

# Influence of non-ideality on condensation to aerosol

S. Compernelle, K. Ceulemans, and J.-F. Müller

Belgian Institute for Space-aeronomy, Ringlaan 3, 1180 Brussels, Belgium

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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 saturation 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  $\alpha$ -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  $\alpha$ -pinene degradation and aerosol formation and taking the activity coefficient into account of all molecules in the aerosol phase. 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. Alternative approaches to deal with these missing parameters are also tested, as well as an activity coefficient calculation method based on Hansen solubility parameters (HSP). 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. The reason is that often, the activity coefficient is on average close to 1 and, specifically for high-VOC experiments, partitioning is not very sensitive on the activity coefficient because the equilibrium is shifted strongly towards condensation. 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 saturation 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 saturation vapor pressure. Hence by its very nature, SOA is a complex mixture of water and organic molecules. The partitioning of a gas to a mixture is determined by the product  $\gamma_i p_i^0$  rather than by its saturation vapor pressure  $p_i^0$ , where  $\gamma_i$  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  $\alpha$ -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). In other studies (Jang and Kamens, 1998; Chandramouli et al., 2003; Erdakos and Pankow, 2004; Erdakos et al., 2006a) a “typical” SOA composition was chosen and the impact of non-ideality investigated. In all instances activity coefficients



Correspondence to: S. Compernelle  
([steven.compernelle@aeronomie.be](mailto:steven.compernelle@aeronomie.be))

were calculated by a UNIFAC method. 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  $\alpha$ -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 saturation 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 (saturation vapor pressures (Hilal et al., 2003b), 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.

There are several limitations in the present approach to model activity coefficients:

- The UNIFAC framework. It cannot distinguish between isomers and e.g. does not take into account proximity effects between the functional groups.
- The available experimentally-derived UNIFAC parameters. These parameters were mostly derived for small monofunctional molecules, whereas polyfunctional are often found in SOA. Parameters fitted to polyfunctional molecules exist only for a few functionalities (hydroxy and acid). However, ideally *all* interaction parameters should be fitted simultaneously to sufficient experimental data for both mono- and polyfunctional molecules. Parameters which have been optimised using a subset of compounds within a given class are not necessarily valid when used to model systems which include combinations of functionalities not included in the original studies. This was e.g. demonstrated when modelling nonideality of a mixed organic/inorganic model (Topping et al., 2005): neglecting organic/inorganic interactions gave better results than using assumed values for interaction parameters.
- The use of SPARC to estimate UNIFAC parameters for functional groups where no experimental data is available. Without activity coefficient data for compounds with these functional groups, it is impossible to estimate the error associated with this approach. We can only validate SPARC indirectly by comparing closely related properties (i.e. vapor pressure and Henry law's constant) of SPARC with experimental data.

Two other approaches to deal with the missing UNIFAC parameters will be presented: a neglective approach, where all unknown interaction parameters are set to zero, and an analogy approach, where all the functional groups with unknown UNIFAC parameters are replaced by the most similar group with known parameters. Finally, we explore another activity coefficient model, based on a group contribution version of HSP (Barton, 1991; Hansen, 2000), which has the advantage that all missing parameters can be inferred from experimental or reliable theoretical data. This model has been used previously to model non-ideality in SOA (Jang et al., 1997; Jang and Kamens, 1998).

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 and on the assumption made regarding the missing UNIFAC parameters.

## 2 Method

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

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

$$K_{p,i} = \frac{RT}{M_{om} \gamma_i P_i^0}, \quad (2)$$

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,  $\bar{M}_{om}$  the mean molecular mass in the aerosol,  $R$  the gas constant,  $T$  the temperature,  $p_i^0$  the saturation vapor pressure, and  $\gamma_i$  the activity coefficient. The saturation vapor pressure is estimated from the group-contribution method of Capouet and Müller (2006).  $\gamma_i$  is a complex function of concentration of all components. It will be useful to rewrite Eq. 1 for molar instead of mass quantities:

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

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

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

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.

## 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  $\gamma_i$  is split into a combinatorial part  $\gamma_i^C$  and a residual part  $\gamma_i^R$ :

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

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

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

with  $r_i = \frac{V_i^{VdW}}{15.17 \text{ cm}^3/\text{mol}}$ ,  $q_i = \frac{A_i^{VdW}}{2.5 \times 10^9 \text{ cm}^2/\text{mol}}$  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 parameters:

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

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

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:

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

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

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

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://unifac.ddbst.com/>), but these are not freely accessible to the community. In Table 1, we define these new functional groups (NFG) 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).

