

Effective Henry's Law Constants of Glyoxal, Glyoxylic Acid, and Glycolic Acid

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Abstract

8 The Henry's law constants of glyoxal, glycolic acid and glyoxylic acid in pure water
were determined over the range of 278 and 308K for the first time by a bubble column
10 technique. These compounds were chosen because of their perceived involvement in the
formation of secondary organic aerosol through in-cloud processing pathways. The
12 experimentally determined Henry's law constants are: glyoxal, $K_H =$
 $4.19 \times 10^5 \times \exp[(62.2 \times 10^3/R) \times (1/T - 1/298)]$; glycolic acid, $K_H =$
14 $2.83 \times 10^4 \times \exp[(33.5 \times 10^3/R) \times (1/T - 1/298)]$; and glyoxylic acid, $K_H =$
 $1.09 \times 10^4 \times \exp[(40.0 \times 10^3/R) \times (1/T - 1/298)]$. The Henry's law constants of glyoxal in the
16 presence of sodium chloride and sodium sulfate were also determined at 298 K. While the
glyoxal K_H is enhanced by less than three times in the presence of chloride in the range of
18 0.05-4.0 M ionic strength, the presence of sulfate at 0.03 M ionic strength increases the
glyoxal K_H by 50 times.

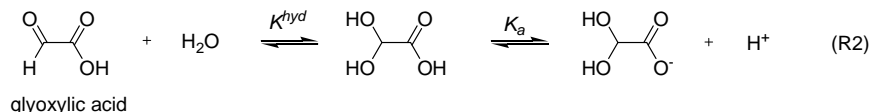
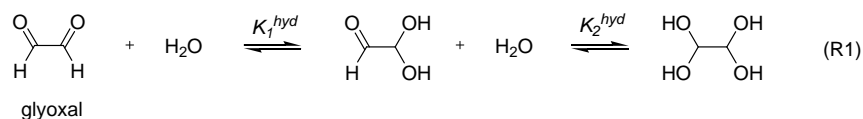
20 1. Introduction

22 The Henry's law constant, K_H , is a key parameter in estimating the magnitude, rate,
and direction of the flux of solutes between gas and aqueous phases [Betterson, 1992]. Recent
research has revealed that a number of C₂ bifunctional compounds (i.e., glycolaldehyde,
24 glyoxal, glyoxylic acid and glycolic acid) are precursors in the aqueous-phase formation of
oxalic acid [Blando and Turpin, 2000; Warneck, 2003]. Oxalic acid is the single most
26 abundant water-soluble organic compound that has been identified in ambient aerosols and
in-cloud processing is its dominant formation pathway [Sorooshian et al., 2006; Yu et al.,
28 2005]. The C₂ bifunctional compounds, especially glyoxal, have numerous volatile organic
compound (VOC) precursors and are relatively abundant in the atmosphere. Typical ambient
30 gas-phase concentrations of glyoxal range from 20 pptv ($\sim 40 \text{ ng m}^{-3}$) in rural environments to
2.0 ppbv ($\sim 4.0 \text{ } \mu\text{g m}^{-3}$) in urban environments [e.g., Munger et al., 1995; Ho and Yu, 2002;
32 Volkamer et al., 2005]. The ambient abundance of the other three C₂ bifunctional compounds
was less frequently measured. The cloud-processing of glycolaldehyde and glyoxal, which
34 are formed mainly in the gas phase, is a potentially important pathway leading to formation
of secondary organic aerosols (SOA). The evaluation of this pathway requires the knowledge
36 of the Henry's law constants of these compounds and their intermediate aqueous-phase
oxidation products (i.e., glycolic acid and glyoxylic acid).

38 Of the four C₂ bifunctional compounds, glycolaldehyde was measured to have a K_H
value of $4.14 \times 10^4 \text{ M atm}^{-1}$ at 298 K and $1.56 \times 10^4 \text{ M atm}^{-1}$ at 318 K [Betterson and Hoffmann,
40 1988]. Two studies in the literature reported K_H measurements of glyoxal; one study provided
a lower limit estimate of $3 \times 10^5 \text{ M atm}^{-1}$ [Betterson and Hoffmann, 1988] and the second study
42 reported a value of $3.6 \times 10^5 \text{ M atm}^{-1}$ in 100% seawater, based on only two measurements
[Zhou and Mopper, 1990]. The K_H values of glycolic acid and glyoxylic acid have not been
44 measured experimentally.

