

Author Reply

We thank the two anonymous referees for their time and effort reviewing the manuscript and for providing constructive feedback. Below is a reply to the reviews and a description how the manuscript has been modified in response to those comments. Some comments have been moved from their sequence of appearance in the original review and those comments have been marked as (non-sequential, moved from pg. XXX). The reason for moving the comments out of sequence are made clear in a preface to the comment.

General overview over revisions:

- (1) In response to several comments we have expanded the introduction to include a broader review of the use of UNIFAC-based approaches for modeling aerosol water interactions.*
- (2) In response to comments regarding liquid-liquid equilibrium calculations and applicability to multicomponent systems we have added a paragraph discussing the envisioned treatment of such systems and potential shortcomings of the proposed approach.*
- (3) In response to comments regarding the automatic mapping of potentially millions of compounds to UNIFAC groups we have added qualifications to the text and added discussion to the problems that need to be solved.*
- (4) In response to comments regarding to extensions including surface tension, we outlined the inclusion of potential modeling approaches.*

Reviewer #1 Evaluation

This work presents a comparison between predicted and measured hygroscopicity, presented as CCN activation potential, for a set of important atmospheric functionalities. The comparison between the measured and predicted kappa values, in itself, is an interesting result and should be published at some level and could equally appear in ACP. My general feeling is that the tone regarding the novelty, and evaluation, of the model basis rather than the application needs to be addressed slightly before accepting for publication in GMD. I raise specific points in the following, with appropriate references, which I believe shouldn't require much effort and ultimately add to the presentation of the work.

Comment: First, on that general note, in the abstract there is the following text: 'The model combines Kohler theory with semi-empirical group contribution methods..' I would suggest, 'Following previous methodologies in the literature, we test the ability of group contribution methods in Kohler theory to...' but of course then add a statement that portrays the attempt to include LLE - 'however, in our approach, we also attempt to account for LLE using'

Response: We made the suggested change.

Revisions: **Following previous methods in the literature, we test the ability of semi-empirical group contribution methods in Köhler theory to predict the effective hygroscopicity parameter, kappa. However, in our approach we also account for liquid-liquid phase boundaries to simulate phase-limited activation behavior.**

Preface: We combined the response to the two separate points raised below regarding the problem of mapping large numbers of computer-generated compounds to UNIFAC groupings.

Comment: Following this, in the introduction the authors state that '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.' I completely agree. However mapping this functionality from detailed chemical mechanisms is not easy. Group contribution methods present the 'keys' to performing this mapping, but selecting those keys from thousands to millions of compounds falls within the remit of chemoinformatics. For the compounds presented in this study, we are able to check the coverage provided by the selected UNIFAC groups. I would suggest qualifying this study with a statement similar to: 'In this study, we test the ability of manually applying such methodologies to ..'. There is also the statement: '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.'

Comment: (non-sequential, moved from pg. C2516) Summary and Conclusions: Page 7463, last paragraph. This text needs a few caveats. 'It is feasible to perform offline computation of $\sim 10^6$ k's..' As far as I can tell, this is based on the information regarding computational cost and seems completely reasonable since you would treat every compound in a binary mixture. Computational time then is the only limit. As mentioned earlier, any automated selecting of the relevant functionalities needs checking against a database of compounds that cover combinations of functionalities. For example, by using the compounds within the Master-Chemical-Mechanism (MCM) database, how many compounds are 'fully' captured with the selected UNIFAC groups? The MCM would provide a nice checkpoint before moving onto using output from GECKO.

Response: *We fully agree with the referee's points. In response we have qualified the statements as suggested. We also added a paragraph discussing issues regarding automated mapping algorithms.*

Revisions: *Added statement of manual mapping*
These predictions are validated by manually mapping chemical composition to UNIFAC groupings and comparing modeled CCN activity against observations from 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.

Added Statement of UNIFAC group coverage
One additional limitation is the need for algorithms that automatically map the computer-generated SMILES structures (e.g. Table 3, Lee-Taylor et al., 2015) to UNIFAC groups. Several of these structures are bridged and even manual mapping of those structures to UNIFAC groupings will necessitate definition of new groups with unknown volume, surface, and interaction parameters. Separate studies are needed to establish the minimal number of new groups that would be needed to obtain optimal coverage for the set of compounds of interest.

