



Common-ion effects on the deliquescence lowering of crystalline ingredient blends



Matthew Allan^a, Lynne S. Taylor^b, Lisa J. Mauer^{a,*}

^a Department of Food Science, Purdue University, 745 Agriculture Mall Drive, W. Lafayette, IN 47907, USA

^b Department of Industrial and Physical Pharmacy, Purdue University, 575 Stadium Mall Drive, W. Lafayette, IN 47907, USA

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ABSTRACT

Deliquescence points (RH_0 , RH_{0mix}) of ionic crystalline food ingredients and blends thereof were determined using water activity and moisture sorption techniques. Measured RH_{0mix} values of ingredient blends with and without a common ion were compared to Ross equation predictions of deliquescence lowering. In binary blends with no common ion, measured RH_{0mix} values ranged from 5% RH lower to 6% RH higher than predicted; however, when a common ion was present, the measured RH_{0mix} was consistently 6–8% RH higher than predicted. In tertiary blends with a common ion, RH_{0mix} values were 15–18% RH higher than predicted. The higher RH_{0mix} in blends with a common ion is caused by counterion dissociation competition from the common ion. At equilibrium, these solutions will have fewer solutes and a greater vapor pressure than assumed by the Ross equation. A modified Ross equation was developed to compensate for the common-ion effect and improve RH_{0mix} predictions.

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1. Introduction

1.1. Deliquescence

Understanding and controlling the effects of water–solid interactions are important for maintaining the physical and chemical integrity of many food ingredients and products. The incorporation of water into a blend of dry ingredients can lead to enhanced degradation, phase transitions, clumping, and/or dissolution (Billings, Bronlund, & Paterson, 2006; Li, Taylor, & Mauer, 2011; Lipasek, Ortiz, Taylor, & Mauer, 2012; Mauer & Taylor, 2010; Salameh & Taylor, 2006; Stoklosa, Lipasek, Taylor, & Mauer, 2012). A critical relative humidity (RH) for many hygroscopic crystalline ingredients is the deliquescence point. Deliquescence is a first-order phase transformation of a crystalline solid to a saturated solution that is initiated at a defined relative humidity (RH_0) at fixed temperatures and isobaric conditions (Mauer & Taylor, 2010). Below the RH_0 , a limited amount of water interacts with the surface of the crystal due to adsorption or capillary condensation at irregularities on the surface and contact points between crystals (Zografi, 1988). Once the RH exceeds the RH_0 , a gradient between the chemical potential of water on the surface of the crystal and the water in the air develops. This creates a driving force for moisture to condense on the surface of the crystal (Mauer & Taylor,

2010). During deliquescence, the solution on the surface of the crystal is not in equilibrium with either the RH or the solid, causing continuous condensation and dissolution. Eventually complete dissolution of the crystal will occur if environmental conditions are maintained above the RH_0 (Djikaev, 2002).

Assuming the kinetics of water sorption do not exceed dissolution rates and the solution remains saturated, the water activity (a_w) of the solution on the crystal surfaces will remain constant during deliquescence. This a_w is equivalent to the RH_0 and is correlated with the chemical potential (μ) at the phase boundary where the saturated solution and the solid phase are both thermodynamically stable. The μ of water in the system is directly correlated to the a_w (ratio of vapor pressures) as shown in Eq. (1) (Mauer & Taylor, 2010; Zografi, 1988) where μ_s is the chemical potential of water in the solution, μ is the chemical potential of pure water, R is the gas constant, T is temperature, p_s is the vapor pressure of the solution, and p_0 is the vapor pressure of pure water.

$$\mu_s - \mu = RT \times \ln\left(\frac{p_s}{p_0}\right) = RT \times \ln a_w \quad (1)$$

1.2. Deliquescence lowering

When two or more deliquescent compounds are blended together, they will have a new deliquescence point, known as the RH_{0mix} , that is lower than the individual compounds' RH_0 s (Salameh, Mauer, & Taylor, 2006). This lowering of the RH_{0mix} is

* Corresponding author. Tel.: +1 (765) 494 9111; fax: +1 (765) 494 7953.

E-mail address: mauer@purdue.edu (L.J. Mauer).

related to the increased total number of solutes in a saturated solution containing multiple ingredients compared to saturated solutions containing only a single ingredient. According to Raoult's law, in an ideal solution there is an inverse relationship between the solute concentration and vapor pressure because water interacts with the solute as hydration shells around the ion (Kotz, Treichel, & Weaver, 2006; Winn, 1995). By having multiple solutes in the saturated solution, the total molar concentration increases, causing the a_w of the saturated solution to decrease, thus lowering the deliquescence point. Deliquescence lowering can also be explained by the Gibbs–Duhem equation (Eq. (2)) where n_i is the number of moles of component i and $d\mu_i$ is the change in chemical potential of component i . In a saturated solution containing two ingredients, the chemical potential of the first ingredient (μ_1) will remain constant when incorporating the second component, which will have its own chemical potential (μ_2). The presence of a second compound in a solution will decrease the chemical potential of water (μ_w) relative to a system only containing one ingredient to balance Eq. (2), which has a direct effect on the a_w as seen in Eq. (1) (Mauer & Taylor, 2010; Wexler & Seinfeld, 1991).

$$n_1 d\mu_1 + n_2 d\mu_2 + n_w d\mu_w = 0 \quad (2)$$

A requirement of deliquescence lowering is physical contact between the crystals (Salameh et al., 2006). At crystal–crystal contact points, the capillary radius approaches 0 and at some distance between the crystals there will be water present according to the Kelvin equation (Billings et al., 2006). It is hypothesized that capillary condensation at crystal–crystal contact points initiates dissolution of these solids. The condensed water facilitates the mixing of the two solutes and the deliquescence lowering described by the Gibbs–Duhem equation (Eq. (2)) to take place (Billings et al., 2006; Mauer & Taylor, 2010). The RH_{0mix} is constant regardless of the ratio of the ingredients in the blend because initially only the eutonic composition deliquesces above the RH_{0mix} (Salameh et al., 2006; Salameh & Taylor, 2005). The eutonic composition can be estimated using the ratio of the individual ingredient solubilities (Kwok, Mauer, & Taylor, 2010).

