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Prediction of cloud condensation nuclei activity for organic compounds using functional group contribution methods

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Abstract

A wealth of recent laboratory and field experiments demonstrate that organic aerosol composition evolves with time in the atmosphere, leading to changes in the influence of the organic fraction to cloud condensation nuclei (CCN) spectra. There is a need for tools that can realistically represent the evolution of CCN activity to better predict indirect effects of organic aerosol on clouds and climate. This work describes a model to predict the CCN activity of organic compounds from functional group composition. The model combines Köhler theory with semi-empirical group contribution methods to estimate molar volumes, activity coefficients and liquid-liquid phase boundaries to predict the effective hygroscopicity parameter, kappa. Model evaluation against a selected database of published laboratory measurements demonstrates that kappa can be predicted within a factor of two. Simulation of homologous series is used to identify the relative effectiveness of different functional groups in increasing the CCN activity of weakly functionalized organic compounds. Hydroxyl, carboxyl, aldehyde, hydroperoxide, carbonyl, and ether moieties promote CCN activity while methylene and nitrate moieties inhibit CCN activity. The model can be incorporated into scale-bridging testbeds such as the Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere to evaluate the evolution of kappa for a complex mix of organic compounds and to develop suitable parameterizations of CCN evolution for larger scale models.

1 Introduction

Organic compounds are an important contributor to the atmospheric submicron aerosol (Jimenez et al., 2009). The organic fraction is projected to increase in the future due to the confluence of a decreasing sulfate and nitrate burden and increases in the global secondary organic aerosol burden (Heald et al., 2008). An important unanswered question is how the organic fraction influences the aerosol's ability to serve as cloud condensation nuclei (CCN), and in turn modulates climate via indirect effects of aerosols on clouds and precipitation (Andreae and Rosenfeld, 2008). Realistic prescribed variations in secondary organic aerosol hygroscopicity have demonstrable impacts on CCN number concentration (Mei et al., 2013) and can change the simulated global aerosol indirect forcing (AIF) by $\sim 1/6$ of the AIF simulated in a control case (Liu and Wang, 2010). To obtain a prognostic understanding of the contribution of the organic fraction to indirect aerosol forcing in future climates, models need improved schemes that map simulated organic aerosol composition to hygroscopicity and CCN activity.

Several organic aerosol types (e.g. freshly emitted diesel oil particles or first generation oxidation products of sesquiterpenes) consist of mostly hydrophobic hydrocarbon chains with few functional groups attached. Pure hydrocarbons with carbon number less than C_{30} are expected to be semi-volatile and in the liquid phase. Over time the compounds evolve by functionalization, fragmentation and oligomerization (Kroll and Seinfeld, 2008; Ziemann and Atkinson, 2012). As functional groups are added to the carbon chain the products usually, but not always, become less volatile (Goldstein et al., 2007), more dense (Kuwata et al., 2012), more viscous (Sastri and Rao, 1992), and more CCN active (Suda et al., 2014).

Laboratory (George and Abbatt, 2010; Poulain et al., 2010; Cappa et al., 2011; Massoli et al., 2010; Lambe et al., 2011; Duplissy et al., 2011; Kuwata et al., 2013; Rickards et al., 2013; Suda et al., 2014) and field studies (Jimenez et al., 2008; Chang et al., 2008; Mei et al., 2013) have demonstrated a robust link between the aerosol oxidation state and the ability of the organic fraction to promote hygroscopic water uptake and CCN activity. Proxies from mass spectrometry such as the fragmentation peak f_{44} or the atomic oxygen-to-carbon ratio are often used to model the increase in hygroscopicity. However, these correlations exhibit significant variability between studies and break down when applied at the compound level (Rickards et al., 2013; Suda et al., 2014).

Chemistry models are already capable of simulating the molecular identities of species present in the condensed phase during multi-day evolution of diluting airparcels (Lee-Taylor et al., 2015). Mapping this speciated aerosol composition to the aerosol hygroscopicity should ultimately permit quantification of changes in CCN number concentration (provided that the size distribution is also simulated) and associated effects on clouds and climate. This work addresses the need for a model that can predict the contribution of a compound with known chemical structure to the CCN activity of a particle of known size. The proposed model uses the UNIFAC equations (Fredenslund et al., 1975) with group interaction parameters form Hansen et al. (1991), Raatikainen and Laaksonen (2005) and Compernolle et al. (2009) to model activity coefficients and free energy of mixing. Liquid–liquid phase boundaries are determined using the area method of Eubank et al. (1992). Molecular volume is estimated from elemental composition and adjustments for functional group composition using the approach of Girolami (1994). The relationship between critical supersaturation and dry diameter is then predicted using Köhler theory (Seinfeld and Pandis, 2006). These predictions are validated against a compiled library of recently published CCN data of mostly weakly oxidized hydrocarbons containing a mixture of alcohol, carbonyl, aldehyde, ether, carboxyl, nitrate, and hydroperoxide moieties. The model is used to predict how the addition of one or more functional groups to otherwise similar molecules promotes CCN activity.

