Applied Occupational and Environmental Hygiene

ISSN: 1047-322X (Print) 1521-0898 (Online) Journal homepage: https://www.tandfonline.com/loi/uaoh20

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To cite this article: Shane S. Que Hee (1996) Simple Glove Permeation Models, Applied Occupational and Environmental Hygiene, 11:2, 117-124, DOI: 10.1080/1047322X.1996.10389306

To link to this article: https://doi.org/10.1080/1047322X.1996.10389306

Simple Glove Permeation Models

Shane S. Que Hee

Department of Environmental Health Sciences and UCLA Center for Occupational and
Environmental Health, UCLA School of Public Health, 10833 Le Conte Avenue, Los Angeles, California 90095-1772

Glove permeation parameters of organic solvents through glove material (nitrile, neoprene, neox-supported neoprene, polyvinyl alcohol, polyvinylchloride, and natural rubber) published by Ansell Edmont were tested with simple physical parameters for the solvent. Some were based on solvent characteristics (Snyder Polarity P′, dielectric constant, solvent/water partition coefficients P, and Hildebrand solubility) and one chromatographic parameter (Snyder elution E°). A simple criterion of permeation resistance with no chemical degradation of the material was applied to rank physical parameters. E° and log P_{hep} were the best such parameters, where P_{hep} is the partition coefficient of the permeant between *n*-heptane and water. E° was then shown to correlate best with log P_{hep} out of all the parameters investigated. E° and hence log P_{hep} were correlated to the breakthrough time (t_b) by the predicted relationship, and qualitatively to the predicted steady-state permeation rate (P_s) data for alcohol permeation through neoprene, polyvinylchloride, and neox-supported neoprene gloves. QUE HEE, S.S.: SIMPLE GLOVE PERMEATION MODELS. APPL. OCCUP. ENVIRON. HYG. 11(2):117–124; 1996.

The permeation process through a barrier can be expressed as:

$$X_{ch} \leftrightarrow X_{chs} \leftrightarrow X_p \leftrightarrow X_{fs} \leftrightarrow X_{com}$$

where at any given time:

X_{ch} = the concentration or mass of the permeant X on the challenge side
X_{chs} = the concentration or mass of X adsorbed on the barrier challenge side
X_p = the permeating concentration or mass of X in the barrier material
X_{fs} = the permeated concentration or mass of X on the far barrier surface to the challenge side
X_{com} = the concentration or mass of X in the collection medium

Each potentially reversible process has a characteristic rate constant, since the concentration gradient of permeant decreases from the challenge to the collection side, that is, equilibrium ($dX_{com}/dt = 0$ where t is time) is usually not attained.

Thus, assuming no leaks and no penetration through microholes at a specified temperature:

$$dX_{com}/dt = -dX_{ch}/dt = dX_{chs}/dt + dX_p/dt + dX_{fs}/dt \tag{1}$$

In a permeation experiment in an American Society for Testing Materials (ASTM) cell, dX_{chs}/dt is high since direct contact occurs on the challenge side. X_{com} is measured as a function of time (dX_{com}/dt) to represent dX_p/dt. If the collection side desorption step is slow, as for when a poor solvent for the permeant is utilized in the collection chamber or if insufficient carrier gas flow occurs in the collection cell to volatilize the permeant molecules for a vapor collection system, the measured dX_{com}/dt contains an artifact due to the collection technique, rather than representing dX_p/dt, the real parameter of interest. The permeation is then assumed to obey Fick's first law:(1–3)

$$dX_p/dt = -D\, dX/dl \tag{2}$$

where:

D = the diffusion coefficient
dX/dl = the concentration gradient of X across the barrier of thickness l

Fick's Law applies if $dX_{com}/dt = dX_p/dt$ (the permeation step is rate limiting), since barrier thickness is evoked in Equation 2. The barrier must be uniform; D must be independent of the concentration of X; and l must remain constant (no swelling or contraction).

dX_p/dt at steady state ($dX_p/dt = dX_{com}/dt$ = nonzero constant) is then calculated by linear regression of the steady-state period from the slope of a plot of total mass X_{com} versus time. The permeation flux through the material is then determined by dividing this rate by the cross-sectional area of the material at the collection side. The extrapolated time of the steady-state period at zero X is the lag time (t_l), also equal to $l^2/6D$.(1–4) The breakthrough time t_b is when X is first detected in the collection medium; it is dependent on detection technique sensitivity, unlike t_l.

The physical properties of the permeant, like the solvent solubility parameter,(5–14) have been correlated to these permeation parameters. Because the nature of the finished glove product is generally a patent secret, predictive models are difficult to develop in terms of finished glove parameters.

