# Thermodynamic Analysis of Moisture Adsorption of *Taraxacum Officinale*' Powder

## Haytem Moussaoui<sup>\*</sup>, Zakaria Tagnamas, Younes Bahammou, Mounir Kouhila, Ali Idlimam, Abdelkader Lamharrar

Team of Solar Energy and Aromatic and Medicinal Plants, ENS Marrakesh- Laboratory of Processes for Energy & Environment ProcEDE, Cadi Ayyad University, Morocco E-mail: Haytem.moussaoui@gmail.com

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**Abstract:** This work aims to model the adsorption isotherms and study the essential thermodynamic properties of Taraxacum Officinale' powder during the moisture adsorption phenomenon at three temperatures 30, 40, and 50°C. The results have been determined by the application of the thermodynamics physical principles to the equilibrium data, which are experimentally measured. The estimated values of the isokinetic and harmonic temperatures and the Gibbs free energy change revealed that the sorption process is non-spontaneous and enthalpy driven. **Keywords:** *Taraxacum Officinale*; Moisture adsorption; Enthalpy; Entropy; Gibbs free energy.

## **1. Introduction**

The Taraxacum Officinale powder is a therapeutic treatment whose benefits have been discovered since ancient times. The benefits of this powder were proven only in the sixteenth century [1]. Taraxacum Officinale has many properties that can act on the liver. They are effective for liver failure and seizures. Taraxacum Officinale powder also regulates intestinal functions. It can be considered as a natural diuretic and depurative. Moreover, its bitter principles stimulate digestive secretions. Also, it is useful against certain skin diseases [2–4].

The determination of the sorption isotherms is an indispensable step and a privileged way to know the distribution and the intensity of the water molecules bonds in the agro-alimentary products. These isotherms make it possible to determine the final water content to be reached in order to optimize the storage and drying conditions of this product and give valuable information about the hygroscopic equilibrium of the product to be dried and stored [5–7].

Knowledge of the thermophysical properties of the powder is a crucial step for the adequate use of the latter. It can also be deemed as a database for the design of industrial dryers as well as the optimization and simulation of drying processes. The essential thermodynamic properties of food products such as heat of sorption, enthalpy, entropy and free energy are necessary for certain thermal processes such as drying [8–10]. The isosteric of desorption heat is the additional heat to the latent heat to evaporate pure water molecules in the hygroscopic range. Knowledge of this parameter is important when designing industrial dryers for product preservation reasons [11].

Differential entropy is calculated from the Gibbs-Helmholtz equation. The knowledge of the change in isosteric heat and in differential entropy of sorption is necessary to characterize the association of molecules in the hygroscopic domain. Enthalpy-entropy compensation theory has been widely studied for different physical and chemical processes [12,13]. In the literature, information about the determination of desorption isotherms and the thermodynamic properties of the Taraxacum Officinale powder is lacking. Indeed, the objective of this work is to determine the desorption isotherms of the *Taraxacum Officinale*'s leaves powder at three temperatures 30, 40, and 50°C, and to analyze the evolution of the isosteric heat of the differential entropy as a function of the equilibrium water content, and finally to verify the existence of enthalpy-entropy compensation theory during the Taraxacum Officinale powder desorption process.

## 2. Material and methods

#### 2.1 Plant material and preparation

The *Taraxacum Officinale*'s powder (figure 1) used in the study was collected in May 2019 in the "OULA SAID" area, Settat, Morocco at harvest stage maturity. This medicinal plant was obtained by the assistance of Mr. Mohammed Benouara, a phytotherapist in Settat.



FIGURE 1. Taraxacum Officinale leaves and its powder

## **2.2 Experimental procedure**

We opted for the static gravimetric method, and we used solutions of saturated salts: KOH, (MgCl2, 6H2O), K2CO3, NaNO3, KCl and (BaCl2, 2H2O). These solutions are prepared in hermetic jars and are kept in a controlled temperature oven. The sample is suspended in the jar, above the salts, and thus remains in an environment stabilized in temperature and humidity. The experiment is carried out for three temperatures 30, 40 and 50  $^{\circ}$ C (figure 2).

