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A new method to determine the water activity and the net isosteric heats of sorption for low moisture foods at elevated temperatures

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ABSTRACT

In recent years, research studies have shown that the thermal resistance of foodborne pathogens in the low moisture foods is greatly influenced by the water activity (a_w) at temperatures relevant to thermal treatments for pathogen control. Yet, there has been a lack of an effective method for accurate measurement of a_w at those temperatures. Thus, the main aim of this study was to evaluate a new method for measuring a_w of food samples at elevated temperatures. An improved thermal cell with a relative humidity and temperature sensor was used to measure the a_w of the three different food samples, namely, organic wheat flour, almond flour, and non-fat milk powder, over the temperature range between 20 and 80 °C. For a constant moisture content, the a_w data was used to estimate the net isosteric heat of sorption (q_{st}). The q_{st} values were then used in the Clausius Clapeyron equation (CCE) equation to estimate the moisture sorption isotherm for all test food samples at different temperatures. For all the tested samples of any fixed moisture content, a_w value generally increased with the temperature. The energy for sorption decreased with increasing moisture content. With the experimentally determined q_{st} value, CCE describes well about the changes in a_w of the food samples between 20 and 80 °C. This study presents a method to obtain a_w of a food sample for a specific moisture content at different temperatures which could be extended to obtain q_{st} values for different moisture contents and hence, the moisture sorption isotherm of a food sample at different temperatures.

1. Introduction

The food industry and research communities are facing immense challenges in addressing emerging food safety concerns associated with the low moisture foods. Three factors have contributed to the complications in this endeavor when considering thermal treatments: 1) vegetative bacterial pathogens become highly resistant to heat in low moisture environments (Villa-Rojas et al., 2013); 2) low moisture foods have historically been considered microbiologically safe until recent highly publicized outbreaks of pathogens in, e.g., almonds, and peanut butters, thus there had been little reported systematic research on such topics (Syamaladevi, Tadapaneni, et al., 2016); and 3) there is an urgent need for food companies to be in compliance with rules under the Food Safety Modernization Act (FSMA), yet there is little literature for the food industry to rely upon in developing validation protocols for different legacy unit operations in production of low moisture foods or novel thermal control methods (Syamaladevi, Tang, et al., 2016). Our recent research suggests that the water activity (a_w) of food at treatment temperatures is a critical factor influencing thermal resistance of vegetative bacterial pathogens (Syamaladevi, Tadapaneni, et al., 2016; Syamaladevi, Tang, et al., 2016; Syamaladevi, Tang, & Zhong, 2016; Tadapaneni, Syamaladevi, Villa-Rojas, & Tang, 2017). Thus, reliable data on the a_w of different foods at high temperatures are needed in developing effective thermal processes for low moisture foods. Yet, there has been a lack of a reported method to determine water activities in food matrices at high temperatures. This research was designed to fill such a gap.

Water activity (a_w) of the food product represents the energy status of water molecules in the food. This thermodynamic property of food is related to fugacity of water from food products which influences various biochemical reaction rates and microbial growth in those food commodities (Labuza, 1975). The change in a_w of food samples at a constant moisture content (MC) over different temperatures can be estimated by determining the moisture sorption isotherms (MSI). MSI shows the relationship between a_w and the equilibrium MC of food samples, and are determined at different temperatures. There are various methods to generate MSI for a food product. The most frequently used method for getting a MSI is the static gravimetric technique where

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Nomenclature

AF	almond flour
a_w	water activity
CCE	Clausius-Clapeyron equation
db	dry basis
E	mean relative percentage deviation
G	Gibb's free energy (J K^{-1} mol^{-1})
ΔH	total enthalpy change for the sorption process (J mol^{-1})
HTC	high-temperature cell
L	specific latent heat of vaporization (J mol^{-1})
MC	moisture content (% db)
m_s	molality of salt (mol kg^{-1} H_2O)
MSI	moisture sorption isotherm
M_w	molar mass of water (kg mol^{-1})
NFMP	non-fat milk powder
Φ	osmotic coefficient
OWF	organic wheat flour
P	vapor pressure (Pa)
q_{st}	net isosteric heat of sorption (J mol^{-1})
R	universal gas constant (8.314 J mol^{-1} K^{-1})
R^2	coefficient of determination
RH	relative humidity
RMSE	root-mean-square error
S	entropy of the system (J K^{-1} mol^{-1})
SEP	standard error of prediction
T	temperature (°C or K)
V	molar volume (m^3 mol^{-1})
ν	stoichiometric number of dissociated solute ions
VSA	vapor sorption analyzer

the food samples are conditioned in closed containers with different saturated salt solutions and the change in weight of the food samples is tracked till they reach equilibrium (Bell & Labuza, 2000). However, the time required for food samples to be in thermodynamic equilibrium with the humidity condition provided by saturated salt solutions may take several days (Levoguer & Williams, 2006). Thus, the determination of MSI for food samples at different temperatures may even take weeks to months. Another way to reduce the equilibration time for the samples is by using humidity generating chambers where a system consisting of a computer program, air flow controllers, and a relative humidity sensor maintains the constant humidity level (Mermelstein, 2009). Many commercial humidity generating devices employ the dynamic dew point isotherm (DDI) or dynamic vapor sorption (DVS) methods to generate the MSI of a sample. However, these devices have limited operating temperature ranges (4 to 60 °C). An alternative method to obtain MSI for food products at elevated temperatures has been reported by Syamaladevi, Tadapaneni, et al. (2016) where the MC of the food sample was controlled, and the a_w of the food sample was measured using a thermal cell a relative humidity and temperature sensor.

