Permeation of Xylene Isomers Through Nitrile Gloves

SHIH-WEI TSAI, SHANE S. QUE HEE

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

ABSTRACT: The physical parameters of the xylene isomers (the positional isomers *o*-, *m*-, and *p*-xylenes and the skeletal isomer ethyl benzene) responsible for the differing permeation behavior of the isomers through lined unsupported 0.41 mm thick nitrile glove material were investigated. An ASTM type permeation cell at 30°C, constant mixing conditions, hexane liquid collection, and capillary column gas chromatography/ mass spectrometry of samples taken from the collection side every ten minutes allowed break through times t_b and steady-state sections to be defined. While pure isomers had distinct break through times t_b (*m*-xylene = *p*-xylene < ethyl benzene = *o*-xylene), steady-state permeation rates P_s (*p*-xylene > *m*-xylene > ethyl benzene = *o*-xylene), lag times t_l (*m*-xylene < *p*-xylene = ethyl benzene < *o*-xylene), and diffusion coefficients D_p (*m*-xylene < *p*-xylene = ethyl benzene < *o*-xylene), such behavior was lost in a equal volume mixture (t_b, t_l, P_s, and D_p were equivalent). The average P_s of the mixture isomers of equal volumes did not differ from that expected from the individual pure isomer P_s values. The results for the pure isomers were attributed to *o*-xylene and ethyl benzene being similarly sterically hindered, the *p*-xylene being the flattest and most symmetrical molecule and having no dipole moment, and *m*-xylene being intermediate in steric structure. The pure isomer t_l were directly related to viscosity divided by the log octanol-water coefficient, while their log P_s was inversely related to dipole moment times the logarithm of the capacity factor for water for a reversed-phase high-performance liquid chromatography column. In an equivolume mixture of the isomers, isomer interactions caused equivalence for all permeation kinetic parameters, indicating that the kinetics of mixture constituents is not predictable from the behavior of the pure constituents, although mass transfer appears additive. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63:** 1713–1721, 1997

Key words: permeation; glove; xylene; ethyl benzene; nitrile

INTRODUCTION

The xylene isomers include the benzene-ring positional *o*-, *m*-, and *p*-xylenes (1,2-, 1,3-, and 1,4-dimethyl benzene, respectively) and the skeletal isomer ethyl benzene. The xylene used in industry is a mixture of all four isomers, usually 44% (v/v) *m*-xylene, 20% *o*-xylene, 20% *p*-xylene, and 15% ethyl benzene.[1] Xylene-range petroleum fractions can also contain trimethyl- and tetramethyl-benzenes, as well as traces (<1%) of toluene and benzene, and are used extensively in the inert components of pesticide formulations.[2] Xylene is used as a solvent in the printing, rubber, and leather industries; as a cleaning agent, as a paint/varnish thinner, an ingredient in coatings, and precursors for aromatic polymers and plastics; and are minor constituents of fuels, gasolines, and cigarette

smoke.[1] The isomers are relatively volatile and are not very water soluble.[1] The major acute human toxicity effect is irritation of mucous membranes, while the major chronic animal effects involve the central nervous system, liver, kidney, heart, and lung.[1] The three positional isomers are excreted as methyl hippuric acids and xylenols in the urine;[1] likewise, ethylbenzene is excreted as mandelic/phenylglyoxylic acids.[1] All are excreted in the breath.[1] Xylene does not appear to be a carcinogen or a point mutagen but causes animal fetal abnormalities at high concentrations.[1] The US EPA has proposed a maximum level of 10 ppm (w/v) xylene/day for lifetime exposures from drinking water.[1] OSHA has mandated an occupational limit of 100 ppm (v/v) time-weighted average for eight hour/day and five day/week exposures; a 15 min short-term exposure limit of 150 ppm (v/v) is also mandated.[1]

