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Determination of the deliquescence point in salt mixtures and in in-situ multicomponent salts with DVS equipment

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Abstract

Accelerated salt induced deterioration occurs by frequently changes across the deliquescence point. Therefore does the actual deliquescence point of the present salts have a major impact on preventive conservation being able to ensure a relative humidity not causing salt phase transition and to in-situ desalination as dissolution of the salts is the essential criterion to enable transport of salt (ions) in the construction.

In the present work deliquescence points were measured with dynamic vapor sorption (DVS) equipment in salt mixtures and the results are shown to be in agreement with values from the literature. Also in-situ-multi salt samples were measured including the difference between the second critical relative humidity and the efflorescence relative humidity being a measure for the critical supersaturation required for crystallization at the specific experimental conditions. The DVS equipment seems to be able to make accurate determinations of the deliquescence points in complex salt systems and could be an expressive determination in in-situ investigations.

Keywords: Deliquescence point, salt mixtures, second critical relative humidity, efflorescence relative humidity, DVS, critical supersaturation

1 Introduction

The precise deliquescence point in constructions is of major importance in relation to preventive conservation being able to ensure a relative humidity not causing salt phase transition and to in-situ desalination as dissolution of the salts is the essential criterion to enable transport of salt (ions) in the construction.

For single salts deliquescence points are and has for decades been well defined [1]. Regarding salt mixtures some deliquescence points are available in the literature as e.g. given in [2] though due to the comprehensive possibilities by far all combinations are available. Two and three component salt mixtures can be thermodynamically calculated [2-5]; however in-situ-multi salt mixtures are difficult to calculate. In the conservation science community is the model ECOS-Runsalt becoming increasingly popular to predict the deliquescence humidities of very complex salt mixtures. However, experimental investigations are desired for validation of the model and for illustration of kinetic effects.

In [2] the deliquescence points of salt mixtures were measured in a cell that can be evacuated and backfilled with water vapor and the phase transformation of the aerosol particle was monitored by laser light scattering. The RH at the transition point was determined by directly measuring the water vapor pressure in the cell. They also developed a theoretical model for the composition and temperature dependence of the deliquescence properties for single- and two-salt aerosol systems.

In preliminary work [6] it was made probable to determine the deliquescence point of single salts with dynamic vapor sorption (DVS) equipment by measuring mass changes during constantly changing partial pressure. In the present work the accuracy of the equipment was determined by salt calibration validation test with single salts. Deliquescence points were measured in salt mixtures at conditions identical to data from the literature and in in-situ-multi salt samples with DVS equipment.

2 Deliquescence point in salt mixtures and multicomponent mixtures

The presence of other ions also impacts the solubility. This effect is opposite to the common ion effect and was called the “secondary salt effect”. If other ions are dissolved, the total ionic concentration of the solution increases and interionic attractions become important. Activities become smaller than the stoichiometric or measured concentrations. Higher concentrations are necessary before equilibrium is established [7].

In case of at least three salts a multiphase region can exist during absorption. At the deliquescence point (Mutual Deliquescence Relative Humidity, MDRH, being the RH at which the mixture starts to pick up moisture) only one component of the solid mixture dissolves completely and subsequently the composition consists of an aqueous solution and undissolved solids following growing into a common saturated solution droplet at the second critical RH (SCRH) at which the dissolution is completed.

Increasing mass after the deliquescence point has been reached is a consequence of continuous water droplet growth by water vapour condensation. At the deliquescence point an equilibrium exists between the solid phase and the aqueous solution. Evaporation will occur until the RH becomes sufficient low and the droplet suddenly crystallizes in a point, expelling the remaining water content. A significant difference between the deliquescence point during absorption and desorption was shown in [8] in case of the salts: KCl-NaCl. According to [2] a significant difference in the deliquescence point during absorption and desorption can exist in salt mixtures consisting of at least 3 salts.

