Physico-chemical properties of green leaf volatiles (GLV) for ascertaining atmospheric fate and transport in fog

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Abstract. Green Leaf Volatiles (GLVs) is a class of biogenically emitted oxygenated hydrocarbons that have been identified as a potential source of Secondary Organic Aerosols (SOA) via aqueous oxidation. The physico-chemical properties of GLVs are vital to understanding their fate and transport in the atmosphere via fog processing, but few experimental data are available. We studied the aqueous solubility, 1-octanol/water partition coefficient, and Henry's law constant (K_H) of five GLVs at 25℃: methyl jasmonate, methyl salicylate, 2-methyl-3-buten-2-ol, cis-3-hexen-1-ol, and cis-3-hexenyl acetate. Henry's law constant was also measured at temperatures and ionic strengths typical of fog. Experimental values are compared to scarcely-available literature values, as well as estimations using group and bond contribution methods, property-specific correlations and molecular dynamics simulations. From these values, the partition coefficients to the air-water interface were also calculated. The large Henry's law constant of methyl jasmonate (8091 ± 1121 M·atm^{-1}) made it the most significant GLV for aqueous phase photochemistry. The HENRYWIN program's bond contribution method from the Estimation Programs Interface Suite (EPI Suite) produced the best estimate of the Henry's constant for GLVs. Estimations of 1-octanol/water partition coefficient and solubility are best when correlating an experimental value of one to find the other. Finally, the scavenging efficiency was calculated for each GLV indicating aqueous phase processing will be most important for methyl jasmonate.

Keywords: green leaf volatiles; aerosols; Henry's constant; volatile organic compounds

1. Introduction

A large body of evidence shows that organic compounds coming from different sources participate in atmospheric reactions, leading ultimately to secondary organic aerosols (SOA) both *via* gas phase and liquid (water) phase processes as in fog (Bateman *et al.* 2011, Blando and Turpin 2000). SOA represent an important fraction of particulate matter and thus play significant roles in climate, air quality and transport of pollutants in the atmosphere (Kanakidou *et al.* 2005).

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Fog processing has been shown to be an important fate mechanism for several organic compounds in the lower atmosphere (Herckes *et al.* 2013). Organic carbon in atmospheric aerosols arises from two sources, viz., natural and anthropogenic. Volatile organic compounds emerging from petroleum sources form a large portion of anthropogenic emissions (McDonald *et al.* 2018). However, natural sources exceed anthropogenic sources by more than an order of magnitude (Guenther *et al.* 1995). Natural sources result primarily from biological species such as plants and microbes and are collectively termed as biogenic volatile organic compounds (BVOC). The global flux of BVOC is estimated at about 1,150 TgC/yr (Guenther *et al.* 1995). Approximately 55% of the material is estimated to be primarily isoprene and monoterpenes, and the remaining 45% is classified as other BVOC. Of the BVOC classified as "other," a significant portion is derived from stress-induced releases from plants, which are termed green leaf volatiles (GLVs). The stress may result from physical injury, pest attacks, diseases, heat waves, water scarcity and climatic changes. Thus, there has been recent work geared to understanding the atmospheric behavior of GLVs (Hamilton *et al.* 2009, Heiden *et al.* 1999, Holopainen 2004, Hoyle *et al.* 2011, Karl *et al.* 2008, Matsui 2006, Mentel *et al.* 2009, Mentel *et al.* 2013, Riipinen *et al.* 2012, Shiojiri *et al.* 2006a, b). While the umbrella term GLV covers many compounds and their derivatives, the focus of this study was on five GLVs crucial to the stress response (Arey *et al.* 1991, Harley *et al.* 1998, Heiden *et al.* 1999, Preston *et al.* 2001): methyl jasmonate (MeJa), methyl salicylate (MeSa), 2-methyl-3-buten-2-ol (MBO), cis-3-hexen-1-ol (HxO), and cis-3-hexenylacetate (HxAC). While to our knowledge MeJa has not been detected in forests it is emitted in the vapor phase (Preston *et al.* 2001), and MBO, HxAC, HxO, and MeSa all have been detected over active vegetation. (Jardine *et al.* 2010, Kim *et al.* 2010, Williams *et al.* 2001). They have been shown to participate in gas phase reactions with ozone and hydroxyl radicals (Hamilton *et al.* 2009, Harvey *et al.* 2014). Our recent work described our experimental work on the oxidation potential of MeJa and other GLVs in fog water (Hansel *et al.* 2015, Richards-Henderson *et al.* 2014), but led to the conclusion that more physico-chemical data is needed to scale laboratory data to natural atmospheric predictions.

Understanding the fate and transport of GLVs in the atmosphere require precise values of various physico-chemical thermodynamic properties (Mackay 2001, Valsaraj 2009). These include basic *equilibrium* data such as saturation aqueous solubility and pure component vapor pressure. In addition, partitioning relationships such as between air and water phases (Henry's law constant) as well as between octanol and water are also required. The latter parameter is also used in estimating other phase partitioning relationships such as soil/water, sediment/water, biota/water, and gas-to-particle partitioning in the atmosphere. A review of the literature clearly suggests that several of the relevant parameters mentioned above are lacking for GLVs. There are property estimations based on bond and group contribution methods, such as the Estimation Program Suite (EPI Suite) and SPARC (Sparc Performs Automated Reasoning in Chemistry) from the U.S. Environmental Protection Agency, which rely on databases and basis sets. Analogously, other predictive methods such as quantum chemical and poly parameter models such as COSMOTherm rely on tested experimental values to validate the methods (Gluge *et al.* 2013, Lyman *et al.* 1990). Both methods are not very reliable because the compounds in their basis sets do not contain any GLV to build the existing correlations. Another important property is the surface concentration of GLVs at the air-water interface; we need this property to estimate the oxidation behavior at the air-water interface of tiny droplets in the atmosphere, for which surface area effects predominate (Donaldson and Valsaraj 2010). Thus, surface adsorption coefficients have to be estimated from surface tension data (Hartkopf and Karger 1973, Valsaraj 2009).

