Determination of Partitioning Coefficients of Numerous Organic Solutes between a Long-Chain Aliphatic Alcohol and the Gas Phase as a Function of Temperature

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Partitioning coefficients of 44 organic solutes between hexadecan-1-ol and the gas phase at temperatures between 333.15 K and 383.15 K were determined with the phase ratio variation (PRV) method based on headspace gas chromatography. It was first established that the PRV method is suitable to determine partition coefficients using a solid matrix containing multiple solutes. Hexadecane/air partition coefficients for nonane and octan-1-ol measured using the PRV method agreed well with data from the literature. Homogeneous "solutions" of solid hexadecano-1-ol were prepared through melting, quick re-coagulation, and grinding. Exact phase ratios were determined by measuring mass and density. Comparison of partition coefficients determined using solutions containing either a single or multiple solutes showed that, in dilute solutions, the impact of the other solutes on the partitioning behavior can be neglected. Using very large phase ratios, the upper limit of partition coefficients that can be measured by the PRV method could be extended to approximately 20 000. The hexadecan-1-ol/air partition coefficients extrapolated to 298.15 K were well-correlated with both liquid-state vapor pressure and the octan-1-ol/air partition coefficient, suggesting that the partitioning behavior of most organic solutes in aliphatic alcohols can be estimated from their vapor pressure with a precision of approximately 1 order of magnitude simply by assuming that the activity coefficient is 1. The free energies, enthalpies, and entropies of hexadecan-1-ol/air phase transfer were derived from the measured data, and the phase transfer enthalpy was found to be correlated with the partition coefficient at 298.15 K.

Introduction

The environmental fate of many organic pollutants is strongly influenced by their distribution between the atmosphere and various liquid and solid phases. Of particular importance is the partitioning from the gas phase into natural organic matter (NOM), such as is present in atmospheric particles, soils, and plant surfaces. These partitioning equilibria, for example, determine the capacity of the terrestrial surface for most organic pollutants and, by controlling pollutant distribution between atmospheric gas and particle phase, also the reactivity and rate of deposition from the atmosphere. Partition coefficients $K_{S/A}$ between organic solvents, such as octan-1-ol, and the gas phase provide important descriptors for studying molecular interactions between solutes and solvents[1] and for approximating and estimating environmental phase equilibria involving organic matter.[2−5] The temperature dependence of these partitioning coefficients is often used to explain the effect of changing ambient temperature on the environmental phase distribution of organic contaminants.[6]

Despite the widespread use of octan-1-ol as a surrogate of NOM, it has been questioned whether their solvation properties are indeed similar. Kömp and McLachlan,[7] for example, concluded that the lipophilicity of the contaminant storage compartment in several grass species is often different from octan-1-ol. Chemicals with a polar functional group attached to a long aliphatic chain have been identified as important constituents in many types of NOM, specifically atmospheric particles[8,9] and epicuticular waxes.[10,11] The alcohols occupy a somewhat peculiar position in the rank of solvents because, like water, they can form hydrogen bonds, but with respect to other properties they are much more similar to organic solvents.[12] Hexadecan-1-ol should constitute a model substance suitable to represent the solvation properties of the long-chain hydrocarbons with a hydrophilic end group because it allows for easy comparison with the solvation properties of hexadecane and octan-1-ol, two solvents that are often used as reference.

Studying environmental phase equilibria involving the gas phase requires techniques that allow the reliable and efficient determination of temperature-dependent partition coefficients between the gas phase and liquid and solid organic matter. Compared to many of the classical methods,[13] which may not be applicable to environmental samples or involve tedious sample pretreatment, techniques based on headspace gas chromatography (HS-GC) have been shown to be particularly suitable for vapor−liquid equilibrium (VLE) research. Among the HS-GC techniques, the phase ratio variation (PRV) method developed by Ettre et al.[14] has some significant advantages: Neither the solute concentration nor the solution matrix need to be known, which is preferable for environmental analysis;[15] there is no need for internal or external standard calibration, which simplifies the quantification process. Whereas inverse chromatography has been instrumental in determining adsorption equilibria from the gas phase to a multitude of environmentally important surfaces,[16] the applicability of this method to measuring partitioning into bulk NOM phases may be limited because of its requirement of very fast equilibration.

Here we report on measurements of the partition coefficients of numerous organic solutes between hexadecan-1-ol and the gas phase with the PRV method. A number of quality control experiments were conducted with the aim to increase the

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applicability range of the PRV method to higher $K_{S/A}$ values and to study the feasibility of using the PRV technique for measuring partitioning into organic solids. To investigate the VLE for a large number of organic chemicals, techniques are needed that can simultaneously determine $K_{S/A}$ for multiple solutes. There is thus a need to consider whether the interaction between solutes is strong enough to influence their partition characteristics. We therefore also measured the partitioning behavior for a number of organic solutes between air and hexadecane or hexadecan-1-ol at different temperatures with or without the presence of other solutes to investigate whether their presence impacts on the partition coefficients determined in dilute solutions.

Theory

Phase Ratio Variation (PRV) Method. A detailed discussion of the theory of the PRV method, its limitations, and possible corrections can be found elsewhere.[14] Briefly, the PRV technique measures the gas-phase concentration in a series of vials containing different volumes of the same solution. It can be shown that the reciprocal of the vapor phase concentrations at equilibrium (C_A*) can be expressed as a function of the phase ratio β, the volume ratio between the gas phase and liquid phase:

$$1/C_A{}^* = (1/C_0)\beta + K_{S/A}/C_0 \qquad (1)$$

where $K_{S/A}$ is the equilibrium partition coefficient between solvent and gas phase, C_0 is the concentration of analyte in the original sample, and the subscripts A and S designate the gas phase and solution, respectively. All the concentrations are expressed on a molar concentration scale.

Assuming that the gas chromatographic response, usually the integrated peak area (A) is proportional to C_A* when the injected volume remains constant, the reciprocal of the peak area can be regressed against β:

$$1/A = (1/(f_iC_0))\beta + K_{S/A}/(f_iC_0) \qquad (2)$$

where f_i is the chemical specific response factor of the GC analysis. In a plot of $1/A$ against β, the partition coefficient $K_{S/A}$ can be derived from the ratio of the intercept ($b = K_{S/A}/(f_iC_0)$) and slope ($m = 1/(f_iC_0)$) of the linear regression:

$$K_{S/A} = b/m \qquad (3)$$

Absolute quantification of C_A* or C_0 is not necessary. However, m and b values are determined by the solute concentration. The partition coefficient is independent of the concentration only for solutions within the Henry's law applicable concentration range (i.e., for dilute solution) or ideal solution. The measurement precision of this method strongly depends on the linearity of the relationship described by eq 2.

Applicability Limits of the PRV Method. The uncertainty of the PRV method depends on obtaining significantly different peak responses within the selected phase ratio range. Specifically, Ettre et al.[14] have pointed out that the uncertainty of the PRV method depends on peak area differences resulting from the changing of β and can be improved by widening the range of phase ratios. The relationship between the area change and phase ratio change can be expressed as follows:

$$\frac{A_2}{A_1} = \frac{K_{S/A} + \beta_1}{K_{S/A} + \beta_2} \qquad (4)$$

From this equation, it is obvious that the peak area change will decrease with increasing $K_{S/A}$ if β remains constant. This limits the application of the method to less volatile compounds. The range of $K_{S/A}$ that can be determined with the PRV methods depends on the range of the phase ratio that can be experimentally achieved. The lower end of the phase ratio range is constrained by the dimensions of the sampling vial, whereas the upper limit is less clearly defined. An upper limit of the phase ratio β of 4 suggested by Ettre et al.[14] would imply that the partition coefficients of most chemicals of environmental interest in organic solvents are too large to be determined by this method, even at elevated temperature. Large phase ratios can be achieved by using a relatively small amount of sample but that will also reduce the sensitivity of the analysis.[17] Considering the smallest mass that can be determined by an electrical balance with reasonable uncertainty (i.e., the relative standard deviation for replicate measurements should be less than a few percent), we suggest that the practical maximum value for the phase ratio is about 4000 if 22.3 mL standard vials and a sensitive detection method are employed. Then, theoretically, the corresponding maximum partition coefficient that can be determined with the PRV method is about 20 000 (i.e., a log $K_{S/A}$ of 4.3).