## 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., 2003b). Vapor pressures are calculated by solute-solute interaction models (Hilal et al., 2003b) 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. The developers of SPARC report a root mean square deviation (RMS) of 0.064 log(mole fraction)

**Table 1.** New UNIFAC groups defined in this work, and their VdW volume and surface parameters.

name	main group	subgroup	$R_k$	$Q_k$
nitrate	CH <sub>n</sub> ONO <sub>2</sub>	CH <sub>2</sub> ONO <sub>2</sub>	2.1246	1.8682
		CHONO <sub>2</sub>	1.8971	1.5562
		CONO <sub>2</sub>	1.6697	1.3282
hydroperoxide	CH <sub>n</sub> OOH	CH <sub>2</sub> OOH	1.5869	1.437
		CHOOH	1.3594	1.125
		COOH	1.132	0.897
		C(=O)OOH	1.7025	1.5217
peroxyacid peroxide	CH <sub>n</sub> OOCH <sub>m</sub>	CH <sub>n</sub> OOCH <sub>m</sub>	0.6904+	0.5920+
			$R_{CH_n} + R_{CH_m}^a$	$Q_{CH_n} + Q_{CH_m}^a$
peroxy acyl nitrate	C(=O)OONO <sub>2</sub>	C(=O)OONO <sub>2</sub>	2.6217	2.2887

<sup>a</sup>  $R_{CH_n}$ ,  $Q_{CH_n}$  are the volume and surface parameters of CH<sub>n</sub>,  $n=0-3$  (Fredenslund et al., 1975).

**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 S1 in Hilal et al. (2008). Experimental saturation vapor pressures were taken from the collection of Pankow and Asher (2008), but aromatic or nitro-compounds were excluded. For the SPARC saturation 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)	0.29 (22)
hydroperoxide	0.35 (3)	0.44 (3)
peroxy acid	1.00 (3)	0.42 (1)
peroxide	0.37 (2)	/ (0)
peroxy acyl nitrate	1.51 (1)	1.81 (1)

for 491 compounds in 41 solvents (including water) for the activity coefficient (Hilal et al., 2003a).

It is impossible to assess the accuracy of SPARC for activity coefficients of the compounds with the NFG, as no experimental data is available for them. Therefore, we compare in Table 2 SPARC generated vapor pressures and Henry law's constants with experimental data, as the best test available. The experimental vapor pressures were taken from Pankow and Asher (2008), and the Henry law's constant data -both experimental and calculated- from Hilal et al. (2008). The vapor pressure model is based on similar principles as the activity coefficient model, while the Henry law's constant is defined as the product of the vapor pressure with the infinite dilution activity coefficient (IDAC) in water:  $H_i = \gamma_i^{\infty, w} p_i^0$ . A poor performance for vapor pressures and/or Henry law's constants probably indicates a poor performance for activity coefficients, while the reverse is not necessarily true. Note

**Table 3.** Molecules used for generating activity coefficient data with SPARC. Molecules with known (unknown) non-CH<sub>n</sub> groups are labeled with RK (RU)

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

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

that except for nitrates, experimental data are very scarce.

From Table 2, one sees that 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 cases. 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 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.

**Table 4.** Solvent-solute combinations used to generate activity coefficient data with SPARC.

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

Most test molecules contain the group  $\text{CH}_n$ . 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  $\gamma_i^j$  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  $\text{CH}_n$  and the unknown groups U were determined. Next, the U–U interaction parameters were derived by fitting to RU–RU data, with the  $\text{CH}_n$ –U interaction parameters kept fixed. Before determining the interaction parameters between groups K and U, we first calculated parameters for the  $\text{CH}_n$ –K interaction from alkane-RK data. For calculating the K–U interaction parameters, these fixed  $\text{CH}_n$ –K parameters were then used, rather than values from the literature. This allowed for a better separation between  $\text{CH}_n$ –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  $\text{CH}_n$ –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  $\gamma$  is on average an acceptable factor  $10^{0.068} \approx 1.2$ .

#### 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

**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  $\sigma$  on  $\log \gamma$  (defined in Eq. 15). Only used for fittings, not for computations.

$m$	$k$	$a_{mk}/\text{K}$	$a_{km}/\text{K}$	$\sigma$
$\text{CH}_n$	$\text{CH}_n=\text{CH}_{n'}$	170.86	−114.95	0.0086
	OH	1184.3	4930.9	0.15
	$\text{H}_2\text{O}$	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
	$\text{CH}_n\text{O}$	649.80	−272.45	0.034
	$\text{C}(=\text{O})\text{OH}$	1879.9	5639.4	0.17

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. However, it was noted before that UNIFAC-Hansen does not describe well water uptake (Cocker III et al., 2001). 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. UNIFAC-Peng was also positively validated by Topping et al. (2005) and Hanford et al. (2008) for mixtures of water with polyfunctional acids. However, as mentioned before, ideally *all* interaction parameters should be simultaneously optimized to relevant polyfunctional compounds.

