EVALUATION OF THE THREE-PHASE EQUILIBRIUM METHOD FOR MEASURING TEMPERATURE DEPENDENCE OF INTERNALLY CONSISTENT PARTITION COEFFICIENTS (K_{OW}, K_{OA}, AND K_{AW}) FOR VOLATILE METHYLSILOXANES AND TRIMETHYLSILANOL

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Abstract: Partitioning equilibria and their temperature dependence of chemicals between different environmental media are important in determining the fate, transport, and distribution of contaminants. Unfortunately, internally consistent air/water (K_{AW}), 1-octanol/air (K_{OA}), and 1-octanol/water (K_{OW}) partition coefficients, as well as information on their temperature dependence, are scarce for organosilicon compounds because of the reactivity of these compounds in water and octanol and their extreme partition coefficients. A newly published 3-phase equilibrium method was evaluated for simultaneous determination of the temperature dependence of K_{AW}, K_{OA}, and K_{OW} of 5 volatile methylsiloxanes (VMS) and trimethylsilanol (TMS) in a temperature range from 4 °C to 35 °C. The measured partition coefficients at the different temperatures for any given compound, and the enthalpy and entropy changes for the corresponding partition processes, were all internally consistent, suggesting that the 3-phase equilibrium method is suitable for this type of measurement. Compared with common environmental contaminants reported in the literature, VMS have enthalpy and entropy relationships similar to those of alkanes for air/water partitioning and similar to those of polyfluorinated compounds for octanol/water partitioning. The temperature dependence of the partition coefficients of TMS is different from those of VMS and is more like that of alcohols, phenols, and sulfonamides. Environ Toxicol Chem 2014;33:2702–2710. © 2014 The Authors. Environmental Toxicology and Chemistry published by Wiley Periodicals, Inc.

Keywords: Partition coefficients Temperature dependence Enthalpy and entropy changes

INTRODUCTION

Volatile methylsiloxanes (VMS) are a group of low molecular weight per-methylated organosiloxane compounds that can be either cyclic (cVMS) or linear (IVMS) in structure. They are used widely in industrial and consumer applications and may also exist as impurities in high molecular weight silicone fluids and elastomers. Some VMS, such as octamethylcyclotetrasiloxane (D4) and decamethylcyclopentasiloxane (D5) have come under increased regulatory scrutiny because of their heavy use and potential for widespread occurrence in the environment [1,2].

Compared with conventional environmental contaminants of similar molecular weights, VMS have relatively high saturated vapor pressures. As a result, volatilization is an important route of emission to the environment for VMS. For example, 90% of cVMS in personal care products are estimated to be released directly to the air during end-user applications, and the remainder is released down the drain to the wastewater system [3]. A pilot study on wastewater treatment processes [4] and a monitoring study of influents and effluents of municipal sewage treatment plants [5] suggest that 90% to 98% of cVMS in the wastewater influent are removed from water by wastewater treatment processes.

Airborne VMS are relatively stable, with OH radicals reaction rate constants ranging from $1 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ to $3 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, corresponding to the global average atmospheric half-lives of approximately 6 d to 15 d [6,7]. Because of the relatively long atmospheric half-lives and high volatility, the released VMS are expected to undergo atmospheric transport, and a small fraction of that can reach remote parts of the atmosphere such as in the Arctic [8]. The occurrence of these compounds in the Arctic air has been verified by recent monitoring studies [9–11]. However, the effects of such atmospheric transport on VMS concentrations in remote ecosystems are estimated to be small, mostly attributable VMS’s unique combination of partitioning properties [8].

Partitioning properties such as air/water (K_{AW}), 1-octanol/air (K_{OA}), and 1-octanol/water (K_{OW}) partition coefficients are very important in determining the chemical fate, transport, distribution, and accumulation of organic contaminants in the natural environment. They are critical inputs in multimedia chemical fate modeling [12,13]. More specifically, K_{AW} is used to estimate the partition equilibrium between air and water under various conditions, including partitioning between air and rain droplets for estimation of wet deposition, volatilization in wastewater treatment processes, and the intercompartment transfer of chemicals between the atmosphere and surface waters [12]; K_{OA} is used to assess the partitioning between organic phases (e.g., soil carbon and biota) and the gas phase [13–17]; and numerous studies have shown that K_{OW} has wide applications in correlating chemical structures with the observed change in some biological, biochemical, or toxic effects [18]. Furthermore, K_{OW} has been found to be related to water solubility, soil/sediment adsorption coefficients, bioconcentration factors for aquatic organisms [18], and internal partitioning between body fluids and biological tissues for common environmental contaminants [19].

Unfortunately, accurate partition coefficients for methylsiloxanes are still scarce as a result of analytical challenges in determining the partition coefficients for this type of compound.
even at room temperature [20,21]. In addition, temperature can also be a major factor influencing the partitioning of organic compounds such as polycyclic aromatic hydrocarbons, polychlorinated biphenyls (PCBs), chlorinated solvents [22,23], and many others [24]. Therefore, the temperature dependences of these partition coefficients are also needed for understanding and predicting the environmental fate, transport, and distribution of VMS, where temperatures can range from −50 °C to greater than 40 °C.

