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**Influence of
non-ideality on
aerosol growth**

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Influence of non-ideality on aerosol growth

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Abstract

Secondary organic aerosol (SOA) is a complex mixture of water and organic molecules. Its composition is determined by the presence of semi-volatile or non-volatile compounds, their vapor pressure and activity coefficient. The activity coefficient is a non-ideality effect and is a complex function of SOA composition. In a previous publication, the detailed chemical mechanism (DCM) for α -pinene oxidation and subsequent aerosol formation BOREAM was presented. In this work, we investigate with this DCM the impact of non-ideality by simulating smog chamber experiments for α -pinene degradation and aerosol formation. Several versions of the UNIFAC method are tested for this purpose, and missing parameters for e.g. hydroperoxides and nitrates are inferred from fittings to activity coefficient data generated using the SPARC model. It turns out that for most experiments, non-ideality has only a limited impact on the interaction between the organic molecules, and therefore on SOA yields and composition, when water uptake is ignored. Still, for ozonolysis experiments with low amounts of volatile organic carbon (low-VOC), the UNIFAC parameterization of Raatikainen et al. leads to significantly higher SOA yields (by up to a factor 1.6) compared to the ideal case and to other parameterizations. Water uptake is model dependent, in the order: ideal > UNIFAC-Raatikainen > UNIFAC-Peng > UNIFAC-Hansen \approx UNIFAC-Magnussen \approx UNIFAC-Ming. In the absence of salt dissolution, phase splitting from pure SOA is unlikely.

1 Introduction

Oxidation of complex VOC molecules (e.g. terpenes, aromatics) leads to a myriad of compounds, many of which having sufficiently low vapor pressures p_i^0 in order to condense and form SOA. In humid conditions, also water vapor will partition appreciably to the SOA phase, notwithstanding its high vapor pressure. Hence by its very nature, SOA is a complex mixture of water and organic molecules. The partitioning of a gas

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to a mixture is determined by the product $\gamma_i p_i^0$ rather than by its vapor pressure p_i^0 , where γ_i is the composition dependent activity coefficient. Including the effect of non-ideality means calculating the activity coefficient explicitly instead of setting each $\gamma_i=1$. UNIFAC (UNiversal Functional group Activity Coefficient) (Fredenslund et al., 1975) is arguably the most popular method to calculate activity coefficients.

Generally one can distinguish two approaches for theoretically predicting SOA formation by VOC oxidation. The first, simplified, approach, like the model of Odum et al. (1996), is based on empirically determined stoichiometric coefficients (EDSC) directly relating the VOC precursor and the final set of oxidation products, which can be explicit molecules or simplified lumped entities. The second approach uses a DCM to predict SOA formation. Focussing on α -pinene as the precursor, some studies on the effect of non-ideality exist using the EDSC approach (Bowman and Melton, 2004; Chang and Pankow, 2008) or using a fixed set of oxidation products (Jang and Kamens, 1998; Chandramouli et al., 2003; Erdakos and Pankow, 2004; Erdakos et al., 2006a) by performing UNIFAC calculations. However, the UNIFAC model used in these studies was either not (Magnussen et al., 1981; Hansen et al., 1991) or hardly (Ming and Russell, 2002) optimized for multifunctional compounds as they occur in SOA.

Examples of DCMs for α -pinene are those developed by Kamens et al. (1999), Kamens and Jaoui (2001), Jenkin (2004) and our own mechanism BOREAM (Biogenic hydrocarbon Oxidation and Related Aerosol formation Model) outlined in a previous publication (Capouet et al., 2008). The BOREAM model was validated versus a wide range of smog chamber experiments. However, neither the impact of non-ideality nor water uptake were explicitly addressed within the DCM approach, except that Kamens et al. (1999) used a RH-dependent water uptake parameterization based on the activity coefficient of water (Jang and Kamens, 1998). Reasons to omit non-ideality are the sake of simplicity, a lack of activity coefficient data for some compounds, and the small expected variation in activity coefficient compared to variation in vapor pressure, at least when the SOA constituents are of similar nature.

Several different UNIFAC parameterizations (Fredenslund et al., 1975; Magnussen

et al., 1981; Peng et al., 2001; Ming and Russell, 2002; Raatikainen and Laaksonen, 2005), are compared in this work, including some that are optimized for multifunctional compounds reminiscent of SOA compounds (Peng et al., 2001; Raatikainen and Laaksonen, 2005). One obstacle we encountered was the absence of parameters in UNIFAC for some functional groups of atmospheric interest. Organic nitrates, hydroperoxides, and (to a lesser extent) peroxy acids are predicted to be abundant products in the oxidation of terpenoid compounds, and are expected to contribute significantly to SOA growth (Bonn et al., 2004; Capouet et al., 2008). There is also experimental evidence for the presence of organic nitrates in SOA (Palen et al., 1992; Presto et al., 2005; Ng et al., 2007) and of peroxides (Docherty et al., 2005), which can originate from hydroperoxides. Therefore, we rely on the model SPARC (Sparc Performs Automated Reasoning in Chemistry) (Carreira et al., 1994), available online (<http://ibmlc2.chem.uga.edu/sparc/>), to generate activity coefficients for species containing these functional groups, and determine the missing parameters by fitting to these data. SPARC provides estimates for various chemical properties (vapor pressures – Hilal et al., 2003; activity coefficients – Hilal et al., 2004; hydration constants – Hilal et al., 2005; – . . .), starting from the molecular structure of the species under consideration, by using a solvation model that includes dispersion, induction, dipole-dipole and hydrogen bonding interactions.

As we shall show below, the activity coefficient is not important for high-VOC dry experiments, but it can be for low-VOC experiments. For humid experiments, the activity coefficient of water affects both the SOA water content and the organics content. Its impact depends on the specific UNIFAC parameterization.

