Deliquescence and deliquescence lowering of food ingredients and blends
– White Paper 20-03

This White paper presents the applicability of DVS analysis to determine the deliquescence point (RH_0) of food powders. The effect of deliquescence lowering was demonstrated on their mixtures.

The effects and problems associated with deliquescence are relevant not only in the food- but also in pharma- and chemical industries. Therefore, this method is useful in R&D and QA of many industrial sectors.

Introduction

Deliquescence describes the transition from a solid to a dissolved state if a critical, material specific relative humidity is exceeded. Deliquescent materials are mostly crystalline with high-water solubility. In dissolved state such materials often cause a strong reduction of the a_w-value by intermolecular interactions [1].

In case of deliquescence, physical and chemical changes of the product are induced which favor caking, decreased solubility and bioavailability, change of appearance and sensory characteristics as well as a degradation of valuable ingredients like vitamins [2].

Furthermore, mixtures of such crystalline ingredients often show a deliquescence lowering, i.e. dissolution at a relative humidity below the deliquescence point of the individual components [3].

Such behavior is typical for many foods but also pharmaceutical ingredients such as sugars, sugar substitutes, organic acids, salts or vitamins.

Especially, for food products which are frequently exposed to changing climatic conditions, e.g. during transport, storage and production, knowledge of the deliquescence behavior is of high importance to draw conclusions about their shelf life and to be able to specifically adapt the recipe. Same applies for pharmaceuticals to guarantee the efficacy of the formulation [4,5].
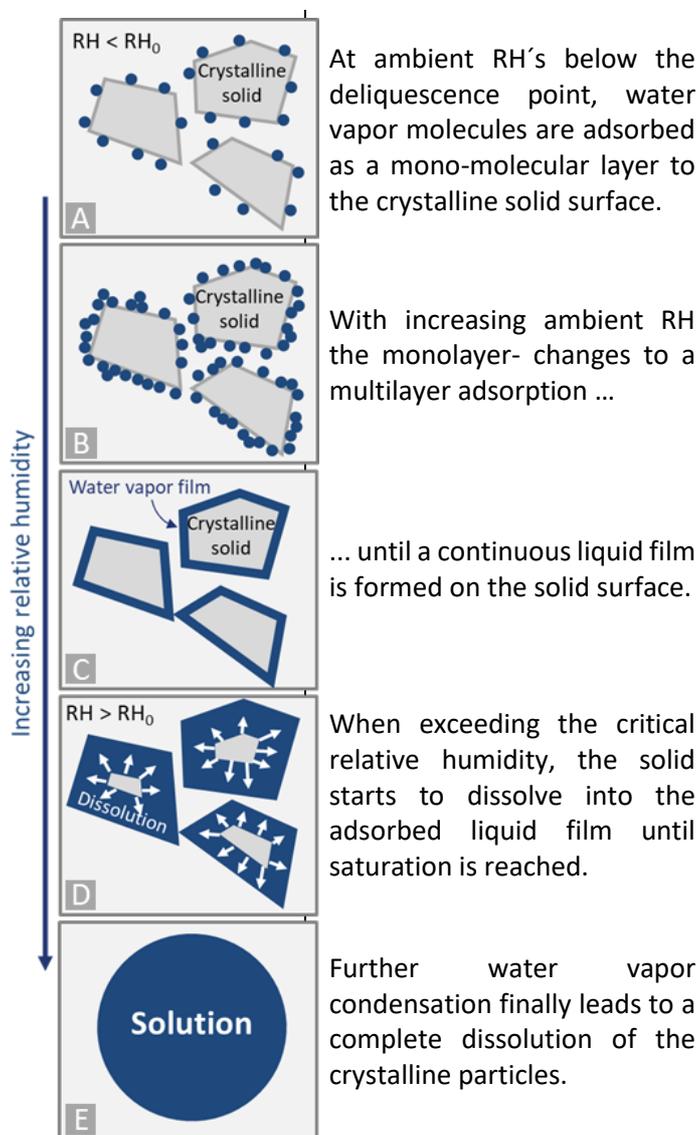

At ambient RH´s below the deliquescence point, water vapor molecules are adsorbed as a mono-molecular layer to the crystalline solid surface.

With increasing ambient RH the monolayer- changes to a multilayer adsorption …

… until a continuous liquid film is formed on the solid surface.