Comment: The proposed model uses the UNIFAC equations..’ On first glance, this sounds as if the approach of UNIFAC within Kohler theory is a new concept. There have been thermodynamic equilibrium models developed around group contribution methods specifically due to the demand for enabling predictions over the wide range of atmospheric functionalities. This should be clear in the paper.

Response: *We now include a broader review of the use of UNIFAC-based approaches for modeling aerosol water interactions.*

Revisions: Chemistry models are already capable of simulating the molecular identities of species present in the condensed phase during multi-day evolution of diluting air-parcels (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. **Thermodynamic models should be able to predict CCN activity. Many thermodynamic models have made use of activity coefficients predicted by the UNIFAC group contribution method (Fredenslund et al., 1975). Several investigators have compared UNIFAC predictions of organic aerosol water content to experimental data (Saxena and Hildemann, 1997, Ming and Russell, 2001, Peng et al., 2001, Choi and Chan, 2002, Mochida and Kawamura, 2004, Marcolli and Peter, 2005, Moore and Raymond, 2008). Some of these comparisons prompted proposed revisions of specific group interaction parameters, e.g. [OH] and [H₂O]. Several thermodynamic models that treat complex phase equilibria of multifunctional multicomponent organic mixtures are based on UNIFAC activity coefficients (Ming and Russell, 2002, Raatikainen and Laaksonen, 2005, Topping et al., 2005, Amundson et al., 2007, Zuend et al., 2008, Compernelle et al., 2009). The development of these models has been driven by the need to enable predictions over a wide range of conditions and compositions, including the effect of liquid-liquid phase separation on gas-to-particle partitioning (Zuend and Seinfeld, 2012, Topping et al., 2013). The prediction of CCN activity of organic compounds has received less attention. Rissman et al. (2007) used the ADDEM model (Topping et al., 2005) with an underlying UNIFAC core to predict the relationship between critical supersaturation and dry for several dicarboxylic acid aerosols. To our knowledge no study to date has systematically focused on the prediction of CCN activity from thermodynamic models.**

Here we build on this body of work to 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 from Hansen et al., (1991), Raatikainen and Laaksonen (2005) and Compernelle 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). **The basic model mechanics are similar to those employed in multicomponent phase equilibrium models (Ming and Russell, 2002, Raatikainen and Laaksonen, 2005, Topping et al., 2005, Amundson et al., 2007, Zuend et al., 2008) but limited in scope to binary compositions and with focus on accurately representing phase and water activity at conditions relevant at the point of CCN activation only.**

Comment: Section 2.2 Molar Volume
Barley et al (2012) reviewed the performance of various methods for predicting molar volume. What is the relative sensitivity of errors in molar volume to derived κ using this method?

Barley, M. H., D. O. Topping and G. McFiggans, The Critical Assessment of Liquid Density Estimation Methods for Multifunctional Organic Compounds, J Phys Chem A 2013 Apr 15;117(16):3428-41.

Response: We added the citation to the text. We also added discussion regarding the sensitivity of derived- κ to the error in molar volume.

Revisions: (1) **Added Barley citation to molar volume validation section (bold text added)**

Girolami (1994) tested this method for 166 liquids and reports agreement with observations $v_s \sim \pm 10\%$. **Barley et al. (2012) reviewed the performance of various methods for predicting molar volume using a test set of 56 multifunctional organic compounds and report similar scatter.**

(2) **Added discussion regarding the sensitivity of κ to error in molar volume (bold text is added).**

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. **We note that uncertainties in molar volume estimation of $v_s \sim \pm 10\%$ stemming from the Girolami et al. (1994) method correspond to $\pm 10\%$ error in predicted κ for these compounds, which is significantly less than the observed scatter in the data (Petters et al., 2009).**

Comment: Section 2.4 Phase equilibrium

The authors are correct in that phase separation can occur, and there are a number of key papers in the literature focusing on the mechanics/numerics of treating this process alone. I find this section a little lacking in detail as it currently stands. For binary systems, it is quite easy to model. A simple root finding method can be used to assess the point of equal chemical potentials and then a calculation of the Gibbs energy used to determine the most stable state. The method proposed here needs to be proven to work from a select number of binary systems that exist in the literature, particularly as this process is then embedded within a Kohler curve designed for multicomponent solutions. For example, how does this perform for systems presented in Zuend et al. 2010?