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2 Method

At equilibrium, gas-particle partitioning is described by the well-known formula of Pankow (1994)

$$\frac{C_{p,i}}{C_{g,i}} = K_{p,i} C_{om}, \quad (1)$$

$$K_{p,i} = \frac{RT}{\overline{M}_{om} \gamma_i p_i^0}, \quad (2)$$

with $C_{p,i}$, $C_{g,i}$, the mass of species i per volume of air in aerosol phase and gas phase respectively, $K_{p,i}$ the partitioning coefficient, $C_{om} = \sum_j C_{p,j}$ the SOA mass per volume of air, \overline{M}_{om} the mean molecular mass in the aerosol, R the gas constant, T the temperature, p_i^0 the vapor pressure, and γ_i the activity coefficient. The vapor pressure is estimated from the group-contribution method of Capouet and Müller (2006). γ_i is a complex function of concentration of all components. It will be useful to rewrite Eq. 1 for molar instead of mass quantities:

$$\frac{C_{p,i}}{C_{g,i}} = \frac{c_{p,i}}{c_{g,i}} = \kappa_{p,i} c_{om}, \quad (3)$$

$$\kappa_{p,i} = K_{p,i} \overline{M}_{om} = \frac{RT}{\gamma_i p_i^0}, \quad (4)$$

$$c_{om} = \sum_j c_{p,j} = \frac{C_{om}}{\overline{M}_{om}}, \quad (5)$$

with $c_{p,i}$, $c_{g,i}$ the mole quantity of species i per volume of air in aerosol phase and gas phase respectively, and c_{om} the mole quantity SOA per volume of air.

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2.1 Activity coefficient calculation by the UNIFAC method

Notwithstanding the existence of several UNIFAC extensions to describe simultaneously ion-organic and ion-water interactions (see e.g. Erdakos et al., 2006a,b; Ming and Russell, 2002; Raatikainen and Laaksonen, 2005), we neglect presently the contribution of dissolved salt to the activity coefficient. This is evidently a valid assumption for the experiments where no inorganic seed is used. Furthermore, the experiments of Cocker III et al. (2001) suggest that, below the deliquescence point of the seed, seeded and seedless experiments give similar results. This indicates that the seed acts as an inert adsorbent and does not dissolve significantly into the liquid phase in such conditions.

The activity coefficient is calculated by the popular group contribution method UNIFAC (Fredenslund et al., 1975). In this method, both the molecule i and the mixture are split into functional groups k . The activity coefficient γ_i is split into a combinatorial part γ_i^C and a residual part γ_i^R :

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R, \quad (6)$$

$$\ln \gamma_i^C = \ln \frac{r_i}{\bar{r}} - \left(\frac{r_i}{\bar{r}} - 1 \right) - 5q_i \left[\ln \left(\frac{\bar{q}}{q_i} \frac{r_i}{\bar{r}} \right) - \left(\frac{\bar{q}}{q_i} \frac{r_i}{\bar{r}} - 1 \right) \right], \quad (7)$$

$$\ln \gamma_i^R = \sum_k v_k^i \left(\ln Z_k - \ln Z_k^i \right), \quad (8)$$

with $r_i = \frac{V_i^{\text{VdW}}}{15.17 \text{ cm}^3/\text{mol}}$, $q_i = \frac{A_i^{\text{VdW}}}{2.5 \times 10^9 \text{ cm}^2/\text{mol}}$ measures of the Van der Waals (VdW) volume V_i^{VdW} ($\frac{\text{cm}^3}{\text{mol}}$) and surface A_i^{VdW} ($\frac{\text{cm}^2}{\text{mol}}$) of molecule i respectively, and \bar{r} , \bar{q} the corresponding mean values over all molecules. v_k^i is the stoichiometric coefficient of group k and Z_k , Z_k^i are the activity coefficients of group k in the mixture and in pure solvent i respectively. r_i , q_i of a molecule can be calculated from the corresponding group

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parameters:

$$r_i = \sum_k v_k^j R_k, \quad (9)$$

$$q_i = \sum_k v_k^j Q_k. \quad (10)$$

These group parameters are usually directly derived from the tables of Bondi (1968), but are sometimes fitted to experimental data. The activity coefficients of the groups are given by the following formula:

$$\ln Z_k = Q_k \left[1 - \sum_m \frac{X_m Q_m \tau_{km}}{\sum_o X_o Q_o \tau_{om}} - \ln \left(\frac{\sum_m X_m Q_m \tau_{mk}}{\sum_k X_k Q_k} \right) \right] \quad (11)$$

$$\ln Z_k^j = Q_k \left[1 - \sum_m \frac{v_m^j Q_m \tau_{km}}{\sum_o v_o^j Q_o \tau_{om}} - \ln \left(\frac{\sum_m v_m^j Q_m \tau_{mk}}{\sum_k v_k^j Q_k} \right) \right] \quad (12)$$

$$\tau_{mk} = \exp \left(-\frac{a_{mk}}{T} \right). \quad (13)$$

The interaction parameters a_{mk} are fitted to experimental data.

2.2 The new UNIFAC groups and their VdW parameters

Currently there are no UNIFAC parameters available for the functional groups nitrate, peroxy acyl nitrate and peroxy acid. Parameters do exist for peroxide and hydroperoxide (The UNIFAC Consortium, <http://134.106.215.86/UNIFAC/>), but these are not freely accessible to the community. In Table 1, we define the new functional groups together with their volume and surface parameters:

The VdW volume and surfaces are calculated as outlined by Bondi (1968), with the atomic radii of Bondi and the bond lengths from Cottrell (1958); Darwent (1970); Benson (1965).

