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ORIGINAL ARTICLE

Moisture Sorption Thermodynamics of *Camellia oleifera*

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Abstract Moisture sorption isotherms of shelled and unshelled *Camellia oleifera* were determined using a gravimetric static method at 20, 30 and 40 °C with water activity ranging from 0.111 to 0.976. Estimated parameters and fitting ability of seven models were evaluated, and the Peleg model provided the best description of the experimental sorption behaviour. The experimental data and the models were also used to obtain thermodynamic functions. The differential enthalpy decreased rapidly as the moisture content increased, when the moisture content exceeded 7 % (dry basis) the value of differential enthalpy tended to zero. The differential entropy showed similar trends. Spreading pressure increased with increasing water activity and decreased with increasing temperature at a given water activity. Net integral enthalpy increased slightly with moisture content to a maximum value, and thereafter decreased with increasing moisture content. However, net integral entropy decreased gradually with increasing moisture content, until reach to a minimum value and then increased slightly with further increases in moisture content.

Keywords *Camellia oleifera* · Moisture sorption · Isotherm · Model · Thermodynamic functions

Notation

T	temperature, °C
a_w	water activity
a_w*	geometric mean water activity (at constant spreading pressure)
C	constant (isotherm model)
K	constant (isotherm model)
K_B	Boltzmann constant (1.380×10^{-23} J K^{-1})
A_m	the area of a water molecule (1.06×10^{-19} m^2)
Δh_d	net isosteric heat of sorption (net differential enthalpy) (kJ mol^{-1})
Δh_{in}	net equilibrium heat of sorption (net integral enthalpy) (kJ mol^{-1})
ΔS_d	net differential entropy (J mol^{-1} K^{-1})
ΔS_{in}	net integral entropy (J mol^{-1} K^{-1})
π	spreading pressure (J m^{-2})
c_1, c_2, c_3	model constants
n_1, n_2	model constants
n	number of experimental data
p	umber of constants in the model
X_{cal}	calculated moisture by model
X_{exp}	experimental moisture content
X_m	monolayer moisture content, g water/g dry solid, GAB constant
EMC	equilibrium moisture content
RMSE	root mean squared error
RSS	residual sum-of-squares
R	universal gas constant (J mol^{-1} K^{-1})
Adj-R^2	adjusted coefficient of determination

Introduction

Camellia oleifera, which originated in China, has a long cultivated and utilized history for over 2,300 years, and is notable as an important source of edible oil obtained from its

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seeds, possessing significant economic and nutritional importance.[38]

Moisture sorption isotherm describes the relationship between equilibrium moisture content and water activity at constant temperature and pressure. Food moisture isotherms and the equations that describe this relationship are important in equipment design for drying, packing and storage, for prediction of shelf-life, and for determination of critical moisture and water activity for acceptability of products that deteriorate mainly by moisture gain.[28,35] EMC (equilibrium moisture content) is defined as the moisture content of a hygroscopic material in equilibrium with a particular environment with respect to temperature and water activity.[35] Numerous correlations have been proposed to present the relationship between EMC and water activity.[31] The models can be divided into several categories: theoretically, for instance, kinetic models based on a mono-layer (BET), kinetic models based on a multi-layer and condensed film (GAB, LewickiI, LewickiII) semi-theoretically (Ferro-Fontan, Halsey), and empirically.[6] Many models are suitable for some particular products only, or for selected ranges of water activity, and parts of these equations reflect the effect of temperature on sorption isotherms. Chirife and Iglesias[9] reviewed some of these models and reported 23 common equations for fitting sorption isotherms to different food material. Some models take into consideration the effect of temperature, among them are the modified Chung-Pfost,[11] modified Henderson,[17] modified Halsay[15] and modified Oswin[27] models. The EMC data are essential for the mathematic prediction of monolayer drying. However, due to the complex composition and structure of foods, mathematical prediction by models has had relative success in representing experimental sorption isotherm data. Attempts to find a general isotherm equation have been unsuccessful, mainly due to that water activity depends on food composition, and the interaction of constituents with water in thermodynamical equilibrium conditions. Thus, it's necessary to assess the applicability of the isotherms equations according to the basic experimental sorption data.[36]

