A Computational Study of the Effect of Glyoxal – Sulfate Clustering on the Henry’s Law Coefficient of Glyoxal

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The figure shows a log-log plot of $\log(K_{H,w}/K_{H,salt})$ (unitless) versus $c_{AS}$ (mol kg$^{-1}$ ALWC). Two equations are compared:

- **Eq. 10 (This work)**: Dashed line
- **Eq. 3 (Kampf et al., 2013)**: Solid line

Different data sets are represented by markers:
- Red circles: AS/FA data
- Blue circles: AS data
- Blue circles with error bars: AS data (non-equilibrium, kinetically limited)

The y-axis represents the log of the ratio of hydration constants, and the x-axis represents the concentration of AS in mol kg$^{-1}$ ALWC.
A Computational Study of the Effect of Glyoxal – Sulfate Clustering on the Henry’s Law Coefficient of Glyoxal

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ABSTRACT We have used quantum chemical methods to investigate the molecular mechanism behind the recently reported (C. J. Kampf et al., Environ. Sci. Technol. 2013, 47, 4236-4244) strong dependence of the Henry’s law coefficient of glyoxal (C$_2$O$_2$H$_2$) on the sulfate concentration of the aqueous phase. While the glyoxal molecule interacts only weakly with sulfate, its hydrated forms (C$_2$O$_3$H$_4$ and C$_2$O$_4$H$_6$) form strong complexes with sulfate, displacing water molecules from the solvation shell and increasing the uptake of glyoxal into sulfate-containing aqueous solutions, including sulfate-containing aerosol particles. This promotes the participation of glyoxal in reactions leading to secondary organic aerosol formation, especially in regions with high sulfate concentrations. We used our computed equilibrium constants for the complexation reactions to assess the magnitude of the Henry’s law coefficient enhancement, and found it to be in reasonable agreement with experimental results. This indicates that the complexation of glyoxal hydrates with sulfate can explain the observed uptake enhancement.

KEYWORDS atmospheric chemistry, secondary organic aerosol, computational chemistry, hydration, solubility
Introduction

Glyoxal, C\textsubscript{2}O\textsubscript{2}H\textsubscript{2}, is one of the smallest and chemically simplest organic molecules known to participate in both chemical and physical atmospheric aerosol processes. Glyoxal itself has a high saturation vapor pressure, but its chemical reactivity makes it an important precursor for secondary organic aerosol (SOA), contributing at least on the order of 1-10 Tg/yr to global SOA formation.\textsuperscript{1,2} In the gas phase, the main sink reactions of glyoxal are photolysis and oxidation by OH radicals.\textsuperscript{3} In the condensed phase, glyoxal molecules react reversibly with water molecules to form covalently bound mono- and dihydrates (denoted C\textsubscript{2}O\textsubscript{3}H\textsubscript{4} and C\textsubscript{2}O\textsubscript{4}H\textsubscript{6}, respectively)\textsuperscript{4}. C\textsubscript{2}O\textsubscript{2}H\textsubscript{2} and C\textsubscript{2}O\textsubscript{3}H\textsubscript{4} further react with organic and inorganic acids to form esters,\textsuperscript{5} with amines,\textsuperscript{6} ammonia\textsuperscript{7} or amino acids\textsuperscript{8} to form a variety of organic nitrogen compounds,\textsuperscript{9} and with themselves to form oligomers and polymers.\textsuperscript{4,10,11,12,13} Many of these reaction products may then participate in SOA formation, and also affect key properties of the formed aerosol such as the visible light absorbance,\textsuperscript{14} the atomic oxygen to carbon ratio (O:C), and thus hygroscopic properties.\textsuperscript{15}