The aim of this article related to organic solvent permeation through gloves is first to review the suitability of several physical parameters relative to permeation parameters; second, to test these parameters with the permeation and degradation data for one glove manufacturer using a simple chemical degradation/permeation discrimination scheme; and third, to select the most promising predictive parameters.

The Chromatographic Model

Assume that the barrier (the glove) acts like a small chromatographic column mimicking a relatively polar stationary phase-solid support in normal phase chromatography(15) with a nonpolar eluent solvent for a permeant. For solvent and solute permeation to occur, interactions (localization) with the glove material must be strong since both must be absorbed to permeate unless pinholes are present. Different solvent and solute breakthrough times can then be interpreted in terms of different solute/solvent/stationary phase-solid support interactions.

According to Snyder,$^{(16-18)}$ eluent strength of mobile phases used for normal phase chromatography of a solute is expressed by the parameter E° developed for elution of solutes from silica, alumina, or bonded phase columns, with n-pentane as a reference solvent E° of zero for an alumina column. No chemical reaction of solute with the column material is assumed. E° accounts for the partitioning interactions between solute and stationary phase-solid support (glove) and solute-solvent solubility/polarity in an empirical manner. Solute retention times increase with column length and decrease with increasing solvent polarity. Increased E° indicates increasing solvent polarity.

Snyder$^{(18)}$ showed that

$$\log K = \log V_a + E_a (S° - A_s E°) \quad (3)$$

where:

K = the partition coefficient for a given solute defined as the concentration of solute in the stationary phase-solid support divided by the concentration of solute in the mobile phase
V_a = the adsorbent surface volume or the volume of an adsorbed monolayer of solvent (mobile phase)
E_a = the average surface activity of the stationary phase-solid support
$S°$ = the adsorption energy of the solute
A_s = the area of stationary phase-solid support required by the adsorbed solute
$E°$ = the Snyder eluent strength

Equation 3 should describe glove challenge in a situation mimicking an impurity or a trace solute in a solvent of known E°.

Most E° for silica columns are 0.77 of the value for alumina, for magnesia columns 0.58, and for Florisil 0.52. This suggests that the relative E° ratios for the same solvents for the same solute on different column materials (gloves) are constant. In glove terms, the P_s and t_b or t_l will differ for different solvents, but their relative order should not change.

Comparing the effect of two mobile phase liquids 1 and 2 for a given solute and a given stationary phase/solid support, Snyder$^{(18)}$ found:

$$\log (K_1/K_2) = E_a A_s (E°_2 - E°_1) \quad (4)$$

The ratio of the two partition coefficients for a given solute on the same column for the two mobile phase solvents depends on the difference of eluent strengths of the solvents when E_a and A_s are constant. When the eluent flow rate F is constant, the retention volume V_R is equal to Ft_R, where t_R is the retention time.

Since

$$V_R = V_M + KV_S = Ft_R \quad (5)$$

where:

V_M = the mobile phase volume (chromatographic dead space volume)
V_S = the volume of the stationary phase-solid support

$$K = (Ft_R - V_M)/V_S \quad (6)$$

For solvents permeating at F corresponding to P_sA/d, where P_s is the steady-state permeation rate in mass time^{-1} area^{-1}, A is the constant cross-sectional area of the exposed glove (as in an ASTM permeation experiment), and d is the density of the solvent, and t_R corresponds to t_b or t_l, where V_M and V_S are constant (same glove material),

$$K_1/K_2 = (P_{s1}At_{b1}/d_1 - V_M)/(P_{s2}At_{b2}/d_2 - V_M) \quad (7)$$

Substituting Equation 7 for K_1/K_2 in Equation 4:

$$\log (P_{s1}At_{b1}/d_1 - V_M)/(P_{s2}At_{b2}/d_2 - V_M) = E_a A_s (E°_2 - E°_1) \quad (8)$$

If $V_M \ll P_sAt_b/d$ term, since it refers to the volume of solvent in the vesicles within the glove material,

$$\log (P_{s1}t_{b1}d_2/P_{s2}t_{b2}d_1) = E_a A_s (E°_2 - E°_1) \quad (9)$$

$$\log (t_{b2}/t_{b1}) = E_a A_s (E°_1 - E°_2) + \log (P_{s1}d_2/P_{s2}d_1) \quad (10)$$

If $t_{b2}/t_{b1} \gg P_{s1}d_2/P_{s2}d_1$ or the latter is constant,

$$\log t_{b2}/t_{b1} = E_a A_s (E°_1 - E°_2) + \text{constant} \quad (11)$$

where the constant is zero if both P_{s1}/P_{s2} and d_2/d_1 are near 1, or $P_{s1}d_2/P_{s2}d_1$ is near 1.