2 Model description

2.1 Köhler theory

The saturation ratio over a curved droplet is given by the Köhler equation

$$S = a_\mathrm{w} \cdot \exp\left(\frac{4\sigma_{\mathrm{s/a}}(T) M_\mathrm{w}}{\rho_\mathrm{w} R T D}\right), \tag{1}$$

where a_w is the water activity, $\sigma_{\mathrm{s/a}}$ is the surface tension of the solution/air interface, T is temperature, M_w is the molecular weight of water, ρ_w is the density of pure water, R is the universal gas constant, and D is the wet drop diameter. Water activity depends on the water content and the amounts and identities of solutes in the nucleus. The principle water content variable used in this work is the mole fraction

$$x_\mathrm{w} = \frac{n_\mathrm{w}}{n_\mathrm{w} + \sum_i n_{\mathrm{s},i}} \quad , \tag{2}$$

where x_w is the mole fraction of water, n_w and $n_{\mathrm{s},i}$ are the number of moles of water and solutes, and i is the number of dry components. The wet drop diameter can be calculated from x_w if the dry diameter, D_d, is specified and it is assumed that the particle is spherical and that the volume of water and solute are additive:

$$D = \langle (x_\mathrm{w} - 1)^{-1} (x_\mathrm{w} - x_\mathrm{w} \sum_i (\varepsilon_i v_{\mathrm{s},i}^{-1}) - 1) D_\mathrm{d}^3 \rangle^{1/3}. \tag{3}$$

In Eq. (3) v_w and $v_{\mathrm{s},i}$ are the molar volume of the water and solutes and ε_i are the volume fractions in the dry particle. Equation (3) is obtained by rearranging Eq. (7) in Petters et al. (2009b). The critical supersaturation required for an aqueous solution droplet to activate into a cloud droplet is found by combining Eqs. (1) and (3) and finding the x_w (or D) that maximizes s_c

$$s_\mathrm{c} = \left\{ \max \left[a_\mathrm{w} \cdot \exp \left(\frac{4\sigma_{\mathrm{s/a}}(T) M_\mathrm{w}}{\rho_\mathrm{w} RT \langle (x_\mathrm{w} - 1)^{-1} (x_\mathrm{w} - x_\mathrm{w} \sum_i (\varepsilon_i v_{\mathrm{s},i}^{-1}) - 1) D_\mathrm{d}^3 \rangle^{1/3}} \right) \right] \right\} \cdot 100\,\%$$

$$x_\mathrm{w} \in [0, 1], \tag{4}$$

where s_c is the critical supersaturation in %. The variables that control s_c are v_s, a_w, and $\sigma_{\mathrm{s/a}}$. In this work it is assumed that surface tension is that of pure water. Discussion on this and other assumptions are provided at the end of this section. First the prediction of v_s and a_w for organic compounds with known chemical structure is described.

2.2 Molar volume

Molar volume is calculated from the molecular formula using the method of Girolami (1994). Each element is assigned a relative volume based on its location in the periodic table. The elemental volumes are summed and scaled by a constant factor to compute v_s. If the oxygen is bound in the form of alcohol [OH] or carboxyl [C(=O)OH] moieties, the actual v_s is smaller due to intramolecular bonding. Therefore v_s is decreased by 10 % for each [OH] or [C(=O)OH] group but by no more than 30 % of the molar volume derived from the elemental composition. Girolami (1994) tested this method for 166 liquids and reports agreement with observations $v_s \sim \pm 10\,\%$.

2.3 Water activity

Water activity is related to the mole fraction via

$$a_w = \gamma_w x_w, \tag{5}$$

where γ_w is the activity coefficient of water. Activity coefficients are estimated using the semi-empirical group contribution method UNIFAC (Fredenslund et al., 1975). The UNIFAC model describes a liquid solution that consists of i components. Each component is divided into k groups. The activity coefficient of component i in solution (γ_i) has contributions from combinatorial (γ^C) and residual parts (γ^R)

$$\ln\gamma_i = \ln\gamma_i^C + \ln\gamma_i^R. \tag{6}$$

The combinatorial part is computed via

$$\ln\gamma_i^C = \ln\frac{\Phi_i}{x_i} + \frac{z}{2}q_i \ln\frac{\theta_i}{\Phi_i} + l_i - \frac{\Phi_i}{x_i}\sum\nolimits_j x_j l_j \tag{7a}$$

$$l_i = \frac{z}{2}(r_i - q_i) - (r_i - 1);\ z = 10 \tag{7b}$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j}; \Phi_i = \frac{r_i x_i}{\sum_j r_j x_j} \tag{7c}$$

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$$r_i = \sum_k v_k^{(i)} R_k;\ q_i = \sum_k v_k^{(i)} Q_k. \tag{7d}$$

In Eq. (7), x_i is the mole fraction of component i, θ_i and Φ_i are the average surface and segment fraction, z is the lattice coordination number, $v_k^{(i)}$ is the number of groups of type k in component i, R_k and Q_k are the group volume and surface area parameters derived from Bondi (1964), and r_i and q_i are the normalized Van-der-Waals volume and surface area. The summation i or j is over all components in the mixture, including component i.

The residual part is computed via

$$\ln\gamma_i^{\mathrm{R}} = \sum_k v_k^{(i)} \left[\ln\Gamma_k - \ln\Gamma_k^{(i)}\right] \tag{8a}$$

$$\ln\Gamma_k = Q_k - \left[1 - \ln\left(\sum_m \Theta_m \Psi_{mk}\right) - \sum_m \frac{\Theta_m \Psi_{km}}{\sum_n \Theta_n \Psi_{nm}}\right] \tag{8b}$$

$$\Theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n} \tag{8c}$$

$$X_m = \frac{\sum_i v_m^{(i)} x_i}{\sum_i \sum_k v_k^{(i)} x_i} \tag{8d}$$

$$\Psi_{mn} = \exp\left(-\frac{a_{mn}}{T}\right) \tag{8e}$$

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In Eq. (8), a_{mn} are empirically determined parameters, Ψ_{mn} is the group interaction parameter of group m with n, X_m is the mole fraction of group m in the mixture, Θ_m is the area fraction of group m, Γ_k is the group residual activity coefficient, and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing only molecules of type i. Equation (8) is also used to compute $\Gamma_k^{(i)}$. The summation n or m is over all different groups in the mixture, and the summation k is over all groups in component i.

