Permeation of Alkylbenzene Isomers of Molecular Weight 120 Through Nitrile Gloves

CHIN-HSIANG TSAI and 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

SYNOPSIS

Factors determining the permeation of eight alkylbenzene isomers of molecular weight 120.19 (three ethyl toluenes, three trimethylbenzenes, and two propyl benzenes) were investigated for a lined nitrile industrial type glove using an ASTM-type cell, liquid collection, and gas chromatography/mass spectrometry. The initial permeation rate P_i correlated inversely with the logarithm of the lag time t_l. The logarithm of the steady-state permeation rate P_s correlated inversely with the logarithm of the breakthrough time t_b. P_s/P_i for a given compound correlated directly with P_s and with t_l/t_b. P_i depended directly on the logarithm of the entropy of fusion divided by the square of the refractive index and divided by the solubility parameter. The t_b was inversely correlated to the logarithm of the water solubility. The logarithm of t_l was most directly correlated to the entropy of vaporization. High P_s for 1,2,4-trimethylbenzene, m-ethyltoluene, and p-ethyl toluene was linked to a common structural similarity to 1,2,4-trimethylbenzene relative to the unhindered geometry of the methyl group in the ethyl side chain. The existence of optimum radii of gyration for enhanced P_s and for long t_b suggested that the protective properties of nitrile followed discontinuous relationships rather than continuous ones and so are not explainable by correlative relationships of continuous functions. © 1996 John Wiley & Sons, Inc.

The alkylbenzenes of molecular weight 120.19 are important constituents of gasoline[1]: 1,2,3-trimethylbenzene (hemimellitene, 123T), 0.73% (w/w); 1,2,4-trimethylbenzene (pseudocumene, 124T), 4.9%; 1,3,5-trimethylbenzene (mesitylene, 135T), 1.32%; isopropylbenzene (cumene, IPB), 0.16%; and n-propylbenzene (NPB, 0.61%). They are also present in gasoline reformate[2]: 124T, 42% (w/w); m-ethyltoluene (MET), 18%; o-ethyltoluene (OET), 9.3%; p-ethyltoluene (PET), 8.8%; 123T, 8.4%; 135T, 7.8%; NPB, 5.3%; and IPB, 0.6%. They are contained in diesel engine exhaust,[1] PET, 135T, and 124T constituting 0.7, 0.4, and 0.4% of emitted hydrocarbons, respectively. They are used as the inert ingredients of many emulsifiable formulation concentrates of pesticides as part of the "xylene" fraction.[3] Thus workers in the pesticide formulating industries, farmers and pilots who mix and spray pesticides,

gasoline pumpers, and personnel repairing gasoline pipelines and transfer lines need to wear the appropriate protective garments to prevent skin absorption. The threshold limit value-time weighted average (TLV-TWA, skin) for cumene is 50 ppm, and that for mixed trimethylbenzenes is 25 ppm.[4]

The comparative permeation of these organic isomers through glove materials has not been studied. Pioneer A-14 nitrile gloves of 0.56-mm thickness protected against cumene[5] with a breakthrough time t_b of 271 min and a steady-state permeation rate P_s of 480 mg m^{-2} min^{-1}. Nitrile is a copolymer of acrylonitrile and 1,3-butadiene with solvent resistance increasing with nitrile content. The rubber is usually made by emulsion polymerization, removing low boiling excess butadiene by vacuum venting and excess acrylonitrile by steam distillation, adding vulcanization agents, antioxidants, and accelerators, and then curing.[6] The nature of any further surface coating usually obtained through dipping is protected by commercial patent and may differ drastically from nitrile's. Thus the protective properties

---

* To whom correspondence should be addressed.

Table I   Selected Pesticide Constants for Molecular Weight 120.19 Isomers

ISO	SG	n	MV	DM	SP	RG	VIS	WS	OW	DC	EFU	SD	ST
123T	0.894	1.512	134	0.56	1.83	4.13	1.019	75	3.66	2.64	8.07	176	31.3
124T	0.876	1.502	137	0.30	1.79	4.20	0.960	57	3.78	2.38	12.9	178	29.7
135T	0.865	1.497	139	0.13	1.80	4.38	0.948	48	3.78	2.35	10.0	178	28.8
IPB	0.862	1.489	139	0.40	1.75	4.32	0.790	50	3.52	2.38	10.0	166	28.2
NPB	0.862	1.490	139	0.35	1.78	4.34	0.860	60	3.63	2.37	11.7	167	29.0
OET	0.881	1.502	136	0.56	1.80	4.08	0.953	93	3.53	nv	13.2	172	30.2
MET	0.865	1.494	139	0.33	1.79	4.27	0.860	94	3.58	nv	10.2	173	29.1
PET	0.861	1.492	140	0	1.78	4.19	0.704	95	3.63	nv	14.4	174	28.8

ISO, isomer; SG, specific gravity at 20°C; n, refractive index at the sodium D line; MV, liquid molar volume in mL mol^{-1} at 20°C; DM, dipole moment of the liquid at 20–30°C in Debye; SP, solubility parameter at 20°C in $(J/m^3)^{0.5}$ multiplied by 10^{-4}; RG, radius of gyration in m multiplied by 10^{10}; VIS, absolute viscosity in centipoise at 20°C; WS, water solubility in mg L^{-1} at 25°C by the shake flask GC method; OW, log K_{OW}, the logarithm to base 10 of the octanol/water partition coefficient at 25°C; DC, dielectric constant of the liquid at 20°C; EFU, entropy of fusion at 25°C in cal K^{-1} mol^{-1}; SD, specific dispersion of 20°C in mL g^{-1}; ST, surface tension at 20°C in dyn cm^{-1}; 123T, 1,2,3-trimethylbenzene; 124T, 1,2,4-trimethylbenzene; 135T, 1,3,5-trimethylbenzene; IPB, isopropylbenzene; NPB, n-propylbenzene; OET, o-ethyltoluene; MET, m-ethyltoluene; PET, p-ethyltoluene; nv, no data. The WS for MET is estimated by the authors.

of the finished glove may not reflect those of the polymer elastomer that forms the bulk of the glove, but of the patented coatings and bulk elastomer. Therefore, direct measurement is the only sure way to ascertain glove protectiveness.

Prediction of glove protectiveness involves utilizing challenge agents as probes, the physical and chemical properties of agents causing permeation or penetration resistance being the direct opposite of those of the gloves. Thus compounds of similar polarity as the glove material will solubilize it and compounds that react chemically with it will degrade it.

