Sorption isotherms and thermodynamic properties of peppermint tea (*Mentha piperita*) after thermal and biochemical treatment

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Abstract
Moisture sorption isotherms of peppermint tea treated by thermal and biochemical process were determined at 30, 40 and 50°C using the static gravimetric method. GAB model found to be the most suitable model for describing the sorption curves among three well-known tested equations. Thermodynamic properties such as differential enthalpy and entropy of sorption were determined from moisture adsorption and desorption data, using the Clausius-Clapeyron equation. The experimental data showed that enthalpy-entropy compensation theory was applicable to the moisture sorption behaviour of peppermint tea.
Key-Words: peppermint, sorption isotherm, thermodynamic properties

1 Introduction

Mentha piperita Lin (Lamiaceae), commonly called peppermint, is a well-know herbal remedy used for a variety of symptoms and diseases [1]. In the popular medicine, it is used to treat nausea, flatulence, vomiting and indigestion [2]. However, plant materials are highly susceptible to microbial contamination [3] due to the medium (water and soil) in which they grow. The decontamination of plant materials is then vital to make them suitable for human consumption and commercialization. Studies should be performed on peppermint tea in order to define theirs longevity after thermal and biochemical process for decontamination [4]. Consequently knowledge of water sorption isotherms of peppermint tea is necessary. The degree to which water is bound is described by the water activity (a_w). The equilibrium moisture content and the water activity at given temperature and pressure related by the sorption isotherm. Desorption and adsorption isotherms could be established, respectively by dehydration or rehydration of the product at fixed conditions of relative humidity and temperature. Moisture sorption isotherm is an extremely valuable tool for food storage because it can be used to predict potential changes in food stability [5].

Further analysis of sorption isotherms data by application of thermodynamic principals can provide important information regarding microstructure and physical phenomena on the food surface, water properties and sorption kinetic parameters [6].

Numerous mathematical equations that describe water sorption of food materials can be found in literatures. Each of the models proposed, empirical, semi-empirical or theoretical, has had some success in reproducing equilibrium moisture content data of a given type of food and in given range of water activity [7]. The GAB models represents a kinetic model based on multi-layer and condensation, and has been successfully applied to various products [8]. Thermodynamic functions calculated from sorption isotherms allow the interpretation of experimental results in accordance with the statement of the theory. These functions include differential enthalpy and differential entropy [9]. The isosteric heat of sorption or differential enthalpy of sorption, gives a measure of the water-solid binding strength. A rapid computational procedure, commonly used for its determination, is the application of the Clausius-Clapeyron equation to the sorption isotherms, at constant moisture content [10]. The differential entropy of material is proportional to the number of its available sorption sites at a specific energy level [11]. Physical phenomena, such as sorption reactions, are often evaluated on the basis of the enthalpy-entropy compensation theory. This states that compensation arises due to changes in the solvent-solute interaction and that a linear relation exists between the enthalpy and entropy of the reaction [12].

The objectives of the present study are to:

- Experimentally investigate the adsorption and desorption isotherms of peppermint tea in the temperature range from 30 to 50°C after thermal and biochemical process for conservation [4];
- Describe the experimental data using selected mathematical models;
- Determine the thermodynamic functions (differential enthalpy, differential entropy);
- Evaluate the application of the enthalpy-entropy compensation theory.

2. Materials and methods

2.1 Raw material

The Sun-dried specimens of peppermint (*Mentha piperita*) were obtained from "Société Impériale des Thés et Infusions" (Marrakesh, Morocco) and used without any sorting or cleaning treatment (figure 1).

Dried peppermint   Fresh peppermint

Figure 1. Dried and fresh peppermint

The adsorption and desorption isotherms were determined by the standard static gravimetric method (figure 2).This method is based on the use of saturated salt solutions to maintain a fixed water activity. The salts used were KOH, ($MgCl_2$, $6H_2O$), K_2CO_3, $NaNO_3$, KCL, and ($BaCL_2$, $2H_2O$). These salts have a range of water activities from 0.05 to 0.9, as given in Table 1 [13].

Table 1. Water activities of the saturated salt solution at three temperature used in the sorption experiments (Greenspan, 1977)

	KOH	MgCl$_2$, 6H$_2$O	K$_2$CO$_3$	NaNO$_3$	KCl	BaCl$_2$, 2H$_2$O
30°C	0.738	0.3238	0.4317	0.7275	0.8362	0.8980
40°C	0.626	0.3159	0.4230	0.7100	0.8232	0.8910
50°C	0.572	0.3054	0.4091	0.6904	0.8120	0.8823

The experimental apparatus is shown in figure 1. It consists of six glass jars of 1L each with an insulated lid. Each glass jar contains a different salt solution with water activities that vary from 0.05 to 0.9, and they

are immersed in a thermostated water bath adjusted to a fixed temperature for 24h to bring the salt solutions to a stable temperature. Duplicate samples each of 0.2 ± 0.001g for desorption and adsorption were weighed and placed in the glass jars. The weight recording period was about 2 days. This procedure was continued until the weight became constant. The equilibrium moisture content was determined by a drying oven whose temperature was fixed at 105 °C (± 0.1°C). The time required for equilibrium was 10 days for desorption and 13 days for adsorption.
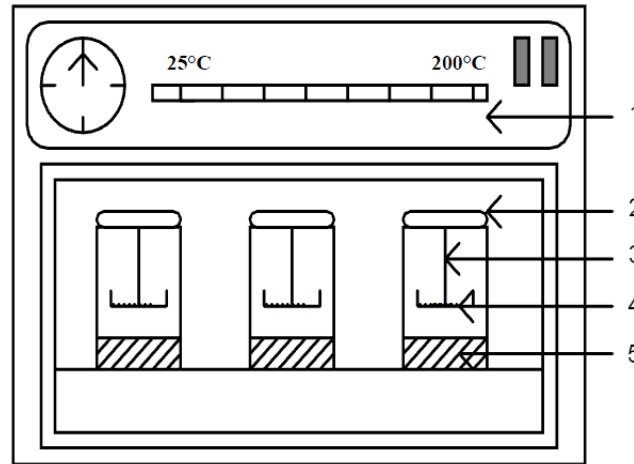
Figure 2. Experimental apparatus for the sorption isotherms measurement : (1) thermostated bath; (2) glass jar containing salt solution; (3) sample holder; (4) product; (5) saturated salt solution

2.2. Modelling equations
Experimental moisture sorption data can be described by many sorption models. Three isotherm equations were chosen to fit experimental sorption data, the selected equations are detailed in Table 2.