For a given homologous series of organic solvents (for example, benzene, toluene, ethylbenzene, and *n*-propylbenzene for nitrile), $t_{b2} > t_{b1}$, $P_{s1} > P_{s2}$, $d_2/d_1 \approx 1$, and $E°_1 > E°_2$, where subscript 1 represents the lowest molecular weight member of the homologous series.

Thus, a plot of $\log t_{bi}/t_{b1}$ versus $(E°_1 - E°_i)$, where subscript i represents a higher homologue than the lowest molecular weight homologue of subscript 1, should be linear with a slope equal to E_aA_s and an intercept equal to the constant if the assumptions are valid for Equation 11. Equations 9 and 10 require specific P_{si} as well as specific t_{bi} for validation, and Equation 8 in addition requires V_M. Unfortunately, manufacturers usually only specify t_b and give a range for P_s for a permeant through a material.

Solvent Polarity Index Model

Miller,$^{(15)}$ Snyder *et al.*,$^{(16)}$ and Snyder$^{(17)}$ also developed a solvent polarity index P′, based on the solubility of a solute in three solvents, *p*-dioxane (a low dipole proton acceptor of P′ 4.8), nitromethane (a high dipole proton acceptor of P′ 6.0), and ethanol (a high dipole proton donor of P′ 4.3). *n*-Octane is defined to have a P′ of zero. Snyder then characterized each solute in this three-dimensional manner with respect to its three solubility types. Eight major polarity classifications were defined. The P′ parameter may be correlated to the parameters of permeation, since the present favored model of permeation postulates that permeation is the result of degree of solubility of the solvent in the glove material, a rationale common to the use of Hildebrand solubilities.$^{(5-14)}$ The potential solvent solubility is related to solvent polarity. The polarity index for mixtures is the polarity index of each component weighted by its volume fraction in the mixture.

The above reasoning suggested a correlational analysis of P_s and t_b with P′ and log P′.

The Liquid–Liquid Partition Model

To permeate, a solute must successfully negotiate hydrophobic and hydrophilic obstacles, that is, it must partition in both types of obstacles. Since many gloves consist of a material that is coated by various polarity films to enhance protection,(3) solute partitioning in different hydrophilic and hydrophobic films is very likely. The simplest way of describing this situation is to assess partitioning behavior of a solute between an organic solvent and water through solute partition coefficients (P_{solv}), defined as the equilibrium concentration (activity) of solute in the organic solvent (C_{solv}) divided by the equilibrium concentration (activity) in water of the same volume as the organic solvent (c_w), so that

$$P_{solv} = c_s/c_w \tag{12}$$

The major P_{solv} are(19) for 1-octanol/water (P_{oct}), diethyl ether/water (P_{dee}), *n*-butyl acetate/water (P_{ba}), chloroform/water (P_{chf}), and *n*-heptane/water (P_{hep}).

A general equation has been proposed(19) to correlate and predict the solubility (S_p) of a nonelectrolyte solute in a given solvent system:

$$S_p = S_{p0} + m(V_m/100) + s\pi + b\beta + a\alpha \tag{13}$$

where:

S_{p0} = the intercept
m, s, b, and a = the regression coefficients reflecting relative contribution of the parameters V_m, π, β, and α, respectively, to the solubility in a given solvent system
V_m = the intrinsic molar volume of the solute(s)
π = the dipolarity/polarizability parameter
β = the hydrogen bond acceptor basicity parameter
α = the hydrogen bond donor acidity parameter

A study(19) for 121 solutes has shown:

$$\log P_{oct} = 5.83\,V_m/100 - 0.74\pi - 3.51\beta - 0.15\alpha - 0.02 \tag{14}$$

$$\log P_{dee} = 5.54\,V_m/100 + 0.02\pi - 3.83\beta - 0.20\alpha - 0.34 \tag{15}$$

$$\log P_{ba} = 6.34\,V_m/100 + 0.91\pi - 3.87\beta + 0.30\alpha - 1.52 \tag{16}$$

$$\log P_{chf} = 6.00\,V_m/100 - 0.14\pi - 3.17\beta - 2.99\alpha - 0.18 \tag{17}$$

$$\log P_{hep} = 6.78V_m/100 - 1.02\pi - 5.35\beta - 3.54\alpha - 0.06 \tag{18}$$

Unlike Equations 14 through 17, the regression coefficients of all intermolecular force parameters for P_{hep} are significant and significantly different from the corresponding parameters of the other models.(19) When the standard deviations of the regression parameters are considered, the intermolecular forces that determine solute P_{oct}, P_{dee}, and P_{ba} are statistically not significantly different. This implies that P_{oct} is the only parameter of this group of three that needs to be considered, especially as many data are available for P_{oct}. While V_m and the β parameters were significant in all systems, the α term was significant only for P_{chf} and P_{hep}. For P_{hep} the π term was also significant, but not for the other solvents.

