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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).

2.3. New high-temperature cell (HTC)

With modifications to the thermal cell with RH sensor as reported by Syamaladevi, Tadapaneni, et al. (2016), an improved version of the thermal cell, i.e. high-temperature cell (HTC), was developed by METER Group, Inc. (Pullman, WA) to measure a_w of food samples at different temperatures (Fig. 1). The newer version of HTC consists of an anodized aluminum alloy cell with a capacitance based RH and temperature sensor (Honeywell HumidIcon™, Morristown, NJ). The sensor with a working accuracy of ± 2% RH was embedded in the lid. The bottom base supported an aluminum cup to hold the samples. For the measurement of RH, the HTC assembly was sealed using screws and an O-ring. The sensor in HTC monitored the RH and temperature of the air in the headspace above the aluminum cup and the corresponding a_w values were recorded on the computer.

The HTC was calibrated using at least four standards (unsaturated salt solutions) provided by AquaLab (METER Group, Inc.). Based on the temperature and molality dependent osmotic coefficients of the salt solutions reported in the literature (Gibbard & Scatchard, 1973; Gibbard, Scatchard, Rousseau, & Creek, 1974), the theoretical a_w values of these standards were computed using the following equation as reported by Tadapaneni et al. (2017):

$$a_w = \exp(-\Phi\ M_w\ \nu\ m_s) \tag{1}$$

where, Φ is the osmotic coefficients, M_w is the molar mass of water (kg mol^{-1}), ν is the stoichiometric number of dissociated solute ions, m_s is the molality of salt (mol kg^{-1} H_2O).

The predicted a_w values from Eq. (1) were plotted against the experimental a_w data from HTC to obtain the linear regression based calibration equation for each HTC device. An extended calibration of HTC requires the a_w measurements at multiple temperatures of each standard solution. The single-temperature calibration involves the measurement of a_w of the standards at a single reference temperature which is an expedited method. The calibration process using both methods improved the accuracy of the a_w data from the HTC which was indicated by the lower values of root mean squared error (RMSE). The RMSE values for the pre-calibration (Fig. 2), extended and single-temperature calibration (Fig. 2) a_w data were determined to be 0.027, 0.009 and 0.012, respectively. In this study, the single-temperature calibration method was applied to all the experimental a_w data obtained from HTC.

2.4. Determination of a_w at different temperatures

Each conditioned food sample of approximately 2 g was placed in the aluminum cup inside the HTC and was sealed properly to prevent any leakage. In the study of Syamaladevi, Tadapaneni, et al. (2016), a hot-air oven was used to increase the temperature of the sample in the first generation thermal cell which took a long time for the sample to reach the target temperatures and attain the equilibrium state at those temperatures. To reduce the come-up time for HTC, i.e. time needed for food samples to reach the target temperature, and the equilibrium state, the HTC was sealed and heated in an oil bath instead of using the hot-air oven method. The HTC was thermally treated at every 10 °C temperature interval from 20 to 80 °C. The RH and temperature were recorded for every 1 min. When there was no change in the RH value for a significant time (approximately 30 min), the sample was considered to be in an equilibrium state at the respective temperature, and the corresponding RH of headspace (or a_w of the sample) was recorded. Fig. 3 shows the typical time-temperature-RH profiles of the headspace in HTC when food samples were treated at different temperatures.

To evaluate the a_w data from HTC, the a_w of the equilibrated food samples were also measured by the Vapor Sorption Analyzer (VSA) (METER Group Inc., Pullman, WA). Due to the limited operating temperature range in VSA, the a_w of each sample was measured by VSA at 10 °C temperature intervals from 20 to 50 °C without opening the lid. The a_w values of OWF, AF, and NFMP were measured using the chilled-mirror dew point sensor in VSA.

Samples in duplicates were measured in both HTC and VSA methods. The samples were weighed before and after each experiment.

2.5. Clausius-Clapeyron equation (CCE)

The derivation of Clapeyron equation is based on the two phases of a pure substance – gaseous (g) and liquid (l) reaching the equilibrium state (Staudt et al., 2013) and the corresponding Gibb's free energy for gaseous form (dG_g in J mol^{-1}) would be equal to the Gibb's free energy for liquid form (dG_l n J mol^{-1}). Thus, the relation can be written as:

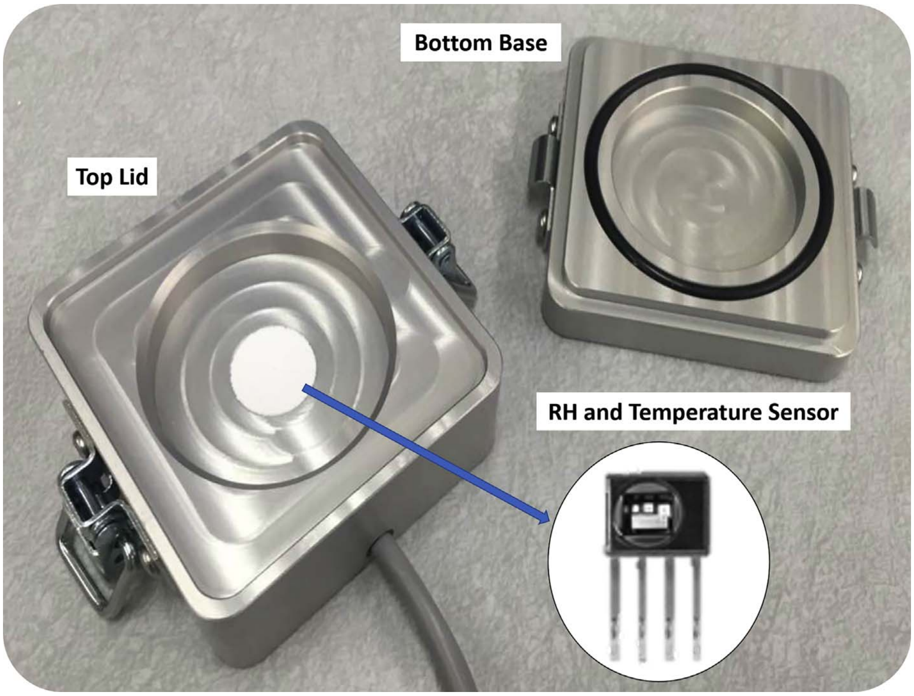

Fig. 1. The high-temperature cell (HTC) developed to measure the a_w of the food samples at elevated temperatures.

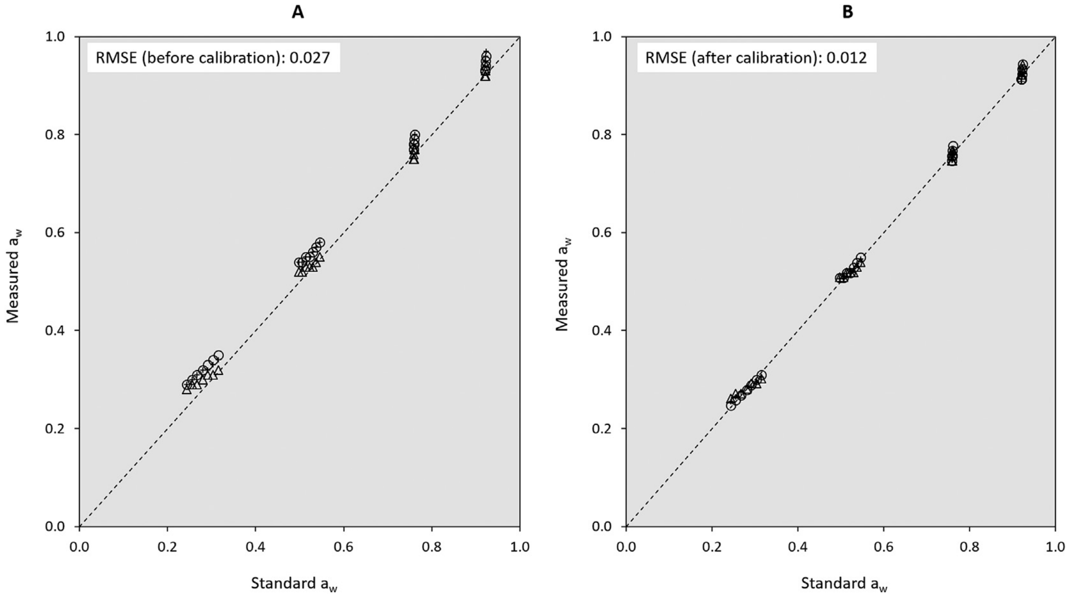

Fig. 2. Comparison of measured (A) vs. calibrated (B) a_w data; different symbols represent data from different HTC systems.

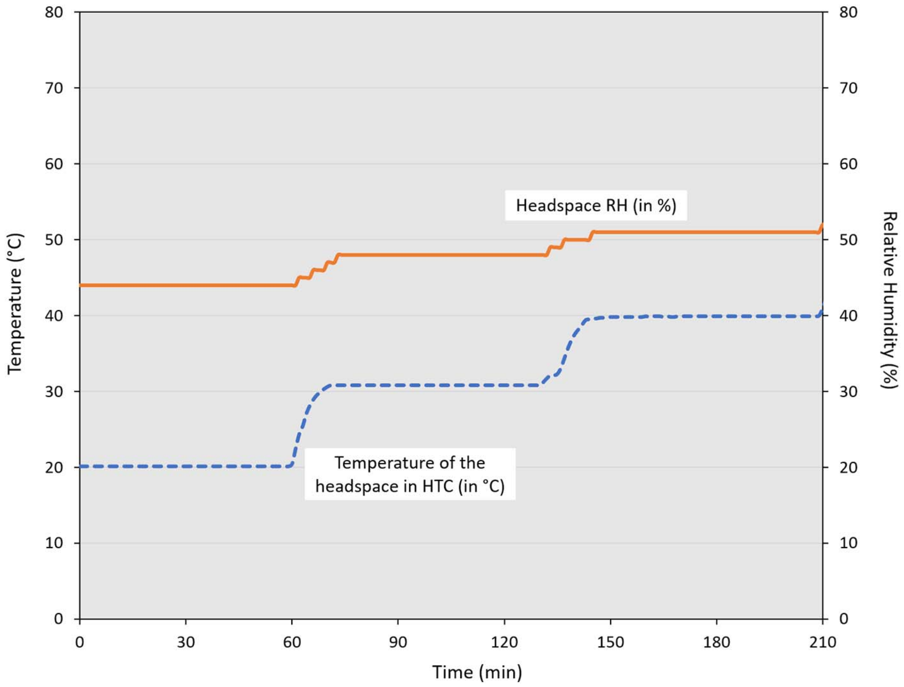

Fig. 3. The time-temperature-RH profile of the headspace in the HTC when heated to different temperatures.

