

Reviewer 1

Interactive comment on “Simulation of SOA Formation from the Photooxidation of Monoalkylbenzenes in the Presence of Aqueous Aerosols Containing Electrolytes under Various NO_x Levels” by Chufan Zhou et al.

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We thank reviewer Dr. Gorkowski for the valuable comments on the manuscript.

Major comment: Dynamic α_i

I understand the mass-based stoichiometric coefficient (α_i), has to be dynamic to capture the full evolution of the aerosol mass. It is not clear on page 5 line 7, if the dynamic reconstruction is a fit to smog chamber data or not. Section 3.1 reads as if α_i was fitted at the beginning and ending conditions of the experiment. Then assuming that is correct, does α_i have any value other than a free parameter? α_i was the major factor that brought the experiments and model into an agreement, is this fit general for the atmosphere or system specific?

Response:

The dynamic reconstruction of α_i is not produced by fitting SOA simulation with α_i to the smog chamber data. The dynamic α_i is created by compositing the two α_i sets at the fresh gas composition (fresh α_i) and the highly aged gas composition (highly aged α_i). The fresh α_i and the highly aged α_i are predicted using the predetermined equations, which are a function of NO_x level near the summer solstice (June 14th, 2018). At a given NO_x level, dynamic α_i is reconstructed using the aging scale factors ($f_A(t) = \log \frac{[HO_2] + [RO_2]}{[HC]_0}$). Under a given NO_x level (HC ppbC/NO_x ppb) the $f_A(t)$ is maximized late afternoon (~4 PM) at near solstice. For the fresh condition, $f_A(fresh)$ is determined at 20% of total hydrocarbon consumption. $f_A(fresh)$ and $f_A(hightly\ aged)$ are $f_A(t)$ values at fresh and highly aged conditions, respectively. For example, $f_A(fresh)$ and $f_A(hightly\ aged)$ at HC/NO_x = 45 for toluene are -3.7 and -2.9, respectively. At HC/NO_x = 2, $f_A(fresh)$ and $f_A(hightly\ aged)$ are -7.2 and -5.2, respectively. We define aging factor ($f_A'(t)$) at time = t as follows

$$f_A'(t) = \frac{f_A(hightly\ aged) - f_A(t)}{f_A(hightly\ aged) - f_A(fresh)}$$

Then, the α_i set is dynamically reconstructed by a weighted average method (Eq. (2) in the manuscript) using fresh α_i set, highly aged α_i set. and $f_A'(t)$.

Minor Comments:

(1) Page 1 line 13: "applied to estimate" would be clearer if changed to "used to estimate"

Response:

This has been corrected in the revised manuscript.

(2) Page 1 line 19: Shouldn't the importance of electrolytes over NO_x or α_i , be expected or is this new insight?

Response:

The impact of hygroscopic seed, NO_x , or aging on SOA growth has been studied by numerous researchers. However, the relative importance of these variables on SOA was not well investigated. Based on our chamber studies and simulation results (Figure 7), we conclude that the effect of an aqueous phase containing electrolytes on SOA yields was more important than that of the NO_x level under our simulated conditions or the utilization of the age-driven α_i set.

(3) Page 1 line 21 and Page 11 line 14: "presence of wet electrolytic seeds" is this mainly the salting-in effect (and not chemical reactions) that causes the increase in SOA mass? From, Figure 7 the small fraction of OM_{AR} in A-D seems to suggest that is the case. Have you run simulations at higher RHs, say 90%?

Response:

Although some compounds (e.g., glyoxal) can be salting in (Kampf et al., 2013). In general, electrolytic inorganic salts results in salting out for most organic compounds (Wang et al., 2014). In this paper, the organic solubility in the salted aqueous phase was predicted using the predetermined polynomial equation, which was produced using the solubility (activity coefficient) of a variety of model compounds, which were parameterized with molecular weight (MW) and organic to carbon ratio (O:C) at different humidity and inorganic compositions. Evidently, the activity coefficient of most organic compound increases as increasing salt concentrations (decreasing humidity) supporting a salting out effect (Section S3 in supporting information). The

sign of the coefficient for humidity in equation 4 is negative. In the revision of the manuscript, equation 4 was updated by including more model compounds and reads now,

$$\gamma_{in,i} = e^{4.789 \cdot \ln(MW_i) - 4.701 \cdot \ln(O:C_i) - 5.484 \cdot FS - 0.098 \cdot (100 \cdot RH) - 12.464}$$

(4) Page 4 line 10: There are theoretical calculations to include in the support the assumption of phase separation. See Zuend, A. and Seinfeld, J. H.: Modeling the gas-particle partitioning of secondary organic aerosol: The importance of liquid-liquid phase separation, *Atmos. Chem. Phys.*, 12(9), 3857–3882, doi:10.5194/acp-12-3857-2012, 2012.