Recently, Kampf \textit{et al.}\textsuperscript{16} reported that the effective Henry's law coefficient K\textsubscript{H,eff} of glyoxal is strongly dependent on the sulfate concentration of the aqueous phase. Similar results have also been found in earlier studies.\textsuperscript{11,17} For example, Ip \textit{et al.}\textsuperscript{17} measured K\textsubscript{H,eff} equal to 4.2×10\textsuperscript{5} mol L\textsuperscript{-1} atm\textsuperscript{-1} in pure water, and larger than 10\textsuperscript{9} mol L\textsuperscript{-1} atm\textsuperscript{-1} in bulk solutions containing sulfate. Kampf \textit{et al.} measured values between 4.5×10\textsuperscript{6} and 4.7×10\textsuperscript{8} mol L\textsuperscript{-1} atm\textsuperscript{-1} in aqueous aerosols containing sulfate, and showed that K\textsubscript{H,eff} increased exponentially with sulfate concentration. They suggested that this is caused by a strong interaction between the glyoxal molecule and the sulfate ion, and like Kroll \textit{et al.}\textsuperscript{11}, they denoted it a “salting-in” effect. “Salting-in” is currently not well understood.
Sulfate, $\text{SO}_4^{2-}$, is one of the major inorganic constituents of atmospheric aerosol particles. Sulfate salts are emitted directly into the atmosphere via sea spray. Additionally, almost all sulfur emitted into the atmosphere in any form, including both biogenic emissions of organic sulfur compounds such as dimethyl sulfide (DMS) and carbonyl sulfide (OCS) from algae, and anthropogenic sulfur dioxide ($\text{SO}_2$) emissions from fossil fuel burning, are eventually oxidized to sulfuric acid via both gas-phase and liquid-phase oxidation processes. Sulfuric acid effectively condenses onto pre-existing aerosol particle, or participates in new-particle formation, in both cases ultimately ending up as sulfate in particles and droplets of various size.$^{18}$ (Note that while sulfuric acid molecules may retain one or both of their protons in the very smallest nanometer-scale clusters, the sulfate ion is the dominant $\text{S(VI)}$ species in all but the most acidic aqueous bulk solutions – including aerosol particles above size of a few nanometers.) Interactions of organic species such as glyoxal with sulfate ions are thus potentially important processes in atmospheric chemistry.

In this study, we investigate the proposed interaction between glyoxal and sulfate ions using quantum chemical methods together with a continuum solvent model, and use the computed free energies for the complex formation reactions to estimate the magnitude of the solubility enhancement as a function of the sulfate molality. In addition to the glyoxal molecule, we have also studied the binding of the glyoxal hydrates $\text{C}_2\text{O}_3\text{H}_4$ and $\text{C}_2\text{O}_4\text{H}_6$ to sulfate.

In principle, assessing the effect of glyoxal – sulfate interactions on the Henry’s law coefficient is straightforward. Quantum chemical calculations can be used to obtain formation free energies for glyoxal – sulfate complexes, both in vacuum and – subject to further approximations – also in the aqueous phase. The free energies are easily converted into equilibrium constants, which can then be used to derive effective Henry’s law coefficients as was
done for the glyoxal hydration reactions by Ervens and Volkamer.\textsuperscript{4} However, the nature of the sulfate ion as well as the surrounding aqueous phase present some problems for this approach. First, accurately treating solvent effects is a difficult task for quantum chemistry. Continuum models can be used as a first-order description, but at least some of the solvent molecules in the first solvation shell should be explicitly included.\textsuperscript{19} Reaction entropies and thus free energies are also very difficult to estimate for non-isomolecular aqueous-phase reactions. Second, small polyanions such as sulfate are in general unstable in vacuum with respect to electron detachment.\textsuperscript{20} Therefore, explicit solvation (by at least three water molecules in the case of sulfate\textsuperscript{20}) is needed in the treatment of the sulfate ion also in “vacuum” calculations. Quantitatively accurate modeling would likely require a combination of continuum solvent models with several tens of explicitly included water molecules,\textsuperscript{21} which severely restricts the level of quantum chemical theory that can be applied, and also presents challenges for configurational sampling of cluster structures.

