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Cross Determination of the Vapor Liquid Equilibrium of Formaldehyde Aqueous Solutions by Quadrupole Mass Spectrometry and Infrared Diode Laser Spectroscopy

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Quantitative measurements of the partial vapor pressure of formaldehyde are performed above aqueous H_2CO solutions of different concentrations (from 10^{-5} to 0.3 molar fraction) using mass spectrometry and IR diode laser spectroscopy. Both experimental techniques allow direct probing of the gas phase concentration collected at equilibrium above the aqueous solutions. A correlation is observed between the polymerization processes occurring in the solution and the partial pressure of H_2CO measured at vapor liquid equilibrium (VLE). A similar correlation is observed from total pressure measurements for which the equilibrium vapor pressure decreases as $[\chi_{H_2CO}^{VLE}]_{liq}$ is increased. A saturation regime of the H_2CO partial pressure is reached as the dissolved fraction of formaldehyde increases above ~0.15 mol frac. Henry's law constants are derived at 295K for the diluted solutions.

Introduction

Formaldehyde plays an important role in chemical industry, where it is a key reactant in many technological processes (*1*). It is a significant component of many manmade materials (solvents, plastics, resins, paper, fertilizers, etc.). The description of the vapor liquid equilibrium (VLE) behavior of the system formaldehyde–water is thus of great importance for the chemical industry. Furthermore, the study of VLE and the determination of thermodynamic properties of formaldehyde solutions have been the focus of several research groups over the last 80 years (*1–6*). Most of these studies were carried out at relatively high temperatures (313–373K) and total pressures between 20 and 760 Torr. However, large discrepancies exist for the gas phase data above concentrated aqueous solutions at lower temperature (293 K), with partition coefficients differing by a factor of 30

(*5*). These discrepancies may illustrate possible experimental pitfalls when the gas phase concentration is measured indirectly, i.e., after recondensation into a liquid.

Formaldehyde is also of great current interest in atmospheric chemistry, as it is a key constituent involved in several important processes occurring in the atmosphere, for instance in the production of HO_x radicals that governs the tropospheric ozone cycle (*7*). It can be directly emitted in the atmosphere by anthropogenic and natural sources, but can also be formed as an intermediate product of the atmospheric hydrocarbons photo-oxidation. Previous studies showed that the reaction of formaldehyde with nitric acid in sulfuric acid aerosols could provide a pathway for HNO_3 conversion to NO_x (*8, 9*). It was shown that the solubility of formaldehyde can be greatly enhanced in such cold acid droplets typically found in the free troposphere, thus efficiently removing H_2CO from the gas phase and increasing in significant levels the formaldehyde content in rain, snow and fog (*10, 11*). More recently, it was demonstrated that the heterogeneous chemistry of formaldehyde is involved in the snowpack chemistry (*12*). The snowpack was found to be photochemically active, producing and emitting formaldehyde into the atmosphere at elevated concentration in coastal and ice-cap sites of Polar regions. The mechanism at the origin of the formaldehyde production remains, however, controversial as the incorporation/partitioning of formaldehyde in ice crystals has to be determined first.

The partitioning of formaldehyde between the gas phase, the liquid and the solid phases is thus an important parameter in both the atmospheric and industrial context. Indeed, the phase in which formaldehyde exists can significantly influence its physical and chemical properties with respect to its behavior and fate in the environment. In previous studies, we investigated the interaction of small organic compounds (formaldehyde, ethanol) with water or ice in many different concentration and temperature regimes using Raman spectroscopy (*13–15*). Thin doped ice films can be produced by simultaneous condensation of the vapor phase sampled at VLE over formaldehyde aqueous solutions. In order to derive meaningful data for the influence of composition on the structure of the condensed film, it is important to determine the concentration of H_2CO in the collected vapor.

We investigate here, quantitatively, the VLE of formaldehyde aqueous solutions of different concentrations at room temperature by directly probing the gas phase above the solutions. The cross determination of the gas phase concentration is performed using mass spectrometry and infrared diode laser spectroscopy techniques in two completely independent set-ups. Vapor pressures at atmospherically relevant formaldehyde concentrations are investigated to derive Henry's coefficients.