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2.3 Obtaining the interaction parameters from SPARC-generated data

In SPARC, molecules are described by a set of molecular descriptors (molecular polarizability, molecular volume, microscopic dipole, hydrogen bond), which are themselves sums over “atomic” fragments (Hilal et al., 2003). Vapor pressures are calculated by solute-solute interaction models (Hilal et al., 2003) and activity coefficients by solute-solvent interaction models (Hilal et al., 2004). The interaction models include dispersion, induction, dipole-dipole and hydrogen bond interactions. The models themselves are calibrated on experimental data.

It is of course impossible to assess the accuracy of SPARC for activity coefficients of the compounds with the new functional groups, as no experimental data is available. However, it was assessed in previous studies (Chattopadhyay and Ziemann, 2005; Asher et al., 2002; Asher and Pankow, 2006) that SPARC produces vapor pressures that compare fairly well with the experimental values of atmospheric relevant species. This is important since the activity coefficient model is built on similar principles as the vapor pressure model. A very recent work evaluates the performance of SPARC to calculate Henry law's constants in water, defined as $H_i = \gamma_i^{\infty, w} p_i^0$ (Hilal et al., 2008), with $\gamma_i^{\infty, w}$ the infinite dilution activity coefficient (IDAC) in water. In Table 2 an overview is given of SPARC's performance for nitrates, hydroperoxides, peroxyacids and peroxy acyl nitrates for vapor pressures and Henry's law constants, by comparing to experimental data collected by Pankow and Asher (2008), and Hilal et al. (2008). Note that, except for nitrates, experimental data are very scarce. SPARC performs reasonably well for nitrates, hydroperoxides and peroxides, but not for peroxy acids and the peroxy acyl nitrate. Still, SPARC is used because of lack of alternative.

We have fitted the unknown interaction parameters to SPARC-generated activity coefficient data (SPARC version 4.2). We limited ourselves to infinite dilution data, as SPARC is mainly tested for those case. For each couple of molecules A and B, both the activity coefficients of solute A in solvent B and solute B in solvent A were calculated. Only smaller molecules were considered since SPARC performs in general

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better for them. They are given in Table 3. Activity coefficients were generated for the combinations given in Table 4. Only solvent-solute combinations of different classes were considered.

Most test molecules contain the group CH_n . The following objective function was used for the fittings:

$$F_{\text{MIN}} = \sum_{i=1}^{N_1} \sum_{j=1}^{N_2} \left[\ln \left(\gamma_i^{j,\text{SPARC}} \right) - \ln \left(\gamma_i^{j,\text{UNIFAC}} \right) \right]^2 + \left[\ln \left(\gamma_j^{i,\text{SPARC}} \right) - \ln \left(\gamma_j^{i,\text{UNIFAC}} \right) \right]^2 \quad (14)$$

where i, j are species belonging to different classes and γ_i^j denotes the activity coefficient of solute i in solvent j .

The interaction parameters were adjusted sequentially. First, by fitting the UNIFAC formula to the data from the alkane-RU combination, the interaction parameters a_{mk} between the group CH_n and the unknown groups U were determined. Next, the U - U interaction parameters were derived by fitting to RU-RU data, with the CH_n -U interaction parameters kept fixed. Before determining the interaction parameters between groups K and U, we first calculated parameters for the CH_n -K interaction from alkane-RK data. For calculating the K-U interaction parameters, these fixed CH_n -K parameters were then used, rather than values from the literature. This allowed for a better separation between CH_n -K and K-U interactions and resulted in generally better fittings. In this manner, the K-U interaction parameters are identical for all different UNIFAC versions. The SPARC-fitted CH_n -K interaction parameters were only used for these fittings, not for the actual computations presented in the next section. The parameters are given in Tables 5, 6 and 7, together with the mean absolute deviation of $\log \gamma$, defined as

$$\sigma = \frac{1}{N} \sum_{i=1}^N \left| \log \left(\gamma_i^{\text{SPARC}} \right) - \log \left(\gamma_i^{\text{UNIFAC}} \right) \right| \quad (15)$$

The mean absolute deviation over all data points is 0.068, hence the deviation on γ is on average an acceptable factor $10^{0.068} \approx 1.2$.

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2.4 Comparison of different UNIFAC versions

We tested the parameterizations of Hansen et al. (1991) (UNIFAC-Hansen), Magnussen et al. (1981) (UNIFAC-Magnussen), Ming and Russell (2002) (UNIFAC-Ming), Peng et al. (2001) (Unifac-Peng), Raatikainen and Laaksonen (2005) (UNIFAC-Raatikainen). UNIFAC-Hansen (Hansen et al., 1991) is actually derived from vapor-liquid equilibrium data of mostly short-chain, monofunctional compounds, but it is also widely used in atmospheric chemistry, probably because it contains the most complete set of functional groups. The other methods replace only some of the interaction parameters and use those of UNIFAC-Hansen for the others. UNIFAC-Magnussen is derived from liquid-liquid equilibrium data. The other three methods contain parameters fitted to multifunctional compounds of atmospheric interest. Both UNIFAC-Peng and UNIFAC-Raatikainen are based on data from mixtures of water with diacids and/or hydroxyacids, but the more recent UNIFAC-Raatikainen is based on a larger data set.

As reported earlier (Raatikainen and Laaksonen, 2005), the results for UNIFAC-Ming were found to be very close to those of UNIFAC-Hansen. Therefore, we omit this parameterization in presenting the results.

3 Results and discussions

3.1 Selection of experiments and model setup

In Table 8 an overview is given of the simulations of smog chamber experiments (SS-CEs) in this work.

