

Measurement of VOC Permeability of Polymer Bags and VOC Solubility in Polyethylene Drum Liner

**Kevin J. Liekhus
Eric S. Peterson**

Published March 1995

**Idaho National Engineering Laboratory
Lockheed Idaho Technologies Company
Idaho Falls, Idaho 83415**

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

**Prepared for the
U.S. Department of Energy
Assistant Secretary for Environmental Restoration and Waste Management
Under DOE Idaho Operations Office
Contract DE-AC07-94ID13223**

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

HH

MASTER

DISCLAIMER

**Portions of this document may be illegible
electronic image products. Images are
produced from the best available original
document.**

ABSTRACT

A test program conducted at the Idaho National Engineering Laboratory (INEL) investigated the use of a transport model to estimate the volatile organic compound (VOC) concentration in the void volume of a waste drum. Unsteady-state VOC transport model equations account for VOC permeation of polymer bags, VOC diffusion across openings in layers of confinement, and VOC solubility in a polyethylene drum liner. In support of this program, the VOC permeability of polymer bags and VOC equilibrium concentration in a polyethylene drum liner were measured for nine VOCs. The VOCs used in experiments were dichloromethane, carbon tetrachloride, cyclohexane, toluene, 1,1,1-trichloroethane, methanol, 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113), trichloroethylene, and p-xylene. The experimental results of these measurements as well as a method of estimating both parameters in the absence of experimental data are described in this report.

EXECUTIVE SUMMARY

Researchers at the Idaho National Engineering (INEL) recently developed a model to estimate the concentration of volatile organic compounds (VOCs) within the innermost layer of confinement of transuranic waste drums given the measured VOC concentration in the drum headspace. The purpose of the model is to reduce the extent of sampling needed to comply with regulatory requirements applicable to waste drums destined for storage at the Waste Isolation Pilot Plant (WIPP). Typically, the waste stored in these drums is contained in polyethylene or polyvinyl chloride (PVC) bags which are located inside a thick-walled polyethylene drum liner.

In support of this program, the VOC permeability of polymer bags and VOC equilibrium concentration in a polyethylene drum liner were measured for nine VOCs. The VOCs used in experiments were dichloromethane, carbon tetrachloride, cyclohexane, toluene, methanol, 1,1,1-trichloroethane, 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113), trichloroethylene, and p-xylene. The VOC permeability of polymer bags was determined using a mixed-gas chromatographic system designed to handle a mixture of gases and VOCs. Polyethylene bags with a thickness of 0.01 cm and PVC bags with a thickness of 0.03 cm were used. The feed side of the membrane was exposed to a continuous feed gas stream for 4 to 8 hours to achieve an equilibrium state. After equilibrium was reached, a sample of the permeate sweep gas was injected into the gas chromatograph to determine VOC content. Two set of permeability tests were conducted. In the first set of tests, VOC permeability of polyethylene and PVC bags at 25°C was determined using gas mixtures containing one VOC in hydrocarbon-free air or 5 VOCs in air. A second set of permeability measurements was performed to identify if a significant concentration and temperature dependence of VOC permeability in polyethylene and PVC existed. Test mixtures for each VOC were prepared at three different concentrations. The experiments were performed at 25°C, 35°C, and 50°C.

An experiment was designed to measure VOC equilibrium concentration in a polyethylene drum liner under saturated vapor conditions and estimate the mass transfer coefficient for VOC adsorption by measuring the rate of VOC desorption. Sample coupons were cut from the lid of a high-density polyethylene drum liner. Each coupon was placed in a 1-L jar which contained a 100-mL beaker containing a liquid VOC. The jar was sealed and the coupon remained in the container for 48 hours at an average temperature of 20 to 22°C. Each coupon was removed from the jar and placed on an analytical balance. The change in the coupon mass was recorded as a function of time. It was assumed that the average VOC concentration in the coupon equals the VOC concentration at the surface. This assumption is most appropriate at the beginning of the experiment (in a saturated coupon) before a concentration gradient has fully developed. For this reason, the mass-transfer coefficient was estimated from data collected within the first 15,000 s of the desorption tests.

Measured VOC permeability of polymers at 25°C was not affected by the presence of other VOCs in the gas mixture. Equations estimating VOC permeability as a function of temperature or concentration were generated for 9 VOC-polymer combinations. A theoretically-based method was used to estimate VOC permeability of polyethylene bags and VOC solubility in a polyethylene drum liner. Two equation parameters were determined from available experimental permeability and solubility data. The parameters can be used to estimated permeability and solubility of other VOCs in the same type of polyethylene.

CONTENTS

ABSTRACT	iii
EXECUTIVE SUMMARY	v
ACRONYMS AND ABBREVIATIONS	ix
1. INTRODUCTION	1
2. BACKGROUND	2
2.1 VOC Permeability in Polyethylene	2
2.2 VOC Solubility in Polyethylene	2
2.3 Estimating VOC Permeability and Solubility	4
3. EXPERIMENTAL EQUIPMENT AND METHOD	7
3.1 VOC Permeability in Polymer Bags	7
3.2 VOC Equilibrium Concentration in Polyethylene Drum Liner	8
4. EXPERIMENTAL RESULTS	9
4.1 VOC Permeability	9
4.2 VOC Solubility	15
5. ESTIMATED MODEL PARAMETERS	18
6. DISCUSSION	20
7. REFERENCES	21
Appendix A—VOC Permeability in Polyethylene and PVC as a Function of Temperature and VOC Concentration	A-1
Appendix B—Antoine Equation Constant	B-1
Appendix C—Solubility Experimental Data	C-1

TABLES

1. VOC permeability of polyethylene and VOC concentration in gas mixtures	10
2. VOC permeability of PVC and VOC concentration in gas mixtures	10
3. Measured TCE permeability of polymer films as a function of temperature and concentration	11
4. Measured TCA permeability of polymer films as a function of temperature and concentration	11
5. Measured carbon tetrachloride permeability of polymer films as a function of temperature and concentration	12
6. Measured dichloromethane permeability of polymer films as a function of temperature and concentration	12
7. Measured toluene permeability of polymer films as a function of temperature and concentration	13
8. Measured p-xylene permeability of polymer films as a function of temperature and concentration	13
9. Measured methanol permeability of polymer films as a function of temperature and concentration	14
10. Measured Freon-113 permeability of polymer films as a function of temperature and concentration	14
11. Measured cyclohexane permeability of polymer films as a function of temperature and concentration	15
12. Calculated vapor pressure at 22°C and estimated VOC mole fraction in gas phase at saturated conditions	16
13. Measured VOC equilibrium concentration at saturated vapor conditions and estimated Henry's constant	16
14. Calculated VOC transfer coefficients for use in Equation (6)	17
15. Measured and estimated VOC permeability in polyethylene bag	18
16. Measured and estimated VOC equilibrium concentration in polyethylene drum liner	19

ACRONYMS AND ABBREVIATIONS

CCl ₄	carbon tetrachloride
EPA	Environmental Protection Agency
DOE	Department of Energy
FID	flame ionization detector
Freon-113	1,1,2-trichloro-1,2,2-trifluoroethane
INEL	Idaho National Engineering Laboratory
NMD	no-migration determination
ppm	parts per million (volume basis)
PVC	polyvinyl chloride
STP	standard temperature and pressure
TCA	trichloroethane
TCD	thermal conductivity detector
TCE	trichloroethylene
VOC	volatile organic compound
WIPP	Waste Isolation Pilot Plant