The permeation of molecular weight 120.19 alkylbenzene isomeric family through nitrile is investigated in the present study to elucidate further the chemical and physical properties of nitrile that favor protection and degradation in terms of the properties of challenge solvents.

METHODS AND MATERIALS

Theory

The physical and chemical properties of isomers should determine permeation behavior through a given glove material. The parameters related to molecular shape may explain permeation behavior for positional and skeletal isomers of the same molecular weight because molecular weight is constant for isomers.

The molar polarization P_M is defined[7] by the Debye equation as

$$P_M = M(E - 1)/[D(E + 2)]$$

$$= (4\pi/3)(a + \mu^2/3RT) \quad (1)$$

where M is the molecular weight; E is the dielectric constant; D is the liquid density; a is the molar polarizability, the induced dipole moment per unit effective field strength, related to molar volume; μ is the permanent dipole moment; R is the ideal gas constant; and T is the absolute temperature.

Table I indicates that liquid phase μ values for the test isomers are almost zero for the symmetrical 135T[8,9] and for PET.[8] The dipole moments for 124T, NPB, and MET are small and about the same; and those for 123T and OET are also the same but bigger.

When the contribution of permanent dipoles is small compared with induced dipoles, the Maxwell relation holds[7]:

$$E = n^2 \quad (2)$$

where n is the refractive index at the same temperature as the dielectric constant, assuming no absorption at that wavelength.

Substitution of eq. (2) in eq. (1) gives the Lorenz–Lorentz equation for molar refraction MR[7]:

$$MR = M(n_D^2 - 1)/[D(n_D^2 + 2)] \quad (3)$$

where n_D is measured at the sodium D line 589.26 nm.

MR and P_M are equal for molecules with no permanent dipole moment, or when n is measured at an infrared nonabsorbing wavelength. For the study

Table II Some Chromatographic Retention Indices and Other Physical Parameters for Molecular Weight 120.19 Alkylbenzene Isomers

ISO	CONN	$C_{18}1$	$C_{18}2$	GCI1	GCI2	VW	AF	MR	EV
123T	3.244	2.526	0.0682	3.035	3.002	0.0818	0.366	40.5	8.1
124T	3.238	2.633	0.0828	3.044	2.991	0.0818	0.379	40.7	8.0
135T	3.232	nv	0.0900	3.035	2.980	0.0818	0.398	40.8	8.0
IPR	3.354	2.633	−0.0555	3.014	2.959	0.0800	0.338	40.4	7.8
NPR	3.471	2.533	−0.0088	3.025	2.972	0.0800	0.346	40.5	7.8
OET	3.388	2.571	0.0170	3.038	2.984	0.0809	0.293	40.4	8.0
MET	3.382	2.630	0.0212	3.030	2.976	0.0809	0.322	40.7	8.0
PET	3.382	2.639	0.0682	3.030	2.977	0.0809	0.324	40.7	7.9

ISO, isomer as defined in Table I; CONN, connectivity index[23]; $C_{18}1$, logarithm of capacity factor in water for a reversed phase 125 × 4.6 mm PE LC-15B silica-based C_{18} column at a flow rate of 1.5 mL min^{-1} using acetonitrile/water elution solvent[20]; $C_{18}2$, logarithm of capacity factor for a reversed phase 160 × 5 mm ID LiChrosorb RP-18 column at a flow rate of 1 mL min^{-1} of 9 : 1 methanol/water[23]; GCI1, logarithm of capacity factor for a gas chromatographic column 3 m × 4 mm i.d. filled with 15% squalane on silanized white support (80/100 mesh) at 100°C with hydrogen carrier flow[22] of 80 mL min^{-1}; GCI2, logarithm of capacity factor for a gas chromatographic column 100 m × 0.25 mm i.d., fused silica capillary column coated with a 0.5-μm crosslinked 100% Petrocol DH film with helium carrier velocity of 31.5 cm s^{-1} at a column temperature program[24] from 30 to 220°C at 1°C min^{-1}; VW, van der Waals volume[14] in m^3 kmol^{-1}; AF, acentric factor[14]; MR, molar refraction[13] in mL mol^{-1}; EV, standard energy of entropy of vaporization in kcal mol^{-1} at 25°C calculated from Rossini et al.[13]

isomers the values of dielectric constants are incomplete[10,11] (Table I). For 135T, the Maxwell relation using the n_D value[12] predicts a dielectric constant of 2.24 compared with the experimental value of 2.35, an acceptable underestimation of about 5%. The ratio of dielectric constants for 123T, 124T, 135T, IPB, and NPB are 1.12, 1.01, 1.00, 1.01, and 1.01 respectively. The respective n_D^2 ratios[10] are 1.01, 1.00, 1.00, 0.987, and 0.987.

Other related quantities often utilized[13] are

$$\text{specific refraction} = (n_D^2 - 1)/[V_m(n_D^2 + 2)] \quad (4)$$

$$\text{specific dispersion} = 10^4(n_F - n_C)/V_m \quad (5)$$

where V_m is the molar volume; subscript F indicates the hydrogen F line of 486.12 nm; and subscript C indicates the hydrogen C line at 656.28 nm.

One alternative model is the Poiseulle equation for viscosity[7]:

$$dV/dt = \pi\, Pr^4/8l\upsilon \quad (6)$$

where dV/dt is the volumetric flow rate, P is the pressure drop or resistance term, r is the radius of the exposed tubing surface area cylinder analogous here to the exposed surface area πr^2, l is the tubing length or here the glove thickness, and υ is the viscosity coefficient.

The mass transfer rate dm/dt for a liquid of density D is then

$$dm/dt = \pi PDr^4/8l\upsilon \quad (7)$$

P can be defined for solute/material combinations and accounts for glove/solvent interactions.

For a given glove material of constant permeation exposure area and thickness at a given temperature

$$dm/dt = \text{const } PD/\upsilon \quad (8)$$

Calculated values for absolute viscosity[14] and experimental values for density as specific gravity[12] and for surface tension[13] are given in Table I for the test isomers.

Other descriptors that have been considered include solubility parameters,[14] liquid molar volumes,[13] radii of gyration,[14] acentric factors,[14] van der Waals volumes,[14] critical temperatures,[13] water solubilities,[15] log octanol/water coefficients,[15] and thermodynamic properties[13] like the standard free energies, enthalpies, and organizational energies of fusion, vaporization, and formation. Some of these are presented for the test isomers in Tables I and II.

