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The Effect of Vapor Polarity and Boiling Point on Breakthrough for Binary Mixtures on Respirator Carbon

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This research evaluated the effect of the polarity of a second vapor on the adsorption of a polar and a nonpolar vapor using the Wheeler model. To examine the effect of polarity, it was also necessary to observe the effect of component boiling point. The 1% breakthrough time (1% t_b), kinetic adsorption capacity (W_e), and rate constant (k_v) of the Wheeler model were determined for vapor challenges on carbon beds for both p-xylene and pyrrole (referred to as test vapors) individually, and in equimolar binary mixtures with the polar and nonpolar vapors toluene, p-fluorotoluene, o-dichlorobenzene, and p-dichlorobenzene (referred to as probe vapors). Probe vapor polarity (0 to 2.5 Debye) did not systematically alter the 1% t_b, W_e, or k_v of the test vapors. The 1% t_b and W_e for test vapors in binary mixtures can be estimated reasonably well, using the Wheeler model, from single-vapor data (1% $t_b \pm 30\%$, $W_e \pm 20\%$). The test vapor 1% t_b depended mainly on total vapor concentration in both single and binary systems. W_e was proportional to test vapor fractional molar concentration (mole fraction) in mixtures. The k_v for p-xylene was significantly different ($p \leq 0.001$) when compared according to probe boiling point; however, these differences were apparently of limited importance in estimating 1% t_b for the range of boiling points tested (111 to 180°C). Although the polarity and boiling point of chemicals in the range tested are not practically important in predicting 1% t_b with the Wheeler model, an effect due to probe boiling point is suggested, and tests with chemicals of more widely ranging boiling point are warranted. Since the 1% t_b, and thus, respirator service life, depends mainly on total vapor concentration, these data underscore the importance of taking into account the presence of other vapors when estimating respirator service life for a vapor in a mixture.

Keywords: mixture, respirators, vapors, Wheeler model

An estimated seven million organic vapor respirator cartridges are used annually in the United States.[1] Activated carbon respirator cartridges are recommended for use by the National Institute for Occupational Safety and Health (NIOSH) for many organic substances. Approval of these respirators by NIOSH and the Mine Safety Health Administration is based on a test challenge using carbon tetrachloride.[2]

Because of the difficulty of accurately predicting their service life during field use, respirator cartridges are typically changed daily, or more often if the wearer detects odor or irritation indicating breakthrough. The use of respirator cartridges is therefore limited to vapors with warning properties (odor, taste, and eye and/or respiratory tract irritation) that can be detected below the threshold limit value (TLV®).[2,3] Even with this restriction, reliance on warning properties to determine the need for respirator cartridge change is deficient because individuals differ in sensitivity, because workers can be desensitized to an odor and no longer notice it, and because the worker's environment frequently contains a variety of compounds that may mask and/or alter each other's warning properties.[2,3] Thus, respirators may be changed less often than required for adequate protection, resulting in potentially hazardous exposures, or changed more frequently than necessary, resulting in inconvenience for the worker and increased

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financial burden on the employer.

These factors highlight the need for accurate models of activated carbon adsorption behavior that are capable of predicting bed service life under the actual conditions of respirator use.[2] Because these conditions often involve mixtures of vapors, models used to predict the service life of organic vapor respirators in the workplace must address mixed vapors.

Since it is impractical to test for all possible combinations of vapors, information is needed about how the physicochemical properties of vapors affect adsorption, and thus breakthrough time. These and other data might then be used with an appropriate model to estimate breakthrough times for untested vapors in mixtures from single-vapor data, or from single-vapor data from analogous vapors (vapors that share characteristics important for estimating breakthrough).[4] Studies of mixtures indicate that properties such as molecular weight, boiling point, vapor pressure, and polarity can affect the relative breakthrough for a vapor in a mixture.[5–8] However, the relative contributions of the various molecular properties are unclear, and the results to date are not generalizable because (1) theoretical models are not used, and/or (2) the effects of these properties have not been systematically studied.

The purpose of this study was to investigate the role of vapor polarity on breakthrough using the Wheeler model. To examine the effect of polarity, it was also necessary to observe the effect of component boiling point. Data from this and other studies may eventually allow the use of models such as Wheeler's to predict breakthrough for vapors in novel mixtures containing physicochemically diverse components. Since several investigators have suggested that the relative polarity of vapors in mixtures may affect their breakthrough time,[7–9] the effect of the polarity of a second vapor on the breakthrough of a polar and a nonpolar vapor was studied.

