

# Effect of Temperature on the Deliquescence Properties of Food Ingredients and Blends

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**S** Supporting Information

**ABSTRACT:** Deliquescence is a first-order phase transformation of a crystalline solid to a saturated solution that is triggered at a defined relative humidity (RH),  $RH_0$ . Previous studies demonstrated that the  $RH_0$  of an inorganic substance with a positive heat of solution ( $\Delta H$ ) will decrease with increases in temperature. In this study, the relationships between  $\Delta H$ , solubility, and deliquescence RH for single-ingredient and multicomponent systems were investigated. The deliquescence RHs of inorganic and organic crystalline solids and their mixtures were measured at temperatures ranging from 20 to 40 °C using a water activity meter and various gravimetric moisture sorption analyzers. The deliquescence behavior as a function of temperature for organic food ingredients was thermodynamically modeled and followed similar trends to those of the previously investigated inorganic ingredients. Furthermore, the models can be used as a predictive approach to determine physical stability and deliquescence RHs of deliquescent ingredients and blends if the storage temperature and ingredient  $\Delta H$  and solubility are known.

**KEYWORDS:** deliquescence, thermodynamics, heat of solution, solubility, temperature dependence, powder mixture

## INTRODUCTION

Ensuring the stability and quality of food ingredients is important for their ultimate application in formulating high-quality food products. Powder or granular ingredients and premixes, often containing both inorganic salts and organic compounds, are widely used in the food industry.<sup>1</sup> Food products are often exposed to fluctuating temperatures and/or relative humidities (RHs) throughout their production, storage, and distribution as well as during abuse or shelf life testing. Water, ubiquitous in the atmosphere, is known to influence the stability of solids and, thus, is an important factor to account for in predicting and/or controlling product quality and shelf life.

For crystalline powders, deliquescence is an important water–solid interaction that induces changes in physical stability and chemical reactivity.<sup>2</sup> The amount of water sorbed by the solid increases dramatically when the environmental RH exceeds its deliquescence point,  $RH_0$ , and this results in dissolution of the solid. The  $RH_0$  is dependent on both the type of crystalline compound and the environmental temperature. Tables summarizing the  $RH_0$  values for individual inorganic and organic crystalline compounds commonly used in foods have been published,<sup>2,3</sup> and most reported values were measured near ambient temperatures (20–25 °C).

The  $RH_0$  of a compound can vary with temperature, depending on the temperature dependence of its solubility. It has been demonstrated that the  $RH_0$  of an inorganic substance with a positive heat of solution (which would lead to an increased solubility with increasing temperature) will decrease with rising temperature.<sup>3,4</sup> Moreover, the extent to which  $RH_0$  decreases with temperature increases will be dependent on the

magnitude of the heat of solution term ( $\Delta H$ ).<sup>3</sup> Therefore, at higher temperatures, lower RHs will induce deliquescence of these inorganic compounds. For many organic compounds, solubility is enhanced by an increase in temperature. This would be expected to lead to a decrease in  $RH_0$ ; however, there are limited reports of temperature effects on the deliquescence behavior of organic crystalline solids.<sup>5</sup>

Powder blends comprised of multiple deliquescent compounds are more sensitive to RH than any of the individual compounds. The presence of multiple deliquescent solids in a blend lowers the deliquescence point (called  $RH_{0mix}$  for multicomponent systems), due to the lowered water activity of the corresponding saturated solution. This is called deliquescence lowering and has been observed for many food ingredient blends.<sup>3,6,7</sup> The Ross equation has been used to determine the onset RH of deliquescence lowering, also termed the mutual deliquescence relative humidity (MDRH).<sup>8,9</sup> Much research has been conducted to determine the deliquescence points of inorganic aerosols, including sodium chloride, sodium bromide, sodium sulfate, and ammonia.<sup>3,10,11</sup> However, information about the behavior of deliquescent blends containing organic ingredients is limited,<sup>12</sup> and documentation of temperature effects on such systems is lacking.

To improve the understanding of temperature effects on the deliquescence behavior of individual crystalline compounds and

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blends, in particular blends containing organic deliquescent solids of relevance to the food industry, this study investigated the relationship between temperature,  $\Delta H$ , solubility, and deliquescence RH ( $RH_0$  for single ingredients and  $RH_{0mix}$  for multicomponent systems) and also established thermodynamic models to predict the deliquescence point as a function of temperature.

## MATERIALS AND METHODS

**Materials.** The deliquescent crystalline ingredients ascorbic acid (A), citric acid anhydrous (C),  $\beta$ -D-fructose (F),  $\alpha$ -D-glucose monohydrate (G), and sucrose (S) were purchased from Mallinckrodt Baker (Phillipsburg, NJ). Xylitol (X), sodium chloride (NaCl), anhydrous sodium bromide (NaBr), and sodium sulfate ( $Na_2SO_4$ ) were purchased from Sigma-Aldrich Chemical Co. (St. Louis, MO). All powders were used as received from the manufacturer. The particle size was determined with a Malvern Mastersizer 2000 with a Scirocco 2000 M dry powder feeder (Malvern Instruments Ltd., Worcestershire, UK) following the manufacturer's directions. A total of 5000 snaps of background and sample measurements were taken within 5 s, and samples were analyzed in triplicate. The mean particle size ( $\mu m$ ) for each deliquescent ingredient used in this study was A,  $842 \pm 6$ ; C,  $432 \pm 6$ ; F,  $425 \pm 18$ ; G,  $340 \pm 16$ ; S,  $631 \pm 2$ ; X,  $587 \pm 5$ ; NaCl,  $395 \pm 25$ ; NaBr,  $519 \pm 9$ ; and  $Na_2SO_4$ ,  $576 \pm 4$ .

**Powder Blends.** All analyses were conducted on all individual powders and in blended systems. Powder blends were made by preparing 1:1 ratios for binary blends, 1:1:1 ratios for ternary blends, and 1:1:1:1 ratios for quaternary blends by weight. Blends represented three categories: (1) inorganic–inorganic blends, (2) inorganic–organic blends, and (3) organic–organic blends. Blends were also formulated to gather information on powders that were acids, salts, and sugars. Blended samples investigated included all binary and ternary ingredient mixtures that were part of the three quaternary mixtures studied (NaCl–C–A–F, NaCl–F–G–S, and F–G–X–S). Quaternary mixtures were chosen as representative samples for a sugar blend, a sugar–salt blend, and a sugar–salt–acid blend, all of which are commonly found in the food industry as premixes (such as seasoning blends and powdered sports drinks).<sup>2</sup> Blends of sucrose and an acid were not used due to possible hydrolysis reactions at elevated temperatures in the presence of moisture, which would influence the deliquescence behavior.<sup>10</sup> The inorganic–inorganic blend studied was NaCl– $Na_2SO_4$ . Inorganic–organic blends included NaCl–A, NaCl–C, NaCl–F, NaCl–G, NaCl–S, NaCl–X, NaCl–C–F, NaCl–C–A, NaCl–A–F, NaCl–F–S, NaCl–F–G, NaCl–S–G, NaCl–C–A–F, and NaCl–F–G–S. Organic–organic blends included A–C, A–F, C–F, F–G, F–S, F–X, G–S, G–X, X–S, C–A–F, F–X–S, F–X–G, F–G–S, G–X–S, and F–G–X–S.