The classical mass transfer treatment for permeation was described elsewhere[16-18] in terms of steady-state permeation rate $P_s = (dm_s/dt)$/exposed surface area, lag time t_l (the time the extrapolated steady-state concentration is zero), and the diffusion coefficient D_p through

$$t_l = l^2/6D_p \quad (9)$$

There is a link[19] between the Snyder elution factor related to the chromatographic capacity factor and the logarithm of P_s and of t_b or t_l. Examining the correlations between t_b, t_l, and P_s is also indicated

as log P_s is correlated to $-\log t_r$.[19] Correlations between the chromatographic capacity factor and octanol/water coefficients,[20] solubility,[21] and solubility parameters[22] for alkylbenzenes were obtained for high performance liquid chromatography (HPLC). Some capacity factors are given in Table II.[20,23,24] The capacity factor is directly related to molecular weight within the normal alkylbenzene homologous series for HPLC.[20-22]

Glove and Permeation Collection Method Selection

The order of decreasing alkylbenzene polarity is benzene, toluene, xylenes/ethylbenzene, and molecular weight 120.19 isomers. Because nitrile does not protect against benzene and toluene but does against xylene,[5,25] it should protect against higher alkylbenzenes, and it does against IPB.[5] Because the ASTM-type liquid collection method was to be used,[16-18] the collection solvent was chosen to be hexane because it did not permeate or degrade nitrile, was miscible with the alkylbenzenes, and was well resolved from them on gas chromatography/mass spectrometry (GC/MS). Nitrile gloves are the gloves most frequently used in industry for protection against organic solvents and aqueous solutions because of great flexibility, low heat stress potential, inexpensiveness, and superior puncture and abrasion resistance.[26] Lined gloves feel more comfortable than unlined ones although they are less flexible.

Chemicals

The gloves were lined unsupported Solvex™ nitrile from Ansell Edmont (Coschocton, OH, catalog no. 37-165 and 37-175, 38 cm long, and 22 mil, 0.56 mm, nominal thickness). Hexane (Optima) from Fisher Scientific (Fair Lawn, NJ) was used as collection medium; sodium dichromate created known humidity atmospheres for glove preconditioning; and concentrated nitric acid was used to clean glassware. The following isomers were obtained with indicated nominal purities from Aldrich Chemical Company (Milwaukee, WI): NPB, 98%; IPB, 99%; 123T, 99%; OET, 99%; MET, 99%; and PET, 99%. Sigma Chemical Company (St. Louis, MO) provided 124T of 99% nominal purity. Similarly, 135T of 99% nominal purity was from Eastman Kodak Company (Rochester, NY). p-Xylene of 99% nominal purity from J. T. Baker (Phillipsburg, NJ) was used as a reference permeation compound because it was the only xylene isomer whose permeation had been investigated for Ansell Edmont nitrile,[27,28] and it was

also the internal standard. Purities were confirmed by GC/MS.

Apparatus

ASTM-type PTC-600 permeation cells[17] were from Pesce Lab Sales (Kennett Square, PA). The exposed surface area between the Teflon-lined sleeves inserted between the Pyrex flanges was 4.34 cm^2. A torque wrench to produce uniform tightening of the cell nuts was from Mechanics Products Inc. (Kent, WA). Micropipets were Eppendorf from Brinkman Instruments (Westbury, NY). The moving tray shaker water bath for immersion of the permeation cell was a Fisher Scientific model 125 no. 429 operated at $30.0 \pm 0.5°C$ and at a horizontal mixing velocity of 8.5 ± 0.5 cm s^{-1}. The micrometer screw gauge to measure glove thickness was from L. S. Starrett Co. (Athol, MA). Vernier calipers were from Mitutoyo (Japan).

For GC/MS, the analysis utilized a Hewlett–Packard 5890A gas chromatograph/5988A mass spectrometer. The fused silica capillary column was a 30 m × 0.317 mm i.d. DB-1701 1.0-μm 14% cyanopropylphenyl bonded stationary phase from J&W Scientific/Alltech (Deerfield, IL). The MS was operated in its 70-eV positive ion electron impact mode. The helium carrier was from Alphagaz (Walnut Creek, CA). A 10-μL Hamilton syringe (Fisher Scientific) was used for injections into the gas chromatograph.

All glassware including vials (1.5 mL) from Wheaton (Millville, NJ) were soaked overnight in 10% (v/v) nitric acid, soaked again in ASTM type II water, and dried in a dustless oven.

Methods

The specific permeation cell procedure based on the ASTM F739-85 method was published elsewhere[17] for the PTC-600 type cell. In summary, gloves were conditioned at least 24 h before use in a desiccator at a relative humidity of $65 \pm 1\%$. Materials were cut from the glove palm after tracing an outline of the outer circumference of the permeation challenge side. The material was interposed between the two Teflon gaskets and Pyrex chambers, and the nuts screwed into the stainless steel flanges to a torque of 30 in.-lb. The whole cell was immersed in the water bath, secured by clamps from a fixed horizontal bar, to test for external leaks. A volume of 10 mL of hexane was first added as the collection medium; the challenge side was partially filled with 15 mL of the alkylbenzene; and mixing was begun when

the alkylbenzene was added. The glove thickness using four measurements was 0.62 ± 0.03 mm.

Aliquots of 0.100 mL were taken every 10 min over 4 h from the collection side during the first experiment for each isomer, with these pipeted into 1.5-mL vials prechilled to $-20°C$ to minimize evaporation. The aliquoted solutions were stored at $-20°C$. They were thawed to room temperature before GC/MS analysis. A volume of 2 μL was injected by the sandwich technique with 1 μL hexane as each of the outer solvent layers. An aliquot from the challenge side at the end of the collection period was also taken for analysis of permeated hexane collection solvent, and by its head space analysis. The volumes of challenge and collection sides were measured at the beginning and end of the sampling period. The thickness of the glove material was remeasured after the sampling period and after external drying.

The operating conditions were: injection port temperature $250°C$; initial column temperature $85°C$ with 4-min solvent delay (none when analyzing backpermeated hexane directly or by head space) that was then increased at $5°C$ min^{-1} to $120°C$, holding for 12 min. The temperatures of the ion source and transfer line were $200°C$. The helium carrier flow rate was 3.00 ± 0.10 mL min^{-1}. Selected ion monitoring was at m/z 91 for p-xylene, NPB, and IPB, and m/z 105 for the trimethylbenzenes and ethyltoluenes.