Xylene absorption after skin exposure has been demonstrated in humans.[1] Gloves are worn for skin protection during solvent handling. The only recommended inexpensive glove for xylene compatible for both water and organic solvent exposures is unsupported nitrile, a polymer of acrylonitrile and 1,3-butadiene.[3] The breakthough time t_b when xylene was first detected by one manufacturer with a flame ionization gas chromatographic detector on the opposite side of this glove (Ansell Edmont 37-165 Sol-Vex™, 0.54 mm thickness) in an air collection medium was 75 min, and the steady-state permeation rate P_s was[4] between 9 to 90 $\mu g/cm^2/min$. Another manufacturer using the same technique reported a t_b of 41 min and a P_s of 122 $\mu g/cm^2/min$ for a similar 0.38 mm thick Best Nitri-Solve™ 727 glove.[5] Forsberg and Keith[6] document a t_b of 27 min and a P_s of 0.2 $\mu g/cm^2/min$ for Ansell Edmont 0.38 mm 37–155 nitrile, t_b of 4 to 5 min and P_s of 2.3 to <900 $\mu g/cm^2/min$ for 0.55 to 0.60 mm Sol-Vex™ 37–165 nitrile; and t_b of 41 to 57 min and P_s of 10 to 280 $\mu g/cm^2/min$ for 0.37 to 0.42 mm thick 37–175 nitrile. Very little attention has been given to individual xylene isomers, although ethyl benzene has been reported to have a t_b of 24 min and a P_s of 192 $\mu g/cm^2/min$ through 0.38 mm 37–155 Ansell Edmont Sol-Vex™ nitrile, and 43 min and 124 $\mu g/cm^2/min$, respectively, through 0.38 mm Best Nitri-Solve™ 727. The only data available for the positional isomers was[7] for *p*-xylene through 0.36 mm nitrile, where the t_b was 12 +/− 5 min and P_s was 420 $\mu g/cm^2/min$.

We have previously reported[8] on the chemical structure–permeation kinetics dependence of a series of trimethyl benzenes, propyl benzenes, and ethyl toluenes through nitrile. We now report a similar study with the same permeation method and the same conditions for the xylene isomers.

METHODS AND MATERIALS

Gloves and Chemicals

The gloves were lined unsupported Ansell Edmont 37-165, 22 mil and 38 cm in length, from Ansell Edmont, Coshocton, Ohio. The xylene isomers were ethyl benzene (certified grade), *p*-xylene (certified grade), *m*-xylene (purified grade), and *o*-xylene (reagent grade) from Fisher Scientific, Tustin, California. Optima hexane from Fisher Scientific was the collection solvent. A challenge mixture containing equal volumes of all xylene isomers was also evaluated.

Apparatus

The permeation cell was a ASTM type PTC-600 permeation cell from Pesce Lab Sales, Kennett Square, Pennsylvania. All glove permeation experiments were at 30.0 +/− 2.0°C in a moving tray shaker water bath (Fisher Scientific model number 125 no. 429) that moved at a horizontal mixing velocity of 8.5 +/− 0.5 cm/s. Gas chromatography/mass spectrometry (GC/MS) utilized a fused silica Bentone 34/Di-*n*-decylphthalate support-coated open tubular (SCOT) capillary column, 30 m long and 0.53 mm internal diameter (Supelco, Bellefonte, Pennsylvania), in a Hewlett-Packard (HP) model 5890A gas chromatograph, connected to a positive ion 70 eV electron impact HP 5988A mass spectrometer. Helium carrier gas (3.0 +/− 0.1 mL/min) was from Alphagaz, Walnut Creek, California. The injector, column, interface, and ion source temperatures were 200, 90, 200, and 200°C, respectively. These conditions allowed resolution of all xylene isomers, a difficult task on almost any other column, and allowed xylene purity as well as the permeation kinetics to be obtained. One microliter aliquots were injected using the sandwich technique via a Hamilton 10 microliter syringe from Fisher Scientific. The mass spectrometer solvent delay for hexane was 4 min. All glassware including 1.5 mL vials from Wheaton (Millville, New Jersey) were soaked overnight in 10% nitric acid, soaked

again in ASTM type II water, and dried in a dust-less oven.

