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The hysteresis cycle of concentration in a solution droplet under changing humidity

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Abstract. For a solution droplet in equilibrium with the atmospheric environment, a relationship exists between radius and concentration, which allows to express the saturation ratio of the droplet as a function of either one of these two parameters. The curves showing the complete behaviour of saturation ratio as a function of radius, for various sizes of NaCl nuclei, were previously presented for both wholly and partially dissolved salt. Here, the dependence of saturation ratio on droplet concentration, rather than on its radius, is examined and plotted for various NaCl nuclei. The occurrence of an analogous, but X-shaped, hysteresis phenomenon, characterizing the behaviour of the solution concentration in a growing-shrinking cycle of a solution droplet under changing humidity, is evidenced and discussed. An insoluble spherical core is assumed to be always present inside the condensation nucleus, so that the onset of the sudden salt re-crystallization is triggered at a well defined concentration value.

List of principal symbols

a_w	Activity of water in a solution
c	Molal concentration (number of solute moles per solvent unit mass)
c_{crys}	Molal concentration when re-crystallization starts
c_{diss}	Molal concentration when deliquescence starts
c_{deli}	Molal concentration when deliquescence ends
m_o	Total mass of salt in a dry mixed nucleus
m_s	Mass of solute in a solution droplet
m_w	Mass of solvent (water) in a solution droplet
s	Solubility of a salt particle
s^*	Standard solubility of the salt
M_{salt}	Molar mass of the salt
M_w	Molar mass of water
r	Droplet radius
r_{deli}	Droplet radius when deliquescence ends
r_{dry}	Radius of the dry nucleus
r_i	Radius of the inner insoluble impurity
r_x	Radius of the residual nucleus inside the droplet
R	Universal gas constant
S	Saturation ratio of a solution droplet
S_{crys}	Saturation ratio at molal concentration when re-crystallization starts

S_{diss}	Saturation ratio at molal concentration when deliquescence starts
T	Temperature
U	Relative humidity
γ	Surface tension of a solution droplet against air
ρ	Density of the NaCl solution
ρ_s	Density of the solid salt
ρ_w	Density of pure water
σ	Supersolubility ratio ($\equiv s/s^*$)
τ	Vapour pressure of a solution droplet
τ_∞	Standard vapour pressure of a NaCl solution
τ_w	Standard vapour pressure of pure water

1 Introduction

The atmosphere contains a large number (up to several thousands per cubic centimetre) of condensation nuclei, that is, of tiny solid particles that play a fundamental role in the formation of clouds and fogs. It is on the surface of these nuclei that the droplets form by condensation of atmospheric water vapour. As soon as the condensation begins, the soluble substance the nucleus is made of starts dissolving in the thin water layer just deposited over the nucleus surface, thus giving rise to the formation of a solution droplet.

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At a fixed temperature, the equilibrium vapour pressure of a solution droplet depends on the curvature of its surface and on its concentration. The vapour pressure increases with the curvature (Kelvin effect) and decreases with the concentration (Raoult effect). The role played by either one of these two effects, mostly of the second one, is fundamental for the equilibria of a solution droplet in the atmosphere.

Whether the nucleus is partially or wholly dissolved in the droplet, the solute mass conservation prescribes a relationship between radius and concentration. Thus, the vapour pressure of a solution droplet, at a given temperature, can be expressed as a function of either one of these two parameters.

Köhler [1] was the first to present, by means of the curves named after himself, the behaviour of the saturation ratio (namely, the ratio of the vapour pressure of a solution droplet to the standard¹ vapour pressure of pure water) vs. the radius for droplets containing wholly dissolved nuclei, that is for unsaturated solutions only (see also [2,3]).

In a previous paper [4], the Köhler curves were extended to droplets containing partially dissolved salt, that is to supersaturated solutions. That paper presented a thermodynamic model of the observed hysteresis phenomenon [5] that characterizes the behaviour of the droplet radius in a growing-shrinking cycle of a solution droplet under changing humidity. The condensation starts when the increasing humidity reaches a critical value, which depends, at a given temperature, on the nature and on the size of the nucleus. Here a jump occurs (deliquescence) which suddenly turns the dry nucleus into a solution droplet with the wholly dissolved salt. After this, a further humidity increase simply causes more vapour to condense onto the droplet.

Under decreasing humidity, evaporation occurs, but the solution does not crystallize at the previous deliquescence humidity (repeating the same path in the opposite direction). Differently, re-crystallization starts at a much lower humidity value, at which another abrupt jump occurs, which suddenly returns the solution droplet into the original dry nucleus.

In this paper the behaviour of the saturation ratio as a function of droplet concentration, rather than of radius, is examined for either partially or wholly dissolved salt. In other words, the sequence of equilibria of a solution droplet in the coordinate plane of concentration and relative humidity is examined. As it can be expected, a hysteresis cycle appears again, but with a completely different shape and behaviour.

