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Determination of Vapor Pressures, Octanol−Air, and Water−Air Partition Coefficients for Polyfluorinated Sulfonamide, Sulfonamidoethanols, and Telomer Alcohols

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Liquid-phase vapor pressures (P_L) and octanol−air partition coefficients (K_{OA}) for *N*-ethyl perfluorooctane sulfonamide, *N*-methyl perfluorooctanesulfonamidoethanol, *N*-ethyl perfluorooctanesulfonamidoethanol, and four fluorotelomer alcohols ($CF_3(CF_2)_nCH_2CH_2OH$, $n = 3, 5, 7$, and 9) were estimated as a function of temperature using a technique based on measuring gas chromatographic retention times relative to those of hexachlorobenzene. The method was calibrated using volatility data for fluorinated aromatic substances, chlorinated benzenes, and pesticides. The fluorinated telomer alcohols were found to have a volatility higher than that of the nonfluorinated alcohols of similar chain length and higher than that of perfluorinated aromatics of comparable molar mass. On the basis of their volatility, the polyfluorinated chemicals are expected to occur predominantly in the atmospheric gas phase. The water−air partition coefficient (K_{WA}) for the three shorter carbon chain length fluorotelomer alcohols was determined as a function of temperature using equilibrium static headspace gas chromatography and the phase ratio variation method. The K_{WA} values of the three fluorinated telomer alcohols extrapolated to 25 °C are of a similar order of magnitude ($1 < \log K_{WA} < 2$) and suggest that rain scavenging is not a very efficient atmospheric deposition process.

Introduction

The polyfluorinated sulfonamidoethanols (FOSEs) and telomer alcohols (FTOHs) are industrial chemicals widely used to incorporate perfluorinated alkyl groups into a variety of polymeric materials. Common FOSEs are *N*-methyl and *N*-ethyl perfluorooctanesulfonamidoethanol, $C_8F_{17}{-}SO_2{-}N(C_2H_4OH)CH_3$ (*N*-MeFOSE) and $C_8F_{17}{-}SO_2{-}N(C_2H_4OH)C_2H_5$ (*N*-EtFOSE), whereas the FTOHs have the generic structure $CF_3(CF_2)_nCH_2CH_2OH$, where *n* is 3, 5, 7, and 9. Designating the number of perfluorinated carbon atoms (X) and nonsubstituted methylene groups (Y), the FTOHs are often referred to as X:Y FTOH. Recently, these compounds have elicited considerable attention within the environmental chemistry community because they are suspected precursors of perfluorooctanesulfonate (PFOS) and the longer-chain perfluoroalkyl carboxylates (PFCAs). These latter groups of chemicals have repeatedly been shown to bioaccumulate in higher animals, including humans, marine mammals and birds.[1,2] The occurrence in organisms is not restricted to industrial and urban regions but extends to very remote regions such as the Arctic.[3] To understand the common occurrence and wide dispersal of the polyfluorinated acids, there is considerable interest in establishing the sources of FOSEs and FTOHs to the atmosphere and to quantify their atmospheric behavior.[4−6]

Volatility information for the precursor chemicals is crucial for assessing the extent of fugitive emissions during their production and nonpolymeric applications and during the manufacturing and use of polymeric products. Similarly, such information is required to evaluate the potential for volatilization from FOSE- and FTOH-containing products after biotic and nonbiotic degradation. Finally, an understanding of the atmospheric fate of these chemicals demands quantitative information on their partitioning into atmospheric particles and water droplets, which in turn is related to volatility. Various parameters are being used to express the volatility of organic chemicals: vapor pressure (*P*) describes the tendency for a chemical to volatilize from its pure form, whereas the octanol−air and water−air partition coefficients K_{OA} and $K_{WA,}$ respectively, describe the equilibrium partitioning of the gas phase with a pure organic solvent and the aqueous phase, respectively. Octanol is often used as a surrogate for a variety of organic and lipid phases. K_{WA} of a solute at dilute concentrations in water is also known as the Henry's law constant. The knowledge of all three volatility-related parameters allows the estimation of a compound's activity in the aqueous phase and in liquid *n*-octanol. Various linear free-energy relationships exist that predict the environmental phase distribution from a chemical's liquid-phase vapor pressure P_L, K_{OA}, and K_{WA}. All three volatility parameters are strongly influenced by temperature.

Here we report on measurements of P_L, K_{OA}, and K_{WA} for these polyfluorinated chemicals as a function of temperature. P_L and K_{OA} were determined with a technique based on gas chromatographic retention times, whereas K_{WA} was measured using equilibrium headspace−gas chromatography. The static headspace technique for K_{WA} determination is considered preferable over more commonly

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employed dynamic bubble-stripping methods, because the latter may lead to significant errors for substances that act as surfactants and adsorb appreciably to the air−water interface and the walls of the experimental vessel.

Methods

Chemicals. *N*-Ethyl perfluorooctane sulfonamide (*N*-EtFOSA), *N*-EtFOSE, *N*-MeFOSE, and four fluorotelomer alcohols (4:2 FTOH, 6:2 FTOH, 8:2 FTOH, and 10:2 FTOH) were obtained from Oakwood Research Chemicals (West Columbia, SC), Dupont (Wilmington, DE), and 3M Corporation (St. Paul, MN). Purity of all chemicals was 97%. Pentafluorotoluene, pentafluorophenol, 1,3,5-trichloro-2,4,6-trifluorobenzene (TCTFB), octafluoronaphthalene, and decafluorobiphenyl were obtained from Aldrich (Oakville, Ont., Canada) with 99% purity.

Method for Measuring Vapor Pressure and Octanol−Air Partition Coefficient

General Description of Method. P_L and K_{OA} values for the test compounds were determined by gas chromatographic retention time (GC-RT) methods described by Bidleman[7] and Wania et al.[8] These methods rely on the measurements of isothermal retention times $t_{R,i}$ of the analytes relative to the retention times $t_{R,ref}$ of a standard reference compound with well-established volatility as a function of temperature. Linearly regressing the logarithm of the ratio of the retention times $t_{R,i}/t_{R,ref}$ at different temperatures with the logarithm of the volatility parameter $P_{L,ref}$ or $K_{OA,ref}$ of the reference compound at those temperatures allows the estimation of the ratio of the energies of volatilization of the analyte and the reference compound from the slope of the following relationships[7,8]

$$\ln(t_{R,i}/t_{R,ref}) = (\Delta_{OA}U_i/\Delta_{OA}U_{ref} - 1)\ln K_{OA,ref} + C \quad (1)$$

$$\ln(t_{R,i}/t_{R,ref}) = (1 - \Delta_{VAP}H_i/\Delta_{VAP}H_{ref})\ln(P_{L,ref}/\mathrm{Pa}) - C \quad (1')$$

This ratio in turn can be used to calculate uncalibrated vapor pressures (P_{GC}) and octanol−air partition coefficients (K_{OA-GC}) and the energy of volatilization for the analytes using

$$\ln(P_{GC}/\mathrm{Pa}) = (\Delta_{VAP}H_i/\Delta_{VAP}H_{ref})\ln(P_{L,ref}/\mathrm{Pa}) + C \quad (2)$$

$$\ln(K_{OA-GC}/\mathrm{Pa}) = (\Delta_{OA}U_i/\Delta_{OA}U_{ref})\ln(K_{OA,ref}/\mathrm{Pa}) + C \quad (2')$$

P_{GC} and K_{OA-GC} values are not necessarily identical to P_L and K_{OA} and have to be converted to P_L and K_{OA-cal} using a number of calibration compounds for which P_L and K_{OA} are well established from techniques other than the GC-RT technique. The P_{GC} and K_{OA-GC} for the calibration compounds are determined in a manner identical to that used for the analytes, and typically a linear regression between the logarithm of the literature values and the noncalibrated property values is obtained.