THE WHEELER MODEL

The Wheeler model has been used to evaluate breakthrough of individual vapors and binary vapor mixtures.[4,10] Several investigators suggest that the Wheeler model is useful for practical estimation of respirator service life.[11,12]

Vahdat et al. effectively used the Wheeler equation to plot complete breakthrough curves of binary mixtures (acetone with m-xylene and acetone with styrene) from single-vapor data (from individual-component adsorption equilibria); however, whether the 1% breakthrough times were accurately predicted was not reported.[4] Jonas found the model useful in predicting breakthrough of binary mixtures of nonpolar vapors with similar boiling points.[10] Thus, it is not known whether the Wheeler model can be used to predict 1% breakthrough and other adsorption parameters for binary mixtures containing vapors with more widely varying polarities and boiling points.

The Wheeler model was developed to predict adsorbent bed behavior in dynamic systems.[13] It is based on a continuity mass balance relationship between the vapor entering an adsorbent bed and the vapor adsorbed before bed penetration occurs, according to the following equation.[14]

$$t_b = \frac{W_e}{C_o Q}\left[W_B - \frac{\rho_B \ln\left(\frac{C_o}{C_x}\right)}{k_v}\right] \quad (1)$$

where W_e = kinetic saturation capacity (g/g);
W_B = mass of the carbon bed (g);
ρ_b = bulk density of the packing (g/mL);
Q = flow rate (mL/sec);
k_v = pseudo first-order rate constant (sec^{-1});
C_o = inlet concentration (mol/mL); and
C_x = exit concentration (mol/mL).

This equation is valid when available adsorption sites greatly exceed the number of adsorbate molecules, thus it is a "pseudo" first-order kinetic model.[15] The pseudo first-order rate constant is valid at low relative breakthrough concentrations ($C_x/C_o<0.04$). A graph of $\ln(C_x/C_o)$ versus the breakthrough time allows the calculation of k_v and W_e. This kinetic model has been validated by Jonas[14,16] and others[11,12] for a number of vapors. However, further data are needed before the Wheeler model is used to estimate 1% breakthrough times for vapors in mixtures containing physicochemically diverse components.

MATERIALS AND METHODS

The effect of component polarity differences on the adsorption and breakthrough of a vapor in a binary mixture was investigated using a gas chromatograph (GC) equipped with both a flame and a photoionization detector (FID and PID). Binary mixtures were selected that contained only one component to which the PID (equipped with an 8.4 eV lamp) responds; the breakthrough of this one component (the test vapor) was studied in the presence of a second vapor (the probe vapor) by analyzing the PID output.

Vapor Selection

The polarity of a molecule may be influenced by several factors, such as molecular structure and functional group. In turn, the polar or nonpolar nature of a molecule can affect properties such as boiling point. To detect an effect of polarity on the adsorption of a vapor in a binary mixture, it was necessary to match component physicochemical properties, such as molecular weight and boiling point, while varying the dipole moment. Mixtures of polar and nonpolar isomers are suited for this purpose, but their ionization potentials (IPs) do not often allow for selective detection of one vapor using the PID. Therefore, the effect of polarity was studied by pairing the same test vapor with polar and nonpolar substituted benzene compounds (which were selected to be as similar as possible except for dipole moment) and then observing the changes in adsorption of the test vapor from one system to another. Para-xylene and pyrrole were selected as test vapors, because they are planar molecules with similar boiling points and also have IPs ≤8.4 eV. Ortho-dichlorobenzene, p-dichlorobenzene, p-fluorotoluene and toluene were selected as probe vapors. The chemical pairings used are shown in Figure 1, and the relevant physicochemical properties of the substances are shown in Table I. Figure 1 shows how p-xylene and pyrrole were each paired with o- and p-dichlorobenzene, p-fluorotoluene, and toluene. Para-xylene or pyrrole are selectively detected in each mixture using a PID lamp with an IP of 8.4 eV. Probe vapor concentration was monitored with the FID. Except for pyrrole, the chemicals selected are commonly used in industry. In addition, the range of polarity (0 to 2.5 Debye) of the selected chemicals is representative of common industrial solvents.

Pairs of compounds were chosen as probe vapors to allow the study of each test vapor in the presence of polar and nonpolar probe molecules that have similar molecular weights and boiling points (see Figure 1). As indicated in Figure 1, test vapors were also combined with pairs of compounds having boiling points above and below them. The test vapors are bracketed to distinguish effects due to polarity differences from those due to boiling point difference between the test and probe vapor.