**Water Activity Measurements.** Water activity values ( $a_w$ ) were measured using an AquaLab 4TE water activity meter (Decagon Devices Inc., Pullman, WA). Discrepancies in the literature about the amount of water added in the preparation of saturated solutions were reported.<sup>3,6,12,13</sup> Winston and Bates<sup>13</sup> reported making saturated solutions by completely dissolving the solid in water, while Hiatt et al.<sup>6</sup> used minimal amounts of water in 4 g of dry sample. Tang and Munkelwitz<sup>3</sup> also reported the comparison for bulk solution and saturated solid-state samples of ammonium sulfate, potassium chloride, and sodium nitrate. In preliminary studies, samples with different amounts of water encompassing the range reported in the literature were prepared and used for water activity measurements. The amount of water was optimized to be 300–600  $\mu L$  for 4 g of sample, similar to a previous report on estimating deliquescence RHs using  $a_w$  measurements,<sup>7</sup> to ensure the formation of saturated solutions with excess solid present. For this study, 4 g of sample were weighed into a water activity sample cup (Decagon Devices Inc., Pullman, WA), and 300–600  $\mu L$  of distilled water was added to each cup.<sup>2</sup> All samples were immediately sealed and equilibrated for 24 h at room temperature ( $22 \pm 3$  °C) prior to further treatments. Samples were then pre-equilibrated at the experimental temperature (20, 25, 30, 35, and 40 °C) in water-jacketed incubators (Forma Scientific Inc.,

Marietta, OH) overnight prior to  $a_w$  measurement in the AquaLab 4TE at the specified temperature (20, 25, 30, 35, and 40 °C) using the single mode measurement technique. All samples were prepared and analyzed in triplicate.

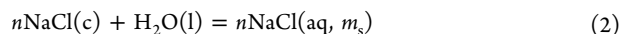
**Deliquescence Point Determination.** Deliquescence points were determined using two different approaches. The first approach used the  $a_w$  of the prepared sample and multiplied the  $a_w$  by 100 to give the deliquescence RH, as described elsewhere.<sup>2,7</sup> The second approach determined the deliquescence RH from a moisture sorption isotherm. Moisture sorption isotherms at selected temperatures were measured using either an SGA-100 symmetrical gravimetric analyzer (VTI Corp., Hialeah, FL) or an SPSx-1 $\mu$  dynamic vapor sorption analyzer (Projekt Messtechnik, Ulm, Germany). Deliquescence RH values were determined from the point in the moisture sorption isotherm at which the sample began to rapidly sorb moisture, indicated by a sharp increase in the slope, similar to the method conducted by Salameh et al.<sup>7</sup>

For the VTI method, samples of 10–15 mg were dried at 60 °C (with the exception of glucose and sucrose, which were dried at 20–40 °C depending on the analysis temperature) and 0% RH in the sorption analyzer for a maximum time of 180 min with an equilibrium criterion of 0.01% wt/wt change in 2 min. Samples of G were not dried at 60 °C because glucose monohydrate converts to an anhydrous form when stored above 40 °C over extended periods of time; instead, G was dried at the same temperature as the testing conditions.<sup>14</sup> Samples containing S were not dried at 60 °C due to possible sucrose hydrolysis at elevated temperatures.<sup>10</sup> Following the drying step, samples were exposed to increasing RHs from 0 to 95%, increasing at 1% intervals around the deliquescence RH. The equilibrium criterion was 0.01% wt/wt within 5 min, and the maximum step time was 60 min. A nitrogen flush was used at a flow rate of 200 mL/min. Results were recorded as percent RH at which deliquescence occurred.

For the SPSx-1 $\mu$  method, samples of 500–1000 mg were added to 2.2 cm aluminum pans in a 24-ring sample holder. The equilibrium criterion was set to a weight change of 0.01% in 15 min with a step time of 5 h, and the time between weighting cycles was set to 15 min. This time was chosen to simulate the conditions of the VTI. The samples were analyzed at 20, 25, 30, 35, or 40 °C from 0 to 95% RH with steps at 1% RH around the  $RH_0$  and  $RH_{0mix}$  values of each sample. Results were recorded as percent RH at which deliquescence occurred.

**Thermodynamic Modeling of Single Components.** Thermodynamic models were developed to describe the temperature dependence of  $RH_0$  using an approach adapted from Tang and Munkelwitz.<sup>3</sup> First, the  $a_w$  and onset deliquescence RH values were measured. The  $a_w$  values were plotted versus the measurement temperature, and a trend line was fit to the data to determine if the  $a_w$ –temperature dependence was linear or exponential. These results enabled further modeling, as described below.

Using NaCl as an example, and according to Tang and Munkelwitz,<sup>3</sup> the deliquescence process could be described as



where g, l, c, aq stand for gas, liquid, crystalline, and aqueous solution, respectively, and  $m_s$  is the molarity of the saturated solution.<sup>3</sup> At the deliquescence point of NaCl, 1 mol of water vapor condensed onto  $n$  mol of NaCl particles and formed a saturated aqueous solution.<sup>3</sup> The Kelvin effect whereby the vapor pressure over a curved surface such as a water droplet is greater than that over a flat surface due to the surface tension can be ignored by assuming the radius of the droplet formed by condensing is larger than 0.1  $\mu m$ .<sup>3</sup>

Therefore, the total heat involved in the deliquescence process could be described as the sum of the heat of solution of NaCl,  $\Delta H_s$ , and the heat of condensation of  $H_2O$ ,  $-\Delta H_v$ , which is opposite to its heat of vaporization,  $\Delta H_v$ .<sup>3</sup>

$$\Delta H = n\Delta H_s - \Delta H_v \quad (3)$$

Therefore, by substituting eq 3 in the Clausius–Clapeyron equation, one obtains<sup>3</sup>

$$\frac{d(\ln p)}{dT} = -\frac{\Delta H}{RT^2} = \frac{\Delta H_v}{RT^2} - \frac{n\Delta H_s}{RT^2} \quad (4)$$

where  $R$  is the gas constant in  $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ .

By definition,

$$\frac{d(\ln p^0)}{dT} = -\frac{\Delta H_v}{RT^2} \quad (5)$$

and water activity is interchangeable with relative humidity, as indicated in eq 6; therefore, the measurement of deliquescence RH using both a water activity meter and a moisture sorption isotherm could be performed.<sup>3</sup>

$$a_w = \frac{p}{p^0} = \frac{\%RH}{100} \quad (6)$$

where  $p^0$  is the water vapor of pure water at temperature  $T$ . Equation 4 could be rewritten as<sup>3</sup>

$$\frac{d(\ln a_w)}{dT} = -\frac{n\Delta H_s}{RT^2} \quad (7)$$

where  $a_w$  is the water activity,  $T$  is temperature in K,  $\Delta H_s$  is the heat of solution of the solute at saturation, and  $n$  is the solubility in moles of solute per moles of water. This, in theory, is the same as the van't Hoff equation<sup>15</sup>

$$\frac{d(\ln K)}{dT} = -\frac{\Delta H'}{RT^2} \quad (8)$$

where  $K$  is the equilibrium constant, which is equivalent to the equilibrium water activity ( $a_w$ ) in this study. The  $\Delta H'$  is the enthalpy change during the deliquescence process, which is the sum of heat of solution, i.e.,  $n\Delta H_s$ , in this study. To simplify the integration,  $n$  can be expressed as a polynomial as a function of  $T$

$$n = A + BT + CT^2 \quad (9)$$

where  $A$ ,  $B$ , and  $C$  are constants.

By substituting eqs 6 and 9 in eq 7 and integrating eq 7 from a reference temperature  $T^*$ , the following equation was obtained

$$\ln \frac{\%RH(T)}{\%RH(T^*)} = \frac{\Delta H_s}{R} \left[ A \left( \frac{1}{T} - \frac{1}{T^*} \right) - B \ln \frac{T}{T^*} - C(T - T^*) \right] \quad (10)$$

where  $T^*$  was chosen to be 298.15 K (25 °C) due to the large amount of deliquescence data reported in the literature for samples at this temperature. In eq 4,  $A$  and  $B$  are used for linear relationships between the temperature and deliquescence RH, while  $A$ ,  $B$ , and  $C$  are used for exponential relationships between the temperature and deliquescence RH.