Methods

The specific permeation procedure is given in detail elsewhere.[8,9] In summary, gloves were conditioned for 24 h at a relative humidity of 65.2 $+/- 0.8\%$ at 21.1 $+/- 0.3°C$ (saturated aqueous sodium dichromate in a desiccator). Material of diameter 3.80 $+/- 0.09$ cm (vernier calipers) was cut from the glove palm, the thickness measured at three points (an average of 0.41 $+/- 0.05$ mm by micrometer screw gauge), and the material was placed between the two Teflon™ gaskets of the permeation cell. The two pyrex chambers were inserted into their aluminum flanges, and the nuts tightened to a torque of 16 in.-lb. (torque wrench). A volume of 10 mL of hexane was pipeted into the collection side, then 15 mL of challenge solution into the challenge side, and the whole cell was immersed in the water bath with mixing then started. Aliquots of 0.100 mL were taken every ten minutes for four hours from the collection side, placed into 1.5 mL vials previously prechilled to $-20°C$, and stored at $-20°C$ until GC/MS analysis using the selective ion mode at m/z 91 (tropylium ion) and 105 (methyltropylium ion). The mass permeated was obtained from calculating the mass injected from an external standards curve and correcting for volume fraction injected and any dilution factor. Glove thicknesses were remeasured after drying. Cumulated mass permeated was then plotted against time of permeation. Linear regression of the steady-state region allowed calculation of P_s and the lag time t_l, the time when this regression line had a permeated mass of zero. Assuming only diffusion was the mass transfer permeation step, the diffusion coefficient D_p was calculated from $l^2/6t_l$. Individual run permeation data were pooled if statistically homogeneous. Correlation to xylene physical and chromatographic parameters (Table I) was then done as done previously for the next higher homologs.[8] The theory for the use of these parameters is provided in Tsai and Que Hee.[8]

Quality assurance and control included tests for contamination (filling both sides before experiments with hexane and analyzing aliquots by GC/MS), for glove pinholes and leaking (above detection limit permeant concentrations at time zero), for back permeation (analysis of headspace and challenge side for hexane), and for evaporation (volumes of both sides measured before and after experiments). Detection limits (signal/noise of 2) were between 200 to 400 pg, and linear ranges were between 200 to 2000 pg. No glove materials swelled, and no back permeation of hexane occurred.

RESULTS

All permeation curves had just one steady-state period and obeyed Type A permeation.[20] Table II shows the individual and average t_b, P_s, t_l, and D_p, for all the permeation experiments. For the average run data, most of the coefficients of variation (CV) are $<25\%$ excepting t_b and D_p for pure m-xylene, t_b and P_s for pure p-xylene, and P_s for pure p-xylene, as well as mixture t_b values for o-xylene and m-xylene. Only the t_b in the grand averages of pure isomers and mixture had CV $>25\%$. Average D_p values calculated from individual D_p data had smaller CV than their averaged corresponding t_l data, except pure m-xylene and pure ethyl benzene.

For the pure isomers, the t_b for m-xylene differed statistically at $p < 0.025$ from those of o-xylene and ethyl benzene; in the mixture, there was no statistical difference in any t_b. The P_s for the pure isomers differed except for o-xylene and ethyl benzene; all P_s in the mixture were equivalent. The t_l for the pure isomers differed for o-xylene and m-xylene, and m-xylene and ethyl benzene; in the mixture, t_l did not differ. The D_p for pure isomers differed for o-xylene relative to m-xylene and p-xylene, and for ethyl benzene relative to m-xylene and p-xylene; all D_p for the isomers in the mixture were equivalent. Corresponding individual run t_l were always greater than the t_b for pure isomers even in the mixture; the averaged t_l were equivalent for the isomers in the mixture.

