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A single parameter representation of hygroscopic growth and cloud condensation nucleus activity – Part 2: Including solubility

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Abstract

The ability of a particle to serve as a cloud condensation nucleus in the atmosphere is determined by its size, hygroscopicity and its solubility in water. Usually size and hygroscopicity alone are sufficient to predict CCN activity. Single parameter representations for hygroscopicity have been shown to model successfully complex, multicomponent particles types. Under the assumption of either complete solubility, or complete insolubility of a component, it is not necessary to explicitly include that components solubility into the single parameter framework. This is not the case if sparingly soluble particles are present. In this work we explicitly account for solubility by modifying the single parameter equations. We demonstrate that sensitivity to the actual value of solubility emerges only in the narrow regime of 1×10^{-1}–5×10^{-3}, where the solubility values are expressed as volume of solute per unit volume of water present in a saturated solution. Since only a few pure compounds fall inside this sparingly soluble envelope and those only make up a small fraction of the total organic fraction most organic species in the atmospheric aerosol can be adequately modeled assuming they are either infinitely soluble in water or completely insoluble .

1 Introduction

The supersaturation required to activate a particle into a cloud droplet depends on the particle size and on its constituent hygroscopicities, and solubilities. Classical Köhler theory provides the relationship between critical supersaturation and dry diameter for particles composed of a single, hygroscopic compound that is fully dissolved at the wet critical diameter, i.e. the diameter where the particle activates. It was recognized early on, however, that particles do not consist of single components but are mixtures of a variety of compounds, some of which may be effectively water insoluble. To treat these cases, extensions of Köhler theory were proposed that decomposed the particle into an insoluble core immersed in an aqueous-ionic solution. As a result, CCN activity

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has often been associated with the water soluble fraction, and, erroneously, with the solubility of the particle. It was not until fairly recently that Köhler equations considering multiple components, each having limited solubility, have been proposed (Laaksonen et al., 1998; Shulman et al., 1996). Accounting for limited solubility has enabled successful prediction of the unusual CCN activities of sparingly soluble compounds (Bilde and Svenningsson, 2004; Hori et al., 2003; Broekhuizen et al., 2004; Henning et al., 2005).

Recently Petters and Kreidenweis (2007), hereafter, PK07, suggested that a single hygroscopicity parameter can effectively model the CCN activity of atmospheric particles, including those containing insoluble components. This framework is built on the premise that (1) water soluble components are fully dissolved at dilutions relevant to CCN activation, and (2) some sparingly soluble components behave as completely insoluble over the full range of relevant dilutions, and do not contribute to water uptake. Hence no explicit treatment of solubility is necessary. Under these conditions it is the aerosol hygroscopicity, i.e. the amount of water per unit volume of dissolved solute, that determines the subsaturated water content and the relationship between particle dry diameter and critical supersaturation. Because the equations in PK07 do not include solubility, deliquescence- and solubility-controlled CCN activation phenomena cannot be modelled. Here we build on PK07 by explicitly including solubility into their framework, using the formulations presented by Raymond and Pandis (2003) and Bilde and Svenningsson (2004). Our equations are valid for the entire range of hygroscopicities and solubilities. We include an algorithm that can be used to efficiently calculate the relationship between critical supersaturation and dry diameter for an arbitrary number of components of specified mass or volume fraction, and selected dry particle size. Finally, we identify a narrow range of solubilities that delineates an effectively insoluble regime from an effectively soluble regime.

2 Generalized κ-Köhler equations

The saturation ratio, S, over an aqueous solution droplet can be calculated from

$$S = a_w \exp\left(\frac{4\sigma_{s/a} M_w}{RT\rho_w D}\right), \tag{1}$$

where a_w is the activity of water in solution, ρ_w is the density of water, M_w is the molecular weight of water, $\sigma_{s/a}$ is the surface tension of the solution/air interface, R is the universal gas constant, T is temperature, and D is the diameter of the droplet. PK07 proposed a hygroscopicity parameter κ that is defined through its effect on the water activity of the solution:

$$\frac{1}{a_w} = 1 + \kappa\frac{V_s}{V_w}, \tag{2}$$

where V_s is the volume of the dry particulate matter (both soluble and insoluble) and V_w is the volume of the water. For a multicomponent system with multiple solutes and water at equilibrium, for which the Zdanovskii, Stokes, and Robinson (ZSR) assumption applies, the total volume of the water is the sum of the water contents due to the individual components, i.e. $V_w{=}\sum V_{wi}$, and the individual V_{wi} are obtained for $a_{wi}{=}a_w$. Applying the ZSR assumption and rearranging Eq. (1) for V_w gives:

$$V_w = \frac{a_w}{1-a_w}\sum_i \kappa_i V_{si}. \tag{3}$$

The total volume of the system (water + solute) is

$$V_T = \sum_i V_{si} + \sum_i V_{wi} = V_s + V_w. \tag{4}$$

In Eq. (2) water uptake is assumed to be continuous over the full range $0<a_w<1$. Not all substances, however, are infinitely soluble in water and a stable solution is formed only for water contents, and thus solution activities, larger than the solubility limit. Here we introduce the dissolved volume fraction of the solute x_i, defined analogously to Eq. (3) in Raymond and Pandis (2003). For complete dissolution, x_i is equal to unity. When x_i is less than unity

$$x_i = C_i V_w / V_{si}, \tag{5}$$

where C_i is the solubility of the solute in water, expressed here as volume of compound per unit volume of water. Effects of dissolution kinetics (Asa-Awuku and Nenes, 2007; Kelly et al., 2007) and curvature enhanced solubility (Padro and Nenes, 2007) are not considered by this expression. Rewriting Eq. (3) gives

$$V_w = \frac{a_w}{1-a_w} \sum_i \kappa_i V_{si} H(x_i), \qquad H(x_i) = \begin{cases} x_i & x_i < 1 \\ 1 & x_i \geq 1 \end{cases}. \tag{6}$$

Defining the individual (dry) component volume fractions as $\varepsilon_i = V_{si}/V_s$ and recognizing that $V_w = V_T - V_s$, Eq. (3) becomes

$$V_T - V_s = \frac{a_w}{1-a_w} V_s \sum_i \varepsilon_i \kappa_i H(x_i), \qquad x_i = C_i V_w / (V_s \varepsilon_i). \tag{7}$$

If we further assume that the volume change of mixing is zero, $V_w = g^3 - 1$, where g is the diameter growth factor ($g = D/D_d$) and D_d is the dry diameter and x_i can be alternatively expressed as

$$x_i = (g^3 - 1) C_i / \varepsilon_i. \tag{8}$$

The volumes can be converted to their volume equivalent diameters, $D_d^3 = 6V_s/\pi$ and $D^3 = 6V_T/\pi$, respectively. Solving Eq. (6) for a_w and combining the result with Eq. (1) yields the generalized κ-Köhler equation:

$$S(D) = \frac{D^3 - D_d^3}{D^3 - D_d^3(1-\kappa)} \exp\left(\frac{A}{D}\right), \tag{9}$$

where $A=8.69251\times10^{-6}\sigma_{s/a}/T$ is a constant that is evaluated at $\sigma_{s/a}=0.072\,\mathrm{J\,m^{-2}}$ and $T=298.15\,\mathrm{K}$ (PK07) and the overall value for κ is given by the following mixing rule:

$$\kappa = \sum_i \varepsilon_i \kappa_i H(x_i), \qquad x_i = (g^3-1)C_i/\varepsilon_i, \qquad H(x_i) = \begin{cases} x_i & x_i < 1 \\ 1 & x_i \geq 1 \end{cases} \tag{10}$$

Note that Eq. (9) is identical to Eq. (6) in PK07 and that for infinitely soluble substances Eq. (10) reduces to Eq. (7) in PK07. Eqs. (9)+(10) apply over the entire range of relative humidity, solution hygroscopicity, and solubility. They can be used to predict deliquescence relative humidity and particle water content in the subsaturated ($S<1$) regime, as well as to predict the conditions for cloud droplet activation. The critical supersaturation (s_c, where $s_c=S_c-1$ and is usually expressed as a percentage) for a selected dry diameter of a particle having hygroscopicity κ is computed from the maximum of the generalized κ-Köhler curve (Eq. (9)). An algorithm for numerically calculating the maximum of Eq. (9) is given in Appendix A.