The above reasoning suggested a correlational analysis of solute P_s and t_b to log P_{oct}, log P_{chf}, and log P_{hep}.

The Solubility Parameter Model

The solubility parameter (δ) was developed by Hildebrand and Scott(20) to describe nonpolar regular solutions whose deviations from ideality (Raoult's Law) are caused by the enthalpy of mixing, that is, only dispersion forces (short range with an intermolecular distance r of dependence of r^{-7}, and on the square of the molecular electronic shape parameter, the polarizability) contribute.

$$\delta = (H/V_m)^{0.5} \tag{19}$$

where:

H = the molar heat of evaporation
V_m = the molar volume of the liquid

The parameter δ has been subdivided into the dispersion (δ_d), polar (δ_p), and hydrogen bonding (δ_h) components(5–7,9–14) to explain the different effects of solvents having the same total δ value. δ^2 is the sum of the squares of the component δ values. The assumptions then are that the dispersive component is H for the closest hydrocarbon analogue; the polar component is accounted for by each hydroxy group contributing 5 kcal to H; and the polar component is the same as the contribution of permanent dipoles to H, that is, the dipole moment to the fourth power. The quantitative treatment for the latter involves the static dielectric constant D, the refractive index n_D at the sodium D line, and the permanent dipole moment μ in Debye units as modeled on the Lorentz–Lorentz and Debye equations:

$$\delta_p^2 = 12{,}108\,(D - 1)\,(n_D^2 + 2)\mu^2/[V_m^2\,(2D + n_D^2)] \tag{20}$$

in units of calories per cubic centimeter for V_m in cubic centimeters.

Since this is the major model in the field, other reviews should be consulted for more details.(5–7, 9–14) The three δ-parameter model resembles the partition model utilizing three solute log P_{solv} values for organic solvents that are proton donors and acceptors and for solvents where dipole moment/polarizability factors dominate. The three δ-parameter model is most closely approached by the one P_{solv} that is dependent on all three component forces, P_{hep}. There is also similarity to Snyder's model for P′ based on three different solute solubilities in solvents that are a proton donor, and high and low dipole proton acceptors.

Gloves having similar solubility parameters to those of a challenge solvent are expected to solubilize in such a solvent or strongly attract and adsorb it according to this model. Permeation is then expected to follow adsorption. The partitioning model is more attractive in accounting for the absorption phenomena that must occur to facilitate the permeation process after the initial adsorption.

Other Models

Use of the universal quasichemical functional-group activity coefficient for polymers to calculate solubilities has led to qualitative but not quantitative predictive success$^{(11)}$ in permeation situations. There are many predictive models, including solvatochromic ones for gas chromatography relative to solute elution, but the gas carrier and the use of elevated temperatures do not mimic permeation conditions, so these were not considered.$^{(21-23)}$ Models based on reverse-phase liquid chromatography are also available.$^{(24-26)}$

Methods

The chemical degradation and permeation data of glove manufacturers are the most accessible sources on which to base glove selection for industrial hygienists. The same types of gloves relative to thickness, manufacture, material type, and test properties in the penetration and permeation tests from a single manufacturer will be used here for the sake of uniformity. Data from different manufacturers for the glove materials of the same type, thickness, temperature, and physical properties can show very different permeation behavior.$^{(6)}$

The permeation and chemical degradation data in the fifth edition of the Ansell Edmont Chemical Resistance Guide$^{(27)}$ were utilized for this study. Gloves in the worst two chemical degradation categories (NR, not recommended as complete glove degradation and P, poor as pronounced degradation) are not tested by Ansell Edmont for permeation. This suggests that solvent physical parameters predictive of permeation resistance should not also predict chemical degradation of the same material. The two categories implying most glove resistance to permeation were also chosen for study. These are E (excellent, since the steady-state permeation rate is <0.9 μg/cm^2/min) and VG (very good, since the steady-state permeation rate is between 0.9 and 9 μg/cm^2/min). Physical parameters allowing the best selectivity were evaluated first on the basis of smallest NR chemical degradation frequency versus highest E permeation frequency. A similar analysis involved an NR-P chemical degradation versus E-VG permeation basis.

The Ansell Edmont Resistance Guide provides both permeation and degradation data for gloves of the following materials: neoprene unsupported [catalog No. 29-840 of palm thickness 15 mil (0.38 mm)], neoprene (Neox™) supported, polyvinyl alcohol (PVA™) supported, and natural rubber [catalog No. 392 of 19 mil (0.48 mm) thickness]. Unfortunately, different nitrile gloves and different polyvinylchloride (PVC) gloves were used for the Ansell Edmont degradation and permeation data. For degradation, the nitrile gloves were Sol-Vex™ 37-145, 11 mil (0.28 mm) thickness. For permeation, the nitrile gloves were Sol-Vex™ 37-165, 22 mil (0.54 mm) thickness. Similarly, Snorkel™ and Everflex™ PVC were used for degradation data but Monkey Grip™ PVC was used for permeation.