$$dG_g = dG_l \tag{2}$$

The thermodynamic relationship of Gibb's free energy (Rizvi, 2014) is:

$$dG = VdP - SdT \tag{3}$$

where V is the molar volume ($m^3\ mol^{-1}$), P is the vapor pressure (Pa), S is the entropy of the system ($J\ K^{-1}\ mol^{-1}$), and T is the temperature (K). For equilibrium condition, Eq. (3) for gaseous and liquid phase can be equated:

$$V_g dP - S_g dT = V_l dP - S_l dT \tag{4}$$

Rearranging the Eq. (4),

$$(V_g - V_l)\, dP = (S_g - S_l) dT \tag{5}$$

And further rewriting the Eq. (5),

$$\frac{dP}{dT} = \frac{(S_g - S_l)}{(V_g - V_l)} \tag{6}$$

where V_g and V_l are the molar volumes ($m^3\ mol^{-1}$) of gaseous and liquid phases, respectively. Using the differential entropy of sorption (ΔS) $S_g - S_l = L / T$, where L is the specific latent heat of vaporization ($J\ mol^{-1}$), Eq. (6) becomes:

$$\frac{dP}{dT} = \frac{L}{(V_g - V_l)T} \tag{7}$$

Taking assumption that the molar volume of the liquid phase (V_l) is negligible in comparison to the molar volume of gaseous phase (V_g) and the vapor phase behaves ideal gas law ($V_g = RT / P$), the Clapeyron Eq. (7) can be stated as

$$\frac{dP}{dT} = \frac{PL}{RT^2} \tag{8}$$

where R is the universal gas constant (8.314 J mol^{-1} K^{-1}). Further expanding the Eq. (8), we get the general form of Clausius Clapeyron relation:

$$\frac{d\ln P}{dT} = \frac{L}{RT^2} \tag{9}$$

Considering that only moisture is exchanged between the two phases in addition to the previous assumptions of Clausius Clapeyron equation, P and L can be substituted with P_w (partial water vapor pressure in Pa) and ΔH (total enthalpy change for the sorption process in J mol^{-1}), respectively:

$$\frac{d\ln P_w}{dT} = \frac{\Delta H}{RT^2} \tag{10}$$

It is known that a_w is a function of partial pressures i.e. $a_w = P_w / P$ and with the Eqs. (9) and (10), the following relation is obtained:

$$d\ln a_w = \frac{\Delta H - L}{RT^2}\, dT \tag{11}$$

Integrating the Eq. (11) at fixed MC, the general form of Clausius Clapeyron equation (CCE) can be obtained as:

$$\ln\left(\frac{a_{w2}}{a_{w1}}\right) = \frac{\Delta H - L}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \tag{12}$$

or:

$$a_{w2} = a_{w1}\exp\left(\frac{\Delta H - L}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right) \tag{13}$$

where a_{w1} and a_{w2} are water activity values of a sample with a fixed MC at temperatures T_1 and T_2, respectively. Thus, by knowing the a_w of the food sample at one temperature and corresponding ($\Delta H - L$) values, the a_w of the same sample at target temperature can be estimated using the derived Eq. (13).

The fit qualities of CCE (Eq. (13)) for the experimental a_w data by HTC and VSA were analyzed by determining the coefficient of determination (R^2), standard error of prediction (*SEP*) and mean relative percentage deviation (*E*). Microsoft Excel (Redmond, WA) was used to calculate R^2, *SEP*, and *E*.

The net isosteric heat of sorption (q_{st} in J mol^{-1}) is the difference between total enthalpy change for the sorption process (ΔH) and the latent heat of water vaporization (L). It provides the key information about the energy requirement for different processes like drying of food samples and state of water molecules in the food products. In the present study, the measured a_w data for different food samples at different temperatures obtained by HTC for the adsorption process was used to plot ln a_w vs. $1/T$, according to Eq. (13). The q_{st} values were estimated from the slope of the plot. These q_{st} values were related to the MC of the food samples following an empirical relation (Zuo, Rhim & Lee, 2015):

$$q_{st} = a\exp(-b\,MC) \tag{14}$$

where a and b are the constants and MC is the moisture content (% db). The R^2 was used to assess the goodness of fit for Eq. (14).

2.6. Moisture sorption isotherms (MSI)

From the Eq. (13), at a constant MC, the a_w of a food sample at different temperatures was estimated. With the assumption that the MC of a sample is constant at different temperatures and the known corresponding estimated a_w values, it is possible to obtain the moisture sorption isotherms (MSI) for a food sample at different temperatures. Similarly, in this study, the predicted a_w for OWF, AF and NFMP samples at a constant MC value, was used to estimate the MSI at 20, 60 and 80 °C.

The predicted MSI from CCE was assessed against the MSI determined by the dynamic vapor sorption method in VSA as described by Syamaladevi, Tadapaneni, et al. (2016) for OWF, AF and NFMP samples at 20 and 60 °C.

