50% of these combinations and within a factor of 10 for 66% of the combinations. Predictions for neoprene rubber were poor. Similarly, as summarized in Table 2, the predicted breakthrough time values were within a factor of 5 of the measured values for 42% of these combinations and within a factor of 10 for 67% of the combinations. In general, this method underestimates the breakthrough times and the steady-state permeation rates.

Applicability and Limitations

The permeation estimation model is based on the assumption of ideal Fick's law behavior. The Fick's law equations used to develop the model assume:

- continuous contact of the liquid chemical over the entire surface area of the polymer for the duration of the exposure. The model does not address intermittent or splash exposures.
- no external phase resistances exist at the downstream clothing material surface (i.e., the inside surface of the clothing material that would contact the skin during clothing use). This assumption may not be appropriate when actual use conditions are considered.
- the diffusion coefficient and clothing material thickness are constants. Effects such as polymer swelling and structural relaxations, which produce concentration dependent and non-Fickian diffusion behavior, are not addressed.

The model does not address multicomponent solutions and was developed to treat only five, generic, "homogeneous" or "isotropic" protective clothing polymers: butyl rubber, natural rubber, neoprene, nitrile rubber, and LDPE. The model currently does not address polymer blends or laminates. Also, the solubility and diffusion coefficient estimation techniques apply only at or near 25°C.

As noted above, the UNIFAP S technique has the critical limitation that it cannot be applied to many chemical/polymer combinations in its present state of development. Whereas the EOS S/CORR D approaches require only basic physical properties of the permeant as input, the Oishi and Prausnitz UNIFAP group contribution technique to estimate S requires specific functional group designations and group parameters as input. Thus, the applicability of the approach is limited by the available functional group parameters. The applicability is fairly broad for butyl rubber, LDPE, and natural rubber but very limited for neoprene and nitrile rubber.

Conclusions and Recommendations

The predictive model evaluated in this study can be used to estimate permeation behavior, however, the accuracy of the model is only fair when tested using a range of organic chemicals and clothing materials. Further improvement of model accuracy is not possible unless a larger set of well-documented permeation data as a function of time are available for model refinement.

The assumption of a constant D may reduce the accuracy of the permeation predictions because, in 50% of the cases analyzed, we found that the permeation behavior as a function of time was more accurately described using a concentration dependent D. The permeation-time data set was too small, however, to develop predictive corre-

lations. The correlations developed previously to estimate constant D values were refined by analyzing a larger set of "average" constant D values compiled under this effort.

Overall, the accuracy of the refined model is fair for predicting the permeation of organic chemicals through butyl rubber, natural rubber, neoprene, and nitrile rubber. The model predictions were often within the range of experimental values reported in cases where multiple or replicate tests were performed. The UNIFAP S/CORR D modeling approach was more accurate than the EOS S/CORR D approach, however the UNIFAP S approach could not be applied in all cases. Other limitations of the model are that it assumes continuous contact of the clothing material with the permeating chemical, it does not address chemical mixtures, and it applies only at 25°C.

Our primary recommendation is that OTS should reevaluate its requirements for a permeation prediction model, specifically regarding prediction accuracy, before further efforts are undertaken for predictive model development. Acceptable model accuracy must be defined and prioritized relative to broad applicability, ease of use, and cost of development.

At present, OTS can use the permeation model to estimate PMN chemical permeation of protective clothing materials so long as they recognize the accuracy and applicability limitations of the model. The model is only useful for order of magnitude estimates. When applicable, we recommend using the UNIFAP S/CORR D approach. The EOS S/CORR D approach should be used only for cases in which the UNIFAP S/CORR D approach cannot be applied because the required group parameters are not available. In any case, the EOS S/CORR D approach is not recommended for predicting permeation through neoprene materials because of the poor accuracy of the predictions.

No efforts to improve the present model's accuracy should be undertaken until a larger set of well documented permeation-time data can be obtained. OTS should contact the NTP and other researchers to obtain additional, existing permeation-time data for model refinement and validation. If such data can be obtained, our specific recommendations are:

- to test the accuracy and applicability of the present model if the data are for LDPE.
- to consider expanding the model to other clothing materials if the data are for materials not included in the present model.
- to pursue approaches to predict the concentration dependence of the diffusion coefficient.
- to expand the range of applicability of the UNIFAP group contribution approach to predicting S. One option would be for OTS to support research to generate the required parameters for specific functional groups not now addressed by the method.
- to evaluate use of the model to estimate chemical mixture permeation.

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