Standard Reference Compound. The accuracy of the GC-RT method depends on the availability of a standard reference compound with a well-established P_L or K_{OA} as a function of temperature. This compound should be of comparable volatility and interact with the gas chromatographic stationary phase in a fashion similar to the analytes of interest.[7] No directly measured K_{OA} values for fluorinated chemicals had been reported at the time of the experiments, and no reliable vapor pressure values for chemicals with longer polyfluorinated alkyl chains could be identified. This prevented the selection of a standard reference compound, which is structurally similar to the analytes of interest. However, previous studies relying on the GC-RT method had successfully employed reference compounds that are quite unlike the target compounds. For example, long-chain hydrocarbons such as octadecane and eicosane have been employed as reference compounds for a variety of chlorinated compounds.[9] The use of a structurally unrelated reference compound is, however, a shortcoming of the present study and emphasizes the need for a calibration.

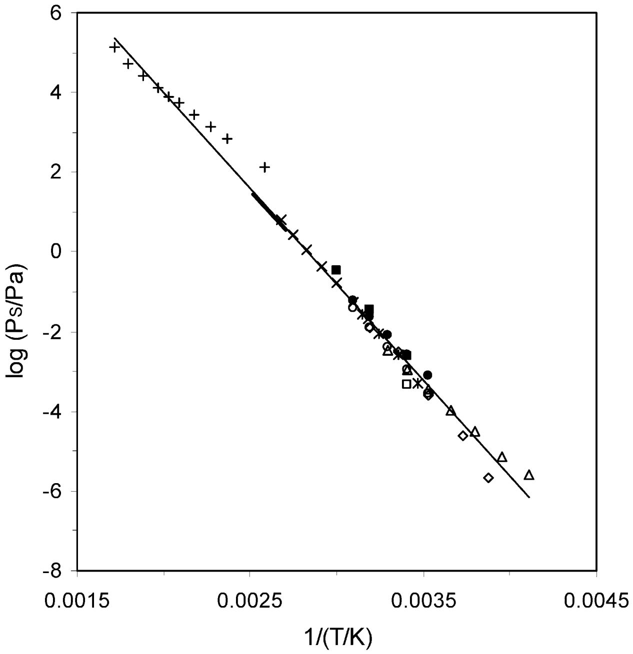

Figure 1. Vapor pressure of solid hexachlorobenzene as a function of reciprocal absolute temperature, reported by studies in the literature: +, Stull;[18] solid line, Sears and Hopke;[14] ×, Rordorf;[17] ■, Gückel et al.;[10] ●, OECD;[15] ○, OECD;[16] *, Farmer et al.;[12] △, Wania et al.;[11] ◇, Liu and Dickhut;[13] □, Dobbs and Cull.[19] The solid line is a linear regression (equation 3 in text) through all data except those by Stull[18] and Dobbs and Cull.[19]

Here, hexachlorobenzene (HCBz) served as a reference compound for both P_{GC} and K_{OA-GC} studies. Its volatility is of comparable magnitude to that of the polyfluorinated organics of interest, and both its P_L and K_{OA} are well known as a function of temperature. Specifically, numerous determinations of the temperature-dependent vapor pressure for HCBz have been reported.[10−19] The observed solid vapor pressure data P_S from these studies were regressed against reciprocal absolute temperature (Figure 1), yielding the following linear relationship over the temperature range −30 to 125 °C

$$\log(P_S/\mathrm{Pa}) = (13.61 \pm 0.33) - (4810 \pm 99)/(T/\mathrm{K})\quad r^2 = 0.985 \quad (3)$$

The solid-phase vapor pressure P_S was converted to the vapor pressure of the supercooled liquid P_L using

$$P_L = P_S/\exp[(\Delta_{fus}S/\mathrm{R})(1 - T_m/T)] \quad (4)$$

and an entropy of fusion $\Delta_{fus}S$ of 48.2 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ (average of values given in refs 20−23) and a melting point temperature T_m of 502 K.[21] Thus

$$\log(P_L/\mathrm{Pa}) = (11.09 \pm 0.33) - (3547 \pm 99)/(T/\mathrm{K}) \quad (5)$$

The temperature-dependent K_{OA} for HCBz has only been measured twice.[24,25] The data from the more recent mea-

Table 1. Vapor Pressure P_{GC} and Octanol−Air Partition Coefficients K_{OA-GC} at 298.15 K (Mean and Standard Deviation), Determined by Gas Chromatography in This Study, Supercooled Liquid Vapor Pressure P_L and Octanol−Air Partition Coefficients K_{OA-lit} at 298.15 K Reported in the Literature, of the Calibration Compounds

compounds	$\log P_{GC}{}^{a}$/Pa	$\log P_L{}^{b}$/Pa	ref	$\log K_{OA-GC}{}^{a}$	$\log K_{OA-lit}{}^{b}$	ref
		Chlorinated Benzenes				
1,2-Cl_2Bz	1.58 ± 0.00	2.23	40[c]	4.99 ± 0.00	4.33	24
1,3-Cl_2Bz	1.68 ± 0.01	2.41	40[c]	4.89 ± 0.01	4.13	48
1,4-Cl_2Bz	1.65 ± 0.00	2.39	40[c]	4.92 ± 0.00	4.18	48
1,2,3-Cl_3Bz	0.92 ± 0.00	1.46	40[c]	5.65 ± 0.00	5.16	24
1,2,4-Cl_3Bz	1.03 ± 0.00	1.52	40[c]	5.54 ± 0.00	4.84	48
1,3,5-Cl_3Bz	1.19 ± 0.00	1.79	40[c]	5.38 ± 0.00	4.64	48
1,2,3,4-Cl_4Bz	0.32 ± 0.00	0.92	40[c]	6.25 ± 0.00	5.61	24
1,2,3,5-Cl_4Bz	0.48 ± 0.00	1.04	40[c]	6.09 ± 0.00	5.53	48
1,2,4,5-Cl_4Bz	0.47 ± 0.00	1.03	40[c]	6.10 ± 0.00	5.65	24
Cl_5Bz	−0.18 ± 0.00	−0.04	41, 42[d]	6.75 ± 0.00	6.29	24
		Fluorinated Aromatics				
pentafluorotoluene	2.47 ± 0.00	3.38	43			
pentafluorophenol	1.46 ± 0.00	2.59	43			
TCTFB	1.22 ± 0.00	1.77	44			
octafluoronaphthalene	1.23 ± 0.00	1.61	45			
decafluorobiphenyl	1.01 ± 0.00	1.27	45			
		Chlorinated Pesticides				
α-HCH	−0.75 ± 0.00	−0.61	46[c]	7.33 ± 0.00	7.61	25
γ-HCH	−0.95 ± 0.00	−1.11	46[c]	7.52 ± 0.00	7.85	25
β-HCH	−1.03 ± 0.00	−1.21	46[c]			
aldrin	−1.69 ± 0.00	−1.23	47[c]	8.27 ± 0.00	8.08	25
heptachlor	−1.51 ± 0.00	−1.33	47[c]			
dieldrin	−2.35 ± 0.00	−1.92	47[c]	8.93 ± 0.00	8.90	25
p,p′-DDE	−2.38 ± 0.00	−2.48	47[c]	9.22 ± 0.00	9.68	25
o,p′-DDT	−2.61 ± 0.00	−2.75	47[c]	9.44 ± 0.00	9.45	25
p,p′-DDT	−3.12 ± 0.00	−3.31	47[c]	9.70 ± 0.00	9.81	25
endosulfan I				8.75 ± 0.00	8.64	25
cis-chlordane				8.83 ± 0.00	8.91	25
trans-nonachlor				8.90 ± 0.00	9.29	25
cis-nonachlor				9.26 ± 0.00	9.67	25

