

Interactive comment on “Secondary organic material formed by methylglyoxal in aqueous aerosol mimics – Part 1: Surface tension depression and light-absorbing products” by A. N. Schwier et al.

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Reviewer 3

We thank Reviewer 3 for his or her constructive comments. We answer specific statements below.

The authors suggest that their surface tension depression is consistent with previous studies and this is true for bulk measurements. However, if the results are to be related to CCN activity, the authors must compare their bulk measurements to particle con-

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centrations at activation. The amounts of dissolved methylglyoxal material at droplet activation will affect the effective surface tension decrease and must be accounted for (Sorjmaa et al, 2008).

We agree with the reviewer on this point. To our knowledge, the concentrations of the methylglyoxal reaction products we have proposed here have not been measured in atmospheric aerosol samples. Kawamura and coworkers have measured methylglyoxal monomer and related compounds (glyoxal, ketocarboxylic acids, and dicarboxylic acids) in ambient aerosols (Sempere and Kawamura, 1994; Kawamura et al., 1996; Kawamura and Yasui, 2005; Ho et al., 2007; Kundu et al., 2009). Methylglyoxal was found to comprise roughly 0.005–0.05% of aerosol mass in urban environments (Kawamura and Yasui, 2005; Ho et al., 2007). However, since methylglyoxal is highly reactive, this value underestimates the total methylglyoxal taken up by the particles. Assuming that all pyruvic acid, glyoxylic acid, and oxalic acid in the aerosol was formed via methylglyoxal oxidation (Carlton et al., 2006) provides a rough upper bound for methylglyoxal uptake of 2% of aerosol mass (Kawamura and Yasui, 2005; Ho et al., 2007). Assuming a particle density of 1 g cm^{-3} this corresponds to an in-particle initial methylglyoxal concentration range of 0.7 mM to 0.28 M.

Since both methylglyoxal and its reaction products are surface-active, the relevant concentration for estimating particle surface tension is the total methylglyoxal uptake. However we also note that the relevant surface tension is that of the droplet at the moment of activation, at which point the surfactant concentration will be lower than that in the aqueous aerosol at lower relative humidities, especially for larger particles. Therefore, using 0.28 M methylglyoxal as an upper bound, we estimate a lower bound of $\sigma/\sigma_w > 0.67$, which corresponds to a critical supersaturation as low as 54% that of a particle with $\sigma = \sigma_w$. CCN activation measurements are planned in order to confirm this effect.

Why did the authors not use similar molarities for NaCl and (NH₄)₂SO₄ in their surface tension measurements? The presented concentrations appear arbitrary.

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Atmospheric aerosols have salt concentrations that exceed bulk saturation concentrations (Tang and Munkelwitz, 1994; Tang et al., 1997). In order to mimic atmospheric aerosol compositions to the extent possible in a bulk solution, the molarities chosen for NaCl and $(\text{NH}_4)_2\text{SO}_4$ are close to saturation for these salts. Different concentrations of NaCl and $(\text{NH}_4)_2\text{SO}_4$ were used because the solubility of NaCl in water exceeds that of $(\text{NH}_4)_2\text{SO}_4$. A few words about this have been added to the experimental section of the manuscript for clarification.

P 15549. The authors should add a few words as to why the sodium solutions had little effect on the methylglyoxal solutions. NaCl solutions are neutral and would not facilitate aldol condensation. It is not explicitly stated but would aid non-chemistry minded readers and help support the conclusions. It should be also mentioned that film forming compounds can affect cloud droplet growth rate and cloud droplet number (Feingold and Chuang, 2002).

The NaCl solutions in our experiment were not neutral, the pH was 2 due to the acidity of the methylglyoxal stock solution, as stated in the manuscript. The notion of NH_4^+ catalyzing or participating in the chemistry of α -dicarbonyls has been developed in a number of recent studies which we have referenced in the manuscript. The role of NH_4^+ in this system is discussed in more detail in the revised manuscript.

The following passage was added to the manuscript upon the reviewer's suggestion: "It should be noted that a film of surface-active organics coating an aqueous particle may also affect the kinetics of particle equilibration with the surrounding water vapor, thereby affecting cloud droplet growth rate and cloud droplet number (Archer and La Mer, 1955; Rosano and La Mer, 1956; Chuang et al., 1997; Feingold and Chuang, 2002; Garland et al., 2005; Ruehl et al., 2009)."

Specific Comments. P 15542 L19: Engelhart et al., 2008 is misspelled P 15545 L11:HOMO-LUMO is not defined nor explained.

We have fixed the spelling error in the manuscript and augmented the following passage

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sage about HOMO-LUMO: ". . . was used to predict the HOMO-LUMO energy difference (and thus UV-Vis absorption wavelengths) of proposed products. When molecules absorb light, their electrons can be promoted from the HOMO (highest occupied molecular orbital) to the LUMO (lowest unoccupied molecular orbital). The energy difference between these levels corresponds to the wavelength of absorption according to $E = hc/\lambda$, where E is the HOMO-LUMO energy difference, h is Planck's constant, c is the speed of light in vacuum, and λ is the wavelength."

Figure 2 and P 15543. Why show data for 282 nm and 550 nm? Do these wavelengths have any significance?

These wavelengths were singled out for analysis because 550 nm is the wavelength where solar spectral irradiance is at a maximum and the most significant peak in our spectra developed at 282 nm (Figure 1a).

Figure 4. Which equation is used to fit the data points? Is it equation 2? It is not clear in the text or from the figure caption.

Referring to pg. 15546, line 24 of the manuscript: "The surface tension depression follows a Langmuir-like dependence on initial methylglyoxal concentration, with a minimum (saturation) surface tension based on a fit to the data using the following equation: (Eq. 2)." The caption to this figure reads: "The best fit curve to each data set based on equation (2) is also shown."

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