In [3] non-ideal mixture of two salts is described. Regarding two salts in a solution as the ambient relative humidity is lowered, one of the salts eventually becomes saturated, and its crystalline phase forms. As the relative humidity is further lowered, more of the solid phase of this salt forms, and the residual solution becomes more concentrated in the other salt. At a certain relative humidity, referred to as the mutual deliquescence relative humidity (MDRH), the two salts crystallize together and form a mixed solid phase at the eutonic composition. The MDRH is always lower than the DRH of the individual solutes.

The resulting dried particles are composed of a pure salt core surrounded by a mixed salt coating, where the core composition is solely determined by the original aerosol composition, but the coating is identical with the eutonic composition and is independent of the original aerosol composition. If the ambient relative humidity is increased, the size of the dried particle remains unchanged until the relative humidity in the atmosphere becomes identical with the water activity of eutonic. The solid coating having 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 saturated solution of eutonic composition. Further increasing the relative humidity results in more water absorption into the particle, and part of the pure salt solid core is dissolved to maintain water equilibrium between the solution and the atmosphere. At a certain relative humidity, which is a function of the overall composition of the original particle, the pure salt solid core is completely dissolved into the solution, and the particle becomes a pure aqueous droplet [3].

3 Principle description of the DVS

The dynamic vapour sorption (DVS) equipment can generate a desired pressure; the pressure is changeable according to a programmable sequence and simultaneously the mass can be recorded. This gives the possibility continuously to increase or decrease the relative humidity.

The pressure within the DVS is generated by control of the supply of dry and moist air respectively. The accuracy of the mixed air supply is checked through calibration tests and preformed with single salts covering RH from 11 to 93 % (LiCl; MgCl₂; MgNO₃; NaCl; KNO₃). The salt calibration principle is based upon the principle that the vapour pressure above a saturated salt solution in equilibrium with its surroundings is a constant at a particular temperature. In case of equilibrium conditions in the vicinity of the deliquescence point, mass change (dm) per change in pressure related to the saturation pressure (d(%P/P₀)) is equal to the pressure (P) multiplied with a constant (c):

$$\frac{dm}{d(\% \frac{P}{P_0})} = c \cdot P \quad (1)$$

At the point where the DVS-generated %P/P₀ is equal to the %P/P₀ above the saturated salt solution, the rate of change of mass is zero defining the deliquescence point, resulting in eq. 1 can be simplified to:

$$\frac{dm}{d(\% \frac{P}{P_0})} = 0 \quad (2)$$

In praxis this means that the change in partial pressure must be appropriate slow throughout the measurements to ensure equilibrium conditions to come into existence. In order to determine the most accurate deliquescence points it is of importance to ensure that the DVS is accurate calibrated which is done with single salt calibration tests. To obtain reliable salt calibration tests it is essential to ensure the salts have been prepared into the right condition prior to the salt calibration test (this is not described in this paper).

4 Materials

4.1 Preparation of salt mixtures

Based on the solubilities of single salts in 100 mL distilled water the soluble mass of two salts was mixed together in 100 mL distilled water in a 1L beaker. The beaker was placed in a pot with boiling water and covered with a slightly curved transparent glass on the top. The solution was heated until the solution was around 100°C or till nucleation occurs at the surface whereupon the beaker is taken up of the pot and placed for cooling in a fume cupboard. Crystals will be formed at the surface and gradually fall down to the bottom. A small amount of the solution was poured into a petri dish to accelerate evaporation. The used masses for preparation of each of the salt mixtures are listed in Table 1.

Table 1: Masses of each single salt added into 100 mL distilled water for preparation of the salt mixture.