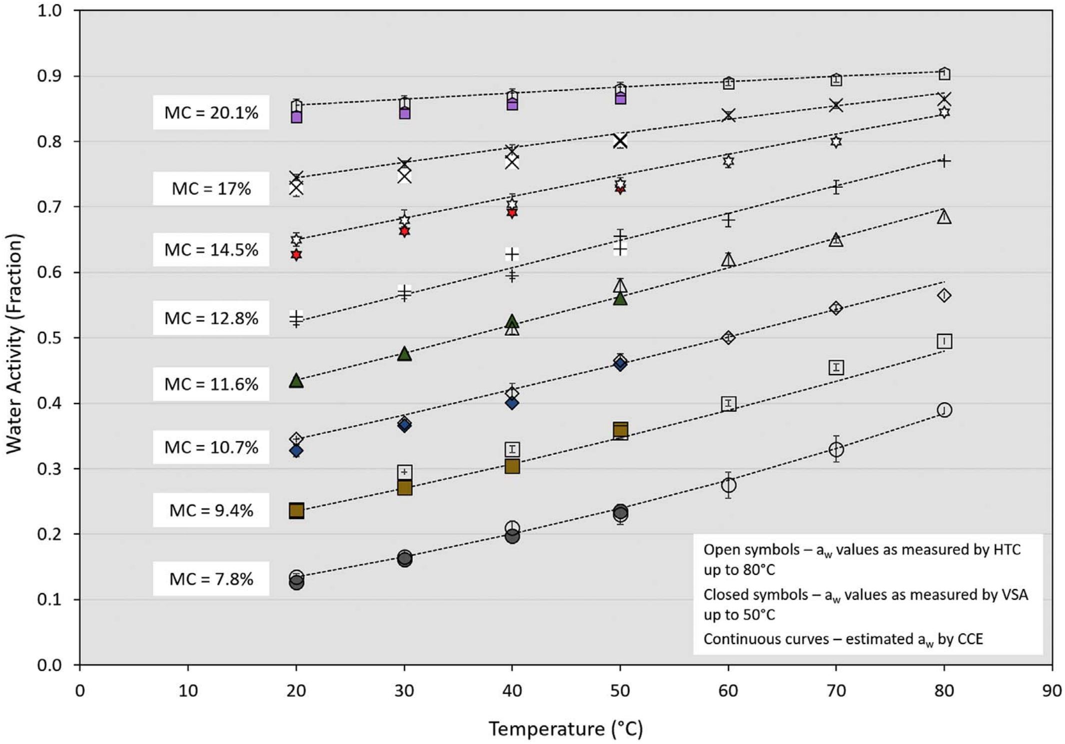

Fig. 4. The estimated and experimental a_w values of organic wheat flour (OWF) at different moisture contents (MC); MC values (in % db) for OWF samples are shown at left with the respective a_w values as indicated by symbols and continuous curves. Scattered data symbols represent means (± SD) of duplicate measurements.

3. Results and discussion

3.1. a_w measured by HTC and VSA

The a_w values for OWF, AF and NFMP samples at eight different MC as measured by HTC at 20 to 80 °C and by VSA 20 to 50 °C are shown in Figs. 4, 5 and 6, respectively. The CCE provided a good fit of the experimental a_w data of OWF, AF and NFMP samples as measured by HTC and VSA based on the high R^2 (> 0.95), low *SEP* (< 0.02) and *E* ($< 10\%$) values.

At any fixed MC, the a_w of OWF samples increased with the sample temperature in a closed system (Fig. 4). For example, at the MC of 11.6% db, the a_w of the sample at 20 °C was observed to be 0.44 as recorded by the HTC. When the same sample in HTC was heated to 80 °C, the a_w of the sample was measured as 0.69. The a_w values from VSA agreed with the data of OWF sample from HTC for 20 to 50 °C.

Likewise, the a_w of AF samples of fixed MC increased as the temperature of the sample was increased from 20 to 80 °C when the MC of the samples was at 2.2 to 4.6% db (Fig. 5). Above 5.7% db, the a_w of the AF sample was relatively stable. The difference between the a_w at 20 and 80 °C was < 0.02. In the NFMP samples, a_w of the sample also increased with the temperature for the samples with MC of 2.8 to 11.9% db. But, for MC above 13.1% db, the difference between the a_w values at 20 and 80°C was < 0.03 (Fig. 6).

In general, the a_w of food powders with hydrophilic macromolecules of a specific MC increases with the temperature (Labuza, 1968). The increase in a_w in such food products is due to temperature induced breakage of molecular bonds between water molecules and —OH groups in foods (Foster, Bronlund, & Paterson, 2005). The degree of increase in the a_w is dependent on the amount of hydrophilic groups (—OH) present in the food product. Similarly, in the present study, the temperature dependence was observed on the a_w of food samples with low MC.

3.2. Net Isosteric heat of sorption (q_{st})

The relationship of q_{st} and the MC of the test food samples are summarized in Fig. 7. In general, the q_{st} values were inversely related to sample MC. For example, with the OWF samples at 7.8% db, the q_{st} was observed to be 14.9 kJ mol^{-1}. As the MC in OWF samples was increased to 20.1% db, the q_{st} was determined to be 0.8 kJ mol^{-1}. For the AF samples, the q_{st} value was computed to be 15.2 kJ mol^{-1} at 2.2% db. With an increase in MC to 10% db, the q_{st} was observed to reach zero. The q_{st} was estimated to be approximately 11 kJ mol^{-1} for the NFMP samples of 2.8% db. As the MC was increased to 15.9% db, the q_{st} decreased to 0.3 kJ mol^{-1}. The exponential relationship for each food sample using Eq. (14) is shown in Table 2. The obtained equation was found to fit the respective experimental q_{st} data as indicated by high R^2 values.

Table 3 lists previously published q_{st} values for the food products with different MC similar to the products used in the present study. The results for the relationship of q_{st} to the MC in the OWF samples for adsorption process are similar to those reported by other studies for wheat flour (Martín-Santos, Vioque, & Gómez, 2012; Moreira, Chenlo, Torres, & Prieto, 2010).

