Direct Measurements of the Deliquescence Relative Humidity in Salt Mixtures Including the Contribution from Metastable Phases

Inge Röig-Dalgaard*

ABSTRACT: Accelerated salt-induced deterioration occurs by frequent changes across the equilibrium relative humidity (RHeq). Therefore, knowledge of the actual RHeq of a salt mixture has a major impact on preventive conservation to ensure that the relative humidity (RH) does not cause a salt-phase transition. In addition, knowledge of the RHeq is essential in relation to in situ desalination as the dissolution of salt is an essential criterion to enable transport of salt (ions) in materials. For decades, it has been possible to determine the RHeq in salt mixtures with thermodynamic-based ECOS-Runsalt software. However, the ECOS-Runsalt model is challenged by the influence of kinetics along with some limitations in regard to possible ion types and combinations. A dynamic vapor sorption (DVS) instrument is used for the direct measurement of RHeq and to deduce knowledge on the physicochemical nonequilibrium process related to the phase changes in salt mixtures. The experimentally measured RHeq values in this study of NaCl–Na2SO4–NaNO3, NaNO3–Na2SO4, NaCl–NaNO3, NaCl–Na2SO4, and (NH4)2SO4–Na2SO4 are in agreement with values from the literature. A comparison with thermodynamically calculated results makes it probable that the phase transition for some salts is significantly influenced by nonequilibrium conditions. The present work bridges some of the existing gaps in regard to improving the accuracy of ECOS-Runsalt, including the effects of kinetics and the possible ions and combinations that may be found in situ. The proposed method makes it possible to determine a more representative RHeq in relation to real conditions for the improved treatment of salt-infected constructs.

INTRODUCTION

Natural changes in climatic conditions as a consequence of seasonal changes may promote the transport of salts (ions), and result in damaging salt-phase changes.1–3 Even timely limited climatic changes (a few hours) may result in salt-phase transitions.4 These salt-phase changes may be avoided or reduced by preventive conservation, such as predicting the equilibrium relative humidity (RHeq) and following the establishment of favorable climatic conditions.5–7 A few examples from praxis, where favorable climatic conditions have been established in terms of climatic chambers to reduce salt-induced wall painting deterioration, can be observed in the Scrovegni Chapel in Padua, Italy, and the Kirkerup, Magleby, Rerby, and Sore Monastery churches in Denmark.

In regard to in situ desalination campaigns, the supply of water has, in many cases, resulted in the redistribution of salt ions and their penetration to various depths,8 e.g., ref 9 is related to the fundamental limitation of this dissolution methodology, which prevented the desired desalination effect. Therefore, for desalination campaigns, knowledge of the RHeq to ensure the dissolution of salts with the lowest possible water supply is desirable.10

For single salts, the RHeq is and has been well defined for decades.12 An example of direct measurements of the RHeq for a single salt is outlined in ref 12. Here, the RHeq of the single salt NaCl is determined with X-ray diffraction under controlled conditions of temperature and relative humidity-X-ray diffraction (RH-XRD), and the disappearance of the respective educt phase peaks in the XRD patterns is used as a criterion for the determination of RHeq along with the reaction time until RHeq.

Regarding salt mixtures, some RHeq values are available in the literature, e.g., given in ref 13, and most two- and three-component salt mixtures can be thermodynamically calculated.5,13–17 However, due to the current comprehensive possibilities, not all combinations are available in the literature. Salt mixtures typically found in historic buildings are even more...
complex and are not limited to three-component salt mixtures. In the conservation science community, thermodynamically based software ECOS-Runsalt is becoming increasingly popular to predict the $R_{Heq}$ of very complex salt mixtures based on measured ionic compositions (in mole or weight) from extracted samples. ECOS-Runsalt software is very user-friendly but is also known to have some limitations in regard to possible ion combinations since it relies on equilibrium conditions that do not include metastable phases. A previous contribution to the direct measurement of the $R_{Heq}$ of single- and two-salt aerosol systems was shown in ref 13 and executed in a cell that could be evacuated and backfilled with water vapor; the phase transformation of the aerosol particle was monitored by laser light scattering. The RH at the transition point was determined by direct measurement of the water vapor pressure in the cell. In addition, they developed a theoretical model for determination by direct measurement of the water vapor pressure of the RH at the transition point was determined by direct measurement of the water vapor pressure in the cell. In addition, they developed a theoretical model for composition and temperature dependence. Another technique used to measure the RH$_{eq}$ of salts is the use of a dynamic vapor sorption (DVS) instrument. In ref 21, it was made probable to determine the RH$_{eq}$ of single salts with a DVS instrument by measuring mass changes during a constantly changing partial pressure across the point of zero mass changes that define RH$_{eq}$. To improve the accuracy of the RH$_{eq}$ for single-salt results, a methodology was developed that took the properties of single salts into account. This work was extended to include salt mixtures, and some preliminary examinations were reported in ref 23.

The present work makes use of the highly accurate calibration of the DVS instrument described in ref 22 to obtain a highly accurate and direct measurement of RH$_{eq}$ for salt mixtures of NaCl, NaNO$_3$, Na$_2$SO$_4$, and (NH$_4$)$_2$SO$_4$. The determination of the RH$_{eq}$ of salt mixtures of NaCl, NaNO$_3$, and Na$_2$SO$_4$ salts is chosen since these results can be compared with results from the literature just as results from the thermodynamically based ECOS-Runsalt program and the improved model presented in ref 24 based on an extended Pitzer formalism on the ion interaction for calculating water activity. The salt mixture (NH$_4$)$_2$SO$_4$ is studied in the present work as an example of a salt that cannot be dealt with in thermodynamically based ECOS-Runsalt software or in the improved model in ref 24 without updating the associated library, and comparisons are, therefore, only possible with experimental results. These new measurement results, along with comparisons with previous experimental results and the results from thermodynamically based ECOS-Runsalt software and the improved model described in ref 24 form the basis for a discussion and assessment of the present suggested methodology for the direct measurement of the RH$_{eq}$ in salt mixtures that includes the contribution of metastable phases.

### EFFECT OF ADDITIONAL SALTS ON THE RH$_{EQ}$

**Salt Mixture Behavior on an Aerosol Scale.** On an aerosol scale, the resulting dried particle is composed of a pure salt core with the least soluble salt surrounded by a mixed salt coating. Thermodynamic analysis and experimental studies have shown that, in general, a salt is heterogeneous with varying thicknesses of the core and coating related to the mass fraction of each single salt, and the core composition is solely determined by the original aerosol composition, whereas the coating is identical to the eutonic composition and is independent of the original aerosol composition. If the ambient RH increases, the size of the dried particle remains unchanged until the RH in the atmosphere becomes identical to the eutonic water activity ($a_w$).