We note that in the case of an inorganic seed, the relative humidity (RH) is well below the deliquescence relative humidity of the pure salts (DRH) (79% for $(\text{NH}_4)_2\text{SO}_4$ – Cruz and Pandis, 2000; Tang, 1979 and 84% for Na_2SO_4 – Cohen et al., 1987) and this DRH will not change significantly by the presence of organics (Cruz and Pandis, 2000; Parsons et al., 2004). This supports our assumption that no salt is dissolved.

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In BOREAM, the continuity equations of the chemical compounds are solved by a Rosenbrock scheme embedded in KPP (Kinetic PreProcessor) (Sandu and Sander, 2005). The first steps of the oxidation are explicit and based on theoretical calculations (Capouet et al., 2008). To limit the number of reactions, secondary chemistry is described by semi-generic and generic reactions, with a partial loss in chemical information. Still, there are >1000 chemical species and >5000 chemical reactions. We used a time step of 10 s. At each time step, \bar{r} , \bar{q} , $\ln Z_k$ -which depend on the mixture composition- are updated and the activity coefficients are recalculated from Eqs. 6–13 and taken into account in the rate constants for evaporation. For generic species, it is assumed that the unspecified part (“LX” in Capouet et al., 2008) has the same average composition of organic molecules as the explicit part.

3.2 Non-ideality effects: with and without water uptake

In Fig. 1 simulated mass yields, with non-ideality included, are compared to mass yields calculated with ideality assumption. Note that all yields presented here are corrected for wall-losses and taken at their maximum:

$$Y = Y(t_{\max}) = \frac{\Delta C_{om, \text{chamber}} + \Delta C_{om, \text{wall}}}{\Delta C_{VOC}}, \quad (16)$$

while the definition of yield can differ in the articles describing the smog chamber experiments. The ability of the BOREAM model to reproduce the experimental yields has been extensively discussed in Capouet et al. (2008). Our goal here is not to further validate the model with experimental SOA data, but rather to investigate the impact of non-ideality. As seen in Fig. 1, non-ideality clearly has an impact on the yields, but the extent depends on the specific experiment and on the employed UNIFAC version.

Deviations from ideality are associated to both interaction of organic molecules with water, and interaction between organic molecules. To distinguish between both effects, we performed SSCEs with the water uptake turned off (Fig. 2), i.e. simulations where water is not allowed to condense on the aerosol. It can be seen that for the

high-VOC SSCEs, the effect of non-ideality on the mass yield is small, for all UNIFAC versions tested. Only the low-VOC SSCEs show significant variability, especially the ozonolysis experiments of Presto et al. (2005) and of Shilling et al. (2008). For these simulations, UNIFAC-Magnussen gives systematically lower, and UNIFAC-Raatikainen systematically higher yields compared to UNIFAC-Hansen (the other UNIFAC versions give results comparable to UNIFAC-Hansen). In what follows we explain this difference.

For an individual species, a measure of its non-volatility is its fraction in the condensed phase

$$f_{p,i} = \frac{C_{p,i}}{C_{T,i}} = \frac{C_{p,i}}{C_{g,i} + C_{p,i}} = \frac{\kappa_{p,i}}{\kappa_{p,i} + 1}. \quad (17)$$

Note that this definition of volatility depends on the amount of aerosol present. When $\kappa_{p,i} \gg 1$, $f_{p,i} \approx 1$ and $C_{p,i} \approx C_{T,i}$ will not be very sensitive to changes in $\kappa_{p,i}$ and therefore in γ_j . We can then define the mean of all $f_{p,i}$ as a non-volatility measure for the SOA

$$\bar{f}_{om} = \sum_j x_j f_{p,j}, \quad (18)$$

with $x_j = \frac{C_{p,j}}{\sum_i C_{p,i}}$ the mole fraction of j in the condensed phase. For \bar{f}_{om} close to unity, the SOA consists largely of low-volatile species, while for \bar{f}_{om} near zero, it consists largely of high-volatile species. The geometrical mean of the activity coefficient is defined as

$$\bar{\gamma} = \exp \left(\sum_j x_j \ln \gamma_j \right). \quad (19)$$

In Table 9 \bar{f}_{om} for the ideal calculation and $\bar{\gamma}$ for UNIFAC-Hansen, UNIFAC-Magnussen and UNIFAC-Raatikainen are presented.

\bar{f}_{om} is generally high, except for the low-VOC SSCEs of Presto et al. (2005) and of Shilling et al. (2008). It follows that the activity coefficient cannot play an important role in the high-VOC experiments.

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For the SSCEs of Nozière et al. (1999), $\bar{\gamma} \approx 1.0$, independently of the UNIFAC version. This can at least partly be attributed to the fact that nitrates and peroxy acetyl nitrates comprise a large fraction of the SOA, and their (SPARC-inferred) interaction parameters do not vary with the applied UNIFAC version. In general, UNIFAC-Raatikainen provides the lowest $\bar{\gamma}$, below unity. UNIFAC-Hansen (and also the other UNIFAC parameterizations) give results below, but much closer to, unity. For the ozonolysis experiments, UNIFAC-Magnussen is even closer to unity compared to UNIFAC-Hansen. Therefore, generally a higher yield is predicted for the low-VOC SSCEs with UNIFAC-Raatikainen compared to the other UNIFAC versions and the ideal case, by up to a factor 1.6. UNIFAC-Magnussen gives the lowest yields for the low-VOC ozonolysis experiments.

In our simulations, the largest SOA contributor for the ozonolysis experiments is pinic acid. The relatively low activity coefficient of pinic acid (0.5–0.7) according to UNIFAC-Raatikainen can largely be attributed to the attractive interaction between the two acid functionalities of the molecule and the alcohol and ketone functions in the mixture, which are much smaller in the other UNIFAC versions.