2 Saturation ratio of a solution droplet

Consider a mixed nucleus, consisting of a spherical core made of an insoluble substance (hereinafter called

“impurity”), coated with a spherical shell of soluble salt. Let r_{dry} be the radius of the dry nucleus and r_i the radius of the inner impurity. Let us assume that a solution droplet forms upon the given nucleus, and denote with r the radius of the droplet and with γ its surface tension against air.

The equilibrium vapour pressure τ of a solution droplet of radius r is expressed by the Kelvin-Köhler law (see, e.g., [6]):

$$\tau = \tau_{\infty} \exp\left(\frac{2M_w\gamma}{\rho_w RT r}\right), \quad (1)$$

where T is the temperature, R is the universal gas constant, ρ_w and M_w are the density and the molar mass of pure water, and τ_{∞} is the standard vapour pressure of the given solution. Note that in this expression only the Kelvin effect is explicit, while the Raoult effect is embedded in the expression of τ_{∞} .

If τ_w is the standard vapour pressure of pure water and $a_w = \tau_{\infty}/\tau_w$ is the water activity in the given solution, equation (1) may be rewritten as:

$$S = a_w \exp\left(\frac{2M_w\gamma}{\rho_w RT r}\right), \quad (2)$$

where $S = \tau/\tau_w$ is the so called *saturation ratio* of the solution droplet. Since γ and a_w only depend, at a given temperature, on the solution concentration (see Appendix B), S is to be regarded as a quantity depending on droplet radius and concentration only. Note that for inorganic compounds, surface tension increases with the concentration [7], while for some organic compounds, a decrease of surface tension with concentration is observed [8].

On the other hand, the constraint of the solute mass conservation results in a relationship between radius and concentration, so that S may be regarded as a function of only one of these two variables. In this section the behaviour of S as a function of the concentration will be obtained, for either partially or wholly dissolved salt.

In both cases, if c is the molal concentration (given as the number of moles of solute per unit water mass), m_s is the solute mass, and M_{salt} is the salt molar mass, the water mass in the solution is $m_w = m_s/(M_{\text{salt}}c)$.

2.1 Partially dissolved salt

The solubility s (i.e., the equilibrium concentration) of a small salt particle exceeds the standard solubility s_{∞} of that salt at the same temperature (for NaCl, at 20 °C, $s_{\infty} = 6.16 \times 10^{-3}$ mol/g). According to the Ostwald-Freundlich law the increase in solubility depends on the size of the solid particle, and it is the greater the smaller the particles (see, e.g., [9]). For a spherical particle it may be shown (see Appendix A) that the super-solubility ratio, defined as $\sigma = s/s_{\infty}$, is linked to the radius r_x of the solid particle through the relationship:

$$\sigma = \exp\frac{\lambda}{r_x}, \quad (3)$$

¹ Throughout this paper by *standard* value we mean the value above a flat interface.

where λ is a characteristic length which, for a given salt, only depends on temperature (for NaCl, at 20 °C, $\lambda \cong 1.41 \times 10^{-7}$ cm).

It is evident that in a droplet where some solid salt is still present, the equilibrium requires $c = s$, so that equation (3) becomes:

$$c = s_\infty \exp \frac{\lambda}{r_x}. \quad (4)$$

On the other hand, if V denotes the entire volume of the droplet, V_x and V_y the volumes, respectively, of the solid and the liquid phase, from $V = V_x + V_y$ it follows:

$$\frac{4}{3}\pi r^3 = \frac{4}{3}\pi r_x^3 + \frac{m_w + m_s}{\rho}, \quad (5)$$

where ρ is the density of the solution that, at a given temperature, can be approximated by means of equation (B.1) (see Appendix B). Furthermore, one obviously has $m_s = 4\pi/3 \rho_s (r_{\text{dry}}^3 - r_x^3)$ by the conservation of salt mass.

In equation (5), replacing m_s with what is given above, m_w with what is given by $m_w = m_s/(M_{\text{salt}}c)$, ρ with what is given by (B.1), and r_x with what is given from equation (4), one eventually gets a relationship between the droplet radius r and the solution concentration c for solution droplets with partially dissolved salt:

$$r^3(c) = r_{\text{dry}}^3 \left(1 + \frac{\rho_s}{\rho_w} \frac{1 - \left(\frac{\lambda}{r_{\text{dry}} \log(c/s_\infty)} \right)^3}{M_{\text{salt}}c} \right). \quad (6)$$

Note that, in a droplet where the salt is partially dissolved, the molal concentration c , as from relation (4), varies from the lower bound

$$c_{\text{diss}} \equiv s_\infty \exp \frac{\lambda}{r_{\text{dry}}} \quad (7)$$

to the upper bound

$$c_{\text{crys}} \equiv s_\infty \exp \frac{\lambda}{r_i}. \quad (8)$$

The above notations (c_{diss} , c_{crys}) will be explained later. For droplets containing partially dissolved salt the behaviour of r vs. c may then be plotted for all concentration values belonging to the interval (c_{diss} , c_{crys}). This behaviour is represented by the dotted curve in Figure 1.