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.

#### 2.5 Activity coefficient calculation by Hansen solubility parameters

The concept of Hansen solubility parameters can be found in e.g. Barton (1991); Hansen (2000). Basically, the cohesive energy density  $E_{\text{coh},i}$  of a molecule is splitted into three contributions, dispersion, polar, and hydrogen bonding. Dividing by the molar volume  $V_i$  and taking the square root of these three parts results in the Hansen solubility parameters  $\delta_{d,i}, \delta_{p,i}, \delta_{hb,i}$ .

$$E_{\text{coh},i} = E_{d,i} + E_{p,i} + E_{hb,i} \quad (16)$$

$$\delta_{t,i}^2 = \delta_{d,i}^2 + \delta_{p,i}^2 + \delta_{hb,i}^2 \quad (17)$$

with  $\delta_{t,i}$  the total or Hildebrand solubility parameter. According to this theory, two compounds will be miscible when

**Table 6.** Same as Table 5, but between known and new groups.

<i>m</i>	<i>k</i>	<i>a<sub>mk</sub>/K</i>	<i>a<sub>km</sub>/K</i>	<i>σ</i>
CH <sub>n</sub>	CH <sub>n</sub> ONO <sub>2</sub>	500.95	-75.718	0.045
	CH <sub>n</sub> OOH	977.56	-23.233	0.045
	C(=O)OOH	1331.0	5853.1	0.15
	CH <sub>n</sub> OOCH <sub>n'</sub>	297.24	-151.61	0.023
	C(=O)OONO <sub>2</sub>	528.50	333.07	0.084
	CH <sub>n</sub> =CH <sub>n'</sub>	CH <sub>n</sub> ONO <sub>2</sub>	10326.	-294.43
CH <sub>n</sub> OOH		475.91	-57.949	0.044
C(=O)OOH		742.38	883.78	0.081
CH <sub>n</sub> OOCH <sub>n'</sub>		606.71	-237.61	0.036
C(=O)OONO <sub>2</sub>		469.27	86.307	0.066
OH		CH <sub>n</sub> ONO <sub>2</sub>	37.631	818.97
	CH <sub>n</sub> OOH	-330.28	342.92	0.051
	C(=O)OOH	1789.0	-457.93	0.090
	CH <sub>n</sub> OOCH <sub>n'</sub>	221.38	820.86	0.065
	C(=O)OONO <sub>2</sub>	-77.526	612.05	0.051
	H <sub>2</sub> O	CH <sub>n</sub> ONO <sub>2</sub>	142.65	681.78
CH <sub>n</sub> OOH		-341.18	795.55	0.015
C(=O)OOH		-329.81	670.32	0.044
CH <sub>n</sub> OOCH <sub>n'</sub>		-7.2937	483.553	0.16
C(=O)OONO <sub>2</sub>		76.211	319.99	0.035
CH <sub>n</sub> C=O		CH <sub>n</sub> ONO <sub>2</sub>	-197.93	188.72
	CH <sub>n</sub> OOH	-350.58	380.94	0.030
	C(=O)OOH	252.05	-98.45	0.035
	CH <sub>n</sub> OOCH <sub>n'</sub>	-286.39	587.21	0.035
	C(=O)OONO <sub>2</sub>	-3.8839	111.76	0.056
	CH=O	CH <sub>n</sub> ONO <sub>2</sub>	402.00	-179.38
CH <sub>n</sub> OOH		-387.63	408.88	0.11
C(=O)OOH		12274.	-520.90	0.11
CH <sub>n</sub> OOCH <sub>n'</sub>		-18.524	509.17	0.055
C(=O)OONO <sub>2</sub>		308.97	-187.02	0.049
CH <sub>n</sub> C(=O)O		CH <sub>n</sub> ONO <sub>2</sub>	1273.8	-356.25
	CH <sub>n</sub> OOH	928.33	-355.00	0.022
	C(=O)OOH	416.00	131.15	0.027
	CH <sub>n</sub> OOCH <sub>n'</sub>	-252.22	449.04	0.027
	C(=O)OONO <sub>2</sub>	426.52	-157.64	0.057
	CH <sub>n</sub> O	CH <sub>n</sub> ONO <sub>2</sub>	1133.1	-289.81
CH <sub>n</sub> OOH		-438.74	490.36	0.20
C(=O)OOH		2221.9	-471.67	0.13
CH <sub>n</sub> OOCH <sub>n'</sub>		-130.54	142.65	0.027
C(=O)OONO <sub>2</sub>		1166.7	-208.91	0.13
C(=O)OH		CH <sub>n</sub> ONO <sub>2</sub>	-100.17	1173.3
	CH <sub>n</sub> OOH	-501.23	1479.0	0.13
	C(=O)OOH	-579.80	1896.1	0.15
	CH <sub>n</sub> OOCH <sub>n'</sub>	79.052	1043.9	0.097
	C(=O)OONO <sub>2</sub>	-340.95	1207.7	0.055

