434g Implications of Deliquescence in Food and Pharmaceutical Products

Adnan K. Salameh, Lisa J. Mauer, and Lynne S. Taylor

The presence of water in food and pharmaceutical systems can produce many undesirable effects on the physical and chemical properties of raw materials and finished products. These effects include phase transformations, chemical degradation, variation in disintegration or dissolution rate, caking, and other changes in flow and compactability. Foods and pharmaceuticals interact with water through a number of mechanisms, one of which is deliquescence. Deliquescence is a moisture-induced phase transformation from solid to solution. A deliquescent ingredient interacts with water vapor from the atmosphere and, at the deliquescence point or critical relative humidity (RH_0), dissolution of the solid occurs and leads to the presence of bulk water with a RH of less than 100%. This RH_0 is characteristic to the solid and has been found to be the same as the RH produced by a saturated aqueous solution of the solid. At RHs below RH_0, deliquescent solids adsorb minimal amounts of moisture via hydrogen bonding at surfaces. On increasing the RH to RH_0, the deliquescent solid will dissolve until saturation is reached, and further increases in RH will result in complete dissolution followed by dilution.

Deliquescent ingredients are typically crystalline solids that are highly water soluble and are capable of producing a significant reduction in colligative properties. Literature reports indicate that the most common category of deliquescent ingredients is salts; however, many other food ingredients, active pharmaceutical ingredients, and pharmaceutical excipients also exhibit deliquescence (including sugars, organic acids, and vitamins common to both foods and pharmaceuticals, as well as pharmaceutical salts such as hydrochloride and sodium salts). The deliquescence of many ingredients, when measured with only one ingredient present, occurs at relatively high RHs (typically 70% RH or above) and is therefore avoidable through selective control of processing, packaging, and storage conditions. However, 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. The deliquescent point for the mixture (RH_{0mix}) is lower than any of the RH_0s of the individual deliquescent ingredients. This phenomenon is supported by the Gibbs-Duhem equation.

The phenomenon of deliquescence in blends of common food and pharmaceutical ingredients and the implications of this moisture induced phase transformation on product quality are not well understood, even though numerous common food ingredients exhibit this behavior. For this study, the RH_0 for individual ingredients and RH_{0mix} for select mixtures of ingredients were measured using a gravimetric water vapor sorption balance. To evaluate the thermodynamics of deliquescence, water activities (a_w) of various saturated solutions were measured using a water activity meter (Aqualab 3TE). Polarimetry was used to monitor the hydrolysis of sucrose in sucrose:citric acid blends. To determine the strength of the agglomerated cakes formed from powder mixtures exposed to RH cycling, a Texture Analyzer (TA.XT2i, Stable Micro Systems) was used to quantify the force required to break such cakes. Optical microscopy was also used to visualize the deliquescence phenomenon.

Results establish that deliquescence lowering occurs in mixtures of common food and pharmaceutical ingredients (including sucrose, lactose, glucose, fructose, citric acid, and thiamine hydrochloride). Visual microscopy images clearly show the deliquescence of two ingredients stored above RH_{0mix} but below RH_0 of either ingredient. There is good agreement between RH_0 estimates from moisture sorption isotherms and a_w measurements. For example, sucrose deliquesces at 86% RH (a_w of a saturated solution is 0.86) and citric acid monohydrate deliquesces at 77% RH (a_w of saturated solution is 0.77). The initial mixture of sucrose and citric acid had RH_{0mix} of 64% RH; however, this mixture showed a gradual decrease in a_w over time. We hypothesized that because chemical reactions occur much more readily in solution, deliquescence-induced dissolution will enhance the degradation of labile food ingredients and that the reduction in a_w over time resulted from the hydrolysis of sucrose to glucose and fructose in the

presence of citric acid. The a_w for a solution saturated with respect to sucrose, citric acid, glucose, and fructose is around 0.46. Polarimetry results indicated that no inversion occurred in citric acid:sucrose mixtures stored at or below 54% RH, but mixtures stored above 54% RH showed significant hydrolysis. To determine the effects of RH cycling on caking and mechanical properties of powdered systems, mixtures of glucose and citric acid were cycled above (72% RH) and below (55% RH) the RH_{0mix} (68% RH). Results show that RH cycling caused caking of the samples, and samples with lower particle size generated cakes that required higher compression forces to break. Results indicate that deliquescence can impact both chemical reactivity and mechanical properties in food and pharmaceutical ingredient mixtures and therefore has implications on quality and functionality of products containing deliquescent ingredients.