The solid coating with an eutonic composition at the particle surface is then dissolved in the absorbed water. Due to surface tension, the remaining pure salt solid core stays at the center of the particle and is surrounded by a saturated solution of the eutonic composition. Further increasing the RH results in more water absorption by the particle, and part of the solid core of pure salt is dissolved to maintain water equilibrium between the solution and the atmosphere. At a certain RH, which is a function of the overall composition of the original particle, the solid core of pure salt is completely dissolved into the solution and the particle becomes a pure aqueous droplet.

**Salt Mixture Behavior Linked to RH and Gravimetric Changes.** In the case of at least two salts (three different ion types), a multiphase region may exist during absorption. At the deliquescence point, mutual deliquescence relative humidity (RH$_{Meq}$) is the RH at which the salt mixture starts to pick up moisture and thereby weight, and only one component in the solid mixture dissolves completely. Subsequently, the solution consists of an aqueous solution and undissolved solids following growth into a common saturated solution droplet at the second critical RH (RH$_{Scop}$) at which the dissolution is completed with increasing water vapor condensation and thereby weight gain.

An increase in the mass after the second critical RH is a consequence of continuous water droplet growth by water vapor condensation and is limited by the contact angle between the salt solution and substrate and may continue until a relatively high weight gain has been reached compared to the necessary weight gain to ensure dissolution of the salt. See Figure 1 for a visualized example of water absorption beyond the saturated solution at RH above RH$_{eq}$.

**Figure 1.** Absorption of water molecules on 25 mg of NaCl(s) followed by vapor condensation in an aluminum pan ($d = 6$ mm) at 95% RH and 25 °C; a 453% weight gain is observed. A weight gain of only 278% is needed to ensure the complete dissolution of NaCl.

The mass increase, which is only related to water vapor condensation, differs in its mass increase function from the previous phase until RH$_{Scop}$ and may therefore be differentiated with another mass increase function. This observation allows for the separation of the abovementioned two phases based on the change in the mass increase function at RH$_{Scop}$ with an increasing RH.

With a decreasing RH (desorption) from RH$_{Scop}$ evaporation from the salt mixture solution occurs simultaneously with expulsion of water, resulting in one continuously decreasing mass function until RH$_{Meq}$ is reached, which is where the salt mixture solution crystallizes. However, in ref 14, it is described that some salt mixtures are much less straightforward and termed nonideal. In such cases, with two salts (A and B) and a decreasing RH, one of the salts (A) eventually becomes saturated during one continuously decreasing mass function ($f(x_A)$) and starts to form its crystalline phase. As the RH is further reduced, more of the solid phase of salt (A) forms at
another decreasing mass function \( f'(x)_{A-B} \), and the residual solution becomes more concentrated in regard to salt (B). At a certain RH, \( RH_{AB} \), the two salts (A + B) crystallize together and form a mixed solid phase with an eutonic composition \( (RH_{AB(A+B)}) \). The \( RH_{SCEq(A+B)} \) is always lower than the \( RH_{eq} \) of the individual solutes \( (RH_{eq(A)} \) and \( RH_{eq(B)}) \).

In the following, \( RH_{eq} \) refers to \( RH_{SCEq} \) in the case of salt mixtures.

**Calculation of the Water Activity in Salt Mixtures.** The presence of additional ions impacts the solubility of each salt component. The equilibrium conditions, expressed as the water activity in salt mixtures (\( a_{mix} \)), can be found by:

\[
\ln(a_{w,mix}) = X_1Y_2\ln(a_{w,12}) + X_2Y_1\ln(a_{w,34})
\]

where \( X_1 \) and \( X_2 \) represent the cationic strength, \( Y_2 \) and \( Y_1 \) represent the anionic strength, and \( a_{w,12} \) and \( a_{w,34} \) represent the water activity in each of these two single salts.

The ionic strength (1) of each ion \( X_1 \) and \( Y_1 \) represents the cationic and anionic fractions for each component, respectively, that is

\[
X_1 = I_1/(I_1 + I_2)
\]

\[
X_2 = I_2/(I_1 + I_2)
\]

\[
Y_1 = I_3/(I_2 + I_4)
\]

\[
Y_2 = I_4/(I_2 + I_4)
\]

This effect is opposite to the common ion effect and is called the "secondary salt effect". If additional ions are dissolved, the total ionic concentration of the solution increases and interionic attractions become important. Water activities in salt mixtures are therefore reduced compared to the stoichiometrically measured concentrations in solution including only the dissolution of one salt.27

**\( RH_{eq} \) in Praxis.** In relation to the determination of the water activity in a solution by measurement, just as for many practical applications, the equilibrium conditions and ideal behavior of water vapor may be assumed. The water activity may then be determined as:

\[
a_w = p_w/p_w^0 = \frac{1}{100} \cdot RH
\]

where \( p_w \) and \( p_w^0 \) are the water vapor pressure above the solution and the saturation vapor pressure, respectively.

Therefore, to determine the water activity of an electrolyte solution, it is sufficient to directly measure the vapor pressure or the relative humidity above a solution of known composition at a constant temperature because the water activity depends on the composition and concentration of the solution.6

Based on examinations of the \( \text{Na}_2\text{SO}_4 \) system, it is proposed that systems including hydrated states should incorporate additional phase equilibria that include the hydration reaction with an equilibrium constant (\( K_{AB} \)), as shown in ref 15

\[
K_{AB} = 1/RH_{AB}
\]

where \( RH_{AB} \) refers to the specific \( RH_{eq} \) for the hydration-dehydration equilibrium. According to ref 6, most salts found in building materials form different hydrates.

**DVS Instrument and Determination of the \( RH_{eq} \).** The introduction of a material sample into a sample chamber in a DVS instrument with connected software enables us to change and program the climatic conditions (temperature, air flow, and continuously changing RH) surrounding the material sample and simultaneously monitor and record gravimetric changes (see Figure 2 for a schematic of the DVS instrument (DVS Advantage 1, Surface Measurements Systems, Alperton London, United Kingdom)).