	NaCl [g]	NaNO ₃ [g]	Na ₂ SO ₄ [g]	(NH ₄) ₂ SO ₄ [g]
NaCl-NaNO ₃	39.1	180		
NaCl-Na ₂ SO ₄	39.1		42.7	
(NH ₄) ₂ SO ₄ -Na ₂ SO ₄			42.7	103.8
NaCl-Na ₂ SO ₄ -NaNO ₃	39.1	180	42.7	

4.2 In-situ-multi-salt sample

The in-situ-multi-salt sample was taken from the upper side of the vault in Rørby church, Denmark, Zealand, in February 2011 and is one of the analysed samples in [9]. The samples consisted mainly of sodium and chloride but did also include potassium, magnesium, nitrate and sulphate. The measured ion contents in the in-situ-multi-salt samples are shown in Table 2 as an average of a trippel determination.

Table 2: The measured ion contents in the in-situ-multi-salt sample as an average of a trippel determination.

	Na ⁺ [wt%]	Ca ²⁺ [wt%]	K ⁺ [wt%]	Mg ²⁺ [wt%]	Cl ⁻ [wt%]	NO ₃ ⁻ [wt%]	SO ₄ ²⁻ [wt%]
Rørby church Feb. 2011	0.36	0.08	0.03	0.02	0.74	0.05	0.09

5 Results and discussion

5.1 Check of the generated RH in the DVS by calibration tests with single salts.

In order to determine the accuracy of the results for salt mixtures initial salt calibration tests were to be made on well-defined single salts with a deliquescence point close to the expected values for the salt mixtures. Salt calibration tests were carried out at 25°C with a salt with a deliquescence relative humidity (DRH) around 70 % RH and with a salt having a lower DRH being NaCl and $\text{Mg}(\text{NO}_3)_2$ with a deliquescence point of 75.29 +/- 0.12 % RH and 52.91 +/- 0.22 % RH respectively [1].

The deliquescence point is found by a combination of the result for the point at which no mass change occur (equation 2) and made more robust by following the development in the desorption and absorption around the deliquescence point (equation 1). The point at which no mass change occurs is represented by the intersection with the X-axis in Figure 1, see the grey lines. By creating a fitted line (see the dotted black line in Figure 1) on basis of the measured values for desorption across the deliquescence point showing mass change per change in RH, the black dotted line is generated. On the basis of this a calculated intersection with the x-axis can be found and thereby a RH found at which no mass change occurs defining the deliquescence point. By creating the same data for the absorption phase the deliquescence point found with the DVS equipment is an average of two determinations with a deviation in the deliquescence point found between the desorption and absorption phase.

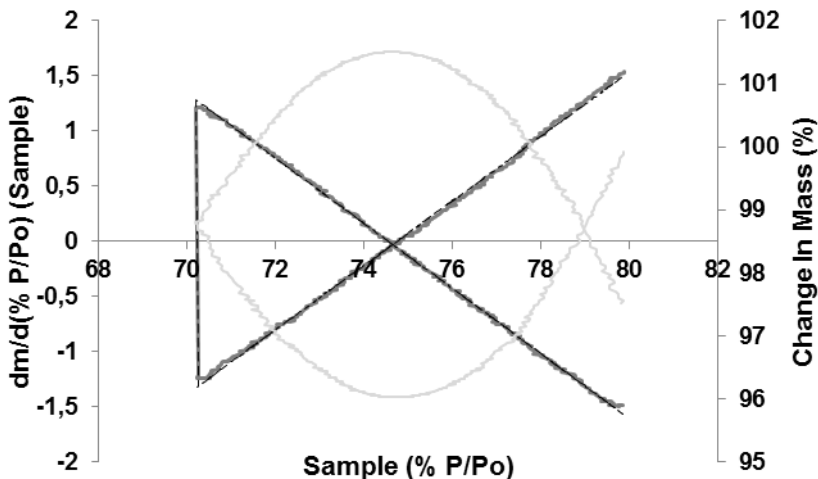


Figure 1: A plot of the salt validation calibration for NaCl. — Measured $\text{dm}/\text{d}(\% \text{P}/\text{P}_0)$ (Sample), — fitted $\text{dm}/\text{d}(\% \text{P}/\text{P}_0)$, — change in mass (%) at 25.0°C.