If now the expression (6) of r in terms of c is replaced with expression (2), the value of the saturation ratio S for droplets with partially dissolved salt can be determined once given the molal concentration c only. Indeed, the surface tension γ and the water activity a_w , as well as the solution density ρ , depend, at a given temperature, only on the solution concentration, as shown, respectively, by equations (B.2) and (A.5) in the Appendices. The final result, valid for supersaturated solutions only, is:

$$S(c) = a_{w\infty} \exp \left[\kappa(1 - c/s_\infty) + \frac{\lambda_w}{r(c)}(1 + hc/s_\infty) \right], \quad (9)$$

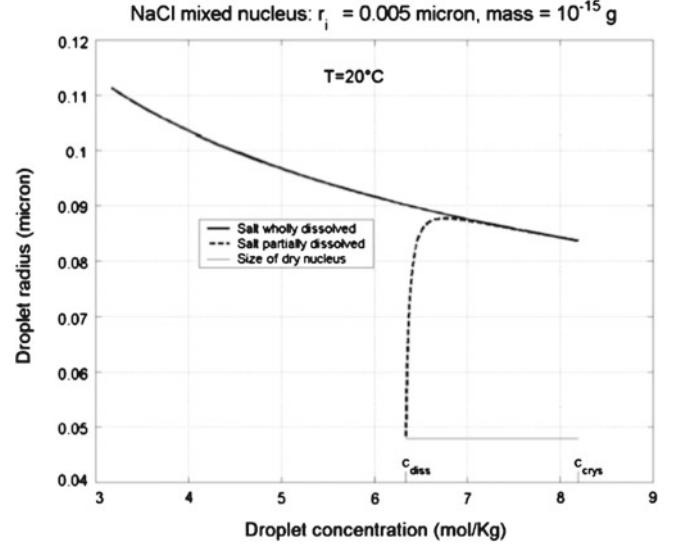


Fig. 1. The twofold dependence of radius on molality for a droplet growing on a mixed NaCl nucleus at $T = 20$ °C: salt partially (dotted line) and wholly dissolved (solid line) lead to different functional relations (see text). Actually, the dotted branch is never followed by a real droplet, since all of its points represent unstable equilibria.

where the explicit expression of $r(c)$ is given by equation (6) and

$$\lambda_w = \frac{2M_w\gamma_w}{\rho_w RT}, \quad (10)$$

is a characteristic length of the solvent (for water, $\lambda_w \cong 1.050 \times 10^{-7}$ cm). Dimensionless constants h and κ are defined in Appendices A and B.

Lastly, we introduce the symbols $S_{\text{crys}} \equiv S(c_{\text{crys}})$ and $S_{\text{diss}} \equiv S(c_{\text{diss}})$, which according to equation (9) represent the lower bound and the upper bound of the saturation ratio in the presence of solid salt inside the droplet. As it will be shown in Section 4, the symbols just introduced, as well as those introduced in the equations (7) and (8), represent the values of concentration and saturation ratio at the beginning of the salt deliquescence and of the salt re-crystallization in the growing-shrinking cycle of a solution droplet under changing humidity, respectively.

2.2 Wholly dissolved salt

Consider now a solution droplet with the salt wholly dissolved. This droplet contains the maximum amount of solute, namely all the salt mass m_o present in the nucleus, but a variable quantity m_w of water, so that the total mass of its liquid phase is $m = m_o + m_w$, where m_w is given by $m_w = m_s/(M_{\text{salt}}c)$ with m_s coinciding with m_o . Hence the mass of the liquid phase is given by:

$$\frac{4}{3}\pi\rho(r^3 - r_i^3) = m_o + \frac{m_o}{M_{\text{salt}}c}. \quad (11)$$

This is just the relationship linking, for a wholly dissolved salt, the droplet radius to the solution concentration.

Using again $m_s = 4\pi/3 \rho_s(r_{\text{dry}}^3 - r_x^3)$ into equation (11), one obtains:

$$r^3(c) = r_{\text{dry}}^3 \left[1 + \frac{\rho_s}{\rho_w} \frac{1 - (r_i/r_{\text{dry}})^3}{M_{\text{salt}} c} \right]. \quad (12)$$

For droplets with a wholly dissolved salt, the behaviour of r versus c may then be plotted for all concentration values comprised between 0 and the maximum concentration c_{crys} . This behaviour is represented by the solid-line curve in Figure 1.

If then we substitute in equation (2) the expression of r implicit in equation (12), as well the expressions (B.1), (B.2) and (A.5) of ρ , γ and a_w in terms of the concentration c valid also for unsaturated solutions, we will be in a position to plot, for each given salt and temperature, the behaviour of the saturation ratio vs. the solution concentration. This is equivalent to a Köhler curve where, instead of the droplet size, the solution concentration is the independent variable.

Figure 1 also shows the values c_{diss} and c_{crys} , given by equations (7) and (8), that represent, respectively, the lower and upper bound for concentration in a droplet, growing on a mixed nucleus, containing the partially dissolved salt.

