Water-Solids Interactions: Deliquescence

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Key Words

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Abstract

Deliquescence is a first order phase transition from solid to solution that occurs at a relative humidity (RH) that is characteristic to the solid ingredient. In blends containing more than one component with deliquescent behavior, the RH of the solid-solution transition will be lowered, leading to some level of dissolution at relatively low RH conditions. Dissolution arising as a result of deliquescence will impact the chemical and physical stability of complex food systems. Because chemical reactions occur much more readily in solution, deliquescence will enhance the degradation of labile food ingredients. RH fluctuations will lead to cycles of deliquescence and efflorescence (crystallization), which will contribute to particle agglomeration and caking. This review addresses the phenomenon of deliquescence, the significance of deliquescence to the food industry, measurement techniques, the kinetics and thermodynamics of deliquescence, the behavior of mixtures of deliquescent salts (including phase diagrams and thermodynamics of binary systems), and consequences of deliquescence on chemical and physical stability of powdered food and nutritional ingredient blends.

INTRODUCTION

Deliquescence: a first order phase transition from solid to solution that occurs at a relative humidity (RH) that is characteristic to the solid ingredient

It is widely recognized that the presence of residual moisture in powder food ingredient blends can lead to many significant changes in physical and chemical properties. These changes can influence the performance of ingredients in storage and during manufacturing processes, as well as the performance of the final food product or ingredient blend. The effect of water on the bulk properties of formulations has been reviewed (Duckworth 1975, Rockland & Stewart 1982, Simatos & Multon 1985, Seow 1988, Levine & Slade 1991, Blanshard & Lillford 1993, Roos 1995, Barbosa-Cánovas et al. 2007), and residual moisture has been found to be implicated in inducing phase transformations, affecting chemical and physical stability, and changes in powder flow and mechanical properties during compaction. Special characteristics enable the water molecule to interact with solids by various modes. These include (*a*) small size (~29 Å^3), which makes it a good penetrant and space filler, and (*b*) the capability to form extensive hydrogen bond networks as a direct result of its ability to act as both a hydrogen bond donor and acceptor. There are five major mechanisms of water-solid interaction. These are adsorption onto the surface of the solid particle, capillary condensation, deliquescence, crystal hydrate formation, and vapor absorption into the bulk of amorphous solids (**Figure 1**). Although known to affect product performance, the interactions of water with food components are not always particularly well understood at a fundamental level, particularly in complex systems. Of the five types of interactions described above, absorption into amorphous materials and deliquescence are likely to have the greatest impact on product performance. There are numerous reports of water absorption into amorphous materials and resulting effects in the food science literature (examples include Bell & Hageman 1994, Bell et al. 1998, Lievonen et al. 1998, Bell & White 2000, Mauer et al. 2000); however, even though numerous common food ingredients undergo deliquescence (such as sucrose, glucose, fructose, citric acid, ascorbic acid, monosodium glutamate, thiamine HCl, sodium diacetate, and NaCl), information about this phenomenon targeted to the food science community is limited. This review addresses the phenomenon of deliquescence, the significance of deliquescence to the food industry, measurement techniques, the kinetics and thermodynamics of deliquescence, the behavior of mixtures of deliquescent salts (including phase diagrams and thermodynamics of binary systems), and consequences of deliquescence on chemical and physical stability of powder food and nutritional ingredient blends.

OVERVIEW OF DELIQUESCENCE

The impact of moisture on the chemical and physical stability of food systems is of great concern, having significant implications for product manufacturability, quality, and shelf-life. Interaction of

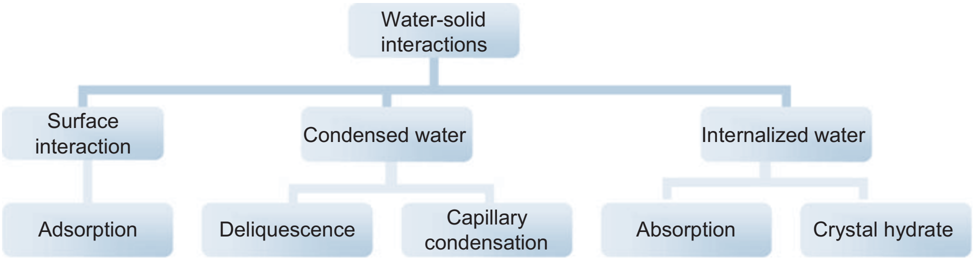

Figure 1

The five types of water-solid interactions.

powders with water can result in a range of deleterious effects including caking and agglomeration of the powder and chemical instabilities that lead to degradation and reduced availability of bioactive compounds. One type of water solid interaction that is of great importance for highly water soluble crystalline compounds is the phenomenon of deliquescence. A crystalline substance is said to deliquesce when it forms a solution when the ambient relative humidity (RH) reaches a certain threshold value (Martin 2000). Deliquescence is a first order phase transformation of the solid to a saturated solution, which is triggered at a well defined relative humidity that depends on the properties of the solid and the temperature (Zografi & Hancock 1994, McNaught & Wilkinson 1997). When this RH is reached, the aqueous solution is the thermodynamically favored phase, and dissolution commences. Below this RH, the crystalline solid surrounded by gaseous water is favorable (Martin 2000). This characteristic RH is termed RH_0 for the purposes of this review and is defined as the RH above a saturated solution of the solid. The reverse process to deliquescence is termed efflorescence. Efflorescence is the process of crystallization and expulsion of water from the crystallized material as the ambient RH is reduced below RH_0. When a substance effloresces, hysteresis is typically observed; i.e., the efflorescence process takes place at an RH value lower than RH_0 (Martin 2000).

RH: relative humidity

***RH_0*:** deliquescence relative humidity of a single ingredient. The RH above a saturated solution of the solid

Efflorescence: the process of crystallization and expulsion of water from a crystallized material as the ambient RH is reduced below RH_0

RH_i: relative humidity of the environment

Many ingredients found in foods are deliquescent. Deliquescence is of particular relevance for powdered foods, where the intent is to maintain the product as a free flowing, low moisture powder. Types of ingredients showing deliquescence include inorganic salts (Adams & Merz 1929), organic salts (Peng & Chan 2001, Cziczo et al. 1997, Salameh & Taylor 2005), sugars (Ruegg & Blanc 1981, Peng et al. 2001b), organic acids and bases (Peng et al. 2001a, Peng et al. 2001b), vitamins (Yamamoto & Takahashi 1952, Hiatt et al. 2008), preservatives, and flavor enhancers. These ingredients are found in a variety of food products including powdered sport beverages, infant formula, seasoning blends, and vitamin supplements. The RH_0 values for a number of chemically different ingredients of relevance to foods are presented in **Table 1**. It can be seen that the susceptibility to RH varies dramatically from ingredient to ingredient and even within a class of ingredients with similar functionality. For example, sucrose deliquesces at a relatively high RH of 85% (25°C) whereas fructose has a RH_0 value of 64%. The difference in RH_0 between these two substances results from their different aqueous solubilities. Higher solubility compounds will tend to have lower RH_0 values. Furthermore, if solubility increases with temperature, RH_0 will be reduced at higher temperatures, as discussed in more detail below. Deliquescent crystalline solids typically have high molal solubilities. The salts commonly used to control RH in desiccator studies are deliquescent, and their deliquescence points (RH_0s) correspond to the environmental RHs created by sealing the saturated salt solutions into desiccators.