When the mixture data were averaged for each parameter, as were the data for the pure isomers, the grand average D_p, t_b, and t_l for all the pure isomers did not differ significantly from the average corresponding parameters for the isomers in the mixture (Table II). This was not so for P_s. When mixture P_s were added, the total mass transfer was 510 $+/- 79$ $\mu g/cm^2/min$. This is not significantly different from the average P_s of the pure isomers, 390 $+/- 250$ $\mu g/cm^2/min$, derived by assuming that each isomer contributes equally at the same time (Table II). The same result occurs when the P_s for

Table I   Selected Physical Constants for the Xylenes, Molecular Weight 106.167

	Isomer			
Parameter	o-Xylene	m-Xylene	p-Xylene	Ethyl Benzene
MP[a]	247.98	225.29	286.42	178.19
BP	417.58	412.27	411.51	409.35
SG	0.88020	0.86417	0.86105	0.86702
n	1.5029	1.4946	1.4932	1.4932
MV	121.14	123.35	123.78	122.68
MR	35.823	35.980	36.029	35.777
SR	0.33744	0.33892	0.33938	0.33701
RI	1.0650	1.0647	1.0649	1.0619
SD	180.1	180.6	182.1	174.7
VIS	0.708	0.549	0.570	0.6003
ST	28.93	27.54	27.22	27.93
CT	632.2	619.2	618.2	619.7
HFU	3.250	2.765	4.090	2.190
EFU	13.106	12.273	14.280	12.291
DM	2.0681	1.0007	0.0	1.9680
SP	1.8453	1.8090	1.7838	1.8043
AF	0.3127	0.3260	0.3259	0.3036
RG	3.8360	3.9370	3.8310	3.8970
VDWV	70.66	70.66	70.66	69.74
SA	146.8	150.3	150.3	144.9
WS	221	160	214	187
OW	3.12	3.20	3.15	3.15
DC	2.544	2.347	2.249	2.381
CONN	2.8274	2.8214	2.8214	2.9713
$\log k'(C_{18}1)$	3.72	4.03	4.12	3.54
$\log k'(C_{18}2)$	2.271	2.317	2.333	2.200
$\log k'(GC1)$	2.9467	2.9369	2.9358	2.9289
$\log k'(GC2)$	2.9424	2.9311	2.9318	2.9267
DIF	12.06	11.87	12.16	12.06

[a] Abbreviations are as follows. MP, melting point[10] in °K; BP, boiling point[11] in °K; SG, density[10] between 4 and 20°C in g/mL; n, refractive index[11] at the sodium D-line at 25°C; MV, molar liquid volume[11] in mL/mol at 25°C; MR, molar refraction[12] in mL/mole at 25°C; SR, specific refraction[12] in mL/g at 25°C; RI, refractivity intercept[12] at 25°C; SD, specific dispersion[12] in mL/g at 25°C; VIS, absolute viscosity[12] in centipoise at 30°C; ST, surface tension[12] in dyne/cm^2 at 30°C; CT, critical temperature[12] in °K; HFU, heat of fusion[12] in kcal/mole; EFU, entropy of fusion[12] in cal/deg. mole; DM, dipole moment[11] in Curie meter ($\times 10^{-30}$); SP, solubility parameter[11] at 25°C in (J/m^3)$^{0.5}$ ($\times 10^4$); AF, acentric factor[11]; RG, radius of gyration[11] in meter ($\times 10^{-10}$); VDWV, van der Waal's volume[11] in mL/mole; SA, total surface area[13] in A^2 recommended by Yalkowsy and Valvani, 1976; WS, water solubility[13] at 25°C in mg/L (Wasik et al., 1983, from HPLC); OW, log K_{ou}^{13} at 25°C recommended by Sangster, 1989; DC, dielectric constant[14] at 29–30°C; CONN, connectivity index[15]; log $k'(C_{18}1)$, logarithm of the capacity factor[15] for Merck LiChrosorb RP-18 column (16 cm $\times$ 5 mm ID) at 1 mL/min of 70 : 30 (w/w) methanol/water using a ultraviolet detector; log $k'(C_{18}2)$, logarithm of the capacity factor in water[16] for a Perkin Elmer HS-5-C$_{18}$ column (12.5 cm $\times$ 4.6 mm ID) at 1.5 mL/min of 50 to 90% acetonitrile/water and 50 to 90% methanol/water mobile phases using a 254 nm detector; log $k'(GC1)$, logarithm of the capacity factor[17] on 15% squalene on 80/100 mesh silanized white support (3 m $\times$ 4 mm ID stainless steel column) at 100°C at hydrogen carrier gas flow of 80 +/ − 0.5 mL/min for a thermal conductivity detector; log $k'(GC2)$, logarithm of the capacity factor[18] on Petrocol DH coated (0.5 μm film) fused silica capillary column (100 m $\times$ 0.25 mm ID) at 1°/min from 30 to 220°C at helium carrier gas flow 31.5 mL/min using a flame ionization detector; DIF, infinite dilution diffusivity[19] ($\times 10^5$) in cm^2/s in supercritical carbon dioxide at 40°C and 160 bar.