Experimental Methods

Preparation of Aqueous Formaldehyde Solutions. Aqueous formaldehyde solutions of different concentrations (between 10^{-5} and 0.3 mol frac.) are prepared according to the classical procedure described in refs *1 and 13*. Briefly, solid paraformaldehyde (Sigma-Aldrich) is depolymerised in double distilled and deionized water (resistivity 18 MΩ cm^{-1}) produced by UHQ PS (Elgastat). The appropriate amounts of paraformaldehyde and distilled water are heated at 373 K during 10 min. Droplets are formed on the cap placed at the top of the flask. This method avoids too much water loss during boiling. To help the depolymerisation, three drops of 0.1 M sodium hydroxide solution are added. After cooling down to room temperature the formaldehyde solutions are reweighted and

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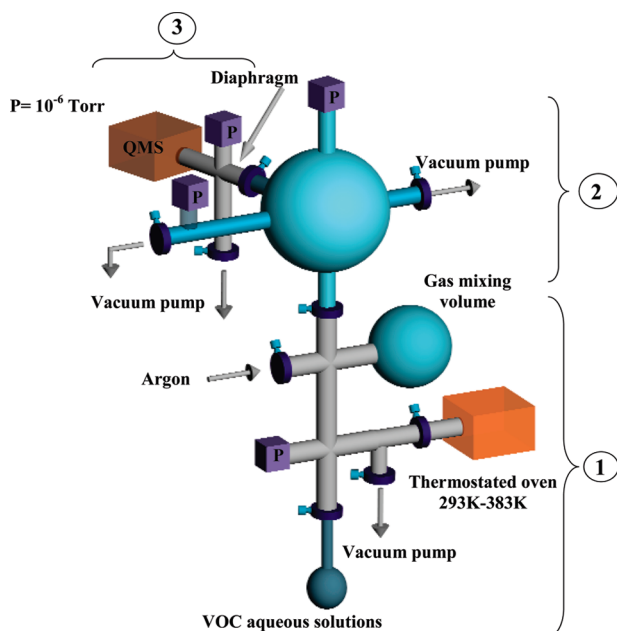
FIGURE 1. Experimental setup used for the determination of gas phase composition of equilibrated aqueous formaldehyde solutions. 1 corresponds to the gas mixture line preparation (H_2CO/Ar, $H_2CO/H_2O/Ar$). 2 corresponds to the intermediate pressure stage (50 Torr); 3 analysis chamber of the quadrupole mass spectrometer (QMS); P refers to pressure gauge. Calibration of the QMS is performed using the flowing argon line and the thermostatted oven in which molecular formaldehyde is produced by sublimation of paraformaldehyde. During the analysis of the gas phase above VOC aqueous solutions, the flowing argon line is used to homogenize the collected vapor mixture of VOC and water. The diaphragm helps to guide the molecular flow to the ionization source of the QMS.

the necessary volume of double distilled water is added in order to compensate for the water loss during boiling. The exact amount of formaldehyde in the liquid samples is determined by adding an excess of sodium sulfite and titrating with a hydrochloric acid solution. The end-point of the titrations is detected by pHmetric measurements. Even though our solutions are not stabilized with methanol, they provide a stable liquid phase over a period of a few days, at least for the most concentrated ones, and up to several months for the others.

Once prepared, the formaldehyde solutions are pumped down to 10^{-1} Torr and are allowed to equilibrate with the gas phase for at least 14 h at room temperature before analysis of the gas phase. This time interval has been found necessary to obtain reproducible results. We assume that it is the time necessary to achieve complete equilibration between the liquid phase and the gas phase, though no data on the equilibration time are available so far. Once equilibrated, total pressure measurements above the solutions are performed using an active strain gauge (AGS 1−1000 Torr, BOC Edwards, accuracy ±0.2% full scale).