In this study, we have attempted to reach a compromise between the mutually exclusive goals of system size and computational accuracy. We have modeled sulfate solvation using a combination of six explicitly modeled water molecules (corresponding to a half-filled first hydration shell, with each oxygen of the sulfate ion solvated by at least one water), and a continuum solvent model for treating the effect of further solvent molecules. Furthermore, we have estimated the equilibrium constants for glyoxal – sulfate clustering by studying the displacement of one water molecule from the sulfate hexahydrate cluster by glyoxal and its hydrates:

$$(\text{SO}_4^{2-})(\text{H}_2\text{O})_6 + \text{C}_2\text{O}_2\text{H}_2 \leftrightarrow (\text{SO}_4^{2-})(\text{C}_2\text{O}_2\text{H}_2)(\text{H}_2\text{O})_5 + \text{H}_2\text{O}$$  \hspace{1cm} (R1)
(SO$_4^{2-}$)(H$_2$O)$_6$ + C$_2$O$_3$H$_4$ $\rightleftharpoons$ (SO$_4^{2-}$)(C$_2$O$_3$H$_4$)(H$_2$O)$_5$ + H$_2$O  \hspace{1cm} \text{(R2)}

(SO$_4^{2-}$)(H$_2$O)$_6$ + C$_2$O$_4$H$_6$ $\rightleftharpoons$ (SO$_4^{2-}$)(C$_2$O$_4$H$_6$)(H$_2$O)$_5$ + H$_2$O  \hspace{1cm} \text{(R3)}

Since the number of separate molecules or clusters does not change in reactions R1-R3, the reaction entropies are fairly small; the translational, rotational and vibrational entropies mostly cancel out. Limiting our analysis to isomolecular reactions avoids at least some of the errors associated with the difficulty of accurately calculating rotational and vibrational entropies for clusters, and especially librational entropies of molecules in the liquid phase.

**Computational details**

All geometry optimizations and frequency calculations have been performed on the Gaussian 09 program suite$^{22}$ using the M06-2X functional$^{23}$ and the 6-31+G(d) and 6-311++G(3df,3pd) basis sets. The M06-2X functional was chosen on basis of recent benchmarks showing its adequate performance in describing sulfur containing compounds and yielding reliable thermodynamics for sulfuric acid - water clusters.$^{24,25,26}$ Solvent effects are taken into account using a Polarizable Continuum Model with the integral equation formalism variant (IEFPCM) IEFPCM.$^{27,28}$

In aqueous solution glyoxal can exist in three different forms: unhydrated, monohydrated and dihydrated. The mono- and dihydrates includes two and four hydroxyl groups, respectively, which greatly complicates the potential energy surface due to internal rotations and various possible hydrogen-bonding patterns. The lowest Gibbs free energy conformations of glyoxal, and
the two hydrates were identified using a systematic rotor approach to construct a rotamer library, which rotates the internal dihedral angles making all possible rotations in increments of 120 degrees. Utilizing this approach narrowed down the energetic relevant conformations (within 3 kcal/mol of the lowest identified) to a single glyoxal, four monohydrate and fourteen dihydrate conformations. The lowest identified conformations are shown in the left-hand side of Figure 1. Structural and thermodynamic data for the displayed clusters is given in the Supporting Information.