Groups within UNIFAC are represented as main groups and subgroups. The main groups evaluated in this work are alkane [CH_n], alcohol [OH], water [H_2O], carbonyl [$CH_nC(=O)$], aldehyde [HC(=O)], ether [$CH_n(O)$], carboxyl [C(=O)OH], nitrate [CH_nONO_2], and hydroperoxide [$CH_n(OOH)$]. Interaction parameters a_{mn} between the main groups that are used in this work are tabulated in Table S1 in the Supplement. Some of the main groups have several subgroups, with each subgroup having unique volume and surface area parameters R_k andQ_k. These are summarized in Table S2.

2.4 Phase equilibrium

For some x_w liquid-liquid phase separation can occur. The normalized Gibbs free energy of the mixture, defined as the actual Gibbs free energy divided by the thermal energy, is needed to compute the number of thermodynamically stable phases in the system. For a binary system consisting of water (w) and a single solute (s), it is calculated from the activity coefficients via standard thermodynamic relationships (Prausnitz et al., 1999; Petters et al., 2009a, b)

$$\Delta g^{\text{mix}} = \Delta g^{\text{ideal}} + \Delta g^{\text{excess}} \tag{9a}$$

$$\Delta g^{\text{ideal}} = x_w \ln x_w + (1 - x_w) \ln x_s \tag{9b}$$

$$\Delta g^{\text{excess}} = x_w \ln \gamma_w + (1 - x_w) \ln \gamma_s, \tag{9c}$$

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where Δg^{mix} is the normalized change in Gibbs free energy of the mixture, $\Delta g^{\mathrm{ideal}}$ is the change in ideal Gibbs free energy of the mixture (Raoult's law) and $\Delta g^{\mathrm{excess}}$ is the excess Gibbs free energy of mixing quantifying the deviation from Raoult's law. In highly non-ideal solutions liquid-liquid phase separation may occur. Two compositions x_a and x_b define the water mole fraction of the two co-existing phases. Computationally, x_a and x_b can be obtained from Δg^{mix} using the area method (Eubank et al., 1992). Briefly, the state space is evaluated by computing the following area for all possible combinations x_{I} and x_{II}

$$A(x_{\mathrm{I}}x_{\mathrm{II}}) = \left|\left[\Delta g^{\mathrm{mix}}(x_{\mathrm{II}}) - \Delta g^{\mathrm{mix}}(x_{\mathrm{I}})\right]\left[\frac{x_{\mathrm{II}} - x_{\mathrm{I}}}{2}\right]\right| - \left|\int_{x_{\mathrm{I}}}^{x_{\mathrm{II}}} \Delta g^{\mathrm{mix}}(x)\mathrm{d}x\right|. \tag{10a}$$

Phase boundaries x_a and x_b exist if condition

$$A(x_a x_b) = \max A(x_{\mathrm{I}}, x_{\mathrm{II}});\ A > 0 \tag{10b}$$

is satisfied. If multiple phases coexist in phase equilibrium, the Gibbs-Duhem relationship dictates that the chemical potential of each component is equal in all phases. Therefore the water activity inside the miscibility gap is constant and the values entering Eq. (4) are subject to the constraint

$$a_{\mathrm{w}} = \begin{cases} a_{\mathrm{w}}(x_a) = a_{\mathrm{w}}(x_b) & \text{for} \quad x_a \le x_{\mathrm{w}} \le x_b \\ \gamma_{\mathrm{w}} x_{\mathrm{w}} & \text{else} \end{cases}. \tag{11}$$

2.5 Model implementation

The model was implemented to run on a personal computer using the commercial MATLAB environment (MathWorks, Inc.). Alternatively, the code runs under the Octave environment, which is available as free software under the GNU General Public License. Correct implementation of the UNIFAC model was confirmed by comparing results from test mixtures against output from existing implementations which is further described in the Supplement. A compound is defined by specifying a count of subgroups comprising the molecule. Equations (6)–(8) are solved to find γ_w for n linearly spaced values within the domain $x_w \in [0.0001, 0.9999]$. Resulting γ_w are parsed through Eqs. (9)–(11) to find the number of stable phases and to define a_w over the entire domain. These a_w are interpolated onto a higher resolution linearly gridded domain (m points) to improve the accuracy of the computation of s_c using Eq. (4). Values for n and m are selected to balance computational speed and solution accuracy. Equations (6)–(8) have linear time complexity. Equations (9)–(11) have quadratic time complexity. Thus the two algorithms have order $O(n)$ and $O(n^2)$, respectively. For $n > 200$, the overall model time complexity is $O(n^2)$. For $n >\sim 800$ and $m = 10\,000$, the resolution is sufficiently high so that the computed s_c becomes independent of the choice of n. All computations in this work were carried out for $n = 1000$ and $m = 10\,000$. Total model execution times for a single compound on an Intel(R) Core(TM) i7-2600 3.4 GHz microprocessor using a single core were 39 s with MATLAB version R2013a (8.1.0.604) 64-bit and 282 s with GNU Octave version 3.8.1 configured for 64-bit.