Measurement of VOC Permeability of Polymer Bags and VOC Solubility in Polyethylene Drum Liner

1. INTRODUCTION

Characterization of transuranic (TRU) waste drums destined for the Waste Isolation Pilot Plant (WIPP) requires detailed characterization of the volatile organic compound (VOC) concentration in the void volume headspaces (drum headspace, the large polymer bag headspace, and the innermost layers of confinement headspace). Extensive sampling is performed to obtain a representative sample from each layer of confinement to identify volatile and gaseous constituents, verify process knowledge of the drum contents, and demonstrate compliance with regulatory requirements. The WIPP conditional no-migration determination (NMD) states that it must be demonstrated that no layer of confinement contains a mixture of gases and VOCs that could become flammable when mixed with air. The NMD also specifies that all layers of confinement in a container will have to be sampled until the U. S. Department of Energy (DOE) can demonstrate to the Environmental Protection Agency (EPA), based on data collected, that sampling of all layers is either unnecessary or can be safely reduced. The DOE must demonstrate to the EPA that a drum headspace sample is representative of the VOCs within the entire void space of the waste container in order to demonstrate compliance in the future when drums could be directly emplaced in the WIPP. A systematic means of describing the VOC concentrations within the innermost layer of confinement, based on the drum headspace concentration, would suggest that the drum headspace sample is representative.

A test program was conducted at the Idaho National Engineering Laboratory (INEL) to investigate the use of a model to estimate the VOC concentration throughout a waste drum void volume given the known or assumed VOC concentration within one layer of confinement and process knowledge of the waste drum configuration. Models describing unsteady-state and steady-state VOC transport were developed.^{1,2} Unsteady-state model equations describe the rate of VOC permeation in polymer bags, VOC diffusion across openings in layers of confinement, and VOC solubilization in a polyethylene drum liner. The VOC solubility in the drum liner is not important under steady-state conditions.

In support of this program, experiments were performed at the INEL to measure the VOC permeability of polymer bags and VOC equilibrium concentration in a polyethylene drum liner. The VOCs used in experiments were dichloromethane, carbon tetrachloride, cyclohexane, toluene, methanol, 1,1,1-trichloroethane (TCA), 1,1,2-trichloro-1,2,2-trifluoroethane (Freon-113), p-xylene, and trichloroethylene (TCE). The experimental approach and results are presented in this report. In addition, the report describes a method for estimating VOC permeability and VOC solubility of polyethylene.

2. BACKGROUND

2.1 VOC Permeability in Polyethylene

The permeability of polyethylene to a number of VOCs has been reported previously by other researchers. The permeability coefficient of carbon tetrachloride and chloroform in polyethylene was measured using a weighed cell method or electrochemical method.³ A pouch method was used for measuring the vapor permeability through a polyethylene film for benzene, carbon tetrachloride, and ethanol.⁴ The gas surrounding the pouch was completely saturated with vapor. Permeability of polyethylene films to benzene and carbon tetrachloride vapors at 35°C has been measured.⁵ Permeation measurement of benzene and cyclohexane through polyethylene films demonstrated the effect of polymer density, vapor pressure, and temperature on VOC permeability.⁶ A gas permeability apparatus specifically designed to allow for the study of permeation of a mixture of gases and vapors has been described.⁷ The apparatus uses the carrier gas method with gas-chromatograph analysis to determine individual permeation values. It also uses in-line detectors to provide simultaneous overall diffusion and permeability data.

2.2 VOC Solubility in Polyethylene

Henry's law provides a good approximation of the equilibrium between the polymer and vapor phases when VOC solubility is small⁸

$$f = Hx \quad (1)$$

where x is the VOC mole fraction in the polymer, f is the fugacity, and H is Henry's constant rigorously defined as

$$H = \lim_{x \rightarrow 0} \left(\frac{f}{x} \right) \quad (2)$$

The pressure of the system is equal to the saturation (vapor) pressure of the VOC at temperature T as x approaches zero. A form of Equation 1 is used to estimate the relationship between the equilibrium VOC concentration in the polymer and the gas phase. In a system at low pressure, fugacity can be approximated by the VOC partial pressure, p^*

$$p^* = yP = H^*X^* \quad (3)$$

where

y = mole fraction of VOC in the gas phase

P = ambient pressure, atm

H^* = Henry's constant, $[\text{cm}^{-3} (\text{STP}) \text{ VOC}] (\text{cm}^3 \text{ polymer}) \text{ atm}$

X^* = VOC equilibrium concentration at standard temperature and pressure (STP),
 $[cm^3 (STP) VOC] (cm^{-3} polymer)$.

In the case of a saturated vapor,

$$H_s^* = \frac{y_s P}{X_s^*} \quad (4)$$

where subscript s indicates saturated vapor conditions. Assuming that H_s^* remains constant over the VOC concentration range of interest, the equilibrium VOC concentration in the polymer can be estimated for any given gas phase VOC concentration as

$$X^* = \frac{y P}{H_s^*} \quad (5)$$

The rate of accumulation in the polymer as the result of VOC solubility is estimated as

$$\frac{dX}{dt} = \eta [X_\infty - X] \quad (6)$$

where

X_∞ = VOC equilibrium concentration in polymer, $[cm^3 (STP) VOC] (cm^{-3} polymer)$

X = average VOC concentration in polymer, $[cm^3 (STP) VOC] (cm^{-3} polymer)$

t = time, s

η = transfer coefficient, s^{-1} .

It is assumed that the VOC concentration is uniform throughout and no concentration gradient is present in the polymer. Integrating Equation (6) yields

$$\ln \left[\frac{X_\infty - X(0)}{X_\infty - X(t)} \right] = \eta t \quad (7)$$

Plotting the term on the left side of the equal sign versus time will generate a straight line with a slope η as long as the initial assumption remains valid.

2.3 Estimating VOC Permeability and Solubility

If the solubility of a gas in polyethylene is proportional to pressure (Henry's law is applicable) and the gas diffusion constant is independent of pressure, then the gas permeability in polyethylene is defined as⁹

$$\rho = DS \quad (8)$$

where

ρ = VOC permeability of polyethylene, $\text{cm}^3 (\text{STP}) \text{ cm}^{-1} \text{ s}^{-1} \text{ atm}^{-1}$

D = VOC diffusivity of polyethylene, $\text{cm}^2 \text{ s}^{-1}$

S = VOC solubility coefficient of polyethylene, $\text{cm}^3 (\text{STP}) \text{ cm}^{-3} \text{ atm}^{-1}$.

The VOC permeability in polyethylene can be estimated using known or estimated values for D and S . The VOC solubility coefficient is estimated to be⁹

$$S = \alpha S_0 \quad (9)$$

where

α = volume fraction of amorphous polymer

S_0 = solubility coefficient in completely amorphous polyethylene, $\text{cm}^3 (\text{STP}) \text{ cm}^{-3} \text{ atm}^{-1}$.

The value of α may range from 0 to 1.0. The value of S_0 is estimated as

$$S_0 = e^{[0.022\epsilon/\kappa - 5.07]} \quad (10)$$

where ϵ/κ is the Lennard-Jones force constant.