THERMODYNAMICS OF DELIQUESCENCE

A schematic of the deliquescence process is shown in **Figure 2**. When the ambient relative humidity (RH_i) is below RH_0, water interacts with the solid through the mechanism of adsorption. Typically, highly crystalline solids adsorb only a few molecular layers of water. For example, below RH_0, sodium chloride adsorbs 2–3 monolayers of water and bulk dissolution is not seen (Foster & Ewing 2000, Barraclough & Hall 1974). Upon increasing the relative humidity, more vapor is adsorbed at the surface, and at some point when the relative humidity of the surroundings exceeds the RH_0 of the solid, a thin film of saturated solution of the solid develops on the particle. This formation of a film of saturated solution on the surface of water-soluble solids with a lower vapor pressure than that of pure water is the basis for the deliquescence process (Zografi 1988). Deliquescent solids have a large colligative effect and their high water solubility leads to a substantial reduction in the water vapor pressure of the saturated aqueous solution compared with pure

Table 1 RH_0 and a_w values of deliquescent individual food ingredients

Single ingredients	RH_0 (%), 25°C	a_w*100, 25°C	References
Ascorbic acid	>95	98	Salameh et al. 2006; Hiatt et al. 2008
Citric acid anydrous	74–75	76–78	Salameh et al. 2006
Citric acid monohydrate	78	78	Peng et al. 2001b; Salameh et al. 2006
EDTA disodium salt	>95	96	
b-D-Fructose	62–63	61–62	Rüegg & Blanc 1981; Salameh et al. 2006
Fumaric acid	>95	99	
α-Glucose anhydrous	89–91	90	Rüegg & Blanc 1981; Peng et al. 2001b; Salameh et al. 2006
α-Glucose monohydrate	91	90	Salameh et al. 2006
β-Glucose	74	74	Salameh et al. 2006
α-Lactose monohydrate	95	99	Salameh et al. 2006
β-Lactose	95	97	Salameh et al. 2006
Malic acid	59	58	
Maltose monohydrate	95	97	Rüegg & Blanc 1981; Salameh et al. 2006
Mannitol	96	98	Ninni et al. 2000; Salameh et al. 2006
Monosodium glutamate	87	87	
Potassium benzoate	85	86	
Potassium chloride	85	85	
Potassium citrate monohydrate	59	61	
Potassium phosphate monobasic	>95	96	
Potassium sorbate	71	70	
Potassium sulfate	>95	97	
Sodium ascorbate	87	87	Salameh et al. 2006
Sodium benzoate	85	86	
Sodium bisulfite	80	79	
Sodium chloride	76	75	Tang et al. 1978
Sodium citrate dihydrate	83	81	
Sodium citrate tribasic dihydrate	86	86	Salameh et al. 2006
Sodium diacetate	70	69	
Sodium hexametaphosphate	54	54	
Sodium saccharine	92	91	
Sorbic acid	>95	100	
Sorbitol	69–91	67	Ninni et al. 2000; Peng et al. 2001b; Salameh et al. 2006
Sucrose	85	85	Ruegg & Blanc 1981; Salameh et al. 2006
Thiamine HCl	89.0	90.0	Salameh et al. 2006; Hiatt et al. 2008
Xylitol	77–79	79	Ninni et al. 2000; Salameh et al. 2006

water vapor pressure, and this causes water to condense at a lower relative humidity (Zografi 1988, Zografi & Hancock 1994). This can be seen by considering the following equations: The chemical potential, μ, of pure liquid water in equilibrium with its vapor can be expressed as

$$\mu = \mu_0 + RT \ln p_0, \tag{1}$$

where p_0 is the vapor pressure, μ_0 is the standard chemical potential, R is the gas constant, and T is the temperature. For a saturated aqueous solution at the same temperature, which has a vapor

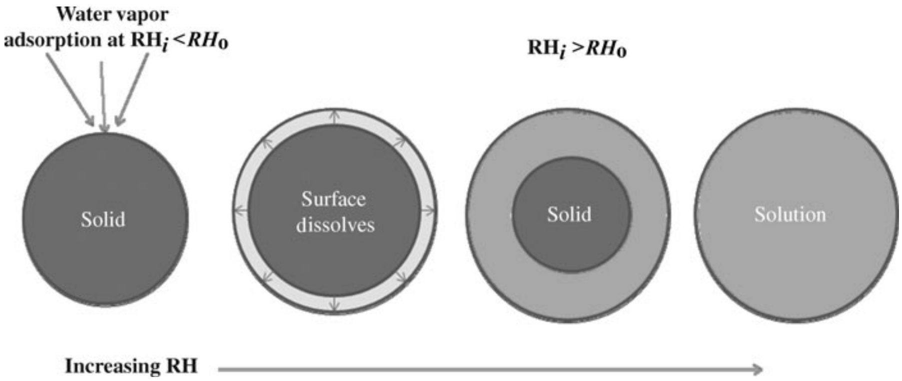

Figure 2

Schematic of the deliquescence process. Adapted from Van Campen et al. (1983a).

pressure p_s which is less than p_0, and a chemical potential μ_s, the difference in chemical potential between water in the solution and pure water can be expressed as

$$\mu_s - \mu = RT \ln\left(\frac{p_s}{p_0}\right). \tag{2}$$

Water in the film of saturated solution will have a lower thermodynamic activity relative to pure water. Thus, a driving force exists for condensation of water when the vapor pressure exceeds p_s, or equivalently when the relative humidity of the surroundings exceeds RH_0. Water vapor condensing into the film raises the vapor pressure of the film to that of the surrounding water vapor pressure. Further dissolution of the solid results until saturation is achieved, bringing the vapor pressure back down to RH_0. Thus, condensation and dissolution alternate until all of the solid dissolves. Equilibration with the atmosphere is reached when complete dissolution and some degree of solution dilution have occurred (Van Campen et al. 1983a).

MEASURING THE CRITICAL RELATIVE HUMIDITY FOR DELIQUESCENCE (RH_0)

Deliquescence, the solid to solution transformation, can be measured by any technique that is sensitive to the phase transformation. Methods for determining RH_0 of a substance can either start with the powder and measure a change in properties with increasing RH, or measure the properties of a saturated solution of the substance in equilibrium with water vapor. Methods that use a powder typically employ gravimetric moisture sorption, and there are two types of measurements that can be made: moisture uptake rates at fixed relative humidities above RH_0 can be determined and extrapolated back to a zero moisture uptake rate (Kontny & Zografi 1995, Salameh & Taylor 2005, Van Campen et al. 1980), or alternatively and more conveniently, a continuous measurement of weight uptake with increasing RH in a temperature and relative humidity–controlled environment, yielding a vapor sorption isotherm. An example of this method showing the deliquescence of fructose, citric acid, and their mixtures is depicted in **Figure 3**. The sharp increase in weight gain is indicative of the deliquescence event. The specific RH_0 is found by extrapolating the linear portions of the isotherm before and after the deliquescence event (Salameh & Taylor 2005). One assumption made with gravimetric measurements is that there is no hysteresis arising from kinetic factors relative to the equilibrium thermodynamic solution measurements. Although such a hysteresis has been shown for highly ordered sodium chloride crystals which are

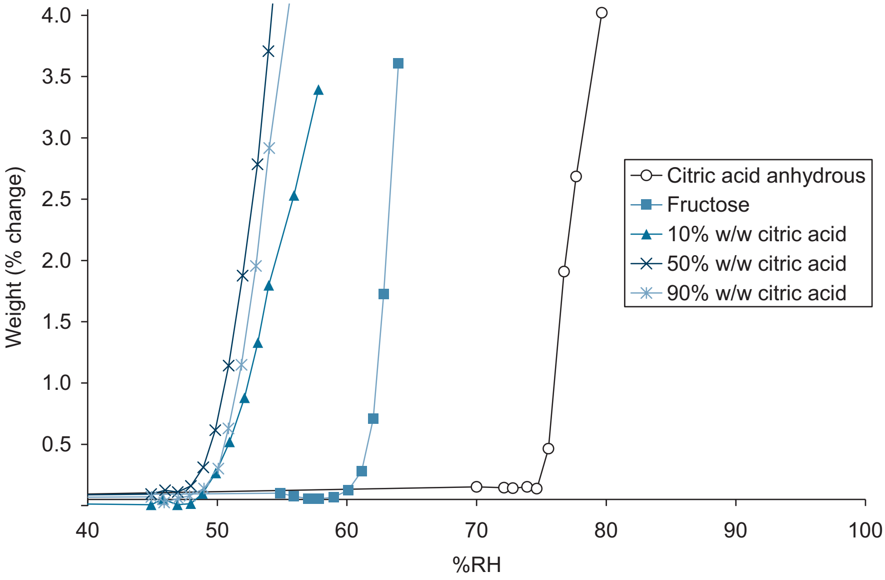

Figure 3

Moisture sorption profiles for citric acid, fructose, and various binary mixtures. It can be seen that deliquescence occurs when there is a sharp increase in the weight gain of the sample. Mixtures deliquesce at a lower relative humidity (RH) than either of the components forming the mixture. Figure adapted from Salameh & Taylor (2006a).

resistant to deliquescence until a slightly higher RH than that found above a saturated solution (Cantrell et al. 2002), it has been shown that the RH_0 measured by this gravimetric method agreed closely to relative humidity or a_w measurements of saturated solutions of the systems (Salameh & Taylor 2005).