2.6 Hygroscopicity parameter

Equation (4) is solved to find s_c for a specified dry diameter, fixed $T = 298.15\,\mathrm{K}$ and $\sigma_{s/a} = 0.072\,\mathrm{J\,m^{-2}}$. The result is expressed in terms of the hygroscopicity parameter κ (Petters and Kreidenweis, 2007) that is defined via

$$s_c = \max_{D \in [D_d, \infty]} \left\{ \left[\frac{D^3 - D_d^3}{D^3 - D_d^3(1-\kappa)} \exp\left(\frac{4\sigma_{s/a}}{\rho_w R T D} \right) \right] - 1 \right\} \cdot 100\,\%. \tag{12}$$

The hygroscopicity parameter is obtained by iteratively seeking the κ value that satisfies Eq. (12) for a given D_d, s_c pair. Kappa values obtained by fitting a D_d, sc pair to Eq. (12) with the assumed temperature and surface tension conceptually correspond to “apparent hygroscopicity at standard state” (Christensen and Petters, 2012). All val-

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ues in this work are apparent κ's. For simplicity these are denoted as κ without further qualification. Observations against which the model is evaluated are summarized in the Supplement and will be discussed further in Sect. 3.

2.7 Model assumptions and limitations

The model approach presented here is limited to liquid organic compounds. This assumption is implied in both molar volume and UNIFAC activity coefficient calculations. Comparison with observational CCN data where the reference phase state may be crystalline should be interpreted with caution. For example, CCN experiments performed with crystalline dicarboxylic acids demonstrate that for some compounds deliquescence, i.e. a solubility-controlled phase transition, must precede droplet activation (Petters and Kreidenweis, 2008). UNIFAC is unable to accurately predict the solubility of these compounds if they existed in their crystalline solid state. If, however, the compound is in metastable aqueous solution, the UNIFAC prediction is expected to be valid. Under atmospheric conditions where the organic compounds are embedded in a matrix comprising a multitude of organic compounds, liquid or amorphous solid is the prevailing stable phase (Marcolli et al., 2004). Furthermore, since metastable states with hygroscopically bound water appear to dominate in the atmosphere (Rood et al., 1989; Nguyen et al., 2014) the liquid assumption may not be a serious limitation. Nonetheless, it is unclear whether the assumption of a liquid-like reference state is a serious limitation if the organic particles are highly viscous (Vaden et al., 2011; Shiraiwa et al., 2011; Zobrist et al., 2011; Renbaum-Wolff et al., 2013).

Other limitations of the UNIFAC method are the problems of accounting for group proximity effects and the inability to distinguish between isomers. Proximity effects occur when polar groups are separated by less than three to four carbon atoms (Topping et al., 2005). Since only the number of groups of type i are specified, all isomers are modeled to have identical κ values. Although experiments show that the location of the functional group has a small and systematic effects on the observed κ (Suda et al., 2014), those effects are relatively small and beyond the resolution of the model presented here.

The application of Eq. (4) assumes that the surface tension is that of pure water. Many organic compounds found in ambient organic aerosol lower the surface tension at the solution/air interface (Tuckermann and Cammenga, 2004; Tuckerman, 2007). However, several studies have demonstrated via experiment and theory that surfactant partitioning between the bulk solution and the Gibbs surface phase greatly diminishes the effect one would predict by applying macroscopic surface tensions in Köhler theory (Li et al., 1998; Rood and Williams, 2001; Sorjamaa et al., 2004; Prisle et al., 2011). Neglecting to account for reduced surface tension and using water activity to estimate CCN activity results in an underestimate of κ of $\sim 30\,\%$ for the strong surfactant sodium dodecyl sulfate (Petters and Kreidenweis, 2013). Including surfactant partitioning in Eq. (4) is possible in principle but will require prediction of surface tension lowering from functional group data and a thorough validation against experimental data.

3 Results and discussion

Experimental data for validation was compiled from the literature. A detailed summary of the compound names, chemical structures, physicochemical properties, CCN observations, and observed κ's is provided in the Supplement (Tables S3–S7). This set features compounds with mostly linear carbon backbones C_4 to C_{18} and O : C ratio between 0.1 and 1. The data are grouped into model compounds for primary organic aerosol (POA, Table S3), functionalized hydroperoxy ethers (Table S4), hydroxynitrates (Table S5), carboxylic acids (Table S6), and carbohydrates (Table S7). Compounds included in Table S3 are long chain molecules that have hydrophobic tails (> 14 methylene groups) and a single terminal carboxyl or hydroxyl group. Representative example compounds are oleic acid or cetyl alcohol. Compounds in Table S4 are C_{14} functionalized hydroperoxy ethers that have 10–12 methylene groups, at least one hydroperoxide and ether group, and a second carbonyl, hydroperxide, or carboxyl group. Compounds in Table S5 are functionalized hydroxynitrates featuring C_{10} to C_{15} carbon backbones with 1–3 hydroxyl and 1–4 nitrate groups. Compounds in Table S6 are C_4–C_{10} carboxylic acids that have 1–2 carboxyl and up to one carbonyl group attached to the carbon backbone. Finally, compounds in Table S7 are C_4–C_{18} carbohydrates that have hydroxyl groups approximately equal to the number of carbon atoms. Data in Table S3 are taken from Raymond and Pandis (2002) and Shilling et al. (2007). Data in Tables S4 and S5 are taken from the Supplement of Suda et al. (2014). Data in Tables S6 and S7 are from various sources are summarized in the Supplement of Petters et al. (2009a), which was updated with new compounds from Christensen and Petters (2012), and data were re-screened for quality. The compounds were selected to provide systematic variation in the number and type of functional groups with otherwise similar structure, i.e. linear or weakly branched alkane backbone with variable carbon chain length.