Drying is one of the key operations employed in the post-harvest processing of *Camellia oleifera* seeds to extend the storage stability. Therefore, the design of effective drying and storage systems for the seed requires knowledge of its energy requirements and the mode of moisture sorption within it.[30] The quantity of energy required is influenced by the association pattern of the water molecules to the solid. However, few literatures have been reported on determining the sorption isothems and analyzing the thermodynamic properties of *Camellia oleifera* sorption. Wu et al.[37] determined adsorption isotherms and did some thermodynamics properties analysis (isosteric heat and adsorbing energy) of Camellia oleifera. But they didn't do a further analysis, such as spreading pressure and integral enthalpy and entropy. Therefore, the thermodynamic properties of sorption are necessary to be analysed, such as enthalpy and entropy of sorption which provided valuable information about the strength of binding and other physical properties. The differential enthalpy is an indicator of the state of water adsorbed by the solid particles, which is in reverse a measure of the physical, chemical and microbial stability of biological materials during storing period.[13] The isosteric heat of sorption is defined as the energy required for evaporating the adsorbed water from liquid to gas status at a determined moisture content, and the net isosteric heat (differential enthalpy) of adsorption is calculated by the result of isosteric heat value minus the heat of vaporization of pure water at the system temperature. Differential entropy is proportional to the number of available sorption sites at a specific energy level.[23] The net equilibrium heat of sorption, or integral enthalpy, provides a measure of the strength of moisture binding, and integral entropy describes the degree of disorder and randomness of motion of water molecules.[24] The spreading pressure, or surface potential, represents the surface excess free energy, and provides an indication of the increase in surface tension of bare sorption sites due to absorbed molecules.[14] Fasina et al.[13] and Fasina et al.[14] studied the thermodynamics of moisture sorption in alfalfa pellets, winged bean seed and gari, respectively.

The objectives of this study were to determine the best mathematical model for *Camellia oleifera* seed and then to estimate its thermodynamic functions including differential enthalpy and entropy, spreading pressure, integral enthalpy and entropy.

Materials and Methods

Raw Material

Unshelled and shelled *Camellia oleifera* were supplied by Jinhao Camellia oil Corp., Ltd (Hunan, China). Prior to the beginning of the adsorption process, unshelled and shelled *Camellia oleifera* were respectively dehydrated in two desiccators with silica gel at room temperature for 10 days to obtain initial moisture content of below 3 %.

Sorption Procedure

In the present work, the equilibrium moisture content of adsorption isotherms were determined using the standard gravimetric static method with the temperature ranging from 20 to 40 °C. Triplicate samples of unshelled and shelled *Camellia oleifera* (8±0.1 g and 5±0.1 g, respectively) were weighed in petri-dishes, and then placed in the desiccators with specified relative humidity in a

Table 1 Water activity of oversaturated solutions at different temperatures

Temperature (°C)	Water activity										
	LiCl	CH_3COOK	$MgCl_2$	K_2CO_3	$Mg(NO_3)_2$	KI	NaCl	KBr	KCl	KNO_3	K_2SO_4
20	0.113	0.231	0.331	0.432	0.544	0.699	0.755	0.817	0.86	0.946	0.976
30	0.112	0.216	0.324	0.432	0.514	0.679	0.751	0.803	0.84	0.923	0.970
40	0.111	0.210	0.316	0.410	0.484	0.661	0.747	0.794	0.83	0.891	0.964

temperature-controlled chamber. Eleven oversaturated salt solutions (LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, $Mg(NO_3)_2$, KI, NaCl, KBr, KCl, KNO_3 and K_2SO_4, respectively) were chosen so as to give a a_w range from 0.111 to 0.976 (Table 1). Samples were weighed periodically until the weight variation was less than 0.001 g, which involved a period of approximately 3 weeks for the samples at lower temperature and 15 days for the samples at higher temperatures. Since the equilibrium was reached, the EMC was determined gravimetrically by drying samples in a convection oven at 105±1 °C for 3–4 h.

Isotherm Models

Many models are detailed in the literatures for description of experimental moisture sorption characteristics. For this work, we selected four two-parameter (Halsey, Oswin, Smith, Caurie), two three-parameter (GAB, Ferro-Fotan) and one four-parameter (Peleg) models for fitting the experimental isotherm data of *Camellia oleifera*. These equations are detailed in Table 2.

The experimental data was analyzed through nonlinear regression statistical analyses using Origin 8.0 software (OriginLab Corporation, Northampton, USA) to obtain the parameters of those models. The suitability of fitting models was evaluated through the Adjusted R-Square (Adj-R^2), residual sum-of-squares (RSS) and the root mean squared error (RMSE), which were defined as:

$$RSS = \sum \left(X_{\exp} - X_{cal}\right)^2 \qquad (1)$$

Table 2 Seven models for fitting the experimental sorption data

Model	Equation
GAB	$\mathrm{EMC} = X_m CK a_w / [(1 - K a_w)(1 - c_2 a_w + CK a_w)]$
Henderson	$\mathrm{EMC} = [-\ln(1 - a_w)/c_1]^{1/c}{}_2$
Oswin	$\mathrm{EMC} = c_1[a_w/(1 - a_w)]^{c}{}_2$
Smith	$\mathrm{EMC} = c_1 - c_2 \ln(1 - a_w)$
Caurie	$\mathrm{EMC} = \exp(c_1 + c_2 a_w)$
Peleg	$\mathrm{EMC} = c_1 a_{w1}^{n} + c_2 a_{w2}^{n}$
Ferro-Fotan	$\mathrm{EMC} = [c_1/\ln(c_2 a_w)]^{1/c}{}_3$

where $X_{\exp}$ is the experimental moisture content, X_{cal} is the calculated moisture by models

$$RMSE = \sqrt{\frac{\sum_{i=1}^{n} \left(X_{\exp} - X_{cal}\right)^2}{n - p}} \qquad (2)$$

where n is the number of data points, p is the number of constants in the model

The RSS value is very important in the non-linear regression process, with the fitting procedure being designed to achieve the minimum value.[32] The lower the calculated values of RSS and RMSE are, the better that the ability of the models to represent the experimental data.[8] These statistical parameters have been widely used as the primary criterion to select the best equation.[12,26,32]