In this work, we used several existing experimental techniques to obtain the above parameters
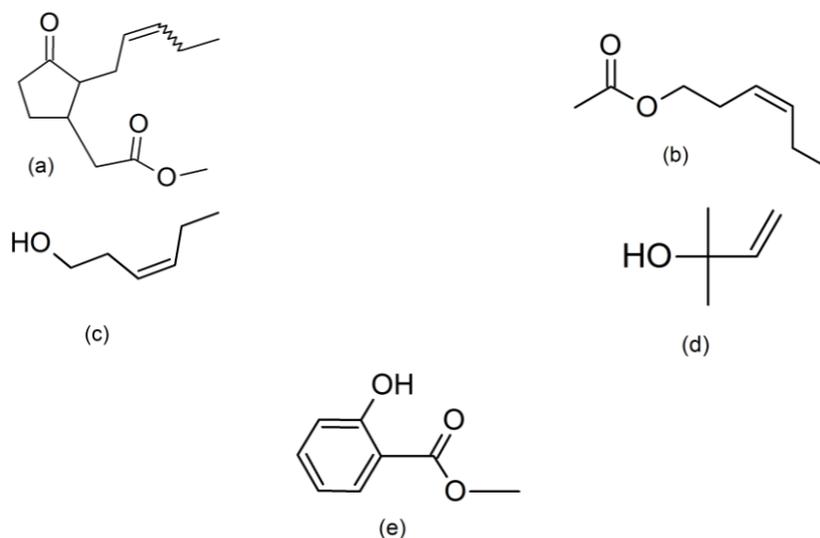
Fig. 1 Molecular Structures of (a) methyl jasmonate (MeJa), (b) cis-3-hexenylacetate (HxAC), (c) cis-3-hexen-1-ol (HxO), (d) methyl buten-2-ol (MBO) and (e) methyl salicylate (MeSa)

for five of the common GLVs that have been detected in the environment. These compounds are: methyl jasmonate (MeJa), methyl salicylate (MeSa), 2-methyl-3-buten-2-ol (MBO), cis-3-hexen-1-ol (HxO) and cis-3-hexenylacetate (HxAC). Their structures are shown in Fig. 1. All data were obtained at 25°C, and the Henry's law constant was also determined at 30 and 35°C. Additionally, the Henry's law constant was also determined for different ionic strength solutions typical of fogwaters. Although pH is another variable, we did not investigate its effects in this series of experiments. We compare our experimental values against predictions using both molecular dynamics (MD) simulations and correlations that exist in the literature.

2. Materials and methods

2.1 Chemicals

Pure samples of each GLV, viz., methyl jasmonate (95%), methyl salicylate (Reagent plus®, ≥ 99%), 2-methyl-3-buten-2-ol (98%), cis-3-hexen-1-ol (natural, ≥ 98 %) and cis-3-hexenylacetate (≥98%) were obtained from Sigma-Aldrich© and used as received without further purification. Ammonium nitrate (ACS Reagent, ≥98%), sodium hydroxide (Sigma-Aldrich, 99.998%), sulfuric acid (BDH, ACS Grade 95-98%) and ammonium chloride (ACROS Organics, 99.5%) were used in ionic strength experiments. LC-MS grade water (Honeywell, B&J Brand®) was used to make solutions. Acetonitrile used was from EMD Millipore© (HPLC grade, ≥99.8%) and 1-octanol from Sigma-Aldrich© (CHROMASOLV© for HPLC, ≥99%). Benzene (anhydrous, 99.8%, Sigma-Aldrich) was used to validate the modified liquid stripping technique used to measure Henry's law constants (Section 2.3)

In order to test the ionic strength effects, ionic solutions were prepared based on the ionic content found in fogwaters sampled at Baton Rouge (LA, USA) (Raja *et al.* 2005): NO_3^- (3 mM), SO_4^{2-} (2 mM), Na^+ (3.3 mM), Cl^- (3 mM), and NH_4^+ (6 mM). Additionally, ionic solutions
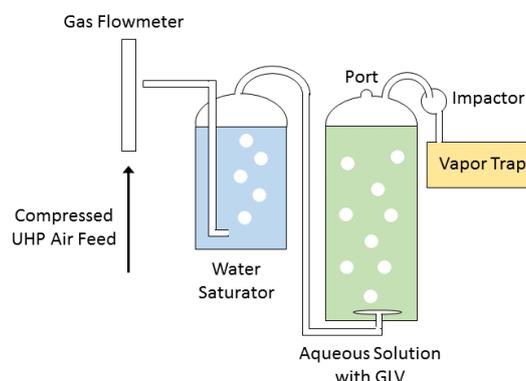
Fig. 2 Gas stripping apparatus for measurement of Henry's constant for GLVs

concentrated by a factor 100 were also used based on the same composition. The ionic solutions had a pH value of 6.

2.2 Chemical analysis

All aqueous sample analyses were conducted using HPLC analysis. An Agilent 1100 HPLC-UV/DAD system was used consisting of the following components: a degasser (G1322A), a quaternary pump (G1311A), an autosampler (G1313A), a column compartment (G1316A) and a diode array detector (G1315A). 4 µL of each sample was injected into a 2.1 mm x 150 mm Pinnacle II PAH column (Restek Corp., Bellefonte, PA, USA) with 4µm particle size, held at 40℃. A water : acetonitrile gradient method with a flow-rate of 0.2 mL/min was used, starting with 60% acetonitrile for one minute, ramping linearly to 100% acetonitrile over 6 minutes, followed by a three minute isocratic hold at 100% acetonitrile, and a final ramping down to 60% acetonitrile over 3 minutes, followed by an 8 minute post time at 60% acetonitrile. The UV absorbance of the GLVs was monitored with an average signal at 195 nm for MeJa, MBO, HxO, HxAC and at 210 nm for MeSa, taking a data point every 2 s using the diode array detector with a slit width of 4 nm. The concentration was determined from the measured peak area *via* a calibration curve obtained from the analysis of standard solutions of known concentrations.

2.3 Determination of Henry's law constants

A modified liquid stripping technique was employed to measure Henry's law constants since this technique is found to be most appropriate for semi volatile organic compounds (VOCs) such as GLVs (Bamford *et al.* 1999, Mackay *et al.* 1979). Fig. 2 is a schematic of the modified equipment used.