[a] This study. [b] Literature value. [c] Literature derived value from data compilation and evaluation. [d] Average value from ref 41 and 42.

surements by Shoeib and Harner[25] are believed to be more trustworthy[8] and were used in this study, yielding the following equation

$$\log K_{OA} = -(2.40 \pm 0.37) + (2914 \pm 107)/(T/\mathrm{K}) \quad r^2 = 0.996 \qquad (6)$$

Instrumentation. Isothermal retention times of the analytes and the calibration compounds at six temperatures in the range 30−80 °C with 10 °C increments on a DB-1 capillary column (0.25 mm i.d. × 1 m long, 0.25-μm film thickness, J&W Scientific, Folsom, CA) were recorded using a Perkin-Elmer Auto System XL gas chromatograph (GC). The operating conditions for the GC were: injection port at 225 °C and detector at 325 °C. Column pressure for hydrogen as a carrier gas was 1 psi with a split ratio of 10:1.

Calibration Procedure. Twenty-four compounds with well-established vapor pressures at 25 °C were selected as the calibration compounds. These compounds should preferably be structurally related to the analytes of interest. Five fluorinated aromatic chemicals with reliably established vapor pressures and volatilities comparable to the analytes of interest were included in the set of calibration compounds, namely, pentafluorotoluene, pentafluorophenol, 1,3,5-trichloro-2,4,6-trifluorobenzene (TCTFB), octafluoronaphthalene, and decafluorobiphenyl. However, even these flourinated substances are structurally quite different from the target compounds. The other calibration compounds were the chlorinated benzenes and a diverse set of organochlorinated pesticides with reliably known volatility. The literature P_L values, their literature sources, and the GC-RT-derived P_{GC} values for these compounds are listed in Table 1. Because of the excellent reproducibility of gas chromatographic retention times, the standard deviation of the P_{GC} values, as determined from duplicate or triplicate experiments, is very small. The calibration curve for vapor pressure, shown in Figure 2, was constructed by regressing the measured P_{GC} of the calibration compounds with their literature P_L values. The following relationship was obtained

$$\log(P_L/\mathrm{Pa}) = (1.17 \pm 0.03)\log(P_{GC}/\mathrm{Pa}) + (0.40 \pm 0.05) \quad r^2 = 0.986 \qquad (7)$$

and used to estimate the P_L values of the polyfluorinated organic compounds of interest from experimentally determined P_{GC}.

The calibration curve for converting K_{OA-GC} to K_{OA-cal} was established by regression of the K_{OA-GC} against K_{OA-lit} using 22 compounds from Table 1. The calibration set does not contain any fluorinated chemicals, because no directly measured K_{OA} value for such substances exists. The following relationship (Figure 3) was found

$$\log K_{OA-lit} = (1.22 \pm 0.03)\log K_{OA-GC} - (1.82 \pm 0.22) \quad r^2 = 0.989 \qquad (8)$$

and used to convert the K_{OA-GC} values for several fluorinated aromatic and aliphatic compounds to calibrated K_{OA-cal} values.

Method for Measuring Water−Air Partition Coefficient

General Description of Method. The partitioning equilibrium between air and water was determined as a function of temperature for 4:2 FTOH, 6:2 FTOH, and 8:2 FTOH using equilibrium headspace−gas chromatography with the phase ratio variation method by Ettre and Kolb.[26]

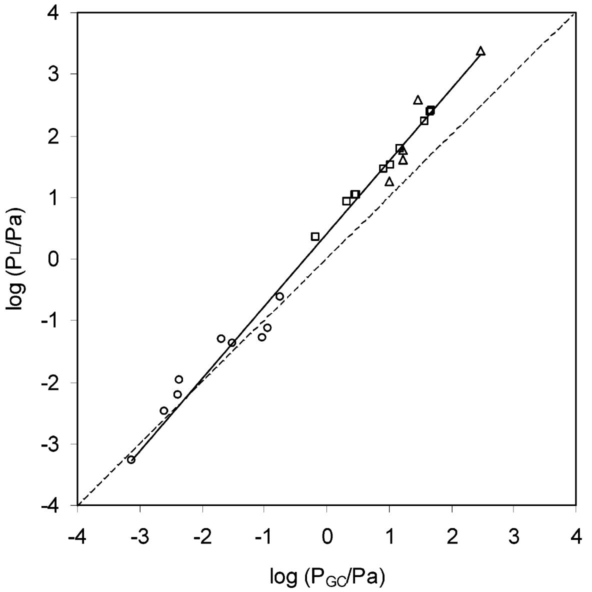

Figure 2. Relationship between the vapor pressure P_{GC} derived from gas chromatographic retention times and the vapor pressure values P_L reported for the calibration compounds in the literature and listed in Table 1 (△, fluoroaromatic compounds; □, chlorinated benzenes; ○, organochlorine pesticides). The broken line corresponds to the 1:1 line, whereas the solid line is the linear regression through all data (eq 7 in text), which is used for calibrating the P_{GC} values of the polyfluorinated chemicals.

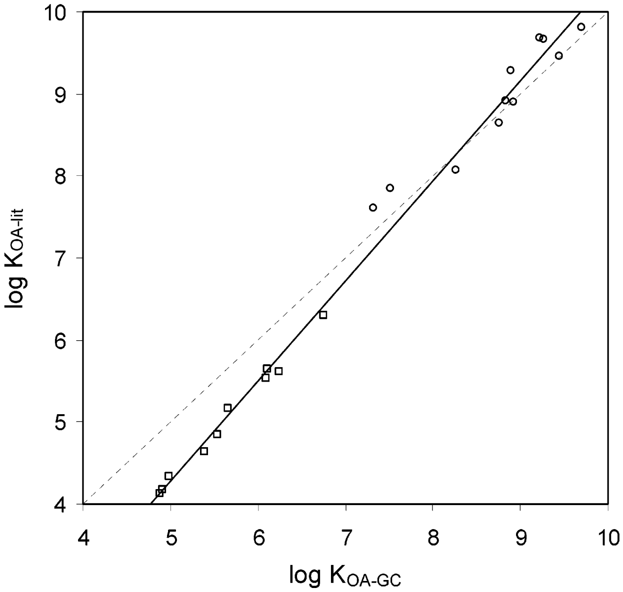

Figure 3. Relationship between the octanol−air partition coefficient K_{OA-GC} derived from gas chromatographic retention times and the K_{OA-lit} values reported for the calibration compounds in the literature and listed in Table 1 (□, chlorinated benzenes; ○, organochlorine pesticides). The broken line corresponds to the 1:1 line, whereas the solid line is the linear regression through all data (eq 8 in text), which is used for calibrating the K_{OA-GC} values of the polyfluorinated chemicals.