the pure isomers are adjusted for actual mass in the mixture. Using averaged isomer data, the pure isomer relationships of t_l with t_b, ln t_l with t_b, P_s with t_b, ln P_s with t_b, P_s with t_l, ln P_s with t_l, ln P_s with ln t_b, and ln P_s with ln t_l were not linear. However, D_p was linearly related to t_b at $p < 0.025$ ($r > +/- 0.9500$), as follows.

$$D_p = -45.2\, t_b + 1798 \quad \text{with } r = -0.991 \quad (1)$$

$$\ln D_p = -0.0536\, t_b + 7.82$$

$$\text{with } r = -0.987 \quad (2)$$

When the unaveraged run data for pure isomers were intercorrelated for $n = 12$, the linear correla-

Table II   Permeation Data Through Lined Unsupported Nitrile for Pure Xylene Isomers and an Equal Volume Mixture of Xylenes at 30°C

Isomer	Run	Thick[a]	t_b	P_s	t_l	D_p
Pure Isomers						
o-Xylene	1	378	30	164	51	467
	2	403	20	246	44	615
	3	458	30	240	61	573
Average +/−		413	26.7	217	52	552
SD		41	5.8	46	9	76
m-Xylene	1	395	10	369	26	1000
	2	464	10	328	20	1794
	3	389	20	361	29	870
Average +/−		416	13.3	353	25.0	1221
SD		42	5.8	22	4.6	500
p-Xylene	1	465	20	716	36	1001
	2	472	20	1016	48	774
	3	480	10	522	31	1239
Average +/−		472	16.7	751	38.3	1010
SD		7.5	5.8	249	8.7	230
Ethyl benzene	1	368	30	132	39	579
	2	384	20	296	36	683
	3	391	30	255	39	653
Average +/−		382	26.7	228	38.0	638
SD		13	5.8	85	1.7	54
Grand average +/−		421	20.8	390	38	854
SD		43	7.9	250	11	370
Mixture						
o-Xylene	1	375	20	109	28	837
	2	423	20	117	41	727
	3	370	30	127	32	713
Average +/−		389	23.3	117.7	33.7	759
SD		29	5.8	9.0	6.7	68
m-Xylene	1	375	20	116	28	837
	2	423	10	115	41	727
	3	370	20	152	38	600
Average +/−		389	16.7	128	35.7	721
SD		29	5.8	21	6.8	119
p-Xylene	1	375	20	117	30	781
	2	423	20	109	43	694
	3	370	20	165	39	585
Average +/−		389	20	130	37.3	687
SD		29	0	30	6.7	98
Ethyl benzene	1	375	30	118	32	732
	2	423	20	130	44	678
	3	370	30	155	41	557
Average +/−		389	26.7	134	39.0	656
SD		29	5.8	19	6.2	90
Grand average +/−		389	21.7	128	6.4	706
SD		25	5.8	19	6.0	91

[a] Abbreviations are as follows. Thick, thickness in micrometers, t_b, break through time in min; P_s, steady-state permeation rate in ug/cm^2/min; t_l, lag time in min; D_p, diffusion coefficient in $(\mu m)^2$/min; SD, standard deviation.