Ultra-high purity compressed air (Alphagaz 1, Air Liquide©) was passed through a flow-meter (Cole Parmer PMR-1) at 30-45 mL/min before entering a 1 L gas-washing bottle containing LC-MS grade water to saturate the air with water vapor. The air was then bubbled through a coarse frit at the bottom of a glass bubble column (100 cm length and 5 cm inside diameter) filled with an aqueous solution of GLV to a liquid height of 75 cm. Solutions of GLV were prepared in 3 media: deionized water, ionic solution based on concentration given above, and ionic solution concentrated by a factor 100. The solutions were used in separate Henry's Constant experiments,

to determine the effect of ionic strength on the air-water partitioning of each GLVs. The air bubbles reached equilibrium through the column, passed through a glass impactor to remove any solid or liquid aerosols caused by bursting bubbles, and then through a XAD-2 polymeric resin trap (ORBO 43 Supelpak-20, Sigma-Aldrich) to collect gaseous GLVs. Each trap has a front and back section; measuring the GLV concentration in these sections separately showed that the maximum GLV in the back section was less than 5%. For this experiment, both front, and back were used. The column was wrapped in a water jacket and insulated to maintain a stable aqueous temperature. The GLVs were desorbed from the XAD-2 trap by soaking in 10 mL of acetonitrile and shaking for two hours. The resulting solution was filtered (PTFE filter, porosity of 0.45 µm, Whatman XD/G) and analyzed by HPLC. Sampling intervals ranged from 15 minutes to 24 hours, and at each time point aqueous samples were taken, the temperature was checked, and the sorbent trap was replaced with a new one. The first time point was not included in data analysis because adsorptive effects of the GLV on the top of the apparatus were apparent. The ratio of the measured average aqueous concentration (C_w) to the air concentration (C_g) gave the Henry's Law constant, K_H [M·atm^{-1}].

2.4 Determination of saturation aqueous solubility

Aqueous solubility S [mM] was measured using a traditional batch equilibration shake flask technique, which has been found to be one of the direct measurements for solubility with very little interference effects (Banerjee *et al.* 1980). Ten 40 mL glass amber vials were each filled with 35 mL LC-MS grade water. Increasing amounts of GLV were added to each vial, with the highest mass added corresponding to double the solubility estimated by the WATERNT program from EPI Suite (EPA 2012). The vials were allowed to equilibrate over several days and gently shaken in a water bath at 25° C. After the equilibration period, the shaker was turned off, and the samples kept in the bath for 24 hours, to allow un-dissolved solute to settle to the bottom or rise to the top. Aliquots of 2 mL were taken from the middle of the liquid volume and centrifuged at 12,000 rpm for 15 minutes. Aqueous samples were then taken from the aliquots and diluted for analysis with HPLC. As the solubility limit was approached and passed, the aqueous concentration plateaued. The solubility limit was determined as the average of these plateau increased GLV concentrations until the plateau was apparent.

2.5 Determination of the octanol-water partition coefficient

Octanol-water partition coefficients were determined using a standard shake-flask method developed by OECD (OECD) and described elsewhere (Ip *et al.* 2009) (Liyana-Arachchi *et al.* 2013b). Solutions containing octanol to water ratios of 1:1, 2:1 and 1:2 (v/v) were prepared in 40 mL vials. Experiments were conducted in duplicate for each ratio. The vials were shaken in a water bath at 25°C to allow for ample contact for equilibrium distribution to be achieved. The concentration in each phase was then determined using HPLC daily until a constant K_{ow} was achieved, viz., when the standard deviation of the K_{ow} between individual solutions was greater than the difference between the daily measurements.

2.6 Computational models and methods

Similar to our previous works (Liyana-Arachchi *et al.* 2013a, b, 2014), the free energies of

hydration ($\Delta G_{hydration}$) of four of the GLVs (namely HxO, HxAC, MBO and MeSa) in a pure water phase were obtained using thermodynamic integration (TI) calculations (Bennett 1976; Hub *et al.* 2012; Shirts *et al.* 2003). The same method was used to determine the free energies of solvation ($\Delta G_{solvation}$) of these GLVs in pure water and in water having an amount of ions (ammonium NH_4^+, sulfate SO_4^{2-} and nitrate NO_3^-, which are typically found in fogwater) equivalent to 100 times the ionic composition of fogwater. Such an ionic system was also studied experimentally here as an example of a highly concentrated salt solution, in order to estimate the maximum effect of ionic strength on the Henry' Law Constant. A simulated system with the correct ionic composition of fogwater was not considered here, mainly due to computational limitations (very large system sizes would be needed in order to have a total number of ions that is statistically relevant and can yield the correct ionic concentration in fogwater). The GLVs were represented using models from our previous work (Liyana-Arachchi *et al.* 2013a, b, 2014). These models are based on the OPLS-AA force field (Jorgensen *et al.* 1996), with some of the atomic charges modified so that the simulations can reasonably match values of the experimental 1-octanol/water partition coefficients. The SPC/E water model was used (Berendsen *et al.* 1987) in this study. For the ionic aqueous system, all the parameters were taken from the literature (Werner *et al.* 2014) for NH_4^+; (Wernersson and Jungwirth 2010) for SO_4^{2-}; and (Thomas *et al.* 2007) for NO_3^-). Sodium ions and chloride ions from Vácha's work (Vácha *et al.* 2009) were added to the system to keep it electrically neutral. A cubic simulation box with the side length of 8.2 nm was used for TI calculation for the simulated aqueous ionic system. This system contains 19112 water molecules, 209 ammonium ion molecules, 70 sulfate ion molecules, 105 nitrate ion molecules, 209 chloride ion molecules and 245 sodium ion molecules. All the TI calculations were run for up to 2 ns, in which the last 1.5 ns of the simulation were used for analysis. All the molecular simulations were performed using GROMACS (Hess *et al.* 2008).

3. Results and discussion

3.1 Henry's law constants

Henry's law is the relationship between the equilibrium concentrations of a compound in the aqueous and air phases. The modified liquid stripping technique used (Section 2.3) requires that the method be first validated using a compound of known Henry's law constant. In this case we chose an aromatic compound, viz., benzene. Using the instrumentation described in this work (Section 2.3), the measured K_H of benzene is 0.19 ± 0.03 M·atm^{-1} that compares well with literature values of 0.19-0.21 M·atm^{-1} (Ashworth *et al.* 1988, Dewulf *et al.* 1995, Karl *et al.* 2003, Mackay *et al.* 1979). Measurements of the gas phase and aqueous phase concentrations were made at regular intervals and the ratio of aqueous to gas phase concentration (per Equation 1) plotted as shown in Fig. 2 for a typical run for MeSa. Clearly the values are large initially and then reach an asymptote; this value is the equilibrium ratio. The measured Henry's law constants for the five GLVs at 25, 30 and 35°C are displayed in Table 1. The existing values of K_H for these GLVs found in the literature are also given in Table 1, but most are available only at 25°C. Between the measured values and those obtained from the literature, there is agreement only for three of the five compounds, viz., MeSa, MBO and HxAC. For MeJa and HxO there is considerable disagreement with the literature values. The cited Henry's law constant value for MeJa used a similar gas sparging method but measured only the decline of the aqueous concentration of MeJa.
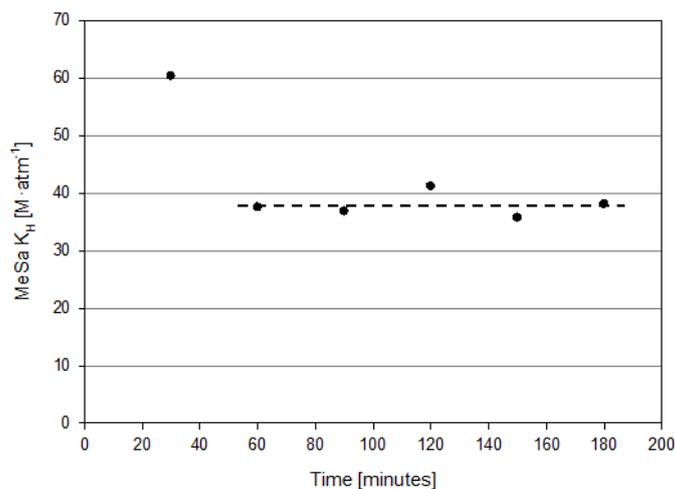
Fig. 3 MeSa K_H vs time at 25 ℃. The dashed line represents the asymptotic value of K_H