Internal standard calibration curves were run on each analysis day. Dilution into the linear region was sometimes necessary. The breakthrough time t_b was defined to be the time when a mass that produced a signal that was three times the blank noise was detected. The detection limits were between 170 and 350 pg, and linear ranges were between 200 and 2000 pg. The average detection limit was about 200 pg, equivalent to a 20 pg mL^{-1} minimum collection concentration.

After analysis of the initial data and no backpermeation of hexane shown, the times for sampling later replicates were optimized to minimize sampling before breakthrough, but yet allowed better definition of t_b and steady-state periods. The sampling periods were 3 h for p-xylene and 4 h for other compounds.

The total mass permeated from the challenge side was calculated from the mass in the 2-μL injection using the internal standard method, correcting for background in the zero time sample, and then for the fraction injected, accounting for volume sampled previously. Cumulated mass permeated was plotted against sampling time. Multiple linear sections were

identified through the linear regression correlation coefficient r and Student t p values, calculating[29] for $n - 2$ degrees of freedom with the formula $r(n - 2)^{0.5}/(1 - r^2)^{0.5}$ for n data pairs. Individual data for t_b, t_l, and dm_s/dt for the linear sections for each run were obtained. Steady-state permeation rates P_s for the faster period and P_i for the slower initial period were calculated by division of dm_s/dt by the exposed surface area. Arithmetic means and standard deviations were determined for all quantities. Mean D_p values were calculated from eq. (9) from mean t_l.

These data were then self-correlated, and correlated to the parameters in Tables I and II with specific combinations through linear–linear, log–linear, linear–log, and log–log analyses. For one permeation period, $P_s = P_i$. Tests of statistical significance were at $p \gtrless 0.05$ or ≤ 0.025 depending on whether one-tailed or two-tailed analyses were appropriate. Analysis of variance techniques detected interactions.

RESULTS

No glove material swelled so that eq. (9) is applicable. No backpermeation of hexane collection solvent was detected. Therefore permeation rates are for the isomers alone. The design of the experiment minimizes the effect of mixing on the collection and challenge sides, making the permeation step rate determining.[19]

Table III shows the individual and mean t_b, t_l, P_s, P_i, and calculated mean D_p. All t_l for the initial permeation period for compounds that exhibited two steady-state periods were not statistically different from t_b. The coefficient of variation (CV) for glove thickness was $< 7\%$. The CV for the t_b of p-xylene was about 35%, but the rest were $< 25\%$ as were all t_l, P_s, and P_i except for the P_s of 124T of CV 46%. The individual cumulated permeated mass versus challenge time data is shown in Figure 1 for p-xylene, IPB, and NPB, in Figure 2 for the ethyltoluenes, and in Figure 3 for the trimethylbenzenes.

Only one steady-state period occurred for p-xylene, IPB, and 135T and two for the rest (Table III). In general, the t_b, t_l, P_s, and P_i differed. Three isomers (124T, MET, and PET) showed a greater P_s than that of p-xylene of lower molecular weight. No isomer had P_i higher than that for p-xylene, nor shorter t_b or t_l.

There were some similarities. P_i and t_b for the three ethyltoluenes were not significantly different, although P_s varied. 124T and NPB also behaved similarly initially but differently for P_s. The three

Table III Individual and Averaged Data for Test Compounds Through Lined Unsupported Nitrile Gloves of Specified Thickness (Nominally 0.56 mm)

COMP	Thickness	t_b	P_i	P_s	t_l	$D_p \times 10^4$
pX	0.60 (0.11)	20	—	720	36	
	0.67 (0.03)	20	—	840	45	
	0.60 (0.07)	10	—	510	39	
Av.	0.62 (0.04)	17 (6)		690 (170)	40 (5)	17 (3)
NPR	0.61 (0.04	40	160	420	90	
	0.63 (0.05)	50	210	380	91	
	0.58 (0.03)	50	280	310	50	
Av.	0.61 (0.03)	47 (6)	220 (60)	370 (60)	77 (20)	8.0 (2.0)
IPR	0.66 (0.05)	60	—	160	96	
	0.61 (0.06)	70	—	140	118	
	0.66 (0.04)	80	—	180	114	
Av.	0.64 (0.03)	70 (10)		160 (20)	110 (10)	6.3 (0.9)
123T	0.66 (0.05)	50	20	60	135	
	0.68 (0.04)	70	30	60	143	
	0.60 (0.04)	50	20	80	162	
Av.	0.65 (0.04)	57 (12)	23 (6)	67 (10)	150 (14)	4.8 (0.7)
124T	0.60 (0.09)	40	280	610	83	
	0.56 (0.04)	40	330	1,360	108	
	0.64 (0.06)	60	240	1,830	109	
Av.	0.60 (0.04)	47 (12)	280 (50)	1,300 (600)	100 (10)	6.0 (1.0)
135T	0.57 (0.04)	110	—	100	162	
	0.63 (0.06)	100	—	100	169	
	0.60 (0.05)	120	—	70	163	
Av.	0.60 (0.03)	110 (10)		90 (20)	170 (4)	3.6 (0.4)
oET	0.61 (0.05)	50	170	520	145	
	0.66 (0.04)	40	150	460	149	
	0.64 (0.04)	40	140	370	131	
Av.	0.64 (0.03)	43 (6)	150 (20)	450 (80)	140 (10)	4.8 (0.6)
mET	0.62 (0.06)	40	130	2,240	187	
	0.63 (0.05)	40	160	1,470	188	
	0.64 (0.03)	50	130	1,690	182	
Av.	0.63 (0.01)	43 (6)	140 (20)	1,800 (400)	186 (3)	3.6 (0.1)
pET	0.62 (0.02)	50	220	810	122	
	0.63 (0.04)	30	220	1,140	107	
	0.64 (0.03)	40	170	920	103	
Av.	0.63 (0.01)	40 (10)	200 (30)	960 (170)	110 (10)	6.0 (0.7)

Permeation rates are in μg cm^{-2} min^{-1} for the initial permeation steady-state period (P_i) and for the second steady-state (P_s). Breakthrough times (t_b) and lag times (t_l) are in min. Diffusion coefficients are in mm^2 min$^{-1} \times 10^{-4}$ (D_p) [calculated from eq. (9)]. COMP, compound as defined in Table I; thickness, average thickness is in mm (standard deviation for n = 3); (—) no data; Av., arithmetic mean; quantities in parentheses are standard deviations for n = 3; pX, *para*-xylene.

trimethylbenzenes varied in their t_b, P_i, and P_s; but P_s for 123T was not significantly different from the sole permeation rate for 135T. There were also no statistical differences for the P_s of 124T and MET, and of NPB and OET. The values of t_l were the same for IPB, NPB, 124T, and PET, and also for 123T and OET.