Application of Equations 9 and 10 is difficult using glove manufacturer data since specific P_s are not provided. Equation 11 is testable since specific t_b are given. Interpretation of t_b data may be difficult since detection limits, detectors, and analytical techniques differ even for the same permeation cell. Thus, only organic solvents were chosen for consideration since their permeation was determined by the ASTM method with collection in a stream of nitrogen followed by flame ionization gas chromatography analysis.

The solvent physical properties evaluated and the sources of the values were: the Snyder E° value for alumina$^{(18,28)}$ (33 values); the Snyder polarity index $P'^{(17,28)}$ (37 values); the octanol/water partition coefficient$^{(29)}$ P_{oct} as log P_{oct} (57 values); the heptane/water partition coefficient$^{(19)}$ as log P_{hep} (25 values); the chloroform/water partition coefficient$^{(19)}$ as log P_{chl} (18 values); the dielectric constant$^{(28)}$ D (37 values); and the Hildebrand solubility parameter$^{(15)}$ δ (30 values). Apart from Hildebrand solubility, the above simple parameters have not been tested before.

Results

The NR-P degradation versus E-VG permeation analysis showed that Snyder P' values, Hildebrand δ, dielectric constants, log P_{oct}, and log P_{chl} produced conflicting and contradictory data for all glove types. Representative results are given in Table 1 for nitrile and unsupported neoprene. For the nitrile gloves, at least one set of NR-P degradation data overlapped with permeation E-VG data, two such overlaps occurred for P' and D, and three for log P_{oct}. For the unsupported neoprene glove, P', δ, and D each conflicted once and log P_{oct} conflicted twice, but log P_{chl} did not conflict.

Comparisons with Snyder E° and log P_{hep} produced the fewest contradictions. The Snyder E° model produced no contradictions between NR degradation and E permeation except for PVC (one contradiction). NR-P degradation and E-VG permeation data comparison (Table 2) revealed one contradiction each for neoprene, natural rubber, and Neox-supported neoprene, two for nitrile, three for PVC, and four for PVA. All of these contradictions were in the 0.58 to 0.65 E° range, and were near boundaries rather than in the middle of bands, unlike the other parameters of Table 1. Thus, for PVC, aniline and amyl alcohol are both resisted with small permeation rates relative to such other NR-P solvents as acetonitrile, diethylamine, dimethylsulfoxide, ethyl acetate, and nitromethane. For PVA, acetone, diethylamine, dimethylsulfoxide, and dioxane are NR-P, while amyl alcohol, aniline, ethyl acetate, and nitromethane are E-VG. The one contradiction for neoprene, natural rubber, and Neox was diethylamine (P, NR, and P, respectively). Amyl alcohol and dimethyl sulfoxide were E-VG for nitrile.

When regions containing more than two E° values within 0.06 units were considered for NR-P degradation/E-VG permeation classification, respectively, the following E° regions were obtained: nitrile, 0.40 to 0.62 (12 E° values)/0.0 to 0.01 (3); neoprene, 0.40 to 0.63 (10)/0.61 to 0.70 (6); Neox, 0.40 to 0.56 (7)/0.61 to 0.70 (3); PVA, none/0.26 to 0.64 (14); PVC, 0.26 to 0.71 (20)/none; and natural rubber, 0.40 to 0.45 (5)/0.61 to 0.70 (5). Only neoprene exhibited overlap, and this was at the boundary discussed above. PVA had the widest protective E° range for E-VG permeation resistance, and PVC had the widest range for NR-P degradation. Generally, t_b were shortest in the NR-P region and longest in the E-VG regions.

The log P_{hep} model produced no contradictions between NR and E data for any of the gloves except for nitrile (one contradiction). The NR-P and E-VG comparison (Table 2) had no contradictions for unsupported neoprene, Neox, and natural rubber; one for nitrile and PVA; and two for PVC.