Response:

We cited the original paper in the manuscript at page 4 line 11.

(5) Page 5 line 26: How did you settle on this formula for the activity coefficients? I suggest adding that discussion to the SI.

Response:

In order to provide better description, Section S3 (“Activity coefficient of organic species in the aqueous phase containing electrolytes”) has been revised and reads now,

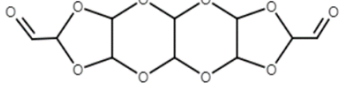
“In the UNIAPR model, the formation of aromatic SOA is simulated with the assumption of organic-inorganic phase separation. To predict the partitioning of organic species on both the organic phase and the inorganic phase, the key model parameters are $K_{or,i}$ and $K_{in,i}$, respectively (described in Section 3.2 of the main manuscript). In order to predict $K_{in,i}$, the calculation of the activity coefficient ($\gamma_{in,i}$) of organic species in the inorganic phase (aqueous phase containing electrolytes) is necessary.

In our study, $\gamma_{in,i}$ was semi-empirically predicted by a polynomial equation, which was fit the theoretical $\gamma_{in,i}$ of various organic compounds to relative humidity (RH), fractional sulfate (FS), and molecular structures (i.e., molecular sizes (MW_i) and polarity ($O:C_i$)). The theoretical $\gamma_{in,i}$ was determined at the maximum solubility of organic species in the electrolytic aqueous phase (SO_4^{2-} - NH_4^+ - H_2O system) using the Aerosol Inorganic-Organic Mixtures Functional Groups Activity Coefficients (AIOMFAC) (Zuend et al., 2011). AIOMFAC was run for the estimation of $\gamma_{in,i}$ of 26 model compounds with diverse MW_i and $O:C_i$ under varying inorganic phase compositions (FS and hygroscopicity linked to RH). The oligomeric products form in aqueous phase, but they deposit to the organic phase due to their poor solubility in inorganic phase.

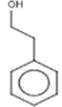
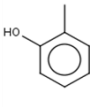
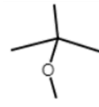
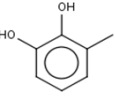

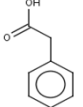
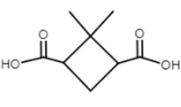
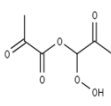
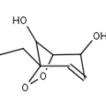
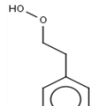
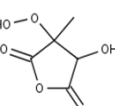
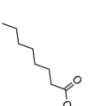
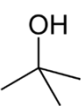
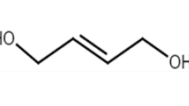
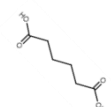

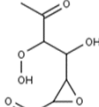
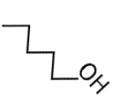
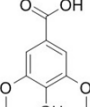
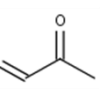
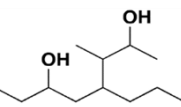
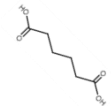
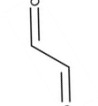
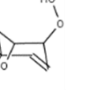
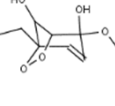
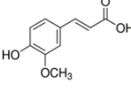
However, some hydrophilic oligomers can dissolve in both organic and inorganic phases. For example, glyoxal-origin oligomers might be hydrophilic and partially soluble in inorganic phase. Hence, the trace amount of glyoxal-oligomer (MW = 290 g/mol and O:C = 1 with mole fraction = 0.01) was included in inorganic phase as seen in Table S4. In Figure S1, the $\gamma_{in,i}$ predicted by AIOMFAC was plotted to that predicted by the polynomial equation (Eq. 4 in the manuscript) along with the one-to-one line for 26 organic species (Table S4). FS ranges from 0.34 to 1.0 and RH ranges from 0.1 to 0.8.”

