



Heat transport model for the deliquescence kinetics of crystalline ingredients and mixtures



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ABSTRACT

Deliquescent crystalline solids undergo the first order dissolution process of deliquescence when the environmental relative humidity (RH) exceeds the deliquescence point (RH₀). The rate at which deliquescence occurs increases as the RH increases above the RH₀ in compressed disks of select deliquescent ingredients; however, a kinetic model for the deliquescence of powdered crystalline food ingredients and blends thereof has not been published. The water vapor sorption rates of commonly used powder food ingredients (citric acid, sodium chloride, sucrose, fructose, sorbitol, and xylitol) and blends were determined using a multi-sample gravimetric moisture sorption analyzer. The water vapor sorption rate was dependent on sample radius, temperature, and sample composition. The heat transport model for the deliquescence of compressed disks was successfully extended to the powder ingredients and blends. Such results enable further understanding of fundamental theories of deliquescence and provide a useful tool in the prediction of water vapor uptake rate during deliquescence in controlled RH chambers.

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1. Introduction

Water is ubiquitous and can affect the physical and chemical stability of powder products through different mechanisms of water–solid interactions (Zografis, 1988). Properties that can be impacted include powder flowability, mechanical properties, chemical stability, and bioavailability (Hiatt et al., 2008; Salameh, 2006; Salameh and Taylor, 2008). There are five mechanisms for water–solid interactions: adsorption onto the surface; absorption into amorphous solids; capillary condensation; crystal hydrate formation; and deliquescence of crystalline solids (Mauer and Taylor, 2010). Of the five mechanisms, absorption and deliquescence bring in the largest amount of water. Deliquescent crystalline solids, including inorganic and organic salts, organic acids and bases, vitamins, sugars, and sugar alcohols, are widely used in the food and pharmaceutical industries.

Abbreviation: *a*, hypothetical spherical sample radius; *a'*, corrected sample radius; *A_s*, effective contacting surface area; *b*, chamber radius; CAA, citric acid anhydrous; *c_n*, normalization coefficient; *d*, sample pan diameter; F, fructose; NaCl, sodium chloride; *r*, sample pan radius; RH, relative humidity; RH₀, deliquescence relative humidity; S, sucrose; So, sorbitol; SPS, SPSx-1μ Dynamic Vapor Sorption Analyzer; X, xylitol; *W_h*, water vapor sorption rate; π, ratio of circumference to diameter.

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Deliquescence is a first order phase transformation of a crystalline solid from the solid state to the saturated solution state. It is triggered when the environmental RH exceeds the critical deliquescence point (RH₀) of the solid (Mauer and Taylor, 2009). At RH values equal to or below the RH₀, water vapor adsorbs onto the solid surface. At RH values above the RH₀, multiple layers of water molecules accumulate onto the solid surface (Adamson, 1978). If the crystalline solid is highly water soluble, dissolution at the solid surface occurs once multi-layer adsorption is established, and a layer of saturated solution is formed at the surface of the solid (Van Campen et al., 1983a). If the environmental RH is maintained above the RH₀, further dissolution of the solid and the subsequent dilution of the saturated solution layer occur until equilibrium is reached.

To quantitatively predict deliquescence behavior, understanding the kinetic basis of the event is necessary. A theoretical heat transport model was developed in a previous study to calculate the kinetics of deliquescence (Van Campen et al., 1983a):

$$W'_h = - \left[\frac{60M_w \cdot 4\pi kab}{\Delta H(b-a)} \left(\frac{RT_c^2}{\Delta H_v - RT_c \ln \frac{RH_i}{RH_0}} \right) + \frac{60M_w \cdot 4\pi a^2 \sigma e}{\Delta H} \left(\frac{4RT_c^5}{\Delta H_v - 4RT_c \ln \frac{RH_i}{RH_0}} \right) \right] \cdot \ln \frac{RH_i}{RH_0} \quad (1)$$

where *W_h*' is the vapor sorption rate in mg/min, and *RH_i* is the

Table 1
Parameters used in deliquescence sorption rate models.

