



The salting behavior of glyoxal in model aerosols containing sulfate

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Glyoxal, the smallest alpha-dicarbonyl, is a ubiquitous component of biogenic environments and urban, arctic, and marine atmospheres. An increasing body of evidence finds small water soluble and polar oxygenated hydrocarbons (OVOC) like glyoxal in the condensed phase despite their high vapor pressures. It is generally believed that multi-phase chemical reactions in cloud or aerosol water form soluble products with lower vapor pressures, and that this lowering of the vapor pressure is the primary cause for the enhanced partitioning. However, our data shows that this could be due to electrostatic forces instead. We have performed a series of simulation chamber experiments to quantify for the first time the time-resolved evolution of glyoxal partitioning to aqueous model aerosols containing sulfate. These measurements show an exponential increase in Henry's law constants with seed particle salt concentrations. This exponential increase is found to be independent of the presence or absence of organics in the seed particles, and can be explained by means of a single parameter, the salting constant K_S , to predict the partitioning of glyoxal over a wide range of environmental conditions (cloud water and concentrated salt solutions of aerosol water). The formalism that we find best explains our data builds on the theory developed by Setschenow in the late 19th century. It is known to the limnology community, but to our knowledge has not previously been used to describe aqueous systems in the atmosphere (aerosols or cloud droplets). The rapid and high monomer partitioning suggests that electrostatic forces triggered by the high dipole moment of glyoxal, rather than vapor pressure, are at the core of the mechanism that causes the high partitioning. This high abundance of glyoxal monomers is compared with oligomeric reservoirs and irreversible reaction pathways (NH₄ or OH radical reactions), and representations for use in atmospheric models are discussed that can explain most of the glyoxal-SOA mass predicted to form in Mexico City. The formalism developed here can easily be extended for atmospheric modeling purposes, but is currently limited by the missing data for Henry's Law constants in the literature.