Table S4: The molecular structures of the oligomeric compound (a) and 26 model compounds (b) with O:C ratios and MW, which were employed to derive the polynomial equation to predict $\gamma_{in,i}$ of organic species in electrolytic aqueous phase. The name of the organic compound with symbol * originates from MCM website (<http://mcm.leeds.ac.uk/MCMv3.3.1/home.htm>).

(a)

#	Oligomer
Structure	
# of GLY	n=5
Formula	C ₁₀ H ₁₀ O ₁₀ (n=5, nonhydrate on both end)
O:C	1.000
MW	290

(b)

#	1	2	3	4	5	6	7
Structure							
Name	phenethyl alcohol	o-cresol	2-methoxy-2-methylpropane	MCATECHOL*	1,7-heptanediol	phenylacetic acid	norpinic acid
Formula	C ₈ H ₁₀ O	C ₇ H ₈ O	C ₅ H ₁₂ O	C ₇ H ₈ O ₂	C ₇ H ₁₆ O ₂	C ₈ H ₈ O ₂	C ₈ H ₁₂ O ₄
O:C	0.125	0.143	0.200	0.286	0.286	0.250	0.500
MW	122.167	108.140	88.150	124.139	132.203	136.150	172.180
#	8	9	10	11	12	13	14
Structure							
Name	C6OTKETO0H*	EBZBPER2OH*	2-phenylethyldihydroperoxide	MMALNHYOOH*	octanoic acid	tert-butanol	1,4-dihydroxy-2-butene
Formula	C ₆ H ₈ O ₆	C ₈ H ₁₂ O ₄	C ₈ H ₁₀ O ₂	C ₅ H ₆ O ₆	C ₈ H ₁₆ O ₂	C ₄ H ₁₀ O	C ₄ H ₈ O ₂
O:C	1.000	0.500	0.250	1.200	0.250	0.250	0.500
MW	176.124	172.180	138.166	162.097	144.214	77.147	88.106
#	15	16	17	18	19	20	21
Structure							
Name	hexanedioic acid	octanol	TLEMUCOOH*	1-pentanol	syringic acid	methylglyoxal	3-methyl-4-propyl-octane-2,6-diol
Formula	C ₆ H ₁₀ O ₄	C ₈ H ₁₈ O	C ₇ H ₁₀ O ₆	C ₅ H ₁₂ O	C ₉ H ₁₀ O ₅	C ₃ H ₄ O ₂	C ₁₂ H ₂₆ O ₂
O:C	0.667	0.125	0.857	0.200	0.556	0.667	0.167
MW	146.142	130.231	190.151	88.150	198.174	72.063	202.338
#	22	23	24	25	26		
Structure							
Name	1-propanol	glyoxal	EBZBPEROOH*	EBENZOLOOH*	ferulic acid		
Formula	C ₃ H ₈ O	C ₂ H ₂ O ₂	C ₈ H ₁₂ O ₅	C ₈ H ₁₂ O ₆	C ₁₀ H ₁₀ O ₄		
O:C	0.333	1.000	0.625	0.750	0.400		
MW	60.096	58.000	188.179	204.178	194.186		