A. Zuend, C. Marcolli, T. Peter and J. H. Seinfeld, *Atmos. Chem. Phys.*, 2010, 10, 7795–7820.

Response: *The suggestion to cross-validate our algorithm to published phase equilibrium model output is excellent. We now do so in the text. We note that the phase boundaries are provided in the model output files and that the model code is available via the supplement. We also revised Section 2.4 and the supplement as follows:*

Revisions: *Addition to Section 2.4*

We note that Eubank et al. (1992) algorithm can be extended to n -components. Other numerically efficient approaches to find phase equilibrium, including those of n -component mixtures, are available in the literature (e.g. Amundson et al., 2005, 2007, Zuend et al., 2010). Comparison for phase boundaries (x_a, x_b) calculated using standard UNIFAC parameters and the Eubank method used in this model, and standard UNIFAC parameter and the algorithm in the UHAERO model (Amundson et al., 2007) are in good agreement and summarized in the supplementary information.

Addition to Supplement

Modelled phase boundaries were compared against published values computed with the UHAERO model (Table 3, Amundson et al., 2007). Three compounds, common to both studies, were compared adipic acid, palmitic acid and pinonic acid. For this comparison the model was executed using the parameters of Hansen et al. (1991), which is identical to the standard UNIFAC calculations in (Amundson et al., 2007). For adipic acid, no phase separation is predicted by either model. For pinonic acid, this model predicts $x_a = 0.9899$, $x_b = 0.5075$ while UHAERO predicts $x_a = 0.9990$, $x_b = 0.5078$. For palmitic acid, this model predicts $x_a = 0.9999$ (limit of model resolution), $x_b = 0.1562$ while UHAERO predicts $x_a = 1 - 1 \times 10^{-7}$, $x_b = 0.1567$ (see Amundson et al., Table 3). Here (x_a, x_b) are the mole fraction of water corresponding to the phase boundary as described in Eq. (10) in the main text.

Preface: We combined the response to the three separate points raised below regarding the inclusion of liquid-liquid equilibrium (LLE) in the model. Our main response is that the current model is not attempting to solve LLE for multicomponent systems. However, discussion regarding this point, and the associated uncertainties, was missing in the manuscript and we address this point.

Comment: Given that study used AIOMFAC, which for organic-water systems gives the same results as UNIFAC, these results should be reproducible. By presenting this information, and also presenting the phase boundaries for the systems presented in the paper, even as supplementary material, one gets a feel for the importance of including, or not, LLE in these calculations. I appreciate the focus of the paper is on organic systems, but what happens when inorganic ions are included in this? UNIFAC can account for ions, but without any organic-inorganic interactions beyond the short-range forces represented within the UNIFAC framework. The challenge when including inorganic-organic interactions in an LLE model becomes a numerical one since molality based terms can induce strongly deviating activity coefficients that can force any ‘root finding’ method to fail.

Comment: Is the method for including LLE assumed to apply for multicomponent mixtures? Parameterised forms of LLE for multicomponent mixtures exist, based loosely on a collaborative dissolution approach or simply on O:C ratios, as benchmarked against more complex methods:

Song, M., Marcolli, C., Krieger, U. K., Zuend, A., and Peter, T.: Liquid-liquid phase separation and morphology of internally mixed dicarboxylic acids/ammonium sulfate/water particles, *Atmos. Chem. Phys.*, 12, 2691-2712, doi:10.5194/acp-12-2691-2012, 2012.