**Thermodynamic Modeling of Binary, Ternary, and Quaternary Systems.** For binary systems, the deliquescence RH of a mixture ( $\text{RH}_{\text{Omix}}$ ) is lower than the individual ingredient  $\text{RH}_0$  values and has been approximated as the product of the  $a_w$  values of a saturated solution of each component, as indicated in the Ross equation:<sup>8</sup>

$$(a_w)_{\text{mix}} = (a_w)_1(a_w)_2 \quad (11)$$

According to Tang and Munkelwitz,<sup>3</sup> the heat of solution for binary systems can be described by

$$\Delta H_s = n_2\Delta H_{s2} + n_3\Delta H_{s3} - \Delta H_1 \quad (12)$$

where the subscripts 2 and 3 refer to the two ingredients in the binary system, and subscript 1 refers to the solvent (water). The last term  $\Delta H_1$  is the differential heat of solution due to the solvent.<sup>3</sup>

By substituting eqs 6, 9, and 12 into eq 7 and then rearranging and integrating, the following equation was obtained:

$$\begin{aligned} \ln \frac{\%RH_{\text{Omix}}(T)}{\%RH_{\text{Omix}}(T^*)} = & \frac{\Delta H_{s2}}{R} \left[ A_2 \left( \frac{1}{T} - \frac{1}{T^*} \right) - B_2 \ln \frac{T}{T^*} \right. \\ & \left. - C_2(T - T^*) \right] + \frac{\Delta H_{s3}}{R} \left[ A_3 \left( \frac{1}{T} - \frac{1}{T^*} \right) \right. \\ & \left. - B_3 \ln \frac{T}{T^*} - C_3(T - T^*) \right] \\ & - \frac{\Delta H_{s1}}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right) \end{aligned} \quad (13)$$

The same method was applied to ternary and quaternary blends of deliquescent ingredients by adding an additional term,  $n_4\Delta H_{s4}$  (for ternary and quaternary blends) and  $n_5\Delta H_{s5}$  (for quaternary blends only) to eq 12, and rearranging and integrating the values into eq 13, similar to the method for binary blends.

The equations used for regressions were

$$\begin{aligned} \ln \frac{\%RH_{\text{Omix}}(T)}{\%RH_{\text{Omix}}(T^*)} = & \frac{\Delta H_{s2}}{R} \left[ A_2 \left( \frac{1}{T} - \frac{1}{T^*} \right) - B_2 \ln \frac{T}{T^*} \right. \\ & \left. - C_2(T - T^*) \right] + \frac{\Delta H_{s3}}{R} \left[ A_3 \left( \frac{1}{T} - \frac{1}{T^*} \right) \right. \\ & \left. - B_3 \ln \frac{T}{T^*} - C_3(T - T^*) \right] \\ & + \frac{\Delta H_{s4}}{R} \left[ A_4 \left( \frac{1}{T} - \frac{1}{T^*} \right) - B_4 \ln \frac{T}{T^*} \right. \\ & \left. - C_4(T - T^*) \right] + \frac{\Delta H_{s1}}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right) \end{aligned} \quad (14)$$

for a ternary system and

$$\begin{aligned} \ln \frac{\%RH_{\text{Omix}}(T)}{\%RH_{\text{Omix}}(T^*)} = & \frac{\Delta H_{s2}}{R} \left[ A_2 \left( \frac{1}{T} - \frac{1}{T^*} \right) - B_2 \ln \frac{T}{T^*} \right. \\ & \left. - C_2(T - T^*) \right] + \frac{\Delta H_{s3}}{R} \left[ A_3 \left( \frac{1}{T} - \frac{1}{T^*} \right) \right. \\ & \left. - B_3 \ln \frac{T}{T^*} - C_3(T - T^*) \right] \\ & + \frac{\Delta H_{s4}}{R} \left[ A_4 \left( \frac{1}{T} - \frac{1}{T^*} \right) - B_4 \ln \frac{T}{T^*} \right. \\ & \left. - C_4(T - T^*) \right] + \frac{\Delta H_{s5}}{R} \left[ A_5 \left( \frac{1}{T} - \frac{1}{T^*} \right) \right. \\ & \left. - B_5 \ln \frac{T}{T^*} - C_5(T - T^*) \right] \\ & - \frac{\Delta H_{s1}}{R} \left( \frac{1}{T} - \frac{1}{T^*} \right) \end{aligned} \quad (15)$$

for a quaternary system.

**Statistical Analysis.** Data were presented as means  $\pm$  standard deviations (when available). All water activity samples were analyzed in triplicate, but not all moisture sorption isotherms were done in triplicate due to time constraints. Nonlinear regression was performed with Matlab R2012a (The MathWorks Inc., Natick, MA). Paired-comparison analyses were conducted using PC SAS 9.3 (SAS Institute Inc., Cary, NC) with  $\alpha = 0.05$  for  $a_w$  measurements of saturated solution and solid state samples and for  $a_w$  versus moisture sorption isotherm deliquescence RH method comparisons.

## RESULTS AND DISCUSSION

**Comparison of Water Activity and Deliquescence RH Measurements.** The  $a_w$  and  $\text{RH}_0$  values of single ingredients are shown in Table 1. The experimental  $\text{RH}_0$  and  $a_w$  results were consistent with previous reports (Table 1) for most



**Table 1. Comparison of Previously Reported and Experimental  $RH_0$  and  $a_w$  Values<sup>a</sup> of Single-Component Systems of Deliquescent Ingredients at 25°C**

system components <sup>b</sup>	lit. reports		experimental	
	$RH_0$ (%)	$a_w \times 100$	$RH_0$ (%)	$a_w \times 100$
A	>95 <sup>6</sup>	98 <sup>6</sup>	97.5	97.0 ± 0.0
C	74–75 <sup>7</sup>	76–78 <sup>7</sup>	75.2	75.2 ± 0.0
F	62–63 <sup>7,28</sup>	61–62 <sup>7,28</sup>	63.4	61.4 ± 0.5
G	91 <sup>7</sup>	90 <sup>7</sup>	91.3	88.5 ± 0.2
S	85 <sup>7,28</sup>	85 <sup>7,28</sup>	86.1	84.8 ± 0.2
X	77–79 <sup>7,29</sup>	79 <sup>7,29</sup>	78.8	78.5 ± 0.0
NaCl	76 <sup>2</sup>	75 <sup>2</sup>	76.1	75.8 ± 0.0
NaBr	58 <sup>17</sup>	44.5 <sup>17</sup>	56.5	57.6 ± 0.0
Na <sub>2</sub> SO <sub>4</sub>	84.2 ± 0.4 <sup>3</sup>	85.4 <sup>17</sup>	88.0	87.2 ± 0.3

<sup>a</sup> $a_w$ , water activity;  $RH_0$ , deliquescent point of a single ingredient. <sup>b</sup>A, ascorbic acid; C, citric acid anhydrous; F, fructose; G, glucose; S, sucrose; X, xylitol; NaCl, sodium chloride; NaBr, sodium bromide; Na<sub>2</sub>SO<sub>4</sub>, sodium sulfate.