To illustrate model initialization and model output two example compounds from the Supplement C_{12} dihydroxynitrate and C_{13} trihydroxynitrate, are presented in Table 1. For some of the compounds density and solubility data are available and those data are included in the Supplement. Table 1 shows how the molecular structure is decomposed into the subgroups understood by the UNIFAC and Girolami (1994) model framework. Detailed model output for the two example compounds is illustrated in Fig. 1. The predicted mole fraction dependence of Δg_{mix} suggests that the C_{13} trihydroxynitrate is miscible with water in all proportions while the C_{12} dihydroxynitrate is not. The dashed black line connecting x_a and x_b encloses the maximum positive area with the Δg_{mix} line and defines the two-phase region. Water activity derived from Δg^{mix} is graphed in the middle panel. It shows that the miscibility gap for the C_{12} dihydroxynitrate occurs at water activity close to unity. Phase gaps at water activity near unity may result in miscibility-controlled cloud droplet activation (Petters et al., 2006), which is analogous to solubility/deliquescence limited cloud droplet activation (Shulman et al., 1998; Hori et al., 2003; Bilde and Svenningsson et al., 2004; Kreidenweis et al., 2006; Petters and Kreidenweis, 2008). Köhler curves in the right panel demonstrate miscibility-limited activation behavior. For the C_{13} trihydroxynitrate, the Köhler curve is smooth and ex-

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hibits a single maximum corresponding to the model critical supersaturation. For the C_{12} dihydroxynitrate two maxima appear. The first maximum corresponds to the point of incipient phase separation x_a. The height of the miscibility barrier depends on the dry diameter. For large dry particles where the Kelvin term does not play a significant role, the supersaturation of point x_a is reduced and the second classical Köhler maximum will control droplet activation. Similar complex Köhler curves have been reported previously (e.g. Bilde and Svenningsson, 2004; Petters and Kreidenweis, 2008). Experiments with pure crystalline sparingly-soluble organic compounds have demonstrated convincingly that the larger maximum indeed controls cloud droplet activation for solubility-limited cases (Hori et al., 2003; Bilde and Svenningsson, 2004; Hings et al., 2008). The s_c vs. D_d relationship for phase-controlled activation does not result in κ that is independent with respect to D_d (Petters and Kreidenweis, 2008). Therefore for compounds having $\kappa_< \sim 0.06$ where phase separation might play a role, the observed s_c, D_d pair is included in the data tables (Table 1, Tables S3–S7) and κ values are computed from the observation and the model (Eq. 12) at the same D_d. Note that the D_d-dependent κ only plays a role in a narrow range of miscibilities. Sufficiently soluble and truly insoluble substances are not affected. In summary, Table 1 and Fig. 1 demonstrate model input, illustrate model mechanics, and identify model outputs.

How well do data-derived and model-derived κ compare? For numerical comparison both κ's are included in Tables S3–S7. A graphical illustration of these is presented in Fig. 2. To improve clarity compounds with predicted and modelled $\kappa < 0.001$ are clustered in the lower left corner. Such low κ's correspond to compounds that are effectively CCN inactive. The range between $\kappa = 10^{-3}$ and 10^{-5} spans a narrow range in the $s_c - D_d - \kappa$ state space that characterizes CCN activity (cf. Fig. 1 in Petters and Kreidenweis, 2007). Resolving these differences is not particularly meaningful for the organic dominated particles that typically have $D_d < 300$ nm. Furthermore, the κ of an internally mixed particle is approximately the weighted volume fraction in the mixture. For $\kappa < 10^{-3}$ the contribution to a mixed particle's κ is insensitive to the exact value. Finally, although state-of-the-science size-resolved CCN measurements can resolve

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differences in $\kappa < 10^{-3}$, compound impurities can interfere. A 1 % impurity having κ similar to ammonium sulphate would contribute ~0.06 to a measured particle κ. In addition, solvent residuals (Huff Hartz et al., 2006; Shilling et al., 2007; Rissman et al., 2007) and control over the dry particle phase state (Raymond and Pandis, 2002; Hori et al., 2003; Broekhuizen et al., 2004; Bilde and Svenningson, 2004) can disproportionally bias the characterization of low κ's. Combined these points justify the definition of $\kappa < 0.001$ as effectively CCN inactive. Compounds in the CCN inactive corner include all compounds from Table S3, the C_{14} and C_{15} hydroxnitrate, and the C_{14}-trinitrate. These compounds all have 11 or more methylene groups and O : C ratios between 0.11 and 0.65. CCN activity of these compounds is satisfactorily predicted by the model.

Nine compounds are predicted to be CCN inactive but have measurements indicating $0.001 > \kappa_{obs} >\sim 0.03$. These are graphed below the dashed line and include C_{14} di- and tetra-nitrate, C_{13} hydroxynitrate, C_{14} and C_{15} dihydroxynitrate, the remaining hydroperoxide ethers from Table S4, and cis-pinonic acid. The observed C_{14} di- and tetra-nitrate are barely larger than the cutoff for CCN inactive. Variation of κ between the C_{14} di- and tri- and tetra-nitrate (cf. Fig. 2, Suda et al., 2014) implies that the trinitrate has lower κ than the di- and tetra-nitrate, which suggests that some random variability in the data is superimposed on the trend. Similarly, the observations show that the C_{14}- and C_{15} dihydroxynitrate are slightly more CCN active than the C_{13} dihydroxynitrate. Although this is possible such behaviour is not plausible due to the well-established hydrophobic nature of the added CH_x groups. One possible explanation for the discrepancies is the sensitivity of observed κ's to trace contamination. Each of the compounds was purified via HPLC (Suda et al., 2014) but degree of purification likely varied between compounds. Furthermore, experimental uncertainty for the HPLC-CCN method used is slightly larger than for standard methods since it requires application of fast flow scans. Finally, the data are from a single set of experiments. More data are needed before attributing the mismatch to either model or measurement error.