One can conclude that for dry, high-VOC oxidation experiments, the influence of non-ideality on mass yield is negligible. UNIFAC-Raatikainen predicts a higher yield for low-VOC ozonolysis experiments.

Most of the deviations from non-ideality (Fig. 1) disappear when no water uptake is considered (Fig. 2). Except for the rather dry experiments of Nozière et al. (1999) and Presto et al. (2005), the non-ideality effects associated with organic-water interaction are therefore far more important than those due to the interaction between organic molecules.

Because of the high volatility of water, $f_w \approx 0$ and $c_{p,w} \approx \kappa_{p,w} c_{g,w}$. $c_{p,w}$ is directly proportional to $\kappa_{p,w}$ and therefore inversely proportional to γ_w . So non-ideality is important for water uptake both in low and high-VOC experiments.

As discussed in Seinfeld et al. (2001), water uptake enhances the SOA yield in two ways: water directly contributes to the total mass, but it also leads to higher gas-to-

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particle partitioning of the organic compounds to the SOA phase since c_{om} in Eq. 3 increases. Fig. 3 shows the yields (both total yield and organics yield) for SSCEs with the settings of Presto et al. (2005) and Ng et al. (2006), but with varying RH, for different UNIFAC models and the ideal case. As discussed above, the low-VOC SSCE of Presto et al. (2005) shows an important variation of yield with UNIFAC version also at low RH, while this is not the case for the SSCE of Ng et al. (2006). Due to the low molar mass of water, the direct contribution of water to the total SOA mass is less important than the increase of organic mass, at least at low and moderate RH.

The repulsive interaction between water and the organics leads to an activity coefficient of water $\gamma_w > 1$. Therefore, water uptake is suppressed compared to the ideal case, leading to a lower c_{om} in Eq. 3. As a consequence, less organic molecules partition to the SOA phase. The amount of water uptake depends on the activity coefficient model, in the order ideal > Raatikainen > Peng > Hansen \approx Magnussen \approx Ming.

Skipping the dry experiments with $RH \leq 10\%$, the activity coefficient of water is typically 1.7–2.0 with UNIFAC-Hansen, 1.0–1.4 with UNIFAC-Peng and 1.0–1.2 with UNIFAC-Raatikainen. The large activity coefficient of water for UNIFAC-Hansen is attributed to the repulsive interaction between H_2O and the group CH_2 , which is only partially compensated by attractive interactions of water with alcohol and acid functionalities. The relatively lower γ_w for UNIFAC-Peng and UNIFAC-Raatikainen is mainly due to more attractive H_2O -OH interactions, and, for UNIFAC-Raatikainen, a less repulsive CH_2 - H_2O interaction.

3.3 Testing phase separation effects

We tested experiments of Kamens and Jaoui (2001); Kamens et al. (1999); Takekawa et al. (2003); Ng et al. (2006) for phase separation effects, using the phase separation algorithm outlined by Erdakos and Pankow (2004). Water and more hydrophilic compounds were put in one phase and the relatively more hydrophobic compounds in the other phase. Afterwards Erdakos' pseudo-diffusion method (Erdakos and Pankow, 2004) was used to test if the system would be stable as a two-phase system or would

return to one single phase. As a criterion to place a compound A initially in the hydrophilic or the hydrophobic phase, the IDAC of A in water, or the IDAC of water in A, was used. Only UNIFAC-Hansen was used, as this method predicts the highest repulsion between organics and water.

5 In all cases, the system returned to a one-phase system. This points to, but is no proof of, a single phase. Earlier calculated phase separation in SOA from α -pinene oxidation involved either addition of salt (Chang and Pankow, 2006), or addition of hydrophobic primary organic aerosol (Erdakos and Pankow, 2004; Chang and Pankow, 2008), while pure SOA (with water) always stayed in one single phase (Erdakos and
10 Pankow, 2004; Chang and Pankow, 2008).

4 Conclusions

UNIFAC interaction parameters for the new groups nitrates, hydroperoxides, peroxides, peroxy acids and peroxy acyl nitrates are derived by fitting to SPARC-generated activity coefficient data.

15 For high-VOC experiments and if no water uptake is allowed, the impact of non-ideality on the mass yield is negligible. For low-VOC ozonolysis experiments, UNIFAC-Raatikainen predicts a higher SOA yield than the other UNIFAC versions and the ideal case. This is primarily due to the stronger attraction between COOH and OH functional groups predicted by UNIFAC-Raatikainen, and the fact that at low SOA mass,
20 the important SOA contributor pinic acid can be considered semi-volatile instead of low-volatile. In general, for experiments with low SOA masses, the gas-particle equilibrium is shifted towards the gas phase, and the SOA yield is more sensitive to variations of the activity coefficient.

When water uptake is included in the model, non-ideality becomes more important.
25 The SOA water content is inversely proportional to the activity coefficient γ_w of water, for both low and high-VOC experiments. The water content is lowered by including non-ideality. A lower water content also leads to a lower gas-to-particle partition-

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ing of organic molecules, and therefore to a lower SOA yield. The water uptake is model dependent, in the order: ideal>UNIFAC-Raatikainen>UNIFAC-Peng>UNIFAC-Hansen≈UNIFAC-Magnussen≈UNIFAC-Ming. As opposed to UNIFAC-Hansen, both UNIFAC-Raatikainen and UNIFAC-Peng were fit to multifunctional molecules (diacids and hydroxy-acids) of atmospheric interest, and can be expected to produce more reliable results. Although UNIFAC-Ming was also developed for multifunctional molecules, we found, as reported earlier (Raatikainen and Laaksonen, 2005), no important difference with UNIFAC-Hansen.