Lambrecht et al. have explored the energy landscape for sulfate-water clusters with three to seven water molecules. They reported 49 different conformations of the sulfate hexahydrate [(SO\textsubscript{4}\textsuperscript{2−})(H\textsubscript{2}O)\textsubscript{6} cluster. These 49 conformations were optimized using M06-2X/6-31+G(d) with PCM solvation to identify the lowest Gibb’s free energy conformation to use as a reference in the water displacement reactions. Similarly, 12 different conformations were extracted from Lambrecht et al. to optimize the sulfate pentahydrates. To construct the (SO\textsubscript{4}\textsuperscript{2−})(C\textsubscript{2}O\textsubscript{2,3,4}H\textsubscript{2,4,6})(H\textsubscript{2}O)\textsubscript{5} clusters we initially scanned the potential energy surfaces of the unhydrated clusters by using a semi-empirically guided methodology as previously described. This scan lead to two different conformations of (SO\textsubscript{4}\textsuperscript{2−})(C\textsubscript{2}O\textsubscript{2}H\textsubscript{2}) clusters, five(SO\textsubscript{4}\textsuperscript{2−})(C\textsubscript{2}O\textsubscript{3}H\textsubscript{4}) clusters and 23 (SO\textsubscript{4}\textsuperscript{2−})(C\textsubscript{2}O\textsubscript{4}H\textsubscript{6}) clusters. Each of these conformations are then hydrated by five water molecules in the same pattern as indicated by the isolated sulfate pentahydrates from Lambrecht et al. Using this procedure allows the exploration of the potential energy surface of the clusters and should yield a good estimate for the equilibrium constant for the binding of glyoxal, mono-hydrate and di-hydrate to sulfate in aqueous solution. Final energetics for the lowest free energy conformations found at the M06-2X/6-31+G(d) were then computed using the larger 6-311++G(3df,3pd) basis set. However, when using this basis set
together with the continuum solvent model, spurious low-lying imaginary frequencies appeared. Therefore, the clusters were reoptimized at the M06-2X/6-311++G(3df,3pd) level of theory in vacuum, and thermal free energy calculations were obtained from this calculation. The solvation effects were then computed by a single-point M06-2X/6-311++G(3df,3pd) calculation with the IEFPCM solvent model.

Results and Discussion

Figure 1 depicts reactions R1-R3, including the most favorable geometries of the reactant and product clusters. The M06-2X/6-311++G(3df,3pd) Gibbs free energies (ΔG at T=298 K) of reactions R1, R2 and R3 are +5.00, -5.44 and -3.68 kcal/mol, respectively. These correspond to dimensionless equilibrium constants (equal to $e^{-ΔG/RT}$, where R is the gas constant) of 0.000216, 9720 and 498, respectively. Based on the computed results, glyoxal itself interacts very weakly with sulfate. The reason for this is that while glyoxal is polar, it lacks hydrogen bond donor atoms (e.g., OH groups) with which to bond to the four acceptor oxygens of the sulfate ion. The glyoxal hydrates, on the other hand, have multiple OH groups capable of acting as H-bond donors. Accordingly, they bond strongly to sulfate, and are easily able to displace water molecules from its solvation shell, as indicated by the large equilibrium constants of reactions R2 and R3. Shifts in the hydration equilibria of glyoxal have been observed experimentally in the presence of sulfate, in good agreement with our calculations.\(^\text{32}\)
Figure 1. Structures of the reactants (left) and products (right) of reactions R1 (top row), R2 (middle row) and R3 (bottom row), calculated at the M06-2X/6-311++G(3df,3pd) level. Color coding: yellow=sulfur, gray = carbon, red=oxygen, white=hydrogen.

The effect of glyoxal - sulfate clustering on the Henry's law coefficient can be assessed in the same way as the effect of glyoxal hydration reactions, which increase the $K_{H, eff}$ value of glyoxal by a factor of 72 700. Applying the law of mass balance to R2 and R3 and reorganizing, we obtain expressions for the concentrations of the sulfate - glyoxal hydrate clusters:

$$[(SO_4^{2-})(C_2O_3H_4)(H_2O)_s] = K_{R2}[C_2O_3H_4][(SO_4^{2-})(H_2O)_6]/[H_2O]$$  \hspace{1cm} Eq1

$$[(SO_4^{2-})(C_2O_4H_6)(H_2O)_s] = K_{R3}[C_2O_4H_6][(SO_4^{2-})(H_2O)_6]/[H_2O]$$  \hspace{1cm} Eq2
where $K_{R2}$ and $K_{R3}$ are the equilibrium constants for reactions R2 - R3, respectively (R1 can be ignored as it is unfavorable). The concentrations of the glyoxal hydrates can be related to the concentration of unhydrated glyoxal as follows:\(^4\)

