



MODELING AEROSOL FORMATION IN α -PINENE OXIDATION EXPERIMENTS: IMPACT OF NON-IDEALITY OF THE AEROSOL MIXTURE

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I. Introduction

The previously published BOREAM model[1] was developed to describe α -pinene oxidation. It has the following characteristics

- The first oxidation steps of α -pinene are treated explicitly by theoretical calculations. Oxidation by OH, O₃ and NO₃ is considered.
- Second-generation oxidation products are lumped together into semigeneric or generic compounds.
- Partitioning to the aerosol phase is described kinetically.
- Vapour pressures are calculated by a group contribution method.[2]
- Agreement with various smog chamber (SC) experiments is generally within a factor two.
- See poster Karl Ceulemans EGU2008-A-09032; AS3.19-1WE3P-0176.

Effects of non-ideality and water uptake were not described previously in the model and are the subject of the present work.

At equilibrium, the gas-liquid partitioning is described by the Pankow[3] formula:

$$C_{p,i}/C_{g,i} = K_{p,i}M_0$$

$$K_{p,i} = \frac{760RTf_{om}}{MW_{om}\gamma_i P_i^0}$$

Nonideality is described by an activity coefficient γ_i different from unity and takes into account that the liquid is a mixture, not a pure compound. The UNIFAC (UNiversal Functional Activity Coefficient)[4] method is used to calculate the activity coefficients γ_i , with three different parametrizations: Hansen et al.[5], Magnussen et al.[6], and Raatikainen et al.[7]. The Raatikainen parametrization should be most appropriate, as it is fitted for polyfunctional compounds.

Unifac parameters for the atmospheric relevant functional groups nitrates, peroxy acyl nitrates, hydroperoxides and peroxyacids do not exist or are not public. We used the SPARC calculator[8] (Spare Performs Automated Reasoning in Chemistry) to produce activity coefficient data. Subsequently, the missing UNIFAC parameters were fitted to these data.

Water uptake can influence partitioning through changes in total mass M_0 , molar mass MW_{om} and activity coefficient γ_i .

II. Simulations without water uptake: impact of activity coefficients

Simulations were run without allowing H₂O to partition to the aerosol phase, both for the ideal case ($\gamma_i = 1$) and for the nonideal ($\gamma_i \neq 1$) case.

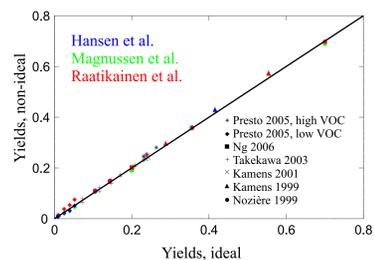


FIGURE 1: Aerosol mass yields, without water condensation, with activity coefficients included versus without (non-ideal case).

experiment	relative deviation
Nozière[9]	7-10 %
Kamens[10]	7 %
Kamens[11]	9 %
Takekawa[12]	6-14 %
Ng[13]	5-7 %
Presto, high VOC[14]	7-8 %
Presto, low VOC[14]	11-42 %

TABLE 1: relative deviation of species concentrations in SOA, for ideal vs. non-ideal case.

Impact on SOA yield and mean molecular mass:

- The impact on the mass yields is very minor (a few % increase), to virtually nonexistent in most cases.
- The mean molecular SOA mass is almost unchanged (not shown).
- **Reason: the mean of the activity coefficient is close to unity.**

Impact on composition:

- For most experiments, the relative error on particulate phase species concentration is small but significant.
- For the low VOC Presto experiments, the error can exceed to 40%.
- **Reason: at low SOA masses, the equilibrium is closer to the gas phase, and the particulate phase is more sensitive to variations in activity coefficient.**

III. Simulations with water uptake: ideal case

When water condensation is allowed, the mass yield increases with relative humidity (RH). As equilibrium between gas and condensed phase is achieved quite rapidly, the molar fraction of water in SOA tends towards RH.

- The increase is due to both water uptake, *and* an increase in organics.
- At lower to medium RH, the increase in total mass yield is mainly due to an increase in organics.
- At higher RH (60%), the two become comparable.
- **Reason: due to the water uptake, also the other aerosol compounds must increase to maintain the equilibrium.**

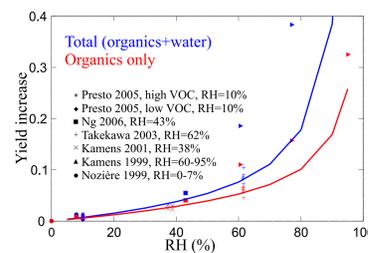


FIGURE 2: Difference between mass yields with and without water condensation, for the ideal case. The line plot is for a theoretical case where only RH is varied.

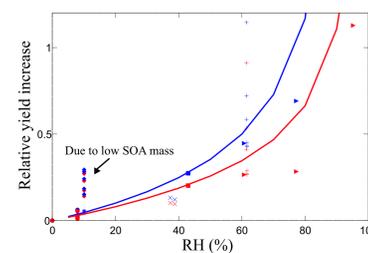


FIGURE 3: Same as on the left, but now for the relative difference.

IV. Impact of non-ideality on water uptake

The non-ideality lowers the mass yield for the higher RH cases.

- Water uptake is suppressed due to an activity coefficient $\gamma_w > 1$.
- Subsequently, the uptake of organics is lowered due to a lower water content.
- For both the Hansen and the Magnussen parametrization, the effect is much stronger compared to the Raatikainen parametrization.

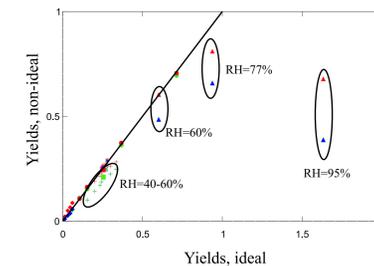


FIGURE 4: Relative deviation of species concentrations in SOA, for ideal vs. non-ideal case. Important deviations occur at higher RH.

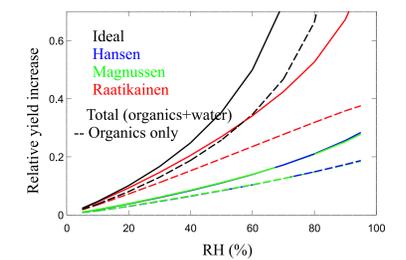


FIGURE 5: Relative difference between mass yields with and without water condensation vs. RH, for a theoretical case where only RH is varied.

V. Testing phase separation effects (Work in progress)

We're investigating the above described systems at varying RH for phase-splitting effects. So far, no evidence of phase-splitting has been found.

VI. Conclusions

- For dry α -pinene oxidation experiments, the impact of non-ideality on SOA yield is unimportant.
- Water uptake enhances partitioning of organic molecules.
- Water uptake is affected by non-ideality, depending on the exact UNIFAC parametrization, in the order: ideal > Raatikainen > Hansen \approx Magnussen.
- At high RH (80-90%), ideal calculations grossly overestimate the yield compared to non-ideal calculations.
- (*Preliminary result*) Phase separation effects do not seem to occur in SOA purely from α -pinene oxidation products, even at high relative RH. This is in agreement with results of Chang and Pankow[15].

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