

On Deliquescence/Efflorescence Induced Hysteresis During Hygroscopic Particle Growth/Evaporation

O. Hellmuth¹⁾, A.K. Shchekin²⁾, I.V. Shabaev²⁾, and J. Katzwinkel¹⁾

¹⁾ Leibniz Institute for Tropospheric Research, Permoserstrasse 15, D-04318 Leipzig

²⁾ St. Petersburg State University, St. Petersburg, Petrodvoretz, Ulyanovskaya 1, 198504 Russia

Abstract. Both thermodynamic and kinetic approaches are employed to interpret data revealing a hysteresis effect during the growth/evaporation of hygroscopic particles in an ambient solvent vapour. For given thermodynamic parameters and material constants, the deliquescence humidity can be determined from the generalised Gibbs-Kelvin-Köhler and Oswald-Freundlich equations. Additionally employing the quasi-steady nucleation kinetics, we can estimate the efflorescence humidity. The predictive power of this approach is demonstrated for the sodium chloride-water system.

Key Words: Hygroscopic growth, hysteresis, deliquescence, efflorescence

NOTIONS AND MOTIVATION

The atmospheric aerosol contains a significant fraction of soluble substances (mostly salts) having a strong affinity for moisture. Due to their ability to absorb water molecules from the ambient air, such substances are called hygroscopic. When the ambient relative humidity (RH) is sufficient high, the water uptake continues until the hygroscopic particle completely dissolves in the absorbed water, in this way forming a pure solution droplet. The transition from partial to complete dissolution is called deliquescence transition, and the RH threshold at which a soluble particle completely dissolves is called deliquescence relative humidity (DRH). Deliquescence transition occurs at subsaturation of the ambient partial water vapour with respect to a flat surface of pure bulk water ($RH < 100\%$), but at water vapour supersaturation with respect to the equilibrium vapour pressure over a curved surface of the solution droplet.

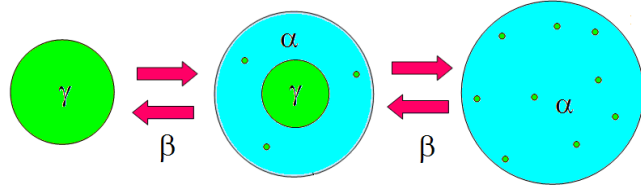
The reverse process, called efflorescence (or crystallisation) transition, leads to hydrosol formation by precipitation of solid crystals from the solution within evaporating droplets. Crystallisation performs via two steps: nucleation and crystal growth. In the nucleation step solute molecules, dispersed in the solvent, start to form clusters on the nanometer scale, which leads to a local increase of the solute concentration. Under certain conditions, these clusters become thermodynamically stable, subsequently constituting an embryo of the new phase (nuclei). To become stable nuclei, clusters need to reach a critical size, which depends on temperature, supersaturation and the droplet size. The crystallisation is driven by the supersaturation of the solution, which depends on ambient temperature and ambient relative humidity. The ambient relative humidity at which efflorescence transition sets in, is called efflorescence relative humidity (ERH).

Due to hysteresis, the aggregate state of atmospheric particles depends not only on thermodynamic state parameters but also on their anamnesis. The aggregate state has a strong impact on atmospheric radiation and chemistry^{1,2}). Solid particles may serve as ice nuclei and influence cirrus formation. Aqueous particles have a larger mass extinction efficiency but a smaller backscattered fraction than their solid counterparts. Furthermore, they act as chemical microreactors for hydrolysis, secondary organic aerosol formation, micellisation, heterogeneous surface reactions etc. Owing to the high variability of the relative humidity in the planetary boundary layer, hysteresis effects were found to effectively impact the partitioning between solid and aqueous phases of tropospheric sulphate-ammonium particles on a global scale¹). Moreover, such effects were reported to have a significant impact on the sulphate direct climate forcing (SDFC). Depending on how these effects were parameterised in a global 3-D chemical transport model, an uncertainty in the SDFC of 23 % on the global scale, but of much higher values on regional scales have been found from sensitivity studies²).

DETERMINATION OF THE DELIQUESCENCE HUMIDITY

In the initial state, the system consists of a soluble solid core (phase γ) with radius R_n , embedded in a solvent vapour (phase β) within fixed volume V at absolute temperature T . In the final state, a droplet of radius R is formed, either including a partially dissolved residual core of radius R'_n , enveloped by a liquid film of thickness $h = R - R'_n$ (phase α), or with a completely dissolved residual core of radius $R'_n = 0$.