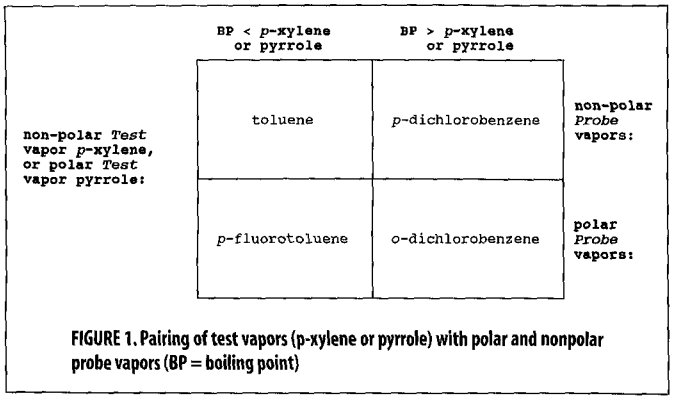

FIGURE 1. Pairing of test vapors (p-xylene or pyrrole) with polar and nonpolar probe vapors (BP = boiling point)

Carbon Bed Challenges

A vapor generation apparatus was constructed to conduct carbon bed challenges. Vapor concentrations were monitored with a GC equipped with a gas sampling valve (GSV) and the PID and FID. Carbon beds were challenged with one or more vapors until the vapor started to appear in the airstream post-carbon bed.

Vapor Generation System

The vapor generation system was constructed of 0.4-cm (ID) stainless steel tubing, and 0.6-cm (ID) borosilicate glass, ball-and-socket tubing. The apparatus is similar to that described by Hall.[17]

The system was functionally divided into two sections; one section for generating vapors, and another section for drawing off the vapors to challenge carbon beds or for sampling with the GC. The vapor generation side of the apparatus was under positive pressure supplied by compressed air. The sampling side was under negative pressure (less than atmospheric) supplied by two vacuum pumps. With this apparatus changes in the flow rate on the vapor-generation side did not affect the flow rate or vapor concentration on the carbon bed side.

The vapor generation side contained three compressed-air (breathing air grade) supply lines; two for generating organic vapors and one for providing additional dilution air. Vapors were generated by passing the dried (anhydrous $CaSo_4$, Drierite, 10-20 mesh), and sieved air (Analabs HGC-149B, 5A pellets) through a chamber containing the liquid or solid organic chemical. Vapor-laden air and dilution air then flowed separately into a manifold and then continued, now mixed together, into a sampling chamber (open to atmosphere) where the vapor(s) could be drawn off. Once the vapor was drawn off the sampling chamber, it entered the negative pressure side of the apparatus where the vapor could be sent through the carbon bed for a challenge experiment or diverted around the carbon bed for sampling with the GC.

Carbon Bed

Activated carbon was obtained from organic vapor respirator cartridges (Chemical Cartridge R51A, 11720C; American Optical Cartridges, Cabot Safety Corp., Southbridge, Mass.). After removal from the cartridge, carbon was sieved with No. 12 (1.7-mm) and No. 20 (0.65-mm) mesh pans and dried in an oven for a minimum of 24 hours at temperatures from 100°C to 120°C. Dried carbon was stored until use in an airtight jar containing desiccant.

The carbon bed consisted of a 14.5 cm long, 0.6-cm (ID) glass tube, fitted with a coarse glass frit, filled with 1±0.005 g of activated carbon. Carbon was gravity-packed into the tube by dropping it from a height of 66 cm. Further packing was accomplished by vibrating the tube during filling, and for one additional minute. This carbon packing method has been verified previously.[18,19]

Bed Challenge

After vapor(s) of the appropriate concentration were generated, the carbon bed was packed, weighed, and placed securely in the vapor generation apparatus. Challenges were conducted at flow rates of 335–350 mL/min and concentrations of 1000–14,000 ppm. When breakthrough began, samples were acquired with the GSV at 45-second intervals. Breakthrough was monitored until bed exit concentration (C_x) was approximately 30% of the challenge, or inlet concentration (C_o).

The breakthrough concentration (C_x/C_o) from 0.25 to 2.50% was regressed with the corresponding breakthrough times, and the regression values were used with the Wheeler equation to calculate W_e and k_v. This process was repeated six times for each chemical pair and for each test chemical alone, and the average W_e and k_v were calculated from these trials.