To verify accuracy and precision of this method, the water−air partition coefficients for benzene, toluene, and chlorobenzene were measured as a function of temperature in the range 45−80 °C, extrapolated to 25 °C, and compared with literature values. In the phase ratio variation method, variable volumes of the same solution of the analytes are equilibrated with the gas phase in closed vials of the same total volume. Each vial experiences a different phase ratio β, which is linearly related to the reciprocal of the headspace concentration. The equilibrium partition coefficient between the solvent and the gas phase can be derived from the slope and intercept of this linear relationship. The theory of the phase ratio variation method is described elsewhere,[26,27] and we only give a brief introduction here. The concentration C^*_A of analyte in the gas phase (in the headspace) at equilibrium is

$$C^*_A = C_{W0}/(K^c_{WA} + \beta) \tag{9}$$

where K^c_{WA} is the water−air partition coefficient (whereby the superscript c indicates that K is expressed on a molar concentration scale), and C_{W0} is the original molar concentration of the analyte in the aqueous solution. β is defined as the ratio of the volumes of the headspace and the aqueous phase. Taking reciprocals of both sides of eq 9, the following relationship is obtained

$$1/C^*_A = K^c_{WA}/C_{W0} + (1/C_{W0})\beta \tag{10}$$

In linear headspace−gas chromatography, the peak area A is proportional to the equilibrium concentration of the analyte, C^*_A

$$A = f_i C^*_A \tag{11}$$

where f_i is a constant. Substituting eq 11 into eq 10 yields

$$1/A = K^c_{WA}/(f_i C_{W0}) + 1/\,(f_i C_{W0})\cdot\beta \tag{12}$$

K^c_{WA} is obtained by dividing the slope $K^c_{WA}/(f_i C_{W0})$ of this relationship by its intercept $1/(f_i C_{0W})$. This means that K^c_{WA} can be determined by simply recording the peak area A resulting from injections of the headspace of a number of vials containing different volumes of the same aqueous solution and then regressing $1/A$ vs β. Specifically, because C_A* is eliminated from eq 12 and C_{W0} is part of both slope and intercept, neither the absolute headspace concentration nor the original concentration in aqueous solution need to be known or quantified.

Sample Preparation. Saturated aqueous solutions of 4:2 FTOH, 6:2 FTOH, and 8:2 FTOH were prepared by stirring in Milli-Q water for 48 h and filtering (0.45 μm). The working standards were 1:50 to 1:1000 dilutions of these saturated aqueous solutions. Concentrations of the three aromatic test compounds in aqueous solution were between 1 and 10 μg·mL^{-1}. Volumes of 1, 2, 3, 4, and 5 mL of these solutions were pipetted into five headspace vials with a total volume of 22.3 mL. Thus, the phase ratios in the vials were 21.30, 10.15, 6.43, and 4.58 and 3.46, respectively. The samples with the aromatic test compounds were equilibrated for 30 min at temperatures of 45, 50, 60, 70, and 80 °C, whereas the solutions of the polyfluorinated telomer alcohols had an equilibration time between 90 and 120 min at four to six different temperatures in the temperature range 35 to 90 °C. The time periods required to ensure equilibration had been established in optimization experiments.

Three sets of vials were prepared and analyzed for each polyfluorinated telomer alcohol at each temperature, whereas only some of the measurements for the three test compounds were replicated. The reciprocal of the averages of the peak areas obtained from replicate measurements were regressed against the phase ratio, and a standard deviation for the partition coefficient was estimated by error propagation from the standard error of the linear regression.

Table 2. Vapor Pressure Determined by Gas Chromatography, P_{GC}, and Supercooled Liquid−Vapor Pressure at 25 °C, P_L, Slopes and Intercepts for the Relationship $\log(P_L/\mathrm{Pa}) = m/(T/\mathrm{K}) + b$, and Enthalpies of Vaporization $\Delta_{vap}H$ Estimated from m, and P_L Values Reported in the Literature

compounds	P_{GC}/Pa	P_L/Pa	m	b	$\Delta_{vap}H$/kJ·mol^{-1}	P_L/Pa
4:2 FTOH	252 ± 11	1670 ± 338	−(1756 ± 67)	9.1 ± 0.2	33.6 ± 1.3	992[30]
6:2 FTOH	145.2 ± 0.5	876 ± 159	−(1907 ± 56)	9.3 ± 0.2	35.5 ± 1.1	713[30]
8:2 FTOH	45.90 ± 0.03	227 ± 35	−(2498 ± 70)	10.7 ± 0.2	47.8 ± 1.3	254 [30]
10:2 FTOH	13.27 ± 0.00	53 ± 7	−(3000 ± 84)	11.8 ± 0.3	57.4 ± 1.6	144[30]
N-EtFOSA	2.38 ± 0.00	7.0 ± 0.8	−(3527 ± 98)	12.7 ± 0.3	67.5 ± 1.9	
N-MeFOSE	0.33 ± 0.00	0.70 ± 0.08	−(3936 ± 110)	13.0 ± 0.4	75.4 ± 2.1	0.0020[6]
N-EtFOSE	0.19 ± 0.00	0.35 ± 0.04	−(4075 ± 114)	13.2 ± 0.4	78.0 ± 2.2	0.0086[6], 0.792[32]

Instrumentation. Peak areas were quantified with a Perkin-Elmer HS-40XL automatic headspace sampler connected to a Perkin-Elmer Auto System XL GC. For the polyflourinated target analytes, a DB-1 capillary column (0.25 mm i.d. × 30 m long, 0.25-μm film thickness, J&W Scientific, Folsom, CA) was used, whereas the three aromatic test compounds were separated on a DB-5 capillary column (0.32 mm i.d. × 30 m long, Supelco). Polyfluorinated analytes were detected by an electron-capture detector at 325 °C and the aromatic test compounds with a flame ionization detector at 250 °C. In both cases, the injection port was kept at 225 °C. Column pressure for hydrogen as a carrier gas was 15 psi (for polyfluorocompounds) and 5 psi (aromatic test compounds). The split ratio was 1:40.