The results of the salt calibration validations test for NaCl is shown in Figure 1. The bright grey color in figure 1 illustrates a continuously changing mass as a function of changing RH. An absence of mass change was measured and imaged in the middle of the graph showing the presence of a deliquescence point. The measured mass change as a function of change in RH occurred continuously as shown as the dark grey line and was very close to the fitted line (black dotted). The fitted line which minimizes experimentally induced circumstances is representative for the actual measured values. A relative little deviation between the desorption deliquescence point and the absorption deliquescence point further make probable that the salt calibration validation tests were performed accurately ensuring the most reliable result.

Figure 1 was made on the basis of the available standard add-ins in excel to the DVS enabling an easy check of the reliability of the obtained data.

The results from the salt calibration validation tests are besides a test of the generated RH used to increase the accuracy of the measured results as deviations from the reference values for single salts must be attributed to experimental induced causes. Several salt calibration tests were carried out with NaCl and $Mg(NO_3)_2$, see Table 3 and table 4.

Table 3: Salt validation calibration tests with NaCl.

	Reference value from the literature	1 th run	2 th run	3 th run	4 th run	5 th run	Average
NaCl	75.29 +/- 0.12	74.65 +/- 0.09	74.58 +/- 0.09	74.51 +/- 0.17	74.40 +/- 0.07	74.69 +/-0.10	74.57 +/- 0.04
Deviation from reference	-	0.64	0.71	0.78	0.89	0.60	0.72

Table 4: Salt validation calibration tests with $Mg(NO_3)_2$.

	Reference value from the literature	1 th run	2 th run	3 th run	Average
$Mg(NO_3)_2$	52.91 +/- 0.22	52.21 +/- 0.03	52.20. +/- 0.02	52.25 +/- 0.11	52.22 +/- 0.05
Deviation from reference	-	0.70	0.71	0.66	0.69

The average of the salt calibration validation test for $\text{Mg}(\text{NO}_3)_2$ was found to 52.22 % RH which is a difference of 0.69 % RH from the reference values of 52.91 % RH \pm 0.22. The average of the measured deliquescence point for NaCl was found to 74.57 % RH meaning a difference of 0.72 % RH from the reference value of 75.29 \pm 0.12 % RH.

The repeated salt calibration validation tests showed an accuracy of the measurements of 0.05 % RH and 0.10 % RH for $\text{Mg}(\text{NO}_3)_2$ and NaCl respectively and make probable the results are reproducible and representative for the preformed measurements.

5.2 Determination of the deliquescence point in salt mix

Since the general definition of the deliquescence point is an absence of mass change at a specific relative humidity this criterion can also be used in case of salt mixtures. The measured deliquescence points for NaCl- NaNO_3 ; NaCl- Na_2SO_4 ; $(\text{NH}_4)_2\text{SO}_4$ - Na_2SO_4 and NaCl- Na_2SO_4 - NaNO_3 are shown in table 5. The deliquescence point for these salt mixtures were previously measured by [2] and [3] at 25°C and used as reference values.

Table 5: Deliquescence point at 25°C for salt mixtures. The recalculated values are the measured values \pm the documented deviation from the reference values (see table 3 and 4).

	Literature % RH	1 th run	2 nd run	3 rd run	Average/ deviation	Re- calculated
NaCl- NaNO_3	68.0 \pm 0.4	66.52 \pm 0.01	66.19 \pm 0.11	66.35 \pm 0.14	66.35 \pm 0.07	67.07
NaCl- Na_2SO_4	74.2 \pm 0.3	73.78 \pm 0.10	73.73 \pm 0.08	73.50 \pm 0.05	73.67 \pm 0.03	74.39
$(\text{NH}_4)_2\text{SO}_4$ - Na_2SO_4	71.3 \pm 0.4	74.61 \pm 1.33	75.75 \pm 0.35	-	75.18	75.90
NaCl- Na_2SO_4 - NaNO_3	71.8 \pm 0.5	65.96 \pm 0.16	-	-	-	66.68

