

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°C: 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 ($8091 \pm 1121 \text{ M}\cdot\text{atm}^{-1}$) 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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- US EPA (2012), *Estimation Program Interface Suite Part 4.11*, US EPA, Washington, D.C., U.S.A.
- Vácha, R., Siu, S.W., Petrov, M., Böckmann, R.A., Barucha-Kraszewska, J., Jurkiewicz, P., Hof, M., Berkowitz, M.L. and Jungwirth, P. (2009), "Effects of alkali cations and halide anions on the dopc lipid membrane", *J. Phys. Chem. A*, **113**(26), 7235-7243.
- Valsaraj, K.T. (2004), "Adsorption of polycyclic aromatic hydrocarbons at the air-water interface and its role in atmospheric deposition by fog droplets", *Environ. Toxicol. Chem.*, **23**(10), 2318-2323.
- Valsaraj, K.T. (2009), "Trace gas adsorption thermodynamics at the air-water interface: Implications in atmospheric chemistry", *Pure Appl. Chem.*, **81**(10), 1889-1901.
- Valsaraj, K.T. (2009), *Elements of Environmental Engineering: Thermodynamics and Kinetics*, CRC Press, Boca Raton, Florida, U.S.A.
- Wadia, Y., Tobias, D.J., Stafford, R. and Finlayson-Pitts, B.J. (2000), "Real-time monitoring of the kinetics and gas-phase products of the reaction of ozone with an unsaturated phospholipid at the air-water interface", *Langmuir*, **16**(24), 9321-9330.
- Werner, J., Wernersson, E., Ekholm, V., Ottosson, N., Öhrwall, G., Heyda, J., Persson, I., Söderström, J., Jungwirth, P. and Björneholm, O. (2014), "The surface behavior of hydrated guanidinium and ammonium ions: A comparative study by photoelectron spectroscopy and molecular dynamics", *J. Phys. Chem. B*, **118**(25), 7119-7127.
- Wernersson, E. and Jungwirth, P. (2010), "Effect of water polarizability on the properties of solutions of polyvalent ions: Simulations of aqueous sodium sulfate with different force fields", *J. Chem. Theor. Comput.*, **6**(10), 3233-3240.
- Williams, J., Pöschl, U., Crutzen, P.J., Hansel, A., Holzinger, R., Warneke, C., Lindinger, W. and Lelieveld, J. (2001), "An atmospheric chemistry interpretation of mass scans obtained from a proton transfer mass spectrometer flown over the tropical rainforest of surinam", *J. Atmos. Chem.*, **38**(2), 133-166.