Recently, 2 related methods were developed for direct measurement of partition coefficients for organosilicon compounds [20,25]. The first method was designed specifically to measure \( K_{\text{OA}} \) in dry 1-octanol and its temperature dependence [25]. A single air-tight syringe was used as an equilibration vessel, with its valve-controlled needle connected to a cold gas trap for minimal loss during gas sampling. The second method was developed for simultaneous determination of the 3 major partition coefficients—\( K_{\text{GW}} \), \( K_{\text{AW}} \), and \( K_{\text{OA}} \) [20]—using a custom-made double-syringe apparatus as the equilibration vessel, which minimized sampling errors and volatile loss for gas and water phases. The new method allows for simultaneous 3-phase (1-octanol/water/air) equilibrium, which ensures the internal consistency of the 3 measured partition coefficients, that is

\[
\log K_{\text{GW}} = \log K_{\text{AW}} + \log K_{\text{OA}} \quad (1)
\]

However, whether this approach could generate data with consistent temperature dependence is still to be determined.

The objectives of the present study were to further evaluate the ability of the double-syringe apparatus to simultaneously measure \( K_{\text{GW}} \), \( K_{\text{OA}} \), and \( K_{\text{AW}} \) for organosilicon compounds and to determine the effect of temperature on the 3 partition coefficients of VMS and their degradation products, silanols.

**MATERIALS AND METHODS**

**Materials**

Five VMS and 1 silanol were used in this experiment: \( ^{14}\text{C} \)-labeled hexamethyldisiloxane (\( ^{14}\text{C-L2} \)), \( ^{14}\text{C} \)-labeled octamethyltrisiloxane (\( ^{14}\text{C-L3} \)), \( ^{14}\text{C} \)-labeled decamethyltetrasiloxane (\( ^{14}\text{C-L4} \)), octamethylocyclotetrasiloxane (\( ^{14}\text{C-D4} \)), \( ^{14}\text{C} \)-decamethylcyclopentasiloxane (\( ^{14}\text{C-D5} \)), and \( ^{14}\text{C} \)-labeled trimethylsilanol (\( ^{14}\text{C-TMS} \)). All were synthesized at Dow Corning. The chemical purity and radiochemical purity of all test compounds were >98%. The specific activities were 206 mCi/g for \( ^{14}\text{C-L2} \), 219 mCi/g for \( ^{14}\text{C-L3} \), 313 mCi/g for \( ^{14}\text{C-L4} \), 393 mCi/g for \( ^{14}\text{C-D4} \), 383 mCi/g for \( ^{14}\text{C-D5} \), and 197 mCi/g for \( ^{14}\text{C-TMS} \). All other chemicals were American Chemical Society reagent grade from Sigma-Aldrich.

**Equilibration apparatus**

The apparatus for sample equilibration was described in a previous article [20]. It consisted of 2 air-tight syringes (100-mL borosilicate glass syringe with a Teflon-faced plunger and rotary Teflon valve) with an air sampling port in 1 syringe and a water sampling port in the other. During the experiment, \( ^{14}\text{C} \)-labeled VMS or TMS dissolved in water-saturated 1-octanol (0.2–1.0 mL) was loaded in the side of the syringe apparatus that had an air-sampling port. Then 1-octanol–saturated water (20–60 mL) was loaded into the other syringe, which had a water sampling port. The air phase in both syringes was connected through a middle valve that was open during the equilibration but closed during the air and water sampling. The syringe system was placed into either an incubator (at 12 °C and 35 °C; Percival I-30BLL) or a walk-in cold room (at 5 °C) for temperature control.

**Water analysis**

Concentrations of \( ^{14}\text{C} \)-VMS and TMS in water were determined by 2 different methods that depended on whether the experiments were conducted at a high or low temperature. Direct injection of 1 mL of water into a high-performance liquid chromatograph with a reversed-phase column and radiochemical detector (RP HPLC/RAM) was used for water samples collected from all L2, L3, and TMS experiments. This method was also used for D4, D5, and L4, which were held at low temperatures and thus had relatively high concentrations of VMS in water. Samples with low VMS concentrations in water (e.g., at high temperatures) were extracted with 1-heptanol before analysis by RP HPLC/RAM as previously described [20].

**Air analysis**

Air samples were obtained from the air/octanol syringe via the air sampling port before and after a set of water samples was taken and the water-containing syringe was completely emptied. The method for air sample collection and analysis was exactly the same as that described by Xu and Kropscott [25]. Briefly, 10 mL of air was expelled through a cryogenic cold trap connected to the air sampling port and immersed in a dry ice/acetone bath within 1 min. The captured organosilicon compounds were dissolved using 1 mL of mixed solvent (60:40% v/v methanol/acetonitrile). A portion of the collected solvent was injected for analysis by RP HPLC/RAM, and the rest was analyzed by liquid scintillation counting (LSC).

**Octanol analysis**

The octanol was sampled through the orifice of the air sampling port using a microsyringe. The concentration of VMS in octanol was usually very high, and therefore the octanol sample was diluted with a methanol/acetonitrile (60:40%) mixture prior to chemical analysis by LSC and RP HPLC/RAM. For TMS, the octanol sample was analyzed by normal-phase HPLC/RAM (NP HPLC/RAM).

**HPLC/RAM analysis**

The HPLC/RAM system consisted of an HP 1100 system equipped with a radiochemical detector (PerkinElmer Flow Scintillation Analyzer Radiomatic 610TR). For RP HPLC analysis, a C-18 column (5 μm, 4.6 mm × 150 mm; Agilent Eclipse XDB-C18) and a linear mobile phase gradient were used: 100% water at time 0; 1% water plus 99% acetonitrile at 5.5 min; 100% acetonitrile at 11 min; 100% acetonitrile at 15 min; and 100% water at 16 min and 20 min. The flow rate was 2.0 mL min\(^{-1}\) for the mobile phase and 6.0 mL min\(^{-1}\) for the scintillation cocktail (Ultima-Flo M; PerkinElmer). For NP HPLC analysis, a normal-phase column (5 μm, 4.6 mm × 150 mm; PrevailTM Silica) and the following linear solvent gradient were used: 94% hexane and 6% tetrahydrofuran (THF) at 0 min to 3 min; 92% hexane plus 8% THF at 4 min; 80% hexane plus 20% THF at 13 min; 65% hexane plus 35% THF at 21 min; and 94% hexane plus 6% THF at 25 min.