Most of the r did not reach a $p \gtrsim 0.05$ level of significance for the self-correlational comparisons

for the parameters in Table III, excluding D_p that was inversely related to t_l [eq. (9)].

The log P_s versus log t_b comparison ($r = -0.74$) was significant:

$$\log P_s = -2.70 \log t_b + 7.24 \qquad (10)$$

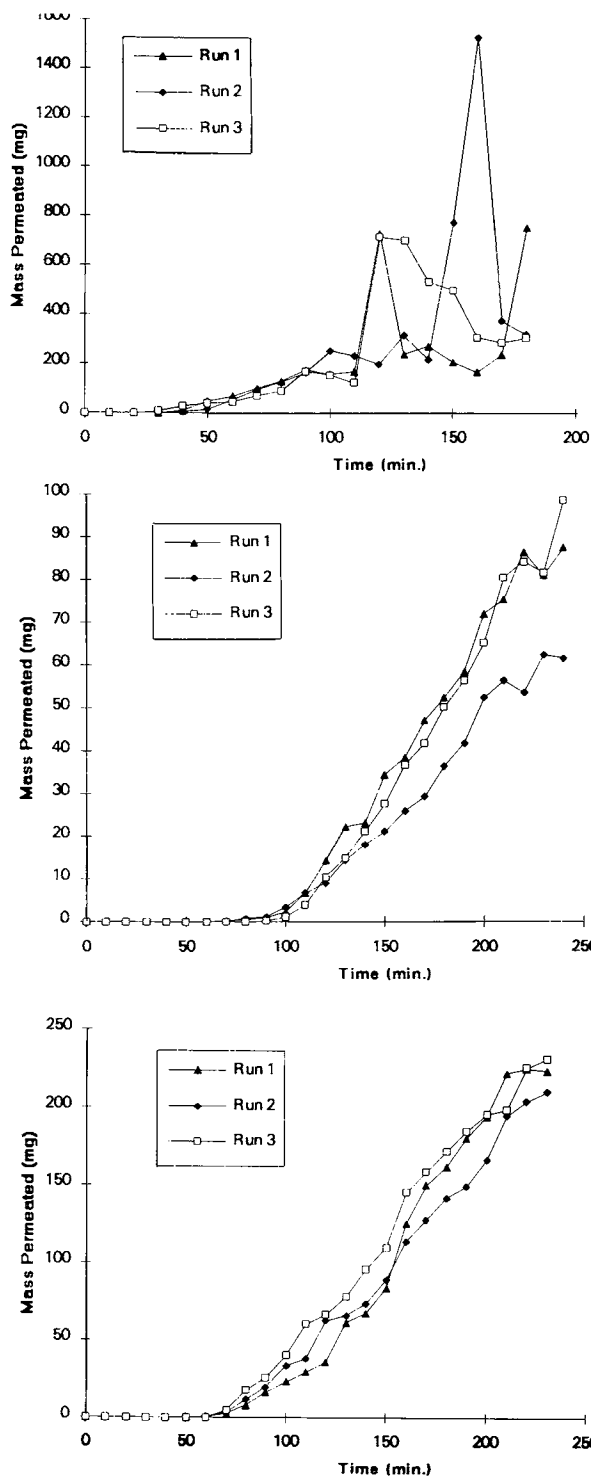where P_s is expressed in μg cm^{-2} min^{-1} and t_b is in min.