The RH can be secured and measured with two independent systems: (1) a mixture of dry and moist air through valves based on prior calibration with single salts (termed open loop) and (2) a direct measurement with a dew point analyzer within the sample chamber (termed closed loop). The accuracy of the open-loop system is checked through calibration tests and performed with single salts covering RH values from 11 to 93% (\( \text{LiCl} \); \( \text{MgCl}_2 \); \( \text{Mg(NO}_3\text{)}_2 \); \( \text{NaCl} \); \( \text{KNO}_3 \)). The salt calibration principle is based upon the principle that the vapor pressure above a saturated salt solution is constant at a particular temperature (eq 6) and may reach equilibrium with its surroundings. For a more comprehensive description of the instrument, see ref 22.

When the actual RH approaches \( RH_{eq} \), the total reaction time increases. When the total reaction time is high (shown for \( t > 2.5 \) h but dependent on salt type), the empirical kinetic equation can be linearized to interpolate the equilibrium conditions (where \( dm/dt = 0 \))22

\[
\frac{dm}{dRH} = c(RH - RH_{eq})
\]
where \( dm \) is the change in the sample mass, \( dR \) is the change in the relative humidity, and \( c \) is an experimentally determined constant.

Furthermore, since each salt differs in atomic composition, thereby resulting in different sizes, atomic structures, etc., each salt also differs in its properties, namely, its water absorption and desorption properties. Therefore, individual salt calibration tests were combined together with the specified salt preparation method in ref 22 to perform a highly accurate calibration. Among others, this takes into account variations of salt crystal size, which influence the \( R_{eq} \).2,29

The salt calibration methods incorporate the following salt properties that influence calibration: the heat of solution, heat of condensation, and kinetics connected to the salt-phase transition. These properties influence the microclimate surrounding the salts during calibration. In addition, both systems (open and closed) are used to ensure and measure the RH within the DVS, thereby supplementing each other and making the RH measurements as accurate as possible.

To achieve a highly accurate direct determination of the \( R_{eq} \), the measured values are adjusted with an experimentally determined difference between the measured values and the well-defined reference values11 for single salts, as described in ref 22.

\section{Materials and Methods}

Preparation of Salt Mixtures. The approach was used to saturate salt solutions, i.e., the solution was saturated with respect to both or all three salts. This saturation was executed by adding the amount of salt corresponding to the solubility of each single salt at 100 °C.10 See Table 1 for the salts and amounts used for each salt mixture.

Table 1. Masses of Each Single Salt Added to 100 mL of Distilled Water for the Preparation of the Salt Mixture

| Salt Mixture               | NaCl (g) | NaNO3 (g) | Na2SO4 (g) | (NH4)2SO4 (g) |
|----------------------------|----------|-----------|------------|---------------|
| NaCl−Na2SO4−NaNO3         | 39.1     | 180       | 42.7       |               |
| NaCl−NaNO3                | 39.1     | 180       | 42.7       |               |
| NaNO3−Na2SO4              | 39.1     | 180       | 42.7       |               |
| NaCl−Na2SO4               | 39.1     | 180       | 42.7       |               |
| (NH4)2SO4−Na2SO4          | 42.7     | 103.8     |            |               |

The salt mixtures were prepared by the addition of the salts into 100 mL of distilled water in a 1 L beaker. The beaker was placed in a pot with boiling water and covered with a slightly curved transparent watch glass on the top. The solution was heated until a temperature of approximately 100 °C was obtained or until nucleation occurred at the surface of the solution, whereupon the beaker was removed from the pot. Next, a small amount of the hot solution was poured into a Petri dish and placed in a fume hood to accelerate evaporation. Over time, crystals formed at the surface and gradually fell to the bottom of the beaker. After complete evaporation of the water, the salt crystals were collected.

Measuring Methods. The measured \( R_{eq} \) was influenced by kinetics and the initial state of the salt, and therefore, the measuring methodology influenced the result in terms of accuracy. The most influential measuring conditions in ref 22 were found to be the preconditioning of the salts. Preconditioning was related to the needed addition of water to the dry salt until \( R_{eq} \) was obtained (see Table 2), and the reasoning was extensively described in ref 22. The initial RH interval was centered around the \( R_{eq} \) found in the literature as an initial approach for the measurement. In case a nonsatisfactory fit with eq 8 was found, an \( R_{eq} \) was read out of the measuring data and subsequently became the center of a new measuring interval. See Table 2 for the used salt preconditioning and measuring conditions.

It should be noted that in most cases, the same measurement duration and RH interval were used. However, to obtain a satisfactory fit with the link described in eq 8, it was necessary to adjust the measurement duration and size of the RH interval in relation to the salt mixture \((NH_4)_2SO_4−Na_2SO_4\). Such adjustments of the measurement duration and RH interval have also been made, when relevant, in previous work.22

\section{Results and Discussion}

Checking the Generated RH in the DVS Instrument by Single-Salt Calibration Tests. Initial salt calibration tests on well-defined single salts are used to ensure the accuracy of the results for salt mixtures. Highly accurate salt calibration tests were carried out following the procedure described in ref 22. Of special relevance are the salt calibration tests for the RH interval in which the salt mixtures are expected to have a \( R_{eq} \) of 55–85% RH. Therefore, calibration tests were carried out with single salts of Mg(NO3)2 and NaCl (see Figure 3). The average measured difference from the reference value in ref 11 and the deviation in the identically performed experiment reveals a measuring inaccuracy between the experimentally determined values and the well-defined values in the literature. Since the single salts used for calibration purposes have well-defined \( R_{eq} \) values and since the determined results in this study are found to have high accuracy, differences between the measured and reference results can be used to recalculate an accurate \( R_{eq} \) \((R_{eq,cal,DVS})\) with the average measured difference. This approach is used in the following. A difference of 0.77% RH and 0.72% RH is found between the well-defined reference values from ref 11 and the determined \( R_{eq} \) for Mg(NO3)2 and NaCl in this study, respectively. Measured salt mixtures with an \( R_{eq} \) of approximately 52 and 75% RH are therefore recalculated to measure the deliquescence point with an added 0.77 ± 0.15% and 0.72 ± 0.12% RH, respectively \((R_{eq,cal,DVS}) = R_{eq,measured} + RH_{diff,relevant} \). It should be noted that the found \( RH_{diff,relevant} \) differs in relation to the actual calibration of the DVS instrument.