Another notable outlier is adipic acid. Here, the observed $\kappa < 0.01$ corresponds to the solubility-limited value that is referenced against its solid crystalline phase state. In contrast, the predicted value $\kappa = 0.14$ is in good agreement with the molar volume prediction ($\kappa = 0.17$, cf. Fig. 4, Christensen and Petters, 2012) and observed κ that adipic acid particles express when solubility limitations are removed (cf. Fig. 1, Hings et al., 2008). This scenario was selected to illustrate the inability of the UNIFAC model to treat solid phases. It therefore cannot capture deliquescence and deliquescence/solubility limited activation. In atmospheric OA multiple organic compounds likely form an amorphous supercooled melt (Marcolli et al., 2004) and metastable aqueous solutions are ubiquitous (Rood et al., 1995). Thus the metastable prediction would be valid to account for adipic acid in the context of atmospheric OA.

A series of carboxylic acids and carbohydrates cluster near the 1 : 1 line at $\kappa >\sim 0.06$. These compounds are generally highly functionalized having at least 2 carboxyl, hydroxyl, or carbonyl group for every 4 carbon atoms. The O : C ratio always exceeds 0.5 and is close to 1 for many of the compounds. For the predictions, activity coefficients approach unity, compounds are miscible in water in all proportions, and model κ's closely track the prediction based on estimated molar volume. Overall comparison of predicted vs. observed κ is approximately within a factor of two and this range is similar to predictions that are based on actual molar volume (cf. Fig. 2, Petters et al., 2009a).

The series of hydroxynitrates, dihydroxynitrates, and trihydroxynitrates for different carbon chain length also cluster near the 1 : 1 line. The spread is within approximately a factor of two and similar to that of the carboxylic acids and carbohydrates. These compounds span the entire range from $\kappa < 0.001$ to $\kappa \sim 0.1$ and have as few as two hydroxyl and one nitrate group per 13 carbon atoms (C_{13} dihydroxynitrate). The model appears to accurately predict the influence of the methylene and hydroxyl groups on the transition from immiscible and CCN inactive to sufficiently miscible and CCN active according to the molar volume of the compound. For the C_{11}, C_{12}, and C_{13} dihydroxynitrates the predicted miscibility-limited activation demonstrated in Fig. 1 seems to adequately explain the transition. The accurate model prediction of this sensitive transition regime is encouraging, especially since no adjustment was made to the a_{mn} group interaction parameters for [OH], [CH_x], and [H_2O] groups.

In summary, Fig. 2 demonstrates four capabilities of the model. First, the model has good skill in correctly classifying effectively CCN inactive compounds ($\kappa < 0.001$). Second, the model captures the molar volume dependent activation of highly functionalized compounds (low molecular weight dicarboxylic acids and polysaccharides). Scatter between predicted and observed κ is approximately within a factor of two and considered acceptable taking into account the considerable diversity in the underlying CCN data. Third, the model predicts that miscibility limitations are the cause for poor CCN activity of weakly functionalized hydrocarbons, and the phase separation information can be used to quantitatively predict the transition between sufficiently miscible and effectively immiscible species. Finally, the model seems to accurately capture the main functional group dependencies observed previously (Suda et al., 2014): a strong promoting effect of hydroxyl, a weak promoting effect for hydroperoxides, a negligible or inhibiting effect of nitrate, and inhibiting effect of methylene groups on CCN activity. How, then, can one quantify the model sensitivity of κ to the addition of functional groups to otherwise similar molecules?

Simulation of homologous series can be used to derive these sensitivities. Figure 3 shows modelled κ's for a series of functionalized *n*-alkanes. The gradual decreasing trend of κ with increasing carbon number is due to the increase in molar volume. A steep decline is observed when a critical carbon number is exceeded. Beyond this point the additional methylene groups reduce the miscibility with water and render the compound effectively CCN inactive. For example, CCN activity for a C_{16} trihydroxyalkane is controlled mostly by molar volume while C_{18} trihydroxyalkane is effectively CCN inactive. The critical carbon number is C_7, C_{12}, C_{16}, C_{20}, and C_{24} for the mono-, di-, tri-, tetra-, and pentahydroxyalkanes, respectively. Starting with an *n*-alkane, the most dramatic effect of adding functional groups is to render the molecule miscible with water. Contrasting the critical carbon number for different homologous series can be used as a measure of a particular groups' ability to transform the molecule such that it is sufficiently miscible in water and can express its molar volume κ. The hydroxyalkane series shows that approximately one hydroxyl group is needed to compensate for the addition of 4 methylene groups (i.e. to maintain miscibility at the composition of the critical carbon number). Expressed as a ratio, $\Delta[CH_n]/\Delta[OH] \sim -4/1$. Similar ratios for the other groups are derived from the shifts in the dihydroxyalkane series upon further functionalization: $\Delta[CH_n]/\Delta[C(=O)OH] \sim -5/2$, $\Delta[CH_n]/\Delta[CH_nC(=O)] \sim -2/3$, $\Delta[CH_n]/\Delta[HC(=O)] \sim -4/2$, $\Delta[CH_n]/\Delta[CH_n(O)] \sim -2/4$, $\Delta[CH_n]/\Delta[CH_n(OOH)] \sim -2/2$, and $\Delta[CH_n]/\Delta[CH_n(OOH)] \sim -2/3$, and $\Delta[CH_n]/\Delta[CH_nONO_2] \sim 1/1$. This leads to a sorting of relative effectiveness of the groups in promoting miscibility, hydroxyl (−4) > acid (−2.5) > aldehyde (−2) > hydroperoxide (−1) > carbonyl (−0.66) > ether (−0.5) > nitrate (1), where the number in parentheses corresponds to the $\Delta[CH_n]/\Delta[n]$. According to this model the addition of nitrate groups is in the same direction as methylene groups, i.e. it reduces miscibility. This finding is consistent with CCN experiments on alkenes reacted with NO_3 radicals (Suda et al., 2014, Supplement), and the known low miscibility of organic nitrates in water (Boschan et al., 1995). Furthermore sorting of the different functional groups is qualitatively consistent with the sensitivity of κ to the addition of functional groups derived from CCN data (Table S5, Suda et al., 2014).

