Determination of Temperature-Dependent Henry's Law Constant of Four Oxygenated Solutes in Water Using Headspace Solid-Phase Microextraction Technique

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Dimensionless Henry's law constants (air/water partition coefficient K_{aw}) of four volatile organic compounds (VOCs), namely, methyl *tert*-butyl ether, vinyl acetate, dimethyl carbonate, and diethyl carbonate, are reported. Applying headspace solid-phase microextraction (HS-SPME) in combination with gas chromatographic analysis, whose response was calibrated by the use of standard gas mixtures, K_{aw} values ($0.001 < K_{aw} < 0.1$) were determined in the temperature range of (10 to 45) °C. Replicated measurements showed a good repeatability (average relative standard deviation 2.5 %, $n = 144$). The results were checked through additional K_{aw} measurements carried out using the inert gas stripping (IGS) technique at 25 °C, receiving intermethod deviations < 5 %. Furthermore, approximate values of hydration enthalpies ΔH_{hyd} and hydration entropies ΔS_{hyd} for the four VOCs were derived from linear van't Hoff fits of the $K_{aw}(T)$ data, demonstrating an enthalpy-driven partition process.

Introduction

Partitioning of volatile organic compounds (VOCs) between air and water has been recognized as a key process of determining their environmental behavior. Accordingly, knowledge of respective air/water partition coefficients K_{aw} (dimensionless Henry's law constants) is crucial for evaluating VOC transport and fate in the environment as well as for the design of efficient remediation procedures. In chemical industry, this information is essential for simulation of thermal separation processes. Because it is directly related to the solvation free energy, K_{aw} is also of interest for solution chemistry.

Unfortunately, accurate data on the air/water partitioning are often scarce and even lacking for many VOCs. Although there are various experimental techniques available,[1] solutes of low and moderate volatility still provide difficulties, calling for further method development and refinement.[1−3] Validated experimental data are also needed to extend the application range of methods for predicting K_{aw} from molecular structure,[4−6] the latter of which also includes models for predicting the temperature dependence of Henry's law constant.[5]

The focus of the present study was to apply a simple experimental method for the accurate determination of air/water partition coefficients of VOCs of moderate aqueous solubility (mole fraction solubility > 0.001) and moderate volatility ($0.001 < K_{aw} < 0.1$). To this end, static gas−liquid equilibration was combined with headspace solid-phase microextraction (HS-SPME) sampling and gas chromatographic analysis. The convenience of SPME for equilibrium studies in highly diluted systems has been recently demonstrated.[2,3,7−12] SPME enables easy headspace sampling of low analyte concentrations, ensuring a high degree of repeatability and accuracy and causing a minimum disturbance of the equilibrated system.[13]

For the determination of K_{aw} in this work, all experimental steps of the HS-SPME method were optimized; then, the entire procedure was thoroughly tested. The method has been applied to four oxygenated VOCs with large industrial production volumes, namely, methyl *tert*-butyl ether (MTBE), vinyl acetate (VAC), dimethyl carbonate (DMC), and diethyl carbonate (DEC), of which only MTBE has been previously studied with respect to air/water partitioning.[14−17] Whereas MTBE, which is used worldwide as a fuel additive, has become a notorious ubiquitous pollutant, the other compounds are still considered to be environmentally benign. VAC is used as a basic material for polymers and glues. DMC and DEC, labeled as green chemicals, find numerous applications, such as being substitutes for toxicologically precarious substances (such as phosgene) in organic synthesis. Widespread industrial usage of these VOCs and the complete lack of information on their air/water partitioning underline the necessity to determine such data. Therefore, for each of these VOCs, we performed ample replicated measurements to determine K_{aw} data at several temperatures in the range of (10 to 45) °C, which enabled us to evaluate the measurement repeatability and to derive approximate values of the solutes' hydration enthalpy and entropy. Finally, a validation of the HS-SPME method was carried out through a comparison with additional K_{aw} measurements by the use of the well-established inert gas stripping (IGS) technique and in the case of MTBE with literature data. Note that HS-SPME and IGS are based on distinctly different working principles, which makes this validation strong.