1.3. Predicting the RH_{0mix}

The RH_0 s of single ingredients have been reported in previous studies, but there are fewer documented deliquescence points of blends (Greenspan, 1977; Mauer & Taylor, 2010; Young, 1967). The RH_0 and RH_{0mix} are most often determined by measuring the a_w of a saturated solution of the ingredient(s), as well as by moisture sorption techniques (Mauer & Taylor, 2010; Salameh et al., 2006). Another approach is to estimate the RH_{0mix} by using predictive equations. Examples of such equations are the Zdanovskii–Stokes–Robinson equation, the Ross equation (Eq. (3)), wherein a_w refers to the water activity of a blend, and $(a^\circ)_i$ is the saturated solution a_w of a single compound), and Raoult's Law (Dupas-Langlet, Benali, Pezron, Saleh, & Metlas-Komunjer, 2013; Kwok et al., 2010; Robinson, Stokes, & Marsh, 1970; Ross, 1975).

$$a_w = (a^\circ)_1 (a^\circ)_2 (a^\circ)_3 \dots \quad (3)$$

The Ross equation was shown to be a good predictor of the RH_{0mix} in multiple studies and is the most common model used for predicting the RH_{0mix} (Salameh et al., 2006). For many deliquescent ingredient blends, the Ross equation prediction of the RH_{0mix} is accurate; however, unexplained larger variations have been noticed in some blends (Mauer & Taylor, 2010; Salameh et al., 2006).

1.3.1. Deviations between the measured and predicted RH_{0mix}

The Ross equation has been used to accurately predict the RH_{0mix} for many ingredient blends, with the greatest accuracy at $a_w > 0.55$ (Dupas-Langlet et al., 2013; Kwok et al., 2010).

Assumptions of the Ross equation include: (1) the blend of ingredients will exhibit no solute–solute interactions, and (2) each ingredient will go into solution at its original solubility constant (K_{sp}). In reality, solutes do interact, and as the solute concentration increases deviations from the behavior predicted by the Ross equation also increase. The deviations of RH_{0mix} from the Ross equation predictions are represented using a parameter, χ (Eq. (4)) (Mauer & Taylor, 2010; Ross, 1975; Salameh et al., 2006).

$$\chi = \frac{\text{(Measured } RH_{0mix})}{\text{(Predicted } RH_{0mix})} \quad (4)$$

The RH_{0mix} can be lower than predicted ($\chi < 1$) for blends with an enhanced solubility, where there is a negative Gibbs free energy of mixing (Kwok et al., 2010). According to the Debye–Hückel theory, enhanced solubilities are expected with increasing concentrations, and therefore the measured a_w values tend to be lower than predicted. However, there are circumstances where the measured RH_{0mix} is greater than the predicted RH_{0mix} ($\chi > 1$). A possible trend we observed when reviewing published datasets was that χ tended to be > 1 when a common ion was present in an ingredient blend (Li, Gupta, Eom, Kim, & Ro, 2014; Mauer & Taylor, 2010). The main objectives of this study were to explore differences in deliquescence behaviors of ingredient blends with and without a common ion in order to investigate the common-ion effect on deliquescence and to improve the prediction of the RH_{0mix} of ingredient blends if the individual ingredient RH_0 values are known.

2. Materials and methods

2.1. Materials

All compounds were reagent grade and water was double distilled and then filtered using reverse osmosis. Sodium ascorbate, ascorbic acid, thiamine HCl, NaCl, NaBr, sodium saccharine, and monosodium glutamate were purchased from Sigma–Aldrich Chemical Co. (St. Louis, MO). Sucrose, KCl, and sodium citrate (disodium citrate) were purchased from J.T. Baker (Phillipsburg, NJ), and calcium ascorbate was purchased from Spectrum (Gardena, CA). All individual ingredients were studied. Ingredient blends with and without a common ion were prepared by mixing equal masses of all ingredients (1:1 for binary blends, and 1:1:1 for ternary blends) prior to the addition of water. Samples were prepared and analyzed at least in duplicate.

2.2. Measurement of deliquescence points (RH_0 and RH_{0mix})

2.2.1. Water activity measurements

The RH_0 and RH_{0mix} of single ingredients and ingredient blends, respectively, were measured using two methods at 25 °C. The first method measured the a_w of a saturated solution of the ingredient(s) using an AquaLab 4TE (Decagon Devices, Pullman WA) chilled dewpoint mirror technique. Equilibrated saturated solutions were prepared by mixing 1–2 g of solids with 100–250 μ L of water, maintaining a 50–125 μ L water/g solid ratio, in high-density polyethylene (HDPE) water activity cups (Decagon Devices Inc.), capping the cups with HDPE lids, and storing the samples at 25 °C for 24 h prior to a_w measurement (Lipasek, Li, Schmidt, Taylor, & Mauer, 2013; Salameh et al., 2006). The chilled mirror systems was validated using a_w standards (Decagon Devices Inc.) as recommended by the manufacturer (Decagon Devices, 2014).

2.2.2. Dynamic dewpoint sorption profile measurements

Dynamic dewpoint sorption profiles (DDI) were also used to determine deliquescence points. The DDI profile has been called a

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