3 The equilibria of a solution droplet in the atmosphere

The behaviour of saturation ratio vs. concentration, $S(c)$ is shown in the right panel of Figure 2, while its behaviour vs. droplet radius, i.e. the corresponding Köhler curve, is shown in the left panel. In both cases, the curves refer to a solution droplet containing the indicated NaCl nucleus, at 20 °C. In each panel, the dotted and the solid portions represent the equilibria of the droplet when the nucleus is, respectively, partially or wholly dissolved.

At the given temperature and in an environment with a given value U of relative humidity, each curve, either the one in the left panel or the other in the right one, indicates, respectively, the size or the molal concentration that a droplet, containing the given mass of salt, must have for it to be in equilibrium.

In Figure 3, we have plotted the upper parts of the behaviour of saturation ratio for five different NaCl mixed nuclei, versus both the molal concentration (right panel) and the radius (left panel) of the droplet. Each of the $S(c)$ curves in the right panel presents a maximum that lies in the supersaturation range at a certain value of concentration, which may be denoted as “critical concentration”, in analogy with the “critical radius” marking the maximum of the Köhler curves in the left panel. Both the maximum value of saturation ratio and the associate critical concentration increase for decreasing salt mass in the nucleus.

Note also that, in the supersaturation range ($U > 1$), for any given relative humidity there are two possible

equilibria for the droplet, no matter which independent variable is adopted. As an example we can consider, among the curves in the right panel of Figure 3, the one relative to the smallest of the five nuclei examined (curve 1): the two equilibrium radii are the intersection points A and B . Of these two equilibria, point A is a stable equilibrium, whereas point B is an unstable equilibrium. As a matter of fact, it is not difficult to show that, even if the droplet happens somehow to be in the state represented by point B , any small fluctuation inducing either a small quantity of vapour to condense or a small quantity of water to evaporate will definitively remove the droplet from its state B . Let us examine both situations.

In the case of a small fluctuation inducing vapour condensation, the concentration decreases so that, on following the curve near B and to its left, the saturation ratio S of the droplet also decreases, thus taking values lower than the ambient humidity U . This causes further vapour to condense upon the droplet, which in turn causes a further decrease in concentration and, as a consequence, a further decrease in saturation ratio, and so on. Thus, a spontaneous condensation process starts which definitively removes the droplet from its previous state B driving it toward increasingly lower concentrations, and increasingly bigger sizes (left panel).

In the case of a small fluctuation inducing evaporation, the droplet concentration increases and on following the curve near B , but to its right, the saturation ratio S increases, thus taking values higher than U . This causes further water to evaporate away from the droplet, which in turn causes a further increase in concentration and, as a consequence, a further increase in saturation ratio, and so on. Thus, a spontaneous evaporation process starts, which definitively removes the droplet from its previous state B driving it toward higher concentrations, and increasingly smaller sizes (left panel).

Note however that, in this case, when the progressive evaporation moves the droplet away from point B , the droplet concentration is driven toward its critical value, where the maximum value of saturation ratio is attained. Even beyond this point, the water keeps on evaporating away from the droplet as long as $S > U$. But, on moving further to the right, the saturation ratio begins now to decrease as the evaporation goes on, so that this spontaneous process ends when the saturation ratio S reaches the value U of ambient relative humidity, that is, when point A is attained. Here the equilibrium is stable, since the effect of any small fluctuations, as it can be easily shown by arguments similar to those above, is to push the state of the droplet back again to point A .

Recently, Shahidzadeh-Bonn et al. [10] investigated the crystallization during evaporation of saturated NaCl solutions on hydrophilic and hydrophobic surfaces, showing the key importance of the liquid-air interfacial properties for the crystal growth and pattern evolution. In the following, however, we neglect the peculiar forms of salt crystallization, and concentrate on the hysteresis behaviour of the solution droplets under changing humidity in the atmosphere.