Parameters	Unit	Values
<i>a</i>	cm	0.290 (S), 0.636 (M), and 1.317 (L) ^a
<i>b</i>	cm	10.26 ^b
<i>M_w</i>	mg/mol	1.8 × 10 ⁴
<i>k</i>	cal/cm sec deg	4.26 × 10 ⁻⁵ (Van Campen et al., 1983a)
ΔH	cal/mol	− $\Delta H_v + (C_{sat} \Delta H_{soln})/55.5$ (Van Campen et al., 1983b)
ΔH_v	cal/mol	10,500 (Van Campen et al., 1983a)
<i>R</i>	cal/deg mol	1.987 (Van Campen et al., 1983a)
<i>T_c</i>	K	298
σ	cal/cm ² sec deg ⁴	1.36 × 10 ⁻¹² (Van Campen et al., 1983a)
<i>e</i>		0.95 (Van Campen et al., 1983b)

Illustration:

Heat transport model.

a, effective sample radius, calculated from the hypothetical sphere sample.*b*, effective chamber radius, calculated from the hypothetical sphere chamber.*M_w*, molecular weight of water.*k*, thermal conductivity. ΔH , heat generated or consumed when one unit of water vapor condenses. ΔH_v , heat of evaporation of water.*R*, gas constant.*T_c*, chamber temperature. σ , Stefan–Boltzmann constant.*e*, emissivity, film surface emissivity approximated from the value of pure water (Van Campen et al., 1983a).^a Hypothetical sample radius at different pan size: S, small; M, medium; L, large.^b The radius of a hypothetical sphere chamber, of which the capacity is equivalent to that of the SPS chamber ($\frac{4}{3}\pi b^3 = 34.0 \text{ cm} \times 35.0 \text{ cm} \times 3.8 \text{ cm}$).**Table 2**
Solubility and heat of solution values for different deliquescent crystalline ingredients.

Compound	<i>C_{sat}</i> , mol/L	ΔH_{soln} , kcal/mol
NaCl (sodium chloride)	6.14 (Van Campen et al., 1983a)	0.928 (Van Campen et al., 1983a)
S (sucrose)	6.18 (Van Campen et al., 1983a)	1.319 (Van Campen et al., 1983a)
F (fructose)	18.5 (Van Campen et al., 1983a)	2.222 (Van Campen et al., 1983a)
X (xylitol)	12.17 (Wang et al., 2006)	5.566 (Mathlouthi and Reiser, 1995)
So (sorbitol)	12.30 (Wang et al., 2009)	−4.828 (Peter, 2011)
CAA (citric acid anhydrous)	8.37 (Apelblat et al., 1995)	4.349 (Apelblat et al., 1995)

Table 3
Heat of solution and *RH₀* values used in modeling the moisture sorption kinetics of different deliquescent ingredients and their blends.

Compound	ΔH , kcal/mol	Estimated <i>RH₀</i> and <i>RH_{0mix}</i> values by linear extrapolation, % (Fig. 2)	Literature <i>RH₀</i> and <i>RH_{0mix}</i> values, %	Predicted <i>RH_{0mix}</i> values by the Ross equation, %
CAA–S–NaCl–F system				
CAA	−9.844	73.17	75.2 (Lipasek et al., 2013)	
S	−10.353	84.47	86.1 (Lipasek et al., 2013)	
NaCl	−10.397	74.21	76.1 (Lipasek et al., 2013)	
F	−9.759	62.19	63.4 (Lipasek et al., 2013)	
CAA–S	−9.697	63.50	64 (Salameh et al., 2006)	61.81
CAA–NaCl	−9.741	57.60	59.2 (Lipasek et al., 2013)	54.30
CAA–F	−9.103	45.20	44.8 (Lipasek et al., 2013)	45.50
S–NaCl	−10.250	62.86	66.2 (Lipasek et al., 2013)	62.69
S–F	−9.612	60.40	57.2 (Lipasek et al., 2013)	52.53
NaCl–F	−9.657	41.57	42.8 (Lipasek et al., 2013)	46.15
CAA–S–NaCl	−9.594	57.27	–	45.87
CAA–S–F	−8.956	44.91	55, 44 (Salameh et al., 2006)	38.44
CAA–NaCl–F	−9.000	45.34	46.4 (Lipasek et al., 2013)	33.77
S–NaCl–F	−9.510	41.73	48.9 (Lipasek et al., 2013)	38.98
CAA–S–NaCl–F	−8.854	45.41	–	28.52
S–F–So–X system				
X	−9.279	78.09	78.8 (Lipasek et al., 2013)	
So	−11.570	70.50	69 (Salameh et al., 2006)	
X–F	−8.539	53.54	53.6 (Lipasek et al., 2013)	48.56
F–So	−10.830	54.56	–	43.84
S–So	−11.423	68.53	–	59.55
X–S	−9.132	70.32	71.5 (Lipasek et al., 2013)	65.96
X–So	−10.350	61.91	–	55.05
X–F–So	−9.609	53.88	–	34.24
X–S–So	−10.203	62.37	–	46.50
X–S–F	−8.392	52.86	50.6 (Lipasek et al., 2013)	41.02
S–F–So	−10.683	55.09	–	37.03
X–S–F–So	−9.462	53.44	–	28.92

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