Table2. Mathematical equation used to describe the sorption isotherms

Model	Equation	Reference
GAB	$X_{eq} = \dfrac{ABCa_w}{[1-Ba_w][1-Ba_w+BCa_w]}$	[29]
LESPAM	$X_{eq} = A.\exp\left(\dfrac{B.a_w}{\theta}\right) + C$	[20]
Modified Oswin	$X_{eq} = (A+B\theta)\left[\dfrac{a_w}{1-a_w}\right]^C$	[30]

Nonlinear regression analysis was used to estimate the model's constants from the experimental data of sorption isotherms for all samples. The suitability of the equations has been evaluated and compared between them using the correlation r, and the mean relative error MRE (%) [14] [15]. These statistical parameters are defined as follows:

$$r = \sqrt{\frac{\sum_{i=1}^{N}\left(X_{eq_{i,pred}} - \overline{X_{eq}}_{i,exp}\right)^2}{\sum_{i=1}^{N}\left(X_{eq_{i,exp}} - \overline{X_{eq}}_{i,exp}\right)^2}} \qquad MRE = \frac{100}{N}\sum_{i=1}^{N}\left|\frac{X_{eq_{i,exp}} - X_{eq_{i,pred}}}{X_{eq_{i,exp}}}\right|$$

2.3. Isosteric heat of sorption

The isosteric (differential) heat of sorption, or differential enthalpy, is an indicator of the state of water absorbed by the solid material. The net isosteric heat of sorption $\left(\Delta h_d\right)$ is the amount of energy above the heat of vaporization of water $\left(\Delta H_{vap}\right)$ associated with the sorption process, and was calculated from the experimental data using the Clausius-Clapeyron equation [16]:

$$\left[\frac{d\left(\ln a_w\right)}{d\left(\dfrac{1}{T}\right)}\right]_{X_{eq}} = \frac{-\Delta h_d}{R} \tag{1}$$

$$\Delta h_d = \Delta H_d - \Delta H_{vap}$$

It is a differential quantity, the value of which corresponds to sorbed molecules at a particular equilibrium moisture content (X_{eq}).

Re-plotting the experimental sorption isotherm in the form $\ln(a_w)$ versus $\dfrac{1}{T}$, for specific moisture content, Δh_d was determined from the slope $\left(\dfrac{-\Delta h_d}{R}\right)$. This procedure is based on the assumption that ΔH_d is invariant with temperature and requires measurement of the sorption isotherms at more than two temperatures [17] [16].

2.4. Enthalpy-Entropy Compensation Theory

The relationship between the net isosteric heat (Δh_d) and the differential entropy $\left(\Delta S_d\right)$ of sorption is given by:

$$\left(-\ln a_w\right)_{Xeq} = \frac{\Delta h_d}{RT} - \frac{\Delta S_d}{R} \tag{2}$$

By plotting $\ln(a_w)$ versus $\dfrac{1}{T}$, for given moisture content (X_{eq}), Δh_d was determined from the slope $\left(\dfrac{-\Delta h_d}{R}\right)$, and ΔS_d from the intercept $\left(\dfrac{\Delta S_d}{R}\right)$. Applying this at different moisture contents allowed the dependence of Δh_d and ΔS_d with moisture to be determined [18].

The compensation theory proposes a linear relationship between Δh_d and ΔS_d :

$$\Delta h_d = T_\beta . \Delta S_d + \Delta G_\beta \tag{3}$$

The isokinetic temperature (T_β) and constant (ΔG_β) were calculated using linear regression.

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3. Results and discussion

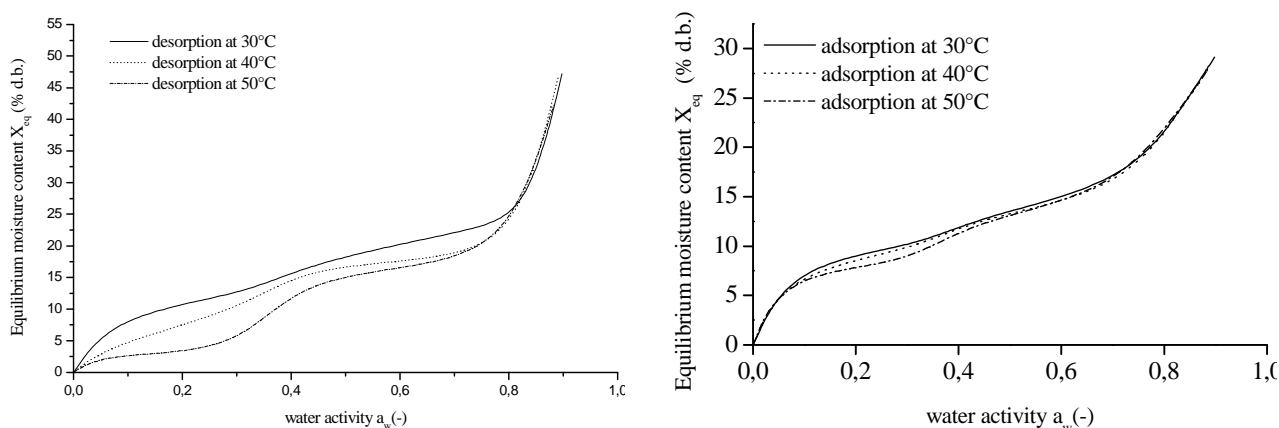*3.1. Adsorption and desorption isotherms*

The experimental results for the equilibrium moisture contents of untreated and treated peppermint tea by a thermal and biochemical process at six water activities for three different temperatures are given in tables 3 and 4.