TABLE 1. Permeant Physical Parameter Regions for NR-P Chemical Degradation and E-VG Permeation Resistance for Snyder P′, Hildebrand Solubility Parameter (δ), Dielectric Constant (D), Log Octanol/Water Coefficient (Log P_{oct}), and Log Chloroform/Water Coefficient (Log P_{chl}) for Ansell Edmont Nitrile (N) and Neoprene (NEO) Gloves

Gloves	Behavior	P′	δ	D	Log P_{oct}	Log P_{chl}
N	NR-P	2.7/3.5	9.0/10.4	2.2/2.3	−1.08/−0.42	−0.25
		4.0/4.8		4.8	0.17/0.73	0.24/0.39
		5.1/5.3		5.7/6.0	1.25/1.93	2.80/2.93
		6.3/6.7		7.6	2.89	3.46
				10.4/12.3		
				18.5/20.7		
				37.6		
	E-VG	0.1	−5.5	1.8/1.9	−1.93/−0.31	−0.85/−0.35
		3.4/3.9	7.0/7.6	2.3	0/0.88	0.34
		4.3/4.6	9.3/10	14	1.23 − 1.40	1.05
		6.9	11.4/11.6	17/20	2.03 − 2.60	
		10.2	12.7/12.8		3.39	
			14.8		5.01	
NEO	NR-P	0.3	8.9/10.7	2.2/2.6	−1.1/−0.42	1.3
		1.6		4.8/5.7	0.29/0.65	2.6/3.5
		2.4/5.3		7.6	1.2/3.0	
		6.0/6.7		9.1		
				10		
				12/13		
				19		
	E-VG	3.4/5.1	−5.5	6.9	−1.93	−0.85/−0.25
		5.8/7.2	9.3/10.2	14/24	−1.4/−1.3	0.34
		10.2	11.3/11.5	33/46	−0.79/0.90	1.05
			12.4		1.2/1.4	1.75
			14.4/14.8		2.0	
					4.2/5.0	

Parameter nonoverlap signifies a parameter that satisfies permeation resistance (E-VG) without contradictory chemical degradation (NR-P) since the latter causes elimination of the material for subsequent permeation evaluation by glove manufacturers.

Snyder P′ values are relative to P′ = 0 for *n*-octane and P′ = 6.0 for nitromethane.(17) Water has a P′ of 10.2. Hildebrand δ values are relative to *p*-dioxane as 10 Hildebrand (cgs units) and water as 21 Hildebrand.(15) Dielectric constants(27) D at 20/25°C are unitless.

/ between two values indicates that there are more than two data points in the range.

When regions containing more than two log P_{hep} values within 0.3 units were considered, definite NR-P/E-VG regions were (number of log P_{hep} values in a region are in parenthesis): nitrile, −0.91 to 0.29 (6)/−2.8 to −0.98 (5); unsupported neoprene, 0.87 to 1.12 (3) and 1.55 to 1.62 (3)/−2.10 to −0.98 (5); Neox-supported neoprene, 1.55 to 1.62 (3)/−2.80 to −0.82 (7); PVA, −2.9 to −1.92 (4)/−0.82 to 0.29 (4) and 2.29 to 2.99 (4); PVC, −0.91 to 0.25 (3) and 0.87 to 1.12 (3) and 1.55 to 1.62 (3)/−2.1 to −1.52 (3) and −0.98 to −0.82 (3); and natural rubber, none/−2.80 to −1.52 (3). Unlike for E°, there are now multiple log P_{hep} regions for each classification. According to the log P_{hep} perspective, the glove of widest permeation resistance range is Neox-supported neoprene and the glove of greatest degradation potential is still PVC, as also predicted by the E° analysis. One overlap for PVC was in the −1.0 to −0.9 VG region where acetone (log P_{hep} of −0.91) is not recommended, whereas butyl alcohol and isobutyl alcohol are resisted. The other overlap for PVC is in the −0.30 to 0.30 region of NR (aniline, ethyl acetate, pyridine, and methyl ethyl ketone) where aniline is resisted. The contradiction for nitrile was in the −2.1 to −0.8 E-VG region (butyl alcohol, isobutyl alcohol) where acetone and phenol were NR.

Discussion

Permeation measurement became important in the early 1980s when materials that passed the degradation NR-P criteria could also show short t_b and high P_s in the remaining F-G-E (fair, good, excellent) degradation classifications. Parameters potentially predictive of E-VG permeation resistance must also necessarily pass the NR-P degradation criterion of the same manufacturer, or, for a permeation E classification, the NR degradation criterion of the same manufacturer must be met. Two such simple physical parameters meet these criteria: the Snyder E° and log P_{hep} values but not log P_{oct} (and hence also log P_{dee} and log P_{ba}), and log P_{chl}, Snyder P′, D, or Hildebrand δ.