Table 1 Values of K_H [M·atm^{-1}]* for GLVs with at various temperatures

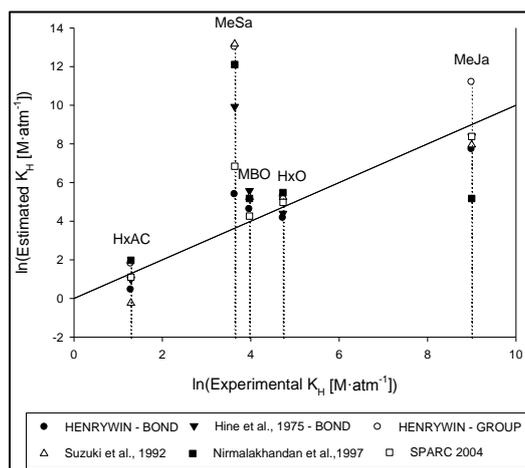| GLV	25°C	30°C	35°C	Literature Values (25°C)
MeJa	8091 ± 1121	6716 ± 1272	4837 ± 272	5018 (Karl *et al.* 2008)
MeSa	37.9 ± 2.1	16.4 ± 0.9	10.0 ± 4.2	33.5 (Karl *et al.* 2008)
MBO	52.9 ± 5.1	40.2 ± 5.4	31.7 ± 2.2	48 (Altschuh *et al.* 1999)
HxO	113 ± 7.1	83.4 ± 8.3	62.7 ± 3.0	25 (T. Karl and W. Lindinger, un-published data, 1998) (Fall *et al.* 1999)
HxAC	3.62± 0.22	3.21 ± 0.17	2.56 ± 0.19	3.3 (Karl *et al.* 2003)

*Values given ±1 Standard deviation

Fig. 4 Comparison of experimental K_H with estimated values. The experimental values are indicated by the intersecting dotted line for each compound. The straight line indicates perfect correlation

These measurements are difficult because MeJa partitions so strongly to the aqueous phase that

a detectable decrease in aqueous concentration can only be achieved with high gas flowrates and long sample intervals. The value for HxO was presumably measured the same way and may suffer from the same problems mentioned above due to its relatively high value. The highest Henry's constant is that for MeJa and the lowest is for HxAC. As K_H increases, the partitioning of compounds is biased towards the aqueous phase. Thus, the chemistry for MeJa in atmospheric systems is going to be determined primarily by the aqueous phase processes. The breakpoint for such behavior is typically $K_H > 1000$ M·atm^{-1} (Gelencser 2005). Hence for all other GLVs the aqueous phase processes are less important.

In addition to the measured values, six quantitative structure-property relationships (QSPRs) were used to determine how literature predictions compare to our experimental values. These relationships correlate the molecular structure with its thermodynamic properties. Countless variations exist; the methods selected here were chosen for their wide applicability and prevalent usage. This study used two *bond contribution* methods: that of Hine and Mookerjee (1975) (Hine and Mookerjee 1975) and EPI Suite's HENRYWIN program (Meylan and Howard 1991). In addition, HENRYWIN's *group contribution* method was used, summing the contribution of functional groups instead of individual bonds. Two methods combining molecular connectivity indices and group contributions were also used, viz., that of (Nirmalakhandan *et al.* 1997) and (Suzuki *et al.* 1992), and finally the SPARC Performs Analytical Reasoning in Chemistry (SPARC) online calculator based on a blend of Linear Free Energy Relationships and Perturbed Molecular Orbital theory (Hilal *et al.* 2003). GLVs present a challenge for property estimation because they have multiple functional groups producing a complex polar character whose hydrogen bonding interactions can be difficult to capture. This is reflected in Fig. 4, which compares the experimentally determined K_H for each GLV with the estimated values from the above methods.

The estimation methods performed satisfactorily for the three lower molecular weight compounds with relatively simple functional group combinations: HxO, HxAC, and MBO, but not for MeSa and MeJa. The range of estimation values for HxO (64.5 M·atm^{-1} to 196 M·atm^{-1}) contained the measured value, with the most accurate being the bond method of Hine and Mookerjee (1975) (81. 7 M·atm^{-1}). For HxAC, the estimations were again all accurate, the range (0.78 M·atm^{-1} to 7.23 M·atm^{-1}) contained the measured value and all estimations were within one order of magnitude, with the best performing being SPARC (3.02 M·atm^{-1}). For MBO, all of the estimations (70.8 M·atm^{-1} to 264 M·atm^{-1}) including the best performing (SPARC, 70.8 M·atm^{-1}) produced values higher than the measured value, showing a consistent overestimation of the distribution towards the aqueous phase. However, the estimation methods were inadequate for predicting K_H of MeJa and MeSa, with the ranges of estimations spread over many orders of magnitude. For MeJa, the range (177 M·atm^{-1} to 72,464 M·atm^{-1}) was very large, but was affected by the excessively high and low values respectively given by the HENRYWIN-GROUP and Nirmalakhandan et al (1997). The best performing was again that of Hine *et al.* (1975). The estimations for MeSa were even more scattered, the range of estimations (216 M·atm^{-1} to 195,588 M·atm^{-1}) spanned many orders of magnitude and did not even include the measured value. Here there were no outliers skewing the range, and even the best performing HENRYWIN-BOND method value was almost 10 times the measured value. For both MeJa and MeSa, the multiple functional groups clearly affected the predictive ability of the methods. For MeSa, especially, all methods appeared to greatly overestimate the hydrogen bonding that the hydroxyl and ester groups would lend, while neglecting the nonpolar character of the aromatic ring. Overall, however, most correctly identified MeJa as having the largest K_H and HxAC as the smallest. The general best