When considering the deliquescence process, one assumption is that the solid particles are surrounded by a saturated solution at RH_0 (Van Campen et al. 1983a). By definition $a_w = RH/100$. Therefore, a_w measurements of saturated solutions can be used to predict RH_0. Typically, the water activity (a_w) in the solution is measured by assuming equilibrium with the headspace above the solution. A measurement of the dew point of the water vapor contained in the headspace then yields the a_w in solution (Ayerst 1965, Richard & Labuza 1990, Roa & Dedaza 1991, Velezmoro et al. 2000). To use a_w measurements to predict RH_0, saturated solutions of the test ingredient(s) can be prepared by mixing approximately 4 g of solid ingredient with small amounts of double distilled water (∼250–500 μl), allowing the test solution to equilibrate to ensure saturation with the solid phase(s), and recording the a_w (Salameh et al. 2006). The a_w measurements can be recorded over time and plotted to ensure equilibrium has been reached. It is important to achieve equilibrium prior to recording the a_w and to avoid adding too much water thereby diluting the system. Although numerous a_w prediction models exist for dilute single and multi-solute solutions (Norrish 1966, Ross 1975, Sloan & Labuza 1976, Vega-Mercado & Barbosa-Canovas 1994), their applicability to deliquescent solid/saturated mixtures with significant solute-solute interactions may be limited.

a_w: water activity

Deliquescence can be visually assessed using a microscope stage with temperature and humidity control. The transformation of initial powder samples into solutions as a response to increasing humidity and/or temperature can be recorded to verify the RH at which deliquescence is observed (Salameh & Taylor 2005).

Other techniques such as conductivity, hygroscopic growth measurements, and infrared spectroscopy have been used to measure or monitor deliquescence; however their applicability to mixtures of food ingredients may be limited. Yang et al. (2002) studied the conductivity of hygroscopic salt deposits and found that a dramatic increase in the conductivity takes place as the salt dissolves and transforms into a saturated solution at or above RH_0. Absorption infrared spectra were used to monitor OH (hydroxyl group)-stretching vibration bands as indicators of hydrogen bonding networks and thin/multilayer film water on salt surfaces, which could be related to RH_0 (Cziczo et al. 1997, Onasch et al. 1999, Cziczo & Abbatt 2000, Foster & Ewing 2000, Brooks et al. 2003, Liu & Laskin 2009). The approach of monitoring hygroscopic growth and particle mobility diameters of salt crystals as a function of relative humidity has been used to determine RH_0 (below RH_0 there is almost no growth) as well as identify that one to four monolayers of water are adsorbed on a NaCl surface prior to deliquescence (Ewing 2004).

KINETICS OF DELIQUESCENCE

The kinetics of deliquescence increase as the RH increases above RH_0. At RHs close to RH_0, the deliquescence process can be extremely slow, taking hours or even days before the system reaches equilibrium. This can clearly be seen from Equation 3, taken from the work of Van Campen et al. (1983a, 1983b, 1983c), who modeled and experimentally studied the kinetics of moisture uptake in single component deliquescent solid systems and reported the results in a series of three articles.

In the first article (Van Campen et al. 1983a), a heat transport model (Equation 3) was developed which quantitatively describes water sorption kinetics above RH_0 in an atmosphere of pure water vapor. This model applies only to situations in which the rate is determined solely by the kinetics of heat transfer away from the surface to the atmosphere. One basic assumption is that a deliquescent solid retains a film of saturated solution surrounding the particle when $RH_i \geq RH_0$ throughout the process of steady-state moisture uptake (Van Campen et al. 1983a). Other major assumptions include (*a*) the solid is initially surrounded by an environment of pure water in which vapor diffusion may be ignored (vacuum conditions), (*b*) in order for vapor to condense at the surface, the heat of condensation must be released and transported to the surroundings, (*c*) the ability of the system to transport the heat to the surroundings is the limiting factor for vapor condensation, (*d*) mass transport in the aqueous film surrounding the solid does not become rate limiting in determining the concentration of material dissolved in the film (zero concentration gradient within the liquid film), (*e*) a zero gradient in temperature exists across the solid and liquid phases, and (*f*) only the conductive flux contributes to the temperature gradient in the vapor film surrounding the surface, and thus a steady-state analysis is valid. For a compressed circular disk sample situated symmetrically near the hemispherical base of a cylindrical chamber, the heat transport model may be represented by the following equation:

$$W_b' = \left[\frac{60M_w 4\pi kab}{\Delta H\,(b-a)}\left(\frac{RT_c^2}{\Delta H_v - RT_c \ln\frac{RH_i}{RH_0}}\right) + \frac{60M_w 4\pi ka^2\sigma e}{\Delta H}\left(\frac{4RT_c^5}{\Delta H_v - RT_c \ln\frac{RH_i}{RH_0}}\right)\right] \times \ln\frac{RH_i}{RH_0}, \qquad (3)$$

where W_b' is the sorption rate, M_w is the molecular weight of water, k is thermal conductivity, a is the effective sample radius, b is the chamber radius, ΔH is the heat generated or consumed per unit moisture condensed, R is the gas constant, T_c is the temperature of the chamber, ΔH_v is the heat of vaporization, RH_i is the relative humidity of the atmosphere, RH_0 is the critical relative humidity, σ is the Stefan-Boltzmann constant, and e is emissivity.

Deliquescence lowering: the RH at which deliquescence occurs when two or more deliquescent powders are in physical contact is lower than for any of the individual components

Equation 3 may be written in a simpler form:

$$W'_b = (C + F)\ln \frac{RH_i}{RH_0}. \tag{4}$$

Here C and F represent the conductive and radiative terms, respectively. C and F were found to contribute equally to heat transport. Both terms were derived to show the dependency of W'_b on the characteristic disk dimensions, a. It can be seen from Equations 3 and 4 that when $RH_i = RH_0$, then the sorption rate is zero.

In the second article by Van Campen and coworkers (1983b), the applicability of the heat transport model was tested for various alkali halides, choline halides, and sugars under vacuum conditions of pure water vapor. Excellent agreement was found between the experimental and calculated values of W'_b, with the latter determined by using the known solubility, RH_0, and heats of solution and condensation, and heats of hydration when necessary. The effect of other factors such as the compression pressure used to make the test compacts, disk size, initial weights, and temperature changes at the surface on the heat transport model were studied as well.

The model was extended in the third and final article in the series by Van Campen and coworkers (1983c) for a system in approximately one atmosphere of air. The model was developed by assuming only mass transport occurs and then combining the resulting equation with the heat transport model. The final combined mass-heat transport model is expressed as

$$W'_{mb} = -\frac{60M_w \cdot 4\pi \cdot c\,DP_0\,(RH_i - RH_0)}{100P_T\left(\dfrac{1}{a} - \dfrac{1}{a'}\right) - \dfrac{c\,DP_0 \cdot \Delta H\,(b-a)RH_0}{14.72\left[kab + 4T_c^3 a^2\sigma \cdot e(b-a)\right]}}, \tag{5}$$

where P_T is the total water vapor and inert gas pressure, c is the total molar concentration in the atmosphere, D is the binary diffusion coefficient, and a'–a is the effective thickness of the vapor diffusion layer, and the other terms are identical to those in the heat transport equation. The model was found to predict well the water vapor sorption by the three salts: potassium bromide, potassium iodide, and choline iodide.

It is apparent from Equation 3 that the kinetics of deliquescence depends on the ratio RH_i/RH_0 and that when RH_i is close to RH_0, the kinetics will be slow. The slow kinetics of deliquescence close to RH_0 have important practical implications. First, in terms of establishing equilibrium behavior, e.g., equilibrium moisture contents, long experimental periods may be required. This may be problematic if the system degrades as a result of deliquescence because the changing composition will influence the equilibrium behavior. Second, if there are RH fluctuations, it is important to realize that the extent of deliquescence will be governed by the extent to which RH exceeds RH_0 and the length of time of the RH excursion above this value as well as particulate characteristics such as specific surface area.