Determination of the \( R_{eq} \) in Salt Mixtures. The general definition of \( R_{eq} \) is the RH at which an absence of mass change exists, provided the temperature is constant. This criterion can and is also applied to salt mixtures since the temperature and the mass fraction of each salt in the mixture is constant.
The measured RH\textsubscript{eq} values for NaCl–Na\textsubscript{2}SO\textsubscript{4}–NaNO\textsubscript{3}, NaCl–NaNO\textsubscript{3}, NaNO\textsubscript{3}–Na\textsubscript{2}SO\textsubscript{4}, NaCl–Na\textsubscript{2}SO\textsubscript{4}, and (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}–Na\textsubscript{2}SO\textsubscript{4} are shown in Table 3. Each measurement was performed in triplicate, thereby allowing the calculation of an average value and deviation. The reproducibility is high for all five salt mixtures, and a standard deviation of ±0.006 to 0.08% RH is obtained (Table 3). This relatively low standard deviation is obtained by ensuring a constant mass change (d\textsubscript{m}) per change in RH (dRH), enabling the determination of the constant c in eq 8 and minimizing the experimental error in the determined RH\textsubscript{eq}. Furthermore, the constant c enables an accurate determination of the intersection with the y-axis (see Figure 4), showing an absence of the mass change at a specific RH, which is the definition of RH\textsubscript{eq}. An example of the measurement output data is shown in Figure 4. In Figure 5, the recalculated measured results are pictured together with results from the literature and the ECOS-Runsalt-calculated results to obtain an overview and to clarify the differences and similarities among the various RH\textsubscript{eq} determination methods. Meanwhile, it is essential to notice that the chosen RH interval in ECOS-Runsalt has a significant influence on the results since this model does not include kinetic effects (see the “ECOS-Runsalt and Kinetics (Influence from the Chosen RH Interval)” section). The recalculated RH\textsubscript{eq} values are the average measured values ± the measured difference from the reference values (shown in Figure 3).

The measured RH\textsubscript{eq} values for NaCl–Na\textsubscript{2}SO\textsubscript{4}–NaNO\textsubscript{3}, NaCl–NaNO\textsubscript{3}, NaNO\textsubscript{3}–Na\textsubscript{2}SO\textsubscript{4}, NaCl–Na\textsubscript{2}SO\textsubscript{4}, and (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}–Na\textsubscript{2}SO\textsubscript{4} are shown in Table 3. Each measurement was performed in triplicate, thereby allowing the calculation of an average value and deviation. The reproducibility is high for all five salt mixtures, and a standard deviation of ±0.006 to 0.08% RH is obtained (Table 3). This relatively low standard deviation is obtained by ensuring a constant mass change (d\textsubscript{m}) per change in RH (dRH), enabling the determination of the constant c in eq 8 and minimizing the experimental error in the determined RH\textsubscript{eq}. Furthermore, the constant c enables an accurate determination of the intersection with the y-axis (see Figure 4), showing an absence of the mass change at a specific RH, which is the definition of RH\textsubscript{eq}. An example of the measurement output data is shown in Figure 4. In Figure 5, the recalculated measured results are pictured together with results from the literature and the ECOS-Runsalt-calculated results to obtain an overview and to clarify the differences and similarities among the various RH\textsubscript{eq} determination methods. Meanwhile, it is essential to notice that the chosen RH interval in ECOS-Runsalt has a significant influence on the results since this model does not include kinetic effects (see the “ECOS-Runsalt and Kinetics (Influence from the Chosen RH Interval)” section). The recalculated RH\textsubscript{eq} values are the average measured values ± the measured difference from the reference values (shown in Figure 3).

### Table 3. Measured and Recalculated RH\textsubscript{eq} at 25 °C

| salt mixture                | RH\textsubscript{eq} 1st run | RH\textsubscript{eq} 2nd run | RH\textsubscript{eq} 3rd run | RH\textsubscript{eq} average/deviation | RH\textsubscript{eq} recalculated |
|-----------------------------|-----------------------------|-----------------------------|-----------------------------|---------------------------------------|----------------------------------|
| NaCl–Na\textsubscript{2}SO\textsubscript{4}–NaNO\textsubscript{3} | 65.96 ± 0.16                | 65.83 ± 0.03                | 65.89 ± 0.01                | 65.89 ± 0.08                           | 66.61                            |
| NaCl–NaNO\textsubscript{3}   | 66.52 ± 0.01                | 66.19 ± 0.11                | 66.35 ± 0.14                | 66.35 ± 0.07                           | 67.07                            |
| NaNO\textsubscript{3}–Na\textsubscript{2}SO\textsubscript{4} | 72.48 ± 0.03                | 72.40 ± 0.01                | 72.53 ± 0.06                | 72.47 ± 0.03                           | 73.19                            |
| NaCl–Na\textsubscript{2}SO\textsubscript{4} (mass fraction = 0.173 Na\textsubscript{2}SO\textsubscript{4}) | 73.78 ± 0.10                | 73.73 ± 0.08                | 73.50 ± 0.05                | 73.67 ± 0.03                           | 74.39                            |
| (NH\textsubscript{4})\textsubscript{2}SO\textsubscript{4}–Na\textsubscript{2}SO\textsubscript{4} | 75.72 ± 0.07                | 75.32 ± 0.08                | 75.66 ± 0.07                | 75.57 ± 0.006                          | 76.29                            |

**Recalculated values are the average measured values ± the measured difference from the reference values (shown in Figure 3).**
and Na₂SO₄ corresponded to the solubility of each single salt at the eutonic composition, the RHₑq was determined to be 71.8 ± 0.5% RH in ref 13. In ref 14, they characterized salt mixtures into two groups: simple and less simple systems. The former is independent of the mole fractions of the salts in this study, which is in contrast to the latter. Additionally, in ref 6, it is shown with examples that the solubility, saturation coefficients and crystallization properties of salt mixtures are strongly dependent on the mixture composition. Since the RHₑq in ref 13 is not comparable with the measured result in this study, it is not shown in Figure 5. However, the difference between RHₑq (ECOS-Runsalt) and ref 13 supports the effect of the specific number of moles on RHₑq.

With the present number of moles being 3.3880, 0.66903, 2.1178, and 0.30061 for sodium, chloride, nitrate, and sulfate, respectively, RHₑq (ECOS-Runsalt) was calculated to be 66.3 with an RH interval limited to the RHₑq ± 1% based on the first scanning (see the “ECOS-Runsalt and Kinetics (Influence from the Chosen RH Interval)” section). However, to obtain a full picture of the formed salt phases, an RH interval ranging between 15 and 98% was applied in ECOS-Runsalt for the NaCl–Na₂SO₄–NaNO₃ salt system, indicating formation of darapskite (NaNO₃·Na₂SO₄·H₂O), nitratine (NaNO₃), halite (NaCl), and thenardite (Na₂SO₄), as shown in Figure 6. As described in the “Effect of Additional Salts on the RHₑq” section, at RHₑq only one component of the solid mixture dissolved completely, being a small amount of thenardite; subsequently, the composition consisted of an aqueous solution and the undissolved solids of halite and nitratine. Following the production of a common saturated solution at the second critical RH (RHₑq), dissolution was completed.