Both glyoxal and glyoxylic acid undergo hydration in water (see reactions (R1) and

46 (R2) below). Glyoxylic acid and glycolic acid also undergo acid dissociation (Reaction (R2)).



48 The experimentally determined values in this work are the effective Henry's law constants,
 which include terms for the hydration constants and the acid dissociation constants in the case
 50 of carboxylic acids [Betterton and Hoffmann, 1988]. That is, for glyoxal, $K_H = K_H'(1 + K_1^{\text{hyd}}$
 $+ K_1^{\text{hyd}}K_2^{\text{hyd}})$; for glyoxylic acid, $K_H = K_H'(1 + K^{\text{hyd}} + K^{\text{hyd}}K_a/[\text{H}^+])$; and for glycolic acid,
 52 $K_H = K_H'(1 + K_a/[\text{H}^+])$, where K_H' is the intrinsic Henry's law constant. The intrinsic
 Henry's law constant can be calculated from the effective Henry's law constant for
 54 compounds with known hydration and acid dissociation constants.

2. Experimental Section

56 2.1 Materials

Glyoxal trimer dihydrate (Sigma), glycolic acid (Acros), glyoxylic acid (Acros), 2,4-
 58 dinitrophenylhydrazine (DNPH) (Sigma) were used as received. A glyoxal solution of ~5
 mM was prepared by dissolving glyoxal trimer dihydrate in water and the solution was
 60 allowed to sit in the dark overnight to ensure complete hydrolysis. The glyoxal solution at
 such a concentration level contained only monomers [Whipple, 1970].

62 2.2 Methods

A bubble-column technique was used to measure K_H . The apparatus, shown schematically
 64 in Figure 1, was modified from the design by Mackay *et al.* [1979] and Betterton and
 Hoffmann [1988]. It consisted of a conditioning column, a stripped column and an absorbing
 66 column of the same dimensions (70 cm long and 4 cm i.d.), all placed in a temperature-
 controlled water bath. The columns were connected using silicone rubber tubing. A heating
 68 tape was used to maintain the tubing connection at least 5°C above the operating temperature

of the water bath to prevent condensation. Glass-wool plugs were inserted to eliminate mist
70 carry-over. The gas exiting the stripped column was collected by an absorbing solution. In a
typical experiment, ultra pure nitrogen gas passed through the first column containing 1 L of
72 water (at a liquid depth of 64 cm) where it was conditioned to the required temperature and
humidity. The conditioned gas was then bubbled through the stripped column containing 1 L
74 of 5 mM solution of the target compound at a flow rate of 250 mL min⁻¹. All solutions were
prepared within three days prior to each experiment. The system was equilibrated at a
76 specific temperature for 12 h before sample collection for K_H measurements at this
temperature. The experiment at each temperature was repeated three times or more.

78 *Mackay et al.* [1979] have shown that the mass transfer rate of a solute from the aqueous
phase to the gas phase in a bubble column is described by the following equation:

$$80 \quad \ln\left(\frac{C_t}{C_o}\right) = -\left(\frac{G}{K_HVRT}\right) t, \quad (1)$$