A study by Pahlevanzadeh and Yazdani (2005) for almond powder reported a steep slope for q_{st} at low MC, similar to what we observed for the AF samples in this study. However, the maximum q_{st} value observed by Pahlevanzadeh and Yazdani (2005) was approximately 4.5 times higher than the maximum q_{st} value determined in this study for a similar range of MC. Moreover, at higher MC, the q_{st} for AF samples in our study approaches zero whereas Pahlevanzadeh and Yazdani (2005) reported q_{st} to be approximately 20 kJ mol^{-1} for MC of 10% db.

In a similar study, it was reported that for adsorption process in skim milk powder, the q_{st} value increased as the MC was decreased (Rückold, Grobecker, & Isengard, 2000). This finding supports observation from our study about the relationship between q_{st} and MC for NFMP samples.

The high q_{st} values obtained at the low MC for all food samples indicate that the water molecules are strongly bonded to the monolayer molecules in the food products, and the amount of energy required to break those bonds is very high compared to samples with higher MC (Abdenouri, Idlimam, & Kouhila, 2010; Lim, Tang, & He, 1995). Several

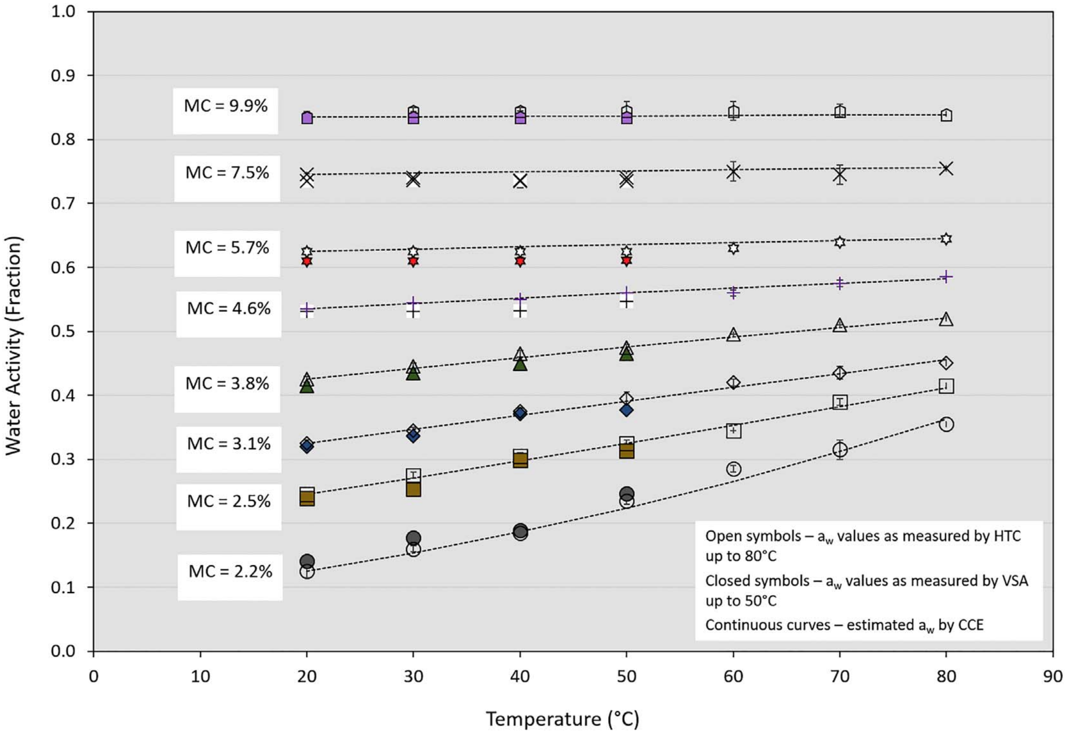

Fig. 5. The estimated and experimental a_w values of almond flour (AF) at different moisture contents (MC); MC values (in % db) for AF samples are shown at left with the respective a_w values as indicated by symbols and continuous curves. Scattered data symbols represent means (± SD) of duplicate measurements.