DELIQUESCENCE IN MULTI COMPONENT SYSTEMS: THE PHENOMENON OF DELIQUESCENCE LOWERING

When two or more deliquescent powders are in physical contact, the RH at which deliquescence occurs is lower than for any of the individual components. A visual example of deliquescence lowering is shown in **Figure 4** and similar examples have been reported in the literature (Salameh et al. 2006, Salameh & Taylor 2005). Citric acid deliquesces at 75% RH, whereas sucrose has a RH_0 of 85% RH. Two of the crystals were placed in contact with each other and two crystals remained as controls (**Figure 4*b***). The RH was then set to 72% RH (25°C) using a controlled humidity microscope stage, and the system was monitored with time. It can be observed that the citric acid and sucrose crystal in contact with each other begin to deliquesce (**Figure 4*c***) and that the extent of deliquescence increases with time (**Figure 4*d***) such that after 18 hours the citric acid has completely dissolved and the sucrose crystal is largely dissolved. However, the control crystals are still intact and show no signs of deliquescence. Another example of deliquescence lowering is shown in **Figure 3**, where it can be seen that the deliquescence RH of a mixture occurs at a lower value than the RH_0 values for either of the pure component powders. It is interesting to note from **Figure 3** that the extent of deliquescence lowering is not affected by the relative composition of the two ingredients in the blend. This result can be rationalized by considering the thermodynamic basis for deliquescence lowering, which is discussed in more detail below.

RH_{0mix}: deliquescence relative humidity for an ingredient blend

History of Deliquescence Lowering

Deliquescence lowering is a well-established phenomenon that was first reported to occur in fertilizers composed of inorganic salts mixtures (Adams & Merz 1929) and has also been widely observed in atmospheric aerosols (Ge et al. 1996, Ge et al. 1998, Wexler & Seinfeld 1991, Tang & Munkelwitz 1993) as well as more recently for food and pharmaceutical systems (Kontny & Zografi 1985, Salameh et al. 2006, Salameh & Taylor 2005, Hiatt et al. 2008, Yamamoto & Takahashi 1952, Ortiz et al. 2009). Deliquescence lowering was first reported by Adams & Merz (1929) who measured vapor pressures above saturated solutions of fertilizers at 30°C. They showed that a mixture of fertilizers generally has a lower vapor pressure at equilibrium than the vapor pressure above a saturated solution of an individual fertilizer, unless a chemical reaction occurred and led to the formation of a double salt which had a higher equilibrium vapor pressure (Adams & Merz 1929). Deliquescence lowering was first shown in pharmaceutical materials by Yamamoto & Takahashi (1952) in a study of the sorption of water by pharmaceutical sugars (glucose and sucrose) and vitamins (ascorbic acid and thiamine). They found that the RH_0 of a mixture of glucose, sucrose, and citric acid was approximately equal to the product of the RH_0s of the individual components, and thus the mixture had a lower RH_0 (called RH_{0mix}). They also reported that varying the composition of the mixture did not affect the RH_{0mix} (Yamamoto & Takahashi 1952). Salameh et al. (2006) first reported deliquescence lowering in food ingredient mixtures containing sucrose, glucose, fructose, citric acid, thiamine HCl, and/or sodium ascorbate. Their study differed from previous reports because the experimental materials were physical blends of particles containing organic ingredients that lacked the intimate contact created by repeated cycles of deliquescence and efflorescence in the inorganic salt containing aerosols (Tang 1976, Tang et al. 1978, Wexler & Seinfeld 1991, Tang & Munkelwitz 1993, Ge et al. 1996). Salameh et al. (2006) found that, even without the intimate contact, deliquescence lowering occurred in all ingredient blends. They also reported that RH_{0mix} was independent of ingredient ratios, that temperature increases can reduce the RH at which deliquescence occurs, and that deliquescence lowering has the potential to affect both chemical and physical stability in powder ingredient mixtures.

Theory of Deliquescence Lowering

Much of the theory around deliquescence lowering has been elucidated by researchers working in the area of atmospheric chemistry, where deliquescence lowering of inorganic salts is important (Tang 1976, Tang et al. 1978, Wexler & Seinfeld 1991, Tang & Munkelwitz 1993, Ge et al. 1996). By starting with the Gibbs-Duhem equation, Wexler & Seinfeld (1991) showed that the RH_0 of an electrolyte will always be lowered by the addition of another electrolyte. The Gibbs-Duhem equation for a general multi-component system of n_i components can be written as follows

$$\sum n_i d\bar{J}_i = 0, \tag{6}$$

where $\bar{J}_i$ is the polar molar quantity of any extensive thermodynamic property. When applied to the chemical potential (μ) it becomes

$$\sum n_i d\mu_i = 0. \tag{7}$$

For a solution of electrolytes (1 and 2) in water (w) at constant temperature and pressure the equation is

$$n_1 d\mu_1 + n_2 d\mu_2 + n_w d\mu_w. \tag{8}$$

If it is assumed that electrolyte 1 is in equilibrium with its solid, i.e., the solution is saturated with respect to electrolyte 1, then the chemical potential will not change with the addition of electrolyte 2, i.e., $d\mu_1 = 0$. However, the chemical potentials of electrolyte 2 and water will change, and thus Equation 8 becomes

$$n_2 d\mu_2 + n_w d\mu_w = 0. \tag{9}$$

Chemical potential (μ) can be defined in terms of activity

$$\mu_i = \mu_i^\circ + RT \ln a_i, \tag{10}$$

where $\mu_i{}^\circ$ is the chemical potential of species i under standard conditions and a_i is the activity of the species i in solution. Combining the previous two equations and substituting $n_2/n_w = M_w m_2/1000$, where m_2 is the molality of electrolyte 2 and M_w is the molecular weight of water, and keeping in mind that $d\mu_i^\circ \equiv 0$, gives

$$m_2 d \ln a_2 + \frac{1000}{M_w} d \ln a_w = 0. \tag{11}$$

Integrating from $m_2' = 0$ to $m_2' = m_2$,

$$\ln \frac{a_w(m_2)}{a_w(0)} = -\frac{M_w}{1000} \int_0^{m_2} \frac{m_2'}{a_2} \frac{da_2}{dm_2'} dm_2'. \tag{12}$$

The evaluation of Equation 12 is difficult for highly concentrated solutions, however, simply by showing that the integrand is greater than zero is sufficient to prove that the RH_0 of the system is lowered by the addition of a second compound. Thus, if the activity coefficient, γ, increases with increasing concentration (as predicted for strong electrolytes at high ionic strength), $d\gamma_2/dm_2 > 0$ and $da_2/dm_2 > 0$, leading to an integrand greater than 0. Thus, the water activity of a saturated solution of component 1 will decrease as component 2 is added until saturated with component 2 when precipitation of component 2 occurs. Further addition will merely increase the amount of salt in the solid phase but will not impact the composition of the solution. A similar analysis can be performed for even more complex multi-component systems to show that the RH_{0mix} of a multi-component mixture is always lower than the RH_0 of the individual salts.