Data Analysis. The measured partition coefficients between air and water are being presented in three different but commonly employed units. The K_{WA}^c values (dimensionless, with the concentrations in both water and air being expressed as molar concentrations), derived from slope and intercept of eq 12, are converted to Henry's law constants K_{AW}^p in units of Pa·m^3·mol^{-1} using

$$K_{AW}^p = RT/K_{WA}^c \tag{13}$$

where R is the ideal gas constant (8.314 Pa·m^3·mol^{-1}·K^{-1}) and T is absolute temperature in K. The superscript p indicates that the concentration in the gas phase is expressed as a partial pressure in units of Pa. The dimensionless Henry's law constant K_{AW}^x, expressed on a mole fraction scale in air and water, can be derived from K_{WA}^c by multiplication with the ratio of the molar volumes υ_A and υ_W of the gas and aqueous phase (m^3·mol^{-1}), respectively

$$K_{AW}^x = (1/K_{WA}^c)(\upsilon_A/\upsilon_W) \tag{14}$$

The temperature dependence of an equilibrium constant K_{AW}^x is described by the van't Hoff equation

$$\mathrm{d}\ln K_{AW}^x/\mathrm{d}(1/T) = -\Delta_{AW}H/R \tag{15}$$

where $\Delta_{AW}H$ is the enthalpy of the air−water phase transition (J·mol^{-1}). If $\Delta_{AW}H$ is independent of temperature over the range investigated, integration of eq 15 yields

$$\ln K_{AW}^x = -\Delta_{AW}H/(RT) + c \tag{16}$$

where c is the constant of integration. Because K_{AW}^x is related to the standard Gibbs energy of the air−water phase transition $\Delta_{AW}G^x$ (J·mol^{-1}) through

$$\Delta_{AW}G^x = -RT\ln K_{AW}^x \tag{17}$$

and

$$\Delta_{AW}G^x = \Delta_{AW}H - T\Delta_{AW}S^x \tag{18}$$

where ΔS^x is the entropy of the air−water phase transition (J·K^{-1}·mol^{-1}), c equals $\Delta_{AW}S^x/R$, and the following relationship can be derived

$$\ln K_{AW}^x = -\Delta_{AW}H/(RT) + \Delta_{AW}S^x/R \tag{19}$$

By use of eq 19, $\Delta_{AW}H$ and $\Delta_{AW}S^x$ were calculated from the slopes and intercepts of the linear regressions between $\ln K_{AW}^x$ and reciprocal temperature. $\Delta_{AW}G^x$ at 25 °C was then calculated using eq 18. Identical values for $\Delta_{AW}G^x$ are obtained by inserting the value of K_{AW}^x extrapolated to 25 °C into eq 17. $\Delta_{AW}G^x$ is the standard free energy computed on the basis of the equilibrium mol fraction in both phases, which is indicated by the superscript x. It is noteworthy to mention that the free energy of transfer is often based on other standard states, such as the unit molar concentration scale. The values of the free energy and entropy of phase transition would then adopt different numerical values.

Results

Vapor Pressures and Octanol−Air Partition Coefficients. Supercooled liquid vapor pressures P_L for 7 polyfluorinated organic compounds and octanol−air partition coefficient K_{OA} for 12 fluorinated organic compounds are listed in Tables 2 and 3, respectively. Table 2 lists the measured vapor pressure P_{GC} and P_L at 25 °C and the enthalpies of vaporization $\Delta_{vap}H$. Table 3 lists the measured octanol−air partition coefficient K_{OA-GC} and K_{OA-cal} and the energy of phase transfer, $\Delta_{OA}U$. The intercepts b and slopes m reported in Tables 2 and 3 allow the estimation of P_L and K_{OA} as a function of temperature. All results are given with confidence limits, which are propagated from the standard errors of slopes and intercepts of the calibration eqs 7 and 8 and the standard deviation of the retention-time measurements. The uncertainty in the measured values derives largely from the uncertainty introduced by the calibration procedure and not by the measurement uncertainty of the retention times, which generally is very small.

Water−Air Partition Coefficient for the Test Compounds. Table 4 lists the measured values of K_{AW}^p for benzene, toluene, and chlorobenzene at each experimental temperature. Duplicate measurements, performed at some of the experimental temperatures, gave good reproducibility with an average relative standard deviation of less than 4%. The relationship between the logarithm of the partition coefficient and reciprocal absolute temperature is highly linear (Figure 4), allowing the linear extrapolation of the partition coefficient to 25 °C and the estimation of the thermodynamic properties associated with the air−water phase transition using eqs 17, 18, and 19 (Table 4). The values of K_{AW}^p for benzene, toluene, and chlorobenzene extrapolated to 25 °C agree very well with Henry's law constants reported in the literature (Table 4), with the

Table 3. Uncalibrated (K_{OA-GC}) and Calibrated (K_{OA-cal}) Octanol−Air Partition Coefficients for Selected Fluorinated Organic Compounds at 25 °C Determined from Gas Chromatographic Retention Times, Slopes, and Intercepts for the Relationship $\log K_{OA} = m/(T/K) + b$, Energies of Phase Transfer, $\Delta_{OA}U$, and K_{OA} Values Reported in the Literature[6]

compounds	$\log K_{OA-GC}$	$\log K_{OA-cal}$	m	b	$\Delta_{OA}U$/kJ·mol^{-1}	$\log K_{OAl}$
4:2 FTOH	4.16 ± 0.01	3.26 ± 0.25	1117 ± 55	−(0.48 ± 0.31)	21.4 ± 1.0	
6:2 FTOH	4.41 ± 0.00	3.56 ± 0.25	1274 ± 50	−(0.71 ± 0.30)	24.4 ± 1.0	
8:2 FTOH	4.91 ± 0.00	4.17 ± 0.26	1865 ± 69	−(2.08 ± 0.35)	35.7 ± 1.3	
10:2 FTOH	5.45 ± 0.00	4.83 ± 0.27	2367 ± 87	−(3.11 ± 0.40)	45.3 ± 1.7	
N-EtFOSA	6.29 ± 0.01	5.86 ± 0.29	2934 ± 108	−(3.98 ± 0.46)	56.2 ± 2.1	
N-MeFOSE	7.05 ± 0.00	6.78 ± 0.30	3303 ± 121	−(4.30 ± 0.51)	63.2 ± 2.3	7.7[6]
N-EtFOSE	7.30 ± 0.00	7.09 ± 0.31	3443 ± 126	−(4.46 ± 0.52)	65.9 ± 2.4	7.78[6]
pentafluorotoluene	4.10 ± 0.01	3.19 ± 0.25	729 ± 30	0.74 ± 0.27	14.0 ± 0.6	
pentafluorophenol	5.11 ± 0.00	4.42 ± 0.26	2089 ± 78	−(2.59 ± 0.37)	40.0 ± 1.5	
TCTFB	5.35 ± 0.00	4.71 ± 0.27	1884 ± 69	−(1.61 ± 0.36)	36.1 ± 1.3	
octafluoronaphthalene	5.34 ± 0.00	4.70 ± 0.27	1923 ± 71	−(1.74 ± 0.36)	36.8 ± 1.4	
decafluorobiphenyl	5.56 ± 0.00	4.97 ± 0.27	2204 ± 81	−(2.42 ± 0.38)	42.2 ± 1.6	