Mass Spectrometry Experimental Setup. Mass spectra in the range 1−200 atomic mass unit (amu) are recorded by a quadrupole mass spectrometer (Pfeiffer Vacuum, model Prisma QMS 200M). A schematic representation of the setup is displayed in Figure 1. The QMS chamber is turbo-pumped down to a residual pressure of 10^{-8} Torr (controlled with a hot cathode PBR 260 Pfeiffer compact full range gauge). The apparatus can work alternatively in scan analog or multi ion detection (MID) modes. The MID mode allows the continuous recording of the time evolution of the ion current for predefined masses. The gas mixing line connected to the

QMS chamber is pumped with a rotary pump (5 m³/h) (residual ~10^{-2} Torr) and serves for preparation of gas mixtures typically at 400 Torr. Because of the large difference of working pressure between the spectrometer chamber and the mixing line, gas expansion can produce substantial fractionation effects. A 4 L round-bottomed flask is added to the system as an intermediate stage (working pressure of 50 Torr) to prevent such effects. It is maintained at a residual pressure of 10^{-5} Torr before gas introduction using a Pfeiffer Vacuum turbo molecular pumping unit (60 L/s). The flask volume allows the storage of an important gas reservoir, thus avoiding any pressure drop during the MID measurements. Gas introduction between the different chambers is performed via manually operated all-metal gas dosing valves (MD5 from K. J. Lesker and UDV 146 from Pfeiffer Vacuum, respectively). The pressure is measured either by the active strain gauge in the 1−1000 Torr range or by an absolute pressure transducer (MKS Baratron model 627B, accuracy 0.15% of reading) in the 0−1 Torr range.

The evolution of the H_2CO signal can be followed either with the parent ion signal at $M/z = 30$ or with the ionization fragment at $M/z = 29$. However, the signal at $M/z = 29$ can also correspond to isotopic nitrogen from residual air present in the mass spectrometer chamber during the gas analysis. To avoid any interference, argon is preferred as carrier gas instead of nitrogen and only the evolution of the ion signal at $M/z = 30$ is considered in the next measurements. It should be noted that the gas analysis of the formaldehyde vapor content performed without any carrier gas is found to be non reproducible. This has to be taken as evidence for an important interaction of formaldehyde and water with the walls of the vacuum line. Therefore, the gas phase collected above the solutions at equilibrium is diluted in argon before being analyzed with the QMS.

The response of the mass spectrometer to formaldehyde (conversion of ionic current into molar fraction) is calibrated using Ar/H_2CO gas mixtures of known composition. Molecular formaldehyde vapor is obtained by heating solid paraformaldehyde at 358 K in a stainless steel oven with adjustable temperatures between 303 and 393 K with 0.1 K accuracy. The Ar/H_2CO gas mixtures are prepared so as to obtain calibration points in the range $10^{-5}−10^{-3}$ formaldehyde molar fraction. The molar fraction of formaldehyde in the gaseous mixture prepared in static conditions is given by

$$[\chi_{cal}] = \frac{P_{H_2CO}}{P_{Ar} + P_{H_2CO}} \qquad (1)$$

where P_{H_2CO} and P_{Ar} are the partial pressures of formaldehyde and argon, respectively. Total pressure of these diluted formaldehyde samples reaches 400 Torr in the mixing line. Supporting Information (SI) Figure S1 displays a typical MID scan showing the time evolution of the ionic current for the corresponding masses of formaldehyde ($M/z = 30$) and argon ($M/z = 40$). The evolution of the pressure in the mass spectrometer chamber is also represented. Signal measurements are taken at the plateau, when the final pressure in the QMS chamber has reached a stable value of 10^{-6} Torr, up from the residual 10^{-8} Torr pressure. Signal variations recorded before reaching the plateau at $P = 10^{-6}$ Torr correspond to the manual adjustment of the gas dosing valve during the introduction of the gas and are not considered here. The signal decreases down to its residual value in a few seconds after closing the valve.

A linear relationship between the H_2CO molar fraction and the spectrometer output is obtained after the analysis of different gaseous mixtures Ar/H_2CO. A calibration curve is given in SI Figure S2.

IR Setup. The optical layout of the infrared tunable diode laser (TDL) spectrometer (*16*) is shown schematically on SI

Figure S3. The cw (continuous wave) radiation of the tunable diode laser (Laser Photonics L5830) is split into two beams. The first beam probes a 10 cm long reference cell filled with a few Torr of pure formaldehyde and is used to stabilize the emission frequency at the top of the line (*17*). The other beam is loosely focused at the entrance hole of a Herriott-type multiple pass cell (MayComm Research Company, volume 7.7 L, base length 50 cm, two gold-coated 4.25-in mirrors with >99% reflectivity) adjusted to an optical length of 34 m. Both beams are focused on HgCdTe liquid nitrogen cooled detectors. The diode frequency is centered at 2829.5 cm^{-1} and modulated at 9.943 kHz. The signal from the multipass cell is demodulated at twice the modulation frequency (2f signal) by a digital lock-in amplifier (SR830, Stanford Research Systems, integration time 100 ms). Other transitions can be probed between 2800 and 2850 cm^{-1}, but this specific line has been preferably chosen due to its strong intensity and absence of interference from any other gas (*18*). This absence of interference is checked before the quantification of formaldehyde in the sample by scanning around the absorption feature.