Diffusion coefficients were estimated based on a correlation with the molecular diameter of the permeating molecule.¹⁰ The diffusion coefficient of a permeant in polyethylene is estimated by the equation

$$D = \frac{D_0}{\tau \beta} \quad (11)$$

where

D_0 = diffusion coefficient in completely amorphous polyethylene, $\text{cm}^2 \text{ s}^{-1}$

τ = geometric impedance factor

β = chain immobilization factor.

The geometric impedance factor accounts for the reduction in the diffusion coefficient due to the necessity of molecules to bypass crystallites and move through amorphous regions of nonuniform cross-sectional area. The chain immobilization factor takes into account the reduction in amorphous chain segment mobility due to the proximity of crystallites. A correlation to estimate D_o at 25°C is

$$\ln\left(\frac{D_o}{\sigma^2}\right) = 3.66 - 1.32[\sigma - 0.5\phi^{0.5}] \quad (12)$$

where σ is the gas molecular diameter in Angstroms (Å) and the quantity $0.5\phi^{0.5}$ is the mean unoccupied distance between two chain segments in the amorphous polymer. The gas molecular diameter is estimated from kinetic theory using experimentally determined viscosities or suitable approximations. The term D_o/σ^2 is expressed in 10^9 s^{-1} . A correlation for β at 25°C is

$$\beta = e^{\gamma[\sigma - 0.5\phi^{0.5}]^2} \quad (13)$$

where γ is a constant and is characteristic of the polymer and the volume fraction of crystallinity. A correlation for τ is

$$\tau = \alpha^{-n} \quad (14)$$

where n is a constant. For linear polyethylenes prepared from Ziegler catalysts and branched, high-pressure polyethylenes, $n=1.88$. For linear polyethylenes prepared from Phillips catalysts and hydrogenated polybutadiene, $n=1.25$. The values of σ and ϵ/κ were obtained through correlations¹¹

$$\sigma = (2.3551 - 0.087 \omega) \left(\frac{T_c}{P_c}\right)^{1/3} \quad (15)$$

and

$$\epsilon/\kappa = (0.7915 + 0.1693 \omega) T_c \quad (16)$$

where

P_c = Critical pressure, atm

T_c = Critical temperature, K

ω = Acentric factor.

In the absence of tabulated values, the acentric factor in Equation (9) can be estimated⁸

$$\omega = \frac{3}{7} \frac{\theta}{1-\theta} \log P_c - 1 \quad (17)$$

where θ equals the ratio of the liquid boiling point, T_b (K), to the critical temperature of the compound. In the case of polar compounds, the values of σ and ϵ/κ were estimated using the Brokaw method⁸

$$\sigma = 1.166 \times 10^{-9} \left[\frac{V_b}{1 + 1.3\delta^2} \right]^{1/3} \quad (18)$$

$$\epsilon/\kappa = 1.18 (1 + 1.3\delta^2) T_b \quad (19)$$

where V_b (m³/kmol) is the liquid molar volume of the polar compound at its normal boiling point T_b (K). The quantity δ is a dimensionless dipole moment estimated as

$$\delta = \frac{1.94 \mu_p^2}{V_b T_b} \quad (20)$$

where μ_p is the dipole moment in debyes (1 debye = 3.162×10^{-25} N^{0.5} m²).

In cases where the VOC equilibrium concentration in the polymer under saturated vapor conditions has not been measured, it is estimated as

$$X_s^* = (y_s P) S \quad (21)$$

where S is calculated using Equations (9) and (10).

3. EXPERIMENTAL EQUIPMENT AND METHOD

The VOCs used in experiments were dichloromethane, carbon tetrachloride, cyclohexane, TCA, Freon-113, methanol, toluene, TCE, and p-xylene.

3.1 VOC Permeability in Polymer Bags

The permeabilities of VOCs in polymer bags were determined using a system capable of analyzing a mixture of gases and VOCs. Compounds that permeate the membrane are swept away from the membrane by an inert carrier gas into a gas chromatograph. The detection system consisted of two Hewlett Packard 5800 Series gas chromatographs. One chromatograph was an HP 5890 Series II, containing two RESTEK 10454 columns, 30 m long, 0.32-mm inside diameter, with flame ionization detectors (FIDs) to determine the concentrations of the feed and permeating gases. The second chromatograph was an HP 5890a which contained two CHROMPACK 007551 columns, 25 m long, 0.32-mm inside diameter, Poraplot Q-coated with thermal conductivity detectors (TCDs) to monitor the components of the compressed air. These columns were chosen for their ability to separate all materials that were being used. The FIDs were insensitive to both the helium sweep gas and the compressed air in the mixture, while the TCDs were insensitive to the minor concentrations of VOCs in the compressed air.

Polyethylene bags with a thickness of 0.01 cm (4 mil) and polyvinyl chloride (PVC) bags with a thickness of 0.03 cm (11 mil) were used. A circular sample of the polymer material was mounted into a 4.7-cm diameter Millipore modified in-line stainless steel filter holder. The feed side of the membrane was exposed to a continuous feed gas stream for 4 to 8 hours to achieve an equilibrium state. The permeate side of the membrane was exposed to a helium sweep gas. The sweep gas transported VOCs from the permeate side of the cell to the detection system. Typical flow rates for the sweep gas were from 1.5 to 2.0 mL min⁻¹ and for the feed gas were from 2.0 to 4.0 mL min⁻¹. These flows were controlled with MKS mass flow controllers. The pressure on the feed side of the membrane ranged from 19 to 20 psi and was monitored with a differential pressure transducer. After equilibrium was reached, a 1- μ m sample of the permeate sweep gas was injected into the gas chromatograph (with FIDs) to determine VOC content.

The VOC permeabilities of polyethylene and PVC were measured in a series of experiments. In the first set of tests, VOC permeability of polyethylene and PVC bags at 25°C was determined using gas mixtures containing a single VOC in hydrocarbon-free air or 5 VOCs in air. The gas mixtures containing a single VOC in air included dichloromethane (1006 ppm), Freon-113 (1010 ppm), TCA (994 ppm), and TCE (300 ppm). Two gas mixtures were used. Gas mixture I contained dichloromethane (1012 ppm), Freon-113 (903 ppm), TCA (977 ppm), carbon tetrachloride (305 ppm), and TCE (310 ppm) was also used. Gas mixture II contained dichloromethane (95.2 ppm), Freon-113 (91 ppm), TCA (101 ppm), carbon tetrachloride (33.9 ppm), and TCE (35.3 ppm).

A second set of permeability measurements was performed to identify if a significant concentration and temperature dependence of VOC permeability of polyethylene and PVC existed. Gas mixtures containing only one VOC of interest were prepared at three different concentrations. The maximum concentrations ranged between 300 and 1000 ppm. The

intermediate and lowest concentrations were approximately 10% to 50% and 1% of the maximum concentration, respectively. The experiments were performed at 25°C, 35°C, and 50°C.