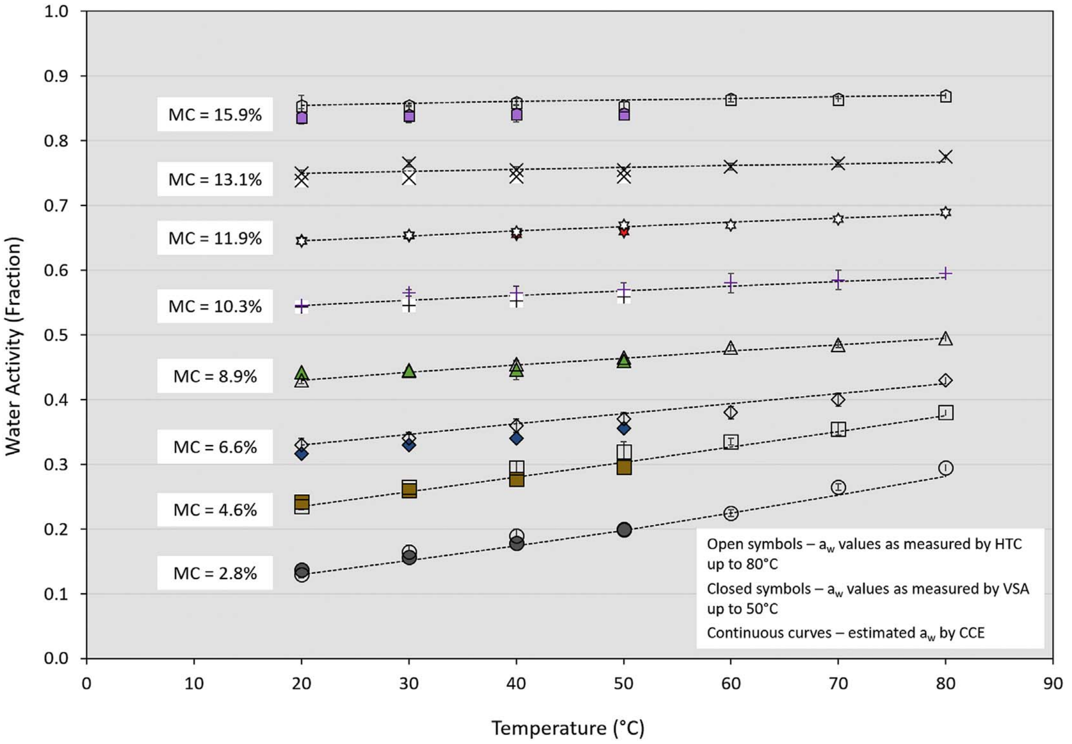

Fig. 6. The estimated and experimental a_w values of non-fat milk powder (NFMP) at different moisture contents (MC); MC values (in % db) for NFMP samples are shown at left with the respective a_w values as indicated by symbols and continuous curves. Scattered data symbols represent means (± SD) of duplicate measurements.

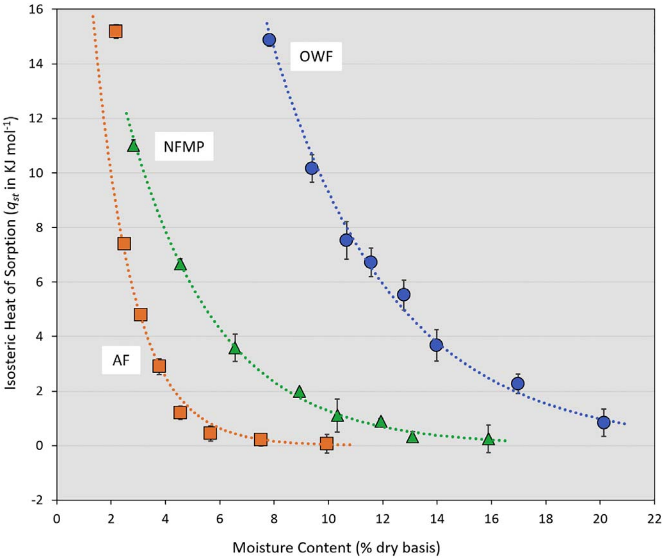

Fig. 7. Net isosteric heat of sorption (q_{st} in kJ mol^{-1}) data for OWF, AF and NFMP samples; Average experimental data of q_{st} for different samples is indicated by respective closed symbols (± SD) and the fit of this experimental values is shown as the respective dotted lines.

Table 2
The fitting equations for the obtained q_{st} values for different MC.

Food sample	Fitting equation	R^2
OWF	$q_{st} = 87.8\ exp(-0.26\ MC)$	0.99
AF	$q_{st} = 39.5\ exp(-0.69\ MC)$	0.96
NFMP	$q_{st} = 26.7\ exp(-0.30\ MC)$	0.98

Table 3
Reported range of q_{st} values for food products as a function of MC similar to the food samples analyzed in the present study.

Type of food sample	MC (% db)	q_{st} (kJ mol^{-1})	Reported by
Wheat flour	≤ 3 to ≤ 28	11 to 0 (adsorption)	Martín-Santos et al. (2012)
	0 to 20	23 to 1.5 (adsorption) 36 to 1.5 (desorption)	Moreira et al. (2010)
Almond powder	≤ 3 to ≤ 10	65 to 20	Pahlevanzadeh and Yazdani (2005)
Skim milk powder	< 5 to ≤ 25	90 to ≤ 45 (adsorption)	Rückold et al. (2000)
	< 5 to ≤ 21	42 to ≤ 0.5 (desorption)	Rückold et al. (2003)

physiochemical and processing factors associated with the food products would influence the binding of water molecules, including three-dimensional structure of food macromolecules and food compositions. Thus, the magnitude of q_{st} value would vary for different food products, as observed in the present study.

The information on q_{st} offers an understanding regarding the status of sorbed moisture in the food product and hence, provides an estimation about the stability kinetics of physiochemical and microbiological aspects in the food products under specified storage settings.

3.3. Moisture sorption isotherms (MSI)

The MSI for OWF, AF and NFMP samples at 20, 60 and 80 °C for adsorption process as estimated by the CCE (lines) and observed by VSA (symbols) are shown in Figs. 8, 9 and 10, respectively.