The Herriott cell is evacuated by a 5 m (*3*)/h rotary pump. Pressure is measured inside the cell with an absolute 0–100 mbar pressure gauge (Keller). Two electromagnetic valves control the injection of the calibration and sample gases inside the multipass cell. A third electromagnetic valve allows isolating the cell from the pumping system. A custom LabVIEW software code controls the acquisition, the opening and closing sequences of the electromagnetic valves, and performs the real time data analysis.

2f absorption signal and pressure are simultaneously acquired during both the pressure increase and the pressure decrease stages, between 1 and 11 Torr.

The signal can be analyzed as a function of pressure as

$$S = a + b(P - cP^2) \qquad (2)$$

where S and P are the 2f signal and pressure, b is the slope close to origin of the S vs P curve, c a positive coefficient representing the line broadening effect that tends to attenuate the signal increase, and a an offset term introduced to take into account the 2f residual mode curvature in the absence of absorbent, coming from interference signals created by the optical elements outside the absorption cell. The curvature term c is fixed to the value determined at high concentration with the calibration point. The molar fraction is proportional to the slope and the absolute mole fraction is obtained when generating formaldehyde at a known mixing ratio using a permeation tube with nitrogen as carrier gas.

With this spectrometer, mole fractions down to about 1 ppb can be determined with a 10% precision, which is mainly limited by the precision on the permeation rate of the tube used for calibration. Validation of the instrument has been demonstrated in indoor H$_2$CO comparative study by the TDL spectrometer vs conventional 2,4-DNPH samplings followed by HPLC analysis (*19*). One of the main advantages of the IR spectrometer and measurement method lies in the fact that small volume samples can be analyzed, as only 7 L at about 12 Torr are needed for one measurement.

As the spectrometer is primarily used for trace gas quantification, it is necessary to avoid as much as possible the contamination by highly concentrated samples, as the formaldehyde can adsorb onto and afterward desorb from all components in the cell and gas handling system. For this reason, all H$_2$O/H$_2$CO samples were adequately diluted with Argon before analysis so as to fall below or about the ppm range.

Results and Discussion

Equilibrium Pressure of Formaldehyde–Water Mixtures. Total pressure measurements (P_{VLE}) as a function of formaldehyde sample concentration are given in Figure 2 and
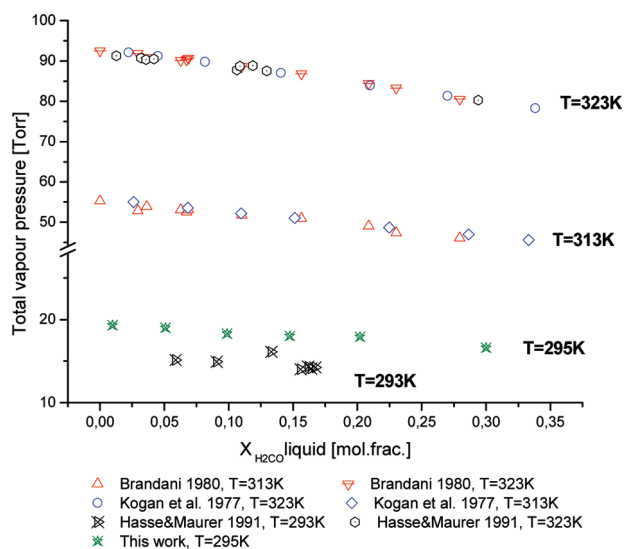
FIGURE 2. Equilibrium total vapor pressure as a function of the H$_2$CO concentration (molar fraction) in the aqueous solutions. Note the decrease of the vapor pressure as the content of dissolved H$_2$CO in the solution increases (see discussion).

compared with literature data. They show a decrease of the pressure as the dissolved fraction of formaldehyde in the aqueous solution increases (see also Table 1). This effect, already observed by Brandani et al., 1980 (*4*), could be explained by the increasing presence of nonvolatile higher-mass oligomers in the solution (see below) and the decrease of the more volatile ones (methylene glycol). Consequently, the contribution of molecular formaldehyde to the vapor pressure, which is mainly given by the dehydration of methylene glycol (*1*), tends significantly to be reduced. This tendency is much more pronounced at higher temperatures but is also noticed at temperatures around 295K.