Taking the determined difference between the RH measured in the DVS and reference values into account being 0.72 % RH at a RH around 75 % RH, the recalculated deliquescence point for NaCl- Na_2SO_4 was found to 74.39 % RH. The present found deliquescence point is in consistence and does not differ significantly from the deliquescence point found by [2] of 74.2 \pm 0.3 % RH. In addition this clarifies that it is possible to measure a significant difference in the deliquescence point between NaCl (75.29 \pm 0.12 % RH) and NaCl- Na_2SO_4 (74.2 \pm 0.3 % RH) meaning two salts have a deliquescence point relative close to each other.

The recalculated value for the deliquescence point for NaCl-Na₂SO₄ was determined to 67.07 % RH. In [3] the deliquescence point for this salt mixture was thermodynamically calculated to 67 % RH whereas in [2] it was measured to 68.0 +/- 0.4 % RH. The setup was described in [8] where the reproducibility of the measurement was described to be better than +/- 2%. They also developed a theoretical model resulting in the same deliquescence point as they had measured. The present measured deliquescence point is in consistence with the thermodynamically calculated result by [3] which is close to but differs significantly from the calculated and measured values by [2].

In two salt calibration validation tests where the deviation was improved by narrowing the interval of the applied RH, the recalculated deliquescence point of (NH₄)₂SO₄-Na₂SO₄ was determined to 76.47 % whereas it was found to 71.3 +/- 0.4 % RH [2]. Likewise was the recalculated deliquescence point for NaCl-Na₂SO₄-NaNO₃ determined to 66.56 % RH whereas it was measured to 71.8 +/- 0.5 % RH in [2].

In case of sodium sulfate there is no unique DRH and the value depends on the nature of the solid phase. At 25°C is the DRH 93.6 % RH for mirabilite, 86.9 % RH for thenardite (Na₂SO₄) and 83.5 % RH for phase III. Regarding the salt mixture NaCl-NaNO₃-Na₂SO₄ two different possible compositions of the solid mixture exist at room temperature being a) NaCl + Na₂SO₄ + Na₃NO₃SO₄·H₂O (darapskite) (MDRH = 69.7 % RH) or b) NaCl + NaNO₃ + Na₃NO₃SO₄·H₂O (MDRH = 66.2 % RH) and a third possibility exists due to the preparation of the salt through evaporation from a boiling solution being c) NaCl + Na₂SO₄ + NaNO₃. In [3] they characterize salt mixtures as simple and less simple systems the former one being independent of the present mole fractions of the salt in contrast to the latter. The differences between the present determined MDRH and the values from the literature [2] is most likely a result of different composition of the solid salt mixture caused by differences in salt preparation and different fractions of each salt. For future work it must be ensured that identical fractions are used for preparation of the salt mixtures and identical salt preparation procedures must be followed to obtain comparable results. Comparison with results from ECOS-runsalt should also be carried out in future work for common validation of results.

The measured deliquescence points for the salts and salt mixtures are in good agreement with reference values both regarding single salt, salt mixtures and found differences can be theoretically explained, making probable the determination of the deliquescence point in in-situ multi salt samples with the dynamic vapor sorption equipment.

5.3 Determination of the deliquescence point in in-situ multi salt samples

In case of an in-situ multi salt sample the deliquescence point and the second critical relative humidity (SCRH) at which the dissolution is complete are unknown. Therefore the below procedure was followed:

- 1) Initially it was necessary to make a relative fast screening of the sample between 0 and 95 % RH to determine the interval where phase changes occur both regarding complete dissolution of the salt at SCRH during absorption and efflorescence relative humidity (ERH) where crystallization is initiated during desorption. It is to be noticed that a fast screening is not carried out at equilibrium conditions which can result in slightly misleading results.
- 2) Based on the results from the initial screening a new test was started within a limited interval with a decreased change in partial pressure as a function of time. The decreased change in partial pressure as a function of time was made to ensure equilibrium conditions throughout the experimental duration.
- 3) Further narrowing of the test interval though still ensuring both the SCRH and ERH were included in the interval and simultaneously decreasing the change in partial pressure as a function of time.