In contrast to most organic solvents used as model substances to describe environmental phase partitioning, natural organic matter is generally solid. Hexadecan-1-ol, with a melting point temperature of 323.15 K, is also a solid at room temperature. To apply the PRV method to solids, a method to accurately determine the volume of the solid samples in the experimental vials is required. In addition, solid samples may be less homogeneous than liquid solutions. The amount of sample in a vial may influence how representative the sample is; a smaller sub-sample likely being less representative. This may constrain the largest phase ratio that can be achieved for solid matrices. A key requirement to increasing the applicability range of the method when applied to solids is to ensure the representativeness of the sample (i.e., to make sure that the solid sample is well mixed).

Thermodynamic Analysis. Phase equilibria involving the gas phase usually are highly dependent on temperature. The phase transfer enthalpy $\Delta_{S/A}H$ is often used to characterize the solvent−solute interaction. Typically, $\Delta_{S/A}H$ is obtained by invoking a form of the van't Hoff equation, for example:

$$\ln K_{S/A} = -\Delta_{S/A}H/RT + c = a/T + c \qquad (5)$$

where R and T are ideal gas constant and absolute temperature. a and c are the regression parameters from the plot of ln $K_{S/A}$ against $1/T$, which is assumed to be linear over relatively small temperature ranges. The partition coefficient based on a mole fraction scale ($\ln K^x_{S/A}$) is related to the standard Gibbs energy of the air−solvent phase transition $\Delta_{A/S}G$ (J·mol^{-1}) through

$$\Delta_{S/A}G = -RT\ln K^x_{S/A} = -RT(\ln K_{S/A} + \ln(V_S/V_A)) \qquad (6)$$

and

$$\Delta_{S/A}G = \Delta_{S/A}H - T\Delta_{S/A}S \qquad (7)$$

where V_S and V_A are the molar volumes of solvent and gas-phase respectively, and $\Delta_{S/A}S$ is the entropy of the phase transition. Thus, eq 5 can be further written as

$$\ln K^x_{S/A} = \ln K_{S/A} + \ln(V_S/V_A) = -\Delta_{S/A}H/RT + \Delta_{S/A}S/R \qquad (8)$$

If the vapor pressure of the solutes in the liquid-state P_L is known, the activity coefficient in a solvent γ_S can be estimated

Table 1. Partition Coefficients between Hexadecane or Hexadecan-1-ol and Air and Their Standard Deviations for Nonane, Octan-1-ol, Butan-1-ol, and Undecane at Different Temperatures between 333.15 K and 383.15 K As Determined by the Phase Ratio Variation Method[a]

	333.15 K	343.15 K	353.15 K	363.15 K	373.15 K	383.15 K
			Log $K_{16/A}$			
nonane		3.31 ± 0.02	3.116 ± 0.004	3.000 ± 0.001	2.824 ±0.002	2.69 ± 0.03
		3.30 ± 0.02	**3.12 ± 0.03**	**3.00 ± 0.02**	**2.85 ± 0.02**	
octan-1-ol		3.47 ± 0.01	3.22 ± 0.03	3.13 ± 0.03	2.98 ± 0.01	2.77 ± 0.04
		3.59 ± 0.10	**3.38 ± 0.01**	**3.16 ± 0.02**	**3.074 ± 0.004**	**2.926 ± 0.001**
			Log $K_{16OH/A}$			
nonane		3.11 ± 0.01	2.88 ± 0.02	2.80 ± 0.02		2.65 ± 0.05
		3.10 ± 0.02	**2.92 ± 0.03**	**2.84 ± 0.02**	**2.75 ± 0.03**	**2.65 ± 0.03**
undecane	4.09 ± 0.17	3.51 ± 0.07	3.47 ± 0.06	3.39 ± 0.03	3.14 ± 0.02	
	4.11 ± 0.14	**3.73 ± 0.08**	**3.56 ± 0.05**	**3.31 ± 0.02**	**3.20 ± 0.04**	**3.08 ± 0.04**
butan-1-ol	3.07 ± 0.20	3.01 ± 0.02	2.92 ± 0.10	2.62 ± 0.09	2.64 ± 0.18	
	3.22 ± 0.03	**3.06 ± 0.13**	**2.68 ± 0.02**	**2.55 ± 0.06**	**2.54 ± 0.08**	**2.50 ± 0.06**
octan-1-ol			4.07 ± 0.14		3.74 ± 0.02	3.65 ± 0.02
		4.35 ± 0.22	**4.11 ± 0.24**	**3.85 ± 0.08**	**3.59 ± 0.04**	**3.55 ± 0.02**

[a] Data in boldface are from measurements in solutions with multiple solutes.

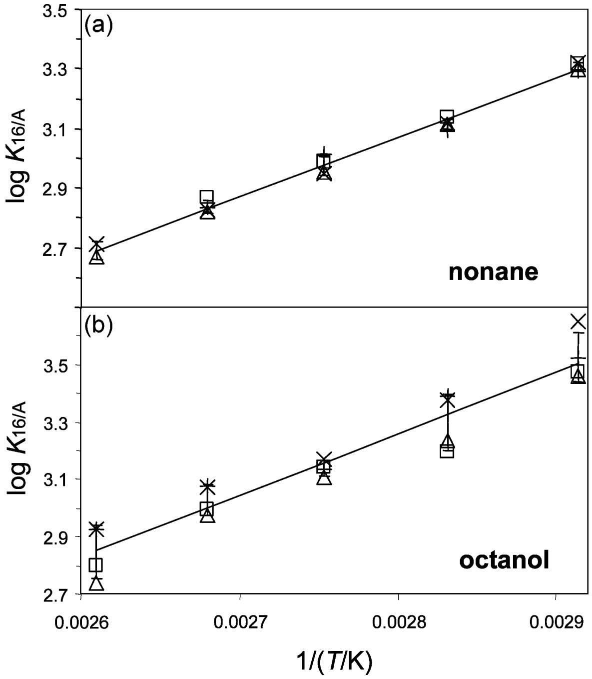

Figure 1. Temperature dependence of the hexadecane/air partition coefficients $K_{16/A}$ for nonane (a) and octan-1-ol (b). The linear regression constants are given in Table 2. Different markers represent different sets of measurements. Standard deviations for the measurements are given as error bars.

from the solvent/air partition coefficient using

$$\gamma_S = RT/(V_S K_{S/A} P_L) \qquad (9)$$

where V_S is the molar volume of the solvent at infinite dilution.

Materials and Methods

Instrumentation. The HS-GC analyses were performed on a Perkin-Elmer HS 40XL automatic headspace sampler combined with a HP 5890 gas chromatograph with flame-ionization detector. The chromatographic separation was carried out on a DB-5 column (30 m × 0.25 mm i.d., film thickness 0.25 μm). The GC oven was set at 323.15 K, which was held for 5.5 min and then increased to 563.15 K with a rate of 40 K/min. The final temperature was held for 5 min. The flow rate of the carrier gas helium was 1 mL/min at 323.15 K. The headspace operating conditions were as follows: The needle temperature was 5 K higher than the HS 40XL oven temperature, and the transfer line was set at 393.15 K. Preliminary experiments showed that nonane reached equilibrium after 60 min. Allowing for differences in the mass transfer characteristics of the solutes, the samples were equilibrated at each specified temperature for 120 min. Vial pressurization time was 3 min, injection time was 0.04 min, and withdrawal time was 0.5 min while the vent is on.