The MSI for the OWF samples from CCE (Fig. 8) shows that at a specific MC, the a_w of the sample increases when heated from 20 to 80 °C. The shift in a_w for OWF when heated in a closed cell as indicated

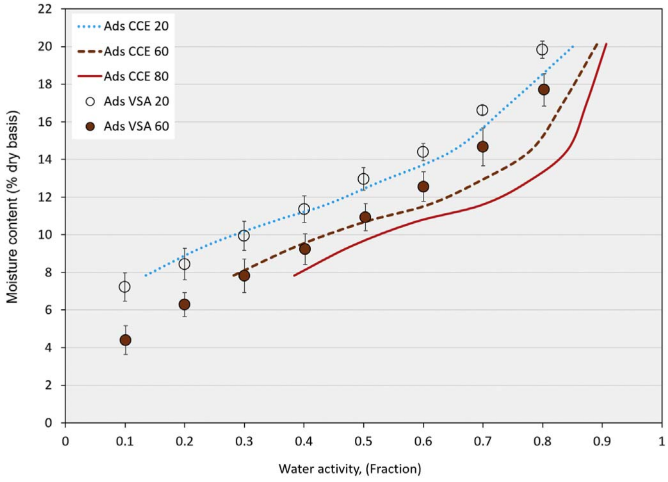

Fig. 8. Moisture sorption isotherms of OWF samples obtained from CCE at 20, 60 and 80 °C (represented by continuous curves) and experimental data from VSA at 20 and 60 °C (represented by symbols).

by the CCE is also observed for the MSI obtained from VSA. To explain, at a MC of 11.6%, the a_w of OWF sample at 20 °C was 0.44 and when the same sample was heated to 60 and 80 °C, the CCE estimated the a_w of the sample to be 0.61 and 0.70, respectively. Similarly, the experimental MSI from VSA also showed that the a_w of the sample for a fixed MC increased when the temperature of the sample was increased from 20 to 60 °C. For instance, at the constant MC of 11%, the a_w at 20 °C was 0.4 and when the temperature was increased to 60 °C, the a_w of the sample was 0.5.

For the AF samples, the MSI estimated by the CCE indicates that as the MC of AF sample was increased, the change in a_w of AF samples at fixed MC decreased as the temperature was increased from 20 to 80 °C (Fig. 9). In the AF samples with MC above 6%, it was estimated that the a_w would remain stable for different temperatures. This trend was confirmed by the experimental MSI data obtained from VSA where the isotherm curves at 20 and 60 °C overlapped above 6% MC indicating no change in a_w of AF sample when the temperature of the sample was increased.

Likewise, the MSI for NFMP samples as estimated by the CCE (Fig. 10) demonstrated that when the MC of the NFMP sample was above 13% db, the a_w remained the same regardless of the sample temperature. The experimental data of MSI for the NFMP samples indicates that at a constant MC, as the temperature was increased from 20 to 60 °C, the a_w of the NFMP was increased by 0.1. This increase in a_w of NFMP sample was observed up to a MC of 13%. With further increase in MC of NFMP samples, the change in a_w of the samples was reduced.

When the food samples are thermally treated in a closed system, the increase in a_w could be attributed to the alleviation of the molecular bonds between food biopolymers and water alleviate which would release free water molecules (Palipane & Driscoll, 1993). As mentioned earlier, this shift in a_w of the samples is highly dependent on the food composition. Depending on the presence of hydrophilic and hydrophobic groups in the food sample and the treatment temperatures, there would be a significant influence on the a_w which may increase or decrease from its initial value.

For carbohydrate-rich food like OWF samples, studies have reported an increase in a_w at specific MC which supports the data for OWF samples observed in the present study (Bandyopadhyay, Weisser, & Loncin, 1980; Syamaladevi, Tadapaneni, et al., 2016).

Even though many studies have reported the MSI for whole almond nuts and shells, there are limited studies available for MSI of almond powder or flour. Pahlevanzadeh and Yazdani (2005) studied MSI of Shokufeh almonds in the nut and powder form over a temperature range of 15–75 °C. They also reported that at constant MC, the a_w values of almond nut and powder were increased as the temperature of the samples was raised which supports the results of AF samples observed in this study. However, a difference was observed in the MSI trends at higher MC (above 5% db) between the reported data of almond powder and the data of the AF samples in the current study. This difference could be attributed to various factors including cultivar of almond kernels used in the study, processing method for turning almond kernels into powder or flour resulting in different particle sizes, and the presence of kernel skin.

The MSI data of the NFMP for both CCE and VSA shows sigmoid-shaped curves which indicate strong interactions between the monolayer of water and the surface of the food (Brunauer, Deming, Deming, & Teller, 1940). The bends observed in the MSI curves could be attributed to physiochemical changes in the sample during the adsorption process. In this study, the effect of temperature on the a_w of the