Table 3. Adsorption and desorption equilibrium moisture contents of peppermint tea obtained at different water activities and temperatures

| Isotherm at 30°C			Isotherm at 40°C			Isotherm at 50°C		
a_w	X_{eq} (% d.b.)		a_w	X_{eq} (% d.b.)		a_w	X_{eq} (% d.b.)	
	des	ads		des	ads		des	ads
0.0738	9.1000	8.1440	0.0626	4.2857	7.3333	0.0572	3.0159	7.2423
0.3238	12.5000	10.0559	0.3159	10.1235	9.6196	0.3054	3.0769	8.1667
0.4317	17.3239	12.8635	0.4230	16.9231	12.6630	0.4091	15.1515	12.2652
0.7275	22.4242	16.3515	0.7100	17.7374	15.4595	0.6904	16.7916	15.2632
0.8362	25.0000	24.0901	0.8232	23.5202	22.9947	0.8120	23.0012	22.5131
0.8980	47.2308	29.1545	0.8910	46.7213	28.3957	0.8823	42.2764	27.6596

Table 4. Adsorption and desorption equilibrium moisture contents of peppermint tea treated obtained at different water activities and temperatures

| Isotherm at 30°C			Isotherm at 40°C			Isotherm at 50°C		
a_w	X_{eq} (% d.b)		a_w	X_{eq} (% d.b)		a_w	X_{eq} (% d.b)	
	des	ads		des	ads		des	ads
0.0738	9.1000	4.5072	0.0626	4.2857	3.4311	0.0572	3.0159	1.4131
0.3238	12.5000	5.8827	0.3159	10.1235	4.4682	0.3054	3.0769	2.5471
0.4317	17.3239	8.6379	0.4230	16.9231	8.2008	0.4091	15.1515	7.709
0.7275	22.4242	13.6842	0.7100	17.7374	12.6222	0.6904	16.7916	11.5752
0.8362	25.0000	24.8889	0.8232	23.5202	23.7564	0.8120	23.0012	19.7742
0.8980	47.2308	28.3867	0.8910	46.7213	26.7885	0.8823	42.2764	25.4202

Figure 3. Sorption isotherms of untreated peppermint tea at 30°, 40° and 50°C

Equilibrium moisture content data obtained for peppermint tea at different water activities and temperatures are plotted in figure 4 .The influence of temperature on the desorption and adsorption isotherms for the full range of water activities can be observed. As can be seen, moisture contents decrease when the temperature increases at constant water activity. This behaviour is typical for many products [19] [20] [21] [22] [23].
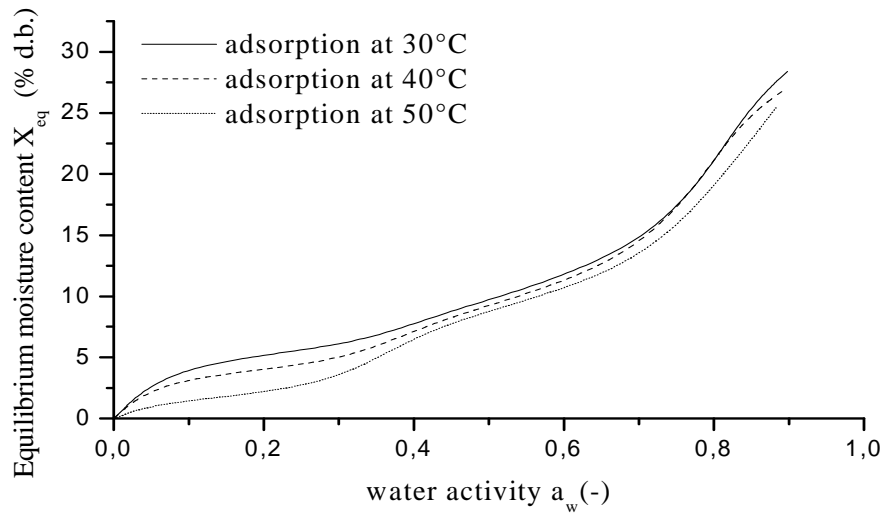
Figure 4. Adsorption isotherms of treated peppermint tea at 30°, 40° and 50°C

The hysteresis effect was observed. Several hypotheses have been put forward to explain hysteresis (Figure 5).
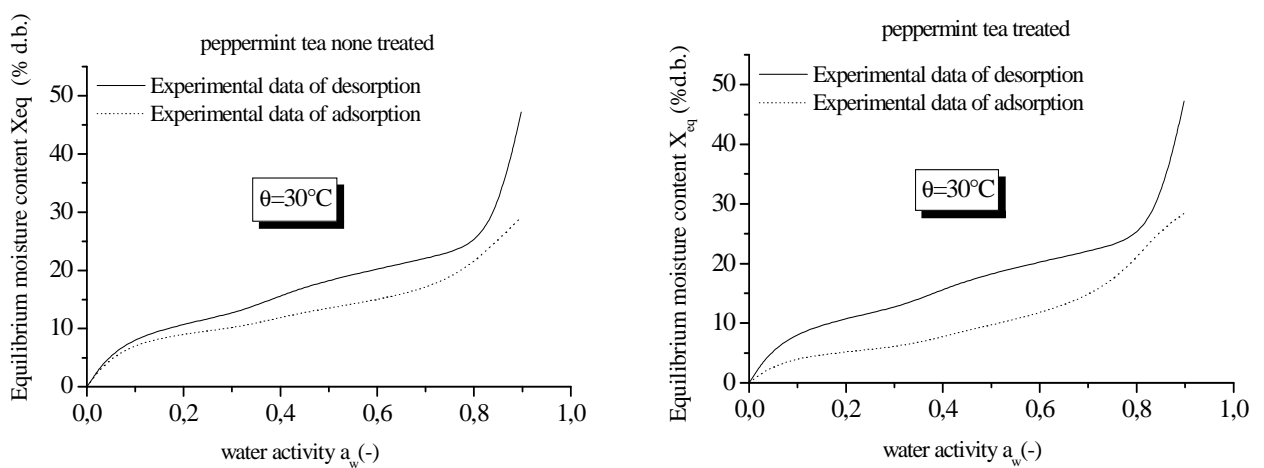
Figure 5. Sorption hysteresis phenomenon of peppermint tea untreated and treated