According to eqs 1 to 3, an accurate knowledge of the sample volume and the volume of the vial is needed to accurately determine the phase ratio and therefore the partition coefficient. Whereas it is difficult to determine the exact volume of a solid sample, its mass is much easier to measure. By assuming that the small amount of analyte added into a sample matrix does not change its density, the volume of the sample can be easily obtained from the total mass and the density of the “solvent”. A Mettler Toledo AG285 balance was used to weigh the mass of the liquid and solid solutions. All the measurements were performed with standard 22.3 mL glass vials, PTBE septa, and patented closures from Perkin-Elmer. Since very small amounts of solution were used to obtain large phase ratios, small differences in the volumes of the headspace vials may affect the regression result. Although standard 22.3 mL glass vials were used to perform all the HS-GC analyses, the exact volume of each vial was determined by filling it with water and weighing it. Vials with similar volume were selected for the measurements. The average volume of the selected vials was (22.520 ± 0.006) mL.

Sample Preparation. All solutes in the partitioning measurements had a purity higher than 95 % and were bought from Aldrich Inc. Hexadecan-1-ol (99 %, Aldrich Inc.) was used as the solid matrix. *n*-Hexadecane (99+ %, anhydrous, Aldrich Inc.) was used to prepare liquid solutions.

Hexadecane stock solutions were prepared as follows: about 10 mL of hexadecane was placed into a 50-mL volumetric flask, and then 50 μL of nonane and/or octan-1-ol was added into the flask by syringe and mixed. An appropriate amount of hexadecane was added to the calibration mark of the flask. Diluted sample solutions were made from the stock solution. Usually, the stock solutions were diluted 100 to 400 times for the HS measurement. Increasing volumes (9 μL or 10 μL, 20 μL, 50 μL, 100 μL, and 1 mL) of diluted hexadecane solution were introduced into headspace vials by syringe for HS-GC analysis.

To get a well-mixed “solid solution”, about 10 g of hexadecan-1-ol was added into a clean empty vial. Then, the vial was put into a 333.15 K water bath and gently shaken until all the hexadecan-1-ol became liquid. About 0.6 to 1 μL of chemical was added into the vial by a syringe. The vial was

Table 2. Parameters Describing the Temperature Dependence of the Partition Coefficients between Hexadecane or Hexadecan-1-ol and Air[a] **and the Partition Coefficients at 298.15 K Predicted by Linear Extrapolation of These Temperature Relationships**

	a	c	R^2	$\Delta_{S/A}H$/kJ·mol^{-1}	log $K_{S/A}$ at 298.15 K
		Hexadecane/Air Partitioning			
nonane	1990 ± 49	−2.50 ± 0.14	0.998	−(38.1 ± 0.94)	4.17 ± 0.21
octan-1-ol	2145 ± 118	−2.75 ± 0.33	0.991	−(41.1 ± 2.26)	4.45 ± 0.51
		Hexadecan-1-ol/Air Partitioning			
nonane	1410 ± 122	−1.05 ± 0.34	0.950	−(27.0 ± 2.3)	3.68 ± 0.53
octan-1-ol	2477 ± 254	−2.92 ± 0.70	0.939	−(47.4 ± 4.9)	5.39 ± 1.11
butan-1-ol	1824 ± 232	−2.34 ± 0.65	0.873	−(34.9 ± 4.4)	3.78 ± 1.02
undecane	2523 ± 270	−3.60 ± 0.76	0.907	−(48.3 ± 5.2)	4.87 ± 1.18

[a] a and c are the slope and intercept; R^2 is the coefficient of determination of the linear regression described by eq 5; and $\Delta_{S/A}H$ is the enthalpy of phase transfer between the organic solvent and air derived from a.

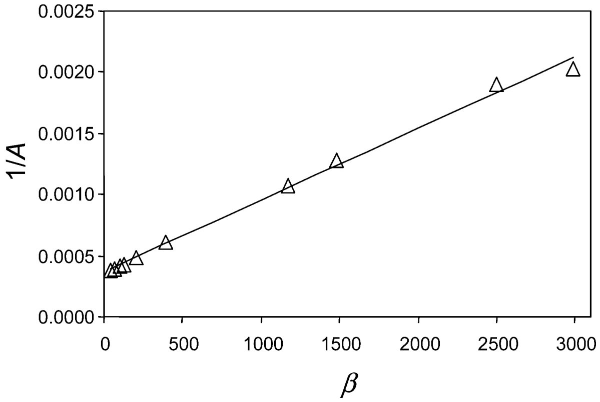

Figure 2. Example of a plot of the reciprocal peak area versus the phase ratio β for nonane in a hexadecan-1-ol solution at 363.15 K. The partitioning coefficient is calculated as the ratio of the intercept and slope of that relationship.

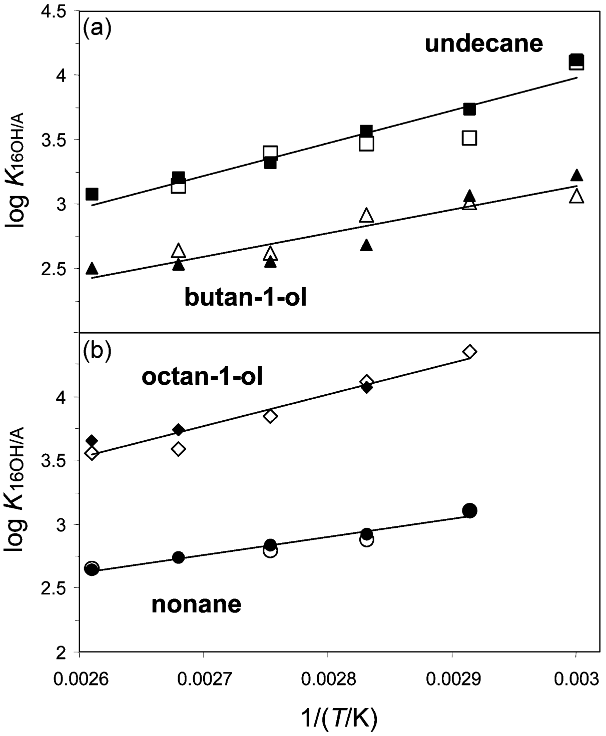

Figure 3. Temperature dependence of the hexadecan-1-ol/air partition coefficients $K_{16OH/A}$ for △, butan-1-ol; □, undecane; ○, nonane; and ◇, octan-1-ol. Open markers are for measurements using solution with a single solute; filled markers for measurements using solution with multiple solutes.