RHₑq (ECOS-Runsalt) for NaCl–NaNO₃ (specifically 2/3NaCl–3/10NaNO₃) was determined to be 67.07% RH (see Table 3). In ref 14, the RHₑq for this salt mixture was thermodynamically calculated to be 67% RH. In ref 13, the RHₑq of the NaCl–NaNO₃ salt mixture at an eutonic composition, where the composition of both salts reached their solubility limit in the solution, was measured to be 68.0 ± 0.4% RH. In ref 15, the deliquescence point was calculated for various aqueous solutions of NaCl–NaNO₃ salts. Since the above salt mixture was an aqueous solution, the results were noncomparable; however, it is noticed that the water activity was relatively strongly influenced by the molar ratio, which may also be the reason for the slightly deviating results between RHₑq (ECOS-Runsalt) and ref 14. With the present number of moles being 2.7868, 0.66903, and 2.1178 for sodium, chloride, and nitrate, respectively, the RHₑq (ECOS-Runsalt) was calculated to be 66.6% RH. According to the ECOS-Runsalt results, only halite and nitratine were present in the salt mixture; additionally, no salt hydrates formed. With the improved thermodynamically based model described in ref 24, the RHₑq was calculated to be 66.76% (by the corresponding author of ref 24). In short, RHₑq (ECOS-Runsalt) ~ RHₑq (litt[24]) < RHₑq (ECOS-Runsalt) < RHₑq (ECOS-Runsalt) (see Figure 5).

The RHₑq (ECOS-Runsalt) was determined to be 73.19% RH for NaNO₃–Na₂SO₄ (see Table 3). In ref 13, the RHₑq for NaNO₃–Na₂SO₄ was found to be 72.2 ± 0.2%, where the number of moles of NaNO₃ and Na₂SO₄ corresponded to the solubility of each single salt at an eutonic composition. Therefore, the number of moles of the above salts was not identical between the present work and ref 13. In ref 16, it was shown that for this specific salt mixture of NaNO₃–Na₂SO₄, RHₑq is a function of the total molality of NaNO₃ and Na₂SO₄. The ratio between NO₃⁻ and SO₄²⁻ significantly affects the RHₑq; thus, the RHₑq in total may vary between 55 and 85% RH. In the present work, x(NO₃) equaled 0.876. In ref 17, the RHₑq was calculated under similar (but not identical) conditions, providing x(NO₃) = 0.9 at 23.5 °C and read 73.8% RH in the graph. Applying ECOS-Runsalt and the present number of moles of 2.7190, 2.1178, and 0.30061 for sodium, nitrate, and sulfate, respectively, RHₑq (ECOS-Runsalt) was calculated to be 73.6% RH, and formation of darapskite, nitratine, and thenardite was observed. With the more advanced thermodynamically based model described in ref 24, the RHₑq was calculated to be 73.52% (by the corresponding author of ref 24); notably, taking into account the presence of darapskite, the relations become further complicated, and with a surplus of NaNO₃, as in this case, a mixture consisting solely of nitratine and darapskite would come into existence. Therefore, RHₑq (ECOS-Runsalt) ~ RHₑq (litt[24]) > RHₑq (ECOS-Runsalt).

The recalculated RHₑq (RHₑq (ECOS-Runsalt)) for NaCl–Na₂SO₄ (specifically 2/3NaCl–3/10Na₂SO₄) was determined to be 74.39% RH (see Table 3). This result was consistent with and
did not significantly differ from the RH<sub>eq</sub> found by ref 13, 74.2 ± 0.3% RH (RH<sub>eq(lit`[13])</sub>). In ref 16, aqueous solutions of NaCl–Na<sub>2</sub>SO<sub>4</sub> salts and their water activity were found to be relatively limited due to the molar ratios of Cl<sup>−</sup> and SO<sub>4</sub><sup>2−</sup>.

With the present number of moles of 1.2703, 0.66903, and 0.30061 for sodium, chloride, and sulfate, respectively, the RH<sub>eq</sub> (ECOS-Runsalt) was calculated to be 74.33%. With the improved thermodynamically based model described in ref 24, the RH<sub>eq</sub> was calculated to be 74.33% (by the corresponding author of ref 24). Therefore, RH<sub>eq</sub> (ECOS-Runsalt) ∼ RH<sub>eq</sub> (ref 24).

Furthermore, the results for RH<sub>eq(ref DVS)</sub>NaCl–Na<sub>2</sub>SO<sub>4</sub> and RH<sub>eq(ref DVS)</sub>(NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> clarified that it was possible to measure a significant difference in the RH<sub>eq</sub> between NaCl (75.29 ± 0.12% RH) and NaCl–Na<sub>2</sub>SO<sub>4</sub> (74.2 ± 0.3% RH), with two salts having an RH<sub>eq</sub> relatively close to each other. This possible differentiation between salts with RH<sub>eq</sub> values relatively close to each other was made possible by the high reproducibility of the RH<sub>eq(ref DVS)</sub> Results that had an accuracy of 0.12% RH (see Figure 3).

The RH<sub>eq(ref DVS)</sub> for (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>–Na<sub>2</sub>SO<sub>4</sub> (mass fraction of 0.173 in regard to Na<sub>2</sub>SO<sub>4</sub>) was determined to be between 75.20 and 76.20% RH based on electrodynamic particle balance measurements of the water activities of highly concentrated solutions and from the phase diagram in ref 25. This result was in agreement with the RH<sub>eq(ref DVS)</sub> of 76.29% RH with a similar mass fraction of 0.173 in regard to Na<sub>2</sub>SO<sub>4</sub>.