Net Isosteric Heat of Sorption and Sorption Entropy

The net isosteric heat, or differential enthalpy (Δh_d), is defined as the isosteric heat of sorption minus the latent heat of vaporization of pure water.[34] The net isosteric heat of sorption gives a measure of the water-solid binding strength. It is evaluated by the Clausius-Clapeyron equation from the best-fitting equation[21]:

$$\left[\frac{d(\ln(a_w))}{d(1/T)}\right]_X = -\frac{\Delta h_d}{R} \qquad (3)$$

where Δh_d is the differential enthalpy, R is the gas constant (universal gas constant J mol^{-1} K^{-1}), T is the temperature.

The value of Δh_d is considered to be invariant with the temperature within small temperature intervals and can be obtained from the slope of the line resulting from plotting ln (a_w) versus 1/T at constant moisture content.

The differential entropy (ΔS_d) is proportional to the number of available sorption sites corresponding to a specific energy level.[23] The relationship between the differential enthalpy and entropy is given by Eq. (4), choosing the pure liquid water as reference system and considering the isothermal transfer of molecules from the liquid to the absorbed state[1]:

$$(-\ln(a_w))X = \frac{\Delta hd}{RT} - \frac{\Delta Sd}{R} \qquad (4)$$

where ΔS_d is the differential entropy.

It is determined from the intercept by plotting $\ln(a_w)$ versus 1/T.

Equilibrium Spreading Pressure

The spreading pressure (π), or surface potential, represents the surface excess free energy, and provides an indication of the increase in surface tension of bare sorption sites due to absorbed molecules.[14] Spreading pressure can be estimated using an analytical procedure described by Fasina et al.[14] from the relationship:

$$\pi = \frac{K_B T}{A_m}\int_0^{a_w}\frac{\theta}{a_w}d(a_w) \tag{5}$$

where the K_B is Boltzmann constant (1.380×10^{-23} J K^{-1}), A_m is the area of a water molecule (1.06×10^{-19} m^2). The moisture ratio θ is given by:

$$\theta = \frac{X_{\exp}}{X_m} \tag{6}$$

Taking into account the formula of the GAB model and substituting θ/a_w, the integral included in Eq. (5) can be developed analytically resulting in the mathematical definition for π (Eq. (7)):

$$\pi = \frac{K_B T}{A_m}\ln\left(\frac{1-Ka_w+KCa_w}{1-Ka_w}\right) \tag{7}$$

where the K and C are the constants of GAB model.

Net Integral Enthalpy and Integral Entropy

The net integral enthalpy (Δh_{in}), or net equilibrium heat of sorption, with moisture content indicates the level to which water-solid interaction is greater than the interaction of water molecules. The integral quantity is calculated in a similar manner to the differential enthalpy of sorption, but at constant spreading pressure instead of constant moisture content[5]:

$$\Delta h_{in} = -R\left[\frac{d\ln(a_w)}{d(1/T)}\right]_\pi \tag{8}$$

The net integral enthalpy of sorption at each spreading pressure is obtained by fitting Eq. (8) to the equilibrium data from the best-fitting equation and then derived from the slope of the line ($-\Delta h_{in}/R$) by plotting the values of $\ln(a_w)$ at constant spread pressure versus 1/T. The integral enthalpy is further used to determine the integral entropy (ΔS_{in}), which describes the degree of disorder and randomness of motion of water molecules, and quantifies the mobility of the adsorbed water molecules.[24] The integral entropy of sorbed water was calculated using [13]:

$$\Delta S_{in} = -(\Delta h_{in}/T) - R\ln(a_w*) \tag{9}$$

where the a_w* is the geometric mean water activity obtained at constant spreading pressure at different temperatures.