they match sufficiently in all three parameters. The parameters can be found from experimental data:  $\delta_{d,i}$  can be calculated from the alkane homomorph,  $\delta_{p,i}$  from the dipole moment  $\mu_i$  (supplemented if available, with the refractive index and the dielectric constant),  $\delta_{t,i}$  from the enthalpy of vaporization  $\Delta H_{\text{vap},i}$ , from which follows automatically  $\delta_{hb,i}$ . We refer to Barton (1991); Hansen (2000) for the precise procedure. The parameters can also be found from group contribution methods, e.g. the one from Hansen and Beerbower (Barton, 1991).

$$\delta_{d,i} = \sum_k c_k^i F_{d,k} / V_i \quad (18)$$

**Table 7.** Same as Table 5, but between new groups.

<i>m</i>	<i>k</i>	<i>a<sub>mk</sub>/K</i>	<i>a<sub>km</sub>/K</i>	<i>σ</i>
CH <sub>n</sub> ONO <sub>2</sub>	CH <sub>n</sub> OOH	545.66	-86.279	0.028
	C(=O)OOH	551.95	221.82	0.037
	CH <sub>n</sub> OOCH <sub>n'</sub>	-308.16	676.62	0.052
	C(=O)OONO <sub>2</sub>	-239.65	474.47	0.044
CH <sub>n</sub> OOH	C(=O)OOH	202.91	-62.0167	0.032
	CH <sub>n</sub> OOCH <sub>n'</sub>	-395.81	1088.8	0.051
	C(=O)OONO <sub>2</sub>	-147.47	392.54	0.051
C(=O)OOH	CH <sub>n</sub> OOCH <sub>n'</sub>	210.57	537.70	0.077
	C(=O)OONO <sub>2</sub>	395.33	-80.543	0.060
CH <sub>n</sub> OOCH <sub>n'</sub>	C(=O)OONO <sub>2</sub>	-2.0795	339.08	0.12

**Table 8.** Group contributions for molar volume and Hansen solubility parameters for new functional groups.

group	$\frac{V_k}{\text{cm}^3 \text{mol}^{-1}}$	$\frac{F_{d,k}}{(\text{Jcm}^3 \text{mol}^{-1})^{1/2}}$	$\frac{F_{p,k}}{(\text{Jcm}^3 \text{mol}^{-1})^{1/2}}$	$\frac{E_{hb,k}}{\text{Jmol}^{-1}}$
-ONO <sub>2</sub>	34	655	880	2700
-OOH	16	375	535	16500
-C(=O)OOH	29	580	585	17500
-OO-	10	360	470	5200 <sup>a</sup>
-C(=O)OONO <sub>2</sub>	51	900	930	5100

<sup>a</sup> Not enough data, hence the same value as for -O- was assumed.

$$\delta_{p,i} = \sqrt{\sum_k c_k^i F_{d,k}^2 / V_i} \quad (19)$$

$$\delta_{hb,i} = \sqrt{\sum_k c_k^i E_{hb,k} / V_i} \quad (20)$$

$$(21)$$

As was the case for UNIFAC, there are no parameters available for the NFG. We can however estimate  $\delta_{d,i}$ ,  $\delta_{p,i}$ ,  $\delta_{hb,i}$  for simple compounds based on experimental  $\Delta H_{\text{vap},i}$  and experimental or theoretical  $\mu_i$ , supplemented if possible with refractive indices and dielectric constants (Hansen, 2000). We note that quantum chemically calculated dipole moments agree in general quite well with experimental values. From these  $\delta_{d,i}$ ,  $\delta_{p,i}$ ,  $\delta_{hb,i}$ , group contribution values for  $F_{d,k}$ ,  $F_{p,k}$ ,  $E_{hb,k}$  can be found. These are given in Table 8.

The HSP activity coefficient can be calculated by the following equation:

$$\ln \gamma_i^{\text{om}} = d_i^{\text{om}} + \frac{V_i}{RT} (1 - \phi_i)^2 A_i^{\text{om}} \quad (22)$$

$$d_i^{\text{om}} = \ln \left( \frac{V_i}{V_{\text{om}}} \right) + 1 - \frac{V_i}{V_{\text{om}}} \quad (23)$$

$$A_i^{\text{om}} = (\delta_{d,i} - \delta_{d,\text{om}})^2 + b_i \left[ (\delta_{p,i} - \delta_{p,\text{om}})^2 + (\delta_{hb,i} - \delta_{hb,\text{om}})^2 \right] \quad (24)$$

The quantities with subscript om are averaged values in the SOA. More details can be found in Jang et al. (1997).