4 Summary and conclusions

This paper describes how functional group contribution methods can be used to estimate the CCN activity of pure organic compounds. Group interaction parameters were taken from a mix of sources and used without further tuning. Model fidelity was evaluated against a database of published CCN data. Weakly functionalized alkanes are correctly classified as effectively CCN inactive (defined as $\kappa < 0.001$). Highly functionalized and water-soluble molecules are predicted to activate in accordance with the estimated molar volume and generally predictions agree with observations within a factor of two. Liquid-liquid phase separation is predicted to occur for compounds with few functional groups and phase separation is predicted to control κ. The model adequately reproduces the observation that hydroxyl groups strongly promote CCN activity while nitrate groups inhibit CCN activity. A few outliers in the model evaluation may be explained by the combination of CCN measurement uncertainty, compound purity, uncertainty in dry particle phase state, and insufficiently tuned group interaction parameters. However, more systematic data on weakly functionalized compounds, including repeat studies, are needed before a retuning of parameters is justified. The model makes new predictions about the relative effectiveness of the groups in promoting miscibility. Most notably, it predicts that hydroperoxides have much less of an effect than hydroxyl, which is slightly surprising since one would expect the hydrogen bonding to be similar. The model state space can serve as a rough guide to define test conditions to quantify via experiment the effectiveness of adding one or more functional groups to a carbon backbone.

Although this work is limited to a few functional groups, the presented framework is general since interaction parameters are available for a wide range of groups. For atmospheric purposes, amines, olefins, and aromatic compounds are the most relevant groups that need to be added. Few, if any systematic CCN data for these groups are available. However, the success of the current model to estimate κ without the need to tune parameters could be taken as indication that first order predictions can be obtained until such data become available.

The computational speed of the model is relatively slow. The slow speed is due to the need to evaluate the entire range of mole fractions in order to determine the phase boundaries. Improvement in model execution speed is likely possible via algorithm optimization. Furthermore, parallel execution of the code is possible. With a regular workstation it is feasible to perform offline computation of $\sim 10^6$ κ's for a large set of compounds produced by the Generator of Explicit Chemistry and Kinetics of Organics in the Atmosphere (GECKO-A) or similar models. Once pure component κ's are predicted, the evolution of the overall OA κ in mixed particles can be calculated quickly using mixing rules (Petters and Kreidenweis, 2007).

Code availability

Source code and example scripts demonstrating model initialization for the compounds presented in this study is available as Supplement to this manuscript.

The Supplement related to this article is available online at doi:10.5194/gmdd-8-7445-2015-supplement.

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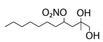
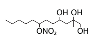
Table 1. Properties for two example chemical compounds. UNIFAC representation indicated the number and type of subgroups to represent the chemical structure MW denotes molecular weight ($g\,mol^{-1}$) and v_s denotes the model predicted molar volume ($cm^{-3}\,mol^{-1}$). CCN reflects the observed supersaturation and dry diameter data pair obtained from the source (Suda et al., 2014) from which observed κ was determined.

Name	Formula	Structure	UNIFAC representation		MW	v_s	Observed CCN	Apparent κ	
			#	Subgroup			s_c (%) D_d(nm)	Observed	Model
C_{12} dihydroxy nitrate	$C_{12}H_{25}O_5N$		2 8 1 1 2	CH_3 CH_2 C $CH(ONO_2)$ OH	263.3	263.3	0.3 222	0.018	0.008
C_{13} trihydroxy nitrate	$C_{13}H_{27}O_6N$		2 8 1 1 1 3	CH_3 CH_2 CH C $CH(ONO_2)$ OH	293.4	257.7	0.3 111	0.1	0.07

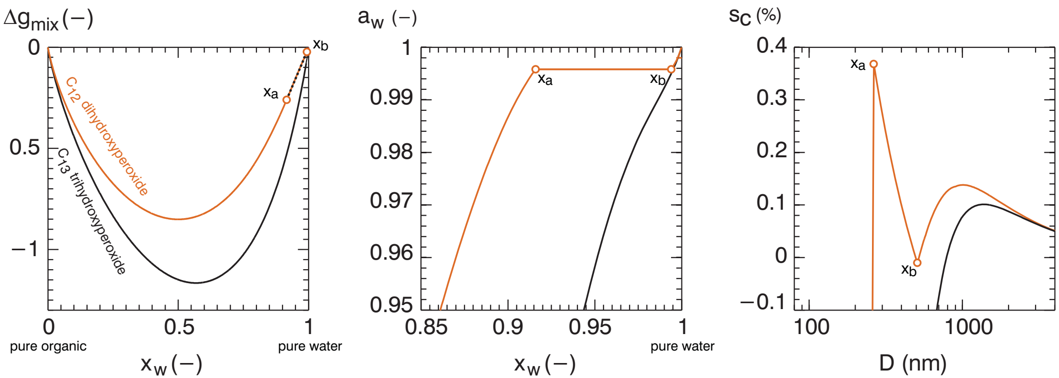


Figure 1. Modeled Δg_{mix} (left), water activity (middle), and Köhler curves (right) for C_{12} dihydroxyperoxide and C_{13} trihydroxyperoxide (see Table 1). Open circles denote the mole fractions x_a and x_b that correspond to the envelope of compositions where liquid–liquid phase separation is predicted for the C_{12} dihydroxyperoxide.