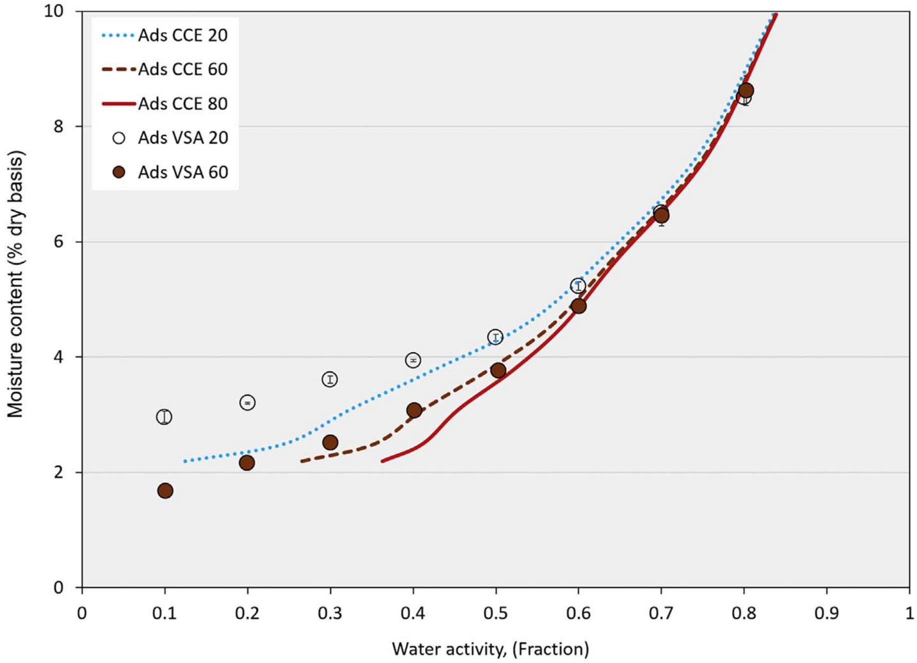

Fig. 9. Moisture sorption isotherms of AF samples obtained from CCE at 20, 60 and 80 °C (represented by continuous curves) and experimental data from VSA at 20 and 60 °C (represented by symbols).

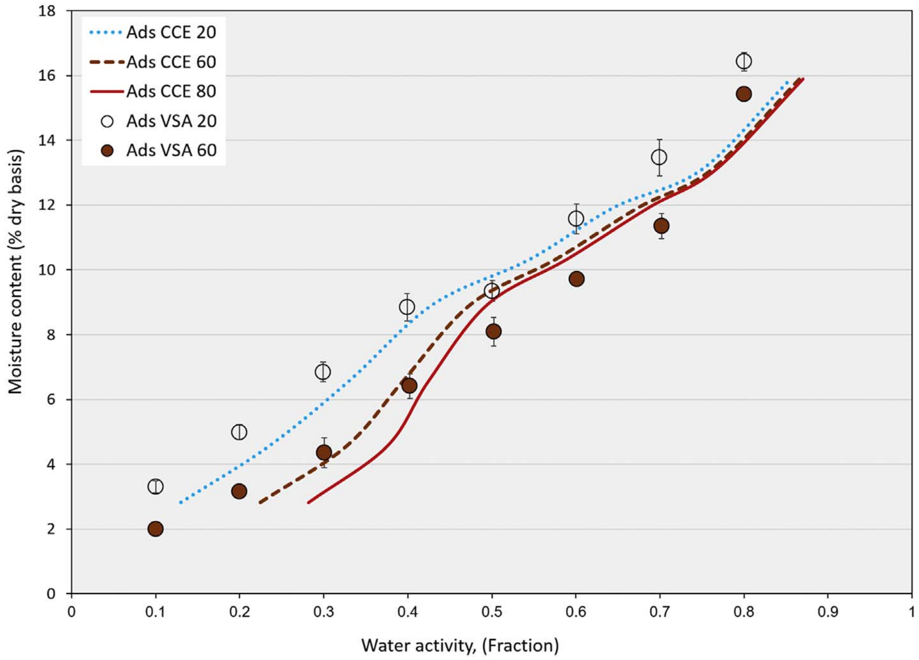

Fig. 10. Moisture sorption isotherms of NFMP samples obtained from CCE at 20, 60 and 80 °C (represented by continuous curves) and experimental data from VSA at 20 and 60 °C (represented by symbols).

NFMP samples was similar to that of the OWF and AF samples. This observed trend was also reported by Štencl (1999) for MSI of skim milk powder where an increase in temperature of skim milk powder led to an increase in the a_w. This behavior implies that the hygroscopicity in the material was greatly reduced when the temperature was increased (Štencl, 1999).

Overall, the CCE appropriately estimates the shift in a_w with an increase in the temperature for the OWF, AF, and NFMP samples. The trends were consistent with the experimental MSI data from VSA. It is important to point out that with the CCE method, the q_{st} of a sample at a specific MC can be readily obtained and be used to obtain MSI of a sample at different temperatures. This process to get the MSI of a food product for a wide range of temperatures would be faster when compared to the conventional MSI generating techniques.

However, studies have reported that the food products which are rich in fat content like peanut butter or peanut oil have demonstrated different behavior for MSI as generally observed in this study. The a_w of very high oil content decreased as the temperature was increased (Loncin, Bimbenet, & Lenges, 1968; Syamaladevi, Tadapaneni, et al., 2016). Thus, further studies are needed to evaluate the effectiveness of CCE in estimating MSI for fat-rich food products.

4. Conclusions

In this study, an improved version of HTC was used to measure the a_w of three different food samples at different temperatures (20 to 80 °C). The experimental a_w data for the food samples obtained from HTC was used to estimate q_{st}. There was a strong influence of MC on the q_{st} which was indicated by the high energy values for sorption at low MC. Using the q_{st} values in the CCE, MSI for all food samples were determined at 20, 60 and 80 °C. For all the tested OWF samples, an increase in sample temperature raised the a_w. However, for AF and NFMP samples, above specific MC, the a_w remained relatively stable as the temperature of the sample was increased.

This study presents an expedited method of determining the a_w at different temperatures. Further studies regarding the application of this approach to estimate the a_w of other food products with different compositions at different temperatures are needed. Knowledge of variations in a_w at the elevated temperatures would offer a better understanding to the food safety personnel in correlating the a_w data to the thermal resistance of pathogens like *Salmonella*, *Listeria* spp. and subsequently, aid in developing the efficient processing techniques.

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