These results cannot be compared with the calculated RH<sub>eq</sub> from ECOS-Runsalt software, as this ion-type NH<sub>4</sub> is not included or used as a default in the improved model in ref 24. ECOS-Runsalt was developed using the molality-based thermodynamic approach of Pitze<sub>19,20</sub> and calculates in regard to mole fractions; thus, ECOS-Runsalt is restricted to the mole fractions of salts that are most commonly encountered in conservation: Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>2+</sup>, Ca<sup>2+</sup>, Cl<sup>−</sup>, NO<sub>3</sub><sup>−</sup>, SO<sub>4</sub><sup>2−</sup>, and H<sub>2</sub>O and excludes mixtures containing both Ca<sup>2+</sup> and SO<sub>4</sub><sup>2−</sup>. Notably, model parameters are provided and validated for the Na<sup>+</sup>–K<sup>+</sup>–Cl<sup>−</sup>–NO<sub>3</sub><sup>−</sup>–SO<sub>4</sub><sup>2−</sup>–H<sub>2</sub>O system in the improved model in ref 24. The need to exclude mixtures containing both Ca<sup>2+</sup> and SO<sub>4</sub><sup>2−</sup> in ECOS-Runsalt is related to practical limitations, as one frequently comes across this combination in praxis. However, this and other limitations are reported to be caused by the fact that it was not possible to refine the system to the extent that had originally been envisaged within the project period.<sup>20</sup>

Having shown consistency among the measured experimental data in this study by the use of the DVS instrument, measurements, and calculations from the literature and thermodynamically calculated values from the ECOS-Runsalt model and improved model in ref 24 for a mixture consisting of up to three salts, the determined RH<sub>eq</sub> with the DVS instrument seemed to be generally valid. According to refs<sup>19,20</sup>, data for quaternary (four ions) or higher mixtures are not required for the parameterization of the model, as experience has shown that the modeling of the thermodynamic properties of multicomponent electrolyte mixtures only requires two or three particle interactions.

**ECOS-Runsalt and Kinetics (Influence from the Chosen RH Interval).** In ECOS-Runsalt, it is assumed that the entire salt system is in equilibrium with its surroundings at all times,<sup>19,20</sup> and therefore does not include the effect of kinetics. However, for some salt mixtures, the kinetics significantly influence the growth of crystals. The kinetics is primarily influenced by the difference between the ambient conditions and equilibrium conditions (RH<sub>actual</sub> − RH<sub>eq</sub>); however, for some salts, the temperature is also of major importance. A visual example of the kinetics influence on deliquescence is shown in Figure 7.

The existence of metastable phases as a consequence of nonequilibrium conditions also influences salt formation. For example, the phase diagram for the binary system of Na<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O is significantly more complex than originally predicted. Experimental investigations can document the existence of two metastable phases, which are caused by the influence of kinetics. In equilibrium models, metastable phases are not predicted. However, in ref 15, metastable equilibrium is incorporated in the thermodynamic models to simulate the existence of metastable phases, which is a necessary part of the Na<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>O system, thereby obtaining a full picture for understanding deterioration mechanisms.

Figure 7. Visualization of the kinetic influence (ΔRH) on a salt (NaCl)-phase transition studied by the application of a cooling stage in an ESEM: (a) reference equilibrium conditions and (b) influence of a change of 0.1% RH for 19 h.31
crystallization of the anhydrous phases proceeds at higher rates than the precipitation of the hydrates. Therefore, the formation of the anhydrous phase is particularly favored at low relative humidity." Since the contribution from metastable phases is not included in the thermodynamically based ECOS-Runsalt model, the presence of metastable phases results in deviating results for the RHeq (ECOS-Runsalt).

To overcome the kinetic influence when using ECOS-Runsalt, it is proposed to apply the same approach, as elaborated for the high accuracy determination of the RHeq for single salts described in ref 22. First, the widest possible RH interval is examined to obtain a rough estimate of the RHeq, first scan followed by the use of the smallest possible interval around the RH (ECOS-Runsalt) was included, RHeq (ECOS-Runsalt) to obtain a more robust result minimizing the kinetic influence. Further it was shown that it might have a significant influence whether the RH interval is 15–98 or 15–95% RH (see Figure 8).

Figure 8. Examination of how the chosen RH interval in ECOS-Runsalt affects the determined RHeq. White square box: the widest possible RH interval being 15–98% (also termed the first scan), dark gray square box: the RH interval limited to 15–95%, and bright gray square box: the RH interval limited to the RHeq ±1% based on the first scan.

Figure 8 shows a significant difference in the RHeq between the calculated results obtained with the widest possible RH interval (15–98%) and the RH interval limited to the RHeq ±1% based on the first scan of 1.5 and 1.2% RH for NaCl–Na2SO4–NaNO3 and NaCl–Na2SO4, respectively. Both salt mixtures form hydrated states according to ECOS-Runsalt. These significant differences can be fully accounted for by following the approach in ref 15, and include a hydration constant of 1/RH (eq 7). Thus, in the NaCl–Na2SO4–NaNO3 salt mixture, a constant for the hydrated phase (caused by the presence of darapskite) was included, RHeq (ECOS-Runsalt including the hydrated phase) = RHeq (ECOS-Runsalt) + 1/RH (ECOS-Runsalt, NaCl–Na2SO4–NaNO3) = 64.8% + 1/0.648 = 66.34% ~ RHeq ±1% = 66.3. Also, when including the hydration constant for the NaCl–Na2SO4 salt mixture, consistency is found between RHeq (ECOS-Runsalt including the hydrated phase) = 74.47% ~ RHeq ±1% = 74.3.

The salt mixture NaNO3–Na2SO4 also formed a hydrated salt (darapskite), and differing by 0.6% RH was dependent on if the RH interval was 15–98% or limited to RHeq ±1%. Taking the hydration constant into account, as proposed in ref 15, as a consequence of the presence of darapskite, RHeq (ECOS-Runsalt including the hydrated phase) = 74.37%. The RHeq (ECOS-Runsalt including the hydrated phase) = 73.98% RH based on results obtained for the interval 15–95% RH ~ RHeq ±1% = 73.6%. It may be considered that the hydration constant should be related to the concentration of the solution, as this would influence the chemical potential, which again would influence the activity, a(w) as stated in ref 6. In ref 6, aqueous solutions of the salt NaNO3–Na2SO4 showed that the water activity was strongly influenced by the molar ratio.

In the case of NaCl–NaNO3, ECOS-Runsalt did not predict the formation of hydrated salts, and a hydration constant was therefore not included; and the difference between the result with the RH interval 5–98% and RHeq ±1% was limited to 0.1% RH.