3.2 VOC Equilibrium Concentration in Polyethylene Drum Liner

An experiment was designed to measure VOC equilibrium concentration in a polyethylene coupon under saturated vapor conditions and estimate the mass transfer coefficient for VOC adsorption by measuring the rate of VOC desorption. Sample coupons were cut from the lid of a high-density polyethylene drum liner. The dimensions of each individual coupon were measured. The coupons were approximately 15 cm long, 1.5 cm wide, and 0.42 cm thick. Each coupon was placed in a 1-L jar which contained a 100-mL beaker containing a liquid VOC. After sealing the jar, the coupon remained in the container for 48 hours at an average temperature of 20 to 22°C. This was done for each VOC. During this time, noticeable swelling of some coupons did occur. Each coupon was then removed from the jar and placed on a Mettler AE240 five-digit analytical balance. The balance was connected to an IBM Model 60 PC using Mettler TOLEDO BalanceLink software for the data recording. The change in the coupon mass as a function of time on the balance was recorded for about two to five days. The weight of the coupons were measured again approximately one month later.

4. EXPERIMENTAL RESULTS

4.1 VOC Permeability

The VOC permeability of a polymer was calculated from experimental data using the equation

$$\rho_i = \frac{\xi y_i V_p \Delta L}{A \Delta P_g} \quad (22)$$

where

ρ_i	permeability of i^{th} VOC, $\text{cm}^3 (\text{STP}) \text{ cm}^{-1} \text{ s}^{-1} (\text{cm Hg})^{-1}$
y_i	volume fraction of i^{th} VOC in permeate stream, $(\text{cm}^3 \text{ VOC}) \text{ cm}^{-3} \text{ gas}$
V_p	volume flow rate of permeate stream, $\text{cm}^3 \text{ s}^{-1}$
ΔL	membrane thickness, cm
A	cross sectional area, cm^2
ΔP_g	VOC partial pressure differential across membrane, cm Hg
ξ	$T_s P_{\text{exp}} / (T_{\text{exp}} P_s)$
T_s	standard temperature = 273.15 K
P_{exp}	pressure on permeate side of membrane, cm Hg
T_{exp}	experimental temperature, K
P_s	standard pressure = 76 cm Hg.

The permeate stream includes all gases and VOCs that permeated across the polymer membrane as well as the inert sweep gas.

Measured VOC permeability of polyethylene and PVC using multicomponent and single VOC-air gas mixtures for 5 VOCs are presented in Tables 1 and 2. The permeabilities of individual VOCs in polyethylene and PVC as a function of temperature are listed in Tables 3 through 11. Some gas concentration values fell below the detection limits of the gas chromatograph indicating that no gas was observed on the permeate side of the polymeric film. Thus, a VOC permeability could not be calculated. Equations estimating VOC permeability as a function of temperature or concentration were generated for 9 VOC-polymer combinations. The equations and the estimates are listed in Appendix A.

Table 1. VOC permeability of polyethylene and VOC concentration in gas mixtures.

VOC	Gas mixture I		Gas mixture II		Single VOC mixtures	
	Conc. (ppm)	Ba ^a	Conc. (ppm)	Ba	Conc. (ppm)	Ba
CH ₂ Cl ₂ ^b	1,012	244 ± 17	95.2	313 ± 21	1,006	232 ± 15
Freon-113	903	27.4 ± 2.6	91.0	54 ± 8.0	1,010	34.3 ± 1.5
TCA	977	138 ± 15	101	209 ± 14	994	83.1 ± 3.4
TCE	310	779 ± 40	35.3	311 ± 22	300	660 ± 15
CCl ₄ ^c	305	224 ± 16	33.9	161 ± 49	— ^d	— ^d

a. 1 Ba = 10^{-10} cm³(STP) cm⁻¹ s⁻¹ (cm Hg)⁻¹.

b. Dichloromethane.

c. Carbon tetrachloride.

d. Not measured.

Table 2. VOC permeability of PVC and VOC concentration in gas mixtures.

VOC	Gas mixture I		Single VOC mixtures	
	Conc. (ppm)	Ba ^a	Conc. (ppm)	Ba
CH ₂ Cl ₂ ^b	1,012	284 ± 16	1,006	295 ± 23
Freon-113	903	24.9 ± 1.7	1,010	36 ± 4.8
TCA	977	43 ± 2.8	994	32 ± 15
TCE	310	267 ± 40	300	148 ± 67
CCl ₄ ^c	305	88 ± 21	— ^d	— ^d

a. 1 Ba = 10^{-10} cm³(STP) cm⁻¹ s⁻¹ (cm Hg)⁻¹.

b. Dichloromethane.

c. Carbon tetrachloride.

d. Not measured.

Table 3. Measured TCE permeability of polymer films as a function of temperature and concentration.

Conc. (ppm)	Temp. (C)	Polyethylene (Ba) ^a	PVC (Ba)
1000	25	496 ± 118	7.78 ± 4.69
1000	35	159 ± 261	168 ± 94
1000	50	1.31 ± 0.60	188 ± 62
300	25	24.2 ± 1.5	22.2 ± 9.4
300	35	33.7 ± 1.6	21.1 ± 1.5
300	50	51.4 ± 3.1	25.4 ± 3.9
11.5	25	1025 ± 854	576 ± 216
11.5	35	447 ± 124	503 ± 149
11.5	50	576 ± 138	597 ± 121

a. 1 Ba = 10^{-10} cm³ (STP) cm⁻¹ s⁻¹ (cm Hg)⁻¹.

Table 4. Measured TCA permeability of polymer films as a function of temperature and concentration.

Conc. (ppm)	Temp. (C)	Polyethylene (Ba) ^a	PVC (Ba)
1000	25	118 ± 6.2	46.0 ± 2.5
1000	35	180 ± 15	70.9 ± 3.2
1000	50	325 ± 20	129 ± 6.7
300	25	98.0 ± 6.5	33.7 ± 2.6
300	35	134 ± 7.5	69.6 ± 9.4
300	50	192 ± 20	126 ± 7.4
10	25	— ^b	— ^b
10	35	— ^b	— ^b
10	50	— ^b	— ^b

a. 1 Ba = 10^{-10} cm³ (STP) cm⁻¹ s⁻¹ (cm Hg)⁻¹.

b. VOC not detected on the permeate side of membrane.

Table 5. Measured carbon tetrachloride permeability of polymer films as a function of temperature and concentration.

Conc. (ppm)	Temp. (C)	Polyethylene (Ba) ^a	PVC (Ba)
295	25	181 \pm 39	— ^b
295	35	298 \pm 72	185 \pm 45
295	50	375 \pm 40	265 \pm 118
50	25	— ^b	— ^b
50	35	— ^b	— ^b
50	50	— ^b	— ^b
5	25	— ^b	— ^b
5	35	— ^b	— ^b
5	50	— ^b	— ^b

a. 1 Ba = 10^{-10} cm³ (STP) cm⁻¹ s⁻¹ (cm Hg)⁻¹.

b. VOC not detected on the permeate side of membrane.

Table 6. Measured dichloromethane permeability of polymer films as a function of temperature and concentration.

Conc. (ppm)	Temp. (C)	Polyethylene (Ba) ^a	PVC (Ba)
1006	25	126 \pm 8.0	102 \pm 15
1006	35	183 \pm 15	212 \pm 29
1006	50	311 \pm 14	323 \pm 8.8
99.1	25	173 \pm 79	287 \pm 201
99.1	35	202 \pm 58	254 \pm 94
99.1	50	390 \pm 126	189 \pm 64
10.3	25	— ^b	— ^b
10.3	35	— ^b	— ^b
10.3	50	— ^b	— ^b

a. 1 Ba = 10^{-10} cm³ (STP) cm⁻¹ s⁻¹ (cm Hg)⁻¹.

b. VOC not detected on the permeate side of membrane.