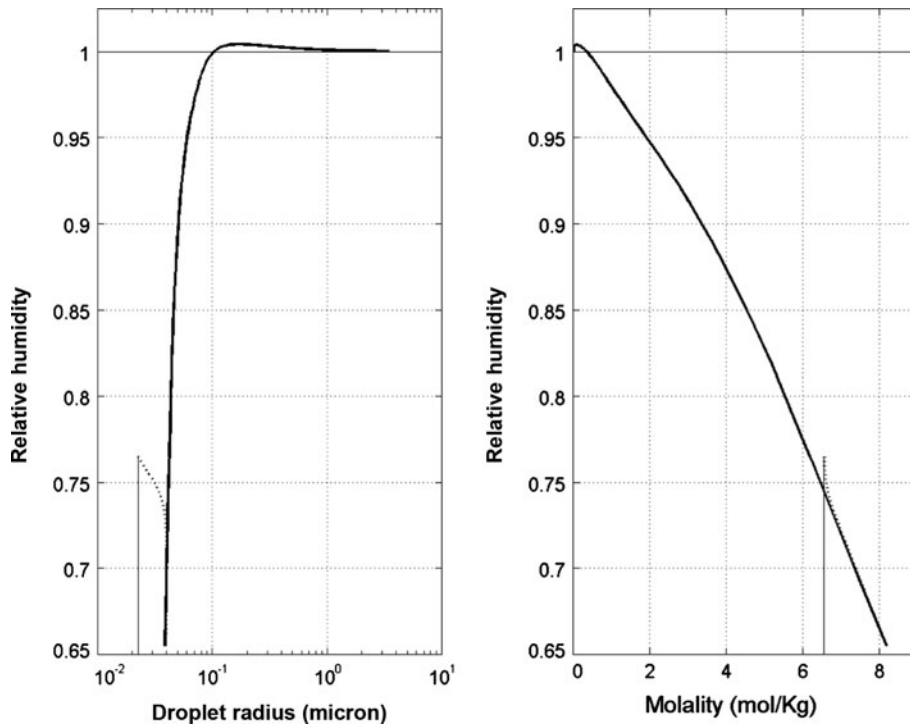


Fig. 2. The behaviour of saturation ratio vs. droplet radius (left panel) and vs. molal concentration (right panel) for a solution droplet growing on a mixed nucleus made of an inner spherical insoluble impurity (5×10^{-7} cm radius), coated with a spherical shell of NaCl (10^{-16} g mass), which corresponds to a dry nucleus radius $r_{\text{dry}} = 0.022 \mu\text{m}$. The temperature is assumed to be $20 \text{ }^\circ\text{C}$. The dotted curves connecting the short vertical thin solid lines (representing the dry nucleus) with the solid curves (representing the equilibria of a droplet with wholly dissolved salt) are the branches of unstable equilibria (see Sect. 4).

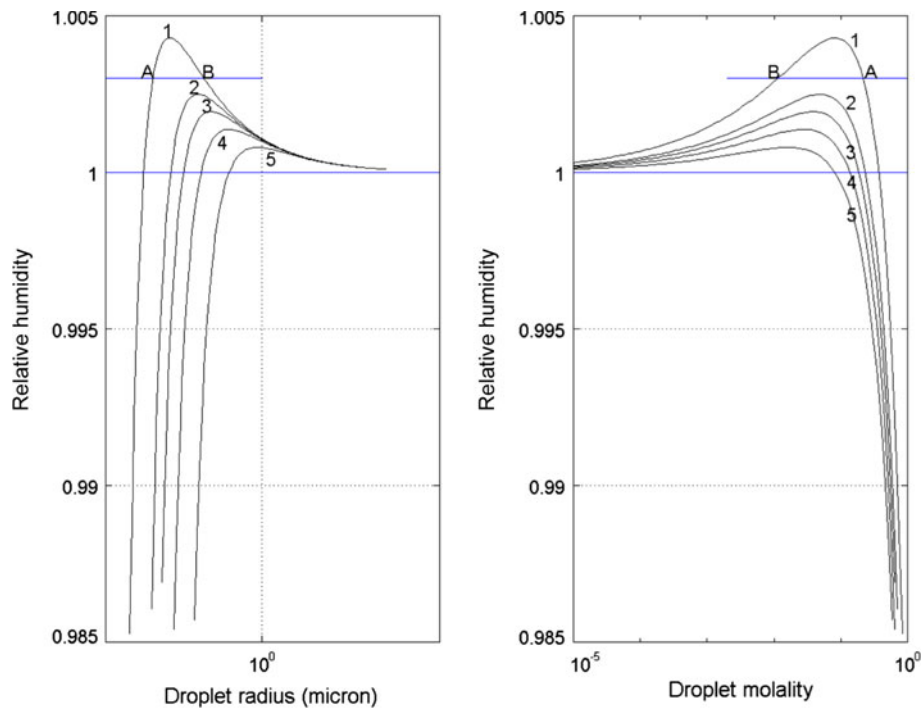


Fig. 3. Behaviour of saturation ratio for five different NaCl mixed nuclei at high humidity with salt masses: (1) 10^{-16} g, (2) 3×10^{-16} g, (3) 10^{-15} g, (4) 3×10^{-15} g, (5) 10^{-14} g.

4 Modelling the concentration hysteresis

Let us consider now Figure 4, which represents a magnification of the lower portions of Figure 2. First of all, we point out that each point belonging to the dotted branch H_1H_3 represents a state of unstable equilibrium. In order to prove this fact, let us assume that, at the ambient relative humidity U , the droplet is in an equilibrium state represented by point B , with radius r , concentration c and saturation ratio $S = U$. At the given humidity value U , there are two other equilibrium states, A and C . Point A belongs to the stable branch representing the dry nucleus (vertical solid line), point C belongs to the stable branch representing the droplet containing the wholly dissolved salt (solid curve). It will be now shown that a droplet in the state B cannot remain there but must move either to state A or to state C . Consider a small fluctuation inducing a small quantity of vapour to condense upon the droplet and, as a consequence, a small quantity of solid salt to dissolve into solution. Thus, the salt solubility increases because of the size reduction of the solid particle inside the droplet, according to the Ostwald-Freundlich law [9]. As a consequence, the solution concentration must increase in order to reach its new equilibrium value, and this can occur only by a further dissolution of the solid salt inside the droplet. At the same time – as apparent from the right panel of Figure 4, an increase in concentration causes the equilibrium vapour pressure to become lower because of the Raoult effect, and even lower because of the Kelvin effect due to the simultaneous increase in droplet size. Then, being now $S < U$, further water vapour will condense upon the droplet and further solid salt will go dissolved, and so on, until the whole salt dissolution is accomplished. It is now evident that, to have a stable equilibrium established with the salt wholly dissolved, the solution droplet cannot but reach point C , representing the only stable equilibrium consistent with the given relative humidity U .