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Experimental Section

Materials. The VOCs used in this study for the HS-SPME experiments were MTBE (purity ≥ 99.5 %), VAC (≥ 99.0 %), DMC (≥ 99.0 %), and DEC (≥ 99.5 %), which were all supplied by Fluka. Bidistilled water was obtained from a GFL 2102 distillation apparatus (GFLmbH, Germany). SPME fibers (Supelco) coated with 100 μm poly(dimethylsiloxane) (PDMS) were used as sampling devices.

For the IGS measurements, VAC (Fluka, purity 99 + %), MTBE (Aldrich, 99 + %), DMC (Aldrich, 99 %), and DEC (Aldrich, 99 + %) were used. Water was distilled and subsequently treated by a Milli-Q water purification system (Millipore).

Headspace Solid Phase Microextraction with Gas Chromatography. The equilibrium apparatus consisted of three jacketed glass equilibrium cells of 200 mL capacity each and was equipped with a magnetic stirring device. (See the Supporting Information.) The cell design allowed for easy headspace SPME sampling and efficient thermostatization of cell contents. The exact volume of each cell was gravimetrically determined with distilled water at ambient temperature. The thermostatization of the cells was provided by an FP 40 circulating thermostat from Julabo (± 0.05 K). SPME fiber holders with 100 μm PDMS fibers were used for the sampling. The PDMS fibers were selected for the present application because the PDMS coating, as a result of its nonpolar character, is less sensitive to the humidity of the sampled air phase than are some other polar coatings (e.g., polyacrylate (PA) or divinyl benzene (DVB)).[18,19] Furthermore, the PDMS fibers, in combination with the flame ionization detection (FID), have been shown to exhibit a broad range of the response linearity.[18]

At the beginning of an experiment, each of the three equilibrium cells was gravimetrically loaded with ~100 mL of solvent water. For thermostatization, the water was stirred at 1000 rpm for about 30 min. Subsequently, a small amount of solute was gravimetrically added to each cell by a gastight syringe such that the solute molar fraction did not exceed 0.001. Accordingly, low solute concentrations effectively ensure the condition of infinite dilution. With stirring continued, the system was then allowed to equilibrate for at least 3 h. Meanwhile, the SPME fiber (along with its holder) was tempered to the experimental temperature in a climate chamber to avoid thermal differences between the sampling matrix and the air phase inside an equilibrium cell. Because any further extension of the equilibration time (up to 24 h) did not affect the measured headspace concentration, the 3 h equilibration period was considered to be sufficient for a complete establishment of the air/water distribution equilibrium of the test chemicals. After equilibration, the air phase of the cell was sampled with the SPME fiber for 15 min. This exposure time was sufficient for establishing the air/fiber partition equilibrium, as determined by preliminary experiments in which we observed that the equilibrium conditions could be reached independently of the stirring speed in only about 5 min. Following the extraction, the fiber was retracted into the assembly sleeve and quickly transported to a gas chromatograph where it was inserted into its injector unit. Thermodesorption of the fiber contents was carried out for 2 min at 250 °C. Prolongation of the thermodesorption showed no remaining substance on the fiber.

The gas chromatograph used in this work was a CP 9001 model from Chrompack International equipped with a thermodesorption unit (injector) for the fiber, a CP SIL 5 MS column (30 m, 0.32 μm i.d., $d_f = 1$ μm) that was also from Chrompack International, and a flame ionization detector (FID). GC control, data acquisition, and evaluation were accomplished by Maitre Chromatography Data System version 2.5 software from Chrompack International.

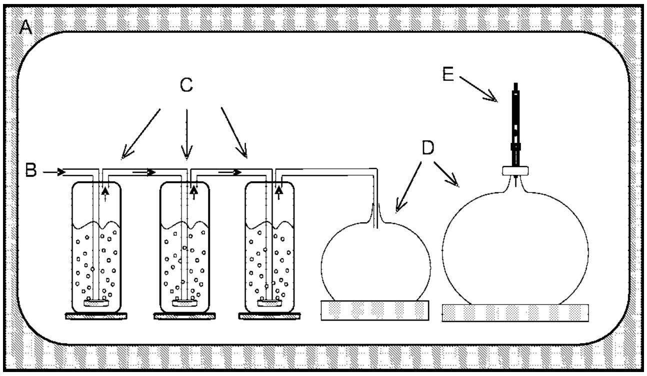

Figure 1. Setup for the generation of vapor phase calibration standards: (A) thermostatting air bath chamber, (B) air flow inlet, (C) washing flasks for air humidification, (D) bulbs for gas standards, (E) SPME fiber with its holder.

