Henry's Law Partitioning and Setschenov Salting of 1,2-ISOPPOOH in Aqueous Solutions Containing Ammonium Sulfate and Sodium Oxalate

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Isoprene is the predominant biogenic emission from plants and contributes approximately 30% of global non-methane volatile organic carbon (VOC) emissions. Isoprene hydroxyhydroperoxides (ISOPOOHs) are a first-generation product of isoprene oxidation in low-NOx conditions. In addition to forming secondary organic aerosol (SOA) precursors through further oxidation, ISOPOOHs can also directly contribute to particle growth by partitioning to the condensed phase. The equilibrium between ISOPOOH in the gas and particle phases is governed by Henry's Law:

\[ K_H = \frac{C_{\text{aq}}}{C_{\text{gas}}} \]

where \( K_H \) is the Henry's Law constant. The presence of salts in the aqueous phase can exponentially affect the equilibrium constant, i.e.

\[ K_{H,x} = K_H \times 10^{C_{\text{salt}}} \]

where \( K_{H,x} \) is the Henry's Law constant in the presence of a salt, \( C_{\text{salt}} \) is the Henry's Law constant in pure water, and \( K_H \) is known as the Setschenov constant.²

This Study

In this experiment, the \( K_H \) for 1,2-ISOPPOOH is determined for ammonium sulfate and sodium oxalate, two major components of atmospheric aerosols. This is accomplished by measuring the gas phase concentrations of 1,2-ISOPPOOH in the head space above aqueous solutions of 1,2-ISOPPOOH with varying concentrations of ammonium sulfate and sodium oxalate. Gas-phase measurement was accomplished using iodine chemical ionization mass spectrometry (I-CIMS). In addition, calibration of the CIMS, combined with quantification of the aqueous 1,2-ISOPPOOH concentration by a colorimetric method⁴, allowed for calculation of the value of the Henry's Law constant for 1,2-ISOPPOOH.

References


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Motivation

Experimental Setup

Partitioning Experiments

Samples were injected into a round-bottom flask and purified nitrogen was flowed through the head space. For each sample, partitioning and sampling lines came to equilibrium within~8 minutes. The stable gas-phase signal was measured for an additional ≥20 minutes. Approximately 11 samples of varying salt concentrations were measured per day.

Aqueous Phase 1,2-ISOPPOOH Quantification

Aqueous phase 1,2-ISOPPOOH measured by colorimetric method adapted from Ranney and Ziemann:

\[ \text{ Peroxide/} \text{I} \rightarrow \text{equilibrium of } I_2 \text{ and } I_3^+ \]

\[ \begin{align*}
\text{(1)} & \quad R_1 + \text{OO-} + 2I^+ + 2H^+ \rightarrow R_1^+ + \text{O}_2 + \text{H}_2^+ \\
\text{(2)} & \quad I_2 + I^+ \rightarrow I_3^+ \\
\end{align*} \]

Absorption of \( I_2/ I_3^+ \) equilibrium mixture measured at 470 nm. Benzoyl peroxide is used as a standard.

Contribution of aqueous phase analysis to the overall error budget is estimated to be 3%.

Gas-phase time series of a typical experiment (0.415 mmol/L 1,2-ISOPPOOH). Samples were measured in order of increasing ammonium sulfate concentration (0 – 3M). Increasing gas-phase signal shows salting-out behavior.

Salting Experiment Results

Salting out is less than expected from parameterization without OOH group, so the OOH group decreases the salting effect.

Henry's Law Constant

Calculation of \( K_H \) (Henry's Law constant without salt) requires quantification of both aqueous and gas phase concentrations. CIMS (gas phase) calibration was accomplished by integration of the total signals from injecting and completely evaporating known volumes of 1,2-ISOPPOOH solutions.

\[ K_H = \frac{q_{\text{aq. conc.}} (\text{M})}{\text{partial pressure (atm)}} \]

\[ \text{llol conc. ccm sample) } \times \text{mol } \times \text{cm } \times \text{cm}^{-3} \]

Integrated signal vs number of molecules injected. The measured 1,2-ISOPPOOH Henry's Law constants.

Ongoing work: Determining \( \Delta H_{sol} \) from Arrenhius plot of temperature-dependent \( K_H \) measurements.

Log(\( K_{H,x}/K_H \)) vs salt concentrations (M). \( K_H \) is determined from the slope. Ongoing work: Determination of mixing rules for salting effects of combined ammonium sulfate/sodium oxalate solutions.