samples.<sup>2,7</sup> There were no differences between  $RH_0$  and  $a_w$  detected for experimental samples of A, C, NaCl, X, or Na<sub>2</sub>SO<sub>4</sub>, while minor differences (where the  $a_w$  was 1–3% RH lower than the  $RH_0$ ) were observed for experimental samples of F, G, and S. This may be due to the prolonged equilibrium time allotted for  $a_w$  samples prior to measurement, since a previous study by Salameh et al.<sup>7</sup> reported that the  $a_w$  of a sample may decrease over time. Additionally, the extrapolation method used for  $RH_0$  determination has a limit of detection of ±1% RH. Therefore, considering the standard deviation and limit of detection, there may be no meaningful differences between the experimental  $RH_0$  and  $a_w$  data for S, G, and F. It is worth noting that anhydrous NaBr forms a dihydrate at 57.7% RH at 25 °C,<sup>16</sup> while anhydrous NaBr has a deliquescence point of 45% RH.<sup>17</sup> Na<sub>2</sub>SO<sub>4</sub> also can form mirabilite from thenardite.<sup>18</sup> In a combined process of deliquescence and hydrate formation at a high RH, the phase changes might be a hydrate formation followed by deliquescence of the hydrate or a partial hydrate formation followed by the simultaneous deliquescence of the hydrated salt until no anhydrous form was present.<sup>18</sup> Although major differences between  $a_w$  and  $RH_0$  for NaBr and Na<sub>2</sub>SO<sub>4</sub> were not observed experimentally (Table 1), multicomponent systems containing NaBr and Na<sub>2</sub>SO<sub>4</sub> were not selected for further investigation to avoid potential discrepancies. Although citric acid may form a hydrate, the deliquescence behaviors of citric acid anhydrous were consistent within the experimental conditions of this study. Further studies are needed to elucidate the relationship between hydrate formation and deliquescence in hydrate-forming crystalline solids.

#### Deliquescence Lowering and the Ross Equation.

Deliquescence lowering was observed in all multicomponent samples (Table 2) and was consistent with  $RH_{0mix}$  values previously reported by Mauer and Taylor.<sup>2</sup> The Ross equation (eq 10) was used to calculate theoretical (predicted)  $a_w$  or  $RH_{0mix}$  values for blended systems at different temperatures based upon  $a_w$  or  $RH_0$  values for the individual ingredients at specific temperatures. These results were then compared to experimental (observed) values for each blended system (Table 2). Differences between the predicted and observed values were seen for many blended systems, particularly in more complex (ternary and quaternary) blends (Table 2), and discrepancies were consistent with previous reports.<sup>7</sup> These discrepancies

between predicted and observed values may be due to solute–solute interactions, which are not taken into account by the Ross equation.<sup>6,8</sup> It is worth noting that the initial composition of the saturated solution is the eutonic composition of the system, regardless of the initial ratio of ingredients in the dry samples.<sup>7</sup> For deliquescence lowering to occur, different ingredients must be in contact with one another. As a mixture increases in complexity, the probability that all ingredients maintain physical contact decreases. This often leads to a higher observed  $RH_{0mix}$  value for the blended system than is predicted by the Ross equation.<sup>2,7</sup> In addition, it has been reported that the Ross equation is better at predicting the  $a_w$  for saturated solutions than it is for predicting the  $RH_{0mix}$  of a powdered blend.<sup>2</sup> Many of the observed results were obtained using moisture sorption isotherms ( $RH_{0mix}$  values), and this may also lead to differences in predicted and observed values.

#### Effect of Temperature on Water Activity and Deliquescence.

The temperature had an effect on the deliquescence RH of both single-component and binary systems (Figures 1–4). For xylitol (X), shown as a representative single ingredient with a positive heat of solution,  $RH_0$  decreased with increasing temperature (Figure 1). It has been reported that ingredients with a positive heat of solution will exhibit increasing solubility with increasing temperature.<sup>19</sup> This will lead to a decreased  $RH_0$  with increasing temperature. Additionally, the magnitude of difference for  $RH_0$  values at different temperatures depends upon the solubility and heat of solution value, as large values lead to greater variation across the temperature range. The  $\Delta H_s$  values for the individual components are shown in Table 3, and all experimentally determined values are positive. In addition, the larger  $\Delta H_s$  values (such as for X and NaBr) led to greater differences in  $a_w$  or  $RH_0$  values across the experimental temperature range (Supporting Information Table A and Figure A). This explains the differences in slopes between the individual components (Figures 2–4 and Supporting Information Figure A). For example, citric acid (C) is more soluble than ascorbic acid (A) (see Supporting Information Table A), leading to a greater slope for  $RH_0$  values across a temperature range for C than for A (Figure 3). X has a greater  $\Delta H_s$  value than the other ingredients studied, leading to a steeper slope for  $RH_0$  values across a temperature range compared to ingredients with smaller  $\Delta H_s$  values (see Supporting Information Figure A).

For multicomponent systems, inorganic–inorganic, inorganic–organic, and organic–organic mixtures were studied. A blend of NaCl–Na<sub>2</sub>SO<sub>4</sub> was chosen as a model for inorganic salt mixtures containing a component with a positive heat of solution (NaCl) and a component with a negative heat of solution (Na<sub>2</sub>SO<sub>4</sub>) value. When  $RH_{0mix}$  was plotted across temperatures, the binary inorganic mixture of NaCl–Na<sub>2</sub>SO<sub>4</sub> (Figure 2) followed the negative linear trend of NaCl rather than the positive polynomial pattern for Na<sub>2</sub>SO<sub>4</sub>. This is similar to the results reported by Tang and Munkelwitz<sup>3</sup> for the inorganic ingredient blend of Na<sub>2</sub>SO<sub>4</sub> and NaNO<sub>3</sub>. However, the slope of the line for the inorganic blend (−0.062) was steeper than for that of NaCl alone (−0.038), but the overall values were relatively small, indicating only slight differences with temperature. This finding is attributed to the  $\Delta H_s$  and individual solubilities of NaCl and Na<sub>2</sub>SO<sub>4</sub>: the  $\Delta H_s$  for NaCl alone was larger than the calculated value of Na<sub>2</sub>SO<sub>4</sub> alone, as seen in Table 3. The magnitude of the change in  $a_w$  or  $RH_{0mix}$  values depends upon the  $\Delta H_s$  term. Therefore, the slope of the blend may follow the trend of NaCl over Na<sub>2</sub>SO<sub>4</sub> due to the

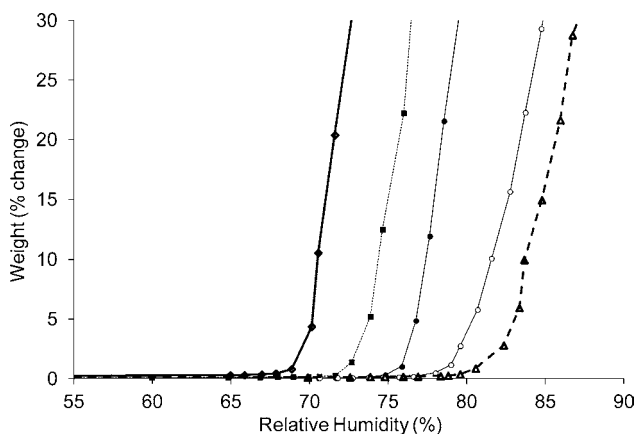
Table 2. Predicted versus Observed  $a_w$  and  $RH_{0mix}$  Values for Binary, Ternary, and Quaternary Mixtures at Various Temperatures