**Table 9.** Simulated experiments in this work.

Experiment	VOC/ppb	Main oxidant	RH (%) <sup>a</sup>	Seed	Notes
Nozière et al. (1999)	305-1500	OH	< 8	nucleation	high NOx
Kamens et al. (1999)	350-820	O <sub>3</sub>	60-95	organic	
Kamens and Jaoui (2001)	940-980	OH	37-39	nucleation	
Takekawa et al. (2003)	55-196	OH	60	Na <sub>2</sub> SO <sub>4</sub>	
Presto et al. (2005), low-VOC	10.8-20.6	O <sub>3</sub>	10	nucleation/organic	
Presto et al. (2005), high-VOC	152-205	O <sub>3</sub>	10	nucleation/organic	
Ng et al. (2006)	108	OH	43	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	
Shilling et al. (2008)	10	O <sub>3</sub>	40	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	dark

<sup>a</sup> Ranges of RH refer to the different input values for simulation, rather than experimental uncertainty.

Similarly with the combinatorial term in UNIFAC,  $d_i^{om}$  takes into account the size effect. The term  $\frac{V_i}{RT}(1-\phi_i)^2 A_i^{om}$  takes into account the intermolecular interactions. A fundamental limitation of Eq. (22) is that the interaction term cannot be lower than zero, hence if size effects are ignored, activity coefficients are not lower than unity.  $b_i$  is a compound-specific factor, but it is not known for most compounds of interest. It varies from 0.12 for (monofunctional) acids, over 0.14 for ketones to 0.19–0.28 for alcohols (Barton, 1991). In this study we put it equal to 0.15, except for water, where a value of 0.32 is recommended (Barton, 1991). Water is difficult to model with the HSP method, and different HSP exist for this molecule. We took the values  $\delta_d=20$ ,  $\delta_p=18$ ,  $\delta_{hb}=18$ , which is recommended for a water+organics mixture (Barton, 1991).

### 3 Results and discussions

#### 3.1 Selection of experiments and model setup

In Table 9 an overview is given of the simulations of smog chamber experiments (SSCEs) 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 (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> (Cruz and Pandis, 2000; Tang) and 84% for Na<sub>2</sub>SO<sub>4</sub> (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.

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

The ability of the BOREAM model to reproduce the experimental yields has already 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. Hence now we do not compare calculated yields versus experimental yields, but calculated yields with versus without activity coefficient correction.

In Fig. 1 simulated mass yields<sup>1</sup>, with non-ideality included, are compared to mass yields calculated with ideality assumption.

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.

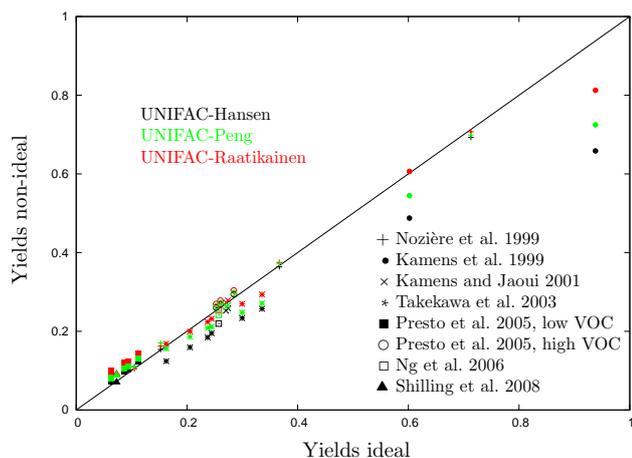
Deviations from ideality are associated to both interaction of organic molecules with water, and interaction between organic molecules. To distinguish between both effects, we performed SSCEs with the water uptake turned off (Fig. 2), i.e. simulations where water is not allowed to condense on the aerosol.

It can be seen that for the high-VOC SSCEs, the effect of non-ideality on the mass yield is small, for all UNIFAC

<sup>1</sup>All yields presented here are corrected for wall-losses and taken at their maximum:

$$Y = Y(t_{\max}) = \frac{\Delta C_{om, \text{chamber}} + \Delta C_{om, \text{wall}}}{\Delta C_{VOC}}, \quad (25)$$

while the definition of yield can differ in the articles describing the smog chamber experiments.