PHASE DIAGRAMS AND DELIQUESCENCE LOWERING

Deliquescence lowering can also be described using a phase diagram (Wexler & Seinfeld 1991). Consider a system composed of two deliquescent solids A and B in equilibrium with their aqueous solution and the vapor phase. A hypothetical phase diagram is shown in **Figure 5**. When the solution is saturated with solute A, the system has a water activity equal to the deliquescence

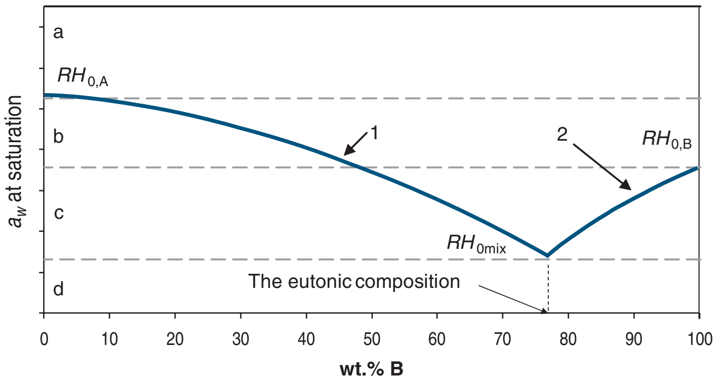

Figure 5

Phase diagram showing water activity at saturation for a hypothetical system of deliquescent components A and B. Figure adapted from Wexler & Seinfeld (1991) and Salameh & Taylor (2006b).

relative humidity ($RH_{0,A}$) of solid A. As solute B is added to the saturated solution, the a_w of the solution will decrease along line 1. This is because the addition of a second highly water soluble component will dilute the amount of water in the system with a corresponding decrease in the relative vapor pressure, as predicted by Raoult's law. When the solutes reach their mutual saturation point, A and B precipitate together and the solution a_w is equal to $RH_{0mix}/100$ [also known as the mutual deliquescence relative humidity (MDRH) (Wexler & Seinfeld 1991)]. The ratio of one solute to the other in solution at this water activity minimum is the eutonic composition. The eutonic composition can be approximated as the ratio of the molal solubilities of the two components, although this estimation does not take into account any changes in the solubility of either component caused by the presence of the other component. Only a solid mixture at the eutonic composition will deliquesce completely at RH_{0mix}; other compositions will partially deliquesce and some of the solid in excess of the eutonic ratio will remain until the relative humidity is raised sufficiently to dissolve all of the solid (Wexler & Seinfeld 1991, Tang et al. 1978).

RH_{0mix} occurs at a global minimum, thus RH_{0mix} (in the absence of the formation of hydrates or any reaction between component A and B to form a new solid form) is always lower than the deliquescence RH of the pure solids. Likewise, commencing from a saturated solution of B, the solution would have a water activity equal to solute B RH_0, and upon adding solute A, a_w decreases along line 2 until RH_{0mix} is reached. The actual physical composition of the system is dependent on the ambient relative humidity. When the ambient RH is above the RH_0 of both solutes (region a), both solids deliquesce and dissolve completely. In region b and to the left of curve 1, the system is composed of solid A in equilibrium with a solution of A and B. To the right of curve 1 in region b, both components are in solution. In region c, when the ambient RH is lower than the individual RH_0 s but higher than the RH_{0mix} (between lines 1 and 2), the system exists as a solution. To the left of line 1 (region c), the system again is composed of solid A in equilibrium with both solutes, and to the right of line 2 the system is composed of solid B in equilibrium with the solutes. In region d, the ambient RH is lower than RH_{0mix} and both components exist as solids.

EFFECT OF TEMPERATURE ON DELIQUESCENCE AND DELIQUESCENCE LOWERING

The RH_0 of a compound can increase, decrease, or remain constant if temperature is varied. If the solubility of an ingredient or mixture of ingredients changes as a function of temperature,

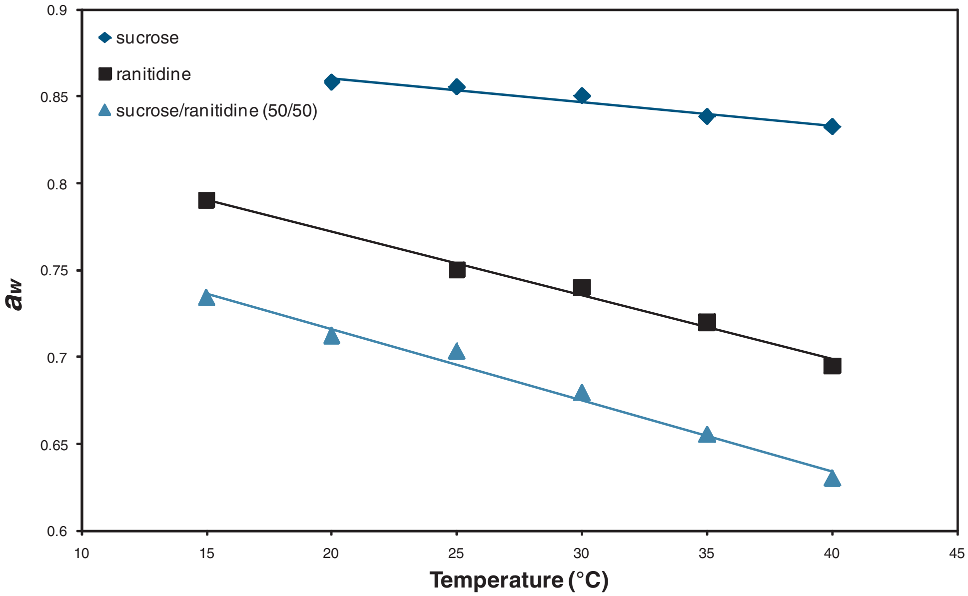

Figure 6

Effect of temperature on the water activity above saturated solutions of sucrose, ranitidine HCl, and a 50:50 wt% binary mixture.

then the deliquescence point of a single component, or multi-component mixtures containing this ingredient, will also change. For most organic compounds, solubility typically increases with an increase in temperature which will lead to a decrease in RH_0 (see **Figure 6**). Here it can be seen that RH_0 decreases for sucrose from approximately 86% RH at 20°C to approximately 83% RH at 40°C. In contrast, the pharmaceutical compound ranitidine HCl (an H_2 receptor antagonist that decreases the production of acid by the stomach and the active ingredient in the well known medicine Zantac^{TM}), has an RH_0 which is much more temperature dependent, RH_0 decreases from 79% to 70% on an increase in temperature from 15°C to 40°C. The binary mixture, which has a lower RH_{0mix} to begin with because of deliquescence lowering, unsurprisingly also shows a decrease in the value of RH_{0mix} as a function of temperature, whereby RH_{0mix} is approximately 73% at 15°C, decreasing to 63% RH at 40°C. These results highlight the importance of considering temperature fluctuations on potential moisture induced phase transformations. Similar temperature dependencies of other organic and inorganic solutes have been reported in the literature and the thermodynamics of temperature effects discussed in more detail (Wexler & Seinfeld 1991, Tang & Munkelwitz 1994, Braban et al. 2003).

EXTENT OF DELIQUESCENCE LOWERING

The deliquescence point of a mixture (RH_{0mix}) is dependent on the individual RH_0 values and has been approximated by the product of the water activities of a saturated solution of each component (Yamamoto & Takahashi 1952, Ross 1975):

$$a_w = (a_w^\circ)_1\,(a_w^\circ)_2\,(a_w^\circ)_3 \cdots .$$

This is known as the Ross equation. Although the Ross equation was not developed to predict deliquescence lowering per se, it has been successfully applied for this purpose (Kontny & Zografi 1985, Salameh et al. 2006, Salameh & Taylor 2005). The Ross equation can be written in terms of the RH_0s using the assumption that a_w is approximately equivalent to $RH_0/100$ by ignoring any kinetic effects. The expression becomes

$$\frac{RH_{0,mix}}{100} = \frac{RH_{0,1}}{100} \cdot \frac{RH_{0,2}}{100} \cdot \cdots \frac{RH_{0,i}}{100}. \tag{13}$$

Ross introduced an empirical interaction parameter to represent the contribution of solute-solute interactions to a_w:

$$\chi = \frac{a_w(observed)}{(a_w^\circ)_1\,(a_w^\circ)_2} \tag{14}$$

where positive deviation in the χ value from unity indicates strong solute-solute interactions and nonideality in the solution. It has been observed that the Ross equation provides reasonable predictions of deliquescence lowering for binary systems (Salameh et al. 2006; **Table 2**) with χ values ranging from 0.94 to 1.28. However, as the number of ingredients in the mixture increased (ternary and quaternary blends), χ values ranged from 0.84 to 2.0 (**Table 2**), indicating that the predictive value of the Ross equation decreases significantly for more complex blends.

In theory, the deliquescence point of a mixture (RH_{0mix}) can be predicted using the individual solute solution a_ws at saturation, given that when a solid mixture deliquesces at RH_{0mix}, a solution saturated with respect to all solutes is produced (Tang et al. 1978, Wexler & Seinfeld 1991). However, as the number of components increases, it has been observed experimentally that the extent of deliquescence lowering predicted by the Ross equation is greater than that experimentally observed, particularly for measurements of powder blends (Salameh et al. 2006) (**Table 2**). The Ross equation better predicted the a_w of the saturated solutions than the RH_{0mix} of the powder blends (Salameh et al. 2006). Possible explanations for these discrepancies are related to the sample physical presentation and the timescale of the experimental measurements. The reduced deliquescence point in powder blends as measured by water vapor sorption requires contact between different ingredients, and as the number of ingredients present in a mixture increases, the likelihood that each ingredient is in physical contact with every other type of ingredient decreases. It is therefore unsurprising that as the number of components increased, differences were seen between this method and the a_w method in which a saturated solution was preformed prior to the measurement (Salameh et al. 2006) (**Table 2**).