Formaldehyde Molar Fraction in the Gas Phase. The formaldehyde molar fraction measured with the QMS or with the IR diode laser is directly converted into molar fraction above the solution by taking into account the argon dilution factor.

The partial pressure P_{H_2CO} above the aqueous formaldehyde solution is then calculated from the measured values of $[\chi_{H_2CO}^{VLE}]_{gas}$ and P_{VLE} as

$$P_{H_2CO} = [\chi_{H_2CO}^{VLE}]_{gas} \times P_{VLE} \qquad (3)$$

All equilibrium vapor pressure measurements are summarized in Table 1 for solutions of dissolved fraction of formaldehyde in the range 10^{-5}–0.3 molar fraction. Due to a better sensitivity of the IR absorption setup, gas phase analysis can be conducted for very diluted solutions (from 10^{-5} to 0.2 mol frac.), whereas QMS measurements are obtained for solutions in the range ~0.01–0.3 mol frac. For these latter solutions, a good agreement is found for $[\chi_{H_2CO}^{VLE}]_{gas}$ when comparing results obtained with the two techniques (Table 1).

Figure 3 displays the formaldehyde molar fraction in the gas phase as a function of the dissolved fraction of formaldehyde in the liquid water system. Our results are compared with data reported previously by Hasse and Maurer (1991) (*5*), Kogan et al. (1977) (*3*), Korzhev and Rossinskaya (1935) (*6*), and Piret and Hall (1948) (*20*) at temperatures between 293K and 313K.

Korzhev and Rossinskaya (1935) (*6*) and Piret and Hall (1948) (*20*) both used vacuum distillation techniques. Their results are found in relatively good agreement with our work. In contrast, the partial pressure measured by a gas saturation method (*3, 5*) is about two times higher than in the present

TABLE 1. Vapor Pressure and Formaldehyde Concentration in the Gas Phase above Aqueous Solutions of Different Mol. Frac. Of Dissolved Formaldehyde at 295 K[a]

liquid phase		gas phase			
X^b (mol frac.)	P_{total} (Torr)	$Y_{QMS}{}^c$ (mol frac.)	$Y_{IR}{}^c$ (mol frac.)	$P_{H_2CO}^{VLE}$ gas (Torr)	Y/X
10^{-5}	19.6		$1.17 \times 10^{-5} \pm 1.2 \times 10^{-6}$ (7)	$2.3\ 10^{-4}$	1.17
10^{-4}	19.2		$7.76 \times 10^{-5} \pm 7.8 \times 10^{-6}$ (6)	$1.5\ 10^{-3}$	0.78
10^{-3}	19.6		$3.34 \times 10^{-4} \pm 3.3 \times 10^{-5}$ (10)	$6.6\ 10^{-3}$	0.33
9.7×10^{-3}	19.3	0.38×10^{-2} (3)	$0.38 \times 10^{-2} \pm 3.8 \times 10^{-4}$ (4)	0.07^d	0.39^d
5.1×10^{-2}	19.	$0.78 \times 10^{-2} \pm 1.09 \times 10^{-3}$ (10)	$0.64 \times 10^{-2} \pm 6.4 \times 10^{-4}$ (3)	0.14^d	0.14^d
9.9×10^{-2}	18.3	$1.07 \times 10^{-2} \pm 3.4 \times 10^{-4}$ (20)	$1.07 \times 10^{-2} \pm 10^{-3}$ (11)	0.20^d	0.11^d
14.8×10^{-2}	18.	$1.73 \times 10^{-2} \pm 1.65 \times 10^{-3}$ (20)	$1.28 \times 10^{-2} \pm 1.3\ 10^{-3}$ (8)	0.27^d	0.10^d
20.2×10^{-2}	17.9	$2.23 \times 10^{-2} \pm 1.45 \times 10^{-3}$ (10)	$2.12 \times 10^{-2} \pm 2.1 \times 10^{-3}$ (4)	0.39^d	0.11^d
30.0×10^{-2}	16.6	$2.26 \times 10^{-2} \pm 1.36 \times 10^{-3}$ (6)		0.38	0.08

