The impact of deliquescence lowering on the caking of powder mixtures

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ABSTRACT

The first step in caking of hygroscopic powders is usually the condensation of water vapor followed by deliquescence of solid particles. If water evaporation subsequently occurs (induced, for example, by the change of ambient conditions) the phenomenon of efflorescence will lead to the formation of solid bridges between particles. Deliquescence takes place at the so-called deliquescence relative humidity (DRH), which corresponds to the vapor pressure of saturated solution of the substance. When two or more deliquescent substances are present, a singular behavior known as "deliquescence lowering" is observed. It was shown that the lowering of deliquescence point favors the caking of powders mixture. Binary blend of NaCl and sucrose was chosen as a model system to investigate the impact of deliquescence lowering on the stability and flowability of powder. Deliquescence lowering was evidenced by ESEM observations and by the quantitative analysis of water uptake. It was shown that mixtures take a large amount of water up while drying step is inhibited. Caking tests, coupled with kinetic measurements of water uptake and loss, are carried out in order to relate the residual water content to the reinforcement of caking of the mixture. The influence of the proportion of two substances in a blend is also analyzed. It was found that the most sensitive composition with respect to caking is close to the one of the eutonic point i.e. the mixture showing the lowest critical relative humidity at a given temperature. This work also shows that the presence of two (or more) solutes deteriorates the mechanical properties and the stability of powders compared to the situation when only one deliquescent substance is present. The determination of the eutonic composition allows anticipating the conditions of reinforced caking.

1. Introduction

The presence of water as liquid or vapor plays a considerable role in physical and chemical stability of powders. The moisture content at which a solid material induces a water vapor pressure equal to that of the surrounding environment defines the hygroscopic behavior of powder. Water sorption often results in the loss of powder flowability due to the agglomeration of particles. This inconvenience is called caking phenomenon and is the state in which the powder cannot be moved by vigorously shaking or tapping the container [1]. The consequences of caking can be severe: from the loss of product to the risk of unreliable product supply or irregular product quality throughout process interruption [2].

Originally, caking process begins by crystal deliquescence when powder is exposed to water vapor pressure higher than the water vapor pressure of saturated solutions of a solid at a given temperature. The foundation of deliquescence is thermodynamical, it is known to occur sharply with increasing relative humidity on reaching free energy equality between the initial (salt particle plus vapor) and final (fully dissolved solution drop plus vapor) states [3]. This leads to the formation of

a saturated solution on the particles surface. For solutions of substances such as sodium chloride (and many other compounds), high affinity of ions and water molecules causes lowering of the equilibrium vapor pressure compared to the substances of low affinity at the same temperature. The affinity between species is expressed via interaction parameter related to the deviation from Raoult's law (direct proportionality between the solution concentration and its vapor pressure): if it is positive, the molecular interactions are repulsive while for attractive interactions the negative interaction parameter is found. One can say that the presence of ions in aqueous solution causes lowering of the water vapor pressure by means of attractive interactions with water molecules [4].

When vapor pressure decreases or temperature increases, evaporation takes place, allowing recrystallization and the formation of solid bridges between particles. Rigid and compact agglomerates are formed after one or several cycles of humidification and drying. Caking scenario of sodium chloride is described in detail in Langlet et al.'s work [5]. Corresponding phase diagram is represented on Fig. 1. The point A is located in the domain where NaCl crystals are in equilibrium with water vapor. The ascending arrow from A to B crossing the liquid-vapor equilibrium corresponds to the vapor pressure change at given temperature. It characterizes the deliquescence of NaCl: crystals become partially or totally dissolved at the point B. Recrystallization can occur by the inverse way from the point B to the point A (or by another way which crosses the liquid-vapor equilibrium).

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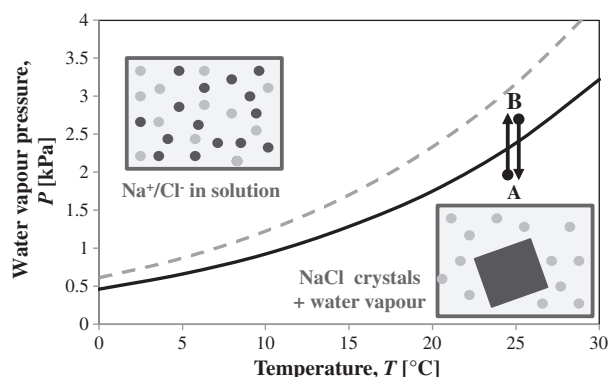E-mail address: marina.langlet@utc.fr (M. Dupas-Langlet).

Fig. 1. Phase diagram of NaCl in the humid air — the cycle ABA corresponds to a sequence of thermodynamic conditions which leads to NaCl caking at 25 °C. The liquid vapor equilibrium of saturated solution of sodium chloride is represented by continued line and the liquid vapor equilibrium of pure water by dotted line.