CONSEQUENCES OF DELIQUESCENCE

Numerous ingredients present in powder food ingredients, premixes, and finished products are deliquescent. If deliquescence occurs, bulk water is condensed which can provide a solvent environment for other nondeliquescent components. Of significance is the observation that the deliquescent point is lowered in mixtures of deliquescent solids which are commonly present in food systems. This will lead to enhanced moisture sensitivity in such systems at RHs commonly found in processing and storage conditions (as low as 38% RH for the blends shown in **Table 2**) and is a possible cause of chemical and physical instability.

Effect of Deliquescence on Chemical Stability

In general, crystalline materials have enhanced chemical stability relative to either amorphous materials or solutions. This is because molecular mobility is restricted in crystalline solids, whereas

Table 2 RH_{0mix} and a_w values for mixtures of model compounds measured at 25°C. All mixtures were prepared using equal masses of components (e.g., binary mixtures were 50:50 w/w)

Mixture composition	a_w *100 observed	RH_{0mix} (%) observed	RH_{0mix} predicted	$\chi a_w{}^1$
Binary systems				
Citric acid monohydrate + Ascorbic acid	75	74	76	0.99
Citric acid monohydrate + EDTA	76		75	1.02
Citric acid monohydrate + Fructose	48	52	47	1.03
Citric acid monohydrate + Fumaric	73		78	0.95
Citric acid monohydrate + Glucose	68		69	0.97
Citric acid monohydrate + Lactose	77		76	1.00
Citric acid monohydrate + Monosodium glutamate	70		67	1.04
Citric acid monohydrate + Potassium benzoate	69		67	1.03
Citric acid monohydrate + Potassium citrate trihydrate	61		48	1.27
Citric acid monohydrate + Potassium phosphate monobasic	56		74	0.76
Citric acid monohydrate + Potassium sorbate	55		54	1.02
Citric acid monohydrate + Potassium sulfate	72		75	0.96
Citric acid monohydrate + Sodium benzoate	88		69	1.28
Citric acid monohydrate + Sodium chloride	62		59	1.05
Citric acid monohydrate + Sodium hexametaphosphate	53		41	1.27
Citric acid monohydrate + Sodium saccharine	76		70	1.08
Citric acid monohydrate + Sorbic acid	76		78	0.97
Citric acid monohydrate + Sucrose	56	65	65	0.85
Fructose + Citric acid monohydrate	50		48	1.05
Sodium benzoate + Potassium sorbate	70		61	1.16
Sodium chloride + Fumaric acid	78		75	1.04
Sodium chloride + Fructose	43	45	47	0.93
Sodium chloride + Citric acid monohydrate	62	58	58	1.06
Sodium chloride + EDTA	73		72	1.01
Sodium chloride + Glucose	71		67	1.05
Sodium chloride + Lactose	72		74	0.97
Sodium chloride + Monosodium glutamate	65		66	0.99
Sodium chloride + Potassium benzoate	67		65	1.03
Sodium chloride + Potassium citrate trihydrate	52		47	1.11
Sodium chloride + Potassium phosphate monobasic	72		72	0.99
Sodium chloride + Potassium sorbate	54	52	53	1.03
Sodium chloride + Potassium sulfate	72		73	0.99
Sodium chloride + Sodium benzoate	74		67	1.10
Sodium chloride + Sodium hexametaphosphate	56		41	1.38
Sodium chloride + Sodium saccharine	72		68	1.06
Sodium chloride + Sorbic acid	75		75	1.00
Sodium chloride + Sucrose	65	65	64	1.02
Sodium chloride + Fumaric acid	78		75	1.04
Sodium chloride + Galactose	71		72	0.98
Sucrose + Fumaric acid	84		84	1.00

(Continued)

Table 2 (*Continued*)

Mixture composition	a_w *100 observed	RH_{0mix} (%) observed	RH_{0mix} predicted	χa_w[1]
Sucrose + Potassium chloride	69		71	0.97
Sucrose + Ascorbic acid	83	85	83	1.00
Sucrose + Ascorbic acid	82		83	0.99
Sucrose + EDTA	83		81	1.03
Sucrose + Fructose	53		52	1.01
Sucrose + Fumaric acid	84		84	1.00
Sucrose + Glucose	78		76	1.03
Sucrose + Lactose	84		83	1.01
Sucrose + Monosodium glutamate	74		73	1.00
Sucrose + Potassium benzoate	68		73	0.93
Sucrose + Potassium citrate trihydrate	52		52	0.98
Sucrose + Potassium sorbate	58	63	59	0.97
Sucrose + Potassium sulfate	82		82	1.00
Sucrose + Sodium benzoate	73		75	0.97
Sucrose + Sodium chloride	64	65	64	1.01
Sucrose + Sodium hexametaphosphate	55	57	46	1.20
Sucrose + Sodium saccharine	75		76	0.98
Sucrose + Sorbic acid	79		84	0.94
Ternary systems				
Citric acid monohydrate + Fructose + Glucose	47		43	1.1
Citric acid monohydrate + Fructose + Potassium sorbate	52		34	1.6
Citric acid monohydrate + Fructose + Sodium benzoate	49		41	1.2
Citric acid monohydrate + Sodium citrate + Potassium sorbate	51		35	1.5
Citric acid monohydrate + Sucrose + Ascorbic acid	56		64	0.88
Citric acid monohydrate + Sucrose + Ascorbic acid	59		64	0.93
Citric acid monohydrate + Sucrose + EDTA	60		63	0.95
Citric acid monohydrate + Sucrose + Monosodium glutamate	60		57	1.06
Citric acid monohydrate + Sucrose + Potassium benzoate	57		56	1.01
Citric acid monohydrate + Sucrose + Potassium citrate trihydrate	53		40	1.31
Citric acid monohydrate + Sucrose + Potassium phosphate monobasic	58		63	0.93
Citric acid monohydrate + Sucrose + Potassium sorbate	56		46	1.23
Citric acid monohydrate + Sucrose + Potassium sulfate	53		63	0.84
Citric acid monohydrate + Sucrose + Sodium benzoate	60		58	1.03
Citric acid monohydrate + Sucrose + Sodium chloride	48		49	0.96
Citric acid monohydrate + Sucrose + Sodium hexametaphosphate	55		36	1.55
Citric acid monohydrate + Sucrose + Sodium saccharine	70		59	1.18
Fumaric acid + Sucrose + Potassium sorbate	71		59	1.21
Fumaric acid + Sucrose + Sodium benzoate	74		73	1.02
Sodium chloride + Fructose + Citric acid monohydrate	40		36	1.10
Sodium chloride + Fructose + EDTA	43		45	0.95

(*Continued*)

Table 2 (*Continued*)