Results and Discussion

Experimental Adsorption Isotherms

The experimental and predicted (Peleg model) sorption isotherms obtained for unshelled and shelled *Camellia oleifera* at a_w ranging from 0.111 to 0.976 and temperature ranging from 20 to 40 °C, are shown in Figures 1 and 2, respectively. The EMC at each water activity represents the mean value of three replications. It can be seen from these figures that, the EMC of both unshelled and shelled *Camellia oleifera* increased with increasing water activity, indicating that, the sorption behavior of *Camellia oleifera* can be precisely described by a sigmoid curve, following the form of TypeIIisotherm according to BET classification.[7] The phenomenon that the EMC increased with increase in water activity may be due to the fact that the vapour pressure of water present in foods increases with that of the surroundings. Also we can find from Figures 1 and 2 that the EMC values decreased with increasing temperature at constant water activity, indicating that the Camellia oleifera became less hygroscopic with increasing temperature. This fact was attributed to the activation of the water molecules caused by the increase in temperature, promoting them to break away from the water binding sites. From a practical standpoint this has many implications, for example, at a given moisture content, the increase in water activity with increasing temperature can lead to increase chemical and microbiological reaction rates and thus, enhanced quality degradation.[26] The One-Way analysis of variance (ANOVA) showed that the

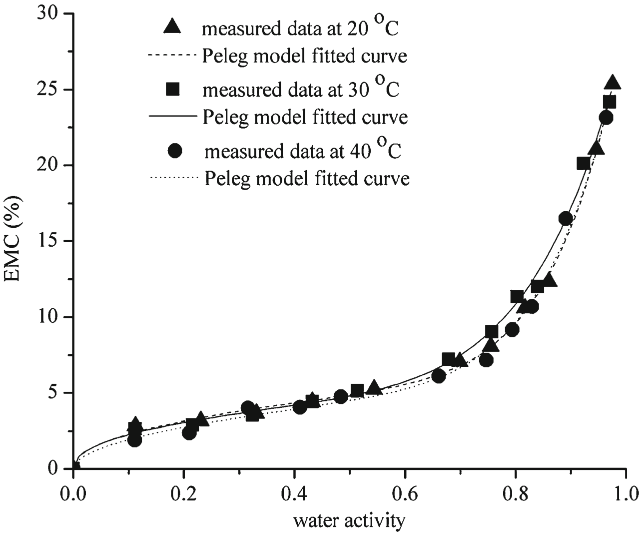

Fig. 1 Sorption isotherms of shelled *Camellia oleifera* at selected temperatures fitted by Peleg model

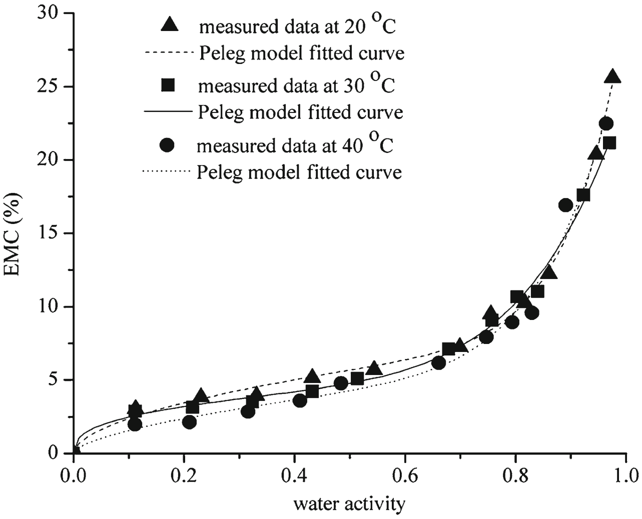

Fig. 2 Sorption isotherms of unshelled *Camellia oleifera* at selected temperatures fitted by Peleg model

effect of temperature in moisture content was insignificantly different (P>0.05) for both shelled and unshelled Camellia oleifera. These were similar with the results of other researchers.[3,10]

In the first segment (with low a_w) of the S-shaped sorption isotherms, *Camellia oleifera* adsorbed relatively lower amount of water, nevertheless, larger amount of water was absorbed at higher water activity. Similar behavior has been reported for walnut kernels.[16] This is probably due to an increase in the number of active sorption sites. According to Van den Berg and Bruin,[35] a general sigmoid sorption isotherm can be divided into three different parts: ranges I (a_w=0–0.22), II(a_w=0.22–0.73) and III(a_w=0.73–1.0). In rangesIIand III, water molecules penetrate newly created pores of the already swollen structure and are mechanically entrapped in the void spaces. Therefore, water uptake particularly at higher water activity would be markedly influenced by the stability of the micro porous structure. By comparing the data in Figures 1 and 2, we found that the EMC of unshelled *Camellia oleifera* was higher than that of shelled *Camellia oleifera* below a_w of 0.755 and the opposite result when a_w was above 0.755. It may be due to the fact that unshelled *Camellia oleifera* has a thick and solid shell which to some extent prevents water penetrating inside the kernel. The One-Way analysis of variance (ANOVA) showed that the difference of moisture content at the same a_w and temperature between shelled and unshelled Camellia oleifera was not significant (P>0.05).