The Clausius-Clapeyron equation (CCE), named after Rudolf J. Clausius and Benoît P.É. Clapeyron, has been reported to describe the changes in a_w of food samples at a constant MC over a wide range of temperatures (Hossain, Bala, Hossain, & Mondol, 2001; Jamali et al., 2006; Labuza, Kaanane, & Chen, 1985). The CCE was originally proposed to estimate the temperature influence on the a_w of a pure system in different conditions by using the net isosteric heat of sorption (q_{st} in J mol^{-1}) (Labuza, 1968; Labuza et al., 1985; Tsami, Maroulis, Marinos-Kouris, & Saravacos, 1990). In applying this equation to a pure system, two assumptions are considered: 1) the MC remains constant during the a_w measurement across different temperatures and 2) q_{st} is constant over the applied temperature range. However, in complex systems like food products, due to various interactions between food components and water molecules, irreversible changes can occur. Thus, it was suggested to determine a_w of food samples with at least 10 °C interval (Labuza et al., 1985).

Most of the studies have reported the application of the CCE in estimating the isosteric heat of sorption and prediction of the a_w of food samples up to 65 °C (Kim, Kim, Kim, Shin, & Chang, 1999; Labuza et al., 1985; Štencl, Janstova, & Drackova, 2010; Tsami, 1991). However, there have been no studies reporting the use of CCE in obtaining the MSI of food samples at higher temperatures. Thus, the objectives of this study were to (1) evaluate a new a_w measuring test cell for low moisture foods covering temperatures up to 80 °C; 2) obtain a_w values of three low moisture food products between 20 and 80 °C; 3) to develop a descriptive model based on CCE for the obtained a_w values.

2. Material and methods

2.1. Food materials

In this study, three food systems were used: 1) soft white organic wheat flour (OWF) (Eden Foods, Clinton, MI), 2) blanched almond flour (AF) (Nuts.com, Cranford, NJ) and 3) non-fat milk powder (NFMP) (Grade A Non-fat dry milk – low heat, Michigan Milk Producers Association, Novi, MI). The proximate compositions of food samples in duplicates were determined according to the standard analytical methods (AOAC, 2012). All the proximate data of samples are reported as a percentage in Table 1. The proximate data indicates that the OWF samples represented a carbohydrate-rich food product (with approximately 79% w/w carbohydrates). The AF samples represented a high-fat product; they consisted of approximately 49% (w/w) fat, 21% (w/w) protein and 23% (w/w) carbohydrate content. The NFMP samples represented a relatively high sugar and high protein product; they consisted of approximately 51% (w/w) milk sugars – mainly lactose and 37% (w/w) protein content.

2.2. Conditioning of food samples

Before the measurement of a_w at different temperatures, the food samples were conditioned to obtain different MC (in % db). The samples were first vacuum dried at 50 °C with the pressure of 10 kPa for approximately two days. Dried food samples were then placed in the jars containing saturated salt solutions to control relative humidity (RH) at room temperature (~21 °C) for approximately three weeks. The supersaturated salts used in this study were LiCl (11.3% RH), CH_3COOK (22.5% RH), $MgCl_2$ (32.8% RH), K_2CO_3 (43.2% RH), $MgNO_3$ (52.9% RH), $NaNO_2$ (65.8% RH), NaCl (75.3% RH) and KCl (84.3% RH) (Greenspan, 1977). The toluene solution was placed in jars with high humidities (75 and 86% RH) to prevent any fungal/mold growth in the samples. After the conditioning period, the MC of all samples were determined using a halogen moisture analyzer (Mettler-Toledo, LLC, Columbus, OH). All conditioned samples were analyzed for MC in duplicates.

Table 1
Proximate composition of food samples (average values ± SD).

	OWF[a]	AF	NFMP
Moisture (% w/w)	8.3 ± 0.2	3.7 ± 0.3	4.1 ± 0.2
Ash (% w/w)	1.6 ± 0.04	3.2 ± 0.1	7.9 ± 0.1
Fat (% w/w)	3.3 ± 0.1	48.8 ± 0.3	0.5 ± 0.04
Protein (% w/w)	7.9 ± 0.5	21.1 ± 0.3	36.8 ± 0.5
Carbohydrate (by difference – % w/w)	78.9 ± 0.6	23.3 ± 0.9	50.7 ± 0.8

[a] Tadapaneni et al. (2017).