The E° correlations suggest that the glove material may act like a normal phase liquid chromatographic column for an organic solvent eluent (chromatographic mobile phase) that is the permeant in an ASTM-type permeation cell. E° not only accounts for the potential affinity of solvent for the glove surface through surface adsorption and bulk solvent partitioning (as do δ and P′), but also the liquid/solid partitioning (solid and permeant-filled glove vesicle partitioning inside the glove material) after absorption together with mass transfer to the column end (collection side of an ASTM cell) that mimics the permeation process. Furthermore, Equations 9 through 11

TABLE 2. Permeant Parameter Regions for NR-P Chemical Degradation Relative to E-VG Permeation Comparison of Snyder Elutability Value and Log (Heptane/Water Partition Coefficient) for Ansell Edmont Nitrile, Unsupported Neoprene, Neoprene Neox Supported, PVA, PVC, and Natural Rubber (NTR) Gloves

	Snyder E°		**Log P_{hep}**	
Gloves	**NR-P**	**E-VG**	**NR-P**	**E-VG**
N	−0.25	0.0/0.01 (3)	−0.91/0.29 (6)	−2.80/−0.98 (5)
	0.30/0.32	0.61/0.62	0.87/1.12	0.45
	0.40/0.62 (12)	0.70/0.71	1.55/1.62	4.18
		0.82/0.88	2.00/2.99	
		1.11		
NEO	−0.25	0.61/0.70 (6)	−0.31/−0.25	−2.10/−0.98 (5)
	0.13	0.88	0.87/1.12 (3)	0.03
	0.20	1.11	1.55/1.62 (3)	0.45
	0.26/0.32 (4)		2.29	
	0.40/0.63 (10)		2.82/2.99	
	0.71			
NEOX	−0.25	0/0.01	−0.31/−0.25	−2.80/−0.82 (7)
	0.15/0.18	0.61/0.70 (3)	0.87/0.90	0.03
	0.26/0.32 (4)	0.82/0.88	1.55/1.62 (3)	0.45
	0.40/0.56 (7)	0.95	2.29	4.18
	0.63	1.11	2.89/2.99	
	0.71			
PVA	0.56 (2)	−0.25/0.01 (4)	−2.90/−1.92 (4)	−0.82/0.29 (4)
	0.62/0.63	0.15/0.18	−1.52/−0.91 (3)	0.87/1.12 (3)
	0.82/0.88	0.26/0.64 (14)		1.56/1.62
	0.95	1.11		2.29/2.99 (4)
				4.18
PVC	−0.25/0.01 (4)	0.61/0.62	−0.91/−0.25 (3)	−2.80
	0.15	0.70	0.29	−2.10/−1.52 (3)
	0.26/0.71 (20)	0.82	0.87/1.12 (3)	−0.98/−0.82 (3)
		1.11	1.55/1.62 (3)	0.03
			2.29	0.45
			2.89/2.99	
			4.18	
NTR	−0.25/0.01 (4)	0.61/0.70 (5)	0.87/0.90	−2.80/−1.52 (3)
	0.15/0.18	0.82/0.88	1.56/1.62	−0.98 (2)
	0.26/0.32 (4)	0.95	2.89/2.99	0.03
	0.40/0.45 (5)	1.11	4.18	0.45
	0.63			1.12

Parameter nonoverlap signifies a parameter that satisfies permeation resistance (E-VG) without contradictory chemical degradation (NR-P) since the latter causes elimination of the material for subsequent permeation evaluation by glove manufacturers.

Snyder E° values on an alumina column are based on E° of *n*-pentane of 0.0. All values within 0.06 units were included in a range, the bracketed numbers being the number of values in the range. Log P_{hep} values within 0.3 units were included in the range, the numbers in the range being bracketed. / signifies a range, with the bracketed numbers indicating total number of values in the range; no bracketed value signifies two values. One number indicates a single datum.

were derived from chromatographic theory in terms of permeation t_b or t_l and P_s measurable in permeation experiments to constitute predictive models.

The log P_{hep} correlations suggest that an organic permeant partitioning between polar and nonpolar regions at the glove surface and inside the glove involve significant contributions from all forces in Equation 18, rather than just one or two forces as for the other partition coefficients embodied in Equations 14 through 17. Since many gloves have both hydrophobic and hydrophilic layers after the manufacturing process,(3) there is a physical basis for the correlation. Solvatochromic theory predicts correlations between log P_{solv} and the forces involved in the glove/solvent interaction, with log P_{hep} the only parameter that accounts for all three types of intermolecular forces for any given permeant.

The failure of total δ and D to explain permeation behavior is well known and is reconfirmed in this study. The more successful three-dimensional δ space approach(6,7,9–14) is replaced in this study through the use of one parameter, log P_{hep}, that depends on three forces that are similarly factored into the three-dimensional δ approach.