Fitting Sorption Data to Various Isotherm Equations

Seven well-known mathematic models, including GAB, Henderson, Oswin, Peleg, Smith, Caurie and Ferro-Fotton equations, were chosen to correlate the experimental data. The parameters for these models were obtained and listed in Table 3. The RSS, RMSE and Adj-R^2 were used to assess the fitting performance between models and experimental data. The lower calculated value of RSS and RMSE indicate the higher agreement of the model to represent the experimental data. The fit accuracy was measured in terms of the coefficient of determination, R^2, which approaches to 1 to guarantee the goodness of the fit. Among these models, the Peleg model seems to be excellent to represent the experimental sorption data of shelled and unshelled *Camellia oleifera* at the three temperatures throughout the entire a_w range. Among these models, the Peleg model was found to have the lowest RSS (0.8136–3.4695, shelled; 2.0821–9.8146, unshelled), RMSE value (0.0103–0.0226, shelled; 0.0201–0.0351, unshelled) and the highest Adj-R^2 value (0.9921–0.9986, shelled; 0.9815–0.9954, unshelled). The comparisons between the best fitting Peleg model and experimental sorption data of shelled and unshelled *Camellia oleifera* were shown in Figures 1 and 2 respectively. The GAB model was found to be the second best model to represent the sorption data, as GAB model had higher value for Adj-R^2 and lower values for RSS, RMSE. The Caurie model gave the worst description of the data, which owns lower Adj-R^2 value and higher RSS, RMSE values compared with other models. However, there is a little difference between our conclusion with others.[37] They found that Henderson model has the highest R^2 and lowest RMSE value. The explanation maybe that Wu et al.[37] takes the temperature effects into account in the Henderson model, by which mean they choose a modified Henderson model, but we did not work like this.

The monolayer moisture content X_m was recognized as the optimum moisture content for good storage stability.[20] This X_m value is the critical moisture content for *Camellia oleifera* to keep quality as deterioration of foods is very small below X_m. The GAB equation was usually applied to calculate this specific value.[29,33] The X_m values of Camellia oleifera calculated from the GAB model at each temperature are presented in Table 3. In this study, the X_m value was independent of the temperature, which were 2.5992–3.1013 % (shelled) and 2.7278–2.9703 % (unshelled) with the involved temperature range.

Differential Enthalpy and Entropy of Sorption

The differential enthalpy (net isosteric heat of sorption, Δh_d) was determined by applying the Clausius-Clapeyron equation (Eq. (3)) to the experimental adsorption data. The values of net isosteric heat of sorption were obtained from the slopes of $\ln(a_w)$ vs. 1/T plots by linear regression analysis, with the assumption that they are invariant with temperature at a specific moisture content.[1] As shown in

Table 3 Estimated parameters of models for the sorption isotherms of shelled and unshelled *Camellia oleifera* at different temperatures

Model	Parameter	20°C		30°C		40°C	
		Shelled	Unshelled	Shelled	Unshelled	Shelled	Unshelled
GAB	X_m(%)	2.5992	2.9065	3.1013	2.9703	2.6532	2.7278
	c_1	172.24	241.57	14.155	28.639	17.838	8.9831
	c_2	0.9213	0.8964	0.9037	0.8902	0.9212	0.9159
	RSS	12.745	20.024	5.1037	2.6004	6.8844	10.262
	RMSE	0.0160	0.0229	0.0293	0.0179	0.0401	0.0941
	R^2	0.9978	0.9964	0.9905	0.9935	0.9844	0.9765
Henderson	c_1	0.1623	0.1337	0.1343	0.1086	0.1796	0.1862
	c_2	1.0318	0.9662	0.9815	0.8800	1.0722	1.0805
	RSS	9.7692	9.7128	12.173	8.6778	15.595	15.085
	RMSE	0.0316	0.0284	0.0248	0.0307	0.0364	0.0372
	R^2	0.9769	0.9771	0.9774	0.9783	0.9647	0.9655
Caurie	c_1	−0.9300	−0.5475	−0.5257	−0.1904	−0.8941	−0.9400
	c_2	4.1908	3.7707	3.7757	3.2778	4.1167	4.1499
	RSS	31.665	40.8697	20.147	15.5012	27.414	23.691
	RMSE	0.1243	0.4334	0.0304	0.0597	0.0422	0.0451
	R^2	0.9461	0.9269	0.9626	0.9612	0.9380	0.9458
Peleg	c_1	23.001	21.9610	22.436	18.6123	23.041	22.039
	n_1	8.3076	9.9073	6.5092	5.9553	7.7687	7.5349
	c_2	6.6274	8.2191	6.1861	5.7826	6.2774	6.3384
	n_2	0.4609	0.5400	0.4382	0.3672	0.5132	0.6078
	RSS	0.8136	2.5916	2.5456	2.0821	3.4695	9.8146
	RMSE	0.0103	0.0202	0.0191	0.0201	0.0226	0.0351
	R^2	0.9986	0.9954	0.9953	0.9948	0.9921	0.9815
Oswin	c_1	5.4366	5.7628	5.8145	5.6917	5.0380	4.9033
	c_2	0.4293	0.4108	0.4285	0.3951	0.4738	0.4767
	RSS	10.221	5.4581	16.602	10.443	11.489	15.837
	RMSE	0.0211	0.0149	0.0278	0.0236	0.0278	0.0423
	R^2	0.9826	0.9902	0.9692	0.9739	0.9740	0.9638
Smith	c_1	0.4616	0.9125	0.5492	1.0565	0.2330	0.0648
	c_2	6.5226	6.3638	6.7955	5.8615	6.5575	6.5242
	RSS	12.705	11.987	10.711	6.4458	16.338	16.340
	RMSE	0.0693	0.0584	0.0393	0.0352	0.0387	0.0407
	R2	0.9784	0.9786	0.9802	0.9839	0.9630	0.9626
Ferro-Fontan	c_1	1.6721	1.7305	1.7775	1.8725	1.6845	1.6731
	c_2	1.1172	1.1308	1.1391	1.1743	1.1130	1.1141
	c_3	0.4882	0.4707	0.4500	0.4615	0.5031	0.5068
	RSS	6.3907	11.863	5.4481	4.3841	8.8356	10.240
	RMSE	0.0124	0.0186	0.0141	0.0177	0.0166	0.0184
	R^2	0.9891	0.9788	0.9899	0.9890	0.9800	0.9766