\[
[C_2O_3H_4] = K_{hyd1}[C_2O_2H_2] \quad \text{Eq3}
\]

\[
[C_2O_4H_6] = K_{hyd2}[C_2O_3H_4] = K_{hyd2}K_{hyd1}[C_2O_2H_2] \quad \text{Eq4}
\]

where $K_{hyd1} = 207$ and $K_{hyd2} = 350$ are the equilibrium constants of the hydration reactions.\(^4\)

Accounting for single and double hydrations, as well as sulfate complexation of both hydrates, the total concentration of glyoxal, $[C_2O_2H_2]_{tot}$, consists of five components: pure glyoxal $C_2O_2H_2$, the hydrates $C_2O_3H_4$ and $C_2O_4H_6$, and the sulfate complexes of the two hydrates. If we assume that the $(SO_4^{2-})(C_2O_3H_4)(H_2O)_5$ and $(SO_4^{2-})(C_2O_4H_6)(H_2O)_5$ clusters are representative of all water-solvated sulfate complexes of glyoxal monohydrate and dihydrate, we can thus write:

\[
[C_2O_2H_2]_{tot} = [C_2O_2H_2] + [C_2O_3H_4] + [C_2O_4H_6] + [(SO_4^{2-})(C_2O_3H_4)(H_2O)_5] + [(SO_4^{2-})(C_2O_4H_6)(H_2O)_5] \quad \text{Eq5}
\]

Inserting the expressions above, and further assuming that the $(SO_4^{2-})(H_2O)_6$ cluster is representative of all solvated sulfate ions (i.e. $[(SO_4^{2-})(H_2O)_6] \approx [SO_4^{2-}]_{aq}$) we obtain

\[
[C_2O_2H_2]_{tot} = [C_2O_2H_2](1 + K_{hyd1} + K_{hyd2}K_{hyd1} + [(SO_4^{2-}]_{aq}/[H_2O])(K_{hyd1}K_{R2} + K_{hyd2}K_{hyd1}K_{R3})) \quad \text{Eq6}
\]

And the effective Henry's law coefficient in the presence of sulfate, $K_{H,salt}$, is simply

\[
K_{H,salt} = \frac{[C_2O_2H_2]_{tot}}{[C_2O_2H_2]}
\]
\[ K_{H,salt} = K_H (1 + K_{hyd1} + K_{hyd2}K_{hyd1} + ([SO_4^{2-}_{aq}]/[H_2O])\{K_{hyd1}K_{R2} + K_{hyd2}K_{R1}K_{R3}\} ) \]

Eq7

Where \( K_H \) is the Henry’s law coefficient of unhydrated glyoxal. Inserting numerical values for the equilibrium constants into Eq7, we obtain a simple equation

\[ \frac{K_{H,salt}}{K_H} = 72,700 + 38,100,000x_{SO4} \]

Eq8

Where \( x_{SO4} = ([SO_4^{2-}_{aq}]/[H_2O]) \) is the mole fraction of sulfate. Alternatively, we can express the ratio of the effective Henry's law coefficient in the presence of sulfate to that in the absence of sulfate but accounting for hydrates (\( K_{H,W} \)):

\[ \frac{K_{H,salt}}{K_{H,W}} = 1 + 524 x_{SO4} \]

Eq9

\( x_{SO4} \) can further be converted into a sulfate molality \( c_{SO4} \) in mol/kg by dividing by the molar density of water (assumed to be 55.5 mol/kg), yielding the expression:

\[ \frac{K_{H,salt}}{K_{H,W}} = 1 + 9.45c_{SO4} \]

Eq10

Eq 10 can be reformulated for easier comparison with Equation 3 in Kampf et al.\textsuperscript{16}:

\[ \log(K_{H,W}/K_{H,salt}) = -\log(1 + 9.45(c_{SO4}) \]