**Liquid scintillation counting**

For aqueous samples, the solution was mixed with an appropriate amount of Ultimate Gold XR (PerkinElmer 77-060802) to obtain a transparent solution that was analyzed by LSC (Packard Tri-Carb 2500TR). Nonaqueous samples were
added to 10 mL of Ultimate Gold scintillation cocktail for LSC analysis.

**Calculation of \( K_{OW}, K_{OA}, \) and \( K_{AW} \)**

The direct results of the above analysis were radioactivity-based concentrations of VMS in all 3 phases, in disintegrations per minutes per mL (DPM mL\(^{-1}\)). The 3 partition coefficients were calculated according to the following equations

\[
K_{OW} = \frac{C_O}{C_W} = \frac{(R_O/S)}{(R_W/S)} = \frac{R_O}{R_W} \quad (2)
\]

\[
K_{OA} = \frac{C_O}{C_A} = \frac{(R_O/S)}{(R_A/S)} = \frac{R_O}{R_A} \quad (3)
\]

\[
K_{AW} = \frac{C_A}{C_W} = \frac{(R_A/S)}{(R_W/S)} = \frac{R_A}{R_W} \quad (4)
\]

where \( C_O, C_W, \) and \( C_A \) are mass-based concentrations of \(^{14}\text{C}-\text{VMS}\) in 1-octanol, water, and air, respectively, when the 3 phases are at equilibrium; \( R_O, R_W, \) and \( R_A \) are the radioactivity (e.g., DPM) of \(^{14}\text{C}-\text{VMS}\) measured in unit volume (e.g., 1 mL) of 1-octanol, water, and air, respectively, when all 3 phases reached equilibrium; and \( S \) is the specific activity of \(^{14}\text{C}-\text{VMS}\) (i.e., in DPM ng\(^{-1}\)).

**RESULTS AND DISCUSSION**

**Equilibrium time**

In the 3-phase equilibrium method, the concentrations of VMS in various phases are directly measured after the equilibrium between the 3 phases is established [20]. As previously demonstrated for D4 at room temperature, when 1-octanol solution with dissolved \(^{14}\text{C}-\text{cVMS}\) initially was loaded into the 3-phase equilibrium system, the increase in aqueous \(^{14}\text{C}-\text{cVMS}\) concentration appeared much more slowly than that in the air, mostly because of the hydrolysis of \(^{14}\text{C}-\text{cVMS}\) in water. A 20-h equilibrium time was required for 3-phase equilibration [20].

To determine the time needed to establish the equilibrium between air and water phases for IVMS in the present study, water from this system was sampled and analyzed at various time intervals ranging from 2 h up to 140 h after the \(^{14}\text{C}-\text{IVMS}/\text{octanol} \) solution was introduced into the apparatus. As measured by radioactivity (Figure 1A), the IVMS concentrations in water tended to be constant after a short equilibrium time, although the total radioactivity or the total concentrations of \(^{14}\text{C}-\text{organosilicon} \) species in water continued to increase as the equilibrium time increased. The continued increase in total radioactivity is attributable to the increased concentrations of hydrolysis products of \(^{14}\text{C}-\text{IVMS} \) in water, based on the HPLC/RAM chromatograms exemplified by L4 (Figure 1B). Nevertheless, the constant \(^{14}\text{C}-\text{IVMS} \) concentrations after 6 h (Figure 1) demonstrated that equilibrium between air and water was established very quickly for IVMS under the current conditions.

**Concentration effects**

Another factor that may influence partition coefficients of hydrophobic compounds such as VMS is the possible concentration effects on activity coefficients in water [21]. As demonstrated in previous studies, \( \log K_{OA} \) values for D4 remained relatively constant as long as the concentration of D4 was less than 0.1 mg mL\(^{-1}\) in 1-octanol [25]. Similarly, all 3 partition coefficients for L2 were relatively constant as the L2 concentration in water varied from 0.7 \( \mu \text{g L}^{-1} \) to 45 \( \mu \text{g L}^{-1} \) (Figure 2) or 0.08% to 5% of its solubility at 25°C [26].

The independence of the measured partition coefficients to the aqueous L2 concentration over this concentration range
suggested that the change in activity coefficients for L2 in all 3 phases was insignificant at these low concentrations.

Based on this finding, all partition coefficients were measured in this low concentration range, as summarized in Table 1. For all VMS except L3, the partition coefficients were measured at less than 5% of their corresponding aqueous solubilities [26]. The high concentrations of L3 in water ranged from 2.7 μg L⁻¹ to 6.3 μg L⁻¹ at 20.8 °C, or 7.9% to 18.5% of its reported water solubility at 23 °C. However, the changes in 13 measurements of partition coefficients at this temperature were also relatively small, judged by the standard deviations given in Table 1.

*Temperature dependence*

As shown in Table 1, temperature has substantial effects on the measured partition coefficients, especially $K_{OW}$ and $K_{OA}$, for any given compound. Generally, a temperature increase resulted in a decrease in $K_{OA}$ values but an increase in $K_{AW}$ and $K_{OW}$ values for all compounds. For L2, a 24 °C increase in temperature resulted in -0.48 log unit, 0.81 log unit, and 0.32 log unit changes in log $K_{OA}$, log $K_{AW}$, and log $K_{OW}$, respectively (corresponding to -0.60 log unit, 1.00 log unit, and 0.35 log unit changes for a 30 °C change in temperature). Similarly for TMS, a 30 °C temperature increase resulted in -0.99 log unit, 1.27 log unit, and 0.28 log unit changes in log $K_{OA}$, log $K_{AW}$, and log $K_{OW}$, respectively.