[a] Errors represent the estimated standard deviation from the mean values for the QMS measurements, and we estimate errors of 10% for the IR measurements (calibration and stability of the permeation tube). [b] $X = [\chi_{H_2CO}^{VLE}]_{liq}$: dissolved fraction of formaldehyde in the liquid. [c] $Y = [\chi_{H_2CO}^{VLE}]_{gas}$: gaseous phase mole fraction, number of measurements indicated in parenthesis. [d] Calculated using a mean value of Y from both IR and QMS measurements.
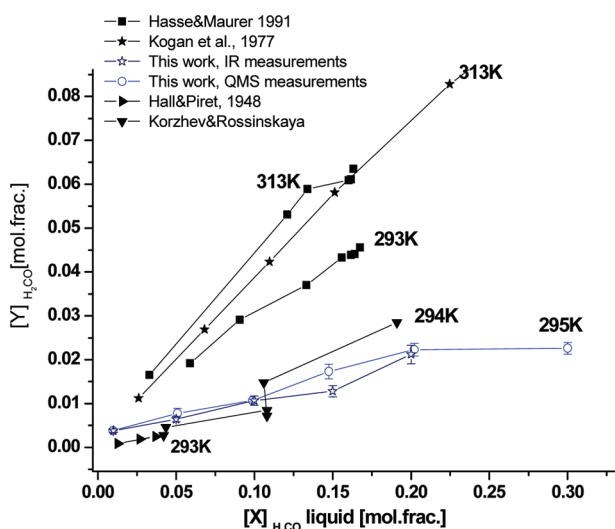
FIGURE 3. Gas phase H$_2$CO molar fraction as a function of the dissolved fraction of formaldehyde in the aqueous solutions at the vapor liquid equilibrium. Results obtained from both techniques (mass spectrometry and IR) are presented. Literature data are reported for comparison.

work. In this latter technique, an adjustment of an inert carrier gas flow is required to avoid the influence of reaction kinetics on the measurement of the gas phase concentration. Even if we do not have any clear explanations for these discrepancies, it should be noted that previous gas phase concentration measurements are all based on the chemical analysis of the recondensed gas phase (in some cases at 230 K), which contrasts with the direct methods presented here. Furthermore, it was recently shown that vapor liquid equilibrium data obtained by inert gas stripping can be biased by surface adsorption artifacts during the bubble bursting process (21). Further work is underway in our group to reduce the possible source of systematic errors on the quantitative determination of the VLE (e.g., added by the argon dilution of the collected vapor). In the QMS setup, an improvement of the sensitivity will greatly enhance the precision of our measurements. This can be achieved for, e.g., by adjusting the distance and orientation between the input molecular flow and the ionization source of the QMS. Such configuration will allow investigating gas solubility at lower concentration such as that expected at lower temperatures.

Above 0.15 mol frac. of dissolved H$_2$CO, the vapor phase formaldehyde concentration seems to reach a maximum value ($Y = 0.022$ mol frac. at 0.2 and 0.3 mol frac aqueous

H$_2$CO (Table 1, Figure 3). This is assigned to the important polymerization occurring in the solution at concentration ≥ 0.15 mol frac. When dissolved in water, formaldehyde is almost completely hydrated into methylene glycol (according to relation 4). Depending on the strength of the solutions, it polymerizes to form polyoxymethylene glycols according to relation (5):

$$CH_2O + H_2O \underset{k_d}{\overset{k_h}{\rightleftharpoons}} HO(CH_2O)H \qquad (4)$$

$$HO(CH_2O)_{n-1}H + HO(CH_2O)H \leftrightarrow HO(CH_2O)_nH + H_2O \qquad (5)$$

where k_h and k_d are the rates of formation and degradation of methylene glycol. Low concentration of dissolved formaldehyde favors methylene glycol formation whereas high concentration favors polyoxymethylene glycols formation. As a result, the concentration of these oligomers and the average degree of polymerization increases progressively as the dissolved fraction of H$_2$CO is increased. Because methylene glycol is volatile and dissociates more efficiently into molecular H$_2$CO and water vapor at VLE than higher hydrates ($k_{d2} > k_{d3} > k_{d4}$, etc. (22)), it is considered to be the only hydrate that exerts any appreciable contribution to the vapor pressure. Higher oligomers possess a low volatility because of their high molecular weight and most of them remain in the liquid or dissociate into methylene glycol or molecular H$_2$CO (1). As the concentration reaches 0.2 mol frac., the proportion of methylene glycol has reduced considerably (13, 22).

