

# DESORPTION ISOTHERMS AND THERMODYNAMIC PROPERTIES OF FRESH AND OSMOTIC–ULTRASONIC DEHYDRATED QUINCES

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Accepted for Publication October 9, 2011

doi:10.1111/j.1745-4549.2011.00671.x

## ABSTRACT

Experiments were conducted to determine the effect of pretreatment osmotic–ultrasonic dehydration on the desorption isotherms of quince by static gravimetric method at 30, 45 and 60°C temperatures. The isotherms exhibited type II behavior, with the sorption capacity decreased with increasing temperature. Out of the six equilibrium sorption models that were evaluated, the Peleg equation gave the best fit to the sorption data. The Hasley equation was further used to estimate the thermodynamic functions (such as net isosteric heat, enthalpy–entropy compensation and spreading pressure) of quince. The net isosteric heat of sorption and differential entropy decreased with increasing moisture contents in an exponential function. A plot of differential heat versus entropy satisfied the enthalpy–entropy compensation theory. The spreading pressure increased with increasing water activity and decreased with increasing temperature. The value of net isosteric heat, differential entropy and spreading pressure of untreated samples are higher than that pretreated sample quince.

## PRACTICAL APPLICATIONS

The desorption isotherms are important in the analysis and design of various food processes, such as preservation, drying, packing and mixing. The net isosteric heat of sorption can be used to estimate the energy requirements of dehydration processes. Combined methods involving osmotic–ultrasonic dehydration and convective air-drying are usually used to obtain a final product with a better quality (i.e., better preserved from undesirable changes) and in this sense, applying an osmotic–ultrasonic dehydration step prior to the dehydration process could be interesting. Nevertheless, when osmotic–ultrasonic dehydration is employed, together with water removal, an acquisition of osmotic solute takes place. In this way, the composition of the final product is changed and the characteristics of the sorption isotherm may be modified. One of the aims of this work was to determine the effect of osmotic–ultrasonic dehydration of quince on its desorption isotherm.

## INTRODUCTION

Desorption isotherms are of great importance in the design of a food dehydration process, because this will determine the degree of drying required to obtain a stable product (Lerici *et al.* 1983; Sereno *et al.* 2001). The study of sorption properties of fruits is of interest because the relationships between moisture content and water activity are essential for the design and optimization of many processes in the food industry such as drying, packaging and storing. An increasing

number of works have been reported in this area during the last two decades (Vazquez *et al.* 1999; Falade and Aworh 2004; Pahlevanzadeh and Yazdani 2005; Yazdani *et al.* 2006; Sopade *et al.* 2010).

Further analysis of sorption isotherm data by application of thermodynamic principles can understand the properties of water and calculate energy requirements associated with the transfer of heat and mass in biological systems. Thermodynamic properties of food relate the concentration of water in food to its partial pressure, which is crucial in the analysis

of heat and mass transport phenomena during dehydration. They determine the end to which food must be dehydrated in order to achieve a stable product with optimal moisture content. The properties also provide an insight into the microstructure associated with the food–water interface (Rizvi 1986). Some thermodynamic functions, used in analyzing sorption behavior of biological systems include net isosteric heat, enthalpy–entropy compensation and spreading pressure.

The net isosteric heat ( $q_{st}$ ) is defined as the difference of the total heat of sorption and heat of vaporization at the system temperature. The heat of adsorption is a measure of the energy released on sorption, and the heat of desorption is the energy required to break the intermolecular forces between the molecules of water vapor and the surface of adsorbent. Thus, the heat of sorption is considered as indicative of the intermolecular attractive forces between the sorption sites and water vapor (Al-Muhtaseb *et al.* 2004b). The differential entropy of a material is proportional to the number of available sorption sites at a specific energy level (Madamba *et al.* 1996). The enthalpy–entropy compensation theory is used to evaluate physical and chemical phenomena such as sorption reaction. The theory states that it is necessary to minimize free energy ( $G$ ) changes because of these phenomena, compensation arises from the nature of the interaction between the solute and the solvent causing the reaction and that the relationship between the enthalpy and entropy for a specific reaction is linear (Fasina 2006). The spreading pressure, or surface potential, represents the surface excess  $G$  and provides an indication of the increase in surface tension of bare sorption sites because of absorbed molecules (McMinn and Magee 2003).

The objectives of the present work were to (1) determine the effect of osmotic–ultrasonic pretreatment on the desorption isotherms of quince; (2) model the desorption isotherm using selected equations; (3) determine the thermodynamic properties; and (4) evaluate the application of the enthalpy–entropy compensation theory to the desorption phenomena.

## MATERIALS AND METHODS

Quinces were purchased from a local market of Mashhad; samples were selected according to its size and ripeness. The quince was peeled and cut into slabs of about 3 mm using a thin blade.