When exceeding the critical relative humidity, the solid starts to dissolve into the adsorbed liquid film until saturation is reached.

Further water vapor condensation finally leads to a complete dissolution of the crystalline particles.

Fig. 1: Schematic drawing of the deliquescence process

Principle of deliquescence

When a solid is exposed to ambient conditions an interaction with the humidity of the surrounding air takes place. As shown in Fig. 1, for relative humidities below the critical value for deliquescence (RH_0) water vapor molecules adsorb to the solid surface as a monomolecular layer (A).

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With increasing ambient RH, the sorption layer increases to a multilayer (B) until the surface is covered with a thin, continuous liquid film (C). If the ambient RH exceeds the critical RH0, the solid starts to dissolve in the surrounding liquid film until the solution is saturated (D). This saturated solution has a lower water vapor pressure compared to a pure liquid which triggers the condensation of further water vapor from the surrounding at lower RH's. The resulting dilution effect causes more of the solid to dissolve again.

This cycle of dissolution/condensation (Fig. 2) is continued until equilibrium with the ambient is reached - i.e. complete dissolution of the solid [5].
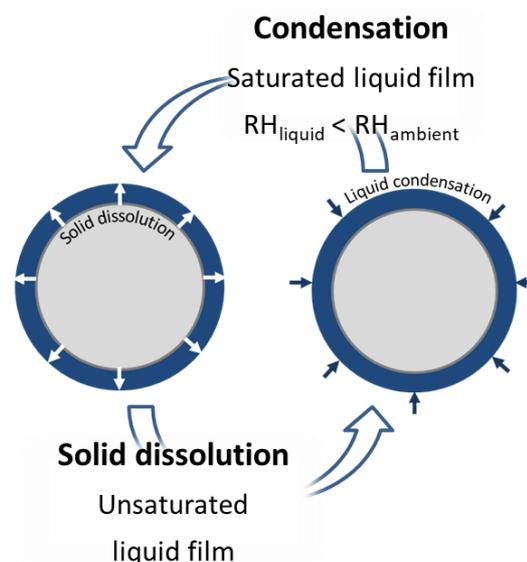
Deliquescence lowering

Blends of crystalline components often show deliquescence below the RH0 of the individual substances. Based on the explanation given above, further solutes in the liquid film cause a stronger reduction of the aw-value of the solution. In consequence, condensation of water vapor and hence induction of deliquescence takes place at lower relative humidities ($RH_{0,mix}$) [5]. Thereby, the mixing ratio has no effect on the extend of deliquescence lowering [3,4].

Calculation of deliquescence lowering: Ross equation

Although this approach was originally intended only for solutions, the Ross equation also proved to be suitable for calculating the critical RH for deliquescence of powder blends (Eq. 1). The approach states that the aw-value of a multi-component solution – or the $RH_{0,mix}$ of a powder blend – is obtained by multiplying the aw-values of the saturated solution (a_w^0) of each component within the mixture.

$$a_w = a_{w,1}^0 \cdot a_{w,2}^0 \cdot a_{w,3}^0 \cdots a_{w,i}^0 \qquad \text{Eq. 1}$$

It was found that the Ross equation overestimates the deliquescence lowering compared to experimental data.

Fig. 2: Schematic drawing of a deliquescence cycle

This discrepancy was attributed to the fact that, for instance, interaction between the solutes or chemical reaction which may lead to changing powder properties are not considered. In addition, a precondition for deliquescence lowering is that the individual components are in contact with each other. In solid mixtures this may not apply to all particles which could also explain a possible deviation [3,4].9.5

Methods

Deliquescence of several food ingredients and their mixtures was analyzed. Measurements were performed in an SPS-1µ (proUmid GmbH, Ulm). Temperature was set to 25 °C. Settings were adjusted as summarized in Tab. 1. The relative humidity was increased from 0 % to 90 % RH. In the relevant region of deliquescence, relative humidity was increased in 1 % steps. In the mixtures, the components were weighed in to equal parts.