formula <sup>b</sup>	determination <sup>c</sup>	$a_w$ or $RH_{0mix}$ <sup>a</sup> values at a given temperature				
		20 °C	25 °C	30 °C	35 °C	40 °C
A–C	predicted	74.5	72.9	70.7	68.9	67.1
	observed	74.8	73.5	71.4	68.7	67.4
A–F	predicted	63.2	61.5	59.5	56.9	53.7
	observed	62.3	58.9	56.8	54.0	51.8
C–F	predicted	49.5	47.7	45.2	42.4	39.4
	observed	48.9	44.8	41.8	37.9	35.1
F–G	predicted	59.4	57.9	55.4	51.7	47.8
	observed	56.1	53.9	51.0	47.7	44.8
F–S	predicted	56.0	54.6	52.7	50.0	46.8
	observed	58.5	57.2	55.4	51.6	47.2
F–X	predicted	52.9	49.9	46.8	42.8	39.1
	observed	55.7	53.6	52.0	48.8	45.6
G–S	predicted	79.2	78.6	76.7	73.8	70.9
	observed	77.9	72.8	71.0	67.8	66.4
G–X	predicted	74.9	71.9	68.1	63.2	59.2
	observed	72.3	67.8	65.0	60.5	55.9
NaCl–A	predicted	74.1	73.5	73.0	72.4	71.9
	observed	75.4	75.0	74.4	74.1	73.5
NaCl–C	predicted	58.0	57.0	55.4	54.1	52.8
	observed	61.0	59.2	58.1	55.8	54.2
NaCl–F	predicted	49.2	48.0	46.6	44.6	42.3
	observed	45.0	42.8	41.7	39.4	38.2
NaCl–G	predicted	69.7	69.2	67.9	65.9	64.0
	observed	71.8	71.1	69.9	68.9	68.4
NaCl–Na <sub>2</sub> SO <sub>4</sub>	predicted	66.4	66.7	67.0	67.1	66.8
	observed	76.3	76.0	75.8	75.3	75.1
NaCl–S	predicted	65.7	65.3	64.6	63.7	62.6
	observed	66.8	66.2	65.4	64.8	63.8
NaCl–X	predicted	62.1	59.7	57.3	54.5	52.3
	observed	56.6	52.8	49.9	46.6	43.4
X–S	predicted	70.6	67.8	64.7	61.1	58.0
	observed	72.3	71.5	70.4	69.0	67.7
C–A–F	predicted	48.3	46.2	43.6	40.8	37.7
	observed	48.8	47.9	44.9	41.9	39.1
NaCl–C–A	predicted	56.6	55.3	53.5	52.0	50.5
	observed	61.0	59.4	57.9	56.3	55.0
NaCl–C–F	predicted	37.6	36.1	34.2	32.0	29.7
	observed	48.9	46.4	43.8	42.2	39.2
NaCl–A–F	predicted	48.0	46.6	45.0	42.9	40.4
	observed	46.1	40.9	38.7	36.6	34.5
NaCl–F–S	predicted	42.6	41.4	39.8	37.7	35.2
	observed	50.3	48.9	48.3	47.2	46.0
NaCl–F–G	predicted	45.2	43.9	41.9	39.0	36.0
	observed	44.4	42.2	40.9	40.0	37.9
NaCl–S–G	predicted	60.2	59.6	58.0	55.7	53.3
	observed	59.1	56.4	54.5	52.8	49.6
F–X–S	predicted	45.7	43.0	39.9	36.2	32.6
	observed	56.3	50.6	47.3	43.8	41.5
F–X–G	predicted	48.5	45.6	42.0	37.4	33.3
	observed	51.2	48.8	47.4	44.8	42.1
F–G–S	predicted	51.3	49.8	47.3	43.7	39.8
	observed	57.0	53.6	50.6	47.4	42.4
G–X–S	predicted	64.7	61.9	58.1	53.4	49.3
	observed	64.8	63.1	60.4	56.2	52.2
F–G–X–S	predicted	41.9	39.3	35.9	31.6	27.7
	observed	59.8	56.1	53.8	50.5	48.4
NaCl–C–A–F	predicted	36.7	35.0	33.0	30.8	28.4
	observed	40.9	39.2	37.6	34.9	33.2

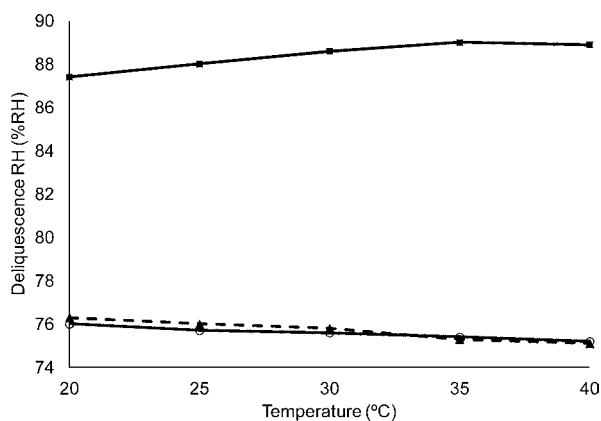
Table 2. continued

formula <sup>b</sup>	determination <sup>c</sup>	$a_w$ or $RH_{0mix}$ <sup>a</sup> values at a given temperature				
		20 °C	25 °C	30 °C	35 °C	40 °C
NaCl-F-G-S	predicted	39.0	37.8	35.8	33.0	29.9
	observed	49.0	48.9	45.8	43.4	40.2

<sup>a</sup> $a_w$ , water activity;  $RH_{0mix}$ , deliquescent point for multicomponent system. <sup>b</sup>A, ascorbic acid; C, citric acid anhydrous; F, fructose; G, glucose monohydrate; NaCl, sodium chloride;  $Na_2SO_4$ , sodium sulfate; S, sucrose; X, xylitol. <sup>c</sup>Predicted values were determined by the Ross equation (eq 11) using measured  $a_w$  and  $RH_{0mix}$  values for the individual components at the specified temperature; observed values were determined using a water activity meter and moisture sorption isotherms.

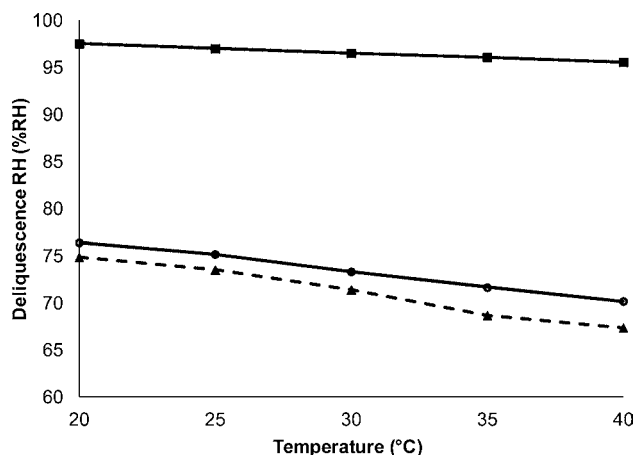


**Figure 1.** Deliquescence point ( $RH_0$ ) determination using moisture sorption isotherms as a function of temperature (°C) for xylitol. Temperatures indicated as 20 °C (---△---), 25 °C (---○---), 30 °C (—●—), 35 °C (—■—), and 40 °C (---◆---).