Gas Chromatograph System

A Hewlett-Packard (HP) 5890 GC equipped with a GSV (0.5-mL sample loop) and a nonpolar methylsilicone gum capillary column (HP-1, cross-linked, 30 m, 0.50 mm ID, 0.88 μm film thickness) was used to monitor vapor concentration. The detector response was calibrated for each chemical using both serial dilution injections and vapor injections (from vapors generated under the same conditions for carbon bed challenges). The HP 3365 *Chemstation*® software program was used to control the GC, to acquire data from its detectors, and to calculate the total area of each chromatogram. *Chemstation* was used to program the GC to inject samples with the GSV at 45-second intervals.

T-tests were conducted to compare the k_v of test vapors alone with that of test vapors with probe vapors. Analysis of variance (ANOVA) was carried out to compare the k_v of test vapors when in the presence of probe vapors, according to probe vapor polarity and boiling point.

TABLE I. Selected Physicochemical Properties of Chemicals Used as Test and Probe Vapors[A]

Chemical	Molecular Weight (g/mol)	Boiling Point (%C)	Dipole Moment (Debye)	Vapor Pressure at 24.4 °C (torr)	Ionization Potential (eV)
Test Vapors					
P-xylene	106.2	138	0.0	8.5	8.4
Pyrrole	67.1	130	1.9	8.0	7.7
Probe Vapors					
O-dichlorobenzene	147.0	180	2.5	1.1	9.1
P-dichlorobenzene	147.0	174	0.0	1.7	8.9
P-fluorotoluene	110.1	117	2.0	17.0	8.8
Toluene	92.2	111	0.4	27.6	8.8

[A]R.C. Weast: *Handbook of Chemistry and Physics*. 60th ed. Boca Raton, FL: CRC Press, Inc., 1980.

RESULTS

As predicted by photoionization theory, the PID detector responded only to vapors with IPs less than or equal to the energy of the 8.4 eV lamp (p-xylene and pyrrole).[20,21] This allowed study of the test vapors in the presence of probe vapors without interference from the probe vapors. Both test and probe vapor were detected by the FID, and as expected, the resulting overlap of the two chromatograms generally precluded accurate analysis of the 1% t_b of the probe vapor. Although test and probe peaks did not always overlap, due to constraints of the GC software, it was not always possible to track the breakthrough of test and probe vapors simultaneously in the breakthrough region of $0.25\%<C_x/C_o<4.0\%$. Several trials were followed until the test vapor reached 100% C_x/C_o, but because the breakthrough region of $0.25\%<C_x/C_o<4\%$ was of interest, trials were normally stopped when the test vapor C_x/C_o reached 30%.

Model Parameters

Average W_es, 1% t_bs, and k_vs (n=6) are displayed (along with the related standard error) in Tables II and III for p-xylene and pyrrole, respectively. Results from trials of test vapor alone are displayed with binary trials matched according to test vapor concentration. Results for test vapors paired with increasing concentrations of toluene and p-fluorotoluene are shown together. (Trials with increasing concentrations of dichlorobenzene isomers were not possible due to the low vapor pressure of these substances.)

Tables II and III also show the predicted W_es for test vapors in mixtures along with the mean percent deviation of the experimental and predicted W_es. The predicted W_e was obtained by multiplying the single-vapor W_e by the fractional vapor molar concentration (mole fraction) of the vapor in each mixture. The predicted 1% t_bs were calculated in a manner similar to that used by Jonas.[10] The k_v and W_e of the test vapor alone were used to calculate the predicted 1% t_b after multiplying the W_e by the mole fraction of the test vapor in the mixture.

Kinetic Adsorption Capacity (W_e)

The W_e for test vapors alone, at concentrations from 0.04 to 0.15 µmol/mL, ranged from 0.41 to 0.42 g/g for p-xylene and 0.33 to 0.37 g/g for pyrrole.

Although the W_e did not change significantly as the concentration of either test vapor alone varied, the W_e was generally reduced in direct proportion to decreasing test vapor mole fraction in binary mixtures.

For p-xylene the experimental W_e was generally higher than predicted, with differences ranging from 0% to –28% for equimolar mixtures and –18% to –35% for mixtures containing >50% probe vapor. The largest deviations are seen with mixtures of toluene, which show increasing deviation (–28% to –35%) with rising concentrations of toluene (0.14 to 0.39 µmol/mL). Increasing deviation with rising probe vapor concentration also occurs with p-fluorotoluene (–9% to –30%).

The agreement between pyrrole's predicted and experimental W_e was better than for p-xylene, with half of pyrrole's predicted W_es occurring within the experimental 95% confidence interval. Agreement was better when pyrrole was paired with either toluene or p-fluorotoluene (–13% to +9% deviation) than when paired with o- or p-dichlorobenzene (+16 to +32% deviation).