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Table 1: Instrument settings

Time between weighing cycles	15.0 min
Min. time per climate cycle	10.0 min
Max. time per climate cycle	5.0 h
Default weight limit	100.0 %
Equilibrium condition	0.01 % / 20 min

Results

In Fig. 3 moisture sorption isotherms of the food ingredients are shown. It can be seen, that at the beginning of the measurement – at lower RH's – only little moisture uptake takes place. With exceeding RH_0 a strong increase in weight and a steep rise of the curve can be observed. The starting point of the steep weight increase was defined as deliquescence point RH_0. Obtained values of RH_0 are summarized in Tab. 2.
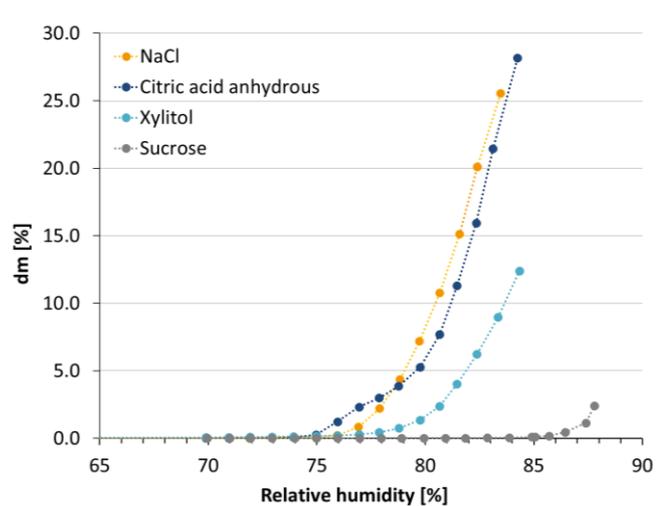

Fig. 3: Water vapor adsorption and onset of deliquescence of food ingredients.

Table 2: Critical relative humidity (RH_0) for onset of deliquescence of food ingredients

Material	RH_0	$RH_{0, Literature}$
Sucrose	85.7	85[1,5], 86.1[4]
Xylitol	78.8	77-79[5], 78.8[4], 79[1]
NaCl	76.9	75[5], 76.1[4]
Citric acid anhydrous	75.9	74-75[5], 75[1], 75.2[4],
NaCl iodized	75.9	
NaCl iodized/fluoridated	73.9	

The results summarized in Fig. 3 and Tab. 2 show that the RH_0 of typical food ingredients can differ considerably. In order to obtain stable products, this should be considered when formulating new products, e.g. replacing sucrose with xylitol, which is frequently used as a healthy sugar substitute, makes the product more susceptible to deliquescence.

Deliquescence lowering

The effect of deliquescence lowering was demonstrated by measuring the water vapor adsorption of binary and ternary blends of these ingredients. Results are shown in Fig. 4A and B.
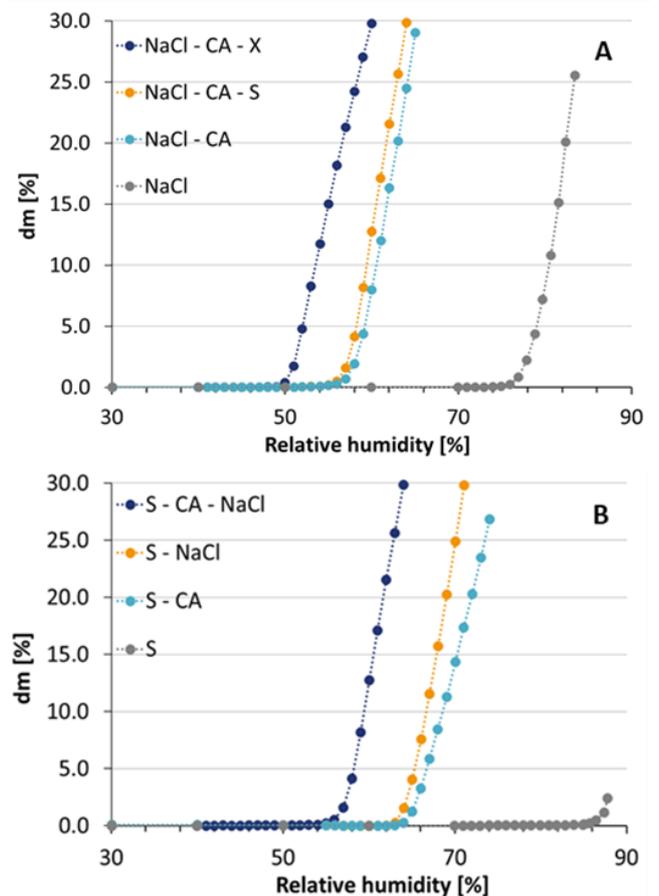

Fig. 4: Deliquescence lowering of several blends of NaCl (A) and sucrose (B) (S: Sucrose, CA: Citric acid anhydrous, X: Xylitol)

As shown in Fig. 4 the deliquescence point is significantly reduced when several deliquescence materials are mixed.