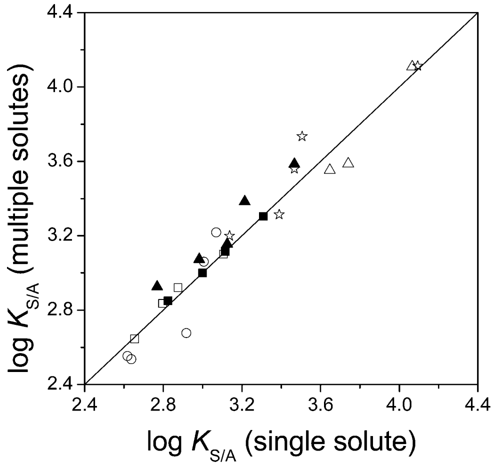

Figure 4. Comparison of log $K_{16/A}$ (filled markers) and $K_{16OH/A}$ (open markers) values for □, nonane; △, octan-1-ol; ○, butan-1-ol; and ☆, undecane measured at different temperatures with or without the presence of other solutes.

capped and shaken for 2 to 3 min and then kept in the water bath for about 30 min. After that, the vial was transferred to the refrigerator to quickly crystallize the solution. To prevent desorption of chemicals, the crystal was kept in the refrigerator and ground into fine particles before usage. Increasing amounts of solid particle sample were placed into headspace vials. The accurate masses of these "solid solutions" were determined gravimetrically. The corresponding phase ratios were calculated from the volume of the vial, the density of hexadecan-1-ol (0.811 g/cm^3 at 333.15 K) and the mass of the "solid solution".

Quality Control Experiments. A number of quality control measurements were performed to confirm the validity of the method. First, the hexadecane/air partition coefficients of two solutes (nonane and octan-1-ol) were measured as a function of temperature and compared with literature values, to verify the ability of the method to reproduce previously determined vapor-organic liquid partitioning equilibria. We then measured individually the hexadecan-1-ol/air partition coefficient of four solutes (undecane, nonane, butan-1-ol, and octan-1-ol) as a function of temperature to confirm the suitability of the method to determine partitioning equilibria between organic solids and the gas phase. Finally, we measured the hexadecane/air and hexadecan-1-ol/air partition coefficient of several solutes simultaneously to verify that the presence of multiple solutes does not influence the measured partitioning coefficients.

Results

Reproducing Previously Measured Hexadecane/Air Partition Coefficients. Table 1 lists the measured hexadecane/air partition coefficients $K_{16/A}$ of nonane or octan-1-ol at various temperatures. Duplicate sets of vials were analyzed at each temperature. The second set was analyzed after the first set was finished. The log $K_{16/A}$ values listed in Table 1 are thus the average of the logarithmic values obtained from two independent

Table 3. Hexadecan-1-ol/Air Partition Coefficients and Their Standard Deviations at Different Temperatures between 333.15 K and 383.15 K As Determined for 44 Organic Solutes by the Phase Ratio Variation Method[a]

		log $K_{16OH/A}$ at					
	R^2	333.15 K	343.15 K	353.15 K	363.15 K	373.15 K	383.15 K
			Alkanes, Alkenes, Alkynes				
nonane	0.950		3.10 ± 0.02	2.92 ± 0.03	2.84 ± 0.02	2.75 ± 0.03	2.65 ± 0.03
decane	0.997	3.61 ± 0.03	3.43 ± 0.03	3.22 ± 0.02	3.09 ± 0.01	2.93 ± 0.04	
undecane	0.907	4.11 ± 0.14	3.73 ± 0.08	3.56 ± 0.05	3.31 ± 0.02	3.20 ± 0.04	3.08 ± 0.04
cyclooctane	0.988		3.13 ± 0.03	2.98 ± 0.02	2.78 ± 0.01	2.66 ± 0.04	2.57 ± 0.03
1-nonene	0.997		3.05 ± 0.06	2.88 ± 0.03	2.697 ± 0.000	2.56 ± 0.03	2.44 ± 0.03
1-heptyne	0.965		2.41 ± 0.03	2.27 ± 0.13	2.08 ± 0.05	2.07 ± 0.01	1.89 ± 0.01
1-octyne	0.997		2.73 ±0.03	2.59 ± 0.01	2.39 ± 0.02	2.23 ± 0.06	2.06 ± 0.05
			Alcohols				
propan-1-ol	0.985		2.48 ± 0.07	2.39 ± 0.03	2.22 ± 0.05	2.16 ± 0.09	2.06 ± 0.04
propan-2-ol	0.925		2.32 ± 0.06	2.23 ± 0.15	2.12 ± 0.10	2.11 ± 0.13	2.07 ± 0.14
butan-1-ol	0.873	3.22 ± 0.03	3.06 ± 0.13	2.68 ± 0.02	2.55 ± 0.06	2.54 ± 0.08	2.50 ± 0.06
2-methyl-1-propanol	0.995		2.82 ±0.07	2.61 ± 0.03	2.45 ± 0.05	2.32 ± 0.05	2.17 ± 0.12
octan-1-ol	0.939		4.35 ± 0.22	4.11 ± 0.24	3.85 ± 0.08	3.59 ± 0.04	3.55 ± 0.02
			Ethers				
propyl ether	0.984		2.28 ± 0.04	2.17 ± 0.03		1.93 ± 0.09	1.74 ± 0.07
isopropyl ether	0.873		2.09 ± 0.09	1.93 ± 0.08	1.80 ± 0.09	1.84 ± 0.12	1.73 ± 0.14
tetrahydrofuran	0.965		2.49 ± 0.10	2.39 ± 0.12	2.24 ± 0.11	2.21 ± 0.06	2.14 ± 0.52
1,4-dioxane	0.522		2.23 ± 0.06	2.35 ± 0.05	2.04 ± 0.07	2.23 ± 0.10	1.22 ± 0.66
			Ketones				
acetone	0.999			1.88 ± 0.05	1.75 ± 0.15		1.47 ± 0.34
butan-2-one	0.790		2.25 ± 0.07	2.22 ± 0.06	2.19 ± 0.08	2.01 ± 0.10	
3-methyl butan-2-one	0.992	2.45 ± 0.04	2.30 ± 0.01	2.21 ± 0.02	2.13 ± 0.10	2.02 ± 0.16	
cyclopentanone	0.978		2.71 ± 0.14	2.52 ± 0.02	2.40 ± 0.05	2.27 ± 0.03	2.21 ± 0.07
			Acetates				
methyl acetate	0.973		1.83 ± 0.04	1.658 ± 0.003	1.61 ± 0.05	1.45 ± 0.04	1.40 ± 0.09
ethyl acetate	0.986		2.09 ± 0.05	2.04 ± 0.11	1.94 ± 0.04	1.89 ± 0.03	1.79 ± 0.03
isobutyl acetate	0.987	2.90 ± 0.09	2.62 ± 0.02	2.52 ± 0.10	2.30 ± 0.09	2.12 ± 0.10	
			Halogenated Aliphatics				
1,2-dichloroethane	0.990		2.26 ± 0.07	2.18 ± 0.04	2.07 ± 0.04	1.98 ± 0.09	1.93 ± 0.02
1,1,2,2-tetrachloroethane	0.995	3.48 ± 0.04	3.27 ± 0.05	3.06 ± 0.04	2.94 ± 0.04	2.73 ± 0.05	
1-iodopropane	0.964		2.50 ± 0.03	2.33 ± 0.06	2.19 ± 0.03	2.122 ± 0.002	2.06 ± 0.03
1,1,2-trichlorotrifluorethane	0.998		1.82 ± 0.11	1.77 ± 0.11	1.72 ± 0.10	1.68 ± 0.17	1.64 ± 0.17
2,2,2-trifluoroethanol	0.983		2.25 ± 0.14	2.18 ± 0.38		2.01 ± 0.15	1.88 ± 0.02
			Alkylated Benzenes				
benzene	0.969		2.57 ± 0.12	2.48 ± 0.07	2.36 ±0.12	2.31 ± 0.07	2.13 ± 0.22
methylbenzene (toluene)	0.983		2.71 ± 0.02	2.56 ± 0.03	2.39 ± 0.02	2.31 ± 0.03	2.22 ± 0.02
1,4-dimethylbenzene (pxy)	0.995	3.22 ± 0.05	3.01 ± 0.08	2.79 ± 0.07	2.67 ± 0.05	2.47 ± 0.06	
1,2,4-trimethylbenzene	1.000				3.21 ± 0.05	3.017 ± 0.002	2.85 ± 0.10
ethylbenzene	0.987		3.01 ± 0.07	2.794 ± 0.001	2.664 ± 0.002	2.56 ± 0.02	2.44 ± 0.02
styrene	0.987		3.23 ± 0.06	2.99 ± 0.07	2.811 ± 0.002	2.68 ± 0.01	2.55 ± 0.03
			Halogenated Aromatics				
chlorobenzene	0.997	3.07 ± 0.02	2.94 ± 0.02	2.82 ± 0.01	2.66 ± 0.02	2.57 ± 0.04	
1,2-dichlorobenzene	0.987		3.80 ± 0.39	3.63 ± 0.36	3.36 ± 0.07	3.16 ± 0.03	2.86 ± 0.07
1,3-dichlorobenzene	0.999	3.71 ± 0.04	3.51 ± 0.04	3.33 ± 0.03	3.16 ± 0.04	2.98 ± 0.06	
bromobenzene	0.994		3.58 ± 0.24	3.37 ± 0.08	3.05 ± 0.02	2.80 ± 0.02	2.61 ± 0.06
iodobenzene	0.696		3.58 ± 0.11	3.22 ± 0.24	3.39 ± 0.01	3.05 ± 0.08	3.08 ± 0.05
4-fluorotoluene	0.985		2.60 ± 0.02	2.52 ± 0.02	2.33 ± 0.04	2.23 ± 0.06	2.11 ± 0.04
			Other Aromatics				
anisole	0.993		3.19 ± 0.03	3.06 ± 0.10	2.87 ± 0.03	2.72 ± 0.04	2.63 ± 0.02
benzaldehyde	0.998	3.62 ± 0.04	3.43 ± 0.05	3.25 ± 0.03	3.11 ± 0.04	2.92 ± 0.07	
indan	0.999				3.32 ± 0.06	3.12 ± 0.02	2.91 ± 0.15
indene	0.978		3.56 ± 0.04	3.40 ± 0.14	3.24 ± 0.05	3.14 ± 0.06	3.07 ± 0.02