Figure 1. Core-shell aggregate in an ambient vapour: phase γ =soluble core; phase α =enveloping liquid film (solvent shell); phase β =solvent vapour.



The equilibrium droplet must satisfy two thermodynamic conditions: (a) external equilibrium between the liquid phase α and the ambient vapour phase β ; (b) internal equilibrium between the liquid phase α and the solid phase γ . Employing the mechanic and thermodynamic concept of the disjoining pressure, $\Pi_D(h)$, one arrives at a generalisation of the Gibbs-Kelvin-Köhler equation of the theory of nucleation on soluble particles for the external equilibrium, Eq. (1), and a generalisation of the Ostwald-Freundlich equation of the theory of solutions for the internal equilibrium, Eq. (2)^{3,4,5}:

$$\mu_v = \mu^\beta \Rightarrow \mu_\infty - \mu^\beta - k_B T a(x) + \frac{2\sigma^{\alpha\beta} v^\alpha}{R} - \left(\frac{R'_n}{R}\right)^2 \Pi_D(R, R'_n) v^\alpha = 0, \quad (1)$$

$$\mu_n^\alpha = \mu'_n \Rightarrow \frac{2v_n}{R'_n} \left(\sigma^{\alpha\gamma} + \int_{R-R'_n}^{\infty} \Pi_D(h) dh \right) - \frac{2\sigma^{\alpha\beta} (v_n^\alpha - v_n)}{R} - k_B T \ln \frac{a(x)}{a_\infty} + \Pi_D(R, R'_n) \left[v_n - \left(\frac{R'_n}{R}\right)^2 (v_n - v_n^\alpha) \right] = 0, \quad (2)$$

where μ^β is the vapour chemical potential of solvent molecules, μ_v and μ_n^α are the chemical potentials of solvent and solute molecules in the liquid solution film, μ_n' is the solute chemical potential of solute molecules inside the solid nucleus residue, μ_∞ is the value of the solvent chemical potential at a flat surface of a pure solvent, k_B is the Boltzmann constant, a and x are the solute activity and concentration in the bulk solution, $\sigma^{\beta\gamma}$, $\sigma^{\alpha\gamma}$ and $\sigma^{\alpha\beta}$ are the surface tensions at the corresponding interfaces, v^α and v_n^α are the partial molecular volumes of the solvent and solute in the solution, v_n is the specific molecular volume of the nucleus matter in solid phase, x_∞ is the value of the solute concentration in the solution saturated at a flat surface of the solid phase of a pure solute.

DETERMINATION OF THE EFFLORESCENCE HUMIDITY

The efflorescence humidity cannot be obtained from the pure thermodynamic approach and requires a kinetic consideration.

According to the nucleation kinetics^{6,7)}, the rate of homogeneous crystallisation J per unit volume of a solution with saturation ratio $S_s = a(x)/a_\infty$ reads:

$$J = J_0 \exp\left(-\frac{W^*}{k_B T}\right), \quad J_0 = n_n \frac{k_B T}{h} \exp\left(-\frac{\Delta g}{k_B T}\right), \quad W^* = \frac{16\pi}{3} \frac{(\sigma^{\alpha\gamma})^3 v_n^2}{(k_B T \ln S_s)^2}. \quad (3)$$

Here, n_n is the molecular concentration in the crystalline nucleus⁶⁾, and Δg is the free energy barrier for a solute molecule to jump from the solution to the crystalline nucleus. The condition for efflorescence is given by:

$$J(\text{ERH}) \cdot V_R(\text{ERH}) \cdot t_{ind} = 1, \quad (4)$$

where t_{ind} denotes the induction time for nucleation, i.e., the time the system spent at constant droplet composition prior to nucleation. The ERH is the relative humidity, at which the saturation ratio $S_s(x)$, referring to the solution with complete dissolved condensation nucleus, is sufficient high to satisfy Eq. (4). For $R'_n = 0$ we obtain from the Gibbs-Kelvin-Köhler Eq. (1) the solute activity as a function of the relative humidity of the ambient vapour:

$$a(\text{RH}) = -\frac{\mu^\beta - \mu_\infty}{k_B T} + \frac{2\sigma^{\alpha\beta} v^\alpha}{k_B T R} = -\ln \text{RH} + \frac{2\sigma^{\alpha\beta} v^\alpha}{k_B T R(\text{RH})}. \quad (5)$$