Article 3 was repeated until equilibrium conditions were ensured through an absence of change in SCRH and ERH at further reduced interval or further decreased change in partial pressure as a function of time; an example of this is given in Figure 2.

The sorption isotherms in Figure 2 represent both brick powder and a salt mixture. Regarding a sorption isotherm for brick powder a weight gain up to 1.5 wt% has been measured dependent on the brick type [10]. The water absorption to the brick powder could partly explain the mass increase at low RH e.g. was a weight gain of 0.3 wt% measured at 40 % RH [10] where the present weight gain at 40 % RH was measured to 0.6 wt%. This implies that at a RH of 40 % there is a significant water uptake and an initial dissolution of the salt mixtures defining the deliquescence point. A more precise deliquescence point could e.g. be calculated by the use of ECOS-Runsalt and verified by measurements with the DVS.

In [11] the water uptake during absorption occurred in a step meaning a sudden increase in absorbed water whereas in contrast the evaporation path yields metastable phases resulting in partly continuous water decrease. Regarding the curved evolution in figure 2 it is seen that the second critical relative humidity (SCRH) during absorption differs significant from the efflorescence relative humidity (ERH) during desorption. At equilibrium there is no difference between the RH at which crystallization starts and the RH at which dissolutions is completed.

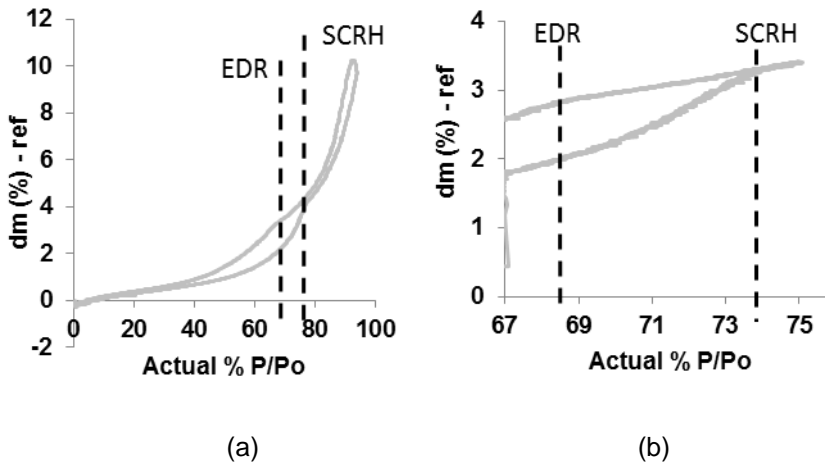


Figure 2: The measured mass change as a function of relative humidity at 25.0°C. The results shown in (a) were obtained from measurements performed in conjunction with a change of 1% RH per hour and in b) with a change of 0.08 % RH per hour.

Table 6: Second critical relative humidity (SCRH) and efflorescence relative humidity (ERH) in three different in-situ samples extracted above the vault in Rørby Church. The results from the three samples were found as a function of different changes in RH/h, intervals and measuring modes.