3.2. Fitting of sorption models to experimental data:

The experimental data of the adsorption and desorption curves of peppermint tea non treated and treated were fitted to three sorption models (Tables 5 to 7). The results reveal the temperature dependence for the sorption behaviour, with an increase in temperature decreasing the sorption capacity. Activation of the water molecules due to the increase in temperature causes them to break away from water binding sites, thus lowering the equilibrium moisture content [22].

The moisture content models were compared according to their correlation coefficient (r), mean relative error (MRE). The isotherms have a sigmoid shape (type II according to the BET classification), which is common for many hygroscopic products. GAB equation gave a satisfactory prediction of the adsorption and desorption equilibrium moisture content of all samples.

The sorption relationships detailed in Table 2 were fitted to the experimental data for two samples. The results of nonlinear regression analysis of fitting the sorption equations to the experimental data are shown in Tables 5 to 7.

Table 5. Results of fitting of adsorption isotherms of untreated peppermint tea

| Model	GAB			Modified OSWIN			LESPAM		
θ (°C)	30	40	50	30	40	50	30	40	50
A	7.2431	6.9961	6.7553	8.7975	-12.838	-17.993	0.2307	0.3164	0.5311
B	0.8330	0.8424	0.8561	0.1632	0.6544	0.6201	149.266	186.1152	206.5667
C	3.4510^{10}	1.6910^{11}	5.9710^{10}	0.3323	0.3427	0.3607	8.9433	8.2047	7.156
r	0.9898	0.9891	0.9906	0.9798	0.9795	0.9776	0.9902	0.9871	0.9888
MRE	1.5230	1.5462	1.4347	2.134	2.1079	2.2024	1.4884	1.6744	1.5618

Table 6. Estimated model coefficients, r, EMR of three equation model fitted to desorption isotherm of fresh peppermint tea

Model	GAB			Modified OSWIN			LESPAM		
θ (°C)	30	40	50	30	40	50	30	40	50
A	7.6288	5.4176	4.8071	-9.775	-17.89	-19.22	0.002571	0.03833	0.403
B	0.9168	0.9865	1.0020	0.8717	0.7727	0.5952	315.2128	308.3612	254.8281
C	9.78610	3.3702	1.5908	0.4257	0.5529	0.657	13.1428	7.0812	3.2457
r	0.9435	0.9540	0.9627	0.9317	0.9544	0.9663	0.9580	0.9348	0.9488
MRE	5.8161	5.7036	5.1026	0.3830	5.7353	4.6789	5.0394	6.8230	5.7415

Table 7. Results of fitting of adsorption isotherms of treated peppermint tea

Model	GAB			Modified OSWIN			LESPAM		
θ (°C)	30	40	50	30	40	50	30	40	50
A	5.1570	5.2835	5.0806	-5.641	-14.9939	-20.7285	1.2515	0.6772	0.9812
B	0.9194	0.9136	0.8977	0.5119	0.6001	0.5054	102.76	161.659	182.20
C	43.1179	12.7205	2.9658	0.506	0.5392	0.614	1.3753	2.7698	0.7312
r	0.9905	0.9818	0.9906	0.9829	0.9802	0.9897	0.9829	0.9868	0.9887
MRE	1.7972	2.4325	1.6863	2.9377	2.5335	1.7668	2.4110	2.0744	1.8515