Employing Eqs. (3) and (4) with $a(\text{RH})$ from Eqs. (5), we arrive at the following equation for ERH:

$$\left[\frac{16\pi}{3} \left(\frac{\sigma^{\alpha\gamma}}{k_B T} \right)^3 \frac{v_n^2}{\ln(J_0 \cdot V_R(\text{ERH}) \cdot t_{ind})} \right]^{1/2} - \ln \frac{a(\text{ERH})}{a_\infty} = 0. \quad (6)$$

RESULTS

For aqueous sodium chloride droplets we will exemplarily show, that Eqs. (1), (2) and (5), (6) allow the size-dependent determination of DRH and ERH within their measurement limits^{8,9}). Vice versa, knowing DRH and ERH, the otherwise difficult to measure surface tension of the liquid-solid interface, $\sigma^{\alpha\gamma}$, can be determined using the present approach.

The behaviour of the growth factor versus relative humidity, which follows from thermodynamic equations (1)-(2), is shown in Fig. 2. There is a hysteresis effect, which manifests itself in the difference between the humidities at which deliquescence and efflorescence set in. The deliquescence humidity corresponds to the threshold value of the chemical potential of a subsaturated vapour for the transition from droplets with a partially dissolved nucleus to droplets with a completely dissolved nucleus. The efflorescence humidity results from Eqs. (5) and (6). In the presentation we will revise the ERH determination by a generalised kinetic approach.

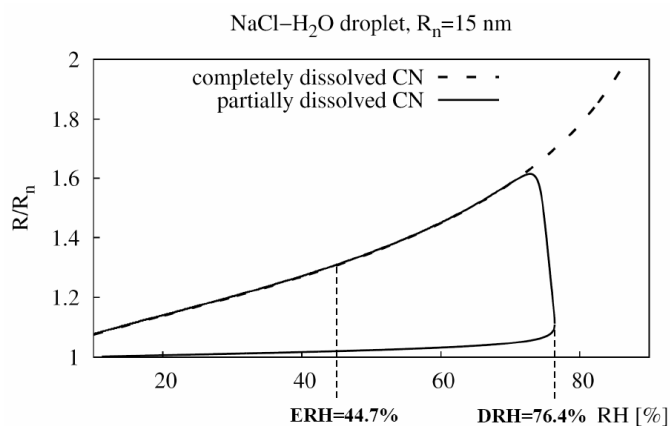


Figure 2. Growth factor vs. relative humidity for NaCl-H₂O droplet with dry particle radius $R_n=15$ nm.

Acknowledgments

This work was supported by the program “The Development of Scientific Potential of High School” (Grant No. RNP.2.1.1/4430).

References

1. Wang, J., Hoffmann, A. A., Park, R. J., Jacob, D. J., and Martin, S. T., *J. Geophys. Res.* 113, D11206, doi:10.1029/2007JD009367 (2008).
2. Wang, J., Jacob, D. J., and Martin, S. T., *J. Geophys. Res.* 113, D11207, doi:10.1029/2007JD009368, (2008).
3. Shchekin, A. K., and Shabaev, I. V., “Thermodynamics and Kinetics of Deliquescence of Small Soluble Particles”, in *Nucleation Theory and Applications*, edited by J. W. P. Schmelzer, G. Röpke and V. B. Priezhev, Dubna: JINR, 2005, pp. 267-291.
4. Shchekin, A. K., and Rusanov, A. I., *J. Chem. Phys.* 129, 154116 (2008).
5. Shchekin, A. K., Shabaev, I. V., and Rusanov, A. I., *J. Chem. Phys.* 129, 214111 (2008).
6. Onasch, T. B., McGraw, R., and Imre, D., *J. Phys. Chem. A* 104, 10797 (2000).
7. Parsons, M. T., Riffell, J. L., and Bertram, A. K., *J. Phys. Chem. A* 110, 8108 (2006)
8. Biskos, G., Malinowski, A., Russell, L. M., Buseck, P. R., and Martin, S. T., *Aerosol Sci. Technol.* 40, 97 (2006).
9. Gao, Y., Chen, S. B., and Yu, L. E., *Atmos. Env.* 41, 2019 (2007).