Table 7. Measured toluene permeability of polymer films as a function of temperature and concentration.

Conc. (ppm)	Temp. (C)	Polyethylene (Ba) ^a	PVC (Ba)
501	25	669 ± 121	66.1 ± 56.0
501	35	926 ± 29	220 ± 102
501	50	1428 ± 108	631 ± 140
51.3	25	220 ± 10	65.2 ± 8.4
51.3	35	317 ± 23	164 ± 9.3
51.3	50	465 ± 19	222 ± 45
10.1	25	428 ± 120	198 ± 44
10.1	35	490 ± 82	527 ± 104
10.1	50	511 ± 67	606 ± 113

a. $1 \text{ Ba} = 10^{-10} \text{ cm}^3 (\text{STP}) \text{ cm}^{-1} \text{ s}^{-1} (\text{cm Hg})^{-1}$.

Table 8. Measured p-xylene permeability of polymer films as a function of temperature and concentration.

Conc. (ppm)	Temp. (C)	Polyethylene (Ba) ^a	PVC (Ba)
1000	25	811 ± 48	9.1 ± 3.1
1000	35	1474 ± 51	480 ± 118
1000	50	1995 ± 192	1890 ± 307
300	25	727 ± 257	— ^b
300	35	1183 ± 379	55.8 ± 15
300	50	1169 ± 113	120 ± 45
10	25	1204 ± 41	— ^b
10	35	1424 ± 57	99 ± 25
10	50	1846 ± 126	205 ± 90

a. $1 \text{ Ba} = 10^{-10} \text{ cm}^3 (\text{STP}) \text{ cm}^{-1} \text{ s}^{-1} (\text{cm Hg})^{-1}$.

b. VOC not detected on the permeate side of membrane.

Table 9. Measured methanol permeability of polymer films as a function of temperature and concentration.

Conc. (ppm)	Temp. (C)	Polyethylene (Ba) ^a	PVC (Ba)
100	25	135 \pm 35	— ^b
100	35	127 \pm 23	— ^b
100	50	128 \pm 33	— ^b
9.9	25	— ^b	— ^b
9.9	35	— ^b	— ^b
9.9	50	— ^b	— ^b

a. 1 Ba = 10^{-10} cm³ (STP) cm⁻¹ s⁻¹ (cm Hg)⁻¹.

b. VOC not detected on the permeate side of membrane.

Table 10. Measured Freon-113 permeability of polymer films as a function of temperature and concentration.

Conc. (ppm)	Temp. (C)	Polyethylene (Ba) ^a	PVC (Ba)
1000	25	— ^b	— ^b
1000	35	— ^b	— ^b
1000	50	— ^b	— ^b
300	25	— ^b	— ^b
300	35	— ^b	— ^b
300	50	— ^b	— ^b
10	25	— ^b	— ^b
10	35	— ^b	— ^b
10	50	— ^b	— ^b

a. 1 Ba = 10^{-10} cm³ (STP) cm⁻¹ s⁻¹ (cm Hg)⁻¹.

b. VOC not detected on the permeate side of membrane.

Table 11. Measured cyclohexane permeability of polymer films as a function of temperature and concentration.

Conc. (ppm)	Temp. (C)	Polyethylene (Ba) ^a	PVC (Ba)
745	25	12.4 ± 1.7	8.31 ± 18.6
745	35	35.2 ± 11.7	8.12 ± 9.37
745	50	161 ± 20	376 ± 251
98	25	21.4 ± 2.7	160 ± 328
98	35	36.3 ± 6.7	25.2 ± 38.8
98	50	85.3 ± 9.8	30.7 ± 5.5
9.7	25	— ^b	53.8 ± 111
9.7	35	— ^b	— ^b
9.7	50	— ^b	25.5 ± 45.7

a. 1 Ba = 10^{-10} cm³ (STP) cm⁻¹ s⁻¹ (cm Hg)⁻¹.

b. VOC not detected on the permeate side of membrane.

4.2 VOC Solubility

The Henry's constant, H_s^{*}, for each VOC was calculated using Equation (4). The VOC vapor concentrations were calculated, assuming an ideal gas, as the ratio of the vapor pressure to the actual system pressure. The VOC vapor pressure (mm Hg) was estimated using Antoine equation

$$\log_{10} P^{vap} = A - \frac{B}{C + T} \quad (23)$$

where A, B, and C are VOC-specific constants¹² and T is temperature (°C). The Antoine constants for each VOC are listed in Appendix B. The actual pressure of the system is the sum of the VOC vapor pressure and atmospheric pressure. The average ambient pressure during the experiments was 646 mm Hg. The calculated vapor pressure at 22°C and estimated VOC mole fraction in the gas phase at saturated conditions are listed in Table 12.

The VOC equilibrium concentration was calculated as the ratio of the total volume of VOC at standard temperature and pressure in the coupon to the coupon volume. The amount of VOC in the coupon upon removal from the jar was calculated as the mass difference of the coupon between the first and last measurements. Coupon shapes were somewhat irregular, so the coupon volume was estimated as the final coupon mass divided by the coupon density. The drum liner density was determined to be 0.964 g cm⁻³. Calculated values of VOC equilibrium concentrations at equilibrium conditions and the corresponding values of H_s^{*} are listed in Table 13.

Table 12. Calculated vapor pressure at 22°C and estimated VOC mole fraction in gas phase at saturated conditions.

VOC	P ^{vap} (mm Hg)	y _s
CH ₂ Cl ₂ ^a	380.8	0.371
CCl ₄ ^b	100.8	0.135
TCA	116.2	0.153
TCE	59.4	0.084
Methanol	107.9	0.143
Cyclohexane	85.1	0.116
Toluene	24.3	0.036
p-xylene	7.34	0.011
Freon-113	296.4	0.315

a. Dichloromethane
b. Carbon tetrachloride

Table 13. Measured VOC equilibrium concentration at saturated vapor conditions and estimated Henry's constant.

VOC	VOC equilibrium concentration cm ³ VOC (STP) cm ⁻³	Henry's constant, H [*] _s cm ³ atm cm ⁻³ VOC (STP)
CH ₂ Cl ₂ ^a	7.321	0.0431
CCl ₄ ^b	5.288	0.0217
TCA	3.235	0.0402
TCE	11.19	0.00640
Methanol	4.471	0.0272
Cyclohexane	9.209	0.0107
Toluene	3.219	0.00957
p-xylene	6.503	0.00147
Freon-113	1.357	0.1973

a. Dichloromethane
b. Carbon tetrachloride

The mass transfer coefficient, η , was estimated by measuring the VOC weight loss from a VOC-saturated coupon. The value of η was estimated using an equation analogous to Equation (7)

$$\ln \left[\frac{m(t) - m_{\infty}}{m(0) - m_{\infty}} \right] = \eta t \quad (24)$$

where

$m(t)$ = coupon mass at time t

$m(0)$ = coupon mass at time $t = 0$

m_{∞} = final coupon mass

The term on the left-side of the equal sign is plotted as a function of time t . The slope of the straight line is the value of η in s^{-1} . The values of η determined for each VOC are listed in Table 14. Experimental data of the coupon mass as a function of time used to determine η are listed in Appendix C.