Kinetic Rate Constant (k_v)

The k_v for test vapors alone ranged from 62.4 to 69.3 sec^{-1} for p-xylene and from 60.6 to 67.6 sec^{-1} for pyrrole. These k_vs are not

TABLE II. Observed (n=6) and Predicted W_e, t_b, and k_v, for p-xylene Alone, and with Probe Vapors at Varying Concentrations

Challenge Vapors and Concentrations mol/mL		p-xylene Mole Fraction	P-xylene W_e, g/g			P-xylene 1% t_b			P-xylene k_v sec^{-1} [A]	
			Experimental[A]	Predicted	Average % Deviation	Experimental[A]	Predicted	Average % Deviation		
Toluene	*P-xylene*									
0.00	0.15	1.00	0.42 (0.002)	NA[B]	NA	64 (0.8)	NA	NA	69.3	(3.3)
0.14	0.14	0.50	0.29 (0.023)	0.21	–28%	45 (1.2)	35	–22%	47.7	(2.0)
0.26	0.14	0.35	0.22 (0.009)	0.15	–33%	32 (0.8)	24	–25%	ND[C]	
0.39	0.14	0.26	0.17 (0.016)	0.11	–35%	24 (0.8)	19	–21%	ND	
P-fluoro.[D]	*P-xylene*									
0.00	0.09	1.00	0.42 (0.003)	NA	NA	106 (0.8)	NA	NA	68.0	(2.4)
0.10	0.11	0.51	0.23 (0.008)	0.21[E]	– 9%	50 (0.4)	48	–4%	51.9	(2.1)
0.24	0.09	0.27	0.14 (0.003)	0.11	–18%	33 (0.4)	30	–9%	ND	
0.44	0.11	0.20	0.12 (0.005)	0.08	–30%	24 (0.4)	18	–8%	ND	
P-dichlo.[F]	*P-xylene*									
0.00	0.05	1.00	0.41 (0.004)	NA	NA	200 (2.0)	NA	NA	62.4	(4.0)
0.04	0.04	0.50	0.23 (0.004)	0.21	–11%	129 (1.6)	123	–5%	78.1	(4.9)
O-dichlo.[G]	*P-xylene*									
0.00	0.05	1.00	0.41 (0.004)	NA	NA	200 (2.0)	NA	NA	62.4	(4.0)
0.05	0.04	0.44	0.18 (0.009)	0.18[E]	0%	98 (0.8)	107	+9%	78.2	(4.9)

[A]Standard error follows in parentheses
[B]NA = not applicable
[C]ND = not determined
[D] p-fluorotoluene
[E]Predicted value within experimental 95% confidence interval
[F]P-dichlorobenzene
[G]O-dichlorobenzene

Table III. Observed (n=6) and Predicted W_e, t_b, and k_v, for Pyrrole Alone and with Probe Vapors at Varying Concentrations

Challenge Vapors and Concentrations mol/mL		Pyrrole Mole Fraction	Pyrrole W_e, g/g			Pyrrole 1% t_b			Pyrrole k_v sec^{-1} [A]	
			Experimental[A]	Predicted	Average % Deviation	Experimental[A]	Predicted	Average % Deviation		
Toluene	*Pyrrole*									
0.00	0.15	1.00	0.33 (0.006)	NA[B]	NA	80 (2.0)	NA	NA	67.6	(3.1)
0.15	0.15	0.50	0.18 (0.002)	0.17	−2%	47 (0.4)	40	−15%	79.8	(4.1)
0.30	0.14	0.32	0.12 (0.002)	0.11[C]	−13%	31 (0.4)	27	−13%	ND[D]	
0.43	0.14	0.25	0.08 (0.003)	0.08[C]	0%	22 (0.8)	21[C]	−5%	ND	
P-fluoro.[E]	*Pyrrole*									
0.00	0.12	1.00	0.35 (0.010)	NA	NA	107 (2.4)	NA	NA	65.0	(3.0)
0.12	0.12	0.50	0.18 (0.004)	0.18[C]	0%	57 (0.4)	52	−9%	68.3	(4.3)
0.22	0.11	0.33	0.11 (0.001)	0.12[C]	+ 6%	36 (0.4)	39	+8%	ND	
0.33	0.11	0.25	0.08 (0.001)	0.09	+ 9%	26 (0.4)	29	+12%	ND	
P-dichlo.[F]	*Pyrrole*									
0.00	0.04	1.00	0.37 (0.007)	NA	NA	303 (9.8)	NA	NA	60.6	(2.9)
0.04	0.04	0.50	0.14 (0.005)	0.19	+32%	129 (2.9)	157	+21%	67.7	(4.4)
O-dichlo.[G]	*Pyrrole*									
0.00	0.04	1.00	0.37 (0.007)	NA	NA	303 (9.8)	NA	NA	60.6	(2.9)
0.04	0.04	0.50	0.16 (0.002)	0.19	+16%	140 (2.4)	153	+9%	73.1	(4.4)