Topping, D, Barley, M and MCFiggans G: Including phase separation in a unified model to calculate partitioning of vapours to mixed inorganic-organic aerosol particles. *Faraday Discuss.*, 2013,165, 273-288

Comment: Could a similar multicomponent or parameterised approach be built into your model? A simple ‘additive’ approach, as per combining kappa values, would not be guaranteed to work. I’m not suggesting the paper needs a full evaluation of multicomponent LLE, as experimental data would be scarce anyway. Nonetheless, there is currently no discussion as to any extension to mixed systems other than a statement at the end of the paper which suggests just combining k values in a mixing rule. It is often interesting to assess errors associated with ‘forcing’ a model into specific states. For example, since an account for LLE is attempted here, why not include gas-particle partitioning depending on the Gibbs energy profile of each possible state? Is it more or less likely that gas-particle partitioning of organic semi-volatiles would represent a shift towards the most stable state under the same conditions? Zuend et al 2012 looked at the effect on

gas-particle partitioning when forcing a one liquid state or allowing LLE to occur:

Zuend, A. and Seinfeld, J. H.: Modeling the gas-particle partitioning of secondary organic aerosol: the importance of liquid-liquid phase separation, *Atmos. Chem. Phys. Discuss.*, 12, 2199-2258, doi:10.5194/acpd-12-2199-2012, 2012.

Comment: (non-sequential, moved from pg. C2516) In addition ‘Once pure component k’s are predicted, the evolution of the overall OA in k in mixed particles can be calculated quickly..’. How does this translate to a k value that has been inferred from a model that treats binary LLE? Is there evidence this holds across the range of compounds across chemical mechanisms or would it not be better to compare with multicomponent methods of LLE to test its suitability?

Response: *The current method for modelling LLE is not assumed to apply for multi-component mixtures or mixtures containing inorganic compounds. The purpose of our proposed model is not to replicate the detail of AIOMFAC or similar more complete thermodynamic models. Specifically, we do not foresee to use the UNIFAC-based model to estimate CCN activity for a single particle as an n-component mixture containing multiple inorganic and organic compounds. Our proposed idea is that the relatively simply binary estimation of the compound’s kappa is sufficient to categorize the compound as insoluble/immiscible (kappa = 0), sparingly miscible (kappa determined by LLE), and miscible (kappa determined by molar volume). Contribution of the mix of organics to overall CCN activity is then estimated using ZSR. The danger of this approach is of course that inorganic-organic or organic-organic interactions between two different compounds are ignored. Furthermore, the issue of co-solubilization, i.e. water attracted by the inorganic compound solubilizing some organic solute, is not explicitly treated. It is quite possible that those effects ultimately matter and will need to be included in complete treatments of the problem. In the meantime, however, we believe that our approach is suitable for the approximate categorization. Uncertainties can be estimated by accounting for the number and mass of components that fall within the LLE regime. Drawing the analogy to the solubility regimes, where only few compounds have solubilities where the exact value of solubility matters, we expect the same to hold for the LLE regime.*

We added a section to the manuscript that reflects this response.

Revisions: **Relationship to other thermodynamic models and application to multicomponent systems. The basic model functionality described here can also be obtained by appropriately initializing other multicomponent equilibrium models (Ming and Russell, 2002, Raatikainen and Laaksonen, 2005, Topping et al., 2005, Clegg and Seinfeld, 2006, Amundson et al., 2007, Zuend et al., 2008) with a set of binary water/organic solutions, parsing the**

output through a phase equilibrium module (if not included in the thermodynamic model itself) and the Köhler model. The predicted CCN activity mostly depends on the underlying set of group interaction parameters. The output should match with the solution presented here if the same interaction parameter matrix is used. The main conceptual distinction between the approach proposed here and the approach employed by the more complex multicomponent models is our focus on predictions for binary organic/water solutions and limitation of the scope to a narrow range of water activities relevant to CCN activation only. Accurate representation of hygroscopic growth at $a_w < \sim 0.99$ is not required and would be of secondary concern when tuning interaction parameters.