Table 14. Calculated VOC transfer coefficients for use in Equation (6).

VOC	η, s^{-1}
$CH_2Cl_2^a$	2×10^{-6}
CCl_4^b	6×10^{-5}
TCA	1×10^{-5}
TCE	6×10^{-5}
Methanol	2.4×10^{-7}
Cyclohexane	3×10^{-5}
Toluene	7×10^{-6}
p-xylene	4×10^{-6}
Freon-113	1×10^{-5}

a. Dichloromethane

b. Carbon tetrachloride

5. ESTIMATED MODEL PARAMETERS

Permeabilities of nine VOCs were estimated using Equation (8). Measured VOC permeabilities across polyethylene were used to estimate the parameter γ in Equation (13). Measured values of VOC solubilities in polyethylene were used to estimate the parameter α in Equation (9). The values of $\alpha = 0.197$ and $\gamma = 0.079$ minimized the error between experimental and estimated values. In all calculations, the quantity $0.5\phi^{0.5}$ in Equations (12) and (13) was assumed to be 0.9 \AA^{10} . An average value of $n = 1.565$ was used in Equation (14). The estimated and experimental permeabilities are listed in Table 15. Experimental permeability values of dichloromethane, carbon tetrachloride, TCA, TCE, and Freon-113 in polyethylene were calculated as the average of the values measured in the first set of permeability tests listed in Table 1. Because of the poor quality of the results from the second set of experiments, no permeability values from these experiments were used in calculating the average. In the absence of any other data, the permeability of cyclohexane, toluene, methanol, and p-xylene in polyethylene were defined from the results in the second set of experiments at 25°C and the maximum concentration. The estimated values are similar to experimental values except in the case of methanol and cyclohexane. The measured and estimated VOC equilibrium concentrations are listed in Table 16.

Table 15. Measured and estimated VOC permeability in polyethylene bag.

VOC	$\rho_{\text{meas}}(\text{Ba})$	$\rho_{\text{est}}(\text{Ba})$
$\text{CH}_2\text{Cl}_2^{\text{a}}$	263	260
CCl_4^{b}	193	200
TCA	143	155
TCE	583	350
Methanol	135	3,170
Cyclohexane	12.4	140
Toluene	669	270
p-xylene	811	270
Freon-113	38.6	40

a. Dichloromethane

b. Carbon tetrachloride

Table 16. Measured and estimated VOC equilibrium concentration in polyethylene drum liner.

VOC	Measured VOC equilibrium conc. cm ³ VOC (STP) cm ⁻³	Estimated VOC equilibrium conc. cm ³ VOC (STP) cm ⁻³
CH ₂ Cl ₂ ^a	7.321	7.304
CCl ₄ ^b	5.288	4.453
TCA	3.235	4.112
TCE	11.19	3.732
Methanol	4.471	6.673
Cyclohexane	9.209	3.756
Toluene	3.219	2.450
p-xylene	6.503	1.297
Freon-113	1.357	4.212

a. Dichloromethane

b. Carbon tetrachloride.

6. DISCUSSION

A comparison of the measured VOC permeability in polymers at 25°C during the first set of tests using a single VOC-air gas mixture and that using a gas mixture containing 5 VOCs indicates that the difference between the methods is not greater than a factor of two. In the second set of permeability experiments, the VOC concentration on the permeate side of the membrane was not found in detectable quantities during permeability tests using PVC. This was attributed to the membrane thickness and the relatively low VOC concentrations used. When VOC permeabilities across PVC were measured, the ratio between average VOC permeabilities across polyethylene and PVC generally did not exceed 2. In some cases, the reported permeabilities at the lowest VOC concentrations were larger than values reported at higher VOC concentrations. This was interpreted as an indication that the experimental setup was incapable of accurately measuring permeabilities at such low concentrations.

In general, VOC permeability increases with increasing temperature or concentration. This trend was observed for many but not all VOCs and was attributed to the narrow range of VOC concentrations. In some cases, the permeability values at the lower concentrations were greater than at the higher concentration. Thus, only the permeabilities reported at the highest and intermediate concentrations were used to determine the concentration and temperature dependence of VOC permeability across the polymer films. In other cases, the permeability values varied over such a range as to suggest these values were not valid as was the case for TCE and p-xylene across PVC.

Two model parameters were determined from available experimental data. The parameters can be used to estimate permeability and solubility of other VOCs in the same type of polyethylene. The discrepancy between the permeabilities in this report and those listed elsewhere² is attributed to different Lennard-Jones parameters being used in calculations. The parameters for dichloromethane, carbon tetrachloride, methanol, and cyclohexane used in original calculations were tabulated values.¹¹ For the purpose of this report, the parameters for dichloromethane, carbon tetrachloride, and cyclohexane were estimated using Equations (15) and (16). The parameters for methanol were estimated using Equations (18) and (19).

The mass-transfer coefficient, η , varied during the course of the desorption experiments. Estimation of the VOC accumulation rate as a function of the VOC equilibrium concentration (for a given VOC concentration in the gas phase) and a constant mass-transfer coefficient is recognized as a simplistic approach. It was assumed that the average VOC concentration in the coupon approximates the VOC concentration at the surface. This assumption is most appropriate at the beginning of the experiment (in a saturated coupon) before a concentration gradient has fully developed. For this reason, η was estimated from data collected within the first 15,000 s of the desorption tests. While it would have been preferable to determine the mass-transfer coefficient from experimental data measuring the weight gain of the coupon as a function of time, it was assumed that the rate of desorption approximates the rate of absorption particularly in the early portion of the experiment.

7. REFERENCES

1. K. J. Liekhus, G. L. Gresham, E. S. Peterson, C. Rae, N. J. Hotz, and M. J. Connolly, 1994, Modeling Unsteady-State VOC Transport in Simulated Waste Drums, EG&G Idaho, EGG-WM-10823, Rev. 1.
2. K. J. Liekhus, 1994, Characterization of Void Volume VOC Concentration in Vented TRU Waste Drums—Final Report, Lockheed Idaho, INEL-94/0252.
3. J. Izydorczyk, J. Podkowka, and J. Salwinski, 1979, Evaluation of Results of Simplified Determination Methods of Polymer Membrane Permeability to Vapors, *J. Appl. Polym. Sci.*, 23, 2265–2269.
4. T. C. Wang, 1975, Pouch Method for Measuring Permeability of Organic Vapors Through Plastic Films, *Proceedings of Am. Chem. Soc. Meeting*, 35(1), 442–447.
5. V. L. Simril and A. Hershberger, 1950, Permeability of Polymeric Films to Organic Vapors, *Modern Plastics*, 97.
6. Y. Takeuchi and H. Okamura, 1976, Permeation of Hydrocarbon Vapors Through Polyethylene Films, *J. Chem. Engng Japan*, 9(2), 136–139.
7. D. G. Pye, H. H. Hoehn, and M. Panar, 1976, Measurement of Gas Permeability of Polymers, II. Apparatus for Determination of Permeabilities of Mixed Gases and Vapors, *J. Appl. Polym. Sci.*, 20, 287–301.
8. R. C. Reid, J. M. Prausnitz, and B. E. Poling, 1987, *The Properties of Gases and Liquids*, 4th ed., McGraw-Hill Book Co., New York.
9. A. S. Michaels and H. J. Bixler, 1961, Solubility of Gases in Polyethylene, *J. Poly. Sci.*, 50, 393–412.
10. A. S. Michaels and H. J. Bixler, 1961, Flow of Gases Through Polyethylene, *J. Poly. Sci.*, 50, 413–439.
11. R. S. Brodkey and H. C. Hershey, 1988, *Transport Phenomena: A Unified Approach*, McGraw-Hill Book Co., New York.
12. *Lange's Handbook of Chemistry*, 13th ed., edited by J. A. Dean, McGraw-Hill, New York, 1984.