The cycle ABA corresponds to the specific situation where temperature is constant, for example 25 °C. In such a case, we can relate the relative humidity and the deliquescence relative humidity to the imposed water vapor pressure, P, the saturated vapor pressure of pure water, P_0, and the vapor pressure of saturated solution of NaCl, P_{sat}:

$$RH = \frac{P}{P_0}.100 \tag{1}$$

$$DRH = \frac{P_{sat}}{P_0}.100 \tag{2}$$

Several authors tried to give a quantitative measurement of caking [2,6,7]. For example, Aguilera et al. [6] reported the "caking index" defined as the weight fraction of sample retained by a mesh, the angle of repose or the ratio of system porosity to initial system porosity. However, a standardized method for characterizing caking is not readily available in literature. Nevertheless, caking degree is clearly dependent on the appearance of lumps. The lumps may be small and isolated perturbing only slightly free flowing or they may connect forming a sticky bulk without free flowing possible. The caked lumps may be held together by strong or weak attachment: this reflects the hardness of the cake. A correct definition of "caking" consists of combining qualitative observations of the lumps and the quantitative examinations of the degree of hardness of the lumps. Crushing by the Instron universal testing technique is commonly used for measuring the degree of hardness of compacts [7].

Caking of pure substances made of organic and inorganic compounds such as NaCl and sucrose, respectively, is well described in the literature [5,6,8,9]. In this study, we propose to focus on deliquescent mixtures, which are often present in numerous areas such as pharmaceutics, food, fertilizers, aerosols, etc [1,10,11]. They are of great interest because of the phenomenon of "deliquescence lowering": the simultaneous deliquescence of two or more crystalline substances takes place at RH lower than their respective DRH, the corresponding DRH being termed the mutual deliquescence relative humidity (MDRH) [12]. The phenomenon of mutual deliquescence lowering is closely related to the attractive interactions between ions and water molecules: in presence of another water-loving species the attractive interactions are enhanced, water evaporation is therefore diminished and equilibrium vapor pressure is lowered [4]. In this study, a higher sensitivity of mixtures with respect to water compared to single substances is demonstrated by means of water uptake measurements and ESEM analysis. Caking tendency may also be reinforced in such mixtures. However, very few works evaluate the impact for the tendency to cake [13]. Instron® technique will also be combined with kinetic measurement of water sorption and desorption in order to

highlight the role of water in compact hardness. The objective of this work is to evidence the reinforced caking in mixtures from simulations of variations of air humidity and to evaluate the influence of the solid composition.

2. Material and methods

2.1. Materials

Sodium chloride and sucrose crystals of micrometric size of purity superior to 99.5% were obtained from Sigma Aldrich (France). In order to analyze mixtures, we define the mass solid fraction, $f_{NaCl/sucrose}$, by the following expression:

$$f_{NaCl/sucrose} = \frac{m_{NaCl}}{m_{NaCl} + m_{sucrose}} \tag{3}$$

The mixtures NaCl-sucrose under study are $f_{NaCl/sucrose} = 0.75$, $f_{NaCl/sucrose} = 0.50$ and $f_{NaCl/sucrose} = 0.16$ (weight basis), the last one corresponds to the eutonic composition, i.e. composition of a mixture with the lowest DRH [13].

Samples under study can be either under the form of powder or compact. The preparation of cylindrical compacts consists of filling the entire volume of a cylindrical form of 13 mm diameter and 20 mm height. Powder mass was approximately equal to 3 grams. An adapted piston moves vertically toward the powder in the cylindrical form until reaching a pressure of 0.25 bar under press. The consolidation of dry crystals is then obtained by mechanical imbrications, maintaining the dry crystals together.

2.2. Methods

2.2.1. Moisture sorption and desorption

Samples, typically of 13 mg approximately, of crystals of micrometric size (purity 99.5% provided by Sigma Aldrich), were submitted to the continuous gas flow of 200 cm³/min at constant temperature of 25 °C. Gas consists of pure nitrogen mixed with water vapor saturated nitrogen in proportion corresponding to the desired relative humidity. Mass variations due to the uptake of water from the gas phase were measured by an accurate microbalance system (DVS, Surface Measurement Systems) with a precision of 0.1 μg. Temperature and humidity were controlled to 0.1 °C and 0.5% RH, respectively.

2.2.2. Environmental scanning electronic microscopy (ESEM)

The environmental scanning electron microscopy instrument (XL30, Philips, The Netherlands) allows the examination of particles under moderate vacuum (up to 50 Torrs for low magnifications). Sample observation is carried out in the environment of controlled temperature, pressure and humidity. Wetting and drying can be induced by varying RH in the observation chamber.

By keeping temperature at 2 °C and by varying the pressure of the water vapor between about 3 and 5 Torrs (400 and 666 Pa), the deliquescence of crystals was observed at imposed RH superior to their DRH (or MDRH in mixtures) while water evaporation and subsequent re-crystallization was observed when the pressure of water vapor is lowered to the values corresponding to RH lower than DRH (or MDRH).

Desired RH in observation chamber is established by increasing the water vapor pressure in step-by-step fashion with steps of 0.1 Torr. Long enough period of time was allowed for steady image to be obtained. However, ESEM images remain qualitative observations of deliquescence and recrystallization of a solid in an atmosphere containing water vapor, with no possibility to affirm the state of equilibrium.

2.2.3. Caking simulations by HydroGen2 Rotronic

Caking conditions are reproduced thanks to the precise control of temperature and relative humidity in the chamber of the HydroGen2