On the other hand, consider any small fluctuation inducing a small quantity of water vapour to evaporate away from the droplet and, as a consequence, a small quantity of solute to crystallize onto the solid particle inside the droplet. Thus, the salt solubility decreases because of the size increase of the solid particle inside the droplet (Ostwald-Freundlich law).

As a consequence, the solution concentration must decrease in order to reach its new equilibrium value, and this can occur only by a further crystallization of the solute. At the same time, as apparent from the right panel of Figure 4, a decrease in concentration causes the equilibrium vapour pressure to become higher because of the Raoult effect, and even higher because of the Kelvin effect due to the simultaneous decrease in droplet size. Then, being now $S > U$, further water vapour will evaporate away from the droplet and further solute will return to the solid phase, and so on, until all the water will have left the droplet and all the salt will have returned solid in the form of a dry nucleus. Now, in order for a stable

equilibrium to be established, the droplet has to reach point A , representing the only stable equilibrium consistent with the given relative humidity U . Hence, in the humidity range $S_{\text{crys}} < U < S_{\text{diss}}$, no solution droplet containing the partially dissolved salt may exist. In this range, either a dry nucleus or a droplet containing the wholly dissolved salt is present.

We are now in a position to model the behaviour of the concentration of a solution droplet in a growing-shrinking cycle of the droplet under changing humidity, a behaviour that is characterized by a hysteresis with two abrupt jumps. Indeed, let us assume that humidity increases starting from a value lower than S_{diss} and in the presence of a dry nucleus. As long as $U < S_{\text{diss}}$, the equilibrium point in the right panel of Figure 4 rises vertically toward point H_1 while the nucleus remains dry. Note that, until deliquescence occurs, the concentration has been given the conventional value ($c = c_{\text{diss}}$), even if no solution exists at this stage, as no solvent has yet condensed onto the nucleus. Nevertheless, even if the nucleus is still dry, it makes sense to attribute the above conventional value to the “concentration” of the dry nucleus. The point is that the equilibrium concentration of a real solution containing some solid salt coincides with the solubility of the salt particle in the solution. Hence, even if no solution exists in the presence of the dry nucleus, the concentration can be assigned a value coinciding with the solubility of a salt particle with the same size as the dry nucleus, a value that is just ($c = c_{\text{diss}}$) (see Eq. (7)).

Now, when the growing ambient humidity reaches the value S_{diss} (point H_1), water vapour starts to condense upon the nucleus and a solution droplet starts to form. But, since a stable equilibrium is forbidden for a droplet having its salt partially dissolved, the only stable equilibrium is the one represented by point H_2 , where all the salt is dissolved. Thus, when humidity reaches the value S_{diss} , a catastrophic jump must occur, which suddenly turns the dry nucleus into a droplet where the salt is already wholly dissolved. This jump, denoted as *deliquescence*, is represented in both panels of Figure 4 by the straight lines H_1H_2 . The end of deliquescence, marked by point H_2 , is characterized by a droplet size $r_{\text{deli}} > r_{\text{dry}}$ and a droplet concentration $c_{\text{deli}} < c_{\text{diss}}$. These values have all been numerically computed for the specific NaCl nucleus and evidenced in Figure 1.

After this spontaneous transition is completed, a further humidity increase simply causes more vapour to condense upon the droplet and the equilibrium point leaves the point H_2 rising along the branch of the curve $S(c)$ represented by the solid line in the right panels of Figure 4 or Figure 2.

Conversely, on slowly decreasing the humidity from values higher than S_{diss} , the water in the droplet starts evaporating causing an increase of concentration, and the droplet traces backwards the same stable equilibrium states achieved during the previous stage described above. However, as the point H_2 is reached, this reversibility in the path of the droplet ceases. Indeed, since point H_2