Appendix A

VOC Permeability in Polyethylene and PVC as a Function of Temperature and VOC Concentration

Appendix A

VOC Permeability in Polyethylene and PVC as a Function of Temperature and VOC Concentration

The following equations were determined by nonlinear regression methods to best estimate the concentration and temperature dependence of VOC permeability, P, across polyethylene or polyvinyl chloride (PVC):

1,1,1-trichloroethane (TCA)

Polymer: polyethylene

(C)oncentrations: 1002 ppm, 494 ppm

(T)emperatures: 298.2 K (25°C); 308.2 K (35°C); 323.2 K (50°C)

$$P = 6.184 \times 10^6 \exp[-3471/T(K) + 8.568 \times 10^{-4} C(ppm)]$$

Conc (ppm)	Temp (K)	P _{act} (Ba)	P _{est} (Ba)
1002	298.2	118.5	128.7
1002	308.2	180.4	187.8
1002	323.2	325.3	316.7
494	298.2	98.0	83.3
494	308.2	134.0	121.5
494	323.2	192.2	205.6

Polymer: PVC

(C)oncentrations: 1002 ppm, 494 ppm

(T)emperatures: 298.2 K (25°C); 308.2 K (35°C); 323.2 K (50°C)

$$P = 7.178 \times 10^7 \exp[-4302/T(K) + 9.981 \times 10^{-5} C(ppm)]$$

Conc (ppm)	Temp (K)	P _{act} (Ba)	P _{est} (Ba)
1002	298.2	46.0	43.0
1002	308.2	70.9	68.7
1002	323.2	129.3	131.4
494	298.2	32.7	40.9
494	308.2	68.6	65.3
494	323.2	126.4	125.4

toluene

Polymer: polyethylene

(C)oncentrations: 501 ppm, 51.3 ppm

(T)emperatures: 298.2 K (25°C); 308.2 K (35°C); 323.2 K (50°C)

$$P = 3.230 \times 10^6 \exp[-2896/T(K) + 2.467 \times 10^{-3} C(ppm)]$$

Conc (ppm)	Temp (K)	P _{act} (Ba)	P _{est} (Ba)
501	298.2	668.5	673.4
501	308.2	925.6	922.8
501	323.2	1427.8	1427.3
51.3	298.2	219.7	222.0
51.3	308.2	317.3	304.3
51.3	323.2	464.6	471.9

Polymer: PVC

(C)oncentrations: 1002 ppm, 494 ppm

(T)emperatures: 298.2 K (25°C); 308.2 K (35°C); 323.2 K (50°C)

$$P = 3.087 \times 10^{11} \exp[-6799/T(K) + 2.022 \times 10^{-3} C(ppm)]$$

Conc (ppm)	Temp (K)	P _{act} (Ba)	P _{est} (Ba)
1002	298.2	66.1	106.7
1002	308.2	219.6	223.6
1002	323.2	630.7	622.3
494	298.2	65.2	43.0
494	308.2	163.9	90.0
494	323.2	222.1	252.3

p-xylene

Polymer: polyethylene

(C)oncentrations: 501 ppm, 49.4 ppm

(T)emperatures: 298.2 K (25°C); 308.2 K (35°C); 323.2 K (50°C)

$$P = 2.403 \times 10^6 \exp[-2433/T(K) + 8.281 \times 10^{-4} C(ppm)]$$

Conc (ppm)	Temp (K)	P _{act} (Ba)	P _{est} (Ba)
501	298.2	811.3	1040.2
501	308.2	1474	1356
501	323.2	1995	1955
49.4	298.2	727.3	715.6
49.4	308.2	1183	932.6
49.4	323.2	1169	1348

cyclohexane

Polymer: polyethylene

(C)oncentrations: 745 ppm, 98 ppm

(T)emperatures: 298.2 K (25°C); 308.2 K (35°C); 323.2 K (50°C)

$$P = 3.001 \times 10^{14} \exp[-8607/T(K) + 8.907 \times 10^{-4} C(ppm)]$$

Conc (ppm)	Temp (K)	P _{act} (Ba)	P _{est} (Ba)
745	298.2	12.4	17.0
745	308.2	35.2	43.4
745	323.2	162.2	158.7
98	298.2	21.4	9.6
98	308.2	36.3	24.3
98	323.2	85.3	89.8

methylene chloride (using data as reported)

Polymer: polyethylene

(C)oncentrations: 1006 ppm, 99.1 ppm

(T)emperatures: 298.2 K (25°C); 308.2 K (35°C); 323.2 K (50°C)

$$P = 2.081 \times 10^7 \exp[-3517/T(K) - 2.276 \times 10^4 C(ppm)]$$

Conc (ppm)	Temp (K)	P _{act} (Ba)	P _{est} (Ba)
1006	298.2	126.4	124.9
1006	308.2	182.7	183.2
1006	323.2	310.8	311.1
99.1	298.2	172.7	153.6
99.1	308.2	201.8	225.2
99.1	323.2	389.8	383.7

methylene chloride (low concentration reduced by one standard deviation)

Polymer: polyethylene

(C)oncentrations: 1006 ppm, 99.1 ppm

(T)emperatures: 298.2 K (25°C); 308.2 K (35°C); 323.2 K (50°C)

$$P = 2.288 \times 10^7 \exp[-3689/T(K) + 2.178 \times 10^4 C(ppm)]$$

Conc (ppm)	Temp (K)	P _{act} (Ba)	P _{est} (Ba)
1006	298.2	126.4	120.7
1006	308.2	182.7	180.4
1006	323.2	310.8	314.3
99.1	298.2	93.4	99.1
99.1	308.2	143.8	148.0
99.1	323.2	263.5	258.9

The following equations were determined by linear regression methods to best estimate the temperature dependence of VOC permeability, P, across polyethylene or polyvinyl chloride (PVC) at a given concentration:

carbon tetrachloride

Polymer: polyethylene

Concentration: 295 ppm

(T)emperatures: 298.2 K (25°C); 308.2 K (35°C); 323.2 K (50°C)

$$P = 1.840 \times 10^6 \exp[-2729/T(K)]$$

Temp (K)	P _{act} (Ba)	P _{est} (Ba)
298.2	181.1	194.9
308.2	297.8	262.3
323.2	375.2	395.6

methylene chloride

Polymer: PVC

Concentration: 1006 ppm

(T)emperatures: 298.2 K (25°C); 308.2 K (35°C); 323.2 K (50°C)

$$P = 2.387 \times 10^6 \exp[-4346/T(K)]$$

Temp (K)	P _{act} (Ba)	P _{est} (Ba)
298.2	101.8	111.8
308.2	211.9	179.4
323.2	322.7	345.1

Appendix B

Antoine Equation Constant

Appendix B

Antoine Equation Constant

Table B-1. Antoine equations constants for VOCs used in solubility experiments.