The representation of these results is shown in figures 6, 7 and 8, which it can be noted that the predicted curve by GAB's model and the experimental data have practically the same rate.
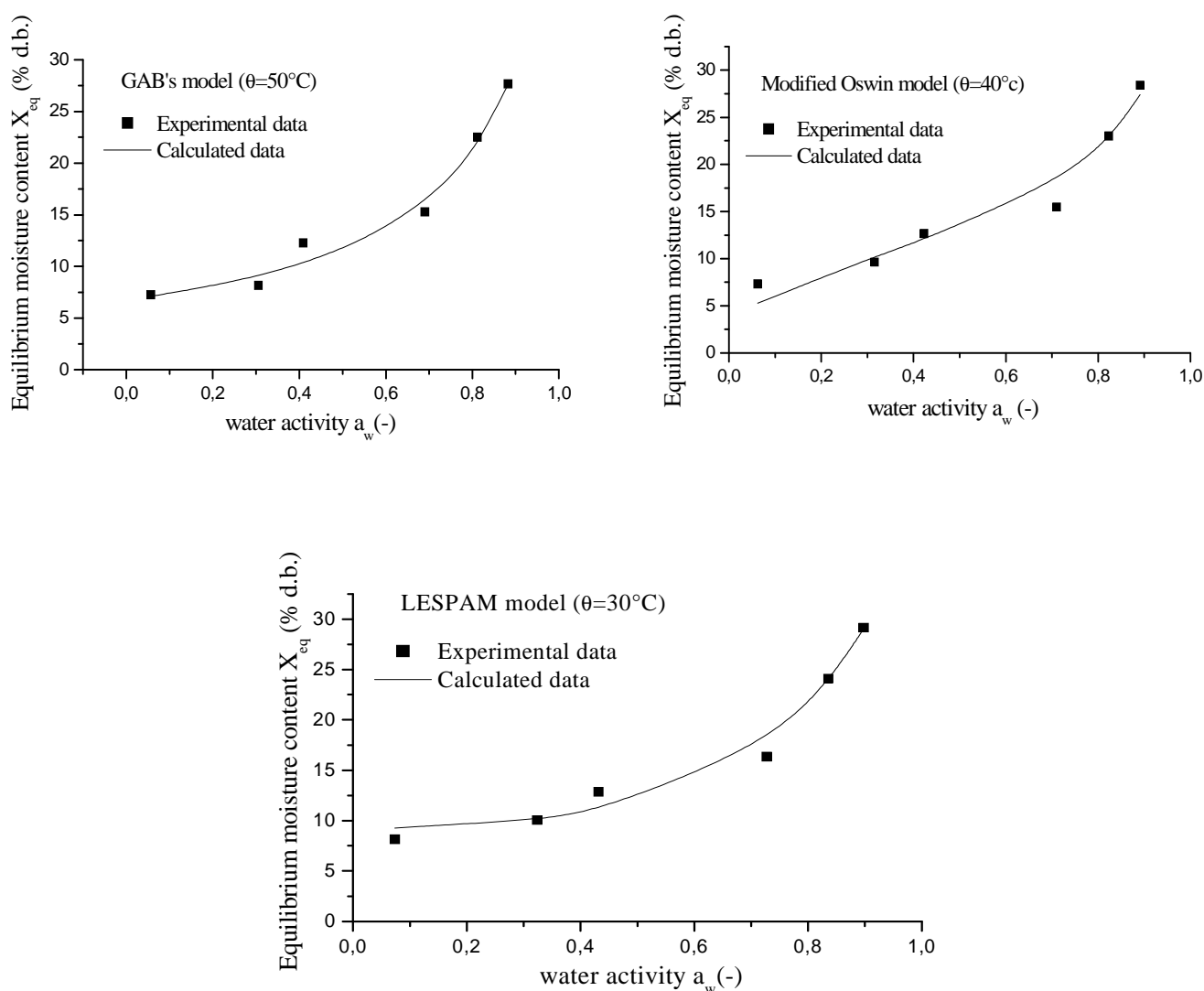