The repulsive interaction between the organic molecules and water does not seem to be large enough to cause a phase-splitting in the SOA, at least when no salt dissolution is considered.

Acknowledgements. This work has been made possible by a grant of the Belgian Science Policy Office in the framework of the SSD program (2006–2009). We also thank L. A. Carreira and A. N. Saravananaraj for help in generating the SPARC output and for useful discussions.

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Table 1. New UNIFAC groups defined in this work.

name	main group	subgroup	R_k	Q_k
nitrate	CH_nONO_2	CH_2ONO_2	2.1246	1.8682
		CHONO_2	1.8971	1.5562
		CONO_2	1.6697	1.3282
hydroperoxide	CH_nOOH	CH_2OOH	1.5869	1.437
		CHOOH	1.3594	1.125
		COOH	1.132	0.897
		C(=O)OOH	1.7025	1.5217
peroxyacid peroxide	CH_nOOCH_m	CH_nOOCH_m	0.6904+	0.5920+
			$R_{\text{CH}_n} + R_{\text{CH}_m}^a$	$Q_{\text{CH}_n} + Q_{\text{CH}_m}^a$
peroxy acyl nitrate	C(=O)OONO_2	C(=O)OONO_2	2.6217	2.2887

^a $R_{\text{CH}_n}, Q_{\text{CH}_n}$ are the volume and surface parameters of CH_n , $n=0-3$ (Fredenslund et al., 1975).

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Table 2. Mean absolute deviation of $\log p_i^0$, $\log H_i$ between SPARC and experiment for certain classes of compounds. $\sigma(\log H_i)$ have been directly taken from Table 3 in Hilal et al. (2008). Experimental vapor pressures were taken from the collection of Pankow and Asher (2008), but aromatic or nitro- compounds were excluded. For the SPARC vapor pressures, SPARC version 4.2 is used. The number of experimental values is given between brackets.

class	$\sigma(\log p_i^0)$	$\sigma(\log H_i)$
nitrate	0.20 (11)	0.30 (23)
hydroperoxide	0.35 (3)	0.60 (3)
peroxy acid	1.00 (3)	0.82 (1)
peroxide	0.37 (2)	/(0)
peroxy acyl nitrate	1.51 (1)	2.05 (1)

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Table 3. Molecules used for generating activity coefficient data with SPARC. Molecules with known (unknown) non-CH_n groups are labeled with RK (RU)

class	formula	<i>n</i>
alkane	CH ₃ (CH ₂) _{<i>n</i>} CH ₃	2–4
alkene (RK)	CH ₃ (CH ₂) _{<i>n-n'</i>} CH=CH (CH ₂) _{<i>n'</i>} CH ₃ ^a	0–2
alcohol (RK)	CH ₃ (CH ₂) _{<i>n</i>} OH	3–5
aldehyde (RK)	CH ₃ (CH ₂) _{<i>n</i>} CH=O	2–4
keton (RK)	CH ₃ C(=O) (CH ₂) _{<i>n</i>} CH ₃	1–3
acid (RK)	CH ₃ (CH ₂) _{<i>n</i>} C(=O)OH	0–2
ether (RK)	CH ₃ (CH ₂) _{<i>n-n'</i>} O (CH ₂) _{<i>n'</i>} CH ₃ ^a	0–2
ester (RK)	CH ₃ C(=O)O (CH ₂) _{<i>n</i>} CH ₃	0–1
nitrate (RU)	CH ₃ (CH ₂) _{<i>n</i>} ONO ₂	1–2
hydroperoxide (RU)	CH ₃ (CH ₂) _{<i>n</i>} OOH	1–2
peroxy acid (RU)	CH ₃ (CH ₂) _{<i>n</i>} C(=O)OOH	0–1
peroxide (RU)	CH ₃ (CH ₂) _{<i>n-n'</i>} OO (CH ₂) _{<i>n'</i>} CH ₃ ^a	0–1
peroxy acyl nitrate (RU)	CH ₃ (CH ₂) _{<i>n</i>} C(=O)OONO ₂	0–1

$$^a n' = \begin{cases} n/2, & \text{for } n \text{ even,} \\ (n-1)/2, & \text{for } n \text{ odd.} \end{cases}$$

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solvent\solute	alkane	RK	RU
alkane	0	x	x
RK	x	0	x
RU	x	x	x

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Table 5. UNIFAC interaction parameters a_{mk} (defined in Eq. 13) between known groups, obtained by fitting to SPARC generated activity coefficients, and the mean absolute deviation σ on $\log \gamma$ (defined in Eq. 15). Only used for fittings, not for computations.

m	k	a_{mk}/K	a_{km}/K	σ
CH_n	$\text{CH}_n=\text{CH}_{n'}$	170.86	-114.95	0.0086
	OH	1184.3	4930.9	0.15
	H_2O	1211.6	567.41	0.057
	$\text{CH}_n\text{C}=\text{O}$	586.57	-180.67	0.049
	$\text{CH}=\text{O}$	644.59	474.88	0.031
	$\text{CH}_n\text{C}(=\text{O})\text{O}$	589.75	-190.83	0.050
	CH_nO	649.80	-272.45	0.034
	$\text{C}(=\text{O})\text{OH}$	1879.9	5639.4	0.17

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Table 6. Same as Table 6, but between known and new groups.