### Ultrasonic Pretreatment

An experimental set of four quince samples was immersed in distilled water and submitted to ultrasonic waves for 0–30 min. The experiments with ultrasonic treatment were carried out in separate 250 mL Erlenmeyer flasks to avoid

interference between the samples and runs. The experiments were carried out under ambient temperature (30°C) in an ultrasonic bath (Schaper model Unique USC 25 kHz, Berlin, Germany) without mechanical agitation. The ultrasonic frequency was 25 kHz. To determine the effect of ultrasonic, the same experimental procedure was carried out without applying ultrasonic. After removal from the distilled water, the samples from each group were drained and were then blotted with absorbent paper to remove the excess water. Weight and moisture content was measured individually. At the end, samples were transferred to the osmotic solution.

**Light Microscopic Analysis.** After the end of ultrasonic pretreatment, the samples were carefully cut into cubes of 5 mm average sides. The sample cubes were fixed with 4% solution of paraformaldehyde in 0.1 M phosphate buffer, pH 7.2 and 1% glutaraldehyde for 24 h at 25°C. The material was then dehydrated in a graded ethanol series and embedded in Historesin embedding kit (Reichert-Jung, Heidelberg, Germany). The tissue blocks were sectioned at 8  $\mu$ m. The Periodic acid-Schiff reagent cytochemical reaction was employed for polysaccharide detection. Photomicrographs of the cell structure were taken using an Olympus BX41 (Olympus, Tokyo, Japan) light microscope with digital image capture system (Fernandes *et al.* 2009).

### Osmotic Dehydration

Each experimental group consisting of three quince slabs was immersed in the osmotic solution for 1, 1.5 or 2 h. The osmotic solution used in each experiment was prepared by mixing food-grade sucrose with distilled water to give a concentration of 40–60 Brix. The osmotic solution to fruit ratio was maintained at 20:1 (weight basis). Experiments were performed with the same constant magnetic agitation. The temperature was monitored by the thermometer set at 50°C. After removal from the solution, the dehydrated samples from each group were drained and were then blotted with absorbent paper to remove the excess solution. Weight and moisture content was measured individually.

The empirical models were generated from response surface methodology to predict osmotic–ultrasonic conditions considered in this research. As a consideration of the osmotic–ultrasonic predrying treatment, it was considered appropriate to maximize water loss and weight reduction and minimize solid gain. The results of the optimum conditions for quinces were found to be 27.25 min for ultrasonic time, 120 min for osmosis time and 50.52% for sucrose concentration (Nosshad *et al.* 2011).

Once osmotic–ultrasonic dehydration was accomplished, samples were strained and blotted smoothly.

## Determination of Desorption Isotherms

The equilibrium moisture contents of quince were determined by a gravimetric technique, which is based on the use of saturated salt solutions to maintain constant water activity at determined values of the samples when equilibrium is reached between atmosphere and food sample. Nine saturated salt solutions selected to give different relative humidity in the range of 0.11–0.90 were used. The salt solutions used and their corresponding relative humidities at different temperatures were taken from data reported by Greenspan (1977) and Kiranoudis *et al.* (1993) given in Table 1. Three replications of the same experiment were carried out. The glass desorption jars were placed in a temperature-controlled cabinet, with an accuracy of  $\pm 1$  C at the selected temperatures 30, 45 and 60C. Equilibrium was reached when the sample weight difference between two successive measurements was less than the balance accuracy 0.001 g. The time required for equilibrium was 3 weeks or more depending on relative humidity and temperature of the samples. In order to inhibit microbial growth, a small quantity of thymol was also placed in the glass flasks in which water activity was greater than 0.5. The moisture contents of the sample were determined by oven method at 105C for 24 h (Munde 2000).

## Data Analysis

**Modeling Desorption Isotherms.** The experimental desorption data of quince at three different temperatures were fitted to six sorption equations shown in Table 2. These mathematical models were reported to be suitable for dehydrated foods, and even foods high in sugar (Falade and Aworh 2004). The parameters of the desorption models were calculated using nonlinear least square regression analysis. Two criteria that were the mean relative deviation modulus ( $P$ ) and the standard error of estimate (SE) were used to evaluate the well fitting of sorption models to experimental desorption data:

**TABLE 1.** WATER ACTIVITY VALUES OF THE SATURATED SALT SOLUTIONS AT THREE TEMPERATURES USED IN THE EXPERIMENT

Salt	Temperature (C)			Reference
	30C	45C	60C	
LiCl	0.113	0.112	0.11	Greenspan (1977)
CH <sub>3</sub> COOK	0.216	0.195	0.16	Kiranoudis <i>et al.</i> (1993)
MgCl <sub>2</sub>	0.324	0.311	0.293	Greenspan (1977)
K <sub>2</sub> CO <sub>3</sub>	0.432	0.432	0.432	Kiranoudis <i>et al.</i> (1993)
Mg(NO <sub>3</sub> ) <sub>2</sub>	0.514	0.469	0.44	Kiranoudis <i>et al.</i> (1993)
NaNO <sub>2</sub>	0.645	0.614	0.59	Greenspan (1977)
NaCl	0.751	0.745	0.745	Greenspan (1977)
KCl	0.836	0.817	0.803	Greenspan (1977)
BaCl <sub>2</sub>	0.9	0.88	0.84	Kiranoudis <i>et al.</i> (1993)