Eq 11

The predicted ratio of Henry’s law coefficients in the presence and absence of sulfate is plotted in Figure 2. The computed ratio is in reasonably good agreement with the experimental data presented by Kampf et al. (Figure 1 in their manuscript).\textsuperscript{16} At low sulfate molalities, equation 10 overpredicts and at high molalities it underpredicts the Henry’s law enhancement by sulfate, but by less than a factor of 5 for the range of molalities that reach equilibrium in the experiments.\textsuperscript{16} Eq 10 is able to explain more than two orders of magnitude of the up to 1000-fold
difference in $K_{\text{H,eff}}$ between pure water and ammonium sulfate / fulvic acid aerosol mixtures.$^{16,17}$ This agreement is surprisingly good, given the various assumptions made above, and the fact that the uncertainties of the Gibbs free energies computed for reactions R1-R3 are probably on the order of ± 2 kcal/mol (due to both errors in the “vacuum” electronic energies and in the approximate treatment of solvation), implying that the equilibrium constants $K_{R2}$ and $K_{R3}$ and thus the predicted effect on the solubility of glyoxal are uncertain by roughly a factor of 30. Note that as the equilibrium constants for hydrate formation, $K_{\text{hyd1}}$ and $K_{\text{hyd2}}$, cancel out when the ratio $K_{\text{H,salt}}/K_{\text{H,W}}$ is calculated, their uncertainties do not significantly affect the predicted relative effect of sulfate on glyoxal solubility.

However, larger differences arise at high molalities (larger than 12 mol/kg, the solubility of ammonium sulfate) between equation 10 and the exponential $c_{\text{SO4}}$ dependence predicted by Setschenow salting theory and supported by experiments at all other molalities.$^{16,34}$ Assuming that the sulfate molality never exceeds that of pure sulfuric acid (around 19 mol/kg), Eq 10 could potentially underpredict partitioning by as much as a factor 200. This could be due to the effect of ionic strength on activity coefficients, as all activity coefficients ratios in our mass balance equations are implicitly assumed to be equal to 1. Fig. 2 partially masks such disagreement at high molality, where limited mass transfer (as demonstrated by Figure 2 in Kampf et al.$^{16}$) leads to non-equilibrium conditions in the experiments.$^{16}$ It should be noted that direct experimental evidence of the functional form of the $K_{\text{H,salt}}$ vs $c_{\text{SO4}}$ relationship at very high $c_{\text{SO4}}$ values is not currently available due to these mass transfer limitations. However, at molalities below 12 mol/kg, equilibrium is attained on the time-scales that are accessible in the laboratory. The available data show enhancements that are a factor 5-6 larger compared to the datapoint near 15 mol/kg, and this decrease in the enhancement with increasing $c_{\text{SO4}}$ is attributed to the limited
mass-transfer above 12 mol/kg. Further, equation 10 significantly overestimates the enhancement below 5 mol/kg. Thus, we assume that the exponential (or in any case stronger than linear) $c_{\text{SO}_4}$ dependence extends beyond 12 mol/kg because the experimental data is better described by the exponential fit below 12 mol/kg, and because of a lack of data at high molalities that would suggest otherwise.

Figure 2. Logarithm of the ratio of Henry’s law coefficients in the absence ($K_{H,\text{w}}$) and presence ($K_{H,\text{salt}}$) of sulfate, respectively, as a function of sulfate molality. (A value of 0 corresponds to a ratio of 1, i.e. no effect.) Experimental data and exponential fit from Kampf et al.$^{16}$ AS =
ammonium sulfate, FA = fulvic acid. Equilibrium and non-equilibrium experimental conditions are indicated separately.