Figure 6. Comparison of experimental and predicted adsorption equilibrium moisture of untreated peppermint tea fitted by three models
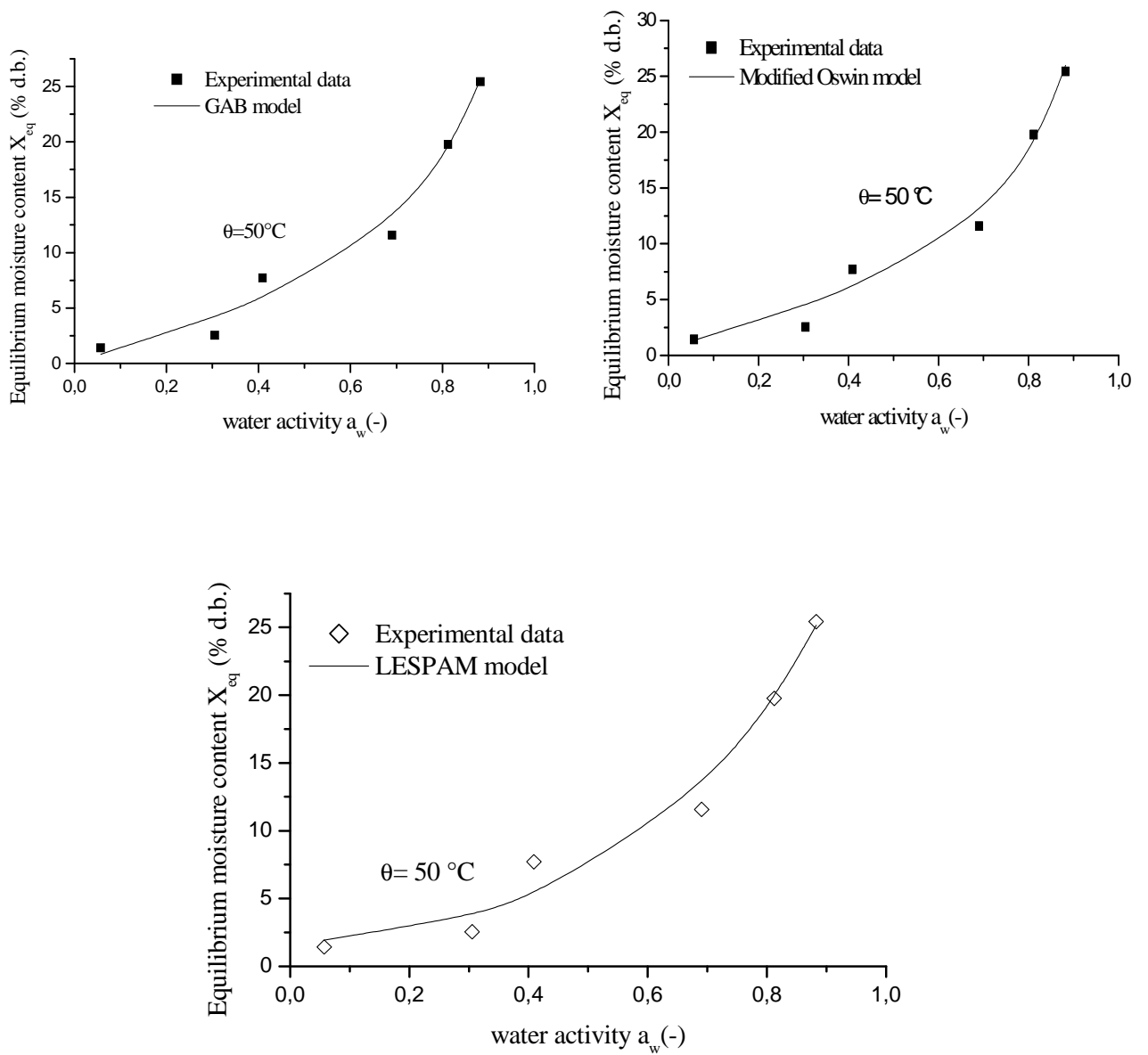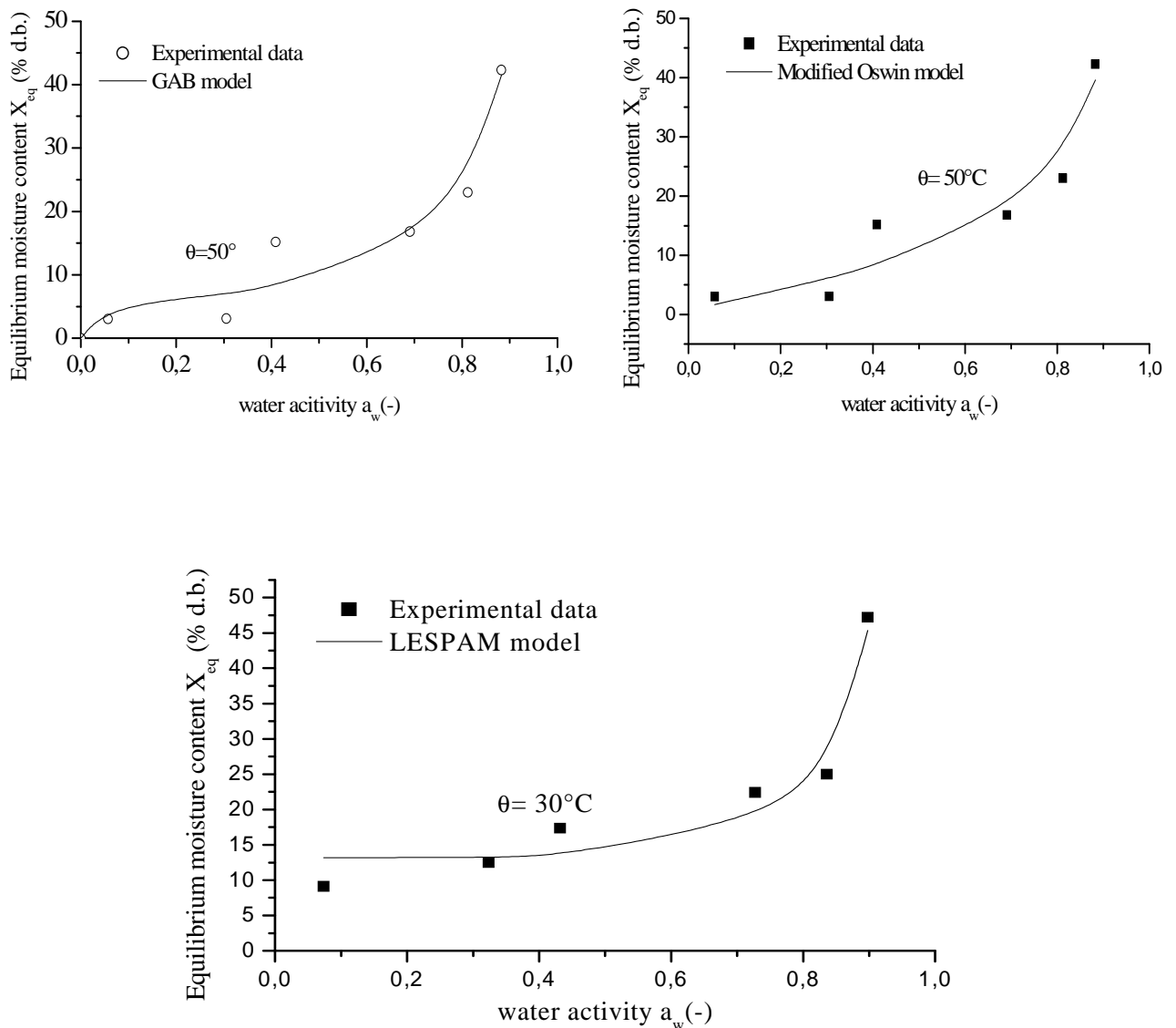
Figure 7. Adsorption isotherms of treated peppermint tea fitted by three models