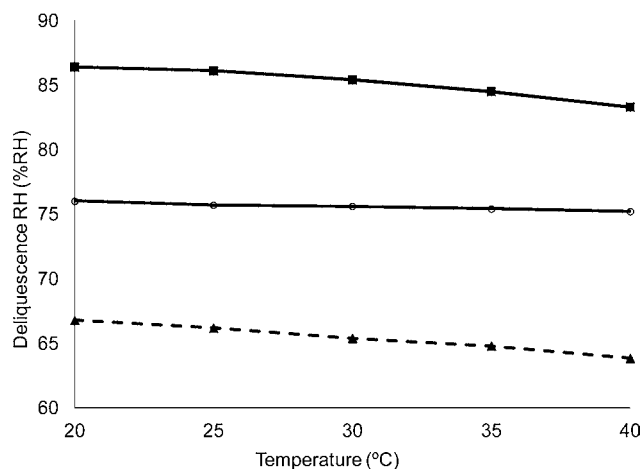


**Figure 2.** Deliquescence point ( $RH_0$  and  $RH_{0mix}$ ) as a function of temperature (°C) for individual components and blends of sodium chloride and sodium sulfate. Samples are  $Na_2SO_4$  (—■—), NaCl (---○---), and NaCl- $Na_2SO_4$  (---▲---).

larger  $\Delta H_s$  value for NaCl. In addition, the solubility of NaCl increases slightly with increasing temperature,<sup>20</sup> while the solubility of  $Na_2SO_4$  varies sigmoidally with temperature (Supporting Information Table A). The solubility of NaCl ranges from 2 to 5 times greater than that of  $Na_2SO_4$  across the temperature range of this study.<sup>21</sup> Therefore, because the solubility of NaCl is greater, the blend of NaCl- $Na_2SO_4$  was more influenced by the behavior of the NaCl, and the trend for the blend  $RH_{0mix}$  values across temperature was similar to the  $RH_0$  of NaCl alone, which is relatively constant. Results were consistent with those reported for inorganic-inorganic blends by Tang and Munkelwitz.<sup>3</sup>



**Figure 3.** Deliquescence point ( $RH_0$  and  $RH_{0mix}$ ) as a function of temperature (°C) for individual components and blends of ascorbic acid and citric acid anhydrous. Samples are C (---○---), A (—■—), and C-A (---▲---).



**Figure 4.** Deliquescence point ( $RH_0$  and  $RH_{0mix}$ ) as a function of temperature (°C) for individual components and blends of sodium chloride and sucrose. Samples are S (—■—), NaCl (---○---), and NaCl-S (---▲---).

Binary blends of organic-organic ingredients were studied, and A-C is shown as a representative sample (Figure 3). The behavior of the individual ingredients was similar to that reported by Hiatt et al.<sup>5</sup> for A and Lipasek et al.<sup>22</sup> for C. The trend of the individual organic ingredients across temperature was similar to that for inorganic ingredients reported by Tang and Munkelwitz.<sup>3</sup> When comparing the single ingredient  $RH_0$ s across temperature, C alone had a steeper slope than A, with slopes of  $-0.3192$  and  $-0.0972$ , respectively. The A-C blend had a slope ( $-0.3948$ ) that was steeper than for the individual components. The deliquescence RH is highly affected by

Table 3. Thermodynamic and Solubility Parameters (A, B, and C)<sup>a</sup> of Single-Component Systems

system <sup>c</sup>	$\Delta H_s^b$ (kJ/mol)		A	B	C	R <sup>2</sup>	RMSE <sup>d</sup>
	reported	calcd					
A	n/a	14.19	-0.281	0.0011		0.9941	0.0005903
C	18.21 <sup>27</sup>	19.98	-0.9484	0.0037		0.9913	0.002344
F	n/a	2.08	0.2223	0.0078		0.9651	0.01225
G	n/a	0.031	3.3863	0.0669		0.9990	0.0002875
S	3.52 <sup>30</sup>	3.87	0.0889	0.0009		0.9476	0.003910
X	23.29 <sup>30</sup>	25.25	-1.9655	0.0073		0.9969	0.004119
NaCl	3.88 <sup>16</sup>	3.46	0.084	0.00008		0.9599	0.0009150
NaBr	19.13 <sup>16</sup>	30.71	-0.2732	0.0014		0.9914	0.005239
Na <sub>2</sub> SO <sub>4</sub>	-9.75 <sup>3</sup>	-1.806	-4.3067	0.0276	0.00004	0.8808	0.003038

<sup>a</sup>For solubility data, see Supporting Information Table A. <sup>b</sup>Heat of solution term for individual components indicated as kJ/mol. <sup>c</sup>A, ascorbic acid; C, citric acid anhydrous; F, fructose, G, glucose, NaCl, sodium chloride; NaBr, sodium bromide; Na<sub>2</sub>SO<sub>4</sub>, sodium sulfate; S, sucrose; X, xylitol. <sup>d</sup>Root mean square error.

solubility and  $\Delta H_s$  values; thus, this difference may be due to the combined effect of the solubility of both ingredients across the temperature range as well as the individual  $\Delta H_s$  values (see Table 3 and Supporting Information Table A). The calculated  $\Delta H_s$  for C (19.98) is larger than that of A (14.19) (Table 3). The solubility of C is much larger than for A (5.7842 and 0.03420 mol solute/mol water, respectively, at 25 °C; see Supporting Information Table A). These results for differences in slope for the organic blend are similar to the results reported for blends of NaCl–KCl by Tang and Munkelwitz.<sup>3</sup> In that study, KCl had a larger  $\Delta H_s$  value and greater solubility range than NaCl alone, and the blended system of NaCl–KCl followed a similar trend to that of KCl alone.

In another binary organic system, A–F mixtures, the slopes of the RH<sub>0</sub>–temperature lines were -0.518 for A–F, -0.094 for A, and -0.428 for F (calculated using data from Table 2). In this case, F has a larger solubility of 0.4173 mol solid/mol water, compared to 0.03420 mol solid/mol water for A (See Supporting Information Table A). However, the calculated heat of solution term for F is much smaller than that for A (2.08 and 14.19 kJ/mol for F and A, respectively, Table 4). Therefore, it was the solubility rather than the heat of solution term that dominated the temperature dependent deliquescence behavior of the A–F binary system.

In the inorganic–organic blend NaCl–A, the slopes of the RH<sub>0</sub>–temperature lines were -0.094 for the binary system, -0.04 for NaCl, and -0.094 for A, respectively (calculated using data from Table 2). Comparing the solubility and heat of solution values, it can be seen that A has a larger heat of solution yet smaller solubility term compared to NaCl (solubility of 0.03420 and 0.1109 mol solid/mol water for A and NaCl, respectively, and heat of solution of 14.19 and 3.46 kJ/mol for A and NaCl, respectively; see Table 4 and Supporting Information Table A). In this case, it was the heat of solution term that most influenced the temperature dependence of deliquescence of the binary mixture. Therefore, both the solubility and  $\Delta H_s$  values of the individual ingredients were determining factors for the behavior of  $a_w$  and RH<sub>0mix</sub> values across temperatures for the blended systems.

Data for another inorganic–organic blend, NaCl–S, are shown in Figure 4. Both NaCl and S had decreasing  $a_w$  values with increasing temperature. In the  $a_w$  vs temperature data, S alone had a steeper slope than NaCl (-0.156 and -0.038, respectively), and the blend of NaCl–S followed a similar pattern to S alone, with a slope of -0.146. The solubility of S and NaCl are similar at 25 °C, 0.1112 and 0.1109 mol solute/