Figure 1 Cumulated mass permeated versus time curves for (top) p-xylene, (middle) isopropylbenzene, and (bottom) n-propylbenzene through 0.62-mm nitrile glove material at 30°C.
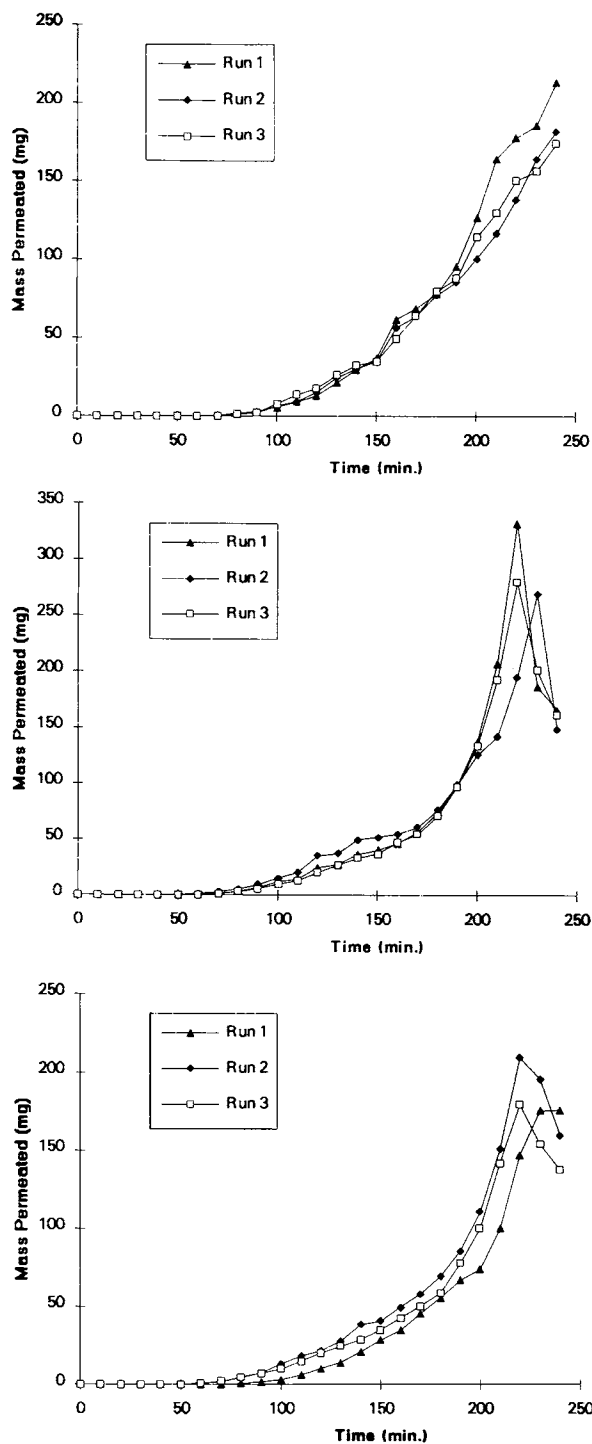
Figure 2 Cumulated mass permeated versus time curves for the three ethyl toluenes through 0.62-mm nitrile glove material at 30°C. (Top) o-, (middle) m-, and (bottom) p-isomers.
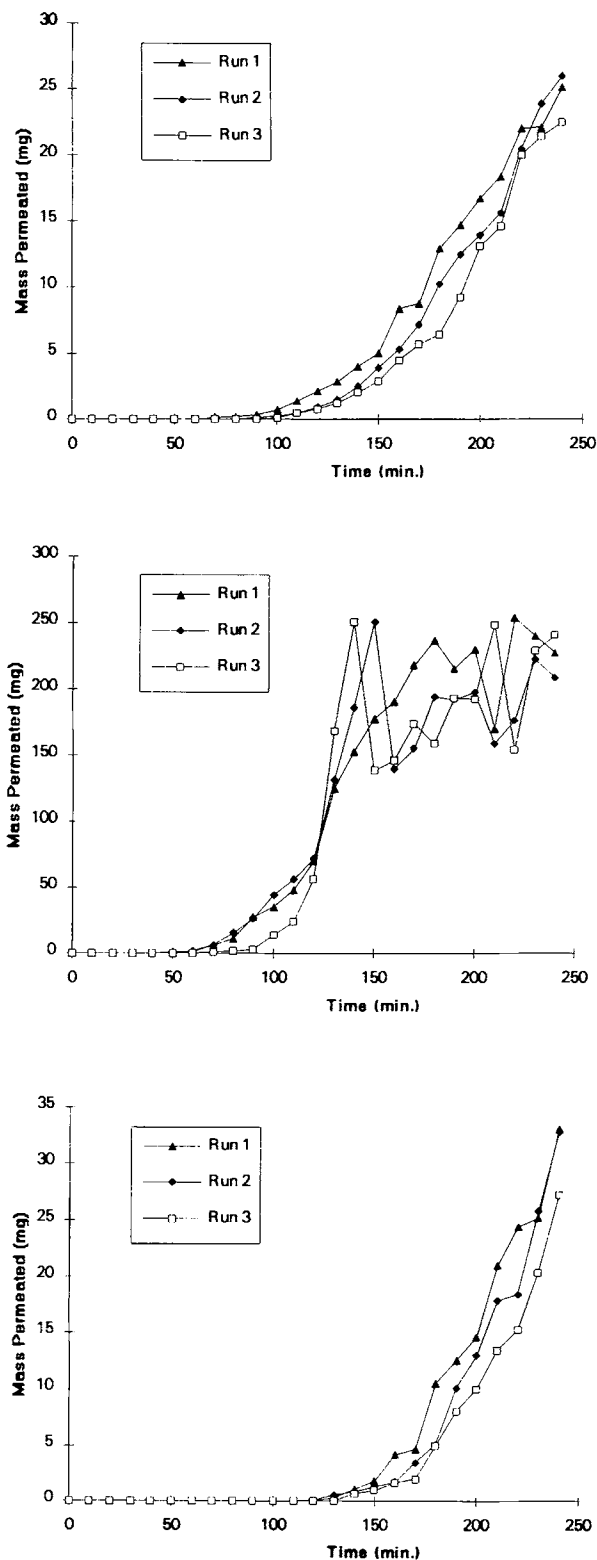
Figure 3 Cumulated mass permeated versus time curves for the three trimethylbenzenes through 0.62-mm nitrile glove material at 30°C. (Top) 1,2,3-, (middle) 1,2,4-, and (bottom) 1,3,5-isomers.

When the three deviant isomers were excluded, $p > 0.05$.

The same occurred for the log P_s versus t_b analysis:

$$\log P_s = -0.016t_b + 3.47 \quad (11)$$

where $r = -0.69$ for $n = 8$. The log–log relationship was similar. All these relationships were dependent on the data for the three deviant isomers.

For the analogous analysis for t_l, there was no significant relationship for P_s at $p \gtrless 0.05$, but there was for P_i. Thus,

$$P_i = -436 \log t_l + 1072 \quad (12)$$

for $r = -0.71$, $n = 8$. When the three deviant isomers were excluded, $r = -0.82$ at $p \gtrless 0.05$ and

$$P_i = -453 \log t_l + 1077 \quad (13)$$

The slope changed only 3.9%, not significant at $p \gtrless 0.025$.

For the P_i versus t_l relationship, $r = -0.69$ for $n = 8$ and

$$P_i = -1.47t_l + 350 \quad (14)$$

When the data for the three deviant isomers are excluded, $r = -0.82$ for $n = 5$ and $p \gtrless 0.05$ with

$$P_i = -1.68t_l + 346 \quad (15)$$

The slope changed 14%. Thus the P_i versus log t_l relationship is stronger than the linear–linear one.

The dependence of permeation rates on $-\log t$ is expected from the Snyder elution factor relationship.[19] An inverse linear dependence of P_s on t_l might be expected from eq. (9). P_i not P_s correlated with t_l and log t_l, however.

When P_s/P_i for a compound was regressed against P_s, the relationship was linear at $p \gtrless 0.05$ with $r = 0.894$ for $n = 8$ obeying

$$P_s/P_i = 0.00544P_s + 0.454 \quad (16)$$

Deletion of the data for the three deviant isomers caused $p > 0.05$.

The same occurred for the log P_s/P_i versus P_s and for the log P_s/P_i versus log P_s regressions:

$$\log(P_s/P_i) = 5.24 \times 10^{-4}P_s + 0.113 \quad (17)$$

where $r = 0.888$ for $n = 8$.

$$\log(P_s/P_i) = 0.548 \log P_s - 0.954 \qquad (18)$$

where $r = 0.78$ for $n = 8$.

Equation (16) has the highest p of eqs. (16)–(18), but all are biased toward the data of the deviant isomers.

The analogous relationships to P_i were not predictive at $p \gtrsim 0.05$.

When the correlations for the t_l/t_b ratio were considered, a very strong linear relationship emerged between P_s/P_i and t_l/t_b at $p \gtrsim 0.05$ if the deviant isomers were included ($n = 8$) or not ($n = 5$):

$$(P_s/P_i) = 3.54 t_l/t_b - 5.14 \qquad (19)$$

for $r = 0.89$ at $n = 8$ and

$$(P_s/P_i) = 1.19 t_l/t_b - 0.62 \qquad (20)$$

for $r = 0.94$ at $n = 5$. Therefore whatever relationships are observed for P_s/P_i will also be observed for t_l/t_b. This tight coupling is only expected for chemically similar compounds but may occur for chemically dissimilar compounds. This should be tested directly.