We envision that the proposed specialized model approach can be used to categorize individual compound into three miscibility regimes, analogous to the solubility regimes defined in Petters and Kreidenweis (2008). **Regime I:** the compound is CCN inactive and can be effectively modeled as $\kappa = 0$. **Regime II:** the compound is CCN active without any additional phase constraints. In turn κ is mostly determined by molar volume and slightly modulated by activity coefficients. **Regime III:** the compounds' CCN activity is limited due to miscibility constraints. In turn κ is highly sensitive to overall water content and can either have $\kappa \sim 0$ or express κ according to its molar volume. Once pure component κ 's are predicted and stored in a database, the overall OA κ in mixed particles can be calculated quickly using the volume weighted mixing rule (Petters and Kreidenweis, 2007). This compound-by-compound treatment of multicomponent mixtures assumes that solute-solute interactions are negligible. Salting-in and salting-out of solution effects are not captured. Effective κ -values for compounds falling into the limited miscibility regime may be misrepresented in this treatment. Whether such effects are important will depend on the fraction of compounds in a mixture that fall into the limited miscibility regime and whether the proposed approach of intermediate complexity – modelling binary solutions coupled with a linear mixing rule – ultimately proves sufficiently accurate model the evolution of ambient OA. In the following we use experimental data to demonstrate that the outlined UNIFAC model is suitable to categorize compounds into these three regimes.

Comment: Discussion Paper
Line 18, page 7452: 'it is calculated'? 'it' being the number of stable phases?

Response: *We reworded appropriately.*

Revisions: For a binary system consisting of water (w) and a single solute (s), Gibbs energy is calculated from the activity coefficients via standard thermodynamic relationships (Prausnitz et al., 1999, Petters et al., 2009)

Comments: The results in figure 2 are very interesting. It would benefit from error bars that are discussed in the supplementary material and model variants. Whilst it is clear in the text, it should also be clear in the figure that the predicted K in the figure is K-CCN. This figure should also have predicted K at 90%RH. Given the practice for inferring k from HTDMA's, and the inclusion of non-ideality with LLE in this paper, this would provide a very interesting set of points for the reader.

Response: (1) *We added typical error bars to the Figure*
(2) *We made clear in the legend that it is kappa-CCN*

(3) *Regarding the point including κ at 90% RH. We are of course aware of the practice, and the interesting points regarding potential disagreements in κ -90% and κ -CCN, some of which we have pointed out in the literature (e.g. Prenni et al., 2007 JGR, Petters et al., 2009 ACP). We prepared the suggested plot and found the general types of relationships one would expect: significantly lower κ -90% than κ -CCN for weakly functionalized compounds and similar κ -90% and κ -CCN for fully miscible compounds. We agree with the referee that such a plot could indeed be of interest to the readers.*

However, we do not believe that such a comparison belongs into this manuscript for two specific reasons. First, this paper focuses completely on the problem of modeling CCN activity (and not kappa or issues with the kappa parameterization – kappa-CCN is merely a convenient expression). Adding the hygroscopic growth dimension would seem quite distracting. Few compounds in the test-set have available hygroscopic growth data. The most interesting systems, the hydroxynitrates and peroxides would not be included. Available data would have to be screened for data quality, methods and measurement artifacts for hygroscopic growth measurements would need to be discussed and model performance would have to be rigorously evaluated. Overall this would significantly change the scope of the work. Second, and more importantly, we point out that we neither do, nor wish to make a claim about the applicability of the current set of parameters for accurately predicting hygroscopic growth factors at $a_w \ll 1$. Our model is tasked to estimate within reasonable accuracy the water activity for highly dilute conditions for binary organic-water systems. Although we did not tune the group interaction parameters, one could envision a tuned set that produces high fidelity predictions for dilute conditions and poor predictions for (more) concentrated solutions. Our approach is therefore distinct from more universal model frameworks such as ADDEM or AIOMFAC, which ought to strive for broad applicability over the entire range of RH and complex multi-component compositions.

Revisions: **Please see the added in response to the previous comment on the inclusion of LLE comparisons which includes discussion regarding the distinction to other thermodynamic models.**

Reviewer #2 Evaluation

This work represents an important advance in linking chemical components of particles to cloud drop activation. Similar codes have been developed previously but this one is unique and important as it is 1) freely available for research and teaching 2) compared to comprehensive data 3) well documented 4) providing insight on the types of functionality that are/not simulated. For these reasons, I fully support publication of a revised manuscript.

Comment: However, there are several issues that I think would much improve the quality of this paper. Here are the issues that I think would improve this manuscript.