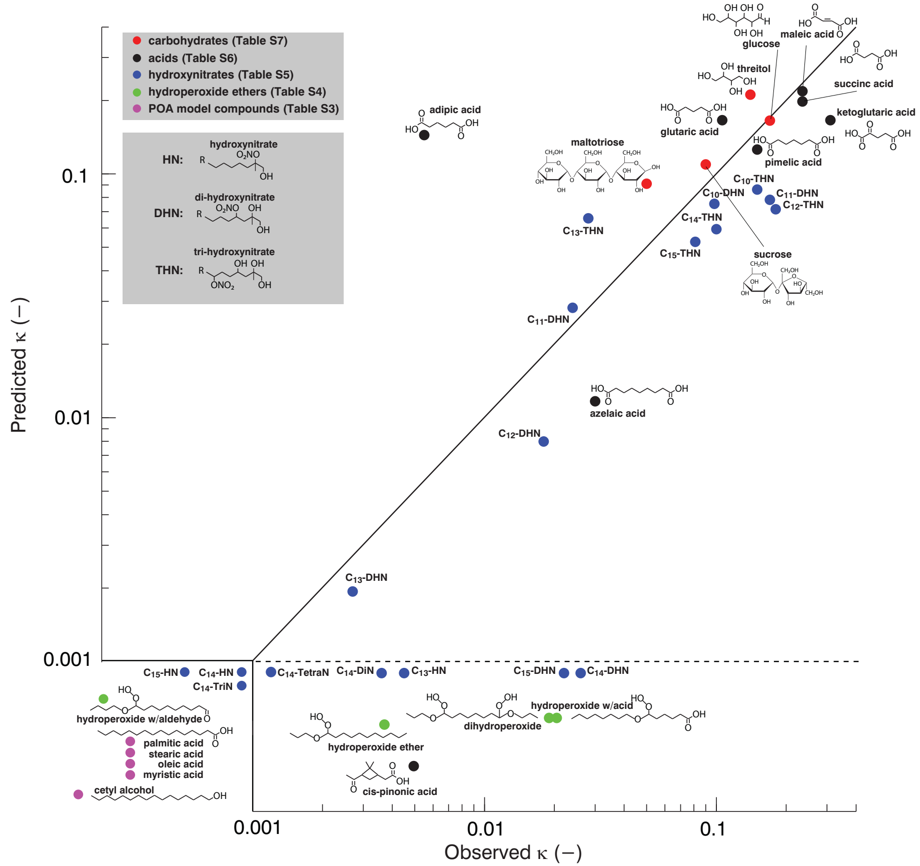


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Figure 2. Model predicted vs. experimentally determined κ-values. Values $\kappa < 0.001$ are classified as CCN inactive and are clustered in the lower left corner of the graph. Colors are used to delineate the grouped source data in the Supplement (SI). Selected structures from the SI are included in the graph. C_x-HN, C_x-DHN, and C_x-THN denote hydroxynitrate, dihydroxynitrate, and trihydroxynitrate and x denotes the total number of carbon atoms. C_{14}-DiN, C_{14}-TriN, C_{14}-TetraN denote the C_{14} dinitrate, trintrate, and tetranitrate, respectively. Points below the dashed line corresponds to compounds with predicted $\kappa < 0.001$ and observed $\kappa > 0.001$.

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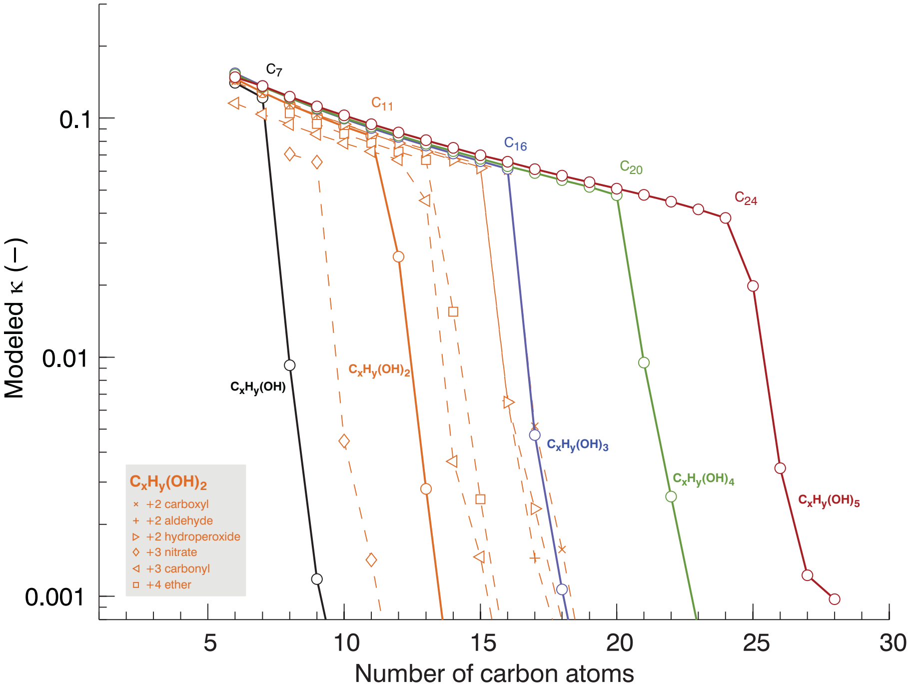

Figure 3. Modeled κ values for homologous series of functionalized *n*-alkanes. Solid lines correspond to alkanes with 1–5 non-terminal hydroxyl groups. Orange dashed lines correspond to further functionalized dihydroxyalkanes as described in the legend. Colored carbon numbers (C_7, C_{12}, C_{16}, C_{20}, and C_{24}) correspond to the largest carbon number without miscibility limited activation for the respective hydroxyalkanes series.

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