[a] R^2 is the coefficients of determination for the relationship between log $K_{S/A}$ and $1/T$.

regression equations, and the standard deviation is calculated from the two individual measurements. The logarithm of the partition coefficients was plotted against the reciprocal of the absolute temperature (Figure 1). The phase transfer enthalpy $\Delta_{16/A}H$ and the partition coefficients at 298.15 K extrapolated from eq 5 are given in Table 2. The extrapolated log $K_{16/A}$ values for nonane and octan-1-ol of 4.17 ± 0.21 and 4.45 ± 0.51, respectively, compare favorably with the measured reference values of 4.18 and 4.56 reported by Dallas and Carr[18] and Mutelet and Rogalski.[19] Considering the need for a temperature extrapolation over a range of 45 K, the standard deviations are also within an acceptable range. These results indicate that it is possible to extrapolate partition coefficients to lower temperature based on determinations at higher temperatures. The method thus should be suitable for the determination of the partition properties of organic solutes in subcooled organic liquids, such as hexadecan-1-ol.

Confirming the Feasibility of Measuring Partition Coefficients Involving Solid Matrices. A sample plot of $1/A$ versus the phase ratio for nonane in a hexadecan-1-ol "solution" at 363.15 K is given in Figure 2. Table 1 lists the measured hexadecan-1-ol/air partition coefficients $K_{16OH/A}$ and their standard deviations. The logarithm of the partition coefficient was again plotted against the reciprocal of absolute temperature

Table 4. Hexadecan-1-ol/Air Partitioning Coefficients at 298.15 K, Enthalpies, Free Energies, and Entropies of Hexadecan-1-ol/Air Phase Transfer Determined from the Linear Regression of the Measured Data in Table 3, Liquid State Vapor Pressure at 298.15 K from Refs 20 and 21, and Octan-1-ol/Air Partition Coefficients at 298.15 K from Ref 24