where G is the gas flow rate (L min⁻¹), V is the volume of the liquid (L) in the stripped
82 column, R is the gas constant (0.082 L atm K⁻¹ mol⁻¹), T is the system temperature (K), C_o is
the initial solute concentration and C_t is the solute concentration after time t (min) in the
84 stripped column. A plot of $\ln(C_t/C_o)$ against time yields a linear correlation with a slope of
($-G/(K_HVRT)$), from which K_H can be calculated. C_t in the stripped column was computed to
86 be $C_o - C_a$, where C_a is the concentration in the absorbing column. C_a was monitored by
removing aliquots of the absorbing solution at different time intervals for chemical analysis.
88 Five or more samples were taken in each experiment at a given temperature. The sampling
time interval between two consecutive samples was 30 min for glyoxylic acid and glycolic
90 acid and varied from 1 to 6 h for glyoxal. An aliquot of 1 mL was withdrawn for glyoxylic
acid and glycolic acid while an aliquot of 10-20 mL was removed for glyoxal. The higher K_H
92 values for glyoxal required longer sampling intervals and larger aliquots of solution for
analysis. C_a was corrected to the volume of the stripped column. Glycolic acid and glyoxylic

94 acid were analyzed using ion chromatography (IC) with 5 mM NaOH as eluent. Glyoxal was
quantified in its DNPH derivative using High-Performance Liquid Chromatography with
96 detection of light absorption at 420 nm.

98 **3. Results and Discussion**

3.1 Validation of the bubble column technique

100 The set-up was first optimized and validated by measuring the K_H of acetic acid and
formaldehyde. Their experimental K_H values are known from previous studies. In the bubble
102 column technique to obtain K_H , the solute in the exit vapor must be in equilibrium with the
liquid. The lower K_H a compound has, the longer it takes to attain the gas-liquid equilibrium
104 [*Mackay et al.*, 1979]. Formaldehyde and acetic acid, having a lower K_H than the three target
compounds, require more stringent conditions (e.g., lower flow rate, higher liquid depth) to
106 attain the gas-liquid equilibrium. A few studies measured the effective K_H of formaldehyde at
298 K, reporting values of $3.0 \times 10^3 \text{ M atm}^{-1}$ [*Betterton and Hoffmann*, 1988], $3.1 \times 10^3 \text{ M atm}^{-1}$
108 in a seawater matrix [*Zhou and Mopper*, 1990], and $6.0 \times 10^3 \text{ M atm}^{-1}$ [*Gaffney and Senum*,
1984]. We measured formaldehyde K_H to be $4.8 \times 10^3 \text{ M atm}^{-1}$, falling within the range of
110 these reported values. Three studies reported the K_H value of acetic acid at 298 K. They were
 $4.1 \times 10^3 \text{ M atm}^{-1}$ by *Johnson et al.* [1996], $5.5 \times 10^3 \text{ M atm}^{-1}$ by *Khan et al.* [1995], and
112 $9.3 \times 10^3 \text{ M atm}^{-1}$ by *Servant et al.* [1991]. Our measurement of acetic acid K_H was $5.0 \times 10^3 \text{ M}$
 atm^{-1} , also in the range of the published measurements. The measurement results for the K_H
114 of formaldehyde and acetic acid have demonstrated that the flow rate in the range of 200-300
 mL min^{-1} and the liquid depth (64 cm) used in this work was adequate to ensure liquid-gas
116 equilibrium.

3.2 The Henry's law constant of glyoxal

118 Measurements of the glyoxal K_H were made at four temperatures and the results are
listed in Table 1. A plot of the K_H measurements as a function of $1/T$ yields a solution

120 enthalpy of $-62.2 \text{ kJ mol}^{-1}$. The measured glyoxal K_H at 298 K was $4.2 \times 10^5 \text{ M atm}^{-1}$, in good
122 agreement with the value of $3.6 \times 10^5 \text{ M atm}^{-1}$ in the seawater matrix measured by *Zhou and*
Mopper [1990] and consistent with the lower limit value of $3.0 \times 10^5 \text{ M atm}^{-1}$ reported by
Betterton and Hoffmann [1988] based on their analytical detection limit ($\sim 5 \text{ }\mu\text{M}$) for
124 aqueous-phase glyoxal.

Recently, *Kroll et al.* [2005] measured the effective glyoxal K_H to be $2.6 \times 10^7 \text{ M atm}^{-1}$
126 in a chamber study. This value was obtained from partition of glyoxal between gas phase and
ammonium sulfate seed particles or mixed ammonium sulfate/sulfuric acid seed particles.
128 The partition of glyoxal onto the two types of seed particles was found to yield the same
effective Henry's law constant. On the basis of this observation, *Kroll et al.* suggested that
130 the high ionic strength (19.5-22.5 M) in the aerosol aqueous phase was responsible for the
enhanced K_H in comparison with the K_H measured in the seawater matrix by *Zhou and*
132 *Mopper*.