3 Discussion and conclusions

We now show that Eqs. (9)+(10) reproduce previously reported complex Köhler curves due to the presence of sparingly soluble components (Shulman et al., 1996; Bilde and Svenningsson, 2004; Hori et al., 2003) and also reproduces the off-kappa-isoline behavior that is observed when plotting critical supersaturation versus dry diameter for sparingly soluble compounds (Hori et al., 2003; Kreidenweis et al., 2006). Four example Köhler curves calculated from Eqs. (9)+(10) are presented in Fig. 1. With no solubility limits imposed the equations predict continuous water uptake over the entire range of $0<\mathrm{RH}<s_c$. For moderately soluble species, $C>1$, as is the case for most inorganic salts, no water uptake is observed until the deliquescence relative humidity (DRH) is reached. The DRH depends on the solubility, the water activity/hygroscopicty of the saturated solution, and the dry particle diameter and is, for moderately soluble compounds, below 95% RH. DRH is expected to increase with decreasing solubility and decreasing particle size, leading to cases where deliquescence only occurs under supersaturated conditions. Since deliquescence must occur prior to growth, cloud droplet activation can be controlled by solubility (e.g. single component examples presented by dashed line in Fig. 1). Multicomponent systems exhibit even more complex behavior. For the illustrative binary solution (dashed-dotted line in Fig. 1), the more soluble compound (compound 1) deliquesces first but only at supersaturated conditions (point A) and is only fully dissolved for water contents corresponding to diameters equal to or larger than that at point B. Some of compound 2 can also dissolve when water is present. The dissolved fraction corresponds to that required to form a saturated solution of compound 2 in the available water, assuming applicability of the ZSR approximation. A second minimum (point D) corresponds to the wet diameter where compound 2 is fully dissolved. Furthermore, the curve shows three maxima (A, C, E), the highest of which, point C, is expected to control cloud droplet activation.

Figure 2 shows isolines of κ in critical supersaturation (s_c) – dry diameter (D_{dry}) space for infinitely-soluble particles (black) and sparingly-soluble particles (blue and yellow). PK07 showed that the CCN activities of pure and complex particle types follow, to a good approximation, lines of constant κ. For certain solubilities and mixtures, off-isoline behavior is observed, leading to a higher sensitivity of critical supersaturation to dry particle diameter (blue curves). For a single sparingly-soluble compound (blue-dashed line) this steep-slope behavior indicates dry diameters where DRH $>s_c$. For particles with $D_d>\sim 120$ nm (point A), DRH$<s_c$ and CCN activity is controlled by the assumed hygroscopicity (κ=0.3). Addition of an infinitely soluble and hygroscopic compound leads to a shift of the steep-sloped region to smaller diameters since the equilibrium water uptake of the infinitely soluble compound leads to partial dissolution of the sparingly-soluble compound. The point of complete dissolution (B, C) is also reached at smaller diameters. Experimentally, the off-isoline behavior has been shown for succinic and adipic acid (Bilde and Svenningsson, 2004; Hori et al., 2003) and perhaps some secondary organic aerosols (Kreidenweis et al., 2006; VanReken et al., 2005) and a humic-like aerosol sample (Ziese et al., 2007). However, to date no ob-

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servations suggest that this behavior is important in atmospheric aerosols. Finally, for very small solubilities, no steep slopes are observed, even in mixtures (yellow lines). The particles behave as if they were composed of an effectively insoluble single component, because the solubility is so small that partial dissolution is unimportant. In fact, the mixed particle hygroscopicity is well approximated by $\varepsilon_1 \kappa_1 = 0.01 \times 0.6 = 0.06$ (solid yellow line), treating the $C=1\times10^{-4}$ compound as $\kappa=0$.

Although Figs. 1 and 2 suggest that solubility can play an important role in cloud droplet activation, it is sufficient to classify a component as effectively infinitely soluble or effectively insoluble. Figure 3 shows the variation of the ratio of solubility peak and classical Köhler peak with solubility for a range of dry diameters, hygroscopicities, and mixing assumptions. By solubility peak we mean any maximum of the Köhler curve at diameters where the particle is not yet fully dissolved. Conversely the classical Köhler peak occurs when all of the solute is dissolved. For convenience we consider this ratio equal to unity when the classical Köhler peak exceeds the solubility peak. Figure 3 shows that sensitivity to solubility emerges only in the narrow regime $\sim 1\times10^{-1} > C > 5\times10^{-3}$, where the solubility values are expressed as volume of solute per unit volume of water present in a saturated solution. This classification is similar to that given by Hori et al. (2003) who introduced type A, B, and C aerosols. Type A particles are moderately soluble and exhibit two local maxima, while type B is insoluble and type C is very soluble. Since only a few pure compounds fall in the type A, or sparingly soluble range (e.g. succinic acid or ammonium oxalate) and those only make up a small fraction of the total organic fraction, the off-isoline behavior seen for the pure sparingly-soluble compounds is likely of little atmospheric relevance. A single kappa with contributions from insoluble compounds (modeled as $\kappa=0$) and infinitely soluble compounds (modeled according to their respective κ_i) can generally be used to describe ambient particles. However, solubility may be important in understanding measured CCN activity obtained for pure compounds in the laboratory.