Mixture composition	a_w *100 observed	RH_{0mix} (%) observed	RH_{0mix} predicted	χa_w[1]
Sodium chloride + Fructose + Glucose	39		42	0.94
Sodium chloride + Fructose + Monosodium glutamate	38		40	0.93
Sodium chloride + Fructose + Potassium benzoate	39		40	0.98
Sodium chloride + Fructose + Potassium citrate trihydrate	38		29	1.32
Sodium chloride + Fructose + Potassium phosphate monobasic	38		45	0.85
Sodium chloride + Fructose + Potassium sorbate	38		33	1.15
Sodium chloride + Fructose + Potassium sulfate	38		45	0.84
Sodium chloride + Fructose + Sodium benzoate	40		41	0.97
Sodium chloride + Fructose + Sodium hexametaphosphate	38		25	1.49
Sodium chloride + Fructose + Sodium saccharine	44		42	1.03
Sodium chloride + Sucrose + EDTA	63		62	1.01
Sodium chloride + Sucrose + Fructose	60		39	1.55
Sodium chloride + Sucrose + Glucose	61		58	1.07
Sodium chloride + Sucrose + Monosodium glutamate	61		56	1.09
Sodium chloride + Sucrose + Potassium benzoate	59		55	1.06
Sodium chloride + Sucrose + Potassium citrate trihydrate	48		40	1.21
Sodium chloride + Sucrose + Potassium phosphate monobasic	60		62	0.97
Sodium chloride + Sucrose + Potassium sorbate	55		45	1.23
Sodium chloride + Sucrose + Potassium sulfate	61		62	0.97
Sodium chloride + Sucrose + Sodium benzoate	62		57	1.08
Sodium chloride + Sucrose + Sodium hexametaphosphate	54		35	1.54
Sodium chloride + Sucrose + Sodium saccharine	63		58	1.08
Sucrose + Fructose + Glucose	52		47	1.1
Sucrose + Lactose + Potassium chloride	65		70	0.9
Quaternary systems				
Citric acid m. + Sucrose + Sodium chloride + EDTA	59		48	1.2
Citric acid m. + Sucrose + Sodium chloride + Fructose	45		31	1.5
Citric acid m. + Sucrose + Sodium chloride + Monosodium glutamate	55		43	1.3
Citric acid m. + Sucrose + Sodium chloride + Potassium benzoate	55		43	1.3
Citric acid m. + Sucrose + Sodium chloride + Potassium phosphate m.	46		48	1.0
Citric acid m. + Sucrose + Sodium chloride + Potassium sorbate	51		35	1.5
Citric acid m. + Sucrose + Sodium chloride + Potassium sulfate	51		48	1.1
Citric acid m. + Sucrose + Sodium chloride + Sodium saccharine	58		45	1.3
Citric acid m. + Sucrose + Sodium chloride + Sodium acetate	71		36	2.0
Citric acid m. + Sucrose + Sodium chloride + Sodium aluminum phosphate	52		32	1.6
Citric acid m. + Sucrose + Sodium chloride + Sodium benzoate	41		44	0.9
Citric acid m. + Sucrose + Sodium chloride + Sodium hexametaphosphate	53		27	2.0

(*Continued*)

Table 2 (*Continued*)

Mixture composition	a_w *100 observed	RH_{0mix} (%) observed	RH_{0mix} predicted	χa_w[1]
Citric acid m. + Sucrose + Glucose + Fructose	44		36	1.2
Citric acid m. + Sucrose + Sodium chloride + Lactose	48		49	1.0
Citric acid m. + Sodium citrate + Potassium sorbate + Sodium benzoate	58		30	1.9
Sodium chloride + Lactose + Monosodium glutamate + Sodium diacetate	64		44	1.4
Sodium chloride + Sucrose + Glucose + Potassium sorbate	47		40	1.2

[1] $\chi a_w = \frac{a_w observed}{a_{w1} * a_{w2}}$ values taken from **Table 1**.

in solutions, mobility is extremely high. Therefore, if deliquescence occurs and a solution is formed, it would be anticipated that chemical stability would be reduced, in particular for compounds readily labile in the solution state. Furthermore, the dissolution of certain compounds may create a specific microenvironment that is conducive to the degradation of another compound. Several literature reports have confirmed that both of these suppositions appear to hold true.

Hiatt et al. (2008) demonstrated that thiamin HCl and sodium ascorbate were much more chemically labile when stored at RHs above their respective RH_0s. Furthermore, when powder blends were prepared with other deliquescent compounds, chemical instability was found to commence when the blends were stored above RH_{0mix}, even though the vitamins alone were stable at this RH. Salameh & Taylor (2006b) showed that the reactivity of sucrose:citric acid physical mixtures at relative humidities below the RH_{0mix} (64%) was minimal over a period of 55 days, whereas at relative humidities above RH_{0mix} degradation proceeded until completion within 55 days, as shown in **Figure 7**. The degradation rates increased with relative humidity for this system, most likely as a result of greater amounts of sucrose being dissolved because sucrose was the excess component relative to the eutonic composition. This was supported by the higher overall amounts of water uptake in the moisture sorption isotherms. Guerrieri et al. observed that small levels of impurities and degradation products decreased RH_0 of a model pharmaceutical salt (Guerrieri et al. 2007) and increased chemical reactivity of the system was observed in the presence of the degradants (Guerrieri et al. 2008). Ortiz et al. (2009) found that an amorphous matrix when plasticized above the glass transition temperature through moisture sorption was able to dissolve deliquescent ingredients, resulting in enhanced reactivity of the system. The chemical stability of this system was further reduced above the RH_0 and RH_{0mix} of the mixtures.

Effect of Deliquescence on Powder Properties

In manufacturing processes, maintaining a free-flowing powder is a necessity for efficient processing (Knowlton et al. 1994) whereby good powder flowability is essential for powder transportation, formulation, and mixing. One process known to result in erratic and poor powder flowability is caking. When a powder cakes, it is transformed from a free flowing powder into lumps, aggregates, and cakes with variable resistance to mechanical handling (Peleg 1983, Aguilera et al. 1995). Formation of liquid bridges is the most common initiator of the caking process in

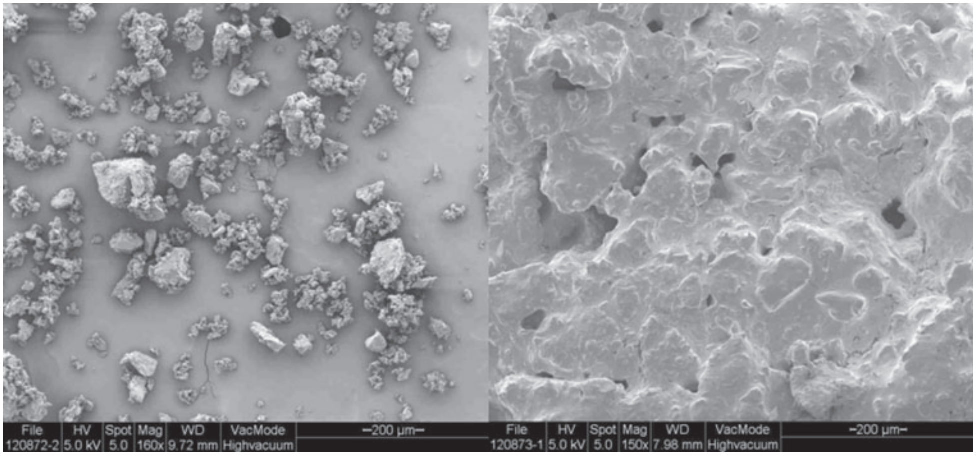

Figure 8

Scanning electron microscopy images of a fructose:citric acid physical mixture kept at 33% relative humidity (RH) showing minimal aggregation (*left*) and fructose:citric acid physical mixture cycled above and below RH_{0mix} showing severe caking of powder (*right*). Figure adapted from Salameh & Taylor (2006a).

powders (Peleg 1983) and caking caused by this mechanism is referred to as humidity caking (Burak 1966). High RH leads to the deliquescence of the solid surface and the formation of a concentrated thin film of solution at the particle surface, which again, upon fusion with other films, leads to the development of liquid bridges. It should be noted that RH_0 is different from the caking point, also termed the critical relative humidity (CRH), which is the minimum RH at which a powder will cake regardless of the mechanism of water uptake (vapor absorption into amorphous regions of the solid or deliquescence) (Teunou & Fitzpatrick 1999, Roge & Mathlouthi 2003).

When liquid bridges are exposed to lower RH conditions, recrystallization may occur resulting in solid bridges and cake formation (Peleg 1983, Roge & Mathlouthi 2003, Purutyan et al. 2005). It has been suggested that deliquescence may play a role in the caking of sucrose (Mathlouthi & Roge 2003, Roge & Mathlouthi 2003). Deliquescence-induced caking in pure glucose, fructose, and citric acid has been reported when the powders were exposed to RH values higher than the individual RH_0 values for these ingredients followed by subsequent storage below RH_0 (Salameh & Taylor 2006a). Physical mixtures of the sugars and citric acid anhydrous showed significant cake formation when cycled between below and above the mixture critical relative humidity. It was found that combinations of glucose and citric acid underwent efflorescence to form crystalline solid bridges when RH was reduced below RH_{0mix}, whereas fructose and citric acid cakes contained amorphous material following storage at low RH. Scanning electron microscopy images are shown in **Figure 8** for fructose and citric acid powder blends before and after storage above RH_{0mix}, showing the caking phenomenon.