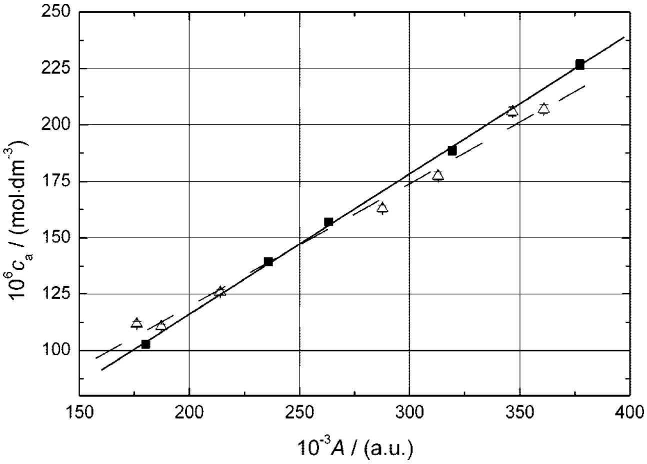

Figure 2. Effect of water on GC response for the HS-SPME method. DMC air phase concentration c_a against its peak area A (calibration points and respective straight line fits): Δ, ---, dry air; ■, −, air saturated with water vapor.

We established a calibration method for the HS-SPME by using the total vaporization technique[20] using an auxiliary setup for the generation of the vapor phase standards shown in Figure 1. The setup consisted of presaturation washing flasks for air humidification and two bulbs of different volumes (2.2 and 6.5 L) for the vapor phase standards. For each solute and temperature, the calibration function was based on 6 to 10 calibration points using the following procedure. First, we thoroughly flushed the bulbs with air saturated with water vapor. This was essential because the impact of air humidity on the uptake of target molecules by the PDMS fiber has been previously observed[19,21] (exemplified in Figure 2), and their closely mimicking in the calibration of the HS measurements was necessary for correct results to be obtained. As soon as the calibration bulb was filled with the humidified air, the liquid analyte was gravimetrically added by injection with a gastight syringe through the septum of the sampling port of the bulb. After 1 h, which was allowed for total analyte evaporation and concentration homogenization, the air-phase standard was ready for sampling. Then, the same fiber and sorption/desorption times (15 min/2 min) as those for the analysis of the equilibrium cell headspace were used.

Calibration points were obtained ad hoc for a range of concentrations that were expected for the equilibrium cell

Table 1. Air/Water Partition Coefficients (K_{aw}) at Different Temperatures for Methyl *tert*-butyl Ether (MTBE), Vinyl Acetate (VAC), Dimethyl Carbonate (DMC), and Diethyl Carbonate (DEC) Together with Their Corresponding Standard Uncertainties ($s(K_{aw})$), Number of Measurements (n), and Relative Standard Deviation (RSD)

substance	method	T/°C	$10^3(K_{aw})^a$	$10^3(s(K_{aw}))$	n	RSD (%)
MTBE	HS-SPME	10	11.3	0.6	6	2.9
	HS-SPME	15	15.6	0.9	5	7.4
	HS-SPME	25	31.9	1	18	3.1
	IGS	25	31.5	0.8	3	0.9
	HS-SPME	35	57.4	1.5	6	1.9
	HS-SPME	45	97.5	5	5	1.3
VAC	HS-SPME	10	9.35	0.4	12	5.1
	HS-SPME	15	12.8	0.6	6	2.7
	HS-SPME	20	16.3	0.8	3	0.1
	HS-SPME	25	20.4	0.9	18	3.9
	IGS	25	19.4	0.5	3	3.1
	HS-SPME	30	25.4	1	3	0.4
	HS-SPME	35	32.3	1	6	2.1
	HS-SPME	45	45.9	2	6	1.6
DEC	HS-SPME	10	1.24	0.06	6	1.2
	HS-SPME	15	2.11	0.1	4	1.9
	HS-SPME	25	4.14	0.2	3	2.6
	IGS	25	4.20	0.1	3	0.7
	HS-SPME	35	7.25	0.2	5	1.1
	HS-SPME	45	12.3	0.3	6	1.3
DMC	HS-SPME	10	1.09	0.06	5	3.0
	HS-SPME	15	1.53	0.1	6	5.6
	HS-SPME	25	2.67	0.1	3	0.3
	IGS	25	2.58	0.05	3	0.4
	HS-SPME	35	4.42	0.2	8	2.6
	HS-SPME	45	6.62	0.4	4	1.8

[a] Mean of n replicates.