tions at $p < 0.025$ with $r > +/- 0.576$) were as follows.

$$t_l = 1.08 \, t_b + 15.8 \quad r = 0.748 \qquad (3)$$

$$\ln t_l = 0.0300 \, t_b + 2.98 \quad r = 0.771 \qquad (4)$$

$$D_p = -37.8 \, t_b + 1642 \quad r = -0.809 \qquad (5)$$

$$\ln D_p = -0.0414 \, t_b + 7.54 \quad r = -0.862 \quad (6)$$

$$D_p = -24.8 \, t_l + 1803 \quad r = -0.764 \qquad (7)$$

$$\ln D_p = -0.0265 \, t_l + 7.70 \quad r = -0.799 \quad (8)$$

$$\ln(D_p t_l) = 0.000537 \, P_s + 10.1 \quad r = 0.675 \quad (9)$$

$$P_s/t_l = 0.0119 \, D_p + 0.786 \quad r = 0.668 \quad (10)$$

$$\ln(P_s/t_l) = 0.00133 \, D_p + 1.05 \quad r = 0.702 \quad (11)$$

The ln (dependent variable) versus independent variable correlations [eqs. (4), (6), (8), and (11)] were more linear than the corresponding untransformed dependent variable versus independent variable correlations [eqs. (3), (5), (7), and (10), respectively]. Similarly, the linear/linear correlation corresponding to eq. (9) was not even significant. Equations (6), (5), (8), (4), and (7) had the most statistical power in that decreasing order. Equations (1), (2), (5), and (6) imply that the run data when analyzed in the formats of individual run or when averaged per isomer showed linear relationships between D_p versus t_b, and ln D_p versus t_b. While individual run t_l and t_b were correlated, the averaged data were not. This implies that individual D_p data should be calculated.

The D_p ratios for an isomer in the mixture relative to the pure isomer were unchanged for ethyl benzene, less than 1 for o-xylene (0.727), and greater than 1 for p-xylene (1.470) and for m-xylene (1.694). The respective P_s ratios were 0.5877, 0.544, 0.173, and 0.363. Ethyl benzene and o-xylene appear to be the determining isomers in the mixture.

DISCUSSION

The data for p-xylene previously reported in the literature for 0.36 mm nitrile are a t_b of 12 +/- 5 min and a P_s of 420 μg/cm^2/min using an air collection technique.[7] In our previous work with 0.62 +/- 0.04 mm thick Ansell Edmont 37–165 nitrile,[8] the t_b were 17 +/- 6 min, P_s of 690 +/- 170 μg/cm^2/min, t_l of 40 +/- 5 min, and D_p of 1,700 +/- 300 μm^2/min. In the present work,

t_b was 16.7 +/- 5.8 min, P_s was 751 +/- 249 μg/cm^2/min, t_l was 38.3 +/- 8.7 min, and D_p was 1010 +/- 230 μm^2/min under the same conditions, except that the nitrile was an average thickness of 0.472 +/- 0.075 mm. The permeation results of both our studies are equivalent, nevertheless, except for D_p. Ethyl benzene has been reported to have t_b of 24–43 min and P_s of 124–192 μg/cm^2/min through 0.38 mm thick nitrile in the air collection technique.[6] Our present results on nitrile of 0.382 +/- 0.013 mm thickness show a t_b of 26.7 +/- 5.8 min and a P_s of 228 +/- 85 μg/cm^2/min. While the t_b are compatible, our P_s are higher. The slightly higher temperature used in the present study may explain this, differences in nitrile glove production, or the presence of a liquid collection medium rather than air.