The sensitivity of partition coefficients to the temperature change is complicated. Both L4 and D4 have 4 Si atoms per molecule, and a 30 °C temperature increase resulted in similar changes in their log $K_{AW}$ (1.21 log units for L4 vs 1.30 log units for D4). However, log $K_{OA}$ for L4 is less temperature sensitive than that for D4, while log $K_{OW}$ of L4 is more temperature sensitive than that of D4.

To better quantify this temperature dependence, all the partition coefficients in Table 1 were plotted against the reciprocal of the equilibrium temperatures ($T$; Figure 3). The results confirmed the linear relationships in the following form in the tested temperature range

$$\log \text{(coefficient for X-to-Y partitioning)} = A_{XY} + B_{XY}/T \quad (5)$$

where $A_{XY}$ and $B_{XY}$ are constants for X-to-Y partitioning (i.e., air-to-water, octanol-to-air, octanol-to-water partitioning). The results of linear regression based on Equation 5, including the coefficients of determination ($r^2$), are given in Table 2. Based on the high $r^2$ values, the temperature change was estimated to account for 80% to 100% of variations in all partition coefficients except in 2 cases. The first case is the $K_{OW}$ for L3, which varied slightly in the tested temperature range. The measured log $K_{OW}$ values were too variable for such low-temperature dependence, resulting in low $r^2$. The second case is D5, which has partition coefficients for only 2 temperatures—enough not to calculate a meaningful $r^2$.

The entropy change ($\Delta S_{XY}$) and enthalpy change ($\Delta H_{XY}$) in Table 3 were calculated from the corresponding intercepts and slopes list in Table 2. The enthalpy change was calculated as

$$\Delta H_{XY} \text{ (kJ mol⁻¹)} = -2.303 B_{XY} R/1000 \quad (6)$$

where $B_{XY}$ is the slope of the regression using Equation 5, $R$ is the ideal gas constant, and 2.303 represents a conversion factor from a 10-based log to the natural log value. The entropy change was calculated as

$$\Delta S_{XY} \text{ (kJ mol⁻¹ K⁻¹)} = 2.303 A_{XY} R/1000 \quad (7)$$

where $A_{XY}$ is the intercept in Equation 5 for the corresponding compounds given in Table 2.

### Table 1. Average equilibrium temperatures (Temp), number of measurements (No. meas.), and range of concentrations in water (Conc in water) for measurements of the 3 partition coefficients and their discrepancies (δ) for TMS and 5 VMS

| Comp  | Temp (°C) | No. meas. | Conc in water (μg L⁻¹) | log $K_{AW}$ | log $K_{OA}$ | log $K_{OW}$ | δ a |
|-------|-----------|-----------|------------------------|--------------|--------------|--------------|-----|
| L2    | 4.2 (0.4) | 4         | 3–38                   | 1.79 (0.13)  | 3.17 (0.06)  | 4.97 (0.07)  | 0.01|
|       | 12.4 (0.1)| 7         | 0.7–42                 | 2.11 (0.06)  | 2.94 (0.16)  | 5.05 (0.15)  | 0.00|
|       | 20.0 (0.2)| 4         | 7–48                   | 2.32 (0.03)  | 2.74 (0.05)  | 5.06 (0.07)  | 0.00|
|       | 28.3 (0.1)| 4         | 2–27                   | 2.60 (0.10)  | 2.69 (0.03)  | 5.29 (0.08)  | 0.00|
| L3    | 4.5 (0.2) | 5         | 6.6–7.7                | 2.50 (0.06)  | 4.25 (0.03)  | 6.75 (0.07)  | 0.00|
|       | 12.1 (0.0)| 5         | 3.5–5.1                | 2.78 (0.10)  | 3.99 (0.03)  | 6.76 (0.10)  | 0.00|
|       | 20.8 (0.4)| 13        | 2.7–6.3                | 3.04 (0.20)  | 3.79 (0.01)  | 6.87 (0.24)  | 0.04|
|       | 35.0 (0.3)| 5         | 1.9–6.0                | 3.24 (0.14)  | 3.51 (0.05)  | 6.75 (0.11)  | 0.00|
| L4    | 4.7 (0.8) | 15        | 0.2–2.1                | 2.62 (0.21)  | 5.39 (0.00)  | 8.01 (0.21)  | 0.00|
|       | 12.2 (0.1)| 14        | 0.04–0.26              | 2.94 (0.19)  | 5.12 (0.05)  | 8.06 (0.23)  | 0.00|
|       | 19.7 (0.1)| 11        | 0.08–0.27              | 3.22 (0.13)  | 4.87 (0.03)  | 8.09 (0.13)  | 0.00|
|       | 34.9 (0.3)| 12        | 0.04–0.17              | 3.83 (0.25)  | 4.38 (0.06)  | 8.22 (0.22)  | 0.01|
| D4    | 5.7 (0.7) | 6         | 1.4–2.0                | 1.79 (0.07)  | 4.81 (0.02)  | 6.59 (0.07)  | -0.01|
|       | 12.2 (0.1)| 7         | 0.9–1.3                | 2.17 (0.08)  | 4.53 (0.08)  | 6.70 (0.07)  | 0.00|
|       | 21.7 b    | 37        | 0.8–1.5                | 2.69 (0.13)  | 4.29 (0.03)  | 6.98 (0.13)  | 0.00|
|       | 34.8 (0.2)| 16        | 1.9–4.0                | 3.09 (0.14)  | 4.04 (0.07)  | 7.13 (0.10)  | 0.00|
| D5    | 24.6 b    | 38        | 0.13–0.24              | 3.13 (0.13)  | 4.94 (0.08)  | 8.07 (0.22)  | 0.00|
|       | 34.8 (0.3)| 12        | 0.001–0.003            | 3.85 (0.37)  | 4.67 (0.10)  | 8.47 (0.40)  | -0.05|
| TMS   | 5.0 (0.3) | 8         | 535–1585               | -3.72 (0.12) | 4.82 (0.08)  | 1.10 (0.09)  | 0.00|
|       | 12.2 (0.1)| 6         | 997–2310               | -3.36 (0.10) | 4.54 (0.08)  | 1.18 (0.06)  | 0.00|
|       | 25.0 (0.3)| 8         | 846–2310               | -2.77 (0.10) | 4.01 (0.04)  | 1.22 (0.13)  | -0.02|
|       | 35.2 (0.3)| 8         | 320–2108               | -2.45 (0.06) | 3.83 (0.07)  | 1.38 (0.02)  | 0.00|