	Sample 1 Closed loop	Sample 2 Closed loop	Sample 2 Open loop	Sample 3 Closed loop
Initial screening $\Delta 1$ % RH per hour	SCRH: 77 ERH: 67	SCRH: 83 ERH: 72	SCRH: 87 ERH: 73.6	SCRH: 84 ERH: 74
Limited interval $\Delta 0.35$ % RH per hour	SCRH: 74 ERH: 67.5	-	-	-
Second limited interval $\Delta 0.18$ % RH per hour	SCRH: 74 ERH: 68	-	-	-
Third limited interval $\Delta 0.08$ % RH per hour	SCRH: 73.8 ERH: 68.6	SCRH: 80 ERH: 74	SCRH: 78.6 ERH: 74.6	-

The measured hysteresis between absorption and desorption for RH between 40 and 80 % is a clear indication that supersaturation occurred during evaporation and differences between the two curves in figure 2 must be attributed to differences between kinetic influences and the state of equilibrium. The supersaturation is dependent on the experimental conditions and is related to the porous structure, material, temperature, RH during evaporation, salt mixture composition and solid phase. The

difference between SCRH and ERH is therefore a measure for the critical supersaturation required for crystallization which clarifies salt induced deterioration RH at the present experimental conditions.

This pattern for the absorption and desorption isotherm including phase change in the sample from Rørby church is in consistence with the theoretical considerations made by [2] which make probable the presence of at least three different salts. The actual presence of at least three different salts is documented by measurements of the ionic contents shown in table 2.

The SCRH will vary in case of varying fractions of the different salts in the mixtures for less simple salt systems. Extracting three different samples from a several hundreds of years old in-situ location it is most probably that these salt systems are less simple and that they do vary in the fraction of the different salts [3].

The measured SCRH was found to be between 73.8 and 80 % RH and the ERH to 68.6 to 74.6 % RH. Such significant differences between SCRH and ERH point has a practical influence on preventive conservation and for dissolution of salts prior to desalination campaigns. According to the present results dissolution of all parts of the salt mixture occurs at RH above 80 % RH and in case of subsequent lowering of the RH to ERH crystallization is initiated which potentially can cause damages. Therefore to avoid salt induced damages the RH should be kept above the SCRH of the salt mixture. Also to carry out desalination the salts must be completely dissolved which only is possible in case of total dissolution of the present salts. Therefore is the SCRH the determining parameter in case of preventive conservation and for desalination.

5.4 Considerations in relation to the practical case (here church vaults)

The present SCRH and ERH were determined at a temperature of 25°C even though this is a high temperature in connection with constructions. This temperature was chosen since most research is carried out at 25°C enabling comparison with the largest amount of data. In future research deliquescence points are also to be made at other temperatures to make the determination of the deliquescence points with DVS valid in a more general context and to make the method more useful for practical purposes.

In case of establishing a climate chamber with steady temperature and RH to prevent further salt induced deterioration determination of the SCRH and ERH gives valuable information on the most appropriate RH. As seen in table 6 the SCRH and ERH can vary considerably as a consequence of varying salt fractions in the salt mixture out of which a sufficient accuracy of the present determined DRH and ERH are concluded.

Prior to desalination treatments climate data including temperature and RH are most often recorded through a year to clarify seasonal variations [12] which makes it possible to determine SCRH and ERH at relevant temperatures. In previous work with electrochemical desalination of an artificial salt contaminated wall section with the single salt NaCl it was shown possible to obtain a high desalination effect when a microclimate was established ensuring a RH above the well-known deliquescence point of this single salt [13]. Therefore knowledge of the deliquescence points and ensuring these can have major impact on the desalination effect and success.

6 Conclusion

It was shown possible to determine ERH and DRH for single salts. The determined ERH and DRH for single salts did not differ significantly. The difference between the determined deliquescence point and reference values from the literature for single salts was used to increase the accuracy of the DVS determined values. A consistence was found between the measured deliquescence point for salt mixtures and values from the literature enabling to determine the deliquescence point in in-situ multi salt samples as shown for a sample lifted from above a church vault in Denmark. For the in-situ multi salt sample a significant difference was found between the SCRH and the ERH being a measure for the critical supersaturation required for crystallization. Due to the extensive possible combinations of salt mixtures, the determination of phase transition with the dynamic vapor sorption equipment seems like an expressive tool useful for in-situ multi salt samples.

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