Atmos. Chem. Phys. Discuss., 8, S5744–S5751, 2008
www.atmos-chem-phys-discuss.net/8/S5744/2008/

Atmospheric Chemistry and Physics Discussions

Interactive comment on "A single parameter representation of hygroscopic growth and cloud condensation nucleus activity – Part 2: Including solubility" *by* M. D. Petters and S. M. Kreidenweis

M. D. Petters and S. M. Kreidenweis

Received and published: 9 August 2008

We thank Ari Laaksonen and the two anonymous reviewers of this manuscript for their comments. In the following we provide individual replies to each review.

Reviewer 1

This manuscript provides an extension of the kappa formalism introduced by the same authors in ACP in 2007 (PK07) to account for compounds with limited solubility. An algorithm to calculate critical supersaturations is provided.

The extension of the kappa formalism is relevant to the scientific community and the first part of the manuscript is clearly written and presents comprehensible equations for

water uptake at sub- and super-saturation as well as critical supersaturations for cloud droplet formation. I find however that the discussion part of the manuscript should be improved: the notation is not consistent and the choice of parameters should be explained better. I also suggest to include a comparison with experimental data or example molecules.

Response: We modified the discussion to clarify the notation as detailed below. The suggestion to add example pairs of solubility and hygroscopicity is a good one and we have modified our figures to correspond to mixtures of calcium carbonate, succinic acid, and sodium chloride.

Specific comments Abstract and page 5946: The last sentences of the abstract and corresponding text on page 5946 that only a small part of the atmospheric aerosol fall into the sparingly soluble envelope and these molecules only make up a small fraction of total organic aerosol fraction is not supported by data or literature references in the manuscript.

Response: We removed this statement from the manuscript

Introduction Page 5941 Lines 7-10: Some references to previous work (e.g. Rissler et al. 2006) on the idea of a single hygroscopicity parameter to effectively model the CCN activity of atmospheric particles should be included.

Response: Done

Generalized k-Kohler equations

Page 5942 line 10: ..Applying the ZSR assumption and rearranging equation (1).. It seems that Equation (1) should be corrected to equation (2).

Response: Done

Also it should be defined that Vs is the sum of the individual Vsi and it should be defined what Vsi is.

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Interactive Comment

Response: Done

Page 5943: line 13: I think it should be Vw/Vs=g3-1 instead of Vw=g3-1,.

Response: Thank you for spotting this mistake

Page 5944: the authors assume that surface tension lowering or surfactant partitioning is not an issue and use the surface tension of pure water. This should be stated explicitly in the manuscript.

Response: Indeed we have assumed the surface tension of pure water in our calculations. We now state that explicitly in the manuscript

Discussion and conclusions The use of symbols and notation should be improved, e.g. in the first part of the manuscript D means droplet diameter, in Figure 3 it means dry particle diameter and it is also used to denote a minimum in the Kohler curve. The use of C and Ci is confusing and should be made consistent. In general the text can be improved by better explaining figures and the choice of kappa and solubility values.

Response: We agree that the notation chosen in the discussion is confusing. We now use unique labels to avoid this.

Page 5944: The use of the words sparingly soluble and moderately soluble is confusing. In Figure 3 the words Insoluble, sparingly soluble and soluble are introduced and clearly defined. It would be much easier to read the discussion if these terms were defined in the beginning of the discussion. It would strengthen the manuscript if examples of solubilities and kappa values of real molecules from the different solubility classes were given.

Response: We now introduce these ranges earlier and give examples for selected compounds.

What type of molecule has k=0.6 and a solubility of 0.02? No such molecule appears in PK07 table 2 as far as I can see. What combinations of kappa values and solubilites

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are realistic?

Response: In general there is no correlation between hygroscopicity and solubility. Many inorganic salts, e.g. calcium carbonate or calcium sulfate, are hygroscopic when they are in solution, but their solubility is small. Conversely, many organic compounds, e.g. polyacrylic acid, are soluble in water in all proportions, but their hygroscopicity is small ($k < 0.1$). Therefore any combination is plausible, in principle. We now present the equations using realistic examples to avoid confusion.

In mixed particles: would it not be more realistic that the deliquescence (A) is below 100

Response: This is correct. In the example the mixture shown in Fig. 1 it is the solubility of the second compound, C2, that regulates the RH at which the mixed particle activated. Had we chosen a more soluble compound for C1 the segment A-B would appear at lower relative humidities.

Page 5944, line 21: It says that moderately soluble species has C>1 and that this is the case for most inorganic salts. Most inorganic salts would be characterized as fully soluble, but still C would be smaller than 1?