a $δ = \log K_{OW} - (\log K_{OA} + \log K_{AW})$.

b From Xu and Kropsch [20],

Standard deviations in parentheses.

TMS = trimethylsilanol; VMS = volatile methylsiloxanes; $K_{AW}$ = air/water partition coefficient; $K_{OA}$ = 1-octanol/air partition coefficient; $K_{OW}$ = 1-octanol/water partition coefficient; L2 = hexamethyldisiloxane; L3 = octamethytrisiloxane; L4 = decamethyltetrasiloxane; D4 = octamethylocyclotetrasiloxane; D5 = decamethylcyclopentasiloxane.
that mutual solubilization of water and 1-octanol has a very small

Therefore, a single set of measured in both cases were indistinguishable (Figure 3).

dependencies for D4, L3, L4, and D5 values measured at different temperatures in dry 1-octanol were

For example, at 25°C, the log $K_{OA}$ value in dry 1-octanol was higher than that in wet 1-octanol by 0.27 log units. A single set of $\Delta H_{OA}$ and $\Delta S_{OA}$ values (Table 3) was calculated for L2 using a combination of all the $K_{OA}$ values for this compound from both studies. Nevertheless, the small difference between the 2 sets of log $K_{OA}$ values confirms the finding in the previous study [20] that mutual solubilization of water and 1-octanol has a very small

Comparison with literature

$K_{OA}$. Currently there is only 1 set of additional $K_{OA}$ values and its temperature dependence measured in dry (not water-saturated) 1-octanol reported for organosilicon compounds [25] (Table 4). At room temperature, the log $K_{OA}$ values measured in the drier octanol phase are similar to those measured in wet 1-octanol in the present study. In fact, when all of these log $K_{OA}$ values were calculated for 1-octanol/water partition coefficient; $K_{OA}$ = 1-octanol/air partition coefficient; $K_{OW}$ = 1-octanol/water partition coefficient.

**Table 2. Results of linear regression analyses based on the equation**

\[ \log K_{OA} = A + B/T \]

along with coefficients of determination ($r^2$) and Pearson correlation probability ($p$ values) with sample sizes ($n$)

effect on the octanol/air partitioning of VMS in the environmentally relevant temperature range.

In addition, a good linear correlation ($p << 0.01$ for 2-tailed test) between $\Delta H_{OA}$ and $\Delta S_{OA}$ was observed for the 5 siloxanes (Figure 4)

$$
\Delta H_{OA} = 640.4 \Delta S_{OA} - 4.15; \quad r^2 = 0.980 \quad (n = 6, \quad p \sim 0.0006)
$$

This kind of correlation between $\Delta H$ and $\Delta S$ is termed the enthalpy and entropy compensation effect [27], because of the cancellation of the 2 terms $\Delta H$ and $-T\Delta S$ in the Gibbs relationship for the physicochemical process of interest

$$
\Delta G_{OA} = -RT \ln K_{OA} = \Delta H_{OA} - T\Delta S_{OA}
$$

where $\Delta G_{OA}$ is Gibbs free energy for the octanol-to-air partitioning process. These effects have been observed for many chemical and biological reactions for groups of similar compounds [28–31] and Henry’s law constants for PCBs [27]. However, others have cautioned that such phenomena may be a statistical artifact in the experimental data [32]. The data in Figure 4 are not enough to either refute or support the existence of such an effect for environmental partitioning processes. However, Figure 4 does show that the measured $\Delta H_{OA}$ and $\Delta S_{OA}$ values for all 6 organosilicon compounds varied in a narrow range similar to those of polyfluorinated compounds but much less negative than those of polychlorinated compounds (Figure 4). This implies that $K_{OA}$ values of organosilicon

\[ \text{Comp} \quad A^b \quad B^b \quad r^2 \quad p \text{ value (n)} \]