Figure 8. Desorption isotherms of fresh peppermint tea fitted by three equations

3.3. Measurement of water activity of treated peppermint tea and its witness

A quality product deserves quality treatment. The heat and process engineering specialists must provide users with accurate information on how to handle a product during storage and conservation. For this purpose, the optimal water activities of conservation (Aw $_{op}$) were determined. The sorption isotherm curve can be described as a polynomial equation of the third degree, the central part or "stage" is the best area of product stability (figure 9).
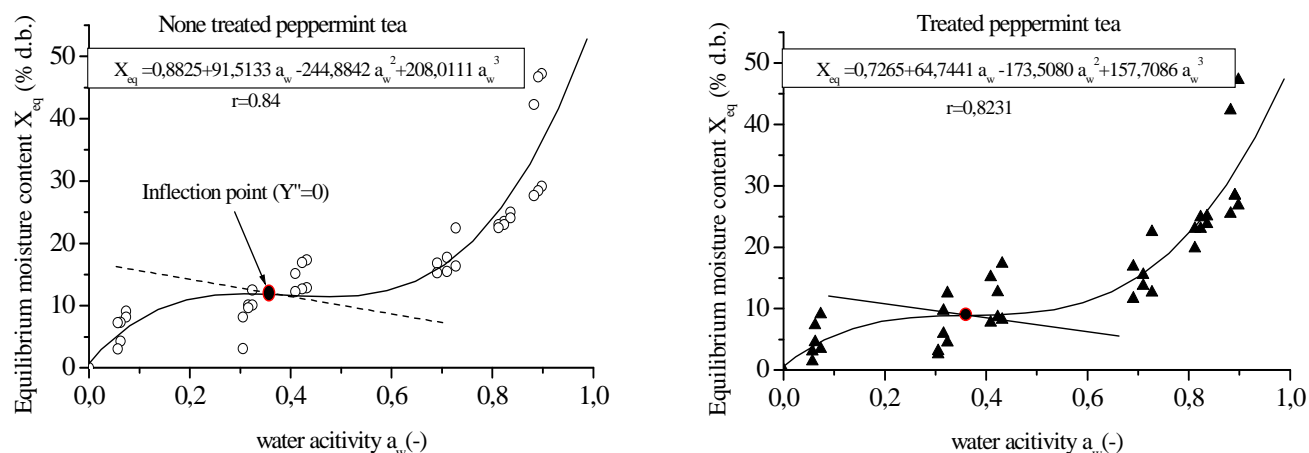
Figure 9. Determination of optimal water activity of conservation of untreated peppermint tea and treated peppermint tea

This calculation method consists of decomposing polynomial of equilibrium moisture content X_{eq}, for all the experimental results for each product based on water activity. It allows calculating the value of the optimal water activity of conservation [20].

The values of the optimal water activity conservation (Table 8) are in perfect agreement with the results obtained for other products [20] [24] [25] [26] .The optimal water activities are ranged in (0.3-0.4).

Table 8.   Optimal water activity of treated and non treated peppermint tea

Samples	Polynomial equation	$a_w(op)$
peppermint tea non treated	$X_{eq} = 0.8825 + 91.5133.a_w - 244.8842.a_w^2 + 208.0111.a_w^3$	0.35
peppermint tea treated	$X_{eq} = 0.7265 + 64.7441.a_w - 173.508.a_w^2 + 157.7086.a_w^3$	0.36

3.4. Isosteric heat of sorption

The differential enthalpy of fresh and non treated and treated peppermint tea was calculated by applying the Clausius-clapeyron equation (1) to the experimental equilibrium isotherm data (table 3, 4). The variation of the heats of adsorption and desorption of the three plants is shown in figure 10.
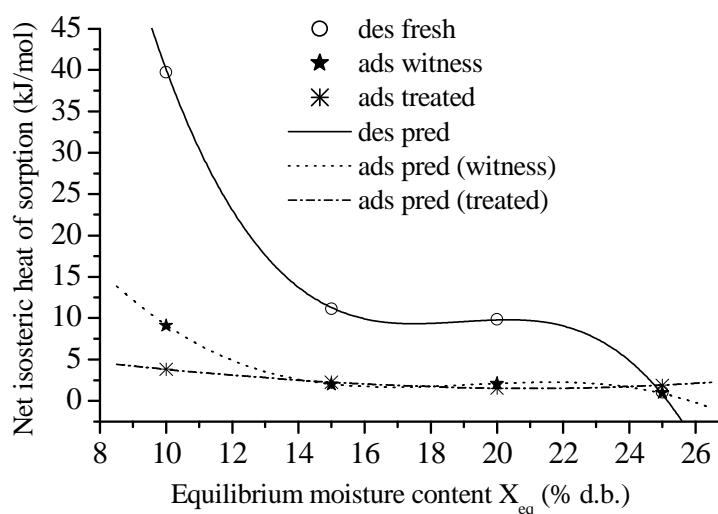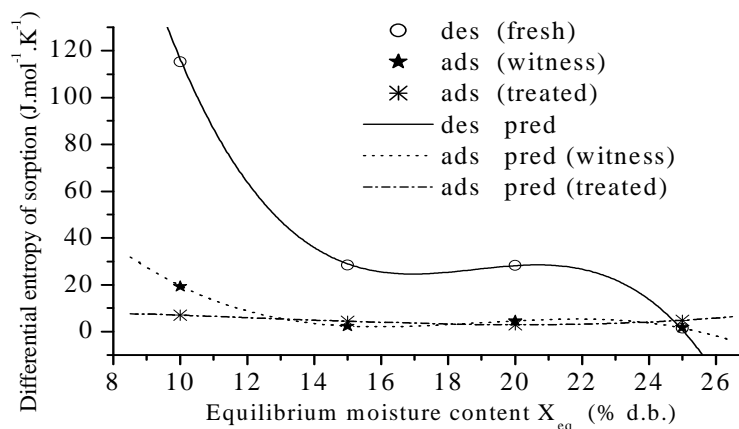
Figure 10. Isosteric heat Δh_d of adsorption and desorption of fresh, untreated and treated peppermint tea as vs equilibrium moisture content

As seen in this figure, at low equilibrium moisture contents, the heat of sorption is high at equilibrium moisture contents (8-14%) [16]. This suggested that the high values of heats of sorption at low equilibrium moisture contents were due to the existence of highly active polar sites on the surface on the product, which are covered with water molecules forming a mono-molecular layer. In addition isosteric heat of desorption is greater than of adsorption at low moisture contents for all samples studied. This indicates that energy required in the desorption process is higher than that in the adsorption process as stated by [27]. However in the case of peppermint tea witness and treated, the adsorption process is almost the same in equilibrium moisture content ranging between 12 and 30%. The variation of isosteric heat of sorption were similar to those observed by other authors for many products: Naji et *al* (2010) [22] for sorption of powdered milk, Boudhrioua et *al*. (2008) [10] for olive leaves, Idlimam et *al*. (2008) [20] for sorption isotherms of *Argania spinosa* and *Zygophyllum gaetulum*, Ait Mohamed et *al*. (2005) [28] for *Citrus reticulate* leaves and *Gelidium sesquipedale*, Jamali et *al*. (2006) [24] for *Chenopodium* and *Citrus aurantium* leaves, Ethmane Kane et *al*. (2008) [19] for *Mentha pulegium*. The isosteric heats Δh_d are adequately represented by polynomial functions (table 9).