Response: We believe that this is a semantic problem that has lead to widespread confusion in the literature. Here we use solubility in its strict thermodynamic sense, i.e. denoting the solute concentration of the saturated solution. In this context a infinitely soluble compound has C = infinity, and all other compounds do have a solubility limit in waterh. However, there are at least two other conceptual uses of the term solubility: 1) fully soluble sometimes means that the particle is fully dissolved at the water contents relevant to CCN activation, and hence its solubility is not important, 2) CCN activity is often associated with the water soluble fraction of the aerosol mass that is obtained from bulk chemical analysis of aerosol filter data.

It is said that Kohler curves using equations 9 and 10 are compared to previously

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complex Kohler curves. Such a comparison is however not made - no Kohler curves from previous work are shown in Figure 1.

Response: We modified Fig. 1 which now is similar to Fig. 1b in Bilde and Svenningsson (2004).

The curve k=0.5, C=infinity is not explained in the text, neither is C=1. It could make the text more clear if figures 1 and 2 were related. The labels A, B and C could have the same meaning (B denotes a Kohler curve minima in figure 1 but a maximum in figure 2).

Response: The labels are now unique and Figs. 1 and 2 are directly related. Specifically we now use the same compounds and mixtures in the both figures and also chose lines styles, weights, and labels consistently.

It should be explained in the text which values of kappa and Ci were studied. I suggest that ABCD in figures 1 and 2 are replaced by other symbols. C and D are used for many things.

Response: We agree that this is confusing and changed our terminology.

Page 5945 Lines 5-10: For mixed particles cloud droplet activation can also be controlled by solubility even though deliquescence is below 100

Response: It is correct that say that DRH=sc. Our new terminology avoids this by specifically labeling the peaks sc1 and sc2, as was done so by Bilde and Svennigsson (2004).

Figure 3 is a nice illustration. It should be pointed out in the figure caption that the four full lines are for single component particles.

Response: Done

Reviewer 2

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General Comments The submitted manuscript presents a method for modeling the cloud activation of a particle. The method, which was previously introduced by the authors, uses a single tunable parameter which represents the overall hygroscopicity of a particle (kappa). In this current contribution, the single parameter method is adapted to include solubility of a particle with a complex composition. The method uses the solubility (here defined as the volume of solute dissolved into a volume of water) of each component of the particle to derive the dissolved fraction of the solute. This enables the isolation of components that are completely solubility (ie, the dissolved volume fraction equals one) and sparingly soluble components (ie, the dissolved volume fraction is less than one). Then two equations, the Kohler equation (which includes the hygroscopicity parameter kappa) and the equation for kappa (which is the sum of each component8217;s solubility) are solved numerically to find the critical supersaturation.

This method is used to calculate Kohler curves and predict deliquescence behavior for hypothetical single-component and two-component particles of varying hygroscopicity and solubility. Figure two shows the effect of adding a small amount (1-5

The authors also suggest that it may be sufficient to classify the components of particles as either infinitely soluble or completely insoluble. This simplification has the potential to be an important tool for predicting the cloud activation of atmospheric aerosols. Although the scope of this contribution is limited to the development of the method, I look forward to the application of the method to experimental data.

Specific Comments The authors contend that because only a few solutes have solubilities in the sparingly soluble region, atmospheric CCN activity can be modeled by classifying components into either completely soluble or insoluble. However, not all organic species have identified, and therefore, not all solubilities are known. Can you elaborate on this point, that is, do we know enough about atmospheric organics for this simplification to be effective?

Response: Indeed not all organic compounds and are known. Our argument is based

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on the observation that off-kappa isoline behavior is only rarely observed, thereby suggesting that the binary categorization in effectively insoluble and effectively soluble is sufficient. We now state explicitly in the manuscript that not all solubilities have been identified, leaving the potential role of the solubilities of those open to future discovery.

The figure captions, especially for figure 1, are lean on helpful details and explanation. Although these can be found in the text, I suggest including an explanation of points A, B, C, etc. the captions for both figure 1 and figure 2.

Response: We have reworked all figures and captions in response to reviewer 1. The labels are now self consistent and explained in the figure captions.

For figure 3, for the dashed line representing a particle with a 5

Response: We agree with the reviewers comment. As suggested by Ari Laaksonen, to add another figure that illustrate the effect of internal mixtures. The sizes are now identical to those chosen in Fig. 3.

Technical Details p. 5940 line 5-6: suggest rewrite for clarity, either "...to successfully model complex, multicomponent particle types." or "...to successfully model complex, multicomponent types of particles."

Response: Done

p. 5942 line 15: rearranging Eq (2), not Eq (1).

Response: Done

Ari Laaksonen

This is a useful manuscript, appropriate for publication in ACP. I have only one comment in addition to what the other two reviewers have said. I believe it would be instructive to generate a figure which shows the following Köhler curves for two-component particles consisting e.g. of 5

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Response: We added the suggested figure. Thank you for alerting us to the issue of critical diameter. We added discussion about this to the manuscript.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 5939, 2008.

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