chemicals	$\log K_{16OH/A}$	$\Delta_{16OH/A}H$ kJ·mol^{-1}	$\Delta_{16OH/A}G$ kJ·mol^{-1}	$-\Delta_{16OH/A}S$ J·mol^{-1}·K^{-1}	$\log P_L$ Pa	$\log K_{8OH/A}$
			Alkanes, Alkenes, Alkynes			
nonane	3.7 ± 0.5	−(27.0 ± 2.3)	−(10.0 ± 3.0)	−(56.8 ± 12.8)	2.76	
decane	4.4 ± 0.3	−(40.9 ± 1.4)	−(13.9 ± 1.8)	−(90.3 ± 7.5)	2.23	
undecane	4.9 ± 1.2	−(48.3 ± 5.2)	−(16.8 ± 6.7)	−(105.6 ± 28.5)	1.72	
cyclooctane	4.0 ± 0.5	−(36.3 ± 2.3)	−(11.6 ± 3.0)	−(82.8 ± 12.5)	2.88	
1-nonene	3.9 ± 0.3	−(39.1 ± 1.3)	−(11.5 ± 1.6)	−(92.4 ± 6.9)	2.85	3.83
1-heptyne	3.1 ± 0.8	−(31.5 ± 3.5)	−(6.9 ± 4.5)	−(82.6 ± 19.0)	3.88	
1-octyne	3.7 ± 0.3	−(43.1 ± 1.5)	−(10.4 ± 1.9)	−(109.8 ± 8.1)	3.23	
			Alcohols			
propan-1-ol	3.1 ± 0.4	−(27.2 ± 2.0)	−(6.8 ± 2.5)	−(68.5 ± 10.7)	3.45	3.68
propan-2-ol	2.7 ± 0.6	−(16.0 ± 2.6)	−(4.3 ± 3.4)	−(39.2 ± 14.4)	3.76	3.38
butan-1-ol	3.8 ± 1.0	−(34.9 ± 4.4)	−(10.6 ± 5.8)	−(81.5 ± 24.5)	3.18	4.19
2-methyl-1-propanol	3.7 ± 0.4	−(39.8 ± 1.6)	−(10.2 ± 2.0)	−(99.3 ± 8.6)	2.95	3.93
octan-1-ol	5.4 ± 1.1	−(47.4 ± 4.9)	−(19.8 ± 6.3)	−(92.7 ± 26.9)	1.04	6.03
			Ethers			
propyl ether	3.1 ± 0.7	−(32.9 ± 2.97)	−(6.5 ± 3.9)	−(88.8 ± 16.3)	3.92	2.97
isopropyl ether	2.5 ± 1.0	−(20.9 ± 4.6)	−(3.5 ± 6.0)	−(58.4 ± 25.3)	4.30	2.66
tetrahydrofuran	3.0 ± 0.6	−(22.6 ± 2.5)	−(6.1 ± 3.2)	−(55.3 ± 13.7)	4.33	2.86
1,4-dioxane[a]	(*3.6 ± 4.0*)	−(*52.5 ± 17.7*)	−(*9.9 ± 23.0*)	−(*143.0 ± 97.4*)	*3.69*	*3.17*
			Ketones			
acetone[b]	2.8 ± 0.3	−(35.3 ± 1.2)	−(5.3 ± 1.5)	−(100.7 ± 6.3)	4.49	2.31
2-butanone	2.7 ± 1.5	−(18.2 ± 6.6)	−(4.5 ± 8.7)	−(46.3 ± 36.6)	4.10	
3-methyl butan-2-one	2.9 ± 0.3	−(24.5 ± 1.3)	−(5.5 ± 1.7)	−(63.7 ± 7.2)		3.04
cyclopentanone	3.4 ± 0.6	−(31.0 ± 2.7)	−(8.4 ± 3.5)	−(75.9 ± 14.8)	3.19	3.67
			Acetates			
methyl acetate	2.4 ± 0.6	−(27.1 ± 2.6)	−(2.9 ± 3.4)	−(81.2 ± 14.3)	4.46	2.31
ethyl acetate	2.5 ± 0.3	−(18.9 ± 1.3)	−(3.5 ± 1.7)	−(51.5 ± 7.1)	4.10	2.70
isobutyl acetate	3.7 ± 0.7	−(44.7 ± 3.0)	−(10.1 ± 3.9)	−(115.8 ± 16.6)	3.42	3.45
			Halogenated Aliphatics			
1,2-dichloroethane	2.8 ± 0.3	−(21.6 ± 1.3)	−(4.8 ± 1.7)	−(56.4 ± 7.0)	4.02	2.78
1,1,2,2-tetrachloroethane	4.3 ± 0.4	−(43.7 ± 1.8)	−(13.4 ± 2.3)	−(101.3 ± 9.9)	2.90	
1-iodopropane	3.1 ± 0.7	−(27.3 ± 3.0)	−(6.7 ± 3.9)	−(69.3 ± 16.7)	3.76	
1,1,2-trichlorotrifluorethane	2.1 ± 0.1	−(11.1 ± 0.3)	−(0.9 ± 0.4)	−(34.5 ± 1.5)	4.68	
2,2,2-trifluoroethanol	2.8 ± 0.5	−(22.8 ± 2.11)	−(5.0 ± 2.7)	−(59.9 ± 11.6)	3.98	
			Alkylated Benzenes			
benzene	3.2 ± 0.6	−(26.5 ± 2.7)	−(7.3 ± 3.5)	−(64.6 ± 15.0)	4.10	2.80
toluene	3.4 ± 0.5	−(31.5 ± 2.4)	−(8.5 ± 3.1)	−(77.0 ± 13.0)	3.58	3.31
p-xylene	4.0 ± 0.4	−(44.1 ± 1.8)	−(12.0 ± 2.3)	−(107.6 ± 9.7)	3.04	3.79
1,2,4-trimethylbenzene[b]	4.7 ± 0.2	−(47.9 ± 0.7)	−(15.9 ± 0.9)	−(107.4 ± 3.7)	2.45	
ethylbenzene	3.8 ± 0.5	−(34.9 ± 2.3)	−(10.6 ± 3.0)	−(81.6 ± 12.9)	3.11	3.72
styrene	4.1 ± 0.6	−(41.6 ± 2.7)	−(12.7 ± 3.5)	−(97.0 ± 15.0)	2.94	
			Halogenated Aromatics			
chlorobenzene	3.6 ± 0.2	−(30.6 ± 1.0)	−(9.8 ± 1.3)	−(69.8 ± 5.5)	3.20	
1,2-dichlorobenzene	5.2 ± 0.9	−(59.1 ± 3.9)	−(18.7 ± 5.0)	−(135.3 ± 21.2)	2.30	4.48
1,3-dichlorobenzene	4.5 ± 0.2	−(42.9 ± 0.7)	−(14.7 ± 0.9)	−(94.6 ± 3.6)	2.49	4.27
bromobenzene	5.0 ± 0.6	−(62.6 ± 2.7)	−(17.8 ± 3.6)	−(150.5 ± 15.1)	2.75	
iodobenzene[a]	(*4.2 ± 2.5*)	−(*29.0 ± 11.1*)	−(*12.8 ± 14.3*)	−(*54.2 ± 60.7*)	*2.13*	
4-fluorotoluene	3.4 ± 0.5	−(32.1 ± 2.3)	−(8.2 ± 3.0)	−(80.3 ± 12.6)	3.45	
			Other Aromatics			
anisole	4.0 ± 0.4	−(36.8 ± 1.8)	−(12.1 ± 2.4)	−(82.8 ± 10.1)	2.66	4.01
benzaldehyde	4.4 ± 0.3	−(41.2 ± 1.1)	−(14.1 ± 1.5)	−(91.2 ± 6.3)	2.23	
indan[b]	5.0 ± 0.4	−(54.1 ± 1.9)	−(17.7 ± 2.4)	−(122.3 ± 10.4)	2.29	
indene	4.3 ± 0.6	−(31.4 ± 2.7)	−(13.4 ± 3.5)	−(60.5 ± 14.8)		

[a] Poor linearity, the data is not reliable, reported in Italics; [b] Only three data points; the uncertainties possibly much larger than what is reported here.

(Figure 3), and the phase transfer enthalpy and the partition coefficients at 298.15 K extrapolated using eq 5 are given in Table 2. Except for butan-1-ol, all plots show very good linearity, and most of the correlation coefficients are larger than 0.90. Because it is impossible to transfer exactly the same amount of a solid solution into two different vials, 10 sample vials with solid hexadecan-1-ol solutions were prepared at the same time and separated into two sets. The $\log K_{16OH/A}$ values and standard deviations given are from one single regression because the linear regressions for the two sets were similar to each other. Even for the solid matrix, the regression coefficients were in most cases larger than 0.99. This confirms that, as a result of the sample preparation procedure, the analytes were close to evenly distributed in the solid matrix. Even small amounts of hexadecan-1-ol, in the range of a few micrograms, are sufficient to represent the partitioning characteristics of that solid solvent. It also suggests that the precision of β as determined by mass and density, which is comparable with the precision of the volume measurement, is within an acceptable range. The experiment confirms the feasibility of using the PRV method for the determination of partition coefficients involving solid matrixes.