Table 2 Measured enthalpy and entropy of each GLV

GLV	A	B	ΔH (kJ·mol^{-1})[*]	ΔS (J·mol^{-1}·K^{-1})[†]	r^2
MeJa	-0.1015	4719.5	36.7 ± 13.2	21.6 ± 21.8	0.969
MeSa	30.50	12221	99.1 ± 28.3	276 ± 47	0.980
MBO	4.913	4706.2	36.6 ± 2.5	63.2 ± 4.2	0.999
HxO	6.518	5412.1	42.5 ± 0.8	76.6 ± 1.3	0.999
HxAC	2.278	3126.3	23.5 ± 10.3	41.3 ± 17.3	0.954

[*]Values given ±2 Standard Errors of the slope. [†]Values given ±1 Standard Errors of the intercept

performing estimators (judged by sum of squared relative errors) were HENRYWIN – BOND program, followed closely by the SPARC program. This is an interesting result given that group contribution methods are thought to be more accurate than bond contribution methods (Staudinger and Roberts 1996). Here, the HENRYWIN-BOND method was not only more applicable (HENRYWIN-GROUP returned an incomplete fragment value when estimating K_H for MBO) but also more accurate than the HENRYWIN-GROUP method, even when omitting MeSa and MeJa from consideration. Thus, for both MeJa and MeSa we believe that the experimental values are more reliable than any prediction methods.

3.2 Henry's law constants at different temperatures

The variation of the Henry's constants with temperature is an important parameter in the assessment of the atmospheric aqueous chemistry. The variation can be expressed using the following expression (Valsaraj 2009)

$$\ln K_H = A - \frac{B}{T} \tag{1}$$

where A and B are constants. From the constants A and B, the enthalpy of phase change from liquid to gas ΔH [kJ·mol^{-1}] and the entropy of phase change ΔS [kJ·mol^{-1}·K^{-1}] for each compound can be found (Bamford *et al.* 1999). The results are shown in Table 2.

The ΔH values ranged from (23.5 ± 10.3) kJ·mol^{-1} to (99.1 ± 28.3) kJ·mol^{-1} for HxAC and MeSa respectively. These are consistent with the ΔH of non-aromatic, oxygenated alkenes (Chickos and Acree 2003). For MBO, HxO, and HxAC they are similar to enthalpy of vaporization for unsaturated counterparts: 50.3 kJ·mol^{-1} for 2-methyl-2-butanol, 61.1 kJ·mol^{-1} for 1-hexanol, and 52.1 kJ·mol^{-1} for hexyl acetate (Chickos and Acree 2003). Double bonds have been shown to decrease the enthalpy of vaporization but generally only by 1-2 kJ·mol^{-1} for alkanes (Baev 2012). The rest of the discrepancy may be attributed to the fact that the cited values of enthalpy of vaporization are calculated as the energy required to vaporize the pure compound from its pure liquid, however the enthalpy required to vaporize the GLV from an aqueous solution may be higher due to hydrogen bonding. The ΔH of MeSa compares favorably with that of other oxygenated aromatics such as benzoic acid (89.5 ± 0.16) kJ·mol^{-1} (Morawetz 1972). The ΔS values ranged from (22 ± 21) J·mol^{-1}·K^{-1} (MeJa) to (276 ± 47) J·mol^{-1}·K^{-1} (MeSa). MeJa, HxO, MeSa, and HxAC have values within the expected range for organic compounds, while MeSa's high value compares well with that of benzoic acid (261 J·mol^{-1}·K^{-1}) (Torres-Gómez *et al.* 1988).

Table 3 K_H [M/atm]* of GLVs at varying ionic concentrations at 25°C

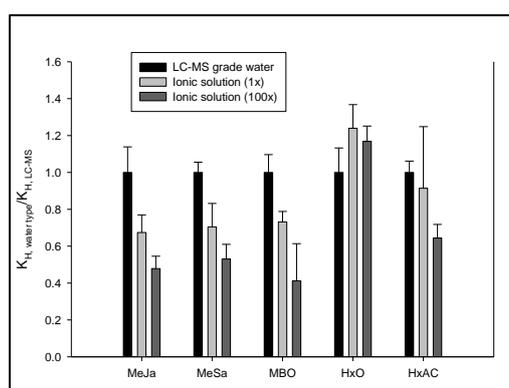| GLV	LC-MS grade water	Ionic solution (1x)	Ionic solution (100x)
MeJa	8091 ± 1121	5454 ± 520	3869 ± 261
MeSa	37.9 ± 2.1	26.7 ± 3.4	20.1 ± 1.6
MBO	52.9 ± 5.1	38.7 ± 2.2	21.8 ± 4.4
HxO	113 ± 15	140 ± 18	132 ± 11
HxAC	3.60 ± 0.22	3.29 ± 1.1	$2.32\ 0.17$

*Values given ± 1 standard deviation

Fig. 5 K_H [M·atm^{-1}] of GLVs at varying ionic concentrations at 25 °C, error bars represent 1 standard deviation

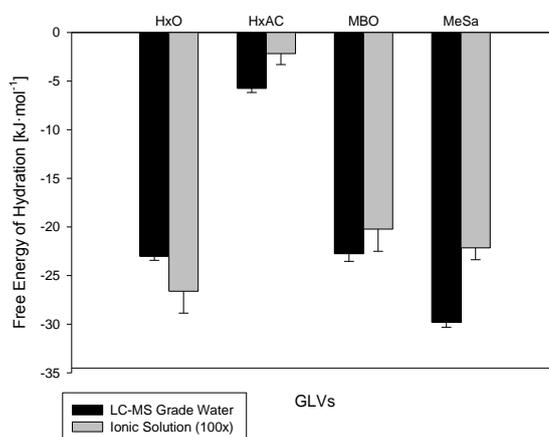
Fig. 6 Comparison of free energy of hydration of different GLVs in pure water and 100 times ions concentration solution obtained from MD simulations

3.3 Henry's law constants and free energies of hydration at varying ionic concentrations

In the literature it has been reported that K_H for glyoxal increases by as much as 50 times in the presence of sodium sulfate (Ip *et al.* 2009). Hence, the extent to which partitioning behavior of

GLVs would be affected by environmentally relevant fogwater composition was determined by performing an experiment at ionic strength comparable to actual fogwater. One solution had an ionic composition similar to the fogwater (0.01 M) and the other one had a composition 100 times (1 M), comparable to that of an industrial wastewater. The K_H obtained in the two solutions and in ultrapure water are displayed in Table 3.