VOC	A	B	C
CH ₂ Cl ₂ ^a	7.4092	1325.9	252.6
CCl ₄ ^b	6.93390	1242.43	230.0
TCA	8.6434	2136.6	302.8
TCE	6.5183	1018.6	192.7
Methanol	7.87863	1473.11	230.0
Cyclohexane	6.84498	1203.526	222.863
Toluene	6.95334	1343.943	219.377
p-xylene	6.99052	1453.430	215.31
Freon-113	6.8803	1099.9	227.5

a. Dichloromethane

b. Carbon tetrachloride

Appendix C

Solubility Experimental Data

Appendix C

Solubility Experimental Data

Coupons of polyethylene drum liner were sealed in a container that also held a 100-mL beaker filled with a liquid VOC and remained in the container for 48 hours. Each coupon was removed from the container and weighed. The mass of coupon was measured as a function of time. Finally, the mass of the coupon was weighed again approximately one month later. The total change of mass is indicative of the VOC solubility in the polymer. The rate of weight loss is assumed to approximate the rate of weight gain during the exposure to a VOC-saturated gas phase. Experimental data from these experiments are summarized in this appendix.

Table C-1. Mass of coupon exposed to cyclohexane as a function of time.

Time, s	Mass, g
0	9.6503
35	9.6466
99	9.6465
125	9.6460
135	9.6458
213	9.6443
661	9.6400
973	9.6380
1304	9.6362
1495	9.6354
3310	9.6291
6903	9.6211
13518	9.6115
14666	9.6077

Time, s	Mass, g
18221	9.6036
18254	9.6035
18385	9.6034
20548	9.6016
32393	9.5913
78537	9.5716
84414	9.5700
85502	9.5696
93764	9.5674
98575	9.5662
103347	9.5649
103830	9.5648
164409	9.5513
165548	9.5511

Final coupon mass: 9.3162 g

Table C-2. Mass of coupon exposed to methanol as a function of time

Time, s	Mass, g
0	7.5365
9	7.5348
34	7.5316
4404	7.5285
8432	7.5282
13590	7.5280
15376	7.5280
19118	7.5282
21030	7.5281
21037	7.5281
23999	7.5281
36027	7.5281
80968	7.5275
80975	7.5275
83681	7.5273
86006	7.5274
88287	7.5273
89473	7.5272
93240	7.5274
97366	7.5273
102492	7.5276
104004	7.5276
105995	7.5276
107143	7.5277
166406	7.5274
167833	7.5274
169964	7.5273

Final coupon mass: 7.4869 g

Table C-3. Mass of coupon exposed to TCE as a function of time.

Time, s	Mass, g
0	9.5542
1	9.5539
7	9.5531
9	9.5530
10	9.5526
17	9.5517
48	9.5482
983	9.5156
14524	9.4175
18564	9.4029
21560	9.3936
23329	9.3886
86762	9.2991
91612	9.2951
100319	9.2883
104937	9.2847
107597	9.2828
110363	9.2808
435350	9.1800

Final coupon mass: 8.9454 g

Table C-4. Mass of coupon exposed to TCA as a function of time.

Time, s	Mass, g
0	9.8680
3	9.8679
5	9.8678
32	9.8671
35	9.8671
44	9.8669
45	9.8668
364	9.8627
710	9.8601
1289	9.8570
7109	9.8424
7382	9.8419
14000	9.8334
15057	9.8323
15588	9.8317
22832	9.8256
23385	9.8252
234447	9.7773
237672	9.7767
243501	9.7764
255298	9.7755
257219	9.7754
257381	9.7754

Final coupon mass: 9.6747 g

Table C-5. Mass of coupon exposed to dichloromethane as a function of time.

Time, s	Mass, g
0	9.6294
91	9.6292
257	9.6289
2918	9.626
4714	9.6247
6498	9.6235
9361	9.6219
11163	9.6209
27836	9.6134
83397	9.5978
85790	9.5972
96725	9.5947
102129	9.5936
108160	9.5921
173521	9.5808
180354	9.5798
182985	9.5794

Final coupon mass: 9.3600 g

Table C-6. Mass of coupon exposed to toluene as a function of time.

Time, s	Mass, g
0	9.5324
94	9.5292
103	9.5290
2171	9.5127
5915	9.5006
10416	9.4915
13056	9.4875
13060	9.4875
14060	9.4861
16931	9.4832
18831	9.4808
21153	9.4784
22040	9.4774
83087	9.4445
84978	9.4436
96076	9.4433
88755	9.4427
88995	9.4426
90468	9.4421
92013	9.4417
93820	9.4412
97191	9.4401
98770	9.4397
102377	9.4388
104330	9.4384
109387	9.4372
163610	9.4262
165296	9.4260
173409	9.4247
176392	9.4243
186223	9.4230
188857	9.4226
190331	9.4224

Final coupon mass: 9.4033 g

Table C-7. Mass of coupon exposed to carbon tetrachloride as a function of time.

Time, s	Mass, g	Time, s	Mass, g
0	9.4458	363	9.4286
11	9.4432	377	9.4283
15	9.4425	564	9.4153
17	9.4422	1383	9.4096
18	9.4420	1904	9.4065
20	9.4416	14214	9.3692
23	9.4411	14566	9.3686
30	9.4402	14825	9.3681
34	9.4397	14947	9.3616
37	9.4392	14961	9.3616
47	9.4379	18566	9.3565
58	9.4367	19690	9.3548
76	9.4358	32706	9.3399
93	9.4351	32874	9.3397
109	9.4345	79312	9.3094
115	9.4343	79743	9.3092
117	9.4342	83096	9.3078
170	9.4327	85103	9.3068
194	9.4321	96319	9.3021
343	9.4289	99124	9.3010

Final coupon mass: 9.1030 g

Table C-8. Mass of coupon exposed to p-xylene as a function of time.

Time, s	Mass, g
0	9.6429
31	9.6427
57	9.6425
2886	9.6338
12705	9.6232
13447	9.6227
17168	9.6203
24180	9.6159
75060	9.5990
81890	9.5973
84367	9.5968
89108	9.5958
94239	9.5947
97845	9.5941
105665	9.5928
106411	9.5927
165354	9.5837
170137	9.5825
170584	9.5824
172787	9.5816
174181	9.5813
182508	9.5805
182513	9.5803
184354	9.5802
186375	9.5797
187809	9.5794

Final coupon mass: 9.3441 g

Table C-9. Mass of coupon exposed to Freon-113 as a function of time.

Time, s	Mass, g
0	8.7714
80	8.7707
202	8.7700
309	8.7695
4430	8.7627
9775	8.7589
34119	8.7503
34995	8.7501
86131	8.7414
91229	8.7407
101016	8.7398
103386	8.7397
107630	8.7392
110759	8.7388
121060	8.7383
121061	8.7382
121074	8.7383
170914	8.7350
172858	8.7348
175431	8.7347
177625	8.7345
184769	8.7342
193025	8.7337
271211	8.7296
289815	8.7287
298983	8.7284
359565	8.7262

Final coupon mass: 8.6693 g