1.1. Setschenow Constants

The presence of salts significantly influences the partitioning behavior of organic compounds between gas phase and aqueous phases. The salt effect is quantified with the empirical Setschenow equation, where $K_s$ is the Setschenow constant (M$^{-1}$).

$$\log K_{\text{air/saltwater}} = \log K_{\text{air/water}} + K_s [\text{salt}]$$

1.2. Environmental Relevance of Salt Effect

**Sea Water**

- Henry’s law constants ($K_{\text{air/water}}$) can increase from freshwater to sea water by as much as a factor of 1.36$^2$.
- The salt effect must be quantified when comparing the behavior of organic compounds in freshwater and marine conditions.

**Atmospheric Water**

- Atmospheric water (cloud, fog and aqueous aerosol) contains a mixture of various inorganic salts, of which ammonium sulfate is often the most abundant.
- Setschenow constants for ammonium sulfate are required for accurate atmospheric phase distribution assessments of organic compounds, including those implicated in secondary organic aerosol (SOA) formation.

2. Objectives

- Test various methods for their ability to provide reliable Setschenow constants.
- Determine Setschenow constants for numerous organic compounds in ammonium sulfate solutions.
- Derive a model that predicts Setschenow constants in ammonium sulfate solutions from molecular structure.

3. Methodology

**Shared Headspace Passive Dosing Method**

$$\log A_{\text{salt}} = \log A_0 - K_s [\text{Salt}]$$

$A_0$ and $A_{\text{salt}}$ are GC peak areas obtained for chemicals in pure water and salt solutions, respectively.

**Negligible-Depletion Solid Phase Micro-Extraction (SPME) Method**

$$\log A_{\text{fiber, salt}} = \log A_{\text{fiber, pure water}} + K_s [\text{Salt}]$$

$A_{\text{fiber, pure water}}$ and $A_{\text{fiber, salt}}$ are GC peak areas obtained for chemicals in fiber for pure water and salt solutions, respectively.

**Negligible-Depletion Headspace Gas Chromatography (HSGC) Method**

$$\log A_{\text{HS, salt}} = \log A_{\text{HS, pure water}} + K_s [\text{Salt}]$$

$A_{\text{HS, pure water}}$ and $A_{\text{HS, salt}}$ are GC peak areas obtained for chemicals in headspace for pure water and salt solutions, respectively.

4. Results

The slope shows Setschenow constants $K_s$.

Increase of $K_s$ with molar size for 2-ketones

5. Conclusions and Future Work

Conclusions

- All the three methods can be applied to determine Setschenow constants of ammonium sulfate for different chemicals.
- The aqueous solubilities of test chemicals decrease in the presence of ammonium sulfate.
- There is an increase of $K_s$ with molar size for 2-ketones.

Future work

- To find out the relation of $K_s$ with polarity, molar size, salt concentration and other factors by measuring more chemicals.
- To develop a predictive model for estimating Setschenow coefficients from chemical structure.

6. References and Acknowledgement

- References

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