The variables in Table I that fit the order of averaged t_l for the pure isomers (m-xylene < p-xylene = ethyl benzene < o-xylene) include the following: viscosity (VIS), specific gravity, refractive index, molar volume (inverse), molar refraction (inverse), specific refraction (inverse), refractivity index, surface tension, critical temperature, acentric factor (inverse), radius of gyration (inverse), total surface area (inverse), water solubility, log octanol-water coefficient (inverse), and dielectric constant. Of these variables, the nearest to $p < 0.025$ was viscosity VIS.

$$t_l = 145 \, \text{VIS} - 50.0 \quad r = 0.928 \qquad (12)$$

When ln t_l was similarly correlated, the VIS correlation was not significant.

$$\ln t_l = 3.74 \, \text{VIS} + 1.34 \quad r = 0.878 \qquad (13)$$

The variables in Table I that may reflect interaction of permeant with the glove material are[21] the dipole moment, the solubility parameter, water solubility, log K_{ow} (inverse), and the chromatographic parameters (inverse for reverse phase log k'). When these were correlated appropriately with t_l, only two combinations, VIS/log K_{ow} and VIS.DIF (where DIF is the infinite dilution diffusivity in supercritical carbon dioxide at 40°C and 160 bar), gave higher r than eq. (12).

$$t_l = 428 \, \text{VIS}/\log K_{ow} - 44.2 \quad r = 0.941 \quad (14)$$

$$t_l = 12.0 \, \text{VIS.DIF} - 49.7 \quad r = 0.953 \quad (15)$$

Equation (15) is significant at $p < 0.025$ ($r > +/-0.95$).

For WS in mg/L, where eq. (16) is expected to be valid,[22]

$$\log K_{ow\text{-calc}} = 4.5 - 0.75 \log WS \qquad (16)$$

Equation (14) becomes

$$t_l = 428 \, VIS/(4.5 - 0.75 \log WS) - 44.2$$
$$= 428 \, VIS/\log K_{ow\text{-calc}} - 44.2 \qquad (17)$$

Substituting the values for WS from Table I, eq. (17) leads to the regression eq. (18) that is still as predictive at $p < 0.025$ as eq. (14).

$$t_l = 438 \, VIS/\log K_{ow\text{-calc}} - 46.1 \quad r = 0.945 \quad (18)$$

The WS values underestimate $\log K_{ow}$ in Table I using eq. (16): 0.35 for m-xylene and ethyl benzene, 0.38 for o-xylene, and 0.40 for p-xylene.

Substituting for t_l as eq. (14) into eq. (8),

$$\ln D_p = -11.3 \, VIS/\log K_{ow} + 8.87 \qquad (19)$$

When $\ln D_p$ was correlated to $VIS/\log K_{ow}$, the resulting correlation was as follows:

$$\ln D_p = -11.5 \, VIS/\log K_{ow} + 9.20$$
$$r = -0.858 \quad (20)$$

While not significant at $p < 0.025$, eq. (20) is close to eq. (19) since the slope for eq. (20) is only 1.8% lower, and the intercept is 3.7% higher than predicted.

Substituting for t_l as eq. (15) into eq. (8),

$$\ln D_p = -0.318 \, VIS.DIF + 9.02 \qquad (21)$$

When $\ln D_p$ was correlated to $VIS.DIF$,

$$\ln D_p = -0.378 \, VIS.DIF + 9.46$$
$$r = -0.880 \quad (22)$$

The r was still not significant at $p < 0.025$, though the r had more power than in eq. (20); however, the slope and intercept of eq. (22) were significantly different from those of eq. (21).

The variables in Table I that fit the order of averaged P_s for the pure isomers (p-xylene > m-xylene > ethyl benzene = o-xylene) are as follows:

molar volume, molar refraction, specific refraction, specific dispersion, surface tension (inverse), critical temperature (inverse), dipole moment (inverse), dielectric constant (inverse), and the reverse phase $\log k'$. Of these parameters, the only one significantly correlated at $p < 0.025$ was the dipole moment DM:

$$P_s = -249 \, DM + 701 \quad r = -0.964 \quad (23)$$
$$\ln P_s = -0.589 \, DM + 6.57 \quad r = -0.992 \quad (24)$$

The log transformed equation is clearly superior in the p value.