**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.

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

$$f_{p,i} = \frac{c_{p,i}}{c_{T,i}} = \frac{c_{p,i}}{c_{g,i} + c_{p,i}} = \frac{\kappa_{p,i}c_{om}}{\kappa_{p,i}c_{om} + 1}. \quad (26)$$

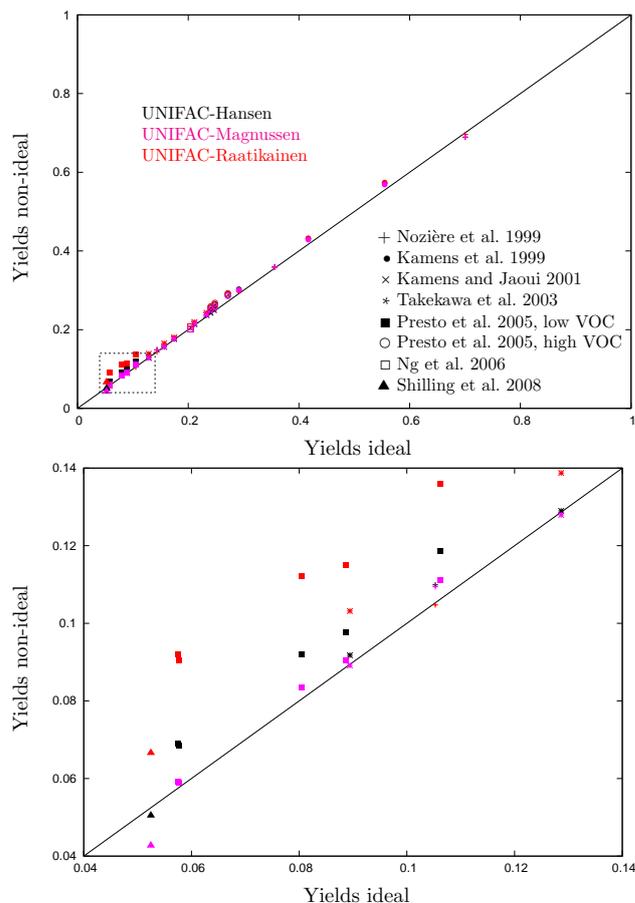
Note that this definition of volatility depends on the amount of aerosol present. When  $\kappa_{p,i}c_{om} \gg 1$ ,  $f_{p,i} \approx 1$  and  $c_{p,i} \approx c_{T,i}$  will not be very sensitive to changes in  $\kappa_{p,i}$  and therefore in  $\gamma_i$ . We can then define the mean of all  $f_{p,i}$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

$$\bar{f}_{om} = \sum_j x_j f_{p,j}, \quad (27)$$

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

$$\bar{\gamma} = \exp\left(\sum_j x_j \ln \gamma_j\right). \quad (28)$$

In Table 10  $\bar{f}_{om}$  for the ideal calculation and  $\bar{\gamma}$  for UNIFAC-Hansen, UNIFAC-Magnussen and UNIFAC-Raatikainen are presented.



**Fig. 2.** Top: 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. Bottom: Magnification of box in left figure to show the low-VOC SSCEs.

$\bar{f}_{om}$  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.

In general, UNIFAC-Raatikainen provides the lowest  $\bar{\gamma}$ , below unity. The other UNIFAC parameterizations give results below, but much closer to, unity. This explains the higher yield 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. The effect is the strongest for the ozonolysis experiments, where according to our simulations the largest SOA contributor 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. UNIFAC-Magnussen gives the  $\bar{\gamma}$  closest to unity

**Table 10.**  $\bar{f}_{om}$  and  $\bar{\gamma}$  of the different SSCEs, without considering water uptake.

Experiment	$\bar{f}_{om}$ ideal	$\bar{\gamma}$ UNIFAC-		
		Hansen <sup>a</sup>	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

<sup>a</sup> Not presented UNIFAC versions give results close to UNIFAC-Hansen.

for the ozonolysis experiments and hence -when it is a low-VOC experiment- also the lowest yields, almost equal to the ideal case.

The SSCEs of Nozière et al. (1999) are a special case as  $\bar{\gamma} \approx 1.0$ , 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.

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 far more important than those due to the interaction between organic molecules. Because of the high volatility of water,  $f_w \approx 0$  and  $c_{p,w} \approx \kappa_{p,w} c_{om} c_{g,w} \cdot c_{p,w}$  is directly proportional to  $\kappa_{p,w}$  and therefore inversely proportional to  $\gamma_w$ . 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-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