m	k	a_{mk}/K	a_{km}/K	σ
CH_n	CH_nONO_2	500.95	-75.718	0.045
	CH_nOOH	977.56	-23.233	0.045
	$C(=O)OOH$	1331.0	5853.1	0.15
	$CH_nOOCH_{n'}$	297.24	-151.61	0.023
$CH_n=CH_{n'}$	$C(=O)OONO_2$	528.50	333.07	0.084
	CH_nONO_2	10326.	-294.43	0.040
	CH_nOOH	475.91	-57.949	0.044
	$C(=O)OOH$	742.38	883.78	0.081
	$CH_nOOCH_{n'}$	606.71	-237.61	0.036
OH	$C(=O)OONO_2$	469.27	86.307	0.066
	CH_nONO_2	37.631	818.97	0.041
	CH_nOOH	-330.28	342.92	0.051
	$C(=O)OOH$	1789.0	-457.93	0.090
H_2O	$CH_nOOCH_{n'}$	221.38	820.86	0.065
	$C(=O)OONO_2$	-77.526	612.05	0.051
	CH_nONO_2	142.65	681.78	0.032
	CH_nOOH	-341.18	795.55	0.015
	$C(=O)OOH$	-329.81	670.32	0.044
$CH_nC=O$	$CH_nOOCH_{n'}$	-7.2937	483.553	0.16
	$C(=O)OONO_2$	76.211	319.99	0.035
	CH_nONO_2	-197.93	188.72	0.034
	CH_nOOH	-350.58	380.94	0.030
	$C(=O)OOH$	252.05	-98.45	0.035
$CH=O$	$CH_nOOCH_{n'}$	-286.39	587.21	0.035
	$C(=O)OONO_2$	-3.8839	111.76	0.056
	CH_nONO_2	402.00	-179.38	0.013
	CH_nOOH	-387.63	408.88	0.11
	$C(=O)OOH$	12274.	-520.90	0.11
$CH_nC(=O)O$	$CH_nOOCH_{n'}$	-18.524	509.17	0.055
	$C(=O)OONO_2$	308.97	-187.02	0.049
	CH_nONO_2	1273.8	-356.25	0.10
	CH_nOOH	928.33	-355.00	0.022
CH_nO	$C(=O)OOH$	416.00	131.15	0.027
	$CH_nOOCH_{n'}$	-252.22	449.04	0.027
	$C(=O)OONO_2$	426.52	-157.64	0.057
	CH_nONO_2	1133.1	-289.81	0.14
	CH_nOOH	-438.74	490.36	0.20
$C(=O)OH$	$C(=O)OOH$	2221.9	-471.67	0.13
	$CH_nOOCH_{n'}$	-130.54	142.65	0.027
	$C(=O)OONO_2$	1166.7	-208.91	0.13
	CH_nONO_2	-100.17	1173.3	0.045
	CH_nOOH	-501.23	1479.0	0.13
	$C(=O)OOH$	-579.80	1896.1	0.15
	$CH_nOOCH_{n'}$	79.052	1043.9	0.097
	$C(=O)OONO_2$	-340.95	1207.7	0.055

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Table 7. Same as Table 6, but between new groups.

m	k	a_{mk}/K	a_{km}/K	σ
CH_nONO_2	CH_nOOH	545.66	-86.279	0.028
	C(=O)OOH	551.95	221.82	0.037
	$\text{CH}_n\text{OOCH}_{n'}$	-308.16	676.62	0.052
CH_nOOH	C(=O)OONO_2	-239.65	474.47	0.044
	C(=O)OOH	202.91	-62.0167	0.032
	$\text{CH}_n\text{OOCH}_{n'}$	-395.81	1088.8	0.051
C(=O)OOH	C(=O)OONO_2	-147.47	392.54	0.051
	$\text{CH}_n\text{OOCH}_{n'}$	210.57	537.70	0.077
	C(=O)OONO_2	395.33	-80.543	0.060
$\text{CH}_n\text{OOCH}_{n'}$	C(=O)OONO_2	-2.0795	339.08	0.12

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Table 8. Simulated experiments in this work.

Experiment	VOC/ppb	Main oxidant	RH (%) ^a	Seed	Notes
Nozière et al. (1999)	305–1500	OH	<8	nucleation	high NO _x
Kamens et al. (1999)	350–820	O ₃	60–95	organic	
Kamens and Jaoui (2001)	940–980	OH	37–39	nucleation	
Takekawa et al. (2003)	55–196	OH	60	Na ₂ SO ₄	
Presto et al. (2005), low-VOC	10.8–20.6	O ₃	10	nucleation/organic	
Presto et al. (2005), high-VOC	152–205	O ₃	10	nucleation/organic	
Ng et al. (2006)	108	OH	43	(NH ₄) ₂ SO ₄	
Shilling et al. (2008)	10	O ₃	40	(NH ₄) ₂ SO ₄	dark

^a Ranges of RH refer to the different input values for simulation, rather than experimental uncertainty.

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Table 9. \bar{f}_{om} and $\bar{\gamma}$ of the different SSCEs, without considering water uptake.

Experiment	\bar{f}_{om} ideal	$\bar{\gamma}$ UNIFAC-		
		Hansen ^a	Magnussen	Raatikainen
Nozière et al. (1999)	0.7–0.9	1.0	1.0	1.0
Kamens et al. (1999)	0.8	0.85	0.86	0.7–0.8
Kamens and Jaoui (2001)	0.8	0.92	0.9	0.7
Takekawa et al. (2003)	0.6–0.8	0.9	0.9–1.0	0.7
Presto et al. (2005), low-VOC	0.5–0.6	0.8	0.9–1.0	0.5
Presto et al. (2005), high-VOC	0.7	0.8	0.9	0.7
Ng et al. (2006)	0.8	0.97	0.98	0.82
Shilling et al. (2008)	0.4	0.89	0.99	0.66

^a Not presented UNIFAC versions give results close to UNIFAC-Hansen.