1) Evaluation of the need for ternary parameters

Response: *We added specific discussion regarding the proposed treatment for multicomponent aerosols.*

Revisions: **We envision that the proposed specialized model approach can be used to categorize individual compound into three miscibility regimes, analogous to the solubility regimes defined in Petters and Kreidenweis (2008). Regime I: the compound is CCN inactive and can be effectively modeled as $\kappa = 0$. Regime II: the compound is CCN active without any additional phase constraints. In turn κ is mostly determined by molar volume and slightly modulated by activity coefficients. Regime III: the compounds' CCN activity is limited due to miscibility constraints. In turn κ is highly sensitive to overall water content and can either have $\kappa \sim 0$ or express κ according to its molar volume. Once pure component κ 's are predicted and stored in a database, the overall OA κ in mixed particles can be calculated quickly using the volume weighted mixing rule (Petters and Kreidenweis, 2007). This compound-by-compound treatment of multicomponent mixtures assumes that solute-solute interactions are negligible. Salting-in and salting-out of solution effects are not captured. Effective κ -values for compounds falling into the limited miscibility regime may be misrepresented in this treatment. Whether such effects are important will depend on the fraction of compounds in a mixture that fall into the limited miscibility regime and whether the proposed approach of intermediate complexity – modelling binary solutions coupled with a linear mixing rule – ultimately proves sufficiently accurate model the evolution of ambient OA. In the following we use experimental data to demonstrate that the outlined UNIFAC model is suitable to categorize compounds into these three regimes.**

Comment: 2) Evaluation of the usefulness of the group contribution

Response: *Several limitations of group contribution method are discussed in the paper. We also added a new limitation regarding the automated mapping of UNIFAC groupings to computer-generated structures*

Revisions: *Added limitation*

One additional limitation is the need for algorithms that automatically map the computer-generated SMILES structures (e.g. Table 3, Lee-Taylor et al., 2015) to UNIFAC groups. Several of these structures are bridged and even manual mapping of those structures to UNIFAC groupings will necessitate definition of new groups with undefined volume, surface, and interaction parameters. Separate studies are needed to establish the minimal number of new groups that would be needed to obtain optimal coverage for the set of compounds of interest.

Other stated limitations

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.

Comment: 3) Evaluation of the predictive capability (if any) of the model beyond interpolation between measurements.

Response: *Please see our response to comment 1) where we lay out the vision for the model use. In addition, we restate the ultimate goal regarding the treatment of OA in the atmosphere. Full evaluation of this capability will require new specifically designed experiments that include CCN measurements of multicomponent aerosol with known quantities of components and components having a relatively wide range of functionalities.*

Revisions: **Please see our response to comment 1)**

Comment: 4) Consideration of the extension of a group-based approach to surface tension prediction.

Response: *We expanded the discussion surrounding surface tension.*

Revisions: The application of Eq. (4) assumes that the surface tension is that of pure water. Many organic compound 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_{app} of ~30% for the strong surfactant sodium dodecyl sulfate (Petters and Kreidenweis, 2013). **We note that estimates of surface tension reduction for pure organic liquids can be obtained from critical pressure and boiling point (Sastri and Rao, 1994) and the Sprow and Prausnitz (1966) expression coupled with UNIFAC activity coefficients (Topping et al., 2005, Rafati et al., 2011). Combined with predictions of critical properties from functional group data (Joback and Reid, 1987), predicted binary surface tensions could be obtained for each compound. Including surfactant partitioning in Eq. (4) is possible using the expressions in Petters and Kreidernweis (2013) or similar approaches (Sorjamaa et al., 2004, Raatikainen and Laaksonen, 2011). Thorough validation against experimental data, including measurements of surface tension and CCN activity are needed before this approach should be adopted.**

Comment: Section 2.7 – is reference to “UNIFAC” here to the generic modeling approach or to this specific (“MDP”) implementation of it? Since the performance is dependent on the parameters used, likely the latter is meant.

Response: *The quality of agreement between measured and modeled is indeed parameter dependent and thus specific to this specific implementation. The limitations regarding group proximity effects, distinction between isomers, and the assumption of a liquid phase are generic at least to the pure UNIFAC approach. We slightly revised the text.*

Revisions: **The UNIFAC approach 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 to within the general accuracy of the specific model implementation.**

References Added

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