Table 4. Henry's Law Constant K_{AW}^{p} of Three Aromatic Test Compounds Measured by HS-GC at Five Temperatures, Their Enthalpies of Air−Water Phase Transitions $\Delta_{AW}H$, and Comparison of K_{AW}^{p} Extrapolated to 25 °C with Values Reported in the Literature

	benzene	toluene	chlorobenzene
$\log(K_{AW}^{p}$/Pa·m^3·mol^{-1}) at 45 °C	2.99 ± 0.03[a]	2.98 ± 0.00[a]	2.79 ± 0.01[a]
at 50 °C	3.03	3.08	2.87
at 60 °C	3.17 ± 0.09[a]	3.16 ± 0.04[a]	2.98 ± 0.05[a]
at 70 °C	3.25	3.26	3.09
at 80 °C	3.36 ± 0.08[a]	3.37 ± 0.04[a]	3.20 ± 0.00[a]
at 25 °C (b)	2.73 ± 0.25	2.74 ± 0.29	2.53 ± 0.13
at 25 °C	2.75[49]	2.83[49]	2.58[49], 2.50[50]
$\log K_{WA}$ at 25°C[b]	0.66 ± 0.25	0.65 ± 0.29	0.87 ± 0.13
$\log K_{AW}^{x}$ at 25°C[b]	2.47 ± 0.25	2.49 ± 0.29	2.27 ± 0.13
Thermodynamic Properties			
$\Delta_{AW}H$/kJ·mol^{-1}	23 ± 1	23 ± 1	24.6 ± 0.5
$T\Delta_{AW}S^{x}$/kJ·mol^{-1}	37 ± 1	37 ± 1	37.5 ± 0.5
$\Delta_{AW}G^{x}$/kJ·mol^{-1} at 25 °C	−(14 ± 1)	−(14 ± 1)	−(12.9 ± 0.6)
$\Delta_{AW}S^{x}$/J·K^{-1}·mol^{-1}	124 ± 3	124 ± 4	126 ± 2

[a] Standard deviation of duplicate measurements. [b] Extrapolation using regression of $\log K_{AW}$ vs 1/ (T/K). Standard deviation derived from error of slope and intercept of that regression.

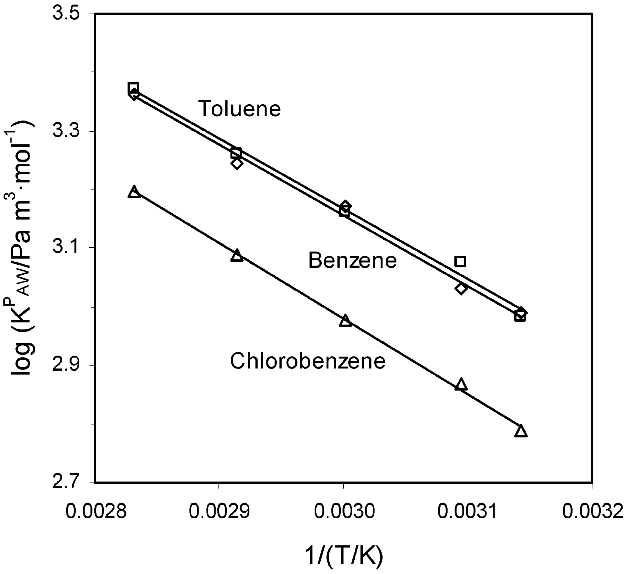

Figure 4. Temperature dependence of air−water partition coefficients for benzene, toluene, and chlorobenzene.

literature values always falling within the confidence limits of our measurements. The size of these confidence limits (the average relative standard deviation of the extrapolated values is 50%) is dominated largely by the uncertainty associated with the extrapolation to lower temperatures. The good agreement of the extrapolated values with literature values at 25 °C gives us confidence in the ability of the method to accurately determine air−water partitioning equilibria of organic chemicals.

Water−Air Partition Coefficients for 4:2 FTOH, 6:2 FTOH, and 8:2 FTOH. Figure 5 displays the relationship between the reciprocal averaged peak area 1/A and phase ratio β as measured for 4:2 FTOH at six different temperatures. The plot reveals that the relationships are highly linear with correlation coefficients between 0.9921 and 0.9997. The slopes, intercepts, and correlation coefficients for all 1/A vs β regressions are given in Table 5. K_{WA}^{c} was calculated from the slope and intercept, and K_{AW}^{p} and K_{AW}^{x} were obtained using eqs 13 and 14. These values are also listed in Table 5. The relative standard deviation of the partition coefficients is on average less than 10% for 4:2 FTOH and 6:2 FTOH and somewhat higher for 8:2 FTOH (on average 25%). The partition coefficient of the latter compound at temperatures below 65 °C could not be determined because of strong sorption effects, which resulted in carry-over in consecutive headspace injections.

The relationship between the logarithm of K_{AW}^{x} of 4:2 FTOH, 6:2 FTOH, and 8:2 FTOH and the reciprocal temperature is highly linear (Figure 6), allowing the extrapolation of the partition coefficients to 25 °C. Table 6 lists these extrapolated values and the thermodynamic parameters for the air−water phase transition of 4:2 FTOH, 6:2 FTOH, and 8:2 FTOH derived from these linear regressions. The extrapolation introduces considerable uncertainty to the partition coefficients.

Discussion

Vapor Pressures and Octanol−Air Partition Coefficients. Figure 7 plots the volatility parameters P_L and K_{OA} against the molar mass of the fluorinated chemicals. Within a group of structurally related substances, volatility expectedly decreases with increasing molecular size. For example, the addition of a $-C_2F_4-$ group decreases the volatility of the telomer alcohols by about 0.6 log units, although the effect is smaller for the smaller FTOHs. In addition to size, polarity is an important factor controlling volatility. For example, pentafluorophenol is about an order of magnitude less volatile than pentafluorotoluene, despite very similar molar mass. This can be explained by the ability of the phenolic compound to undergo hydrogen bonding with itself and with octanol. Similarly, the 10:2 FTOH is almost 2 orders of magnitude more volatile than the FOSEs of comparable molecular mass, indicating that the polar sulfonamide group greatly increases intermolecular interactions and thus lowers vapor pressure.

Interestingly, 4:2 and 6:2 FTOH are also considerably more volatile than the perfluorinated naphthalene and biphenyl, which do not have any polar functional groups

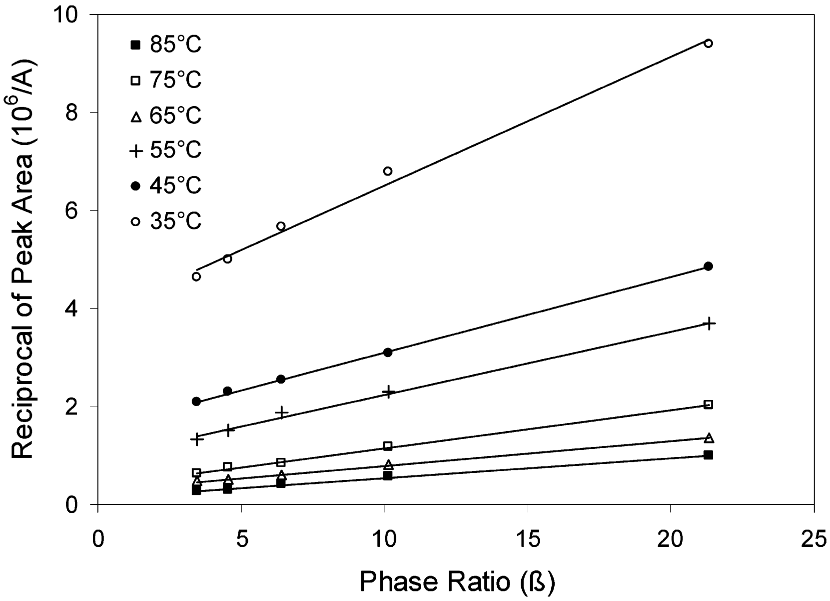

Figure 5. Reciprocal of peak area (1/*A*) vs phase ratio (β) for 4:2 FTOH in gas/water systems, at six temperatures.