Figure 3, the net isosteric heat has a strong dependence on moisture content, which indicated that the value of the energy required for sorption decreased with increasing moisture content. This reflects the water binding strength: initial occupation of highly active polar sites on the surface (with the strongest interactive energy), followed by the progressive filling of the less available sites with lower bonding activation energies.[34] The magnitude of Δh_d, however, indicated that the binding energy between water molecules and sorption sites located at the solid surface was greater than the energy holding the water molecules in the liquid phase. Values of the isosteric heat of sorption at a specific moisture content provide an indication of the state of the adsorbed water and hence, a measure of the physical, chemical and microbiologic stability of the food material under given storage conditions.

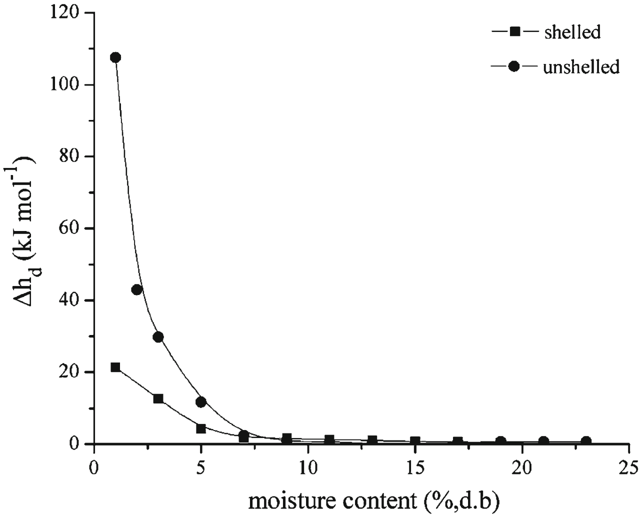

Fig. 3 Differential enthalpy of sorption at different moisture contents for different *Camellia oleifera* forms

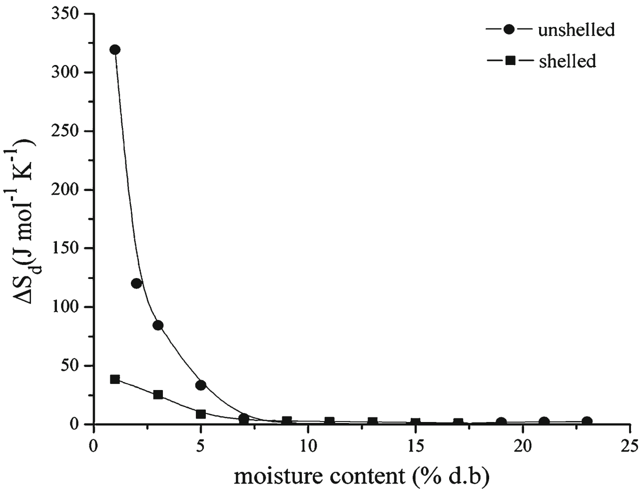

Fig. 4 Differential entropy of sorption at different moisture contents for different *Camellia oleifera* forms

The net isosteric heat of sorption of shelled and unshelled *Camellia oleifera*, at a specific moisture content (1 %), were comparative, with values of 21.37 and 107.59 kJ mol^{-1}, respectively. Irrespective of the moisture content, unshelled *Camellia oleifera* exhibited a dramatically higher net isosteric heat of sorption than that of the shelled ones, with this being particularly evident at moisture content less than 7 %. It may be attributed to the fact that the presence of shell may have a blocking effect of heat and mass transfer. The values of both decreased closely to zero at higher moisture contents (>7 %), indicating that the moisture molecules laid on the solid surface tend to exist in the free form.