**TABLE 2.** EQUATIONS DESCRIBING THE SORPTION EQUILIBRIUM ISOTHERMS

Name of the equation	Equation
Peleg (Peleg 1993)	$M = m_1 a_w^{n_1} + m_2 a_w^{n_2}$
G.A.B. (van den Berg and Bruin 1984)	$M = M_0 C K a_w / [(1 - K a_w)(1 - K a_w + C K a_w)]$
Halsey (Halsey 1948)	$M = \left[ \frac{-a}{\ln a_w} \right]^{1/r}$
Caurie (Caurie 1970)	$M = \exp(A + B a_w)$
Henderson (Henderson 1952)	$M = [-\ln(1 - a_w)/A]^{1/B}$
Chen (Chen 1971)	$a_w = \exp[k - c \exp(-bM)]$

$$P = \frac{100}{N} \sum_{i=1}^N \frac{|X_{ei} - X_{pi}|}{X_{ei}} \quad (1)$$

$$SE = \sqrt{\frac{\sum_{i=1}^N (X_{ei} - X_{pi})^2}{N - n}} \quad (2)$$

Where  $X_{ei}$  and  $X_{pi}$  were the experimental and predict moisture content values, respectively;  $N$  and  $n$  was the number observation and the number of constants in each model, respectively. A model is considered acceptable if it has a  $P$  value of less than 10% (Lomauro *et al.* 1985). The model with lowest SE and  $P$  and highest regression coefficient ( $r^2$ ) was selected.

## Isosteric Heat of Sorption and Entropy of Sorption-

The isosteric heat of sorption ( $Q_{st}$ ) is a differential molar quantity derived from the temperature dependence of the isotherm at a constant amount of sorbed water moles. The net isosteric heat of sorption ( $q_{st}$ ) is the amount of energy above the heat of vaporization of water ( $H_L$ ) associated with the sorption process, and is calculated from the experimental data using the Clausius–Clapeyron equation (Tsami 1991; Tolaba *et al.* 2004; Pahlevanzadeh and Yazdani 2005):

$$q_{st} = -R \left[ \frac{d \ln(a_w)}{d(1/T)} \right]_X \quad (3)$$

$$Q_{st} = q_{st} + H_L \quad (4)$$

The  $Q_{st}$  is calculated from Eq. 4 by plotting the sorption isotherm as the natural logarithm of water activity versus  $1/T$ , for specific moisture content, and determining the slope, which equals  $-q_{st}/R$ . The application of method requires the measurement of sorption isotherms at more than two temperatures. Sorption entropy is proportional to the number of available sorption sites at a specific energy level. For a thermodynamic system, the relationship between the isosteric heat ( $q_{st}$ ) and the differential entropy of sorption ( $s_d$ ) is given by:

$$\ln(a_w)_x = \frac{Q_{st}}{RT} - \frac{S_d}{R} \quad (5)$$

**Enthalpy–Entropy Compensation Theory.** Enthalpy–entropy compensation theory or isokinetic relationship is used to evaluate physical and chemical phenomena that prevail in the sorption processes. This theory proposes a linear relationship between  $Q_{st}$  and  $S_d$  (Leffler and Grunwald 1963):

$$Q_{st} = T_1 S_d + G \quad (6)$$

Plotting  $Q_{st}$  against  $S_d$ , isokinetic temperature ( $T_1$ ) and the  $G$  at  $T_1$  can be calculated using linear regression.  $T_1$  represents the temperature at which all reactions in the sorption series proceed at the same rate. Krug *et al.* (1976) and Polatoglu *et al.* (2010) recommended a test for the compensation theory, which involves the evaluation of the  $T_1$  respect to the harmonic mean temperature  $T_{hm}$ , which is defined as:

$$T_{hm} = \frac{n}{\sum_{i=1}^n (1/T)} \quad (7)$$

Where  $n$  is the number of isotherms.

The compensation theory only can be applied if  $T_1 \neq T_{hm}$ . If  $T_1 > T_{hm}$ , the process is enthalpy-driven, while if the opposite condition is observed, the process is considered to be entropy-controlled.

**Spreading Pressure.** The spreading pressure is the force applied in the plane of the surface that must be exerted perpendicular to each unit length of edge to keep the surface from spreading. This parameter is not subject to direct experimental measurement; it can be estimated using an analytical procedure that can be used to obtain the empirical relationship between moisture content and water activity (Smith *et al.* 2001). Halsey equation was used to obtain the parameters  $a$  and  $r$ , which are used in the following equation that defines the spreading pressure (Moreira *et al.* 2008):

$$\phi = \frac{K_B T}{A_m} a^{1/r} \left[ \frac{1}{\left( \frac{1}{r} - 1 \right) (-\ln(a_w))^{1/r}} \right]_{0.05}^{a_w} \quad (8)$$

Where  $\phi$ , spreading pressure,  $J/m^2$ ,  $A_m$  area of a water molecule,  $1.06 \times 10^{-19} m^2$ ,  $K_B$  Boltzmann's constant,  $1.38 \times 10^{-23} J/K$ ,  $a$  and  $r$  Halsey parameters,  $a_w$  water activity,  $T$  absolute temperature,  $K$ .