[A]Standard error follows in parentheses
[B]NA = not applicable
[C]Predicted value within experimental 95% confidence interval
[D]ND = not determined
[E]P-fluorotoluene
[F]P-dichlorobenzene
[G]O-dichlorobenzene

significantly different for either test vapor. The k_v for p-xylene in mixtures ranged from 47.7 to 78.2 sec^{-1}. Results of t-tests indicate that the k_v is significantly different for p-xylene alone compared with p-xylene in the presence of each probe vapor. The k_v of p-xylene decreases when p-xylene is in the presence of toluene or p-fluorotoluene, and increases when p-xylene is accompanied by either p- or o-dichlorobenzene (see Table II).

The k_v for pyrrole in mixtures was similar to that of pyrrole alone, ranging from 67.7 to 79.8 sec^{-1}. The k_vs for pyrrole in the presence of toluene or o-dichlorobenzene were similar (79.8 and 73.1 sec^{-1}) as were the k_vs for pyrrole with p-fluorotoluene or p-dichlorobenzene (68.3 and 67.7 sec^{-1}). Results of t-tests indicated that the k_v for pyrrole alone was significantly different when compared with the k_v of pyrrole with toluene ($p=0.03$) or o-dichlorobenzene ($p=0.02$), but not when compared with pyrrole with either p-fluorotoluene or p-dichlorobenzene.

ANOVA comparing the k_vs of p-xylene in binary mixtures indicates that it is not significantly different when compared on the basis of polarity of the probe vapor ($p=0.64$), but that significant differences occur when k_vs are compared according to probe boiling point ($p<0.001$). There was no interaction between polarity and boiling point ($p=0.66$).

ANOVA comparing the k_vs of pyrrole in binary mixtures indicates that it is not significantly changed by the polarity or boiling point of the probe vapors used. However, the interaction term for polarity and boiling point was significant at $p=0.05$.

Test Vapor 1% t_b

The predicted 1% t_b for p-xylene in the presence of either toluene of p-fluorotoluene was consistently underestimated (p-xylene took longer to break through than predicted). The predicted 1% t_b for pyrrole in the presence of toluene was consistently underestimated and in the presence of o- and p-dichlorobenzene was overestimated.

The 1% t_b is plotted with the total vapor concentration in Figure 2 for p-xylene and Figure 3 for pyrrole.

DISCUSSION

The variance between experimental and predicted W_c was similar to that reported by Jonas for mixtures of benzene, carbon tetrachloride, and chloroform, where expected W_cs for individual components in binary mixtures were calculated using the W_c for each vapor alone and its mole fraction in each binary vapor trial.[10] The differences between observed and expected W_cs in that study ranged from −10% to +20%.

For p-xylene, in all but two challenges the predicted W_c was outside of the experimental W_c 95% confidence interval. However, the differences between the experimental and predicted W_c were relatively small and of limited practical consequence. The differences were also within the range of variability of the adsorption space (mL/g) of carbon used in organic vapor respirator cartridges, which vary by as much as 30%.[22]

The decrease in W_c for a vapor as its mole fraction in a mixture is reduced conforms with results reported by Jonas for different binary vapor mixtures of carbon tetrachloride, chloroform, and benzene.[10] Cohen et al. also reported that the W_c decreased in proportion to vapor concentration for mixtures of carbon tetrachloride and hexane.[9] In both of these studies better agreement was found between experimental and predicted W_cs when the binary system consisted of vapors having similar boiling points and vapor pressures. Cohen et al. reported pronounced variation from expected W_c for mixtures of pyridine and carbon tetrachloride.