Table 9. Isosteric heat Δh_d of adsorption and desorption of fresh and untreated peppermint tea

	Δh_d (kJ.mol^{-1})
Fresh peppermint tea	$318.67-49.65\,X_{eq}+2.64\,X_{eq}^2-0.05\,X_{eq}^3$ r = 1
Non treated peppermint tea	$78.71-12.35\,X_{eq}+0.65\,X_{eq}^2-0.01\,X_{eq}^3$ r = 1
treated peppermint tea	$8.59-0.54\,X_{eq}+0.003\,X_{eq}^2-3.07\,10^{-4}\,X_{eq}^3$ r = 1

The differential entropy is plotted as a function of equilibrium moisture content in figure 11. Once again the entropy data display a strong dependence on moisture content. The experimental adsorption and desorption data conform to polynomial relations as represented by the following equations (Table 10).

Figure 11. Differential entropy ΔS_d of adsorption and desorption of fresh, non treated and treated peppermint tea as a function of equilibrium moisture content

Table 10. Differential entropy ΔS_d of adsorption and desorption of fresh peppermint and non treated end treated peppermint tea

	ΔS_d (J.mol^{-1}.K^{-1})
Fresh peppermint tea	$1003-159.08\,X_{eq}+8.54\,X_{eq}^2-0.15\,X_{eq}^3$ $r=1$
Non treated peppermint tea	$209.91-34.41\,X_{eq}+1.86\,X_{eq}^2-0.033\,X_{eq}^3$ $r=1$
treated peppermint tea	$7.15+0.75\,X_{eq}-0.11\,X_{eq}^2+0.003\,X_{eq}^3$ $r=1$

The Δh_d and ΔS_d values for adsorption and desorption, at given moisture contents, were calculated by linear regression equation using Equation 2. It was assumed that, at specific moisture content, Δh_d and ΔS_d did not vary with temperature [18].

Figure 12, shows a linear relation, with a correlation of determination (r =1). This indicates that compensation exists. The parameters T_β and ΔG_β (Equation 3) were calculated from the data by linear regression, and the values are detailed in Table 11.

Table 11: Characteristic parameters for $\dfrac{\Delta h_d}{\Delta S_d}$ relationship

	T_β (K)	ΔG_β (J.mol^{-1})
Fresh peppermint tea	735.5	338.9
Non treated peppermint tea	412.1	446.34
treated peppermint tea	368.1	570.8
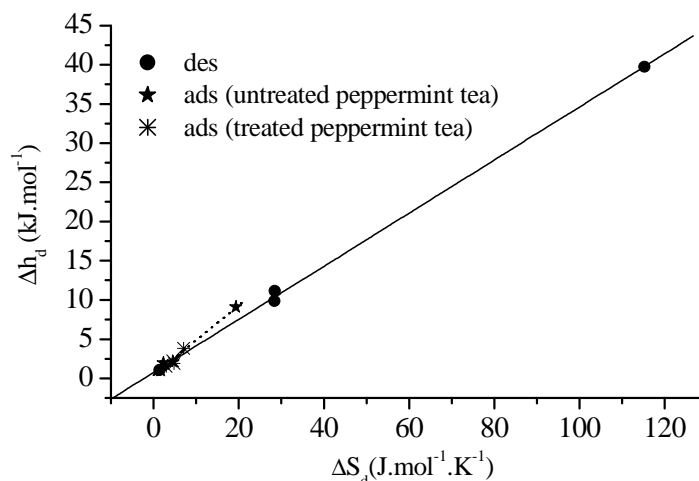
Figure 12. $\dfrac{\Delta h_d}{\Delta S_d}$ relationship for adsorption and desorption in peppermint tea

Conclusion

The sorption curves provide valuable information about the hygroscopic equilibrium of aromatic and medicinal plants. They give a clear idea on the stability domain of the plant after drying. So, these curves are indispensable in the pharmaceutical industry, especially in the operation of storage and conservation of aromatic and medicinal herbs [29].

The sorption isotherms of peppermint tea treated by thermal and biochemical treatment of conservation [4] were determined by experiment and then described by three models. These isotherms were compared to untreated peppermint tea. The water activities of treated and untreated peppermint tea have been determined, these values are in the range of optimal conservation of products, and consequently our combined treatment is promising. The experimental results show that the sorption isotherms of fresh peppermint tea, untreated and treated peppermint tea take a type II sigmoid form and that the GAB model gives a better fit for the sorption isotherms of peppermint tea samples.

The net isosteric heat of sorption and differential entropy values of all samples of peppermint tea decreased with increasing moisture content. The isosteric heat of sorption versus entropy data satisfies the enthalpy-entropy compensation theory.

Nomenclature

A, B, C   model coefficients
ads   adsorption
a_w water activity
$a_w(op)$ optimal water activity
d.b.   dry basis
des   desorption
GAB   Guggenheim, Anderson and De Boer model
LESPAM   Laboratory of Solar Energy and Medicinal Plants
MRE   mean relative error (%)

Pred	predicted
R	universal gas constant (8.3145 J.mol^{-1}.K^{-1})
r	correlation coefficient
T_β	isokinetic temperature (K)
$X_{eq_{i,exp}}$	experiment equilibrium moisture content (% d.b)
$X_{eq_{i,pred}}$	predicted equilibrium moisture content (% d.b)
θ	temperature (°C)
ΔS_d	entropy of sorption, J.mol^{-1}.K^{-1}
Δh_d	isosteric heat of sorption, J. mol^{-1}
ΔG_β	free enthalpy at the isokinetic temperature, J.mol^{-1}

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