The ECOS-Runsalt model was validated with water activity measurements. Direct vapor pressure measurements were obtained above single-salt solutions (a deviation of approximately 0.2%). Attempts were also made to use standard RH and T sensors for the measurements of water activities with a sensor. A Testo 601 instrument (Testotherm) was used to test solutions of LiCl and NaCl and standard solutions of known water activity. The deviations for these measurements were approximately 3–4% RH, and the authors described that such a deviation was insufficient to obtain water activities or osmotic coefficients with the accuracy required for the determination of binary model parameters. However, they reported that this type of measurement was much less time consuming than direct measurements and might be helpful for model validation.19,20

Therefore, it may be argued that the reason for the ECOS-Runsalt calculation of RHeq deviating from RHeq measured with the DVS instrument and the experimental results from the literature is caused by the following: (1) equilibrium conditions are assumed at all times and do not include hydration reactions and (2) the precision of the validation data. However, applying the presently used approach, to have a first scan of the widest possible RH interval as an input for subsequently applying the RHeq ±1% interval, it seems feasible to minimize the kinetic influence.

The abovementioned assumptions are further supported by the fact that the improved thermodynamically based model described in ref 24 provides results that differ by only ±0.33% RH from the measured RHeq (re-cal DVS) for three out of the five salt mixtures in this study; thus, it is possible to calculate with the proposed model.

### CONCLUSIONS

The present work contributes to enabling a more accurate determination of RHeq in salt mixtures, thereby preventing or minimizing accelerated salt-induced deterioration. This determination is through the direct measurement of RHeq in salt mixtures utilizing a DVS instrument. As a consequence of using a previously developed methodology for highly accurate calibration of the equipment, it is possible to determine RHeq with similar high accuracy (<0.2% RH).

The direct measurements of RHeq take into account the fractioning of salts in mixtures, which has been recently reported to influence RHeq due to metastable phases.

There was consistency among the measured experimental data in this study with the DVS instrument, experimentally measured data and thermodynamically based calculations from the literature, and thermodynamically calculated values by the ECOS-Runsalt model and an improved thermodynamically based model for a mixture consisting of two or three salts. This consistency was found for all five salt mixtures that were studied (NaCl–Na2SO4–NaNO3, NaCl–NaNO3, NaNO3–Na2SO4, NaCl–Na2SO4, and (NH4)2SO4–Na2SO4), and the use of the DVS instrument for the determination of RHeq seemed to be...
generally valid. This result makes it possible to directly measure the RH<sub:eq</sub> in salt mixtures with an arbitrary number of ion types, which would occur in real-world, in-situ applications. Therefore, the proposed methodology could be the advancement needed for the accurate determination of RH<sub:eq</sub> and for subsequent decisions on favorable climatic conditions to avoid or reduce phase transitions without restricting validity to specific ion types and combinations.

Through the proposed direct measurements of RH<sub:eq</sub> of salt mixtures forming hydrates, it was identified that the use of thermodynamically based ECOS-Runsalt software, in some cases, resulted in significantly different RH<sub:eq</sub> values, if focus on the kinetics was not included. This observation was found when comparing the experimentally determined RH<sub:eq</sub> in this work with the experimentally determined results from previous research and with the improved thermodynamically based model described in ref 24. This result may be explained by the fact that in the ECOS-Runsalt model, equilibrium conditions were assumed at all times and did not include the contribution of metastable phases together with the precision of the validation data. Additionally, some ions (e.g., NH<sub>4</sub><sup>+</sup>) and combinations of ions (Ca<sup>2+</sup> and SO<sub>4</sub><sup>2-</sup>) were not included in ECOS-Runsalt software. Thus, some limitations of ECOS-Runsalt software were revealed. However, ECOS-Runsalt software provides fast results on RH<sub:eq</sub> creating a reasonable overview of the present phases. Further, the present direct measurement of RH<sub:eq</sub> in salt mixtures utilizing a DVS instrument enabled to propose a new approach when using ECOS-Runsalt, which seems to result in more accurate results if focus on the kinetics is included by choosing the appropriate RH interval.

Finally, having the possibility to determine the RH<sub:eq</sub> including the metastable contribution in salt mixtures may be of value for obtaining new theoretical insights.

**AUTHOR INFORMATION**

**Corresponding Author**

Inge Rörg-Dalgaard — Department of Civil Engineering, Technical University of Denmark, 2800 Kgs. Lyngby, Denmark; orcid:0000-0002-0977-4630; Email: ird@byg.dtu.dk

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.1c00538

**Funding**

This project was financially supported by the Aage and Johanne Louis-Hansen Foundation.

**Notes**

The author declares no competing financial interest.

**ACKNOWLEDGMENTS**

Clifford Price is acknowledged for providing access to the executable ECOS file and Michael Steiger is acknowledged for constructive comments on the manuscript.

**REFERENCES**

(1) Arnold, A.; Zehnder, K. Monitoring Wall Paintings Affected by Soluble Salts. In The Conservation of Wall Paintings; Cather, S., Ed.; The Getty Conservation Institute: London, 1991; pp 103–135.

(2) Gupta, S.; Pel, L.; Kopinging, K. Crystallization behavior of NaCl droplet during repeated crystallization and dissolution cycles: An NMR study. J. Cryst. Growth 2014, 391, 64–71.

(3) Flatt, R. J.; Mohamed, N. A.; Carusoc, F.; Derluyn, H.; Desarnaud, J.; Lubelli, B.; Espinosa-Marzal, R. M.; Pel, L.; Rodriguez-Navarro, C.; Scherer, G. W.; Shahidzadeh-K; Steiger, M. Predicting salt damage in practice: A theoretical insight into laboratory tests. RILEM Tech. Lett. 2017, 2, 108–118.

(4) Sawdy, A.; Heritage, A. Evaluating the influence of mixture composition on the kinetics of salt damage in wall paintings using time lapse video imaging with direct data annotation. Environ. Geol. 2007, 52, 303–315.

(5) Laue, S.; Schaab, C.; Dresse, D.; Krauthäuser, D.; Hellmeieger, G.; Vogl, J. Long-term investigations and monitoring of the salt loaded Crypt of St. Maria im Kapitol, Cologne. In Monument Future: Decay and Conservation of Stone, Siegsemsd, M.; Middendorf, B., Eds.; Mitteledterleuscher Verlag, 2020; pp 345–350.

(6) Steiger, M. Salts in porous materials: Thermodynamics of phase transitions, Modeling and preventive Conservation. Restor. Build. Monuments 2005, 11, 419–432.

