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## Caking of sucrose: Elucidation of the drying kinetics according to the relative humidity by considering external and internal mass transfer

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## ABSTRACT

Hygroscopic powders are prone to caking when they are submitted to variations of ambient relative humidity (*RH*) during process, transport and/or storage. The increase of *RH* above a characteristic threshold induces the formation by direct sorption of a saturated aqueous solution through a process called deliquescence, forming liquid bridges between the particles. When the *RH* decreases below this threshold, these liquid bridges recrystallize into solid bridges to form an agglomerate. In this work, the thermodynamics and kinetics of sucrose deliquescence and efflorescence were determined by gravimetric analysis. The influence of the drying *RH* on efflorescence was studied. In particular, two drying mechanisms were highlighted and modeled according to the imposed *RH*. An innovative method based on the representation of the water uptake/loss rates as a function of the imposed *RH* was established to determine the deliquescence *RH*.

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### 1. Introduction

Many industries handle powders and have to face a loss of their flowability, which impacts the product manufacturability, quality and shelf-life. This loss of flowability is a widespread phenomenon called caking which occurs during processing, handling and storage of powders. Caking may result in costly losses of product, process interruptions and customers' complaints due to irregular product quality.

A general definition of caking is the "spontaneous and undesired formation of a coherent mass from individual grains" (Afrassiabian et al., 2016). This is a slow process amplified by the variations of the environmental conditions: temperature, relative humidity (*RH*) and mechanical stress. One of the primary causes of caking is the interaction between particles and water in the surrounding atmosphere (Scholl and Schmidt, 2014). In particular, many industrial products contain hydro-soluble crystalline materials characterized by a *RH* threshold called Deliquescence Relative Humidity (*DRH*).

Deliquescence is a phase transition of a solid to its saturated

solution at a well-defined *RH* dependent on the material nature and the temperature (Mauer and Taylor, 2010). Below this threshold, the solid phase surrounded by moist air is thermodynamically favorable whereas above the *DRH*, the aqueous solution is the most stable phase (Langlet et al., 2013; Mauer and Taylor, 2010). Partially deliquesced crystals are surrounded by a saturated aqueous solution that links them through liquid bridges, causing wet caking. Further deliquescence leads to the complete dissolution of the crystals followed by the dilution of the solution.

The reverse process, called efflorescence, corresponds to the crystallization of the solid associated with water release to the gas-phase. This phenomenon occurs at a high-enough sucrose concentration, generally at a *RH* well below the *DRH* (Martin, 2000). A hysteresis is then typically observed between deliquescence and efflorescence. When partially deliquesced crystals are submitted to a *RH* below the *DRH*, the liquid bridges recrystallize into solid bridges. An agglomerate of crystals is spontaneously formed.

The mechanical strength of these solid bridges depends on the environmental conditions (temperature, *RH*, pressure, mechanical stress) and on the crystal properties: solubility in water, morphology and particle size.

This work focuses on partial deliquescence and efflorescence of sucrose, a well-known crystalline sugar, with a *DRH* value of 85% at

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### Nomenclature

$\alpha$	Condensation/evaporation coefficient (–)
$D$	Apparent diffusion coefficient ( $\text{m}^2/\text{s}$ )
$DRH$	Deliquescence Relative Humidity (%)
$ERH$	Efflorescence Relative Humidity (%)
$K$	Knudsen coefficient (m.s)
$m$	Mass of sucrose with water (g)
$m_0$	Mass of sucrose crystals (g)
$m_w$	Mass of water (g)
$p^0$	Vapor pressure at standard conditions ( $p^0 = 1 \text{ bar}$ )
$p_w$	Partial vapor pressure (bar)
$p_w^*$	Saturated vapor pressure (bar)
$p_s$	Partial vapor pressure in equilibrium with the sucrose aqueous solution (bar)
$p_{s,sat}$	Partial vapor pressure in equilibrium with the sucrose saturated solution (bar)
$R$	Ideal gas constant ( $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$ )
$RH$	Relative Humidity (%)
$T$	Temperature (K)
$\mu_w^0$	Chemical potential of water vapor at standard conditions ( $p^0 = 1 \text{ bar}$ )
$\mu_w^*$	Chemical potential of pure water ( $\text{J}/\text{mol}$ )
$X_w$	Water content in the aqueous solution

25 °C (Dupas-Langlet et al., 2015; Salameh et al., 2006). Sucrose is one of the most common and widely used sugars in the food and pharmaceutical industries (Edrisi Sormoli et al., 2013). This has generated a huge amount of information about the sucrose-water binary system, alone or in blends, published over the years (Khaddour et al., 2010; Lipasek et al., 2012; Yao et al., 2011). However, there is only little information provided on the mechanisms and kinetics of sucrose drying. How does the drying  $RH$  affect them? Can we understand the governing mechanisms?