The magnitude of these values relative to the value in LC-MS grade water is given in Fig. 5. For MeJa, MeSa, MBO, and HxAC the K_H value is clearly affected by the ionic strength of the liquid phase. HxO is the only GLV that appears unaffected. Our MD simulations of free energies of solution gave the results shown in Fig. 6, which exhibit trends that are similar to those observed from Fig. 5. The free energies of hydration shown in Fig. 6 decrease in magnitude (i.e., become less negative) in the presence of salts for all GLVs except HxO. These results indicate that it is more difficult to solvate HxAC, MBO, MeJa, and MeSa when the ion concentration increases in water. These results are in general agreement with previous findings that ionic species introduce a "salting-out" effect (Peng and Wan 1998), which reduces a compound's aqueous solubility and shifts its air-water partitioning behavior towards the gas phase. The higher molecular weight GLVs with carbonyl groups (HxAC, MeSA, MeJa) all show this effect. Regarding HxO, 1-alkanols have previously been shown to have a decreased salting out effect from sodium sulfate than 2-ketones due to the ability of the alcohol group to hydrogen bond with water more than the carbonyl (Falabella *et al.* 2006). The fact that MBO undergoes salting out can be attributed to steric hindrance to water accessing its hydroxyl group. The simulation results also suggest that HxO partitions more to the aqueous phase when salts are present (its free energy of hydration becomes more negative), which is in agreement with the experimental results shown in Fig. 5.

3.4 Aqueous solubility

The measured aqueous solubility of GLVs are presented in Table 4. The solubility of MBO (1959 ± 36 mM) clearly dwarf that of the other GLVs, unsurprising because it is the lightest molecular weight GLV and its hydroxyl group lends significant hydrogen bonding opportunity. The solubility of HxO (162 ± 6 mM) was also relatively large because of the hydroxyl group bonded to the first carbon, but less than MBO because of its extra carbon atom and straight-chain enol structure which exposes more non-polar surface area to interact with water. The other three GLVs exhibited modest aqueous solubility, as both MeJa (4.52 ± 0.09 mM) and HxAC (3.12 ± 0.17 mM) were under 5 mM while MeSa was just over (5.11 ± 0.06 mM). Neither HxAC nor MeJa has any alcohol groups, but ester groups lend enough polar character to solubilize appreciably. The straight chain structure of HxAC clearly limits its solubility, and it is interesting to note the difference in solubility between HxO and HxAC by simply replacing HxAC's hydroxyl group with a carboxyl group. MeSa's aromatic ring dampened the influence of the aromatic alcohol and ester group-the increased bulk also contributed to its low solubility. However, even though the differences in solubility are large, even the least soluble GLV should not be expected to reach its aqueous saturation value in environmental conditions.

Many estimations were performed to obtain the aqueous solubility of GLVs including: EPI Suite's WATERNT bond contribution method (Meylan and Howard 1995), the group contribution method of Marrero *et al.* (Marrero and Gani 2002), and SPARC. In addition, solubility is also commonly estimated by using correlations with either experimentally determined or estimated log(K_{ow}) values. This arises by manipulating the fugacity equations of an analyte, eventually giving Eq. (2) (Chiou *et al.* 1982)

$$\log(K_{OW}) = -\log(S) - \log(\bar{V}_0^*) - \log(\gamma_0^*) + \log\left(\frac{\gamma_w^*}{\gamma_w}\right) \tag{2}$$

where $\bar{V}_0^*$ is the molar volume of octanol, γ_0^* is the activity coefficient of the solute in octanol saturated water, γ_w^* is the solute activity coefficient in water saturated with octanol, and γ_w is the solute activity coefficient in pure water. If one assumes that the solute forms an ideal solution in octanol, and that the analyte's solubility is the same in pure water as water saturated with octanol, $\log(K_{ow})$ can be directly correlated with $\log(S)$. Numerous coefficients for the linear relationship between the two properties have been published (Banerjee *et al.* 1980, Chiou *et al.* 1977, Meylan and Howard 1996). In the idealized case, the slope should be -1, though others have found (Isnard and Lambert 1989) that over a large training set this does not bear true. This discrepancy has been attributed to non-ideal behavior resulting from the mutual saturation of water and octanol (Chiou *et al.* 1982). While octanol is only slightly soluble in water, water is highly soluble (2.3 M (Chiou *et al.* 1982)) in octanol which directly affects molar volume $\bar{V}_0^*$ and could affect the γ_0^* term, depending on the analyte. Correlations of this type are used not only for small functional organic molecules, but complex, multifunctional molecules and pharmaceutical drugs. Finally, Jain *et al.*

Table 4 Measured aqueous solubility and $\log(K_{ow})$ of GLVs

GLV	Solubility [mM]	$\log(K_{ow})$
MeJa	4.52 ± 0.09	2.55 ± 0.02
MeSa	5.11 ± 0.06	2.36 ± 0.02[a]
MBO	1959 ± 36	0.69 ± 0.02[b]
HxO	162 ± 6	1.52 ± 0.02[c]
HxAC	3.12 ± 0.17	2.48 ± 0.02[c]

[a] (Liyana-Arachchi *et al.* 2013a)
[b] (Liyana-Arachchi *et al.* 2013b)
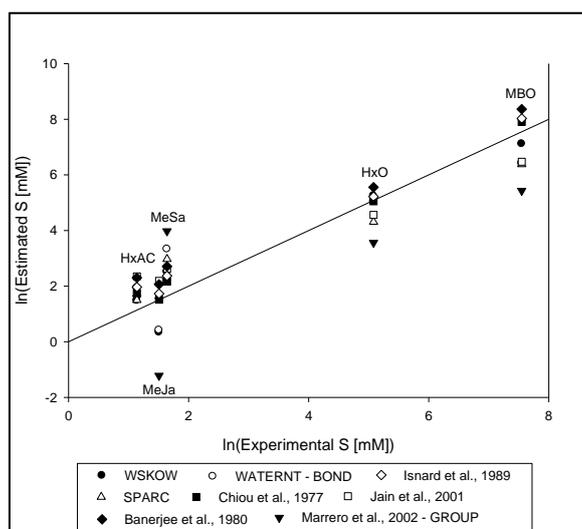[c] (Liyana-Arachchi *et al.* 2014)

Fig. 7 Comparison of experimental and predicted aqueous solubility of GLVs in ln scale

(Dewulf *et al.* 1995) presents the General Solubility Equation which begins by defining K_{ow} as the solubility of the analyte in octanol, C_o, divided by the analyte solubility in water, S. By assuming all organic analytes are fully miscible in octanol, a simple correlation between log(S) and log(K_{ow}) is found.