We measured K_H of glyoxal in NaCl and Na₂SO₄ solutions to investigate the effect of
134 ionic strength. A series of experiments were conducted in NaCl solutions of different ionic
strength ranging from 0.05 to 4.0 M. The measured K_H was $1.90 \times 10^6 \text{ M atm}^{-1}$ at an ionic
136 strength of 0.05 M and dropped by $\sim 50\%$ to $8.50 \times 10^5 \text{ M atm}^{-1}$ when the ionic strength
increased to 4.0 M. The K_H value measured in the highest ionic strength NaCl solution was
138 twice that measured in pure water. The enhancement of K_H was possibly facilitated by the
weak hydrogen bonding formed between Cl⁻ ion and the -OH groups in the hydrated form of
140 glyoxal [*Wan and Yu*, 2007]. Further increase in the NaCl concentration lowered the K_H . It
was likely a result of shift in the hydration equilibrium in favor of the aldehyde form since Cl⁻
142 and Na⁺ ions compete for water molecules to form hydration shells [*Schartzenbach et al.*,
2003], leading to more prominent salt-out effect with increasing NaCl concentration.

144 In the experiments carried out in Na₂SO₄ solutions, the ionic strength varied from
0.0003 to 0.03 M while the concentration of glyoxal was fixed at 10 mM. The corresponding

146 sulfate:glyoxal molar ratio ranged from 0.01:1 to 1:1. K_H was found to increase significantly
with increasing SO_4^{2-} concentration and reached a value of $2.40 \times 10^7 \text{ M atm}^{-1}$ in the solution
148 having the highest ionic strength (0.03 M). This value was similar to the K_H value derived by
Kroll et al. in their chamber study, but it was ~ 50 times higher than the K_H measured in pure
150 water and 12 times higher than the K_H measured in the NaCl solution at an ionic strength of
0.05 M. More experiments were conducted, in which the SO_4^{2-} concentration was further
152 increased to 0.15 M (ionic strength 0.225 M, and sulfate:glyoxal = 15:1) to make the
sulfate:glyoxal ratio closer to those observed in ambient clouds and aerosols. It was found
154 that the resulting effective K_H was too high ($>10^9 \text{ M atm}^{-1}$) for measurement by our method,
since a 6-h collection time was not long enough to obtain sufficient glyoxal in the absorbing
156 column for analysis. Our measurement results pointed to that sulfate was a more important
factor than the ionic strength in affecting the glyoxal K_H . We have yet to understand the
158 reactive interaction of sulfate ions with the hydrated glyoxal forms.

3.3 The Henry's law constants of glyoxylic and glycolic acid

160 The measured K_H values of glyoxylic and glycolic acid at four temperatures are given
in Table 1. The solution pH was not controlled in the experiments. Consequently, the
162 concentrations of the acids and their respective acid dissociation constants determined the
resulting solution pH (Table 1). Plots of $-\ln K_H$ versus $1/T$ yielded ΔH values of -33.5 and -
164 40.0 kJ mol^{-1} for glycolic acid and glyoxylic acid, respectively. Our measured ΔH for
glycolic and glyoxylic acids are in good agreement with ΔH values for the other carboxylic
166 acids. *Khan et al.* [1995] reported ΔH values of pyruvic, pentanoic, and hexanoic acid as -
42.3, -54.7, and -52.4 kJ mol^{-1} , respectively.