Appendix A

In the case of multiple components with limited solubility, analytical approximations to Eqs. (9)+(10) do not exist and the maximum must be found numerically. Since multiple maxima can exist, gradient-based search algorithms may terminate at a local, and not the global, maximum. Thus the entire domain must be searched efficiently. We provide an implementation of our algorithm in the scripting language Python in Table A1. Python is a powerful high-level object-oriented scripting language that is available for all major computing platforms and is distributed at no cost under the GNU public license. The algorithm calculates the critical saturation ratio using a single dry diameter as input. Input and outputs are listed in detail in Table A2. Arrays containing any number of components having properties of κ_i, ε_i, and C_i can be passed to the algorithm. Optionally, temperature and surface tension values as well as parameters constraining the accuracy of the algorithm can be modified in the function call. The algorithm scans the wet diameter (or growth factor) in geometric increments given by “inc” until a termination criterion “gmax” is reached, and returns the maximum value found. Decreasing “inc” allows for arbitrary accuracy of the returned solution, although accuracy is limited by the maximum recursion depth of the interpreter. The number of iterations per function call are given by ln(gmax)/ln(inc). We find that gmax=10 and inc=1.01 give generally satisfactory results, thereby limiting the number of iterations to ~200. Program flow control is recursive to minimize the computational overhead and optimize the algorithm for speed. Table A3 gives two example calls to the function “Sc” defined in Table A1. Example 1 is a 100 nm particle that is composed in equal proportions of two components having κ=0.6 and κ=0.2. The compound with κ=0.6 is infinitely soluble while the substance having κ=0.2 is sparingly soluble, i.e. C=0.1. Default parameters of the algorithm are not modified. Example 2 is a single component system having κ=0.6 and is infinitely soluble. The calculation is performed at 273 K instead of the default temperature.

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Table A1. Python implementation of the algorithm to find numerically the critical saturation ratio for a specified dry diameter. Note that the "dot" function performs the dot product on two vectors and is imported from the numerical python (NumPy) library. The "exp" function is imported from the math library. All remaining functions are built into Python. Explanations for variables used are given in Table A2. Example function calls are summarized in Table A3. Lines starting with the # symbol indicate comments.

```
# include all functions from the math and numpy library
from math import *
from numpy import *

# definition of the function Sc see Table 2 for details
def Sc(Dd, ki, ei, Ci, T=298.15, sigma=0.072, gmax=10, g=1+1e-11, inc=1.01):
    # calculate the A parameter in equation 9
    A = 8.69251e-6*sigma/T
    # returns H(xi) as defined in equation 10
    xi = map(lambda x: x if x < 1 else 1, Ci*(g**3.0 - 1.0)/ei)
    # calculates the dot product of the hygroscopicity and solub. vectors in Eq. 10
    k = dot(ki, ei*xi)
    # defines the function given by equation 9
    S = lambda D, Dd, k, A: (D**3.0-Dd**3.0)/(D**3.0-Dd**3.0*(1.0-k))*exp(A/D)
    # implementation of a pairwise max function; f(2,3) returns 3
    f = lambda x,y: x if x > y else y
    # returns 1 when g > gmax otherwise return the larger value S(g*Dd) or S(g*Dd*inc)
    return 1 if g > gmax else reduce(f,[S(g*Dd,Dd,k,A), \
    Sc(Dd,ki,ei,Ci,T=T,sigma=sigma,gmax=gmax,inc=inc,g=g*inc)])
```

Table A2. Variable definitions, types, definition, units, inputs and outputs (I/O) for the function Sc shown in Table A1. Array inputs take values for each specified compound. Some inputs have a predefined value while retaining the option of a user defined input. N/A denotes not applicable.