Our mass spectrometric measurements performed at $T = 295$ K provide further evidence for these findings. SI Figure S4 displays the residual signal and the mass spectrum corresponding to the gas phase collected above an equilibrated aqueous solution of 0.099 mol frac. H$_2$CO at 295K. No signal corresponding to methylene glycol at $M/z = 48$ can be observed in the B panel which suggests that the vapor phase contains only molecular formaldehyde and water. Earlier VLE works at 373 K (20) estimate that the gas mixture above the liquid contains about 5% methylene glycol vapor and 95% of its dissociated products: molecular formaldehyde and water vapor. As the partial pressure of formaldehyde is known to decrease as the temperature decreases, the methylene glycol contribution will be even smaller at 295 K and apparently is below the detection limit of our QMS or has completely dissociated once vaporised. Hence, when the H$_2$CO dissolved fraction is increased above 0.15 mol frac., the reduced proportion of methylene glycol in the solution affects considerably the formaldehyde vapor pressure at VLE (i.e., also Y ($=[\chi_{H_2CO}^{VLE}]_{gas}$)). This can explain the saturation regime of Y observed above 0.15 mol frac.
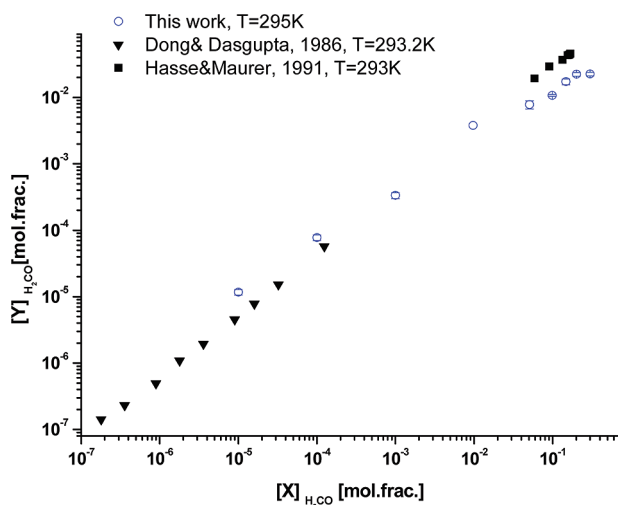
FIGURE 4. Gas phase H₂CO molar fraction as a function of the dissolved fraction of formaldehyde in the water system at the vapor liquid equilibrium compared with literature data. Gas phase mol frac. from Dong and Dasgupta (*23*) data are obtained assuming the total vapor pressure above the solutions are constant and equal to that of pure water at *T*= 293 K.

Figure 4 displays the IR results for the concentration range $10^{-5}-10^{-2}$ mol frac. together with the data reported by Dong and Dasgupta (1986) (*23*) for low formaldehyde concentration in the liquid phase. Our results are in relatively good agreement with this earlier study. From Figure 4 slight differences may be observed between the two sets of measurements that can be attributed to the temperature dependence of the vapor pressure. In their work, Dong and Dasgupta (*23*) showed an increase of vapor pressure of formaldehyde with temperature. Our experimental points follow this trend in comparison to their measurements at lower temperature (293 K). Nevertheless, other effects inherent to the limits of accuracy of our system can not be completely excluded. The partition coefficients derived from both studies suggest a net decrease of solubility as the dissolved fraction of formaldehyde approaches 10^{-3} and 10^{-5} with Y/X increasing from 0.3 to ~1.2, respectively (Table 1).

Information about the solubility of formaldehyde can also be derived from our data at 295 K by determining the Henry's law coefficient. The intrinsic Henry's law constant is defined as the ratio of the formaldehyde free molecules in the aqueous phase [H₂CO] to its partial pressure in gas phase at equilibrium:

$$H = \frac{[H_2CO]}{P_{H_2CO}}; [M/atm] \qquad (6)$$

Since the formaldehyde is hydrated to different degrees in water, an apparent Henry's law constant needs to be introduced as

$$H^* = \frac{\{[H_2CO] + [CH_2(OH)_2]\}}{\mathbf{P}_{H_2CO}}; [M/atm] \qquad (7)$$

where [CH₂(OH)₂] represents the concentration of methylene glycol.