168 3.4 Atmospheric Implications

The knowledge of K_H makes it possible to assess the phase distribution, which in turn
170 is a necessary step in evaluating the fate of glyoxal, glycolic acid and glyoxylic acid and their
potential contributions to secondary organic aerosol. The partitioning of atmospheric species

172 into cloud droplets involves multiple steps and the key step is transport across the interface
[Schwartz, 1986]. The characteristic time to achieve interfacial equilibrium is strongly
174 dependent on the Henry's law constant and can be calculated with the knowledge of K_H and
the accommodation coefficient of a species using the following equation [Betterson, 1992;
176 Schwartz, 1986]:

$$\tau_H = [(r^2/(3D_g) + 4r/(3\alpha v)]R_gTK_H \quad (2)$$

178 where r is the radius of cloud droplet, D_g is the gas phase diffusion coefficient, α is the mass
accommodation coefficient, and $v = (8R_gT/\pi M)^{1/2}$ is the mean thermal velocity of molecules
180 in the gas phase (M is the molecular weight). Schweitzer *et al.* [1998] reported an average
accommodation coefficient of glyoxal by water droplets to be 0.023 in the temperature range
182 of 263-283 K. If we assume an accommodation coefficient of 0.01 (a lower value typically
employed in cloud physics computation [Schwartz, 1986]), a cloud droplet radius of 5.0 μm
184 and a temperature of 288 K, the characteristic times required to achieve gas-droplet
equilibrium are 54 s for glyoxal, 4 s for glycolic acid (pH = 3), and 1.6 s for glyoxylic acid
186 (pH = 3). The calculations indicate that the gas-droplet equilibrium could be readily
established under atmospheric conditions.

188 Using the K_H values measured in pure water, we calculate that with the typical liquid
water content of clouds of 0.1-1 g m^{-3} (i.e., 10^{-7} - 10^{-6} v/v), 78-97% of glyoxal, 17-67% of
190 glycolic acid, and 6-38% of glyoxylic acid partition into the cloud water at equilibrium at 5°C
(Figure 2). In other words, glyoxal predominately resides in clouds at equilibrium while a
192 smaller but still significant fraction of glycolic acid and glyoxylic acid is in clouds at
equilibrium. The significant partitioning of glyoxal in cloud water predicted by its Henry's
194 law constant is confirmed by field measurements. Munger *et al.* [1995] observed that up to
50% of glyoxal was partitioned in the aqueous phase during cloudy periods encountered in
196 the Shenandoah National Park, USA during September 1990. Glyoxal in cloud/fog water was
also detected in Riverside, California, USA [Munger *et al.*, 1990].

198 If we do not consider the enhancement by salt like NaCl or sulfate, the K_H values
predict that in wet aerosols (typical liquid water content in the range of 1-100 $\mu\text{g m}^{-3}$), the
200 fractions of glyoxal, glycolic acid, and glyoxylic acid in particle phase are negligible (Figure
2). The effective glyoxal Henry's law constant in pure water is apparently not high enough to
202 explain its observed presence in particle phase. *Matsunaga et al.* [2004] measured gas-
particle partitioning of glyoxal in a forest atmosphere in Japan in August 2002 and reported
204 that the fraction of glyoxal residing in the particle phase ranged from zero to 100% and
average at 46%.

206 In addition to liquid water content, atmospheric factors such as other constituents in
cloud water/aerosols, acidity, and ionic strength could significantly affect the partitioning of
208 glyoxal, as demonstrated by the observed higher K_H values in the presence of NaCl and
 Na_2SO_4 in this work. *Volkamer et al.* [2007] compared direct measurements of gas-phase
210 glyoxal in Mexico City to experimentally constrained model prediction and concluded that
there must be an additional glyoxal sink. They suggested reversible partitioning to aerosol
212 liquid water with a K_H as high as $4 \times 10^9 \text{ M atm}^{-1}$ to be a possible sink to account for the
discrepancy between the model prediction and the measurements. Certain strong interactions
214 between glyoxal with other aerosol constituents have to be involved to account for the high
effective K_H suggested by *Volkamer et al.*, since this suggested K_H value is four orders of
216 magnitude higher than the K_H in pure water. Such a high K_H is possible and in general
agreement with our lower-limit estimate for K_H in the presence of 0.15 M sulfate and 10 mM
218 glyoxal. It is apparent that further work is needed to quantify the effects of sulfate, acidity,
and ionic strength on partitioning of glyoxal between the gas and aqueous phases.

