

Interactive comment on “Cloud droplet activation: solubility revisited” by L. T. Padró and A. Nenes

Anonymous Referee #3

Received and published: 17 April 2007

The paper focuses on the treatment of solubility in theoretical predictions of critical supersaturation. The curvature of small particles enhances the solubility in water, thereby providing more solute to the solution and suppressing the critical supersaturation required for activation. The results are used to re-interpret published CCN data for organic species, where many compounds studied behaved as if they were fully dissolved (i.e., did not require a high supersaturation to reach their deliquescence point before activating).

The premise of the paper is interesting, and it is great that the authors have provided some new measurements of interfacial energy to apply in the theory. However, I believe the paper needs to be extensively revised before publication, for the following reasons.

(1) The property being talked about here, “solubility” is of course the same property that controls “deliquescence”. Deliquescence of particles, including nanoparticles, has

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been discussed extensively in the recent literature. Mirabel, Reiss and Bowles (2000) present a clear formulation for an idealized system in which drops form “promptly” upon deliquescence, showing that deliquescence RH of dry crystals exposed to water vapor decreases (for high assumed interfacial energy) with decreasing size. In that work, only one phase, dry or dissolved, was allowed to exist. They briefly consider an alternative case, presented their equation (17), to treat the possibility of phase coexistence (core, solution, vapor). Russell and Ming (2002) built upon this work but relaxed the requirement for the particle to be dry at deliquescence, as well as considering nonideality of solutions formed. They presented a “coated” model and showed that a multiple-equilibria region could exist. Djikaev et al. (2001) also built on the work of Mirabel et al. and considered the possibility of coexistence between a liquid film of solution and a solid core. None of this work is referenced in the manuscript.

(2) Using equation (1) as a starting point is not as conceptually satisfying as the treatments in the above-mentioned papers, which begin from a more fundamental thermodynamic basis and show more clearly where approximations are made. The equations derived here have several simplifying assumptions that are not explicitly mentioned. For example, one is that the activity of the saturated solution can be expressed by Raoult's Law (mole fraction).

(3) It seems the basic argument for manifestation of CES is that, when CES is important, the particles are not required to transition through a high-RH (sometimes even supersaturated RH) deliquescence transition. “Bulk solubility”, when it is assumed that one can calculate the DRH from the solubility alone, controls the S at which a selected dry size particle will begin to take up water (deliquesce) and dissolve (e.g., as shown in Figure 6c). If CES is active then the particle behaves as if it deliquesced at much lower S_c (even if that means it formed a metastable solution), such that the deliquescence can not even be seen in plots such as those in Fig. 6. In this case “classical” Kohler theory will predict the critical supersaturation. So the problem can be stated as trying to understand how deliquescence occurs for submicron particles, and thus the

referencing of prior work in this area is important.

(4) Equation 9 seems to have an error. The second term on the right-hand side should express the mass of solute dissolved in the water present in a drop of size D_p . Unless the drop is very dilute, the volume of water cannot be expressed by $(\pi/6) \cdot D_p^3$, but the equation should rather read

$$d_{\text{core}}^3 \rho_s = d_{\text{dry}}^3 \rho_s - (D_p^3 - d_{\text{dry}}^3) C_{eq}$$

As written equation (10) applies close to the critical supersaturation, but introduces errors if used to describe the process of deliquescence. Equation (10) should read

$$d_{\text{core}}^3 \frac{\rho_s}{(\rho_s + C_{eq})} + \frac{D_p^3 C_{\text{bulk}}}{(\rho_s + C_{eq})} \exp\left(\frac{4M_s \gamma_{sl}}{RT \rho_s d_{\text{core}}}\right) = d_{\text{dry}}^3$$

where C_{eq} is $C_{\text{bulk}} \cdot \exp(\text{term containing } d_{\text{core}})$, so the equation has become more complicated to solve for d_{core} . The authors have to review this point, decide if equation 9 is in error, and show whether their calculations need to be corrected.

(5) The title of section 2.3 is “When is bulk solubility not enough to explain CCN activity?” The interpretation of the ratio Φ presented in this section is not clear. I would argue that $\Phi > 1$ means that, for the conditions (s_c , and selected compound) being studied, observation of activation under those conditions requires existence of a metastable solution at activation. This is because $\Phi > 1$ at activation (as derived here) means that not all of the dry particle should have been dissolved by this point, under bulk-solubility rules. (However, the criterion *ignores* the possibility of a high DRH, which may control the critical supersaturation if the particle is initially dry and needs to be deliquesced first. So it is not clear that the criterion can be interpreted as has been done in the paper.)