| Comp      | A  | B  | $r^2$ | $p$ value (n) |
|-----------|----|----|-------|---------------|
| Octanol/water |    |    |       |               |
| L2        | 8.59 (1.15) | -1011 (333) | 0.823 | 0.0930 (4)    |
| L3        | 6.97 (0.92)  | -53 (267)    | 0.019 | 0.8600 (4)    |
| L4        | 10.12 (0.23) | -590 (66)    | 0.976 | 0.0120 (4)    |
| D4        | 12.57 (0.71) | -1666 (207)  | 0.970 | 0.0150 (4)    |
| D5        | 20.15         | -3596        | NA    | NA            |
| TMS       | 3.68 (0.55)   | -718 (160)   | 0.910 | 0.0460 (4)    |
| Octanol/air$^a$ |    |    |       |               |
| L2        | -1.78 (0.76)  | 1394 (219)   | 0.803 | <0.0001 (12)  |
| L3        | -2.80 (0.49)  | 1953 (120)   | 0.964 | <0.0001 (12)  |
| L4        | -3.54 (0.06)  | 2448 (158)   | 0.960 | <0.0001 (11)  |
| D4        | -3.37 (0.82)  | 2282 (138)   | 0.968 | <0.0001 (11)  |
| D5        | -3.45 (0.48)  | 2470 (40)    | 0.978 | <0.0001 (9)   |
| D6$^b$    | -4.39 (0.33)  | 3001 (96)    | 0.996 | 0.0003 (5)    |
| TMS       | -5.67 (0.94)  | 2910 (276)   | 0.982 | 0.0090 (4)    |
| Air/water |          |               |       |               |
| L2        | 11.77 (0.36)  | -2766 (103)  | 0.998 | 0.0010 (4)    |
| L3        | 9.99 (0.99)   | -2064 (288)  | 0.962 | 0.0190 (4)    |
| L4        | 14.92 (0.25)  | -3421 (73)   | 0.999 | <0.0001 (4)   |
| D4        | 15.68 (1.20)  | -3859 (350)  | 0.984 | 0.0080 (4)    |
| D5        | 24.87         | -6472        | NA    | NA            |
| TMS       | 9.41 (0.58)   | -3648 (169)  | 0.996 | 0.0020 (4)    |

$^a$In the equation, A and B are constants and $T$ is the equilibrium temperature in Kelvin.

$^b$Standard deviations in parentheses.

$^c$log $K_{OA}$ values measured in the present study and those reported in Xu and Kropscott [25] were combined in the regression.

$^d$log $K_{OA}$ values for D6 were not measured in the present study. The values shown here are from Xu and Kropscott [25].

L2 = hexamethyldisiloxane; L3 = octamethyltrisiloxane; L4 = decamethyltetrasiloxane; D5 = decamethylcyclotetrasiloxane; TMS = trimethylsilanol; $K_{OA}$ = 1-octanol/air partition coefficient.

Figure 3. Temperature (T) dependence of partition coefficients for trimethylsilanol (TMS) and 5 volatile methylsiloxanes (VMS) measured in the present study (blue triangles and circles), and log $K_{OA}$ values measured in dry 1-octanol from Xu and Kropscott [25]. L2 = hexamethyldisiloxane; L3 = octamethyltrisiloxane; L4 = decamethyltetrasiloxane; D5 = decamethylcyclotetrasiloxane; $K_{AW}$ = air/water partition coefficient; $K_{OA}$ = 1-octanol/air partition coefficient; $K_{OW}$ = 1-octanol/water partition coefficient.
Table 3. Values (and standard deviations) of enthalpy ($\Delta H$) (kJ mol$^{-1}$) and entropy ($\Delta S$) kJ mol$^{-1}$ K$^{-1}$ changes for the three partitioning processes and their overall internal consistency

| Comp | Octanol/water | Octanol/air | Air/water | Overall consistency$^a$ |
|------|---------------|-------------|-----------|------------------------|
|      | $\Delta H_{\text{OW}}$ | $\Delta S_{\text{OW}}$ | $\Delta H_{\text{OA}}$ | $\Delta S_{\text{OA}}$ | $\Delta H_{\text{AW}}$ | $\Delta S_{\text{AW}}$ | $\delta (\Delta H)$ | $\delta (\Delta S)$ |
| L2   | 19.4 (6.4)    | 0.164 (0.022) | -26.7 (4.2) | -0.034 (0.015) | 53.0 (2.0) | 0.225 (0.007) | -6.9 | -0.027 |
| L3   | 1.0 (5.1)     | 0.133 (0.018) | -37.5 (2.3) | -0.054 (0.008) | 39.5 (5.5) | 0.191 (0.019) | -1.0 | -0.004 |
| L4   | 11.3 (1.3)    | 0.194 (0.004) | -46.9 (3.0) | -0.068 (0.011) | 65.5 (1.4) | 0.286 (0.005) | -7.3 | -0.024 |
| D4   | 31.9 (4.0)    | 0.241 (0.014) | -43.7 (2.6) | -0.065 (0.009) | 73.9 (6.7) | 0.300 (0.023) | 1.7 | 0.006 |
| D5   | 68.8          | 0.386        | -47.3 (2.7) | -0.064 (0.009) | 123.9      | 0.476        | -7.8 | -0.026 |
| TMS  | 13.7 (3.1)    | 0.070 (0.011) | -55.7 (5.3) | -0.109 (0.018) | 69.8 (3.2) | 0.180 (0.011) | -0.4 | -0.001 |

$^a$,$\delta (\Delta H) = \Delta H_{\text{OW}} - (\Delta H_{\text{OA}} + \Delta H_{\text{AW}})$; $\delta (\Delta S) = \Delta S_{\text{OW}} - (\Delta S_{\text{OA}} + \Delta S_{\text{AW}})$.

compounds are less sensitive to temperature change than those of most polychlorinated pollutants.

$K_{\text{AW}}$ values for VMS reported in the open literature vary greatly, depending on the methods of determination (Table 4). At water solubility limits, $K_{\text{AW}}$ values estimated from the saturated vapor pressure [33,34] and water solubilities [26] are valid. They are smaller than those obtained in dilute solutions in the present study, presumably because of the increased activity coefficients of the VMS as they are diluted in water [21]. The rest of the directly measured values from the early literature [35–37] are much smaller than those calculated based on saturated vapor pressure and aqueous solubility or measured in the present study (Table 4). These early measurements are questionable because of flawed analytical methodologies, as discussed in detail elsewhere [21].