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Table 1. Summary of Effective Henry's law constants for glyoxal, glyoxylic and glycolic acid

Aldehyde	Temp. (K)	K_H (M atm ⁻¹)	pH	$K_{H, \text{intrinsic}}$ (M atm ⁻¹)	Reference
Glyoxal	298	3.6×10^5			Zhou and Mopper [1990]
	288, 298, 308, 318	$\geq 3.00 \times 10^5$			Betterton and Hoffmann [1988]
	278	$(1.60 \pm 0.11) \times 10^6$	7		This work ^d
	298	$(4.19 \pm 0.87) \times 10^5$	7	1.90 ^a	This work ^d
	308	$(1.53 \pm 0.16) \times 10^5$	7		This work ^d
	318	$(4.97 \pm 0.30) \times 10^4$	7		This work ^d
Glyoxylic acid	278	$(2.72 \pm 0.53) \times 10^4$	2.76		This work ^d
	288	$(1.90 \pm 0.21) \times 10^4$	2.64		This work ^d
	298	$(1.09 \pm 0.09) \times 10^4$	2.64	28.67 ^b	This work ^d
	308	$(4.97 \pm 0.51) \times 10^3$	2.84		This work ^d
Glycolic acid	278	$(8.95 \pm 0.75) \times 10^4$	3.09		This work ^d
	288	$(4.82 \pm 0.47) \times 10^4$	3.11		This work ^d
	298	$(2.83 \pm 0.31) \times 10^4$	3.12	2.37×10^4 ^c	This work ^d
	308	$(2.24 \pm 0.29) \times 10^4$	2.95		This work ^d

^a The intrinsic K_H at 298 K for glyoxal was calculated from its effective K_H using a hydration constant of 2.2×10^5 M measured by *Wasa and Musha* [1970].

^b The intrinsic K_H at 298 K for glyoxylic acid was calculated from its effective K_H using a hydration constant of 3.0×10^2 M [*Sørensen et al.*, 1974] and an acid dissociation of 3.47×10^{-4} M for the hydrated form of glyoxylic acid [*Smith and Martell.*, 1977].

^c The intrinsic K_H at 298 K for glycolic acid was calculated from its effective K_H using an acid dissociation of 1.58×10^{-4} M [*vel Leitner and Dore*, 1997].

^d The K_H values as a function of temperature in the form of $K_H = K_{H,298K} \times \exp\left[-\frac{\Delta H}{R} \times \left(\frac{1}{T} - \frac{1}{298}\right)\right]$ derived from measurements at different temperatures in this work are:

Glyoxal: $K_H = 4.19 \times 10^5 \times \exp\left[\frac{62.2 \times 10^3}{R} \times \left(\frac{1}{T} - \frac{1}{298}\right)\right]$; glycolic acid: $K_H = 2.83 \times 10^4 \times \exp\left[\frac{33.5 \times 10^3}{R} \times \left(\frac{1}{T} - \frac{1}{298}\right)\right]$; and glyoxylic acid: $K_H = 1.09 \times 10^4 \times \exp\left[\frac{40.0 \times 10^3}{R} \times \left(\frac{1}{T} - \frac{1}{298}\right)\right]$.