Variable	Type	Definition	Units	I/O	Optional	Default
Dd	scalar	dry diameter	m	in	no	N/A
ki	array	hygroscopicity	unitless	in	no	N/A
ei	array	volume fraction of solute in mixture	unitless	in	no	N/A
Ci	array	solubility (volume solute/volume water)	unitless	in	no	N/A
T	scalar	temperature	K	in	yes	298.15
sigma	scalar	solution surface tension	$N\ m^{-2}$	in	yes	0.072
gmax	scalar	maximum growth factor considered	unitless	in	yes	10
g	scalar	initial growth factor considered	unitless	in	yes	$1+10^{-11}$
inc	scalar	growth factor increment	unitless	in	yes	1.01
Sc	scalar	critical saturation ratio	unitless	out	no	N/A

Table A3. Example calls to the Python function Sc shown in Table A1. The string "inf" is the Python representation for infinity. See text and Table A2 for details.

Description	Dd	hygroscopicity	volume fraction	solubility
Example 1	`Sc(100e-9,`	`array([0.6,0.2]),`	`array([0.5,0.5]),`	`array([inf,0.1]))`
Example 2	`Sc(100e-9,`	`array([0.6]),`	`array([1]),`	`array([inf]), T = 273.0)`

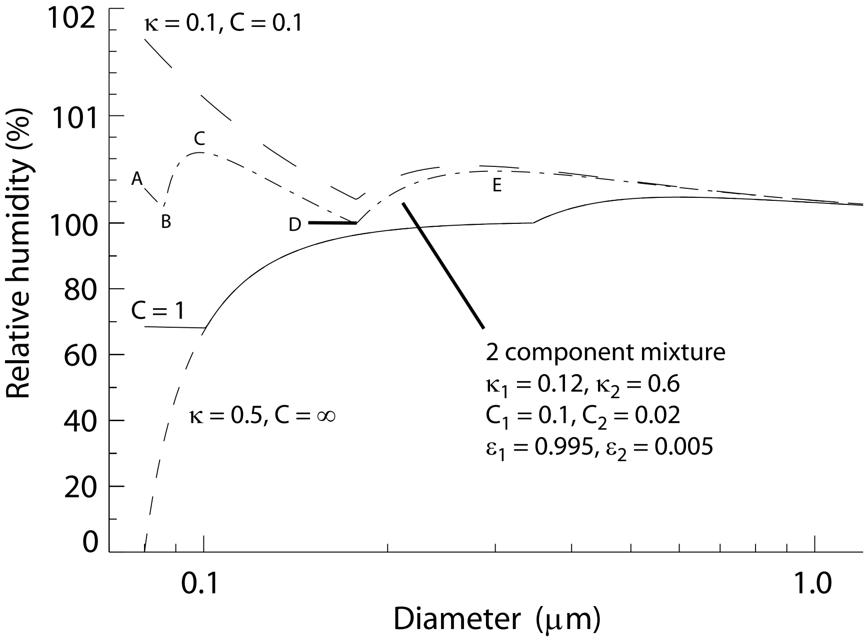

Fig. 1. Four example Köhler curves calculated from Eqs. (9)+(10). Note the break in scale at RH=100%.