Table 5. Slopes, Intercepts, and Correlation Coefficients (r^2) of the Linear Regression of Reciprocal Peak Area 1/*A* vs Phase Ratio β and Air−Water Partition Coefficients for Three Polyfluorinated Telomer Alcohols Derived from These Regressions

compound	T/°C	slope	intercept	r^2	K^{c}_{WA}	K^{p}_{AW}/Pa·m^3·mol^{-1}	K^{x}_{AW}
4:2 FTOH	35	3.88×10^{-6}	2.63×10^{-7}	0.9921	14.8 ± 1.0	174 ± 11	95 ± 6
	45	1.57×10^{-6}	1.53×10^{-7}	0.9994	10.2 ± 0.2	258 ± 5	142 ± 3
	55	9.56×10^{-7}	1.29×10^{-7}	0.9959	7.4 ± 0.5	369 ± 25	202 ± 14
	65	2.93×10^{-7}	5.09×10^{-8}	0.9997	5.7 ± 0.1	489 ± 10	268 ± 6
	75	3.66×10^{-7}	7.82×10^{-8}	0.9994	4.7 ± 0.2	618 ± 22	339 ± 12
	85	1.42×10^{-7}	4.07×10^{-8}	0.9935	3.5 ± 0.5	856 ± 135	469 ± 74
6:2 FTOH	45	2.31×10^{-5}	2.10×10^{-6}	0.9957	11.0 ± 0.6	240 ± 13	131 ± 7
	55	2.16×10^{-5}	3.27×10^{-6}	0.9935	6.6 ± 0.6	413 ± 38	226 ± 21
	65	1.32×10^{-5}	3.15×10^{-6}	0.9877	4.2 ± 0.8	671 ± 124	368 ± 68
	75	7.45×10^{-6}	2.62×10^{-6}	0.9989	2.8 ± 0.2	1019 ± 79	558 ± 43
	85	4.54×10^{-6}	2.27×10^{-6}	0.9996	2.0 ± 0.1	1487 ± 99	815 ± 54
8:2 FTOH	65	2.57×10^{-6}	5.95×10^{-7}	0.9839	4.3 ± 0.9	650 ± 134	356 ± 73
	75	6.08×10^{-7}	2.43×10^{-7}	0.9988	2.5 ± 0.2	1158 ± 108	634 ± 59
	85	2.52×10^{-7}	1.74×10^{-7}	0.9974	1.4 ± 0.3	2055 ± 469	1126 ± 257
	90	2.69×10^{-7}	2.52×10^{-7}	0.9946	1.1 ± 0.5	2825 ± 1268	1548 ± 694

but are of similar molecular mass. This may be related to the formation of intramolecular hydrogen bonding in the FTOHs,[28,29] which presumably reduces the extent to which the hydroxyl group can form intermolecular hydrogen bonds.[30]

Air−Water Partition Coefficients. The air−water partition coefficients of the three fluorinated telomer alcohols are of a similar order of magnitude. This suggests that an increase in the fluorinated chain length reduces the water solubility of these substances to a similar extent as the vapor pressure. Similar dependencies for structurally related halogenated substances have previously been noted. For example, the Henry's law constants of the polychlorinated biphenyls change only slightly with the degree of chlorination, despite large differences in the vapor pressure and aqueous solubility.[31] The temperature dependence of the air−water partition coefficient of the FTOHs shows larger differences, with 8:2 FTOH having double the enthalpy of the phase transition of the 4:2 FTOH (Table 6). As a consequence, the extrapolated K^{x}_{AW} of 8:2 FTOH at 25 °C is smaller than that of 4:2 FTOH even though it is higher at the actual experimental temperatures (Figure 6). Again, an increase in the temperature dependence of air−water partitioning with increasing molecular size is consistent with findings for other groups of structurally related halogenated compounds, such as the PCBs. However, the differences in $\Delta_{AW}H$ typically tend to be less dramatic than observed for the FTOHs.[31] One should stress that the K^{x}_{AW} data and thermodynamic properties for the 8:2 FTOH should be considered somewhat less reliable than for the other two compounds because of the limited number of experimental temperatures. In particular, the extrapolated value at 25 °C is subject to significant uncertainty.

Comparison with Literature Values. Very recently, Shoeib et al.[6] and Stock et al.[30] have reported vapor pressure and octanol−air partition coefficients for some of the polyfluorinated substances investigated here. These data are listed in Tables 2 and 3 for comparison. The vapor pressure values for the telomer alcohols obtained by Stock et al.[30] with a boiling-point method are comparable to our numbers, i.e., are generally within a factor of 2 of each other (Table 2). The values for 8:2 FTOH are in excellent agreement, but the decrease in vapor pressure with fluorinated chain length reported here is larger than that measured by Stock et al.[30] so that their P_L value for 10:2 FTOH is higher than the one reported here, whereas their P_L for the smaller FTOHs are lower than our numbers. According to our measurements, 10:2 FTOH has a vapor pressure 1.5 orders of magnitude lower than 4:2 FTOH, whereas that difference is less than 1 order of magnitude according to Stock et al.[30]

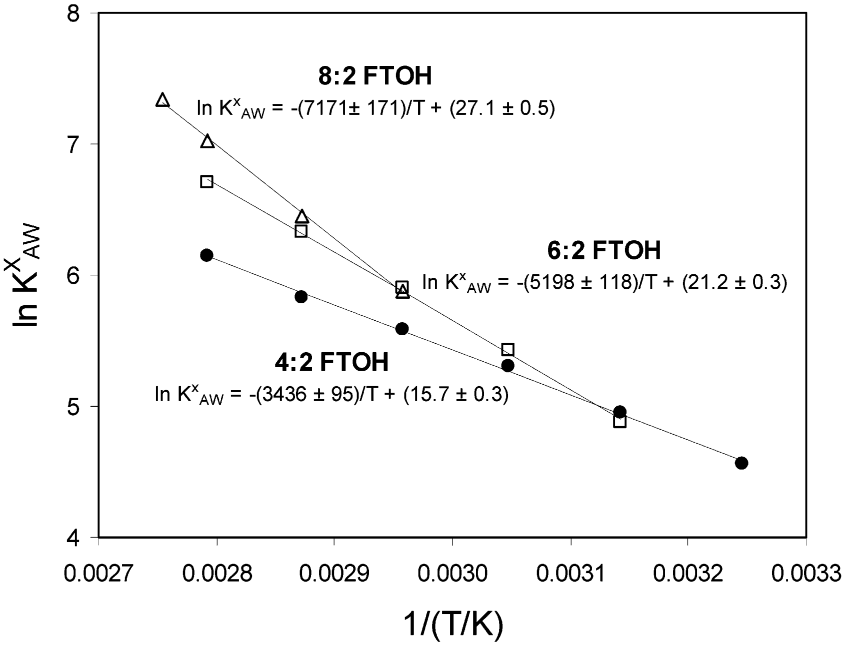

Figure 6. Temperature dependence of the air–water partition coefficient K^x_{AW}, expressed on a mol fraction scale, for three polyfluorinated telomer alcohols.