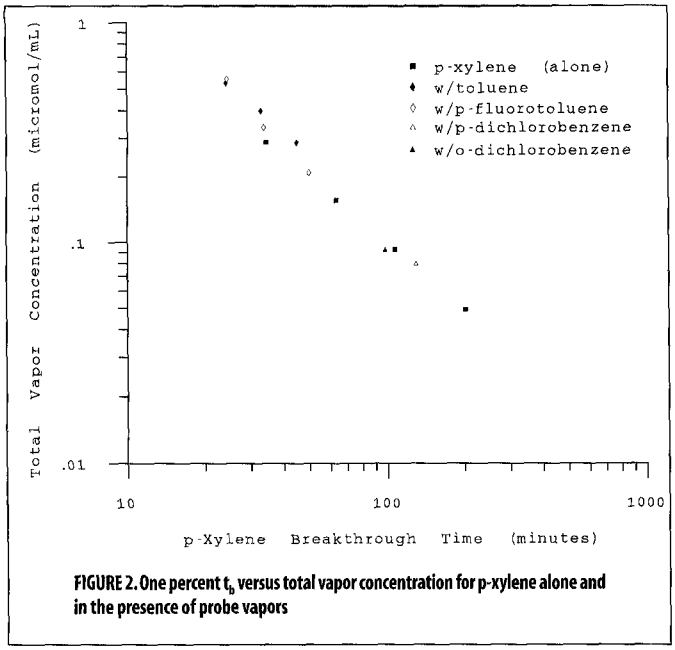

FIGURE 2. One percent t_b versus total vapor concentration for p-xylene alone and in the presence of probe vapors

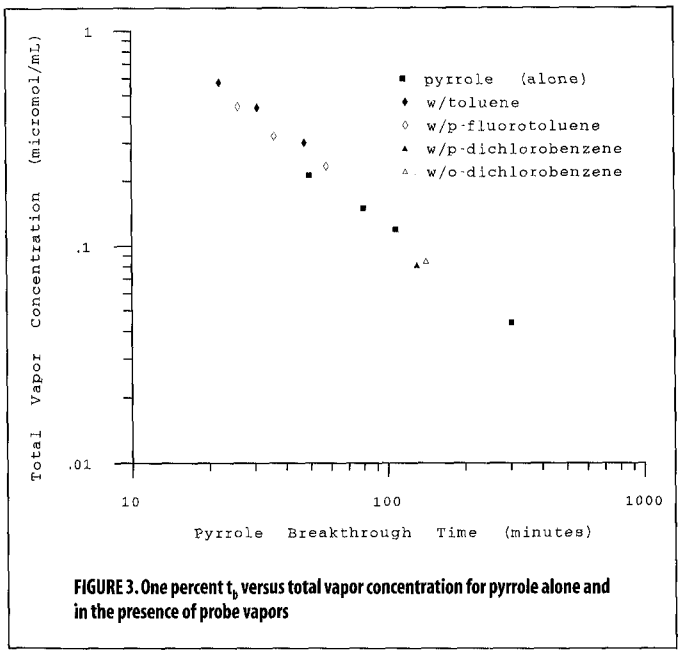

FIGURE 3. One percent t_b versus total vapor concentration for pyrrole alone and in the presence of probe vapors

The W_c was reduced only slightly for pyridine alone, compared with pyridine in an equimolar mixture with carbon tetrachloride (from 0.59 g/g to 0.48 g/g). It appears that the higher boiling point pyridine (115.5°C) displaces carbon tetrachloride (boiling point = 76°C). However, the authors suggested that the displacement was the result of the polar nature of pyridine.[9]

Displacement of a lower boiling vapor by a higher boiling vapor is also suggested by the larger than expected W_c for p-xylene in the presence of toluene or p-fluorotoluene. The effect is more pronounced with toluene, possibly because it has the lowest molecular weight and boiling point of the probe vapors, and both of these factors may cause it to be displaced more readily.[5,6,8,23]

In summary, the reduction of W_c with decreasing test vapor mole fraction is not systematically influenced by the polarity difference between the test and probe vapors. There is no consistent variation from the expected W_c due to probe boiling point; however, the displacement of lower boiling point vapors by higher boiling point vapors is suggested by the uniform underestimation of W_cs for p-xylene with either toluene or p-fluorotoluene and the overestimation of W_cs for pyrrole with o- and p-dichlorobenzene.

The magnitude and range of k_v for test vapors are similar to previously reported k_vs for carbon tetrachloride on comparable carbon (mean=75.6 sec^{-1}, CV=9.4%).[10] Jonas also found the k_v of carbon tetrachloride to be unaffected by vapor concentration.[10]

The ANOVA and t-tests suggest that the k_v of p-xylene changes when p-xylene is in the presence of another vapor. The changes in k_v appear to depend on the relative difference between the boiling point of p-xylene and the accompanying probe vapor (i.e., k_v decreases with lower boiling point probe, k_v increases with higher boiling point probe). However, because molecular weight often varies along with boiling point, i.e., higher molecular weight compounds have higher boiling points, a study that examines the effect of boiling point while controlling for molecular weight is needed to address this question.