The next most correlated parameters were the molar refraction MR, the specific refraction SR, and the dielectric constant DC, whose r were -0.846, 0.846, and -0.809, respectively. Log transformation of P_s improved these r but still did not reach significance (respective r were -0.906, 0.906, and -0.845). No combination of these three variables with DM improved the r of eq. (24). The partitioning variables were then compared as for t_l above. Thus, the r values > 0.992 were shown by the following:

$$\ln P_s = -0.164 \, DM.\log k'(C_{18}1) + 6.59$$
$$r = -0.996 \quad (25)$$
$$\ln P_s = -0.265 \, DM.\log k'(C_{18}2) + 6.57$$
$$r = -0.993 \quad (26)$$

Equation (25) is the equation of greatest statistical power.

There were no significant relationships of averaged t_b with the variables in Table I (t_b values obeyed m-xylene = p-xylene < o-xylene = ethyl benzene). The nearest to significance was molecular surface area SA [eq. (27)]. No combination of variables improved p, even though the variables that best correlated next were the acentric factor AF ($r = -0.922$), the molar refraction MR ($r = -0.921$), the specific refraction SR ($r = -0.921$), and the reverse phase chromatographic capacity factor for water, $\log k'$ ($C_{18}1$), with $r = -0.906$.

$$t_b = -2.41 \, SA + 378$$
$$r = -0.938 \quad p = 0.030 \quad (27)$$

The equation with most statistical power of eqs. (1) through (11) that contains t_b is eq. (1). Substitution of eq. (27) into the latter produces

$$D_p = 109 \text{ SA} - 15,288 \qquad (28)$$

On correlating D_p with SA,

$$D_p = 103 \text{ SA} - 14,458 \quad r = 0.882 \qquad (29)$$

This was not significant at $p < 0.025$, but eqs. (28) and (29) are similar.

If instead eq. (27) is substituted into eq. (2),

$$\ln D_p = 0.129 \text{ SA} - 12.4 \qquad (30)$$

On correlating $\ln D_p$ with SA,

$$\ln D_p = 0.123 \text{ SA} - 11.5 \quad r = 0.879 \qquad (31)$$

The correlation is not significant at $p < 0.025$, but eqs. (30) and (31) are similar.

The variables from Table I that were considered in their correlation to t_b also were considered for D_p since D_p and t_b were linearly correlated [eq. (1)]. Again, there was no correlation at $p < 0.025$, eqs. (29) and (31) having the best correlations. Correlation coefficients were lower for D_p than the same variable correlated to t_b.

The above relationships for the xylene isomers have some similarities to those found for the congeneric isomers with one more carbon.[8] For the latter, there was no factor that correlated with t_l. An additional complication was the presence of two steady states for the molecular weight 120 isomers rather than just one as for the xylene isomers. For the initial steady-state rate in the latter study, an inverse dependence on DC (approximated by the square of the refractive index n^2 using the Maxwell Relation[8]), while not statistically significant alone, was implicated in combination with other parameters. It might be noted that n^2 underestimates xylene DC by 11, 4.8, 0.84, and 6.3% for o-, m-, and p-xylenes and ethyl benzene, respectively.

The ortho isomer is sterically hindered and it has the lowest P_s and D_p and longest t_l and t_b; whereas the para isomer, the flattest and most symmetrical, has the highest P_s and D_p and the longest t_b and the second longest t_l. If ethyl benzene has its methyl group bent, the latter will be close to the ortho position of the ring, a situation likely for a constrained environment like inside nitrile during permeation. This explains why ethyl benzene has about the same t_l and t_b as o-xylene and about the same P_s and D_p. m-Xylene is then intermediate between o-xylene/ethyl benzene and p-xylene. This holds for all variables except for t_l. In the mixture, such considerations are negated by isomer interactions with themselves and nitrile. The same type of steric dependence mechanism appeared to operate for the molecular weight 120 pure isomers.[8] More work needs to be done to determine how permeation kinetics is related to pure isomer physical and chromatographic parameters and then to determine the mechanism in mixtures.

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