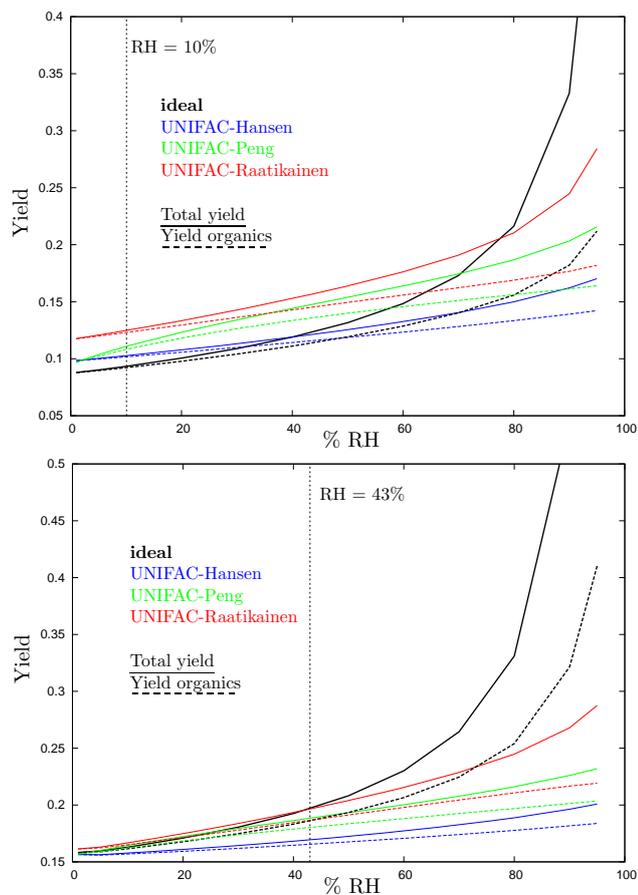
molecules partition to the SOA phase. The amount of water uptake depends on the activity coefficient model, in the order ideal > Raatikainen > Peng > Hansen  $\approx$  Magnussen  $\approx$  Ming.

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<sub>2</sub>O and the group CH<sub>2</sub>, which is only partially compensated by attractive interactions of water with alcohol and acid functionalities. The relatively lower  $\gamma_w$  for UNIFAC-Peng and UNIFAC-Raatikainen is mainly due to more attractive H<sub>2</sub>O–OH interactions, and, for UNIFAC-Raatikainen, a less repulsive CH<sub>2</sub>–H<sub>2</sub>O 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.

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  $\alpha$ -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

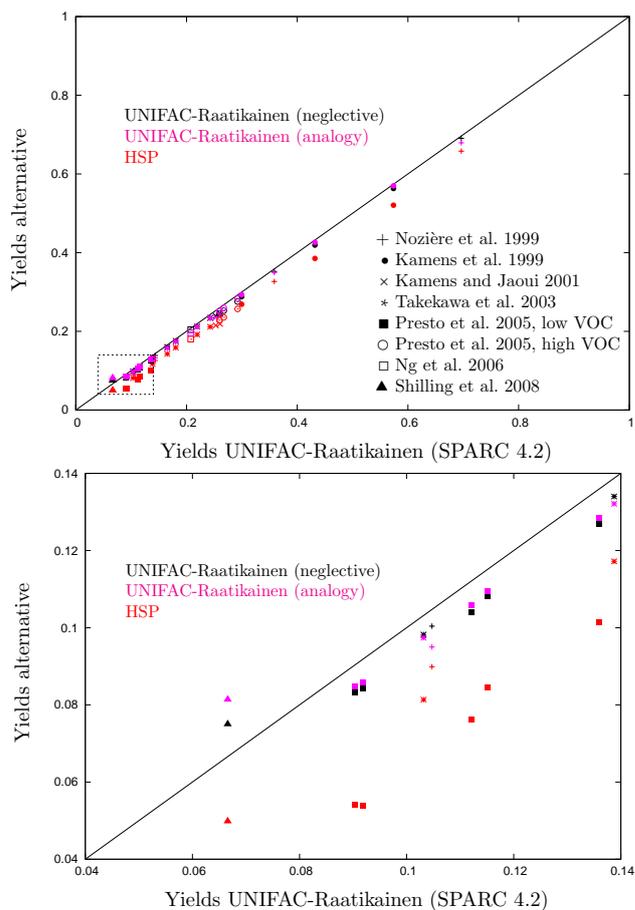


**Fig. 3.** Total (full line) and organics-only (dashed line) mass yield vs. RH, for the ideal case and for several UNIFAC-parameterizations, using the settings of two smog chamber experiments from Presto et al. (2005) (top), and Ng et al. (2006) (bottom). The vertical dashed line indicates the RH at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

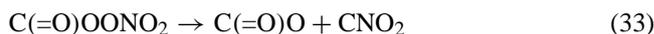
SOA (with water) always stayed in one single phase (Erdakos and Pankow, 2004; Chang and Pankow, 2008).