Statistical interaction occurs in the ANOVA of pyrrole's k_v, because the k_v is increased to a lesser extent when the probe vapors are p-fluorotoluene and p-dichlorobenzene than when the probe vapors are toluene and o-dichlorobenzene. The k_v for pyrrole was always increased in the presence of a second vapor compared to the k_v of pyrrole alone.

In Jonas' study of binary mixtures of benzene, chloroform, and carbon tetrachloride, the data indicate that the k_vs of vapors alone were different from the k_vs of vapors in mixtures.[10] The k_vs were increased in the presence of a second vapor by 9% to 73%, except for chloroform with benzene, where the k_v was reduced by 2%. Whether the differences were statistically significant was not reported. In that study Jonas did not evaluate the effect of polarity, boiling point, vapor pressure, or molecular weight of the components on the k_v, and there is no discernable pattern to the change in k_v due to these factors.

The 1% t_b appears to decrease in proportion to increasing total vapor concentration for both vapors without regard to the nature of the probe vapor present. This is illustrated in Figure 2 for p-xylene and Figure 3 for pyrrole, where the 1% t_b is plotted with the total vapor concentration. These data suggest that the 1% t_b for test vapors is largely a function of the total concentration of the vapor mixture, independent of the polarity and boiling point of the accompanying probe vapor.

Although all but one of the predicted 1% t_bs are outside the experimental 1% t_b 95% confidence interval, these differences are small in practical terms. The agreement between experimental and predicted 1% t_bs (–25% to +21%) is acceptable and is similar to the variation reported by Jonas and Sansone (–12.4% to +17.8%) for sequential binary mixtures of benzene and carbon tetrachloride.[24] In that study the vapors were introduced sequentially, with a second vapor added after first partially saturating the carbon with the first vapor. Then the t_b of the second vapor was predicted with the Wheeler model using single-vapor data with the assumption that W_c was constant at 0.49 g/g.

The predicted 1% t_b for either p-xylene or pyrrole in the presence of toluene was consistently underestimated. This may be the result of these test vapors "displacing" toluene and delaying their own breakthrough. Some of the results reported here and by others suggest that higher boiling point vapors displace the lower boiling point vapors at high breakthrough concentrations.[5,23] The p-xylene data support this, since the 1% t_b for p-xylene with the lower boiling point compounds is consistently underestimated and

is overestimated with the higher boiling point o-dichlorobenzene. With pyrrole mixtures, however, the direction of the deviation of experimental and predicted 1% t_bs is not all consistent with displacement as a function of vapor boiling point. For example, if the higher boiling point vapor always displaced the lower boiling point vapor, the predicted 1% t_b of pyrrole with p-fluorotoluene should always be too low. However, this occurs only when the concentration of p-fluorotoluene exceeds that of pyrrole. This suggests that other factors, such as vapor polarity or molecular weight, may contribute to or mitigate the displacement of one vapor by another. However, in the case of the vapors studied, the effect of these factors does not prohibit relatively accurate prediction of the 1% t_b (±25%) for a vapor in a mixture from its single-vapor data (using the Wheeler model).

CONCLUSIONS

In general, the test vapor's W_e varied in proportion to its mole fraction in the mixture, and the W_e and k_v did not appear to be systematically affected by the polarity of the accompanying probe vapor. However, the p-xylene k_vs were significantly different ($p<0.001$) when compared across probe boiling point, and there was significant interaction ($p=0.05$) between polarity and boiling point for pyrrole in the presence of probe vapors.

The 1% t_b for test vapors depended largely on the total concentration of the vapor system and for practical purposes is not affected by the polarity or boiling point (for the ranges tested) of the accompanying probe vapor. Reasonably good estimates of the 1% t_b (±25%) for a vapor in a mixture were obtained with the Wheeler model using single-vapor data.

While the polarity and boiling point of the vapors in the range tested appear to be practically unimportant in predicting service life, an effect due to vapor boiling point is suggested, and tests with vapors of more widely ranging boiling point are warranted. These data underscore the need to take into account the presence of other vapors (noxious or otherwise) when estimating the service life of a respirator for a vapor in a mixture. This research suggests that it is possible to estimate the service life of a respirator for a vapor, in the range of boiling points and polarities tested, in a binary mixture using the Wheeler model and (1) the carbon capacity for the vapor, and (2) the mole fraction of the vapor in the mixture. However, before this approach can be more broadly generalized, further investigation of more diverse mixtures is required.

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