## RESULTS AND DISCUSSION

Figure 1 shows the equilibrium moisture content of fresh and pretreated dried quince slices. All isotherms show an increase

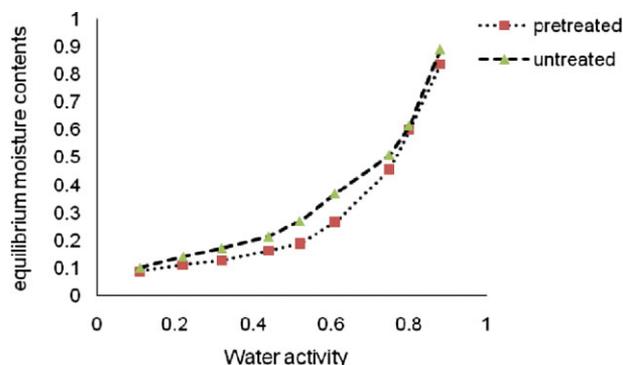


FIG. 1. MOISTURE DESORPTION ISOTHERMS OF QUINCE AT 45°C

in equilibrium moisture content with increasing water activity, at each temperature (Sopade *et al.* 2010). The shape classification of the isotherm is type II classification of Brunauer *et al.* (Brunauer *et al.* 1938). The variety and total amount of hygroscopic materials present in the particular heterogeneous mixture of hydrophilic substances affects the characteristic shape of moisture isotherms (Bolin 1980). The microscopic image analysis of the fresh fruit showed typical thin-walled cells with normal morphology and no visible intercellular spaces (Fig. 2A). After ultrasonic treatment, the cells became more distorted and microscopic channels began to form (Fig. 2B). In the process of osmosis, sugar may have entered into the micro-channel; the composition of the quince is changed. Figure 2 also shows the effect of pretreatment on desorption isotherms of quince, both fresh and pretreated dried quince slices sorbed low moisture in the low and intermediate  $a_w$  range, but sorbed more moisture at higher  $a_w$ . Moisture content increases considerably at high water activity values. This fact is related to the crystalline sugars transition to the amorphous state (Saltmarch and Labuza 1980).

### Effect of Temperature on Desorption Isotherm of Fresh and Pretreated Dried Quince Slices

In general, moisture content is expected to decrease with increasing temperature at a constant water activity (Hill and Rizvi 1982; Moreira *et al.* 2010). As said by Kaya *et al.* (2007), this can be explained by the excitation states of molecules, which because of temperature augmentation, increase their distance apart and hence attractive forces between them decrease. Subsequently increasing temperature lessens the water sorption degree. This finding is consistent with the results of various researchers (Moreira *et al.* 2002; Kaymak-Ertekin and Gedik 2004; Timoumi *et al.* 2004).

A similar trend was obtained in pretreated dried quince slices until inversion of temperature occurred at  $a_w \sim 0.8$ . Figure 3 shows the effect of temperature on desorption

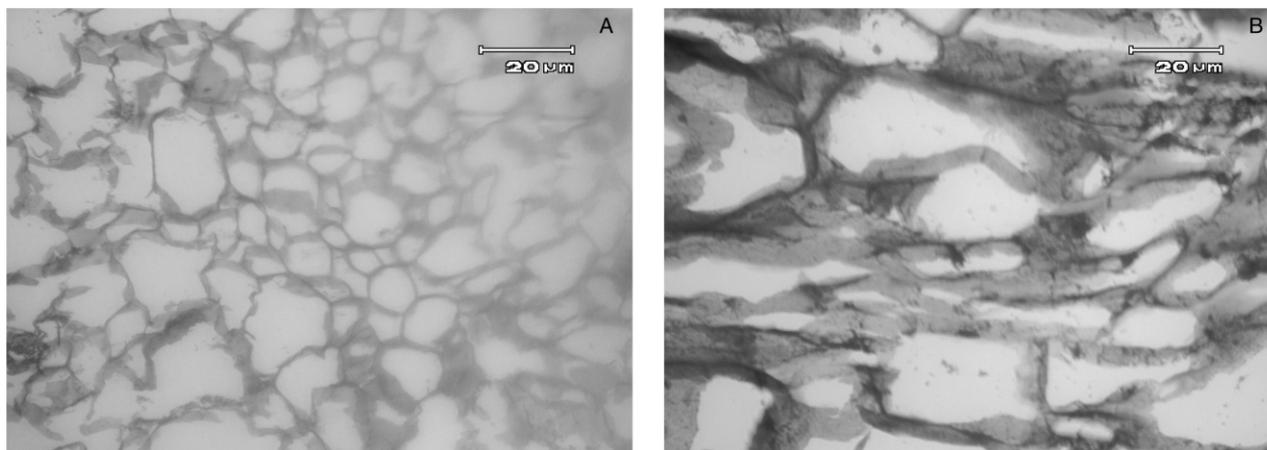


FIG. 2. PHOTOMICROGRAPHS OF QUINCE CUBES BEFORE PROCESSING (RAW FRUIT) (A) AND AFTER ULTRASONIC PRETREATMENT (B)