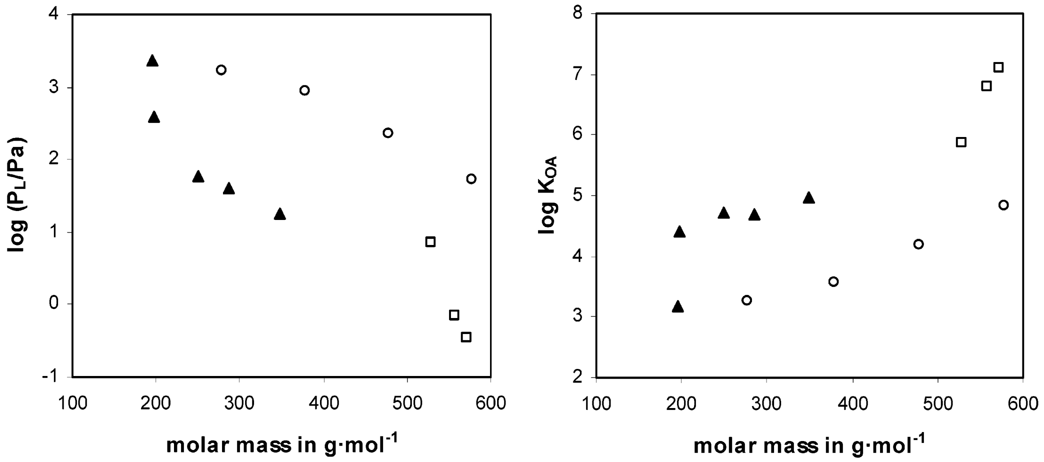

Figure 7. Vapor pressure P_L and octanol–air partition coefficients K_{OA} for various fluorinated chemicals (○, FTOHs; □, FOSEs/FOSA; ▲, fluorinated aromatics) as a function of molar mass.

Table 6. Air–Water Partition Coefficients Extrapolated to 25 °C and Thermodynamic Parameters for the Air–Water Phase Transition for Three Polyfluorinated Telomer Alcohols

compounds	4:2 FTOH	6:2 FTOH	8:2 FTOH
log K_{WA} at 25 °C	1.30 ± 0.19	1.47 ± 0.24	1.82 ± 0.32
log(K^p_{AW}/ Pa·m^3·mol^{-1}) at 25 °C	2.09 ± 0.19	1.92 ± 0.24	1.57 ± 0.32
log K^x_{AW} at 25 °C	1.83 ± 0.19	1.66 ± 0.24	1.31 ± 0.32
$\Delta_{AW}H$/kJ·mol^{-1}	28.6 ± 0.8	43.2 ± 1.0	59.6 ± 1.4
$T\Delta_{AW}S^x$/kJ·mol^{-1}	39.0 ± 0.7	52.7 ± 0.9	67.1 ± 1.2
$\Delta_{AW}G^x$/kJ·mol^{-1} at 25 °C	−(10.4 ± 1.1)	−(9.4 ± 1.3)	−(7.5 ± 1.9)
$\Delta_{AW}S^x$/J·K^{-1}·mol^{-1}	131 ± 2	177 ± 3	225 ± 4

The liquid vapor pressure values for the perfluorooctyl sulfonamides reported by Shoeib et al.,[6] obtained with a generator column method, are almost 2 orders of magnitude lower than our values (Table 2). On the other hand, a P_L value reported for *N*-EtFOSE by 3M Corp.[32] is actually slightly higher than our number for this chemical. The K_{OA} values for the perfluorooctyl sulfonamides measured by Shoeib et al.[6] using a direct method are in better agreement with our measurements but still differ by up to an order of magnitude (Table 3). We note that the GC-RT method employed here may be overestimating the volatility of the target substances by not accounting fully for their ability to form hydrogen bonds in the pure liquid and octanol phase. This possibility cannot be excluded, because of the use of a nonpolar stationary phase and mostly nonpolar calibration compounds. We have previously used the GC-RT technique for polar phenolic compounds and obtained good agreement with directly determined vapor pressure values,[33] but the possibility exists that the true volatility of the polyflourinated chemicals investigated here is lower than reported in Tables 2 and 3.

Comparison with Nonfluorinated Analogues. Because experimental values of the K_{AW} for the FTOHs have not been reported previously, no direct comparison with literature values is possible. It is illuminating to compare the properties of the fluorinated telomer alcohols with the corresponding nonfluorinated analogues, i.e., hexan-1-ol, octan-1-ol, and decan-1-ol. As Stock et al.[30] have already noted, this comparison reveals that partial fluorination of the alkyl chain increases the vapor pressure of the alcohols by about 1–2 orders of magnitude. A comparison of the respective air−water partition coefficients similarly suggests that the FTOHs have K_{AW}s that are approximately 1−2 orders of magnitude higher than those of the nonsubstituted alcohols.[34] This agrees qualitatively with recent findings by Chen et al.,[35] who noted that the CFC replacement chemical $CF_3CF_2CH_2-OH$ had a K_{AW} approximately 1 order of magnitude higher than its nonfluorinated analogue propan-1-ol.

However, the concurrent increase of both P_L and K_{AW} with fluorination would imply that the water solubility of the fluorinated and nonfluorinated alcohols is of a comparable magnitude. This is in conflict with a recently reported[5] water solubility for 8:2 FTOH of 148 $\mu g \cdot L^{-1}$, which corresponds to a value of 0.00032 $mol \cdot m^{-3}$ or about 3 orders of magnitude below the water solubility of decan-1-ol. Assuming that the vapor pressure values for 8:2 FTOH is well established as a result of the measurements reported here and by Stock et al.,[30] this suggests that the K_{AW} for 8:2 FTOH reported here is too low and/or the water solubility is higher than 148 $\mu g \cdot L^{-1}$. We reiterate that derivation of the K_{AW} value for 8:2 FTOH at 25 °C involved an extrapolation over a considerable temperature range, and an error in the slope of the log K_{AW} vs $1/T$ relationship could have resulted in a significant underestimation of the value at 25 °C. The surprisingly strong increase in $\Delta_{AW}H$ with increasing length of the fluorinated chain (Table 6) indicates that that this possibility cannot be discounted. Clearly additional measurements of the water solubility and air−water partition coefficient of polyfluorinated chemicals are required to better constrain the distribution properties of these substances.

Implications for Environmental Fate. The volatilities of the polyfluorinated chemicals investigated here are so high (log $K_{OA} < 7$ and log $P_L > 0.1$) that, based on commonly employed empirical relationships,[36,37] we would not expect them to sorb appreciably to atmospheric particles but to remain in the atmospheric gas phase, even at fairly low atmospheric temperatures. The validity of these empirical relationships for polyfluorinated chemicals, however, remains to be established.[4,6] Because at environmentally relevant temperatures the fluorotelomer alcohols have a log K_{WA}^{c} between 1 and 3, rain scavenging will not be an efficient process of atmospheric deposition for these chemicals. This process is only believed to become important for chemicals with a log K_{WA}^{c} above 4.[38] However, wet deposition will not be quite as inefficient as estimated by Ellis et al.,[5] who suggested an atmospheric lifetime of 8:2 FTOH with respect to wet deposition in the millions of years. The air−water exchange is controlled by the water-side resistance for chemicals with a log K_{WA}^{c} below 1, whereas the air-side resistance becomes dominant for substances with a log K_{WA}^{c} above 3.[39] The FTOHs thus belong to the group of compounds whose transfer across the air−water interface is controlled by both air- and water-side resistances.

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Note Added in Proof

Kaiser et al.[51] report a vapor pressure equation for 8:2 FTOH, which yields a value of 7 Pa at 25 °C, which is considerably lower than the value reported here and by Stock et al.[30]

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