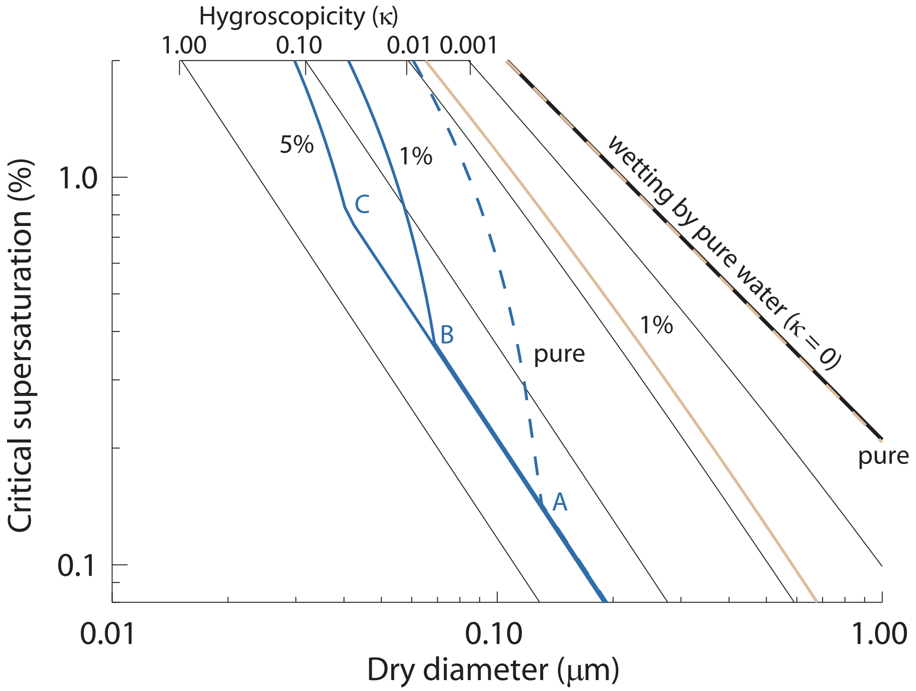

Fig. 2. Predicted CCN activity for single- and two-component mixtures. Blue: assumed hygroscopicity and solubility of dominant component, κ=0.3 and C=5×10^{-1}. Dashed line: pure component; activation proceeds based on the deliquescence RH, which is determined by the water activity of the saturated solution. Solid lines: addition of 1% and 5% by volume of a hypothetical substance that is infinitely soluble, with κ=0.6. Yellow: assumed hygroscopicity and solubility of dominant component, κ=0.3 and C=1×10^{-4}. Dashed line: pure component. Solid line: addition of 1% by volume of a hypothetical substance that is infinitely soluble, with κ=0.6.

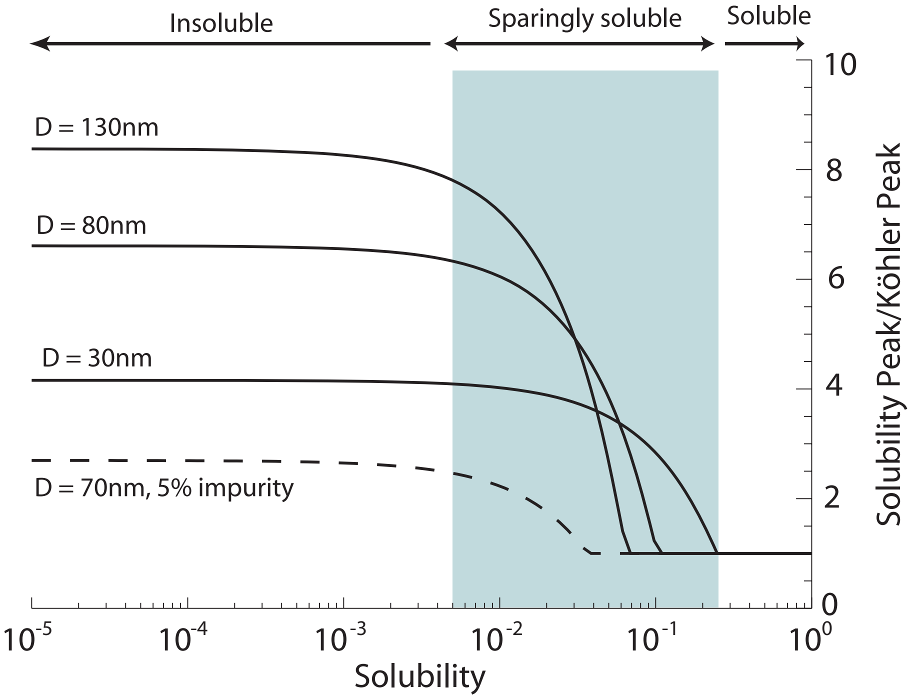

Fig. 3. Ratio of solubility peak to classical Köhler peak with solubility C for particles having assumed κ=0.2 and dry diameters of 130, 80, and 30 nm (solid lines). The ratio is set to unity if the Köhler peak dominates and cloud drop activation proceeds via classical theory. The dashed line represents a 70 nm particle of mixed composition, with 95% by volume of a substance with κ_1=0.2 and 5% of an infinitely soluble substance with κ_2=0.5. The plot delineates three solubility regimes that impact CCN activity in the size range $30<D_{\mathrm{dry}}<500$ nm: (1) $C <\sim 5\times10^{-3}$, where solubility of that compound is negligible, regardless of the value of κ, and the compound may be treated as insoluble. (2) $C >\sim 1\times10^{-1}$ where DRH$<s_c$ and cloud droplet activation is determined by particle hygroscopicity. (3) $1\times10^{-1}>C>5\times10^{-3}$ where cloud droplet activation is highly sensitive to particle solubility.