isotherms of pretreated dried quince slices. As shown, crossing of the temperature isotherms occurred at  $a_w \sim 0.8$ . The “unusual” temperature effect on isotherms above 0.6 (0.8 in this study) was a result of dissolution or increasing solubility of sugars in the high  $a_w$  region (Ayrancl *et al.* 1990; Tsami *et al.* 1990). At water activity values higher than 0.8, there was an inversion in the effect of temperature (i.e., equilibrium moisture content increased with temperature) because of an increase in solubility of sugars in water. The intersection (or inversion) point depends on the composition of the food and the solubility of sugars (Weisser *et al.* 1982). For sultana raisin and currant, the inversion point was about 0.55, likewise, 0.65 for fig, 0.70 for prune, 0.75 for apricot (possessing the lowest sugar content of fruit) (Tsami *et al.* 1990) and 0.65 for quince jam (tapada nova) (Sa and Sereno 1993).

### Fitting of Sorption Models to Experimental Desorption Data

The results of the estimated parameters and comparison statistics for the sorption models of quince are presented in Table 3. The goodness of the fit was provided for the higher values of  $r^2$  and the lowest values of SE and  $P$ . It can be seen in Table 3 that the Peleg model is the best fit to the experimental data over almost the whole range of water activity and temperature for both fresh and pretreated dried quince slices. According to (Peleg 1993), this model fitted as well as or better than the Guggenheim–Anderson–De Boer (GAB) model but its constants had no physical meaning. It is reported that the Peleg model gave good fit for isotherms of some foods (Al-Muhtaseb *et al.* 2004a; Arslan and Togrul 2005). Figures 3 and

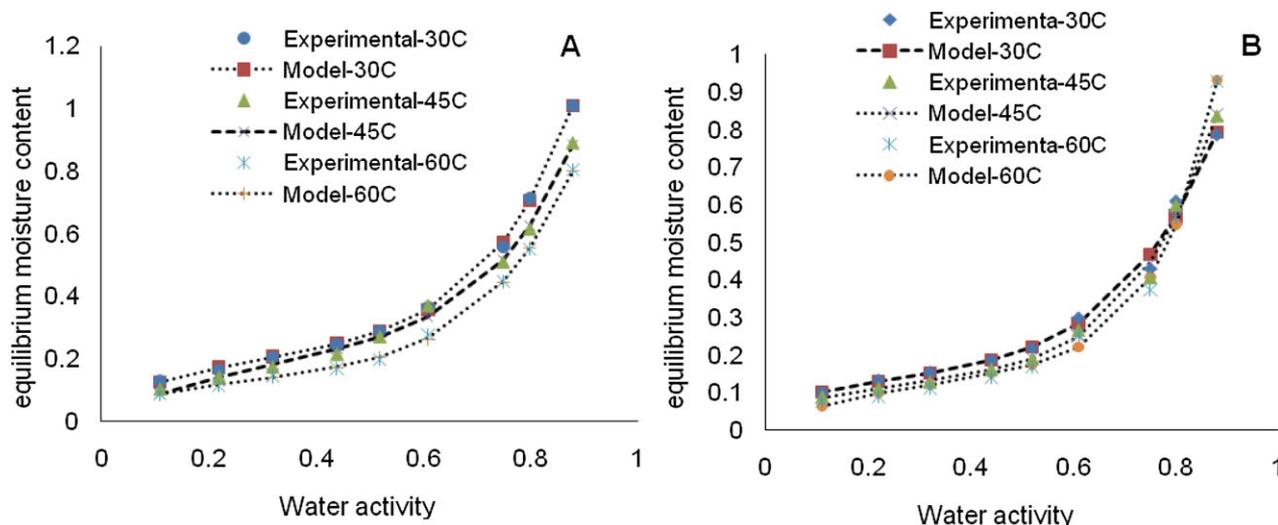


FIG. 3. EXPERIMENTAL AND CALCULATED EQUILIBRIUM MOISTURE CONTENT BY PELEG MODEL OF (A) UNTREATED QUINCE (B) PRETREATED QUINCE

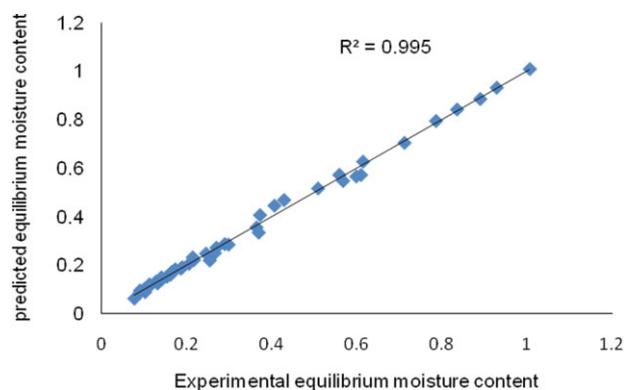
**TABLE 3.** ESTIMATED VALUES FOR THE FIT PARAMETERS AND ASSOCIATED STATISTICS FOR DESORPTION MODELS APPLIED TO DESORPTION DATA FOR QUINCE AT DIFFERENT CONDITION