The temperature dependence on the Henry's law constant is usually established according to the van't Hoff equation from which H* is shown to increase as the temperature decreases. From our experimental data at $T = 295$ K, one derives a value of $\sim 1840 \pm 240$ M/atm for a dissolved fraction of formaldehyde of 10^{-5} mol frac. (5.5×10^{-4} M), $\sim 2830 \pm 370$ M/atm at 10^{-4} mol frac. (5.5×10^{-3} M) and $\sim 6440 \pm 840$ M/atm at 10^{-3} mol frac. (5.5×10^{-2} M). In comparison, some

discrepancies exist in literature for the Henry's law constant obtained by different experimental methods (e.g., 3407 ± 200 M/atm (for the concentration range $10^{-4}-10^{-3}$ M), 6300 ± 1440 M/atm ($10^{-3}-10^{-2}$ M) and 3400 ± 300 M/atm ($10-10^{-4}$ M) at 298K (*23-25*) and 4296 ± 294 M/atm ($10^{-4}-10^{-3}$ M) at $T = 295$ K (*23*)). Our results indicate a decrease of solubility (increase in formaldehyde partial pressure) as the dissolved fraction of formaldehyde decreases. Additional data at intermediate concentrations are needed to confirm the trend observed. Moreover, a significant negative deviation from Henry's law at concentrations of dissolved H₂CO higher than 0.01 mol frac. (Figure 4) is observed. This behavior is consistent with the important oligomerization occurring in the solution as the dissolved fraction of H₂CO is increased.

The potentiality of this method to derive thermodynamic parameters was suggested in our preliminary Raman studies and permitted to calibrate the composition of thin ice films produced by vapor deposition of gas mixtures (H₂O/H₂CO) collected above different H₂CO aqueous solutions at VLE (*15*). The systematic study presented here demonstrates the feasibility of the principle on a quantitative basis.

It should be mentioned that no information exists concerning the solubility of VOC compounds like formaldehyde in ice at low temperature. It is thus difficult to determine the incorporation mechanism of such compounds in natural snow and therefore to establish the role of snow in the transfer of organic compounds from the atmosphere to the Earth's surface. A number of authors assumed that the ice surface (between 243 and 273 K) behaves to a first approximation as liquid water with respect to the incorporation of volatile organics, so that air/ice partitioning coefficients can be calculated according to the aqueous solubility of the compound and to its Henry constant (*26-29*). Using extrapolated gas solubility from equilibrium data obtained at room temperature to estimate partitioning at lower temperature can however seriously bias the results for volatile organic species like aldehydes. Indeed, the solubility in the disordered layer present at the ice surface at such temperatures is likely to differ strongly from that in the bulk water. For instance, a VOC like H₂CO can be incorporated in variable amounts in ice or water. This modifies the gas phase composition of the surrounding atmosphere. In rimed snow samples formed in mixed clouds that contain both ice crystals and supercooled water droplets, the condensed phase composition is predicted to be order of magnitudes higher than that observed in natural snow samples. At 258 K, an extrapolated Henry constant as high as 121×10^3 M/atm has been applied to discuss estimates of the repartition of formaldehyde between gas phase and rimed snow samples (*29*). A Henry constant of ~900 M/atm seems however more appropriate to describe the measured H₂CO fraction in snow at that temperature. Postdepositional processes are then suggested to explain these discrepancies. Our understandings of the H₂CO incorporation mechanism in ice or snow will therefore greatly beneficiate from the determination of the temperature dependence of the VOC solubility in water-ice (or acid doped-ice) samples at temperatures relevant for the troposphere.

Supporting Information Available

Figures S1, S3, and S4. Calibration curve is given in Figure S2. This curve does not pass through zero as we still have residual gases that cannot be pumped out of the QMS chamber. Thereby, we have chosen to define the zero point of the calibration curve by introducing pure argon at the typical working pressures (50 Torr in the flask and 10^{-6} Torr in the QMS) and measure the formaldehyde residual signal. This material is available free of charge via the Internet at http://pubs.acs.org.

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