DISCUSSION

The p-xylene results show that the average t_b of 17 ± 6 min was longer than observed by Mickelsen and Hall[27] of 12 ± 5, $n = 7$ min, probably because the nitrile in the present study was 0.62-mm thick compared with 0.36 mm. The t_b is shorter than quoted for mixed xylene by Ansell Edmont.[25] The selective ion monitoring GC/MS method is more sensitive than the flame ionization and photoionization GC methods. Technical xylene, being a mixture of all xylenes and ethylbenzene, may also not permeate like p-xylene. The permeation is type A.[30] The P_s for a thinner 0.36-mm glove from Ansell Edmont was reported[28] to be 4200 mg m^{-2} min^{-1}. The results for IPB permeation through Pioneer A-14 nitrile gloves of the same nominal thickness as those of the present study were[5] a t_b of 271 min and a P_s of 480 mg m^{-2} min^{-1}. The corresponding results of the present study were 70 ± 10 min and 1600 ± 200 mg m^{-2} min^{-1}. A more sensitive technique would explain the shorter t_b. The material being lined may explain the observed higher P_s, or a more optimized collection system. Type A permeation behavior[30] was shown for the isomers by NPB, IPB, 123T, 135T, and OET. Type B behavior appeared to fit 124T, MET, and PET, the ones that showed much greater P_s than their corresponding P_i.

Explanation of isomer permeation behavior must account for: the three ethyltoluenes showing the same t_b and P_i; the similar initial equivalence of 124T and NPB; the same t_b of NPB, 124T, and the three ethyltoluenes; the same P_s for 135T and 123T; and the same t_l for IPB, NPB, 124T, and PET, and for 123T and OET.

When all the physical parameters mentioned in the Theory section (Tables I and II) were regressed to the parameters in Table III, few correlations were significant.

For the initial permeation period, the only parameters allowing equivalence of the ethyltoluenes were the van der Waals volume, the solubility parameter, and the connectivity parameter (Table II); the last is related to polarizability defined in eq. (1). The parameters that appeared to link 124T and NPB were molar volume, dielectric constant, and water solubility. The only parameter related to P_i at $p \gtrsim 0.025$ was the entropy of fusion S_f ($r = 0.75$) with the solubility parameter ($r = -0.58$) and dielectric constant ($r = 0.67$ for $n = 5$) not significantly so. When S_f divided by the solubility parameter S_p and by the square of the refractive index n (assuming the Maxwell relation) was regressed, the linear–linear plot had an r of 0.78, and the P_i versus log comparison had an r of 0.81. The relationship is

$$P_i = 748 \log S_f/(n^2 S_p) - 170 \qquad (21)$$

The units of the parameters and those for subsequent equations are defined in Tables I and II.

Equating eqs. (21) and (12),

$$\log t_l = 2.85 - 1.72 \log[S_f/(n^2 S_p)] \qquad (22)$$

Equating eqs. (21) and (14),

$$t_l = 354 - 509 \log[S_f/(n^2 S_p)] \qquad (23)$$

Neither prediction was significant at $p \gtrsim 0.025$ (r values about -0.50 for $n = 8$), probably because eq. (21) does not have enough p.

The parameters that allowed equivalence of t_b for ethyltoluenes, NPB, and 124T were solubility parameter and molar volume. A correlation analysis of all physical parameters revealed significant dependence on t_b at $p \gtrsim 0.025$ for log water solubility ($\log s_w$).

$$t_b = -134 \log s_w + 303 \qquad (24)$$

and $r = -0.72$ for $n = 8$. When the three deviant isomers are excluded, $p \gtrless 0.025$.

When eq. (24) is substituted into eq. (10),

$$\log P_s = 2.70 \log(134 \log s_w + 303) + 7.24 \quad (25)$$

This equation is not predictive at $p \gtrless 0.025$ ($r = 0.50$ for $n = 8$).

The other parameters near significance in the linear–linear analysis for t_b were directly for acentric factor a_f and radius of gyration r_g and inversely for connectivity c_n and for the chromatographic capacity factor for water $C_{18}1$. The best p was for

$$t_b = 106 \log[a_f/(s_w c_n)] + 38.6 \quad (26)$$

and $r = 0.75$ for $n = 8$,

$$t_b = 137 \log[a_f/(s_w c_n)] + 35.8 \quad (27)$$

and $r = 0.83$ for $n = 5$. When eq. (26) is substituted into eq. (10),

$$\log P_s = -2.70 \log[106 \log[a_f/(s_w c_n)]$$
$$+ 38.6] + 7.24 \quad (28)$$

Equation (28) is not predictive at $p \gtrless 0.025$ (r is -0.52 for $n = 8$).

The parameters that are near constant for isomers with the same t_l include refractive index, solubility parameter, chromatographic capacity factor for water, van der Waals volume, and molar refraction. After a complete correlational analysis of the parameters of the Theory section, there was no parameter that was correlated at $p \gtrless 0.025$. The closest were the standard entropy of vaporization S_v (significant at $p \gtrless 0.05$), the standard entropy of fusion, the van der Waals volume, and the specific dispersion in increasing p. There was no parameter or combination of parameters significant at $p \gtrless 0.025$. For the correlation with S_v,

$$\log t_l = 0.843 S_v - 4.61 \quad (29)$$

for $n = 8$, $r = 0.70$. Excluding the three deviant isomers:

$$\log t_l = 0.845 S_v - 4.62 \quad (30)$$

for $n = 5$, $r = 0.83$. When eq. (29) is substituted into eq. (12),

$$P_i = -436(0.843 S_v - 4.61) + 1072 \quad (31)$$

No correlation of P_i to S_v exists at $p \gtrless 0.025$ (r is -0.52 for $n = 8$).

Considering P_s, the rates of 135T and 123T, 124T and MET, and NPB and OET were not significantly different. The solvent parameters that might explain these relationships include solubility parameter, molar refraction, entropy of vaporization, and the chromatographic capacity factor for water $C_{18}1$. There were no significant correlations of P_s or P_i on specific gravity/density based on eq. (8), probably because P also varies. The three isomers that deviated in the faster permeation period were 124T, MET, and PET, all having the common structural feature of being similar in configuration to 124T if the methyl group of the ethyl in the two ethyltoluenes is visualized to be bent toward the adjacent sterically unhindered ring position. The equivalence of NPB and OET could arise through a common five-membered type ring making them appear almost annulated, the methyl group of the straight chain compound being close to the ortho position, and the methyl group of the ethyl group of the ethyltoluene being close to the ring methyl.