The differential entropy of sorption is was obtained from the Y-axis intercept at $1/T=0$ ($\Delta S_d/R$) by plotting the $\ln(a_w)$ vs. $1/T$ as it was previously explained (Eq. (4)). The results of these calculations are shown in Figure 4 and represent mean values of ΔS_d for the temperature interval studied. Once again the differential entropy data displayed a strong dependence on moisture content. It decreased sharply with increasing moisture content below 7 %, and then keeps nearly zero from 7 % on. Unshelled *Camellia oleifera* exhibited higher differential entropy than that of the shelled ones, irrespective of moisture content, with this being particularly evident at moisture contents less than 7 %.

Equilibrium Spreading Pressure Curves

The equilibrium spreading pressures of *Camellia oleifera* at different temperatures, evaluated using Eqs. (5)–(7), are presented in Figure 5. As observed, the spreading pressure increases with increasing water activity and decreases with increasing temperature at a given water activity. The spread pressure increases more smoothly than the corresponding isotherms in terms of moisture content. The sinusoidal behaviour of the isotherm tends to disappear: at higher temperatures (i.e. T=40 °C) π may be considered to have a linear dependence versus a_w. The values of spreading pressure and trends with respect to water activity and temperature are comparable to those reported for alfalfa pellets and winged bean, and gari,[13] cowpea,[2] and two-phase SOB.[22] Once again, the values of π of unshelled *Camellia oleifera* were higher than corresponding values of shelled ones. These curves were employed for computing the integral enthalpy and entropy involved in the moisture adsorption on *Camellia oleifera*.

Net Integral Enthalpy and Entropy

If the differential thermodynamic parameters facilitate a qualitative comprehension of the water adsorption on

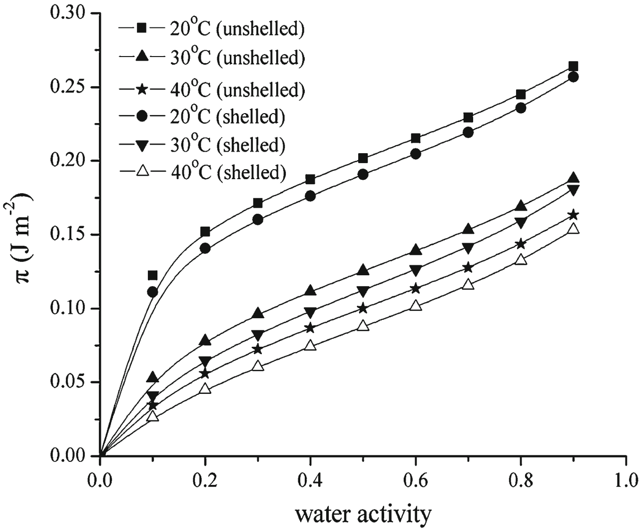

Fig. 5 Spreading pressure isotherms versus a_w for different *Camellia oleifera* forms

Camellia oleifera, the integral ones provide valuable quantitative information about the system. For example, the value of integral enthalpy can provides an Information for the theoretical minimum amount of energy required to remove a given quantity of water from food, and also provides insight into the microstructure associated with the food as well as the theoretical interpretation of physical phenomena occurring at the food –water interface[30]. The values of net integral enthalpy for water adsorption on *Camellia oleifera* were obtained following the procedure already described, using the spreading pressure curves and Eq. (8). The results are shown in Figure 6. It was clearly observed that the curves of net integral enthalpy show two different linear intervals characterized by different slopes: the greater the slope, the more intense the water molecules binding to the solid is, indicating of two kinds of water molecules binding to the solid surface. Thus, two kinds of water molecules in *Camellia oleifera* under equilibrium conditions can be considered: the molecules belonging to the monolayer directly joined to the solid surface, and those present in the multilayer.[22] The net integral enthalpy increases to a maximum value (69.66 and 82.98 kJ mol^{-1} for shelled and unshelled *Camellia oleifera*, respectively), which occurred around the monolayer moisture content, and then decreases with increasing moisture content. This can be explained: more accessible sites on the surface are firstly occupied during adsorption, followed by the high-energy sites (but less accessible) on the surface until the monolayer is completely covered with high binding energy. And then, the molecules disposal on multilayer takes place, what means the integral enthalpy would be mainly given by the free water contribution so the dynamical properties of the water adsorbed to the solid are equal to the pure water. Hence, it can be extrapolated that the curve would tend to constant value (the slope would be 0). The same trend is observed by other authors, such as McMinn & Magee for potato,[25] Durakova & Menkov for chickpea flour,[12] and Liébanes et al. for two-phase SOB.[22] It can be also found that the net integral enthalpy values of unshelled *Camellia oleifera* were greater than those of shelled at a specific moisture content.

The net integral enthalpy represents the additional energy that required for drying *Camellia oleifera* with respect to the evaporation of pure water. This quantity of evaporating energy depends on the dryness degree to be reached during the drying procedure: the lower the final moisture content (>Xm), the more energy is required, affecting substantially to the energetically balance of the system and drying effectiveness. For calculating the total energy required to remove the water from the solid surface, the corresponding evaporation enthalpy of pure water must be summed up, since only net values are presented here.