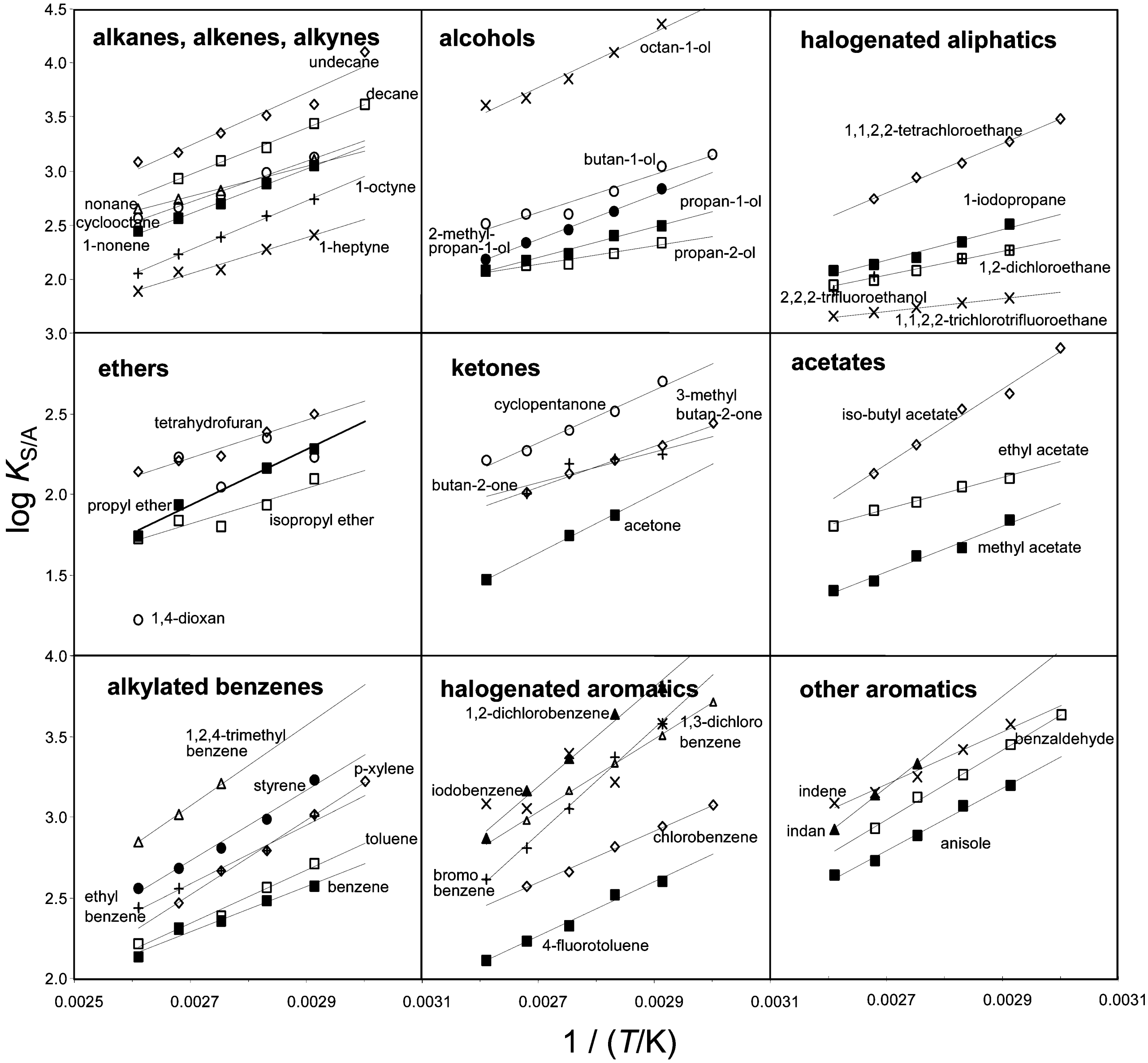

Figure 5. Measured temperature dependence of the hexadecan-1-ol/air partition coefficients for different classes of organic chemicals.

Simultaneous Determination of the Partitioning Properties of Multiple Analytes. Hexadecane/air and hexadecan-1-ol/air partition coefficients for a number of solutes were determined at a number of temperatures using solutions with multiple solutes. The results of these experiments are included in Table 1. Figure 4 compares the partition coefficients measured in solutions with a single or multiple solutes. The points in Figure 4 are close to the diagonal 1:1 line, and a two-paired sample *t*-test further confirmed that the partition coefficients are not significantly different. The simultaneous determination of the partition coefficients of multiple solutes is therefore possible with this method. It should be noted, however, that the more chemicals are introduced into a solution, the more impurity peaks will appear in the chromatogram. Baseline shifts and impurities can strongly affect the veracity of the integration of peak areas, especially in the case of large phase ratios, when the amount of solute in the vial is small. Unfortunately, the slope of the regression equation tends to depend strongly on the peak area value measured at the largest phase ratio, and a few percent error in the area integration may cause large differences in the partition coefficient value. Thus, a precondition for the simultaneous analysis of multiple analytes is that good peak resolution and clean chromatograms can be obtained. It should also be avoided to try to simultaneously measure the VPE of highly volatile and less volatile compounds.

Measurement of Hexadecan-1-ol/Air Partition Coefficients for Numerous Solutes. Hexadecan-1-ol/air partition coefficients $K_{16OH/A}$ for 44 volatile organic compounds belonging to different chemical classes were measured at temperatures between 333.15 K and 383.15 K. The solutes included alkanes, alkenes, alkynes, alcohols, ethers, ketones, acetates, halogenated alkanes, several alicyclic compounds, and alkylated and halogenated benzenes. The partition coefficients and their corresponding standard deviations are listed in Table 3. The measured $K_{16OH/A}$ values range over approximately 3 orders of magnitude from 15 to 25 000, encompassing the entire applicability range of the PRV method. Except for a few individual data points, most of the measurements have a relative error well below 10 %.

The extrapolated $K_{16OH/A}$ values at 298.15 K and free energies $\Delta_{16OH/A}G$, enthalpies $\Delta_{16OH/A}H$, and entropies $\Delta_{16OH/A}S$ of phase transfer derived from the temperature-dependent relationships are given in Table 4. Figure 5 shows the relationships between the experimentally determined log hexadecan-1-ol/air partition coefficients and reciprocal temperature. Whereas 39 of the 44

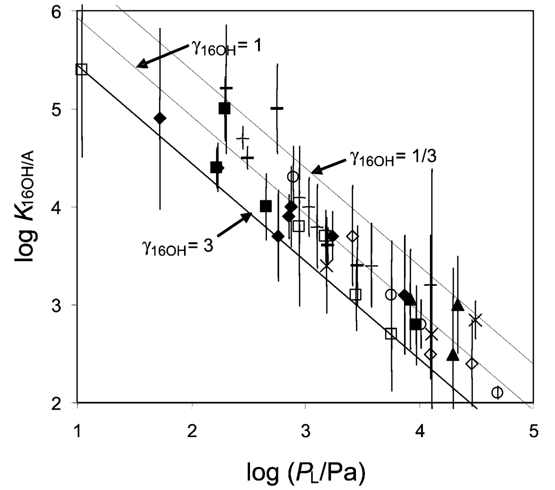

Figure 6. Relationship between the logarithm of the hexadecan-1-ol/air partition coefficient log $K_{16OH/A}$ at 298.15 K and the logarithm of the liquid-state vapor pressure log P_L (in Pa) at 298.15 K of 40 organic solutes. Different classes of solutes are represented by different markers: ◆, alkanes, alkenes, alkynes; □, alcohols; ▲, ethers; ×, ketones; ◇, acetates; ○, halogenated aliphatics; +, alkylated aromatics; —, halogenated aromatics; and ■, other chemicals. The diagonal lines correspond to activity coefficients in hexadecan-1-ol γ_{16OH} of 0.3333, 1, and 3, respectively.

relationship are linear with correlation coefficients R^2 above 0.90 (Table 3), there are two relationship (those for 1,4-dioxan and iodobenzene) that have poor linearity with R^2 values below 0.70. The entries for log $K_{16OH/A}$, $\Delta_{16OH/A}G$, $\Delta_{16OH/A}H$, and $\Delta_{16OH/A}S$ for these two compounds in Table 4 are therefore not reliable, which is reflected in large standard deviations. It also should be noted that for three chemicals (acetone, 1,2,4-trimethylbenzene, and indan) there are only data points at three different temperatures. Thus the thermodynamic properties reported for these three substances in Table 4 probably have much larger uncertainties than it appears. For the remaining compounds the logarithm of $K_{16OH/A}$ at a temperature T can be estimated from the entries in Table 5 using:

$$\log K_{16OH/A} = -(\Delta_{16OH/A}H/RT + \Delta_{16OH/A}S/R - \ln V_{16OH}/V_A)/\ln(10) \quad (10)$$

At 298.15 K, V_{16OH} equals 0.296 L·mol^{-1} and V_A is 24.46 L·mol^{-1}, so that eq 10 simplifies to

$$\log K_{16OH/A} = -(\Delta_{16OH/A}H/RT + \Delta_{16OH/A}S/R + 4.415)/2.303 \quad (11)$$

Discussion

Figure 6 plots the log $K_{16OH/A}$ at 298.15 K against the logarithm of the liquid-phase vapor pressure log P_L of 40 solutes.[20,21] No vapor pressure values could be found for indene and 3-methyl butan-2-one, and the extrapolated values for 1,4-dioxan and iodobenzene are not included. A strong relationship exists between the two parameters:

$$\log K_{16OH/A} \text{ at } 298.15\text{ K} = -(0.98 \pm 0.06) \log(P_L/\text{Pa}) \text{ at } 298.15\text{ K} + (6.8 \pm 0.2) \quad n = 40 \quad R^2 = 0.88 \quad (12)$$