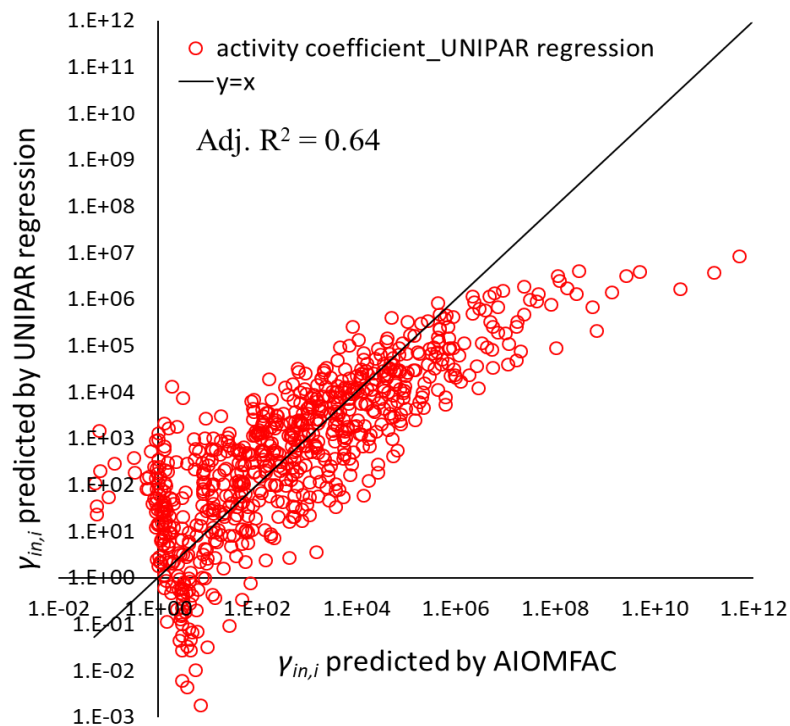


Figure S1: The $\gamma_{in,i}$ predicted by AIOMFAC was plotted to that predicted by the polynomial equation (Eq. 4 in the manuscript) along with the one to one line.

(6) **Page 11 Line 3:** "RH is insignificant" only at these experimental conditions. Maybe change to "RH is insignificant for our experiments, discussed in Section 4.2."

Response:

We changed the sentence to "... the effect of RH on SOA growth is insignificant in our simulation, discussed in Section 4.2."

(7) **Figure 5:** I find the figure's y-axis labels a bit cramped. Add a little more white space between the three panels to improve readability.

Response:

Figure 5 has been revised based on the comment the reviewer as follows,

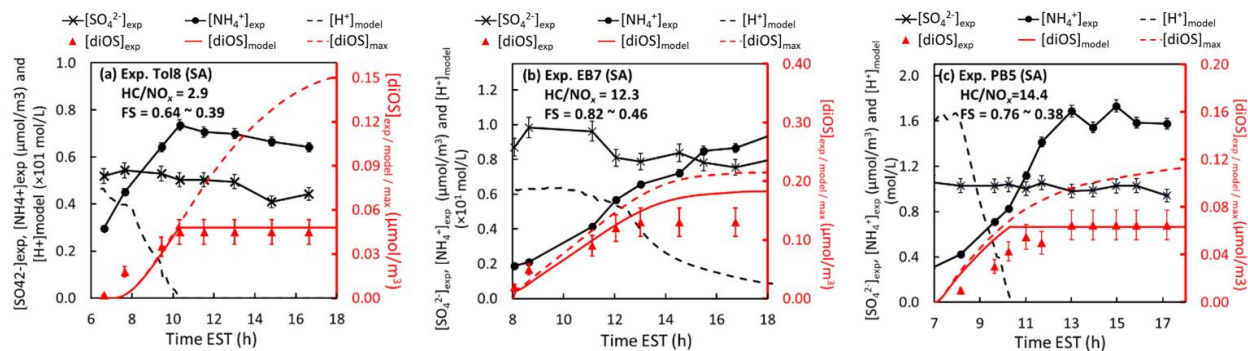


Figure 5: Time profiles of measured inorganic sulfate concentration ($[SO_4^{2-}]_{exp}$), ammonium concentration ($[NH_4^+]_{exp}$), diOS concentration ($[diOS]_{exp}$), the predicted proton concentration ($[H^+]_{model}$), diOS concentration ($[diOS]_{model}$), and the maximum diOS concentration ($[diOS]_{max}$) (assuming there is no ammonia neutralization in the system) for SOA generated from (a) toluene (HC/NO_x = 2.9, OM-to-sulfate mass ratio (OM:sulf) = 1.4), (b) ethylbenzene (HC/NO_x = 12.3, OM:sulf = 1.4), and (c) n-propylbenzene (HC/NO_x = 14.4, OM:sulf = 0.7). The degree of neutralization is indicated by FS, which is ranging from 1 (for sulfuric acid) to 0.33 (for ammonium sulfate). “SA” stands for experiment with direct-injection sulfuric acid seeded aerosols. The ion and diOS concentrations were corrected for the particle loss to the chamber wall. The experimental conditions are available in Table 1.

Reference

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Zuend, A., Marcolli, C., Booth, A. M., Lienhard, D. M., Soonsin, V., Krieger, U. K., Topping, D. O., McFiggans, G., Peter, T., and Seinfeld, J. H.: New and extended parameterization of the thermodynamic model AIOMFAC: calculation of activity coefficients for organic-inorganic mixtures containing carboxyl, hydroxyl, carbonyl, ether, ester, alkenyl, alkyl, and aromatic functional groups, *Atmospheric Chemistry and Physics*, 11, 9155-9206, 10.5194/acp-11-9155-2011, 2011.