PREVENTING DELIQUESCENCE

Deliquescence occurs when the ambient RH exceeds the RH_0 of the deliquescent ingredient or RH_{0mix} of deliquescent ingredient blends. It logically follows that storing ingredients below this

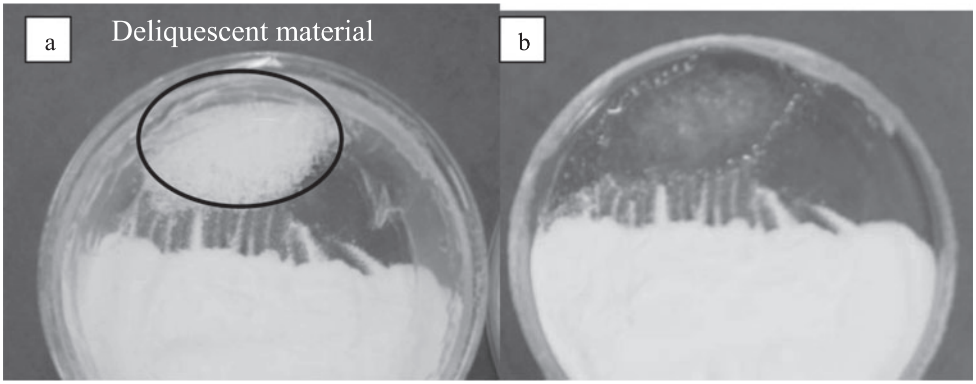

Figure 9

Corn starch equilibrated at 75% relative humidity (RH) for one week and placed in a sealed Petri dish with a mixture of deliquescent ingredients (pre-equilibrated at 11% RH) at a 9:1 ratio: (*a*) Immediately after sealing the dish; (*b*) 65 hrs after sealing the dish, the deliquescent ingredients have deliquesced.

critical RH would prevent deliquescence. In an ideal scenario, ambient RH would be maintained at levels below deliquescence throughout the product life cycle. However, the control of RH to required levels in practical applications can be difficult because water is ubiquitous in the environment where food ingredients and products are processed, stored, distributed, and used. Temperature fluctuations can exacerbate problems. Additionally, moisture transfer will occur between nondeliquescent and deliquescent ingredients in a closed system, even when the initial RH of the deliquescent ingredients was well below RH_{0mix} (**Figure 9**). Therefore, not only is environmental RH a concern, but also moisture associated with coformulated nondeliquescent ingredients. Coating or encapsulating deliquescent ingredients and/or blending with anticaking agents can prevent (or slow) contact with water, thereby inhibiting deliquescence, and/or provide a physical barrier between deliquescent ingredients to avoid deliquescence lowering. After production, barrier packaging can protect products from environmental fluctuations in RH. However, more information is needed to not only provide a mechanistic understanding of the different modes of water introduction into products and effects of movement thereafter, but also to intelligently design products to optimize quality and stability.

SUMMARY POINTS

1. Deliquescence affects a wide spectrum of powder food ingredients.
2. Deliquescence is a little-recognized phenomenon that has very important consequences.
3. Deliquescence lowering is the phenomenon in which blends of deliquescent ingredients undergo deliquescence at lower than expected humidities and has important implications on stability of food systems.
4. More attention should be given to deliquescence and deliquescence lowering to improve understanding of deleterious effects of water on food quality traits.

T_g: glass transition temperature

FUTURE ISSUES

1. Better understanding of deliquescence in multi-component systems is needed, in particular interactions between deliquescent and hygroscopic amorphous ingredients.
2. Better understanding of temperature and RH fluctuations on deliquescence is needed.
3. More information is needed on the kinetics of deliquescence.
4. Better understanding is needed of more complex blends and effects of ingredient intimacy, particle size, and control techniques (e.g., encapsulation).
5. A mechanistic understanding of the interplay between different phase transformations (deliquescence and T_g), different modes of water introduction into products, and movement thereafter is needed.

DISCLOSURE STATEMENT

The authors are not aware of any affiliations, memberships, funding, or financial holdings that might be perceived as affecting the objectivity of this review.

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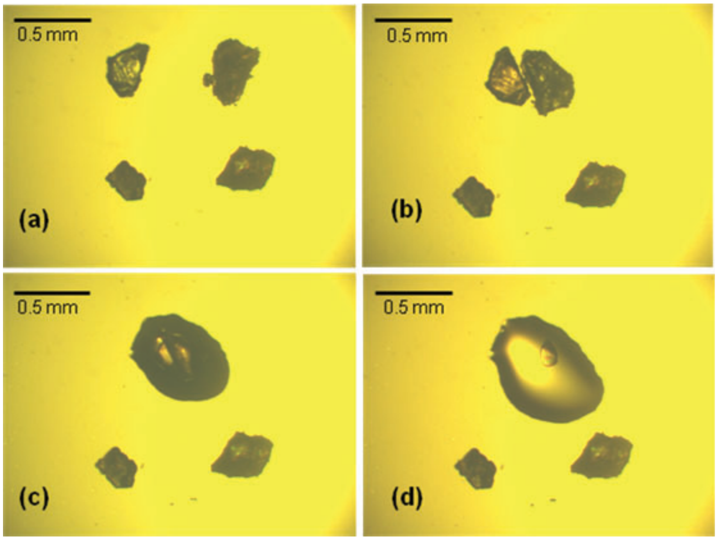

Figure 4

Visualization of deliquescence in mixtures of sucrose and citric acid anhydrous. (*a*) Sucrose crystals (*right*) and citric acid crystals (*left*) are placed on a microscope slide. (*b*) A sucrose and a citric acid crystal are placed in contact and loaded into a controlled temperature, controlled relative humidty (RH) microscope stage. Time = 0 min. (*c*) After 6 hours stored at 72% RH, 25°C, (*d*) after 18 hours stored at 72% RH, 25°C, complete deliquescence of citric acid crystal has occurred with partial deliquescence of the sucrose crystal. Noncontacting crystals remain intact.

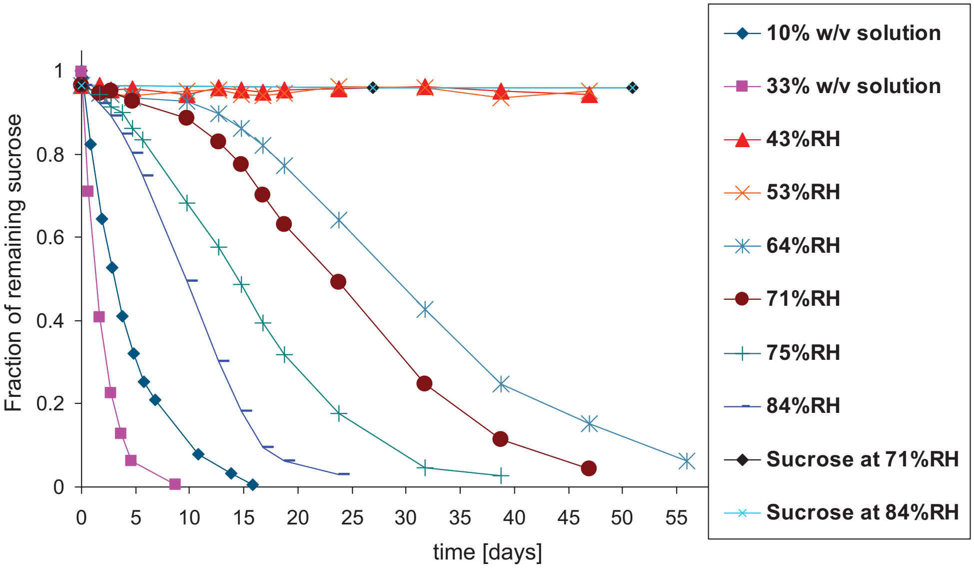

Figure 7

Sucrose inversion kinetic profiles in solutions and physical mixtures of sucrose and citric acid anhydrous stored at various relative humidities at 22°C. Figure adapted from Salameh & Taylor (2006b).

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Errata

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