If E° and log P_{hep} data measure similar phenomena, they should be correlated. When E° was correlated with all the independent variables utilized in this study (Table 3) via z-parameter probabilities,(30) log P_{hep} showed the best p_z to E°. The order of decreasing correlation was: log P_{hep} > log P_{oct} >

TABLE 3. Correlation Analyses of Parameters (Snyder Polarization P′, Log P_{chl}, Log P_{hep}, Log P_{oct}, Hildebrand Solubility δ, and Dielectric Constant D) with Snyder E° for the equation: Parameter = m E° + b

Parameter	n	m	b	r	z	p_z	t
P′	28	5.66	0.94	0.81	1.13	0.03	7.04
Log P_{chl}	13	−6.78	5.28	−0.94	1.74	0.04	26.8
Log P_{hep}	17	−7.76	4.69	−0.96	1.95	<0.01	47.4
Log P_{oct}	27	−4.49	3.30	−0.83	1.19	<0.01	7.44
δ	28	13.1	4.72	0.58	1.74	0.07	4.46
D	31	33.7	−3.16	0.73	0.93	0.03	5.75

n, number of paired data; m, slope in appropriate units; b, intercept in appropriate units; r, correlation coefficient; z parameter = 0.5 ln (1 + r)/(1 − r); p_z, probability relative to z parameter; t, Student's *t* value.

Snyder P′ and D > log P_{chl} with all $p_z < 0.05$. δ is not linearly correlated to E° at $p_z < 0.05$. As log P_{oct} did not fare well in the NR-P degradation/E-VG permeation analysis, only log P_{hep} has promise as a simple partition parameter correlated to glove permeation parameters. Since there are fewer log P_{hep} values, correlational analysis with E° will have more statistical power in light of the fact that E° correlates significantly with log P_{hep}, and the latter does pass solvent-glove NR-P degradation and E-VG permeation criteria (Table 2).

If E° holds promise as a permeation predictor, Equations 9 to 11 should be correlated in the predicted manner to t_b or t_l and P_s. Typical of most glove manufacturers, the only specific data provided for individual permeants by Ansell Edmont are for t_b, whereas P_s data are given through the nonspecific E-VG-G-F-P-NR P_s system defined through tenfold differences in P_s, where E means $P_s < 0.9$ μg/cm^2/min and permeation NR signifies $P_s > 9$ mg/cm^2/min as alluded to above in the Methods section. Manufacturers provide no t_l data. The predicted correlation for Equation 11 should be obeyed best for homologous series, since a general correlation is not expected because of functional group differences (this was not observed at $p < 0.05$). There are four homologous series with three or more homologues that have t_b data, namely, monofunctional alcohols, polychlorinated methanes, alkyl acetates, and aromatic hydrocarbons. Decreasing polarity occurs in a homologous series with increasing molecular weight of homologues in hydrophobic functional groups like methylene (monofunctional alcohol, alkyl acetates, and aromatic hydrocarbons) and halogen (polychlorinated methanes) groups. Ansell Edmont classification range P_s decrease with increasing molecular weight (MW) and decreasing E° of monofunctional alcohols for nitrile and PVC, increasing chlorination for the polychlorinated methanes for nitrile and PVC, and increasing chain length of aromatic hydrocarbons for nitrile. This shows that most permeation occurs with the most polar homologues of homologous series for nitrile and PVC. More specific manufacturer P_s data are required to test the applicability of Equations 9 and 10. Qualitatively there is an inverse relationship of permeant MW to P_s and E° for nitrile and PVC for these homologous series, consistent with Equations 9 and 10, but the logarithmic nature of the relationships cannot be tested except with explicit P_s and t_b.

There is no dependence on solvent MW for the t_b for natural rubber and nitrile for the monofunctional alcohols, and for nitrile for the alkyl acetates. For monofunctional alcohols with methyl alcohol as reference, Equation 11 is obeyed for neoprene and PVC (excluding amyl alcohol), with not significantly different slopes (2.27 and 2.54 E°$^{-1}$ units, respectively), unlike for Neox (the slope is 5.30 for only three data points).

Explicit P_s and t_l data as well as t_b data should be supplied in manufacturer catalogs to facilitate permeation model research.

Conclusions

E° and log P_{hep} best discriminate organic solvent permeation resistance from avid chemical degradation for the glove materials of one manufacturer. Both also correlate the best of all parameters investigated, indicating that they may describe common phenomena. The theoretical predictions for both E° and log P_{hep} relative to t_b are valid for specific homologous series.

Recommendations

Distinctive E° and log P_{hep} regions can be utilized to select gloves that will protect workers handling single solvents from permeation and chemical degradation. Glove manufacturers should supply explicit P_s and t_l data as well as t_b for individual permeants to facilitate further permeation model development because of their standardized permeation analysis conditions and detection limits.

Acknowledgments

This project was supported by grant 1 R01 OH02951 from the National Institute for Occupational Safety and Health of the Centers for Disease Control. Partial support also came from the UCLA Center for Occupational and Environmental Health.

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