On the other hand, the variation in net integral entropy with the moisture content for *Camellia oleifera* is shown in Figure 7. The net integral entropy of water adsorption decreases gradually with increasing moisture content to a minimum value around the monolayer moisture content, and then increases with further increasing moisture content. The minimum net integral entropy of adsorption (−217.13 and −257.12 Jmol^{-1} K^{-1}) are observed at the moisture content of 3.90 % and 2.92 % for shelled and unshelled *Camellia oleifera* respectively. The initial decrease in the net integral entropy indicates the loss of rotational freedom or degree of randomness of the water molecules as the readily available sites become saturated and the strongest binding sites are occupied. The subsequent increase shows the appearance of more freely held water molecules and the formation of multilayers[16]. In all cases the net integral entropy of absorbed water is negative in magnitude. Iglesias & Chirife[18,19] explained that this behaviour might be attributed

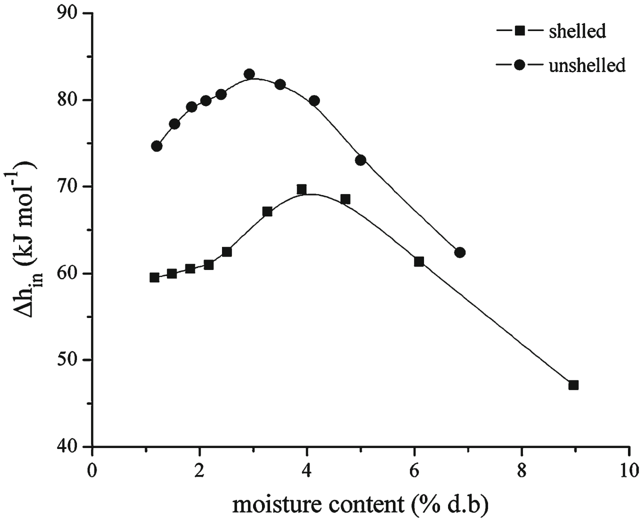

Fig. 6 Net integral enthalpy of sorption at different moisture contents for different *Camellia oleifera* forms

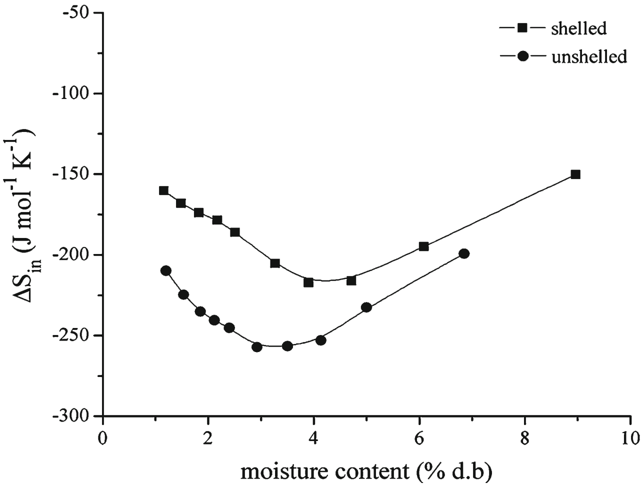

Fig. 7 Net integral entropy of sorption at different moisture contents for different *Camellia oleifera* forms

to the existence of chemical adsorption or structural modifications of the adsorbent. Similar trends have been reported for sugar beet root[18,19], winged bean seed,[14] walnut kernels[16] and sesame seed.[4]

Conclusions

The moisture sorption isotherms of *Camellia oleifera* (shelled and unshelled) at three temperatures were determined. *Camellia oleifera* presents TypeIIisotherms. Water sorption isotherms were slightly dependent on temperature. Equilibrium moisture content decreased with increasing temperature at a given water activity and increased with increasing water activity at a given temperature. The Peleg model was found to be the most appropriate equation for representing *Camellia oleifera* sorption isotherms. The differential enthalpy of sorption decreased with increasing moisture content and tended towards zero at a moisture content above 7 %. The differential entropy showed a same behaviour. The values of differential enthalpy and entropy for unshelled *Camellia oleifera* are higher than shelled ones. Spreading pressure increased with increasing water activity, and decreased with increasing temperature. Net integral enthalpy of sorption increased slightly with moisture content to a maximum value (69.66 and 82.98 kJ mol^{-1} for shelled and unshelled *Camellia oleifera*, respectively) around the monolayer moisture content, and then decreased with increasing moisture content. The net integral entropy of adsorption decreased gradually with increasing moisture content to a minimum value (−217.13 and −257.12 J mol^{-1} K^{-1} for shelled and unshelled *Camellia oleifera*, respectively) around the monolayer moisture content, and then increased with further increase in moisture content, reflecting transition from occupation of easily accessible sites to increased localized binding, followed by formation of mobile multilayers.

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