Furthermore, the real number of water molecules displaced from the sulfate hydration shell by glyoxal hydrates may differ from unity. This would affect our predictions in two ways. First, the expression for $K_{H,salt}/K_{H,W}$ would then depend on $[H_2O]^{1-n}$, where $n$ is the number of displaced water molecules. Since the water and sulfate concentrations are inversely related, this would imply a stronger dependence of $K_{H,salt}/K_{H,W}$ on $c_{SO4}$ for $n > 1$ and a weaker dependence for $n < 1$. Second, entropy contributions become non-negligible when $n \neq 1$. Entropic effects would tend to reduce uptake compared to Eq 10 if $n < 1$, and increase it if $n > 1$. In order to reconcile deviations between Eq. 10 and experimental data visible in Fig. 2 at low and high sulfate molality (Eq. 3 in Kampf et al.) by entropic factors alone, ignoring the other effects described above, entropy contributions ranging from about -3 to +10 cal/Kmol (implying free energy effects between +1 and -3 kcal/mol at 298 K, respectively) would be required. These values are on the order of 10-30% of the typical entropy change associated with the clustering or declustering of one molecule in the gas phase, which is reasonable given that the translational and librational motion of “free” molecules is more restricted in the liquid phase. It is presently unclear whether the entropy contributions further increase with sulfate molality as a result of increasing competition by sulfate ions for limited water molecules. In other words, glyoxal might displace a greater number of water molecules at higher sulfate molalities, which would create a positive feedback between molality and entropy, and could in principle explain the experimentally observed\textsuperscript{16,34} exponential dependence of $K_{H,eff}$ on $c_{SO4}$.

\textbf{Atmospheric implications and conclusions}
In contrast to surface partitioning–based mechanisms for the enhanced uptake of organic molecules into aerosol particles, the mechanism for glyoxal uptake enhancement presented here is a bulk effect, primarily because most sulfate mass resides in the particle bulk. For liquid aerosol particles consisting of a single aqueous phase, and in the absence of mass transfer limitations, the uptake thus depends on the aerosol volume rather than the surface area. This does not contradict the observations that other reactions and mechanisms involving glyoxal are surface-active, or that the uptake of glyoxal onto particles with multiple phases may depend on the surface area. Indeed, glyoxal-sulfate interactions are not limited to bulk processes, but can also affect surface partitioning and reactivity. In particular, under conditions where diffusion of glyoxal into the bulk is mass-transfer limited, enhanced surface partitioning due to sulfate may be a pre-requisite for surface reactivity.

Since the presented mechanism involves strong and specific interactions between glyoxal hydrates and sulfate ions, the magnitude of the enhancement mainly depends on the concentration of sulfate ions, and is thus likely to be relatively insensitive to the presence of most other (organic or inorganic) solutes, as indicated by the experimental results of Kampf et al. and Ip et al. The latter noted especially that the effect of chloride ions on glyoxal was at least a factor of 15 smaller than that of sulfate, implying that other monoanions probably have only minor effects as well. On the other hand, multiply charged small molecular anions such as phosphate or oxalate can probably form complexes with glyoxal hydrates similarly to sulfate, and could thus be expected to have large effects on whenever they are present in solutions in their polyanionic forms (e.g. oxalate rather than hydrogenoxalate or oxalic acid). However, the atmospheric concentrations of oxalate and especially phosphate are in general much smaller than that of sulfate, and their overall effects on aerosol glyoxal uptake are thus likely minor.
proposed glyoxal uptake enhancement by sulfate is also likely to be mostly independent of pH, except for very acidic solutions (pH < 3), where a significant part of the sulfate ions are converted into bisulfate. Indeed, a strong reduction in $K_{H, \text{eff}}$ (> factor 20) is observed\textsuperscript{42} if sulfuric acid is added to ammonium sulfate, confirming that monoanions interact less strongly with glyoxal\textsuperscript{17} also for sulfate/bisulfate. For atmospheric modeling purposes,\textsuperscript{15,43} the glyoxal uptake into aerosol particles can thus probably be adequately described by a simple parameterization involving only the sulfate molality.\textsuperscript{16}

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