Although there are no measured $\Delta H_{\text{AW}}$ and $\Delta S_{\text{AW}}$ values in the current literature for any organosilicon compounds, the $\Delta H_{\text{AW}}$ and $\Delta S_{\text{AW}}$ values measured in the present study for VMS and TMS can be compared with those of common environmental contaminants in the literature (Figure 5). As shown in Figure 5, $\Delta H_{\text{AW}}$ and $\Delta S_{\text{AW}}$ values for VMS and TMS have ranges similar to those for other compounds. However, the enthalpy–entropy relationship is different. As demonstrated in Figure 5, $\Delta H_{\text{AW}}$ and $\Delta S_{\text{AW}}$ values of the similar compounds are linearly related, presumably reflecting strong enthalpy–entropy compensation effects for all compounds tested. For example, 5 VMS follow a straight line ($p << 0.01$ for 2-tailed test)

$$\Delta H_{\text{AW}} = 292.0 \Delta S_{\text{AW}} - 15.2; \quad r^2 = 0.996 \quad (n = 5), \quad p \sim 0.0001$$

Both $\Delta H_{\text{AW}}$ and $\Delta S_{\text{AW}}$ values increase as the molecular weight increases beyond L3, similar to that found for $\Delta H_{\text{OA}}$ and $\Delta S_{\text{OA}}$ values described in the previous section. However, L2 does not follow this pattern; the exact reason for this abnormality is not currently known.

More importantly, the parallel $\Delta H_{\text{AW}}$-vs-$\Delta S_{\text{AW}}$ lines in Figure 5 suggest that the iso-equilibrium temperatures are very similar for various groups of compounds, although the actual log $K_{\text{AW}}$ values vary at this iso-equilibrium temperature. As expected, VMS are highly hydrophobic compounds, and the $\Delta H_{\text{AW}}$ values of 5 VMS are located near those of the highly hydrophobic compounds such as alkanes and Freons. Although 3 volatile fluorotelomer alcohols possess some polarity, they are also located close to VMS. In contrast, TMS behaves more like alcohols and ketones. Nevertheless, log $K_{\text{AW}}$ for VMS had the weakest temperature dependence relative to other environmental contaminants of similar $\Delta S_{\text{AW}}$ values.

$K_{\text{OW}}$. Values of log $K_{\text{OW}}$ have been reported in the literature; however, as with values of log $K_{\text{AW}}$, they range widely among methods (Table 4). One source of experimentally measured log $K_{\text{OW}}$ values for VMS is recent studies using the slow-stirring method coupled with microextraction and gas chromatography/mass spectrometry analysis [38]. The slow-stirring method is designed to minimize the formation of octanol microdroplets in the aqueous phase; the reported log $K_{\text{OW}}$ values are very close to those obtained in the present study for the same temperatures. Another experimental study of log $K_{\text{OW}}$ for cVMS available in the open literature is that of Bruggeman et al. [39]. The measurements were made using an indirect method that relied on correlation of log $K_{\text{OW}}$ to measured HPLC retention times or indices on an octadecylsilyl-bonded silica column using alkylbenzenes as correlation standards. As analyzed recently by Xu et al. [21], there are 2 major issues with this method that render the log $K_{\text{OW}}$ values for cVMS unreliable. First, the octadecl-functionalized stationary phase is not a good surrogate for 1-octanol [40]. Second, alkylbenzenes are poor analogues for VMS compounds with respect to their molecular size and potential for van der Waals and hydrogen bonding interactions.

The linear relationship ($p << 0.01$ for 2-tailed test) between $\Delta H_{\text{OW}}$ and $\Delta S_{\text{OW}}$ (Figure 6) was also observed for siloxanes

$$\Delta H_{\text{OW}} = 259.1 \Delta S_{\text{OW}} - 31.5; \quad r^2 = 0.953 \quad (n = 5), \quad p \sim 0.004$$

The $K_{\text{OW}}$ values of IVMS and TMS show little temperature dependence, however, whereas those of cVMS have substantially more temperature dependence. The positive $\Delta H_{\text{OW}}$ and $\Delta S_{\text{OW}}$ values for all 6 organosilicon compounds are similar to those for benzoates, phthalates, and some phenolic compounds, but are different from those for CBs, PCBs, and sulfonamides, which usually have negative $\Delta H_{\text{OW}}$ values (Figure 6).

In short, the enthalpy and entropy compensation effects were observed for the 3 partition coefficients of all tested VMS, as shown by the linear relationship between their corresponding $\Delta H$ and $\Delta S$ values. Relative to common environmental contaminants in the literature, VMS have enthalpy and entropy compensation effects similar to those of alkanes for air/water partitioning and similar to polyfluorinated compounds for 1-octanol/air partitioning, but more like benzoates and phenolic compounds for 1-octanol/water partitioning.
**Table 4. Comparison of the room temperature partition coefficients for VMS and TMS**