Model	Constants	Temperature (C)					
		Untreated			Pretreated		
		30C	45C	60C	30C	45C	60C
GAB	$M_0$	0.161684	0.158007	0.124637	0.149649	0.147382	0.112544
	C	16.4444	9.25389	8.675703	6.548117	3.539481	4.632819
	K	0.957733	0.939247	0.965402	0.934093	0.949597	1.003357
	P	3.291	3.992	6.443	12.04	14.141	12.154
	$r^2$	0.996	0.997	0.995	0.968	0.989	0.99
	SE	0.015	0.0255	0.0184	0.0358	0.0347	0.0246
Chen	K	-0.18284	-0.1623	-0.19732	-0.20875	-0.21068	-0.20835
	c	4.942162	3.476633	4.472133	5.128343	4.727659	3.847414
	b	7.93329	7.006348	10.84678	10.7913	11.95072	12.01243
	P	6.719	9.219	8.203	8.806	10.63	11.873
	$r^2$	0.987	0.983	0.979	0.976	0.972	0.966
	SE	0.0336	0.0388	0.0444	0.0446	0.0505	0.0555
Halsey	a	0.124093	0.124776	0.095557	0.095436	0.101121	0.103217
	r	1.380986	1.261928	1.256831	1.326084	1.198889	1.10752
	P	3.68	2.297	5.075	8.069	9.622	8.677
	$r^2$	0.997	0.996	0.992	0.989	0.986	0.985
	SE	0.0152	0.0172	0.0196	0.0326	0.0348	0.0321
	Henderson	A	1.500473	1.581163	1.701097	1.583375	1.664992
B		1.499827	1.593619	1.699714	1.58609	1.667783	1.771337
P		17.757	14.55	18.931	19.93	21.669	19.147
$r^2$		0.97	0.981	0.965	0.962	0.957	0.965
SE		0.0564	0.0392	0.0476	0.0572	0.055	0.0431
Peleg		$m_1$	1.432465	1.166024	0.230892	1.308266	1.203571
	$n_1$	5.783734	6.245384	0.448449	4.522687	4.367713	0.280908
	$m_2$	0.342486	0.391053	1.172271	0.185907	0.146314	1.02292
	$n_2$	0.457008	0.670402	5.467987	0.255964	0.208181	4.32328
	P	1.937	4.666	2.444	2.51	2.498	2.079
	$r^2$	0.999	0.996	0.999	0.999	0.999	0.999
	SE	0.0092	0.0203	0.008	0.0084	0.0089	0.007
	Caurie	A	-2.85523	-2.89788	-3.37171	-3.29398	-3.48946
B		3.181676	3.090013	3.522823	3.604396	3.725532	3.671633
P		14.392	9.754	15.668	15.535	15.672	13.209
$r^2$		0.977	0.983	0.982	0.986	0.988	0.991
SE		0.0494	0.0365	0.0355	0.0358	0.0307	0.0227

GAB = Guggenheim–Anderson–De Boer model;  $M_0$  = monolayer moisture;  $r^2$  = regression coefficient; SE, standard error of estimate.

4 show the experimental and calculated equilibrium moisture content at the different process condition that was predicted by the Peleg model. It is apparent in the figures that the predicted data closely banding around the straight line, which indicated the sufficiency of the model, proposed in describing the desorption behavior of quince.

From Table 3, it is obvious that the monolayer moisture content ( $M_0$ ) measure of the desorption possibility for both GAB model decreased with increasing temperature. The temperature dependence of the monolayer value has been linked (Iglesias *et al.* 1975) to the physic–chemical changes induced by temperature in reduced sorption active sites (Iglesias and Chirife 1976; Sopade *et al.* 1996).  $M_0$  should decrease with increasing temperature as the absorbed molecules gain