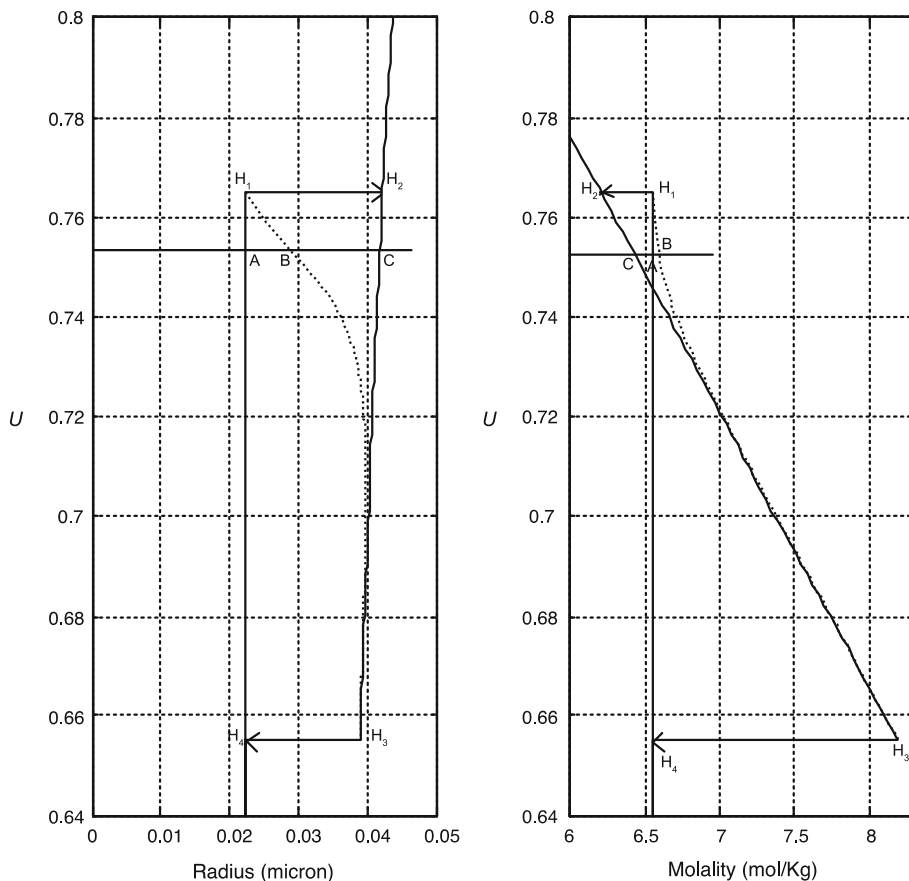


Fig. 4. A magnification of the lower portions of Figure 2 evidencing the hysteresis of radius (left panel) and of concentration (right panel). Note, in both panels, the two abrupt jumps, H_1 - H_2 and H_3 - H_4 , indicated by the two horizontal arrows, the upper jump representing the deliquescence of the dry nucleus, the lower one the re-crystallization of the salt with the reappearance of the dry nucleus. The dotted line in each panel represents the branch of unstable equilibria. Points A , B , C represent three equilibrium states of the solution droplet at the given humidity U , of these B is unstable.

belongs to a branch of stable equilibria, there is no need now for a sudden phase transition to occur toward the point H_1 . Only when humidity is further lowered to the value S_{cryst} and point H_3 is reached, the solute starts to re-crystallize over the inner insoluble core. But, for a reason similar to that mentioned above, the only stable equilibrium is the one represented by point H_4 , in which the nucleus becomes dry again. Thus, when the ambient humidity reaches the value S_{cryst} , an inverse abrupt jump H_3H_4 occurs, which suddenly returns the droplet, previously containing the wholly dissolved salt, to its original state of dry nucleus.

An experimental evidence of the process depicted in Figure 4 has been recently discussed by Desarnaud and Shahidzadeh-Bonn [11]. By investigating the deliquescence and re-crystallization of micro droplets of sodium chloride, it is shown that after complete deliquescence, followed by evaporation, a concentration much higher than the solubility of the salt is observed before nucleation and crystal growth, in agreement with the behaviour at point H_3 of the hysteresis cycle.

5 Conclusions

The behaviour, under variable humidity, of droplets of saturated NaCl salt solution is an important topic for a wide range of applications, that go well beyond atmospheric sciences.

The model presented in this paper predicts that, in a growing-shrinking cycle of a solution droplet in the atmosphere, the behaviour of the concentration, as well as that of its size (see, e.g., [12]), is characterized by a hysteresis phenomenon. The existence of a hysteresis, as shown in Section 4, is the result of the combination of two effects, that is the change in vapour pressure due to the dissolved salt (Raoult effect) and the change in solution concentration due to the salt particle size inside the droplet (Ostwald-Freundlich law), whereas the Kelvin effect is negligible. The concentration hysteresis exhibits an X-shaped interlaced path in the (c, S) plane, characterized by a concentration decrease in both abrupt jumps of the hysteresis, that is, either at the salt deliquescence H_1H_2 or at the solute re-crystallization H_3H_4 .

On the contrary, the size hysteresis is characterized by a size increase in the first jump, but a size decrease in the second one. Also, note that the concentration decrease caused by the abrupt salt dissolution is opposite in direction to the variation that would occur had the dissolution process followed the virtual path indicated by the branch H_1H_3 of the unstable equilibria.

It is worth noting that the characteristic X-shaped form of the concentration hysteresis does not depend on the nature of the salt under study, that is, the form of this hysteresis is present whatever the salt considered. Indeed, for any hygroscopic salt it may be easily shown that point H_3 in the (c, S) plane is not found, with respect to the vertical line H_4H_1 , on the same side where point H_2 lies.