| Comp   | T (°C) | $\log K_{OW}$ | $\log K_{AW}$ | $\log K_{OA}$ | $\delta^a$ | Source          |
|--------|--------|---------------|---------------|---------------|-------------|----------------|
| L2     | 25     | 5.20          | 2.49          | 2.89          | $-0.19$     | Present study  |
|        | 25     | 4.76          | 1.98          |               | $-1.3$      | [41]           |
|        | 25     | 2.60          | 2.98          |               |             | [26] (solubility) |
|        | 25     | 0.27          |               |               |             | [33] (VP)      |
|        | 25     | 4.2           |               |               |             | [25]           |
|        | 25     | 6.79          | 3.07          | 3.75          | $-0.03$     | Present study  |
|        | 25     | 5.35          | 2.52          |               | $-2.13$     | [41]           |
|        | 25     | 3.16          |               |               | $-0.01$     | [26] (solubility) |
|        | 25     | 2.13          |               |               |             | [33] (VP)      |
|        | 25     | 4.8           |               |               |             | [35]           |
|        | 25     | 6.60          |               |               |             | [39]           |
| L3     | 25     | 8.14          | 3.45          | 4.66          | 0.03        | Present study  |
|        | 25     | 5.93          | 3.12          |               | $-2.36$     | [41]           |
|        | 25     | 3.04          |               |               | $0.04$      | [26] (solubility) |
|        | 25     | 1.91          |               |               |             | [33] (VP)      |
|        | 25     | 6.11          |               |               |             | [35]           |
|        | 25     | 4.8           |               |               |             | [39]           |
|        | 25     | 8.13          |               |               |             | [38]           |
| L4     | 25     | 6.98          | 2.74          | 4.28          | $-0.04$     | Present study  |
|        | 22     | 6.98          | 2.69          | 4.29          | 0           | [20]           |
|        | 25     | 5.09          | 2.69          |               | $-2.55$     | [41]           |
|        | 25     | 2.43          |               |               | $0.04$      | [26] (solubility) |
|        | 20     | 4.31          |               |               |             | [34] (VP)      |
|        | 25     | 0.53          |               |               |             | [35]           |
|        | 28     | 1.37          |               |               |             | [36]           |
|        | 25     | 4.45          |               |               |             | [39]           |
|        | 25     | 6.49          |               |               |             | [38]           |
| D5     | 25     | 8.09          | 3.16          | 4.95          | $-0.02$     | Present study  |
|        | 25     | 8.07          | 3.13          | 4.94          | 0           | [20]           |
|        | 23     | 5.71          | 2.43          |               | $-2.18$     | [41]           |
|        | 25     | 2.25          |               |               | $0.04$      | [26] (solubility) |
|        | 25     | 5.2           |               |               |             | [34] (VP)      |
|        | 25     | 8.03          |               |               |             | [39]           |
|        | 23     | 0.74          |               |               |             | [38]           |
|        | 28     | 1.1           |               |               |             | [37]           |
|        | 25     | 4.95          |               |               |             | [35]           |
| TMS    | 25     | 1.39          | $-2.24$       | 3.62          | 0.01        | Present study  |
|        | 25     | 1.14          | $-2.74$       |               | 0.26        | [41]           |

$^a\delta = \log K_{OW} - (\log K_{OA} + \log K_{AW})$.

$K_{AW} = \text{air/water partition coefficient}; K_{OA} = 1\text{-octanol/air partition coefficient}; K_{OW} = 1\text{-octanol/water partition coefficient}; VP = \text{saturated vapor pressure};$ VMS = volatiles methylsiloxanes; L2 = hexamethyldisiloxane; L3 = octamethyltrisiloxane; L4 = octamethylcyclotetrasiloxane; D4 = decamethylcyclopentasiloxane.

**Internal consistency of partition coefficients and their temperature dependence**

One important characteristic of the 3-phase equilibrium method is its ability to generate internally consistent partition coefficients for any given compound at any given temperature. This was demonstrated for room temperature partition coefficients for D4, D5, D6, and dimethylsilanol by Xu and Kropscott [20], and for all compounds tested in the present study (Table 1). In addition, the internal consistency should also hold for enthalpy and entropy for all 3 partitioning processes for any given compound. In other words, for complete internal consistency among the partition coefficients, the discrepancies $\delta(\Delta H)$ and $\delta(\Delta S)$ as defined in Equations 12 and 13 should be equal to 0 for a given compound

$$\Delta H_{OW} = \Delta H_{OA} + \Delta H_{AW} + \delta(\Delta H) \quad (12)$$

$$\Delta S_{OW} = \Delta S_{OA} + \Delta S_{AW} + \delta(\Delta S) \quad (13)$$

For all 6 organosilicon compounds, $\delta(\Delta H)$ varied between $-7.8 \text{kJ mol}^{-1}$ and 1.7 $\text{kJ mol}^{-1}$, whereas $\delta(\Delta S)$ varied between 0.005 $\text{kJ mol}^{-1} \text{K}^{-1}$ and 0.027 $\text{kJ mol}^{-1} \text{K}^{-1}$ (Table 3). These values are not so different from the standard errors of $\Delta H_{OW}$ and $\Delta S_{OW}$, respectively. At temperatures between 0 °C and 35 °C, these discrepancies in $\Delta H$ and $\Delta S$ resulted in a maximum difference in partition coefficients between 0.15 log units and $-0.25$ log units. Judged by this effect, such discrepancies can be considered relatively small.

**CONCLUSIONS**

The suitability of the 3-phase equilibrium method for simultaneous determination of the temperature dependence of $K_{AW}$, $K_{OA}$, and $K_{OW}$ values was successfully demonstrated for 5 VMS compounds and TMS at temperatures between 4 °C and 35 °C. As expected, for any given compound, the measured partition coefficients at the different temperatures and the enthalpy and entropy changes for the corresponding partition processes all were internally consistent. The enthalpy and entropy compensation effects were observed for 3 partition coefficients of all VMS tested. Compared with literature data for common environmental contaminants, VMS have enthalpy and entropy relationships similar to those of alkanes in air/water.
partitioning, and similar to polyfluorinated compounds in octanol/air partitioning, but more like benzoates and phenolic compounds in octanol/water partitioning. The temperature dependence of the partition coefficients of TMS is different from those of VMS and more like that of alcohols, phenols, and sulfonamides.

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