**FIG. 4.** COMPARISON OF EXPERIMENTAL AND CALCULATED EQUILIBRIUM MOISTURE CONTENT VALUES BY PELEG MODEL

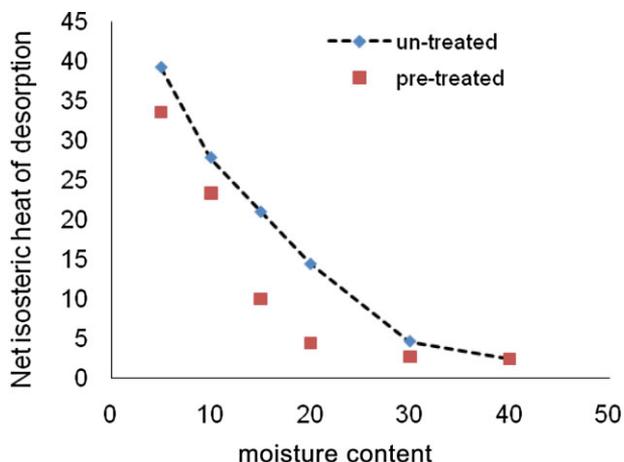


FIG. 5. NET ISOSTERIC HEAT OF DESORPTION OF QUINCE AS A FUNCTION OF MOISTURE CONTENT

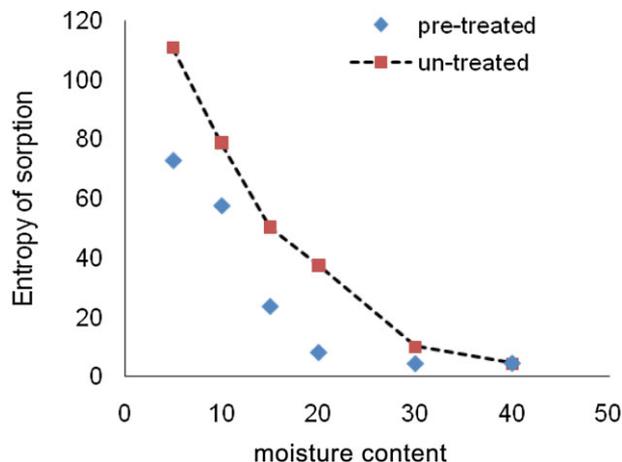


FIG. 6. DIFFERENTIAL ENTROPY OF DESORPTION FOR QUINCE AS A FUNCTION OF MOISTURE CONTENT

kinetic energy (Diosady *et al.* 1996). The samples pretreated have lowered the monolayer moisture ( $M_0$ ) content as compared with the control sample. A similar result was reported by Mazza (1982); that the addition of sugar lowers the  $M_0$  content of potatoes.

### Isosteric Heat of Sorption and Sorption Entropy

Figure 5 shows the net isosteric heat of sorption ( $q_{sn}$ ) values as the function of the equilibrium moisture content for desorption isotherms. As seen from Fig. 5, for both isotherms, the  $q_{sn}$  decreases with increasing moisture content. The decrease of the heats of sorption indicates that the water–solid interactions are strong in the range of low equilibrium moisture

contents and they decrease with the increase in the equilibrium moisture content (Nourh ne *et al.* 2008; Stencl *et al.* 2009). At increasing moisture content, the most active sites become occupied and sorption occurs on the less active site giving lower heats of sorption (Quirijns *et al.* 2005). Untreated samples show the highest heat of sorption at low water content, and this means that the energy required for drying quince to a safe water activity will be higher for untreated samples than for pretreated samples.

Figure 6 shows the differential entropy for quince as functions of moisture content. The results show the strong dependence of differential entropy on moisture content with an exponential trend similar to that of the net isosteric enthalpy. The differential entropy of the untreated samples exhibits a slightly higher magnitude than that for pretreated samples;

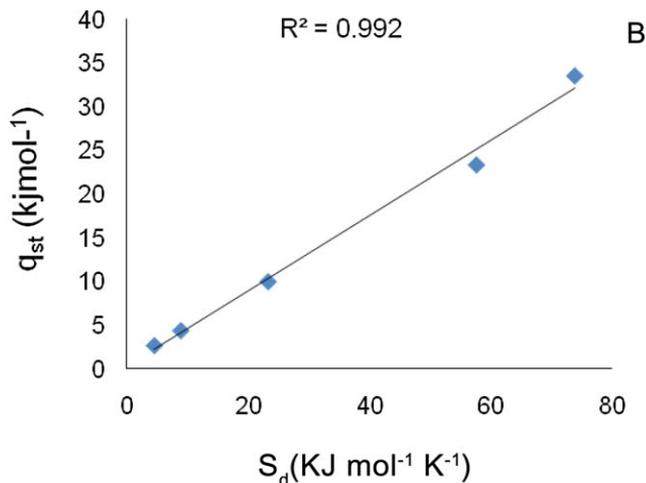
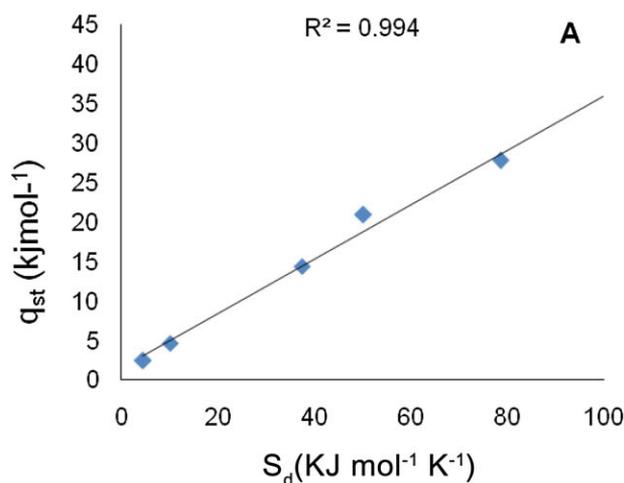