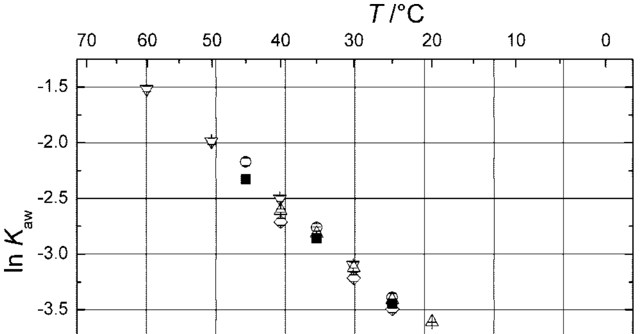

Figure 3. Temperature dependence of air/water partition coefficient of MTBE: ■, this work (HS-SPME); ○, Hiami et al.;[14] Δ, Arp et al.;[15] ▽, Atik et al.;[16] ◇, Fukuchi et al.[17] (Air/water partition coefficients were calculated from the reported limiting activity coefficients using vapor pressure data of Krähenbühl and Gmehling.[26])

headspace. For all solutes and temperatures studied, the calibration data (analyte's air-phase concentration vs analyte's peak area) exhibited a very good linearity. Straight line fits with small but statistically significant intercepts were found to represent the calibration data adequately with coefficients of determination of $r^2 \geq 0.994$ and relative standard deviations of fits of about 3 %.

We determined the air/water partition coefficients from the HS-SPME measurements using the following formula

$$K_{aw} = \frac{c_a}{c_w} = \frac{c_a}{\left[c_w^0 - c_a\left(\frac{V_a}{V_w}\right)\right]} \tag{1}$$

where c_a and c_w are the solute equilibrium concentrations in the gas and the liquid phase, respectively, V_a and V_w are the volumes of the respective phases, and c_w^0 is the initial solute concentration in the liquid phase. Calculations of standard uncertainties were performed according to error propagation law.

Inert Gas Stripping Method. To validate the performance of the applied HS-SPME technique, we carried out some parallel measurements by the IGS method. In this method, an entraining inert gas is passed through a highly dilute solution, and the rate of the solute elution is measured with periodic analysis of the outlet gas by gas chromatography. We have implemented a refined version of the IGS method and have applied it to a large number of aqueous[22,23] as well as nonaqueous systems.[24,25] The typically achieved standard uncertainty of below 3 % over a broad K_{aw} range ($0.0001 < K_{aw} < 1$) allows us to use it as a reference technique for validation. In the following, we confine the IGS description to aspects that are relevant to the present application; for more details, the reader is referred to the literature.[22−24]

Two equilibrium cells of similar design[22,23] but of different capacities (13/17 cm^3 and 35/47 cm^3 (liquid loading/total volume)) were alternatively used to accommodate different solute volatilities (air/water partition coefficients). The flow rate of the stripping gas (nitrogen) was controlled with an Aalborg DFC 26 mass flow digital controller and was checked against a bubble flow meter. The flow rates were set from (7 to 18) cm^3·min^{-1} to give small relative rates of the solute elution (~0.01 min^{-1}). Presaturation of the stripping gas with the solvent vapor was used in all experiments. The process of the solute elution was monitored during (3.5 to 8) h; the sampling interval was from (12 to 30) min.

The employed gas chromatograph was a Hewlett-Packard Model 5890 II with an FID. The instrument was equipped with two pneumatic gas sampling valves that have (125 and 250) μL sampling loops and a wide-bore (0.53 mm) 15 m long capillary column DB-WAX ($d_f = 1$ μm). The gas sampling valves were kept at 150 °C, and the GC analysis was performed in the splitless injection mode at a constant oven temperature of 50 °C. The operation of the entire GC, including the controls of the carrier gas flow rate and all zone temperatures, sample injection, data acquisition, and processing, was provided by an interfaced personal computer using Agilent ChemStation software.