### 3.4 Alternative ways to treat the missing UNIFAC-parameters

Fitting to SPARC-generated activity coefficients (SPARC fitting approach) is only one way to deal with the missing UNIFAC-parameters  $a_{mk}$  of the NFG. They could be put to zero (the neglective approach), or the NFG could be replaced with their closest known analogs (the analogy approach). For the analogy approach, we took the following replacements



**Fig. 4.** Mass yields without water uptake. Top: On the horizontal axis mass yields are calculated with UNIFAC-Raatikainen, with SPARC-inferred parameters for the missing functional groups (cfr. supra). Vertical axis: mass yields with activity coefficients calculated in alternative ways. Black: UNIFAC-Raatikainen, but with zero  $a_{mk}$  for the missing functional groups. Magenta: UNIFAC-Raatikainen, but with missing functional groups replaced by their closest known analogs. Red: calculated with the HSP method. Bottom: Magnification of box in left figure to show the low-VOC SSCEs.



The first analogy was also made by Chang and Pankow (2008).

Results for mass yields are shown in Figs. 4–5, where the UNIFAC-Raatikainen was used for the known parameters.

Without water uptake, yields with the neglective or the analogy approach are slightly lower than with the SPARC fitting approach, except for the SSCE of Shilling et al. (2008), where it is higher. The differences are much smaller (up to a factor 0.9 for the low yields) than between e.g. UNIFAC-Hansen and UNIFAC-Raatikainen. Hence the results for the SSCEs without water uptake, presented in Sect. 3.2, are not

too sensitive on the way the missing UNIFAC-parameters are dealt with.

When considering water uptake (Fig. 5), the neglective approach gives again results very close to the SPARC fitting approach.

For the analogy approach, there are important differences for the SSCEs of Kamens et al. (1999), where much higher yields are predicted compared to the SPARC fitting approach or the neglective approach. This can be explained by the very high RH of these SSCEs, and the direct proportionality of water uptake to  $\gamma_w$ . Thus, for calculations at high RH, the results will depend largely on the assumption made for the interaction between the unknown UNIFAC groups and water. This is especially true for hydroperoxides and peroxy-acids, which are probably strongly hydrogen-bonding.

### 3.5 Results with the HSP method

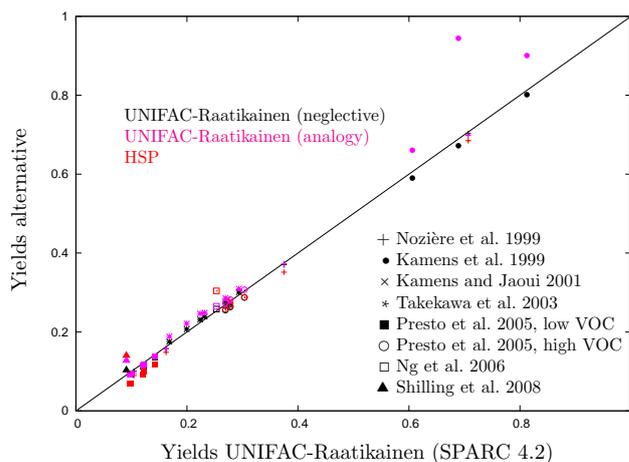
An alternative activity coefficient method is also tested, which presents the advantage that all necessary parameters are known or can be established from available experimental or trustworthy theoretical data: the HSP method. It was already used by Jang et al. (1997) to calculate IDACs in aerosol and was found to give in general approximately similar results to UNIFAC.

Without considering water uptake, mass yields calculated with the HSP method are systematically lower than with UNIFAC-Raatikainen (Fig. 4) or without activity coefficients (not shown). Since in our system all organic molecules are about the same size, the activity coefficient is mainly determined by the interaction part. From Eq. (22) it can be seen that  $\gamma_i$  is almost always greater than unity, which explains the low yields. This is different from the UNIFAC-method, where the interaction part of the activity coefficient can be, and often is, smaller than unity (see e.g. Table 10). When considering water uptake, the HSP calculated mass yield can be higher compared to UNIFAC or the ideal case, due to the size factor in Eq. (22). We note that the calculations did not converge for the high RH experiments of Kamens et al. (1999) and Takekawa et al. (2003).

## 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.

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



**Fig. 5.** Same as Fig. 4, but with water uptake. Note that some HSP-calculated mass yields for Kamens 1999 fall outside the figure, and that no mass yields for Takekawa et al. (2003); Kamens et al. (1999) could be calculated with the HSP method.

at low SOA mass, 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. The SOA water content is inversely proportional to the activity coefficient  $\gamma_w$  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 partitioning 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  $\approx$  UNIFAC-Magnussen  $\approx$  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.

If no water uptake is allowed, the results are not very dependent on the way the missing UNIFAC interaction parameters are treated. This is no longer the case, however, when water uptake is allowed and the RH is very high (>60%). Therefore, experimental characterization of the nonideality effects of the missing functional groups would be beneficial.

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.

An alternative way to calculate activity coefficients, based on HSP, give significant different results than UNIFAC. Given that the UNIFAC parameters, as opposed to HSP, are based on activity coefficient data, the HSP method is probably not appropriate for SOA calculations.

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