Tab. 3 summarizes the experimentally determined deliquescence points as well as deliquescence lowering predicted by the Ross equation [Eq. 1]. The a_w- values of saturated solutions of the individual compounds were used for calculation.

The values in brackets show literature data of $RH_{0,mix}$ for some binary mixtures. The comparison shows a fairly good agreement with these data.

Table 3: Deliquescence points of food ingredient blends. a_w-values for calculation were obtained from literature data [4].

Mixtures	$RH_{0,Mix}$	$RH_{0,Mix}$ (calc.)[4]
NaCl/Citric acid	58.0 (59.2[4])	57.0
NaCl/Citric acid/Xylitol	51.0	44.75
Sucrose/Citric acid	65.0 (64[1])	63.77
Sucrose/NaCl	64.1 (66.2[4])	64.28
Sucrose/Citric acid/NaCl	57.0	48.34
Sucrose/Citric acid/Xylitol	55.0	50.06

Comparing experimental and calculated data it reveals that deliquescence lowering is overestimated by the Ross equation. In particular for the ternary blends there is a clear deviation from theoretical values (Tab. 3). However, this observation is consistent with literature reports [1,4,5].

This discrepancy may be explained by solute-solute interactions which are not considered in the Ross approach. Furthermore, although the mixing ratio is irrelevant, in powder blends deliquescence only takes place if the particles are in direct physical contact with each other.

Especially for more component systems this is most likely not guaranteed for all particles. A further point to consider is the influence of the analysis methods. For example, in the present application $RH_{0,mix}$ values were obtained by DVS measurements, whereas a_w-values of the saturated solution were measured by a dew point mirror method [1,4,5].

Influence of minor components on deliquescence

The results presented above show the effect of deliquescence lowering when mixing several crystalline food ingredients.

However, also minor components which are added to a product can influence deliquescence. As an example, Fig. 5 shows the water vapor sorption of pure NaCl and of table salt enriched with iodine or iodine and fluoride. Results show that RH_0 is reduced from 76.9 % to 75.9 % and 73.9 % (Tab. 2).
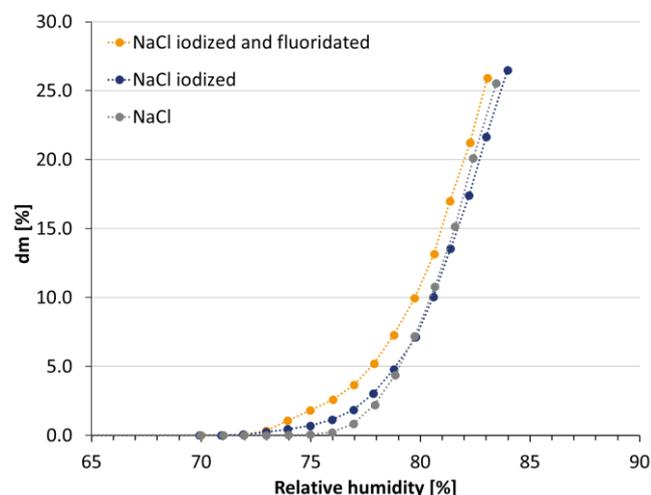

Fig. 5: Water vapor sorption and deliquescence of NaCl and NaCl enriched with iodine and fluoride.

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Conclusion

Dynamic water vapor sorption measurements were used to determine deliquescence points of some typical food ingredients. In addition, deliquescence lowering was detected in binary and ternary mixtures of these substances.

A comparison with literature data showed a good agreement with values given for RH_0 and $RH_{0,mix}$.

Knowledge of deliquescence is of importance regarding product quality, shelf life and for new product development. In this context, the change of climate conditions, e.g. during the production- and distribution chain should also be considered.

Results show that dynamic water vapor measurements are a well suited to accurately determine the onset of deliquescence of different materials. The multisampling capacity of the SPS devices additionally provides not only a precise but also a time-saving option.

Deliquescence of food ingredients with color change and caking

References

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