Air/water partition coefficients were determined from the IGS measurements using the following formula

$$K_{aw} = \left(\frac{V_w}{D}\right)\left(\frac{-\mathrm{d}\ln A_1}{\mathrm{d}t}\right)\left(1 - \frac{P_2^S}{P}\right)\xi \tag{2}$$

where V_w is the volume of the highly dilute solution loaded into the stripping cell, D is the flow rate of the neat stripping gas at temperature T and pressure P of the cell, $(\mathrm{d} \ln A_1)/(\mathrm{d}\, t)$ is the slope of the semilogarithmic plot of solute peak area A_1 against time t, and P_2^S is the saturated vapor pressure of the solvent water at the temperature of the cell. The volume V_w was determined gravimetrically using the density of neat water. The last term in eq 2

$$\xi = \left[1 - \left(\frac{-\mathrm{d}\ln A_1}{\mathrm{d}t}\right)\left(\frac{V_a}{D}\right)\right]^{-1} \tag{3}$$

is a correction factor that is close to unity (for systems studied in this work, $1 < \xi < 1.02$) and accounts for the amount of

Table 2. Temperature Dependence of Air/Water Partition Coefficient of Four VOCs: Calculated Parameters A and B of the Linear van't Hoff Plot, Standard Deviation of the Fit (s_{fit}), Coefficient of Determination (r^2), Hydration Enthalpy (ΔH_{hyd}), and Hydration Entropy ($T \cdot \Delta S_{\mathrm{hyd}}$) at 298.15 K along with Their Standard Uncertainties

substance	A / K	B	s_{fit}	r^2	ΔH_{hyd} / $\mathrm{kJ \cdot mol^{-1}}$	$s(\Delta H_{\mathrm{hyd}})$[a] / $\mathrm{kJ \cdot mol^{-1}}$	$T \cdot \Delta S_{\mathrm{hyd}}$ / $\mathrm{kJ \cdot mol^{-1}}$	$s(T \cdot \Delta S_{\mathrm{hyd}})$[a] / $\mathrm{kJ \cdot mol^{-1}}$
MTBE	−5602	15.170	0.032	0.999	−46.6	0.8	−37.9	0.8
VAC	−4075	9.764	0.032	0.997	−33.9	0.8	−24.2	0.8
DMC	−4645	9.623	0.042	0.998	−38.6	1.1	−23.9	1.1
DEC	−5770	13.789	0.091	0.993	−48.0	2.4	−34.2	2.4

[a] Calculated by error propagation law from regression statistics.

solute in the vapor space (volume V_a) of the cell. Equation 3 disregards the change in the stripping gas flow rate that is due to the solute evaporation in the cell, which was found to be negligible for the solutes and conditions examined.

Results and Discussion

Using the HS-SPME procedure, we measured air/water partition coefficients for MTBE, VAC, DMC, and DEC at five temperatures in the range of (10 to 45) °C. Extensive replication of experiments was carried out to evaluate measurement repeatability. The results are summarized in Table 1. The measured K_{aw} values span two orders of magnitude from about 0.001 for DMC at 10 °C to 0.1 for MTBE at 45 °C. Replicated measurements showed a very good measurement repeatability (average relative standard deviation 2.5 %, $n = 144$). The combined standard uncertainties, which we estimated from the error propagation law considering contributions from all possible sources of error, also have favorable values (on average about 5 %). Among the four oxygenated VOCs studied, MTBE exhibits the highest volatility from aqueous solution. The K_{aw} values of the solutes decrease in the order MTBE > VAC > DEC > DMC, thus following the increase in relative oxygen content of the molecules. All four VOCs exhibit a higher affinity for the aqueous phase than for the air phase.

To validate the HS-SPME results, we carried out additional K_{aw} measurements by the IGS technique at 25 °C. The respective results are also included in Table 1. The intermethod deviations are below 5 %, which can be regarded as an excellent agreement, keeping in mind that the two methods are based on different measurement principles; the measurements were carried out in two different laboratories and even with two different solute samples. Note that under such conditions, literature air/water partitioning data are typically observed to deviate much more; a 20 % tolerance is thus often accepted as a reasonable accord.