The present approach combines qualitative observations with quantitative measurements at controlled temperature and  $RH$ . The thermodynamics of sucrose deliquescence and efflorescence are studied via the sorption isotherm at 25 °C while the kinetics of water uptake and loss are precisely determined by gravimetric analysis at several  $RH$  conditions. The choice of the models used to fit those kinetics data is discussed, providing a better understanding of the mechanisms of moisture sorption and drying. Furthermore, a new method for accurate determination of the  $DRH$  is presented.

## 2. Theoretical aspects

To understand the deliquescence phenomenon, the vapor pressure – temperature diagrams of water and of the binary sucrose-water system are represented in Fig. 1 at temperatures between 20 and 40 °C.

For pure liquid water in equilibrium with its vapor at a given temperature  $T$ , the liquid-vapor coexistence curve can be estimated by Rankin equation shown as a thick line in Fig. 1a. At equilibrium, the chemical potential is the same in every present phase (Atkins, 1994). Thus, for water:

$$\mu_{w(l)}^* = \mu_{w(g)}^* \quad (1)$$

where  $\mu_{w(l)}^*$  and  $\mu_{w(g)}^*$  are the chemical potentials of pure liquid water and vapor.

Assuming water vapor behaves like an ideal gas, the chemical potential of the gas phase is:

$$\mu_{w(g)}^* = \mu_w^0 + RT \cdot \ln \frac{p_w^*}{p^0} \quad (2)$$

where  $\mu_w^0$  is the chemical potential of water vapor at standard conditions ( $p^0 = 1 \text{ bar}$ ).  $p_w^*$  is the saturated vapor pressure,  $R$  the ideal gas constant.

The equation of liquid-vapor equilibrium is obtained by combining these two equations:

$$\mu_{w(l)}^* = \mu_w^0 + RT \cdot \ln \frac{p_w^*}{p^0} \quad (3)$$

The vapor phase is at saturation ( $p_w^*$ ) when in equilibrium with the liquid. In all other cases it is under-saturated and characterized by a partial vapor pressure  $p_w$  defined as a percentage of  $p_w^*$  (Equation (4)), called Relative Humidity ( $RH$ ).

$$p_w = RH \cdot p_w^* \quad (4)$$

The values of vapor partial pressure at different  $RH$ s are also represented in Fig. 1a.

With a solute present in water (like sucrose), the vapor pressure in equilibrium with the formed solution is reduced (Zografis, 1988). The chemical potential of the aqueous solution becomes:

$$\mu_{w(l)} = \mu_w^0 + RT \cdot \ln \frac{p_s}{p^0} \quad (5)$$

where  $\mu_{w(l)}$  is the chemical potential of the sucrose aqueous solution and  $p_s$  the new equilibrium vapor pressure such as  $p_s < p_w^*$ .

Combining Equations (3) and (5):

$$\mu_{w(l)} = \mu_{w(l)}^* + RT \cdot \ln \frac{p_s}{p_w^*} \quad (6)$$

The decrease of the equilibrium vapor pressure with respect to pure water means that water condenses at a lower  $RH$  equal to  $p_s/p_w^*$ . At saturation,  $p_s$  is called  $p_s$  and the  $DRH$  is defined as  $p_{s,sat}/p_w^*$ .

Like most organic compounds, sucrose solubility depends on temperature, as it is observed on its solubility diagram in Fig. 2. As the solubility increases with the temperature, more solute is present and the decrease of  $p_{s,sat}$  is accentuated. Thus, the  $DRH$  decreases with the temperature, from approximately 86%  $RH$  at 20 °C to approximately 83%  $RH$  at 40 °C (Mauer and Taylor, 2010).

The values of  $p_{s,sat}$  as a function of the temperature constitute the saturated solution – vapor equilibrium curve represented as a dotted line in Fig. 1 b. Below this curve, the sucrose crystals coexist with the under-saturated vapor. Above the curve, the equilibrium phase is a diluted aqueous solution.

However, even if solid crystals are stable below the  $DRH$ , water molecules interact with them at much lower  $RH$ s. The early stages of adsorption occur typically between 5% and 35%  $RH$  with a few layers of water molecules at the surface of solids (Afrassiabian et al., 2016). With the increase of  $RH$ , the adsorbed layer becomes thicker, particularly in confined spaces such as contact points between particles or surface asperities which can be assimilated as mesopores (pore size between 2 and 50 nm). When the adsorbed layer reaches a 3 nm thickness in those spaces, water molecules become mobile and form a liquid-like meniscus (Afrassiabian et al., 2016). This phenomenon is called capillary condensation and is made possible by a decrease of the saturated vapor pressure within pores (Gomez and Saleh, 2012) that can be estimated by the Kelvin equation:

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