In all, eight different estimations for solubility were used: two based only on molecular structure, the other six were correlations using previously determined experimental values of log(K_{ow}) to estimate S. These estimated values are plotted against the experimental values in Fig. 7.

For MeJa, both the group and bond contribution schemes under predicted the solubility, presumably due to difficulty to decipher the effect of the many multifunctional groups. The correlations all predicted it very well, with the best performing being Chiou *et al.* (1977) (4.54 mM). MeSa again proved to be difficult for group contribution schemes to predict, with both group and bond methods overestimating the solubility, again over-predicting the extent of hydrogen bonding due to the aromatic hydroxyl and ester groups. The correlations were much closer, but still over predicted slightly, with the best method again being the correlation of Chiou *et al.* (1977) (8.72 mM). The range of predictions for MBO (228 mM to 4289 mM) was very large, and erred by deviating both positively and negatively from the measured value. Both group contribution methods under-predicted, and the closest correlation value was from EPI Suite's WSKOW program (based on Meylan *et al.* 1996), some 65% of the measured value (1230mM). For HxO however, the methods showed better accuracy, especially the WATERNT method. The best was again that of Chiou *et al.* (1977) (156 mM), but all methods except the group method of Marrero *et al.* (2002) provided acceptable estimations. For HxAC, all methods provided very good estimations, including both group contribution methods and SPARC, however all slightly overestimated the value. The closest came from WSKOW (4.39 mM). The two best performing estimations were those of Chiou *et al.* (1977) and EPI Suite's WSKOW program, both from measured log(K_{ow}) values. Either the correlation of Chiou *et al.* (1977) or WSKOW program had the best solubility estimation for every GLV. Overall, all methods generally identified MBO as the most soluble, HxO as less soluble than MBO, and MeSa, MeJa, and HxAC as far less. As in the prediction of Henry's Constants, the group contribution method appeared to struggle with both MeJa and MeSa, the two most complex GLVs. Since group contribution methods predict properties "from scratch", it is somewhat unfair to compare them to the correlations based on accurate experimental values. Neither the Chiou *et al.* (1977) nor WSKOW correlations used the ideal-case slope of -1, yet were more accurate in this case than the other correlations which were closer to ideality. Past papers have found that grouping monofunctional compounds by class increases correlational accuracy and pushes the slope toward unity (Tewari *et al.* 1982). However, for multifunctional compounds like GLVs, using a general correlation trained on a varied dataset of compounds with a wide variety of functional groups appears to be the best choice. This may be because of non-ideal conditions as specified above affecting the process. When estimating the aqueous solubility of multifunctional compounds such as GLVs, a correlation with an experimentally determined log(K_{ow}) is preferable to group contribution methods, as noted elsewhere (Meylan and Howard 1996).

3.5 1-Octanol/water partition coefficient

In previous works from our laboratory, the log(K_{ow}) values for MBO, HxO, HxAC, and MeSa were measured (Liyana-Arachchi *et al.* 2013a, b, 2014). They are presented in Table 4 along with
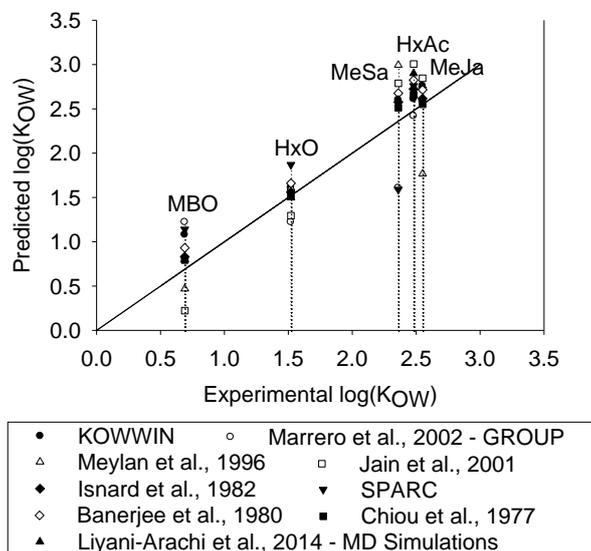
Fig. 8 Comparison of Experimental and Predicted octanol/water partition coefficients of GLVs

the measured value for MeJa. The values reflected the solubility trends well: MBO partitions strongly to the aqueous phase, followed by HxO, then MeJa, MeSa, and HxAC far behind. These values are plotted in Fig. 8 against estimated values obtained from EPI Suite's bond contribution program KOWWIN (Meylan and Howard 1995), the Marrero *et al.* (2002) group contribution method, SPARC, MD simulations from previous works, and the same log(S) vs log(K$_{ow}$) correlations as the previous section. Here again, the Chiou *et al.* (1997) correlation is clearly the most accurate. This is unsurprising, given that the KOWWIN and WATERNT estimations are both based on the same bond/fragment contribution methodology (Meylan and Howard 1991), and the other correlations fared worse than Chiou *et al.* (1977) in predicting solubility from log(K$_{ow}$). The correlation from Chiou *et al.* (1977) was the most accurate for every GLV except HxAC. Unlike for aqueous solubility, however, the KOWWIN fragment contribution method produced acceptable results.

It is again shown that the correlation from Chiou *et al.* (1977), containing a non-unity slope is the most accurate predictor of log(K$_{ow}$). It has previously been shown that alkanes and alkenes deviate consistently downwards from the ideal line (Chiou *et al.* 1982), caused by a large γ_0^* term which indicates significant analyte interactions with the octanol phase. It is not anticipated that the small amount of octanol dissolved in water would cause such large deviations from ideality in the $\frac{\gamma_w^*}{\gamma_w}$ term for compounds already fairly soluble in water. For multifunctional compounds such as GLVs, measuring either log(K$_{ow}$) or S will aid significantly in predicting the other. If no values are available, caution should be taken in estimating the solubility from group or fragment contribution methods, especially if the compound of interest is an aromatic with polar functional groups.