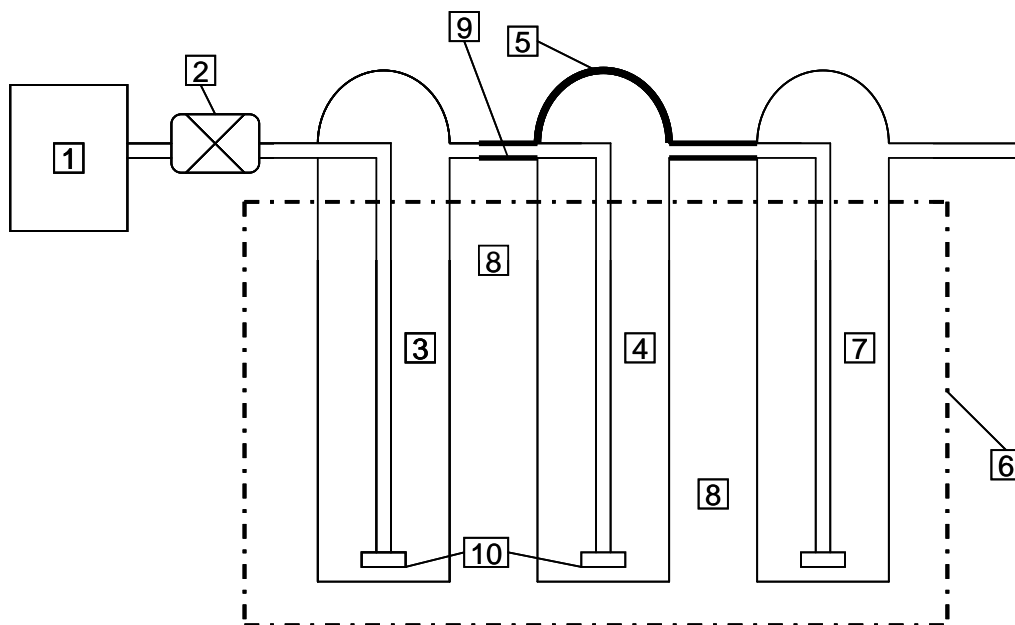


Figure 1. Schematic diagram of the bubble-column setup. (1) Nitrogen carrier gas tank, (2) Flow meter, (3) Conditioning column containing pure water, (4) Stripped column solution containing the target compound, (5) Heating tape, (6) Water bath, (7) 1L of pure water to collect sample, (8) Thermometer, (9) Glass wool, and (10) Stainless steel slip-on inlet filters with porosity of 10 μm

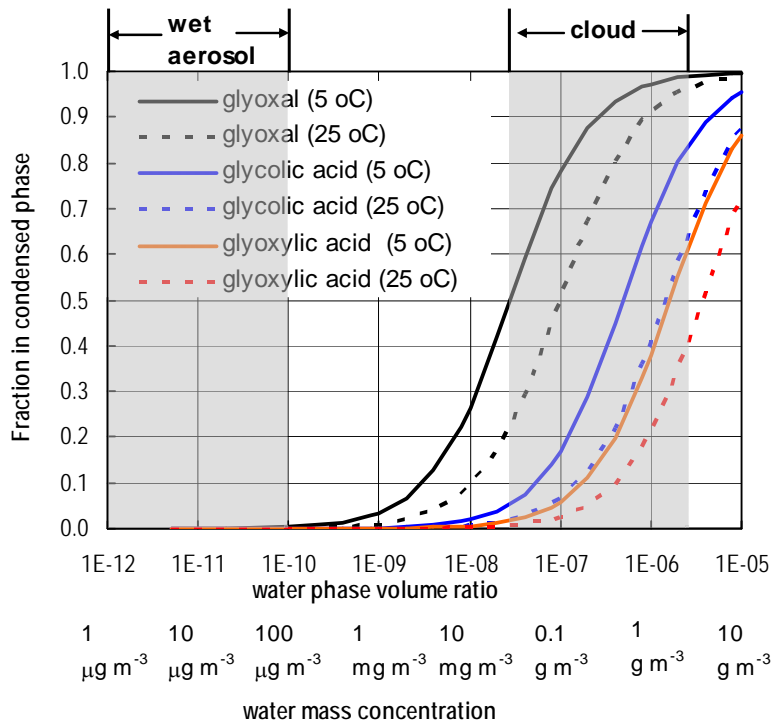


Figure 2. Calculated fractions of glyoxal, glycolic acid, and glyoxylic acid in cloud water and in wet aerosols as a function of water phase volume ratio, assuming Henry's Law Constant (HLC) values measured in pure water. (The shaded areas indicate the typical range of liquid water content for wet aerosols ($1\text{-}100\ \mu\text{g m}^{-3}$) and for clouds ($0.05\text{-}3\ \text{g m}^{-3}$)).