The coefficient of determination suggests that vapor pressure alone can explain more than 88 % of the variability of $K_{16OH/A}$ among the investigated solutes. We had previously observed a similar relationship with a slope close to −1 between vapor pressure and the octan-1-ol/air partition coefficient for a large number of nonpolar organic chemicals[22] but did not necessarily expect such strong correlation for a much more diverse set of substances. The strong correlation implies that the solutes must have quite similar activity coefficients in hexadecan-1-ol, γ_{16OH}. Figure 6 also includes lines corresponding to activity coefficients in hexadecan-1-ol of 0.3333, 1, and 3. Virtually all of the γ_{16OH} data, derived from P_L and $K_{16OH/A}$ using eq 9, fall between these lines, highlighting that the γ_{16OH} values for the solutes are all within 1 order of magnitude of each other. Obviously the molecular interactions of the solutes with hexadecan-1-ol are quite comparable to those between the solutes and their pure liquid phase. No clear relationship between the compound class and the activity coefficients is apparent, in particular there are no indications that nonpolar, monopolar, and dipolar substances fall on different regression lines as has for example been observed when comparing partitioning into octan-1-ol and olive oil.[23]

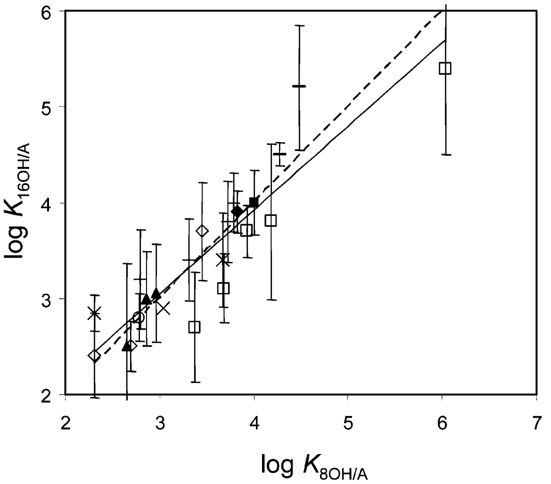

Figure 7. Relationship between the logarithm of the hexadecan-1-ol/air partition coefficient log $K_{16OH/A}$ at 298.15 K and the logarithm of the octan-1-ol/air partition coefficient log $K_{8OH/A}$ at 298.15 K of 23 organic solutes. Different classes of solutes are represented by different markers: ◆, alkanes, alkenes, alkynes; □, alcohols; ▲, ethers; ×, ketones; ◇, acetates; ○, halogenated aliphatics; +, alkylated aromatics; —, halogenated aromatics; and ■, other chemicals. The dashed line is the 1:1 line.

Because the octan-1-ol/air partition coefficient, $K_{8OH/A}$, is so widely used in the environmental field, we further compared $K_{16OH/A}$ with $K_{8OH/A}$ values for 23 compounds reported by Abraham et al.[24] Figure 7 shows a relatively good linear relationship between log $K_{8OH/A}$ and log K_{16OH}, at 298.15 K:

$$\log K_{16OH/A} = (0.88 \pm 0.09) \log K_{8OH/A} + (0.42 \pm 0.32) \quad n = 23 \quad R^2 = 0.82 \quad (13)$$

It seems that the $K_{16OH/A}$ values of the more volatile compounds are somewhat higher than their $K_{8OH/A}$ values. However, considering the experimental uncertainties, such differences are not significant.

A close inspection of Figure 5 reveals that the log $K_{16OH/A}$ versus 1/T relationship are steeper for compounds with higher $K_{16OH/A}$ values. A linear regression between the ln $K_{16OH/A}$ at 298.15 K and the phase transfer enthalpy $\Delta_{16OH/A}H$ (Figure 8) yields the following relationship:

$$\Delta_{16OH/A}H/\text{kJ·mol}^{-1} = (5.2 \pm 0.4) \ln K_{16OH/A} \text{ at } 298.15\text{ K} - (9.0 \pm 3.6) \quad n = 42 \quad R^2 = 0.79 \quad (14)$$

As the partition coefficient increases by one ln unit, an additional 5.2 kJ of energy is required to desorb 1 mol of a chemical from hexadecan-1-ol to air. Equation 14 allows the approximate

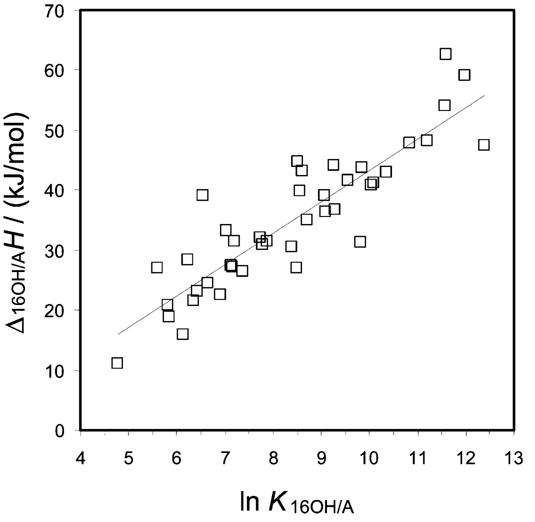

Figure 8. Relationship between the hexadecan-1-ol/air partition coefficient ln $K_{16OH/A}$ of 42 organic compounds at 298.15 K and the enthalpy of hexadecan-1-ol/air phase transfer $\Delta_{16OH/A}H$ in kJ/mol.

estimation of $\Delta_{16OH/A}H$, and therefore of the temperature dependence of $K_{16OH/A}$, if the partitioning coefficient is only known at 298.15 K. Compared with similar equations derived by Goss and Schwarzenbach,[25] this energy is slightly higher than that for the heat of evaporation and heats of adsorption of organic compounds to mineral surfaces.

Conclusions

One of the findings of this study is that the solvation behavior of a diverse group of organic chemicals in a long-chain aliphatic alcohol such as hexadecan-1-ol is not very different from that in octan-1-ol. The observation that the lipid storage compartment of grassland species had solvation properties quite different from those of octan-1-ol can thus not be attributed to the fact that epicuticular wax components have typically a chain length much longer than eight. In fact, it does not even appear that the solvation into a long-chain aliphatic alcohol is very different from the solvation a solutes experiences in its own pure liquid phase, as activity coefficients close to 1 indicate. In other words, the partitioning behavior of most organic solutes in aliphatic alcohols can be estimated from their liquid-phase vapor pressure with a precision of about 1 order of magnitude simply by assuming that the activity coefficient is 1.[22] This is comparable to the precision of the log $K_{16OH/A}$ values at 298.15 K determined in this study by extrapolation (the precision of the partition coefficients at the experimental temperatures is much higher).

Bulk phase partitioning of organic compounds from the gas phase into many organic solvents therefore seems to be much more amenable to simple approximation through vapor pressure than adsorption to surfaces or bulk phase partitioning into water or other solvents with very strong hydrogen bonds. If it should turn out that it is possible to similarly approximate the partitioning into NOM through vapor pressure, this would suggests that differences in the environmental phase distribution between different organic chemicals are controlled to a much greater extent by differences in their (i) solvation behavior in water, (ii) adsorption behavior on environmentally relevant surfaces, and (iii) vapor pressure, than by differences in the solvation behavior in NOM because the latter would appear to be relatively small.

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