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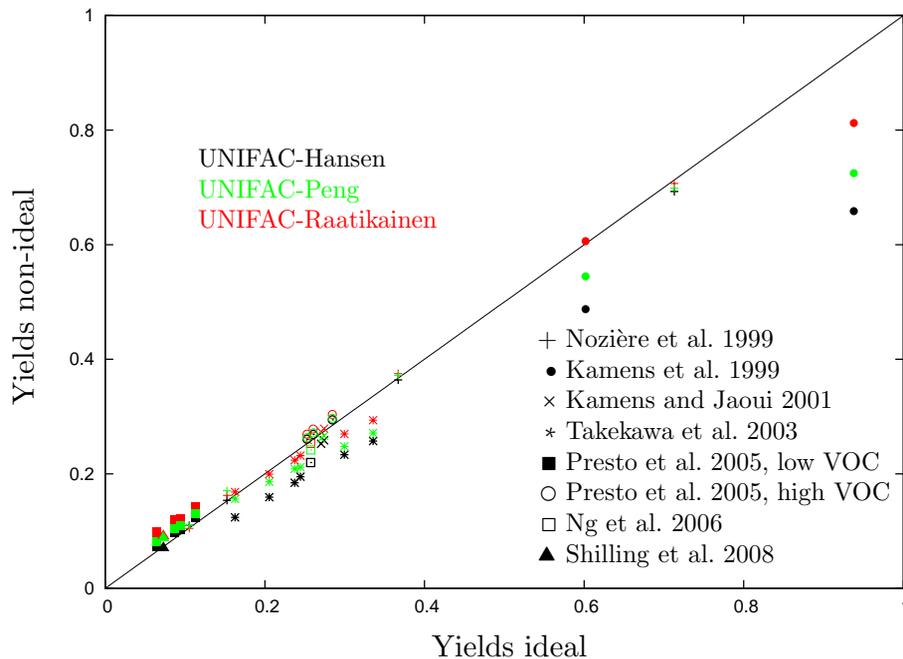


Fig. 1. Aerosol mass yields with activity coefficients included (non-ideal case) versus without (ideal case). Not presented UNIFAC parameterizations give results very close to UNIFAC-Hansen.

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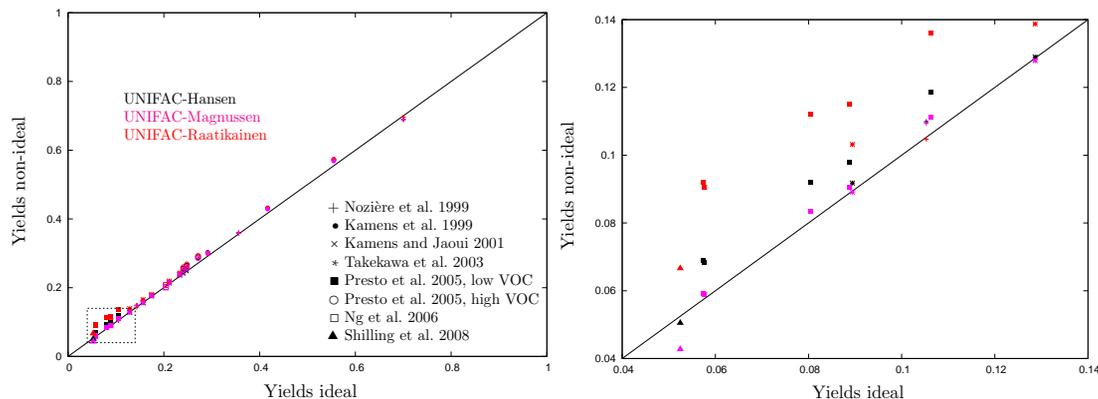


Fig. 2. Left: Aerosol mass yields with activity coefficients included (non-ideal case) versus without (ideal case), without allowing water uptake. Not presented UNIFAC parameterizations give results very close to UNIFAC-Hansen. Right: Magnification of box in left figure to show the low-VOC SSCes.

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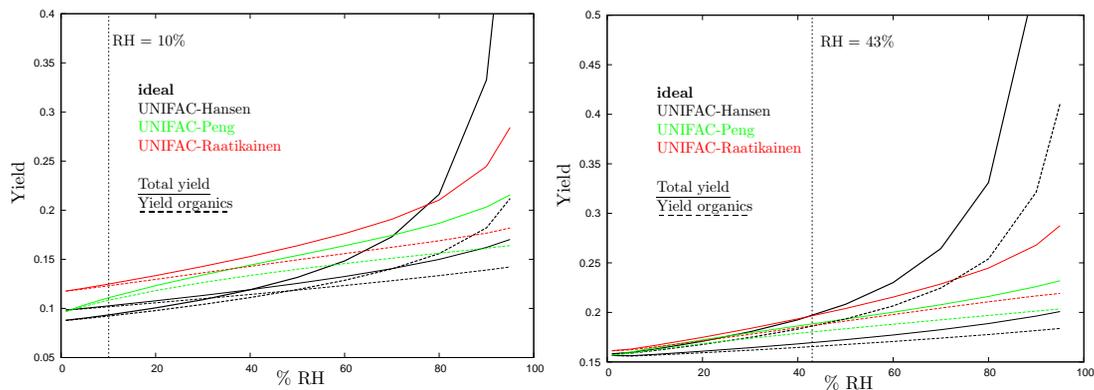


Fig. 3. Total (full line) and organics-only (dashed line) mass yield vs. RH, for the ideal case and for several UNIFAC-parameterizations, using the settings of two smog chamber experiments from Presto et al. (2005) (left), and Ng et al. (2006) (right). The vertical dashed line indicates the RH at which the experiment was actually performed. Not presented UNIFAC-parameterizations give results very similar to UNIFAC-Hansen.

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