Table 4. Fitting Parameters ( $\Delta H_1$ ) of Binary-, Ternary-, and Quaternary-Component Systems

system <sup>a</sup>	$\Delta H_1^b$ (kJ/mol)	R <sup>2</sup>	RMSE <sup>c</sup>
NaCl–A	0	0.9642	0.00219
NaCl–C	-0.5324	0.9883	0.002915
NaCl–F	-0.8102	0.9545	0.01619
NaCl–G	-0.904	0.9760	0.003127
NaCl–Na <sub>2</sub> SO <sub>4</sub>	-14.28	0.6949	0.003613
NaCl–S	-0.006076	0.9848	0.002218
NaCl–X	-3.651	0.9970	0.005706
A–C	-0.2386	0.9775	0.004684
A–F	-0.4922	0.9800	0.01019
C–F	-3.647	0.9968	0.003075
F–G	-3.142	0.9912	0.008749
F–S	-1.639	0.9166	0.03554
F–X	4.16	0.9744	0.0127
G–S	-3.979	0.9291	0.02366
G–X	-1.657	0.9876	0.01577
X–S	4.502	0.9927	0.002242
C–A–F	0.09907	0.9283	0.01089
NaCl–C–F	1.046	0.9934	0.003033
NaCl–C–A	8.606	0.9951	0.001671
NaCl–A–F	-10.17	0.9296	0.04178
NaCl–F–S	3.822	0.9632	0.006564
NaCl–F–G	0.9192	0.9632	0.02259
NaCl–S–G	-21.9	0.9805	0.01853
F–X–S	5.091	0.9592	0.02793
F–X–G	4.034	0.9857	0.01028
F–G–S	3.869	0.9758	0.03557
G–X–S	-0.4078	0.9711	0.01505
F–G–X–S	4.577	0.9889	0.01078
NaCl–C–A–F	1.758	0.9898	0.003165
NaCl–F–G–S	-0.8931	0.8309	0.01544

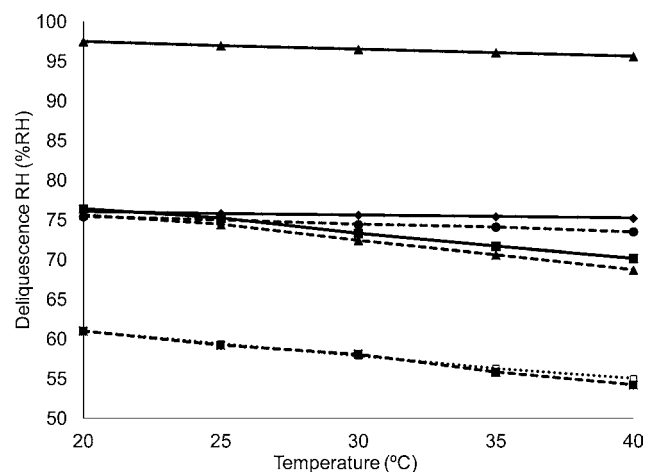
<sup>a</sup>A, ascorbic acid; C, citric acid anhydrous; F, fructose; G, glucose monohydrate; NaCl, sodium chloride; Na<sub>2</sub>SO<sub>4</sub>, sodium sulfate; S, sucrose; X, xylitol. <sup>b</sup>Experimentally determined heat of solution term for water. <sup>c</sup>Root mean square error.

mol water,<sup>20,23</sup> respectively, but the solubility of S has greater variation with changes in temperature.<sup>23</sup> In addition, the  $\Delta H_s$  values are similar, 3.87 kJ/mol for S and 3.46 kJ/mol for NaCl. The slopes of both NaCl and S deliquescence RHs across temperature were relatively small compared to other ingredients studied (such as C in Figure 3), and this can be explained by the small solubility and  $\Delta H_s$  values. These trends



are consistent with the observations made for the inorganic blends studied by Tang and Munkelwitz.<sup>3</sup> Unlike the steeper slope of the  $a_w$  vs temperature relationship that was obtained in the binary mixtures compared to those of the individual ingredients, the slope of NaCl–S blends is larger than that of S but smaller than that of NaCl. Blends containing ingredients with large solubility and  $\Delta H_s$  values had greater variation in  $a_w$  and  $RH_{0mix}$  values across temperature, while blends containing ingredients with smaller solubility and  $\Delta H_s$  values for both ingredients had less variation in  $a_w$  and  $RH_{0mix}$  values with temperature.

To investigate a more complex mixture, the ternary blend of NaCl–C–A was chosen, and results are presented in Figure 5.



**Figure 5.** Deliquescence point ( $RH_0$  and  $RH_{0mix}$ ) as a function of temperature ( $^{\circ}C$ ) for individual components and binary and ternary blends of sodium chloride, citric acid anhydrous, and ascorbic acid. Samples are NaCl (—◆—), C (—■—), A (—▲—), C–A (–▲–), NaCl–C (–■–), NaCl–A (–●–), and NaCl–C–A (·□·).

The three appropriate binary mixtures and individual components are also shown for comparison. All three ingredients and their mixtures have decreasing  $a_w$  with increasing temperature (see Supporting Information Table B). The slopes of the  $a_w$ –temperature lines for NaCl–C–A, NaCl, C, and A were  $-0.3016$ ,  $-0.04$ ,  $-0.318$ , and  $-0.094$ , respectively. The temperature dependence of the ternary mixtures followed that of C rather than the other two components. This can be understood by considering that C possesses a higher solubility in solution than the other ingredients (see Supporting Information Table A; solubilities for C, A, and NaCl at  $25^{\circ}C$  are 0.1507, 0.0342, and 0.1109 mol solute/mol water, respectively<sup>20,24,25</sup>). The  $\Delta H_s$  of the individual ingredients can also influence the behavior of the blends. The  $\Delta H_s$  value for C (19.98 kJ/mol) is much larger than for NaCl (3.46 kJ/mol) (Table 3). Despite the differences in the  $\Delta H_s$  values, the solubility differences between the ingredients in the ternary blend also contributed to the behavior of the NaCl–C–A blend. Therefore, the blend behaved most like the ingredient with the greatest  $\Delta H_s$  and the highest solubility. These results were consistent with those reported for binary blends (Figures 2–4). Overall, from eqs 3 and 12, the overall heat of solution term is described as the sum of the product of solubility and heat of solution of the individual components, and therefore, both solubility and  $\Delta H_s$  are important to the  $RH_{0mix}$  in a multicomponent system. The ingredient with the largest solubility and  $\Delta H_s$  values contributes

the most to the  $a_w$  and  $RH_{0mix}$  values. If the  $\Delta H_s$  values for individual ingredients are relatively small or similar, the solubility values will determine which ingredient will have the most effect on the stability of the system (e.g., A–C), and vice versa (F–G). This is important for formulating powder premix blends, because the ingredient with the largest solubility and  $\Delta H_s$  will be the most influential on determining physical stability.

**Mathematical Modeling.** Mathematical models have been established for inorganic systems;<sup>3</sup> however, for organic food ingredients, the combined effects of temperature, heat of solution, and the composition on the deliquescence properties of the system have not yet been reported. Therefore, mathematical modeling accounting for the simultaneous influence of the above-mentioned factors is necessary to further understand the thermodynamics of the phenomenon as well as to predict the stability of complex food powder systems containing organic ingredients, because organic ingredients often behave differently than inorganic ingredients.<sup>26</sup> The solubility information for the individual ingredients was collected from literature reports (see Supporting Information Table A) and was fit to eq 9. In addition, the  $a_w$  and  $RH_0$  values for individual ingredients were determined over a range of temperatures, and eq 10 was used to correlate solubility,  $a_w$  or  $RH_0$ , and temperature, with results shown in Table 3. The A, B, and C values correlate to the solubility (obtained using eq 9), and root-mean-square error (RMSE) and  $R^2$  values correspond to the fit of the model for the experimental heat of solution term. Both linear and polynomial approaches were used to fit the data,<sup>3</sup> and in most cases, the linear fit resulted in  $\Delta H_s$  values near those reported in the literature (data available for C, NaCl, S, and X). For mathematical modeling, two systems (G, NaBr) had no significant difference between the linear and polynomial models, and therefore, the linear model was chosen for simplicity. One ingredient (A) had both positive and negative  $\Delta H_s$  values resulting from linear and polynomial fitting, respectively. Upon the basis of the observed increasing solubility and decreasing  $RH_0$  values for A with increasing temperature, a positive  $\Delta H_s$  was logical.<sup>3</sup> For  $Na_2SO_4$ , the polynomial model was the only option due to this ingredient's nonlinear solubility values (see Supporting Information Table A). All  $R^2$  values for the models were high, 0.9476–0.9990 for all samples except  $Na_2SO_4$  with a value of 0.8808, indicating that the models may be used not only for inorganic<sup>3</sup> but also for organic ingredients to predict the effects of temperature on water activity if the heat of solution and solubility are known for the ingredient.