Nevertheless, assuming that it has been determined that observed activation is only consistent with the presence of a metastable solution at activation, whether this

metastable solution is produced through retention of water during particle generation, as a result of impurities, through CES, or was simply estimated to be metastable because of inaccurate thermodynamic input data, cannot be ascertained from this criterion alone. The paper really does not make clear that these other possible alternatives are equally likely. In fact, based on prior CCN studies looking at the role of impurities, I would argue that experiments which begin with impure organic reagents (unavoidable, of course) and use atomization from aqueous solution to generate particles cannot possibly create uncontaminated particles. If the compound is hygroscopic and soluble, the presence of the contaminants is generally not important. Unfortunately, for compounds that are weakly hygroscopic, or that are only slightly soluble, even trace amounts of soluble impurities will have a strong effect on observed CCN activity.

In light of this, I'm a little puzzled by the statement (p. 2327-8) that unexpected behavior in CCN activity was always attributed to retention of residual water in prior studies. Bilde and Svenningsson, for example, showed very convincingly that the presence of trace amounts of impurities could explain the enhanced activation of slightly soluble organic species. Their point was that it is nearly impossible to create an impurity-free particle from an aqueous solution of such slightly soluble organics.

(6) The authors argue that d^* and $d_{\text{core,min}}$ are separate concepts and offer that when $d^* = d_{\text{core,min}}$ the particle will crystallize. However, d^* and $d_{\text{core,min}}$ are not independent concepts. In fact, equation (4) expressed the supersaturation in solution and thus the core size in equilibrium with that supersaturation, which is the definition of d^* . d_{core} as calculated by equation (4) follows directly from the free energy argument made in homogeneous nucleation theory and thus $d_{\text{core,min}}$ is equivalent to d^* . d^* cannot be chosen independently of the assumed sc and compound properties, as done here (i.e. set to 5 nm).

On pg. 2335 the authors state that "aerosol that is initially wet can retain its water at very low relative humidity, as long as the nucleation embryo size $d^* < d_{\text{core,min}}$ ". In the absence of a preexisting core a nucleation event must generate a thermody-

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namically stable cluster of size d^* first. The generation of such clusters is currently not well understood, but theory holds that at least two additional processes must be considered: a) formation of the distribution of unstable clusters that form in supersaturated solutions, b) energy of activation for diffusion of solution molecules across the solution-cluster boundary. Since these processes are not included in equation (13) and no experimental data is offered to support its validity, it seems unlikely that equation (13) can correctly predict the onset of crystallization, as suggested in the manuscript. Therefore equation (13) presents a necessary but not sufficient condition for particle crystallization.

Other points:

The units of C_{eq} (moles m^{-3}) stated at the stop of p. 2330 work for equations 3 and 8, but do not work in equations 9 and 10. In the latter the units must be mass / volume water, or molecular weight should be included in the equation.

p. 2329, line 6: Should state that Seq is **approximated** by this equation. In the first term in the exponential, density of water is missing from the denominator.

p. 2329, line 11: the van't Hoff factor is usually referred to as "i" and is approximated by $\nu \cdot \phi$. ν is the number of moles each molecule of solute produces.

It is confusing to have a single-component equation presented as equation 1, then write equations 2 and 3 and construct Figure 2 for two solutes (s and ss). Equation 4 could possibly apply for more than one solute, but all remaining equations refer to the system of one pure solute + water. I don't see the purpose of writing the equation for more than one solute since that case is never applied. Further, the notation gets confused, because the slightly soluble (please do not use the term "partially soluble") substance is given the subscript "ss" but that subscript is not used in the remaining equations.

p. 2331: Equation (5) is an approximate equation for critical supersaturation that does not apply for compounds with low hygroscopicity (e.g., high MW). Similarly for such

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compounds and for smaller dry particles, the approximation that the wetted particle consists mostly of water can break down, and therefore the computation of n_{bulk} is also in question. Therefore the use of these approximations to derive equation (8) must introduce some inaccuracies for such compounds.

Table 1: the bulk solubilities are functions of temperature, so the T of the measurement needs to be reported (and compared with T of experiments). The solubilities for the sparingly soluble compounds are probably rather uncertain; this should be mentioned.

Table 2 has an error for leucine at $SS=1\%$; this value is higher than for $SS=1.2\%$. I believe the correct entry should be less than one, which means leucine probably passes the criterion for most (perhaps all, considering uncertainties) of the supersaturations.

The data in Fig. 8 attributed to Raymond and Pandis do not match the values reported in their paper.

References:

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Interactive comment on Atmos. Chem. Phys. Discuss., 7, 2325, 2007.

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