In Figure 3, the K_{aw} temperature dependence of MTBE as determined by HS-SPME is compared with respective literature data from four different sources. As can be seen from Figure 3, our HS-SPME measurements are in reasonable agreement with the literature results. Note that at lower temperatures, our data have somewhat larger deviations (> 15 %) from both Hiami et al.[14] and Arp and Schmidt[15] and are closer to the data of Fukuchi et al.[17] (∼5 %). However, for VAC, DMC, and DEC, no comparison with literature results is possible because the literature information here is totally lacking.

For a more detailed analysis of the thermodynamics of the air/water phase transfer of the four compounds, conventional straight line fits of the measured $K_{\mathrm{aw}}(T)$ data in the van't Hoff coordinates

$$\ln K_{\mathrm{aw}} = \frac{A}{T} + B \tag{4}$$

provide a reasonable approximation in the temperature range investigated. To get some insight into the thermodynamics of the air/water phase transfer of the compounds studied, we inferred corresponding contributions of hydration enthalpy and entropy from

$$\Delta H_{\mathrm{hyd}} = -RT^2\left(\frac{\mathrm{d} \ln K_{\mathrm{aw}}}{\mathrm{d}\, T}\right) = R \cdot A \tag{5}$$

$$T \cdot \Delta S_{\mathrm{hyd}} = -RT \cdot B \tag{6}$$

Table 2 lists the calculated parameters A and B together with some statistical characteristics of regression. Moreover, hydration enthalpies and entropies and their corresponding standard uncertainties are reported in Table 2. Values of the standard deviation of the fit s_{fit} and the found coefficient of determination r^2 indicate that the fits are quite good despite the simple temperature dependence of K_{aw} given by eq 4. Note that when $K_{\mathrm{aw}}(T)$ data over a temperature range that is broader than those studied in this work are considered, the straight line fit (eq 4) and the derived ΔH_{hyd} (eq 5) and $T \cdot \Delta S_{\mathrm{hyd}}$ (eq 6) values should be considered to be approximate because the temperature dependency of ΔH_{hyd} cannot be neglected, which results in a significant curvature of the van't Hoff plot. (Large positive hydration heat capacities that are comparable to those determined for some alcohols and ethers[27] are also expected for the presently studied solutes.) The considerably negative hydration enthalpies indicate that despite the somewhat hydrophobic nature of the solutes, aqueous solvation is favorable through solute−solvent interactions overcompensating the energy penalty needed for cavity formation. In the case of MTBE with a molecular surface largely determined by its methyl groups, ΔH_{hyd} is most likely governed by van der Waals interactions, whereas the greater oxygen contributions to the molecular surface of VAC, DMC, and DEC provide more opportunity for H-bonding interactions with water (at the cost of water−water H-bonding). The largest exothermic hydration enthalpy (i.e., the strongest effect of temperature on K_{aw}) is exhibited by DEC and further decreases in the sequence DEC > MTBE > DMC > VAC. In accordance with the expectation, ΔS_{hyd} is negative for all four compounds, reflecting the increase in order upon phase transfer from the gas phase into aqueous solution. When the contributions of ΔH_{hyd} and $T \cdot \Delta S_{\mathrm{hyd}}$ are compared, it appears that for all four VOCs, the air/water phase transition process at ambient and near-ambient temperatures is enthalpy driven.

Among the four VOCs, only MTBE and VAC belong to the chemical domain of our recently developed group contribution model for predicting ΔH_{hyd} from molecular structure.[5] The accordingly predicted values are $-49.8\ \mathrm{kJ \cdot mol^{-1}}$ (MTBE) and $-30.0\ \mathrm{kJ \cdot mol^{-1}}$ (VAC) and thus agree reasonably well with our experimental measurements. With respect to DMC and DEC, the new experimental data provide an opportunity to extend the existing prediction schemes to the chemical class of carbonates.

Conclusions

Although all four oxygenated VOCs investigated here are industrial chemicals that are applied worldwide, current knowledge of their air/water partitioning behavior in literature had been insufficient or even totally lacking. The present work partially compensates for this data gap. The applied HS-SPME in combination with GC analysis provides reliable K_{aw} data in the temperature range of (10 to 45) °C. To ensure the accuracy of measurements, it is inevitable to calibrate the SPME fiber in the standard gas atmosphere at a temperature and air humidity that are identical to those of the air/water distribution experiment.

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Supporting Information Available:

Drawing of the equilibrium cell used for the experiments. This material is available free of charge via the Internet at http://pubs.acs.org.

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