The experimental  $\Delta H_s$  values obtained through modeling and those previously reported in the literature were similar, such as for S (3.87 and 3.52 kJ/mol, calculated and reported, respectively), X (25.25 and 23.29 kJ/mol), and NaCl (3.46 and 3.88 kJ/mol) reported in Table 3. Discrepancies were found in NaBr and  $Na_2SO_4$ , as shown in Table 3. However, these differences might be due to the formation of hydrates of NaBr and  $Na_2SO_4$ . The heat of hydration might affect the experimental measurements of heat of solution during the dissolution/deliquescence process of these two anhydrous salts. The heat of solution values for another hydrate-forming ingredient, citric acid anhydrous, are similar (19.98 and 18.21 kJ/mol, calculated and reported). The reported value was for citric acid anhydrous and is quite similar to the calculated value in our study but different from the reported  $\Delta H_s$  of citric acid monohydrate (29.06 kJ/mol<sup>27</sup>). Such agreement might indicate



that citric acid anhydrous did not form a hydrate during deliquescence under our experimental conditions. Further research is needed to investigate the competing mechanisms of deliquescence and hydrate formation for crystalline ingredients that may undergo both events. Overall, the mathematical model developed for inorganic ingredients was successful at estimating  $\Delta H_s$  values for organic ingredients.

Binary-, ternary-, and quaternary-component systems followed the models presented in eqs 6 and 7, respectively, and results are shown in Table 4. Values were extracted from the experimental data by fitting  $\Delta H_s$  terms and solubility values for the individual components into eqs 6 and 7. Therefore, the only unknown variable was  $\Delta H_1$ , the heat of solution from water. The  $\Delta H_1$  differed for different systems, indicating that different ingredients have different interactions with water. As discussed by Tang and Munkelwitz,<sup>3</sup> this  $\Delta H_1$  term varies depending upon the salts within the solution and the interaction of the salt with the water. This term was previously used in models by Tang and Munkelwitz to describe differential heat of solution due to the solvent.<sup>3</sup> In their work, the heat of solution of each ingredient was included in the equation, and therefore, this  $\Delta H_1$  term should be subtracted from the total heat of solution: once for a binary system, twice for a ternary system, three times for a quaternary system, and  $(n - 1)$  times for an  $n$ -component system. In this study, we combined all the correction factors in one term, and therefore  $\Delta H_1$  is the correction factor that accounts for all discrepancies in a multicomponent system. It is important to note that the  $\Delta H_1$  term was usually small relative to the heat of solution values and could be neglected in most cases.<sup>3</sup>

Overall, these results indicate that the model, previously only utilized in binary inorganic blends, can be extended to binary organic blends and ternary and quaternary blends containing both inorganic and organic ingredients. In addition, the  $\Delta H_1$  values are small relative to the heat of solution values for the individual components (Table 4). The  $R^2$  and RMSE values for the results indicated good correlation of the experimental data to the models.

In summary, the temperature dependence of the deliquescence properties of organic ingredients and their mixtures can be predicted from thermodynamic models. Although simplified solubility calculations were used, experimentally estimated  $\Delta H_s$  values were similar to those previously reported in the literature. The models established from aerosols by Tang and Munkelwitz<sup>3</sup> can be applied to concentrated solutions of both inorganic electrolyte and organic ingredients and blends thereof. Overall, the behavior of the blends followed similar trends to the individual ingredient that had greater changes in solubility with increasing temperature as well as larger  $\Delta H_s$  values, rather than individual ingredients with lower solubility and/or  $\Delta H_s$  values.

This work enhanced the understanding of the thermodynamic basis of the impact of temperature on deliquescence and deliquescence lowering of food ingredients and blends. Premixes are commonly used in the food industry, and it has been documented that blends of deliquescent ingredients are more sensitive to moisture (i.e., deliquesce at a lower RH) than any of the single ingredients of which they are comprised. For example, X deliquesces at 79% RH at 25 °C but becomes more sensitive to environmental moisture as the temperature increases. At 35 °C, X deliquesces at 73% RH. If X was blended with F, the resulting deliquescence point ( $RH_{0mix}$ ) of the blend would be lowered to 54% RH at 25 °C or 49% RH at

35 °C. If a third ingredient was added to the blend, for example F, X, or G, the  $RH_{0mix}$  would be further reduced to 49% RH at 25 °C and 45% RH at 35 °C. Because temperature and humidity fluctuate in manufacturing facilities, especially in the summer months, it is possible that the temperature and/or RH could reach or exceed these deliquescence threshold levels, thereby creating physical instability in the product.

The thermodynamic models developed and applied in this study could be used to determine the physical stability of powder blends at different storage conditions if the solubility and heat of solution variables are known, without needing to collect data for all ingredients and blends across all temperatures of interest. For example, for a single ingredient, such as X, if its deliquescence point at a certain temperature (reference  $RH_0$ , 25 °C in this work) and its solubility and heat of solution terms (as presented in Table 3) are known, then its  $RH_0$  at any temperature could be calculated using eq 10. Similarly, by knowing the reference  $RH_0$ , solubility, and heat of solution terms of each individual component in a blended system, the  $RH_{0mix}$  of the powder mixture at any temperature could be calculated using eqs 13, 14, and 15 for binary, ternary, and quaternary systems, respectively. The measured  $RH_{0mix}$  values of F–X (54%) and F–X–G (49%) mixtures at 25 °C, combined with the solubility and heat of solution terms listed in Table 3, enable the calculation of  $RH_{0mix}$  values for F–X and F–X–G at 35 °C using eqs 13 and 14. The calculated values are 48.9% and 43.9% RH for F–X and F–X–G, respectively, which are very close to the measured experimental values of 48.8% and 44.8% RH. High  $R^2$  values were obtained for most ingredient systems in this work (Table 4), suggesting the robustness and accuracy of these models. For complex systems with more components present, similar thermodynamic models could be established. Therefore, this thermodynamic modeling could assist the food industry in predicting the deliquescence properties of powder ingredients and blends across relevant temperatures. The effects of possible ingredient substitutions in blends on the deliquescence properties could be determined and the information used to select the best ingredients for a premix to enhance storage stability. Once the deliquescence RH is determined across the temperature range of interest, then recommendations can be developed to store ingredients and products at temperatures and RHs below these levels, or product handling systems and packages could be designed for products that are sensitive to conditions to which they will unavoidably be exposed. Careful consideration in formulating and storing ingredient blends could avoid some physical and/or chemical instabilities that have been problematic in blended systems under conditions where the individual ingredients were stable.

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

The determination of  $a_w$  and  $RH_0$  for single-component and multicomponent systems of deliquescent ingredients at temperatures from 20 to 40 °C. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## Notes

The authors declare no competing financial interest.

## ABBREVIATIONS USED

A, ascorbic acid;  $a_w$ , water activity; C, citric acid anhydrous; F, fructose; G, glucose; RH, relative humidity;  $RH_0$ , deliquescence point of an individual crystalline ingredient;  $RH_{0mix}$ , deliquescence point of a mixture of crystalline ingredients; S, sucrose; X, xylitol;  $\Delta H_s$ , heat of solution for an individual component;  $\Delta H_1$ , heat of solution for water.

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