On the contrary, the X-shape never occurs in the hysteresis for the droplet size. As a matter of fact, it is evident that points H_2 and H_3 have to lie on the same side with respect to the vertical line H_1H_4 . In other words, unlike what happens to their analogous concentrations, the radii r_{deli} and r_{cryst} , which denote the size of droplets effectively containing some water, are both greater than the radius r_{dry} of the dry nucleus.

Finally note that the existence of a hysteresis in the droplet behaviour is already detectable in the twofold functional relation linking droplet size and concentration, a relation that, consisting of two branches, fails to be univocal.

The primary root of hysteretic behaviour is to be traced back to this lack of univocal behaviour.

This work is in memory of our dear friend and colleague Vincenzo Malvestuto, who passed away while still working at this paper.

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Appendix A

Expression for solubility and pressure ratio

For the sake of clarity, here we briefly refer to the derivation of equation (3) (Eq. (3.7) of [4]). We consider a solution of sodium chloride near its saturation point. An equilibrium expression for the chemical potentials of the salt in the solid $\mu_s^{(x)}$ and liquid phase $\mu_s^{(y)}$, where x denotes the number of solid salt moles and y the moles of solute. The equilibrium relation reads:

$$\mu_s^{(y)} - \mu_s^{(x)} = \frac{2M_s\varepsilon}{\rho_s r_x}, \quad (\text{A.1})$$

where M_s is the molecular weight of the salt, ε the specific surface free energy of the crystal-solution interface, r_x and ρ_s the radius and the density of the salt particle, respectively. For a saturated bulk solution, equilibrium requires equal chemical potential for the solid and liquid phase, $\mu_{s\infty}^{(x)} = \mu_{s\infty}^{(y)}$, where the label ∞ indicates any quantity of the saturated bulk solution. Also, at the same pressure and temperature, for a given chemical compound in the crystalline form we have that $\mu_{s\infty}^{(x)} = \mu_{s\infty}^{(y)}$. We hence have that equation (A.1) is also valid with the left-hand side changed into $(\mu_s^{(y)} - \mu_s^{(x)})$.

To further proceed, we use the relations linking chemical potential to the solute activity a and to the water activity a_w :

$$\mu_s^{(y)} - \mu_{s\infty}^{(y)} = RT \log \frac{a}{a_\infty}, \quad (\text{A.2})$$

$$\mu_w^{(y)} - \mu_{w\infty}^{(y)} = RT \log \frac{a_w}{a_{w\infty}}, \quad (\text{A.3})$$

from which we have:

$$\log \frac{a}{a_\infty} = \frac{2M_s\varepsilon}{RT\rho_s r_x}. \quad (\text{A.4})$$

A relation linking water activity with concentration for supersaturated solution can be obtained by fitting data (see [13]),

$$a_w = a_{w\infty} \exp[\kappa(1 - c/s_\infty)], \quad (\text{A.5})$$

where $a_{w\infty} = 0.752$ is the water activity of a NaCl saturated solution at $T = 20^\circ\text{C}$, the fitting constant is $\kappa = 0.473$, c is molality and s_∞ the molal bulk solubility.

An analytic expression for the solute activity a is obtained by re-writing the Gibbs-Duhem relation for chemical potentials in terms of the water and solute activity, thanks to equations (A.2) and (A.3):

$$Y_w d \log a_w + Y_s d \log a = 0. \quad (\text{A.6})$$

By using equation (A.5) and the definition of molality ($d \log a / d \log a_w = -1/(1. e - 3M_w s_\infty)$), we have the relation:

$$\log \frac{a}{a_w} = \frac{\kappa}{(1. e - 3M_w s_\infty)} \log c, \quad (\text{A.7})$$

obtained after integration. Since at equilibrium the normalized molality coincides with the supersolubility ratio $c = \sigma$, where $\sigma = s/s_\infty$, we can finally write:

$$\sigma = \exp \frac{\lambda}{r_x}, \quad \lambda \equiv 2. e - 3 \frac{M_w M_s s_\infty \varepsilon}{\kappa \rho_s RT} \quad (\text{A.8})$$

For NaCl at 25° , taking $\varepsilon = 276 \text{ erg/cm}^2$, gives $\lambda = 1.41 e - 7 \text{ cm}$.

Appendix B

Density, surface tension and water activity of NaCl solutions

For both unsaturated and supersaturated NaCl solutions, once the temperature has been fixed, the density may be well approximated by the following relationship (see [4], Eq. 4.2):

$$\rho(c) = \rho_w \frac{1 + M_{\text{salt}}c}{1 + (\rho_w/\rho_s)M_{\text{salt}}c}, \quad (\text{B.1})$$

where ρ_w is the density of pure water at the given temperature and ρ_s is the density of the solid salt.

As far as the surface tension of an electrolyte solution is concerned, its dependence on the molal concentration can be represented (see [4], Eq. 3.9, with a slight notation change) as:

$$\gamma(c) = \gamma_w(1 + hc/s^*), \quad (\text{B.2})$$

where γ_w is the surface tension of pure water against air and h a dimensionless positive constant, depending on the salt, typically comprised between 0.1 and 0.2. Here the value of the constant h is 0.139.