(7) Bollingtoft, P.; Larsen, P. K. In The Use of Passive Climate Control to Prevent Salt Decay in Danish Churches, Mauersalze und Architektur: Tagungsbeiträge, Leitner, H.; Laue, S.; Siedel, H., Eds.; 2002; pp 90–93.

(8) Brajer, I.; Larsen, P. K. In The Salt Reduction Treatment on the Wall Paintings in Tristred Church, Salt Weathering on Buildings and Stone Sculpture, Ottoson, L. M.; Ottoson, L. M.; Rörg-Dalgaard, I.; Larsen, P. K.; Brajer, I.; Bollingtoft, P.; Marciniak, M.; Svane, M., Eds.; 2008; pp 219–228.

(9) Pel, L.; Sawdy, A.; Voronina, V. Physical principles and efficiency of salt extraction by poulticing. J. Cult. Herit. 2010, 11, 59–67.

(10) Rörg-Dalgaard, I. Desalination for Preservation of Murals by Electromigration and Regulated Climate. In Structural Studies, Repairs and Maintenance of Heritage Architecture XI, Brebbia, B. A., Eds.; WIT Press: 2009; Vol. 109, pp 71–82.

(11) Greenspan, L. Humidity Fixed Points of Binary Saturated Aqueous Solutions. J. Res. Natl. Bur. Stand. 1977, 81A, 89–96.

(12) Linnow, K.; Steiger, M. Determination of equilibrium humidities using temperature- and humidity-controlled X-ray diffraction (RH-XRD). Anal. Chem. Acta 2007, 583, 197–201.

(13) Tang, I. N.; Munkelwitz, H. R. Aerosol Phase Transformation and Growth in the Atmosphere. J. Appl. Meteorol. 1994, 33, 791–796.

(14) Ge, Z.; Wexler, A. S.; Johnston, M. V. Deliquescence Behavior of Multicomponent Aerosols. J. Phys. Chem. A 1998, 102, 173–180.

(15) Steiger, M.; Asmussen, S. Crystallization of sodium sulfate phases in porous materials: The phase diagram Na<sub>2</sub>SO<sub>4</sub>-H<sub>2</sub>O and the generation of stress. Geochim. Cosmochim. Acta 2008, 72, 4291–4306.

(16) Clegg, S. L.; Brimblecombe, P.; Liang, Z.; Chan, C. K. Thermodynamic Properties of Aquous Aerosols to High Supersaturation: II-A Model of the System Na<sup>+</sup>-Cl<sup>-</sup>-NO<sub>3</sub><sup>-</sup>-SO<sub>4</sub><sup>2-</sup>-H<sub>2</sub>O at 298.15 K. Aerosol Sci. Technol. 1997, 27, 345–366.

(17) Lindström, N.; Heitmann, N.; Linnow, K.; Steiger, M. Crystallization behavior of NaNO<sub>3</sub>-Na<sub>2</sub>SO<sub>4</sub>, salt mixtures in sandstone and comparison to single salt behavior. Appl. Geochem. 2015, 63, 116–132.

(18) De Clercq, H. The Effect of Other Salts on the Crystallization Damage to Stone Caused by Sodium Sulphate, In Salt Weathering on Buildings and Stone Sculpture, Ottoson, L. M.; Rörg-Dalgaard, I.; Larsen, P. K.; Brajer, I.; Bollingtoft, P.; Marciniak, M.; Svane, M., Eds.; 2008; pp 307–316.

(19) Bionda, D. RUNSALT - A graphical user interface to the ECOS thermodynamic model for the prediction of the behaviour of salt mixtures under changing climate conditions, 2005. http://science.sdf-eu.org/runsalt/.

(20) An Expert Chemical Model for Determining the Environmental Conditions Needed to Prevent Salt Damage in Porous Materials. In European Commission Research Report 11, (Protection and Conservation of European Cultural Heritage), Price, C. A., Eds.; Archetype Publications: London, 2000; pp 1–136.

(21) Rörg-Dalgaard, I. Determination of the Deliquescence Point in Salt Mixtures by Utilizing the Dynamic Vapour Sorption Method, In The 3th International Workshop on Crystallization in Porous Media, Diaz, T. Eds.; 2012; pp 37–38.
(22) Rörig-Dalgaard, I.; Svensson, S. High accuracy calibration of a dynamic vapor sorption instrument and determination of the equilibrium relative humidity of single salts. *Rev. Sci. Instrum.* **2016**, *87*, No. 054101.
(23) Rörig-Dalgaard, I. Determination of the Deliquesce Point in Salt Mixtures and in In Situ Multicomponent Salts with DVS Equipment, In *Salt Weathering on Buildings and Stone Sculptures 2014*, De Clercq, H., Eds.; 2014; pp 223–236.
(24) Steiger, M.; Kiekbusch, J.; Nicolai, A. An improved model incorporating Pitzer’s equations for calculation of thermodynamic properties of pore solutions implemented into an efficient program code. *Constr. Build. Mater.* **2008**, *22*, 1841–1850.
(25) Koloutsou-Vakakis, S.; Rood, M. J. The \( (NH_4)_2SO_4-Na_2SO_4 \)-H\(_2\)O system: comparison of deliquescence humidities measured in the field and estimated from laboratory measurements and thermodynamic modelling. *Tellus B* **1994**, *46*, 1–15.
(26) Ge, Z.; Wesler, A. S.; Johnston, M. V. Multicomponent Aerosol Crystallization. *J. Colloid Interface Sci.* **1996**, *183*, 68–77.
(27) De Rijck, G.; Schreven, E. Elemental bioavailability in nutrient solutions in relation to precipitation reactions. *J. Plant Nutr.* **1998**, *21*, 2103–2113.
(28) Heng, J. Y. Y.; Williams, D. R. *Vapour Sorption and Surface Analysis, chapter 8 in Solid State Characterization of Pharmaceuticals*, 1st ed.; Storey, R. A.; Ymén, I., Eds.; Blackwell Publishing Ltd, 2011; pp 245–285.
(29) Desarnaud, J.; Shahidzadeh-Bonn, N. Salt crystal purification by deliquescence/crystallization cycling. *EPL* **2011**, *95*, No. 48002.
(30) Weast, R. C. *CRC Handbook of Chemistry and Physics 1983–1984*, 64th ed.; CRC: Boca Raton, 1983.
(31) Rörig-Dalgaard, I. Transition at the Deliquesce Point in Single Salts, In *Proceedings of the 4th International Workshop on Crystallization in Porous Media*, Shahidzadeh, N., Eds.; 2014.