A complete correlational analysis revealed that there was no one parameter or combination of parameters that could be correlated to P_s at $p \gtrless 0.025$, although the best correlation was shown at $p \gtrless 0.05$ to the reverse phase capacity factor for water at $r = 0.63$. This implies that there might be an optimum condition rather than a simple dependence, linear or exponential.

When the quantities in Table III were plotted against the solvent parameters in Tables I and II, the ones showing one optimum for P_s containing at least two data points in either a symmetric or hyperbolic dependence were connectivity between 3.36 and 3.40 units, the solubility parameter between 1.78 and 1.80 $(J/m^3)^{0.5}$, the radius of gyration between 0.413 and 0.430 nm, and the logarithm of the reverse phase capacity factor for water between 2.573 and 2.640. These parameters also define the susceptibility parameters for the nitrile glove material in terms of solvent parameters. There were no optima for t_l. The analogous quantities for t_b resistance were the radius of gyration 0.432–0.438 nm, water solubility 48–50 mg/L, and the entropy of fusion 8–10 cal K^{-1} mol^{-1}. These parameters define the optimum resistance to permeation of nitrile in terms of alkylbenzene parameters. The only common parameter for t_b resistance and enhanced P_s is the radius of gyration, a measure of rotatory molecular volume. The two regions do not overlap but are close. The existence of optima explains the lack of correlations. Much the same conclusions were shown by the Que

Hee study for the Snyder elution factor analysis of Ansell Edmont data.[19]

The three deviant isomers may form charge transfer type complexes with the unsaturated butadiene and nitrile groups more avidly than the other isomers without allowing swelling, but may permit type B permeation behavior characteristic of an extra process, the exact nature of which needs further investigation.

REFERENCES

1. K. Verschueren, *Handbook of Environmental Data on Organic Chemicals*, 2nd ed., Van Nostrand Reinhold, New York, 1983.
2. S. Coffey, *Rodd's Chemistry of Carbon Compounds*, 2nd ed., Elsevier, New York, 1971.
3. Weed Science Society of America, *Adjuvants for Herbicides*, Weed Science Society of America, Champaign, IL, 1982.
4. American Conference of Governmental Industrial Hygienists, *1994-95 Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices*, ACGIH, Cincinnati, OH, 1994.
5. K. Forsberg and L. H. Keith, *Chemical Protective Clothing Performance Index Book*, Wiley, New York, 1989.
6. M. Grayson, *Kirk-Othmer Concise Encyclopedia of Chemical Technology*, Wiley–Interscience, New York, 1985.
7. W. J. Moore, *Physical Chemistry*, 3rd ed., Prentice–Hall, Englewood Cliffs, NJ, 1962.
8. A. L. McClennan, *Tables of Experimental Dipole Moments*, Vol. 1, W. H. Freeman, San Francisco, CA, 1963, p. 332.
9. A. L. McClennan, *Tables of Experimental Dipole Moments*, Vol. 2, Rahara Enterprises, San Francisco, CA, 1974, p. 369.
10. J. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds*, Vol. 2, Elsevier, New York, 1965.
11. E. W. Washburn, *International Critical Tables of Numerical Data, Physics, Chemistry and Technology*, Vol. VI, McGraw–Hill, New York, 1929.
12. D. R. Lide and G. W. A. Milne, *Handbook of Data on Organic Compounds*, 3rd ed., CRC Press, Boca Raton, FL, 1994.
13. F. D. Rossini, K. S. Pitzer, R. L. Arnett, R. M. Braun, and G. C. Pimentel, *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds: American Petroleum Institute 44*, Carnegie Press, Pittsburgh, PA, 1953.
14. T. E. Daubert and R. P. Danner, *Physical and Thermodynamic Properties of Pure Materials*, Hemisphere Publishing Corporation, New York, 1989.
15. D. Mackay, W. Y. Shiu, and K. C. Ma, *Illustrated Handbook of Physical-Chemical Properties and Environmental Fate for Organic Chemicals*, Vol. 1, Lewis Publishers, Boca Raton, FL, 1992, p. 93.
16. M. Mikatavage, S. S. Que Hee, and H. E. Ayer, *Am. Ind. Hyg. Assoc. J.*, **45**, 617 (1984).
17. J. Harville and S. S. Que Hee, *Am. Ind. Hyg. Assoc. J.*, **50**, 438 (1989).
18. S. S. Que Hee, in *Chemical Protective Performance in Chemical Emergency Response, ASTM OH-010370-55*, J. L. Perkins and J. O. Stull, Eds., ASTM, Philadelphia, PA, 1989, p. 157.
19. S. S. Que Hee, *Appl. Occup. Environ. Hygiene*, to appear.
20. P. M. Sherblom and R. P. Eganhouse, *J. Chromatogr.*, **454**, 37 (1988).
21. N. N. Nirmilakhandan and R. E. Speece, *Environ. Sci. Technol.*, **22**, 328 (1988).
22. Z. Hongwei and H. Zhide, *Chromatographia*, **33**, 575 (1992).
23. J. H. Knox, J. Kriz, and E. Adamcova, *J. Chromatogr.*, **447**, 13 (1988).
24. C. M. White, J. Hackett, R. R. Anderson, S. Kail, and P. S. Spock, *J. High Resolution Chromatogr.*, **15**, 105 (1992).
25. Ansell Edmont, *Ansell Edmont Chemical Resistance Guide*, 5th ed., Ansell Edmont, Coshocton, OH, 1990.
26. G. A. Mellstrom and A. S. Boman, in *Protective Gloves for Occupational Use*, G. A. Mellstrom, J. E. Wahlberg, and H. I. Maiibach, Eds., CRC Press, Boca Raton, FL, 1994, p. 21.
27. R. L. Mickelsen and R. C. Hall, *Am. Ind. Hyg. Assoc. J.*, **48**, 941 (1987).
28. R. L. Mickelsen, M. M. Roder, and S. P. Berardinelli, *Am. Ind. Hyg. Assoc. J.*, **47**, 236 (1986).
29. G. W. Snedecor and W. G. Cochran, *Statistical Methods*, 8th ed., University of Iowa Press, Ames, IA, 1989.
30. G. O. Nelson, B. Y. Lum, G. J. Carlson, C. M. Wong, and J. S. Johnson, *Am. Ind. Hyg. Assoc. J.*, **42**, 217 (1981).