FIG. 7.  $Q_{st}$ – $S_d$  RELATIONSHIP FOR DESORPTION IN UNTREATED (A) AND PRETREATED QUINCES (B)

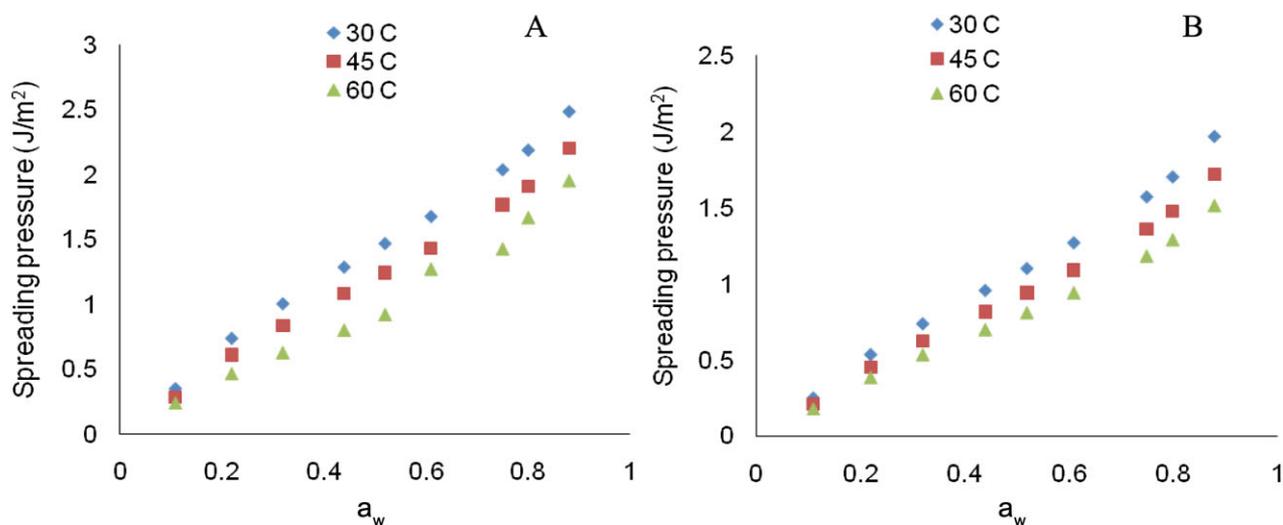


FIG. 8. VARIATION OF SPREADING PRESSURE WITH MOISTURE CONTENT AND TEMPERATURE FOR (A) UNTREATED QUINCE AND (B) PRETREATED QUINCE

however, the difference rapidly decreases to become negligible at high moisture contents. This behavior indicates that water molecules are more mobile during untreated samples than pretreated samples.

### Enthalpy–Entropy Compensation Theory

Plotting differential enthalpy versus differential entropy, a linear correlation is found (Fig. 7). This means that the theory of compensation could be applied in the range of moisture contents studied. The values for the parameters  $T_1$  (Eq. 6) calculated from the data by linear regression for desorption and values of them were determined as 371.1 and 397.5 K for untreated and pretreated samples, respectively. Krug *et al.* (1976) showed that the compensation theory could be confirmed to apply if the calculated  $T_{hm}$  was significantly different from  $T_1$ . The  $T_{hm}$  was calculated by Eq. (7) and the obtained results are  $T_{hm} = 318$  K for untreated and pretreated samples, as these values are significantly different from the value of  $T_1$ , the suitability of the isokinetic theory is confirmed and, additionally, as in all cases of  $T_1 > T_{hm}$ , the processes can be characterized as enthalpy driven.

### Spreading Pressure

The spreading pressures of untreated and pretreated samples at different temperatures were evaluated using Eq. (8). Spreading pressures of quince are plotted in Fig. 8. The results show that the spreading pressure decreased with increasing temperature and increased with increasing water activity (Aviara and Ajibola 2002) for melon seed and cassava. For starch powders, Al-Muhtaseb *et al.* (2004b) noted similar

changes with respect to temperature and water activity. The values of spreading pressures untreated samples are higher than the pretreated sample.

### CONCLUSIONS

It can be concluded from this study that the osmotic-ultrasonic pretreatment decreased the equilibrium moisture content of the product. Desorption isotherms of untreated and pretreated quince were typical type II sigmoid shape. The equilibrium moisture content decreased with increasing temperature at constant water. The Peleg equation was found to be the best model for predicting the moisture sorption data for both fresh and pretreated dried quince slices. The  $Q_{st}$  was high at low moisture contents decreasing with moisture content increases; the differential entropy has an analogous behavior to the isosteric heat. Spreading pressure increases with increasing water activity, and decreases with increasing temperature, the osmotic-ultrasonic pretreatment decreased the value of net isosteric heat, differential entropy and spreading pressure. The plot of isosteric heat versus entropy data satisfies the enthalpy–entropy compensation theory.

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