3.6 Implications for secondary organic aerosol production in fog droplets

In order to consider the impact GLVs will have on aqueous phase (fog water) SOA production,

Table 5 K_{SW}, K_H, and K_{SA} for all GLVs at 25°C

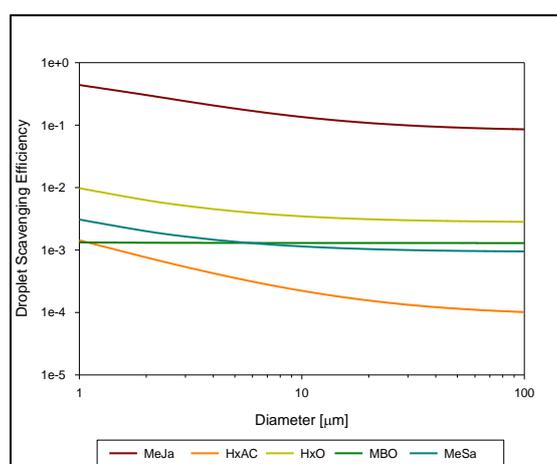| GLV	$K_{sw} \cdot 10^{-4}$ [m][*]	$K_{wa} \cdot 10^{-3}$[*]	$K_{sa} \cdot 10^{-4}$ [m]
MeJa	13.4 ± 0.87	198.0 ± 27.4	2648
MeSa	3.87 ± 1.76	0.927 ± 0.041	3.59
MBO	1.71 ± 1.53	1.29 ± 0.12	0.050
HxO	4.28 ± 2.95	2.76 ± 0.37	16.7
HxAC	25.4 ± 15.7	0.088 ± 0.005	2.24

[*]Values given ± 1 Standard Deviation

Fig. 9 Droplet scavenging efficiency for GLVs at 25 ˚C

it is necessary to examine not only their reactions in the bulk aqueous phase, but also their heterogeneous reactions with gas-phase oxidants while adsorbed at the air-water interface. This "surface phase" can be a significant site for oxidation of VOCs in aqueous droplets with large surface area to volume ratios such as fog and clouds (Wadia *et al.* 2000) (Mmereki and Donaldson 2003) (Liyana-Arachchi *et al.* 2013b). The amount of analyte residing at the air-water interface is represented by the surface concentration C_s [mol·m^2]. In previous works the C_s of GLVs was measured at varying bulk concentrations C_w (Liyana-Arachchi *et al.* 2014). By taking the ratio C_s/C_w at equilibrium, a surface to bulk aqueous partition coefficient K_{sw} [m] was calculated, giving an indication of the extent to which a compound partitions to the air-water interface of an aqueous body vs its bulk. Furthermore, an air-surface partition coefficient K_{sa} [m], defined as the ratio of surface aqueous concentration (C_s) to bulk air concentration (C_a) at equilibrium was obtained by multiplying the dimensionless air-water partition coefficient K_{wa}, equivalent to RTK_H, with K_{sw}. These values are given for the GLVs in Table 5. With these three coefficients, in an air-water system containing GLV at equilibrium, if either bulk aqueous, surface aqueous, or gas phase concentration is known, the two other parameters can be calculated.

Due to its large K_H, MeJa has the largest concentration in both bulk and surface aqueous phases. This has significant implications in fog where the high MeJa concentrations will render it the primary SOA source compared to the other GLVs studied here. This is illustrated by considering the example of an ensemble of fog droplets in a finite volume of air, and a GLV in

equilibrium between the two. By assuming the liquid water content, L, in the finite volume is that of dense fog (1 [g $\cdot$m^{-3}] (Seinfeld and Pandis 1998)), and that this water exists only as spherical droplets, the fraction of total GLV in the volume partitioned into the bulk and surface aqueous phases, the droplet scavenging efficiency, can be calculated as a function of droplet diameters (Valsaraj 2004). The relation is given in Eq. (3) below.

$$\zeta = 1 + \frac{6}{d}(K_{sa}/K_{wa}) \qquad (4)$$

Here ε is the droplet scavenging efficiency, n_w and n_s are the number of moles of analyte in the bulk and surface aqueous respectively, n_o is the total number of moles in the ensemble, L is the liquid water content, and ζ is the deviation from conventional Henry's Constant relationship for bubbles in water, defined in Eq. (4) below. Note that K_{wa} is the dimensionless air-water partition constant.

$$\varepsilon = \frac{n_w + n_s}{n_o} = \left(1 + \frac{1}{LK_{wa}\zeta}\right)^{-1} \qquad (3)$$

Here d is the droplet's diameter, ζ in practice denotes the enhancement in uptake if the surface phase is significant, and approaches 1 as the surface-to-air partition constant, K_{sa} approaches 0. The droplet scavenging efficiency is calculated for each GLV and the results are shown in Fig. 9, which emphasizes the importance of MeJa in aqueous phase processing. MeJa's large K_H gives it a scavenging efficiency which is orders of magnitude greater than that of any other GLV, both at small droplet diameters where interfacial adsorption is significant, and at larger diameters where K_H is the sole determinant of aqueous partitioning. At droplet diameters of 1 μm, almost half of the MeJa in the system can be found in the surface or bulk aqueous phases of the droplet. Even at droplet diameter 50 μm where the surface phase is a negligible store for MeJa, almost 7% of the total MeJa molecules reside in the droplet. For most of the other GLVs, the air-water interface is a significant store, especially at small droplet sizes. Only MBO does not show any significant variation due to droplet size, due to its low K_{sw}.

4. Conclusions

In this study, various physical properties of five GLVs (methyl jasmonate (MeJa), methyl salicylate (MeSa), 2-methyl-3-buten-2-ol (MBO), cis-3-hexen-1-ol (HxO) and cis-3-hexenylacetate (HxAC)) were determined. Experimental values of the Henry's law constant varied as MeJa>HxO>MBO>MeSa>HxAC; aqueous solubility varied as MBO>HxO>MeSa>MeJa>HxAC; and that of 1-octanol/water partition coefficient varied as MeJa>HxAC>MeSa>HxO>MBO. Estimation methods were also tested to predict each property, which, indicated that for oxygenated, multifunctional compounds such as GLVs, a bond contribution method is more accurate than a group contribution method for predicting properties. The effects of temperature (K_H decreased with increasing T, Table 1) and ionic strength (K_H decreased with increasing I, Table 3) relevant to natural fog water samples were estimated, and confirmed by MD simulations. The surface to bulk aqueous and the air-surface partition coefficient at 298K that are necessary for determining fog droplet scavenging efficiencies were determined from the physico-chemical thermodynamic properties and were found to vary as MeJa>HxO>HxAC>MeSa>MBO. This information can provide data on the partitioning characteristics of various compounds in natural water samples of different types. For example, the

scavenging efficiency as a function of the size of atmospheric water droplets were determined as a function of droplet size. From this, the amount of GLV in fog water is shown to be significant, especially for MeJa. This is also relevant for any aqueous media with large surface area to volume ratios such as clouds and fog, and emphasizes the importance of aqueous phase photochemistry to fully elucidating SOA formation mechanisms. The physical properties determined in this study plugs a major hole in the unavailability of their most important physico-chemical properties and, can be very useful in further studies and models to determine the fate of GLVs in the atmosphere and their contribution to SOA production from the aqueous phase.

Acknowledgments

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