The mass of the product used for desorption is  $0.500 \pm 0.001$  g. The monitoring of mass losses for desorption and mass gain for adsorption is ensured by a precision balance of  $\pm 0.001$  g. The hygroscopic equilibrium is obtained when the exchange between the product and the ambient air is finished. As soon as the wet masses are determined, the samples are introduced into an oven at 105 °C. for 24 hours in order to determine their dry masses. The product undergoes a pre-drying stage before being submitted to the adsorption study phase. The pre-drying step is carried out in an oven heated to a temperature of 50 °C until the maximum dehydration of the product [14–16].

$$EMC=X_{eq}=\frac{M_{h}-M_{s}}{M_{s}}$$
(1)







FIGURE 2. Experimental apparatus for the sorption isotherms measurement

#### 2.3 Mathematical modeling of sorption isotherms

Several authors have proposed mathematical models in the empirical form to describe the graphical relationship between the equilibrium water content, the ambient relative humidity, and the temperature. In this work, we chose the Guggenheim Anderson-Boer (GAB) model. The expression of the GAB model is presented in the table 1.

<b>TABLE 1.</b> Guggenheim Anderson-Boer (GAB) model				
Authors	Model	Parameters	Reference	
Guggenheim Anderson-Boer (GAB)	$MC = \frac{ABCa_{W}}{\left[\left(1-Ba_{W}\right)+\left(1-Ba_{W}+CKa_{W}\right)\right]}$	A, B, C	[14]	

The correlation coefficient (r) is one of the first criteria for predicting the best equation that describes the sorption isotherms. In addition to the correlation coefficient, the standard error of estimate (SEE) is used for the same purpose [17,18]. These statistical parameters are calculated as follows:

$$r = \sqrt{\frac{\sum_{i=1}^{N} \left(Xeq_{i,pre} - \overline{Xeq}_{i,exp}\right)^{2}}{\sum_{i=1}^{N} \left(Xeq_{i,exp} - \overline{Xeq}_{i,exp}\right)^{2}}}$$

$$ESH = \sqrt{\frac{\sum_{i=1}^{N} \left(Xeq_{i,exp} - Xeq_{i,pre}\right)^{2}}{d_{f}}}$$
(2)
(3)

Where N is the number of data points; Xeqi,exp is the experimental moisture content (%d.b); Xeqi,pre is the predicted moisture content (%d.b).

## 2.4 The Specific surface area of adsorption

Calculating the specific surface area of sorption is very useful in determining the strong bonds that exists between water and solid. In this regard, the calculation of the specific surface area of sorption is conducted via the following equation [9]:

$$SS = \frac{M_0 \times N_A \times A_m}{M_{wat}} = 35.3M_0 \tag{4}$$

Where SS designates the solid surface area of sorption (m2.g-1 solids);  $M_0$  refers to the monolayer moisture content (g/100 g, d.b); NA is the number of Avogadro (6.02 1023 molecules.mol<sup>-1</sup>); Am is the area of a water molecule (1.06 10-19 m<sup>2</sup>/molecule). Finally, the Mwat represents the molecular weight of the water (18 g.mol<sup>-1</sup>).

#### 2.5 Net isosteric heat of adsorption

In the hygroscopic domain where water is strongly bound to the product, the heat required to evaporate a water molecule is the sum of the latent heat of phase change and the heat of sorption. The heat of sorption can be determined from the desorption isotherms [19].

The application of the Clausius-Clapeyron equation to sorption isotherms (equilibrium isostatic pressure) at different temperatures is a widely used procedure for calculating the isosteric heat of sorption or the differential enthalpy of sorption, which is only valid for constant water contents.

$$-\left(\frac{d\ln(P_{v})}{d\left(\frac{1}{T}\right)}\right) = \frac{\Delta H_{a}}{R}$$
(5)

The net sorption enthalpy ( $\Delta$ ha), equation (7) is defined by the subtraction of equation (5) predefined from the equation corresponding to pure water (6).

$$-\left(\frac{d\ln(P_{vsat})}{d\left(\frac{1}{T}\right)}\right) = \frac{\Delta H_{vap}}{R}$$
(6)

$$-\left(\frac{d\ln\left(\frac{P_{v}}{P_{vsat}}\right)}{d\left(\frac{1}{T}\right)}\right)_{EMC} = \frac{\Delta H_{a} - \Delta H_{vap}}{R} = \frac{\Delta h_{a}}{R}$$
(7)

## 2.6 Differential entropy of adsorption

The sorption differential entropy ( $\Delta S$ ) is another helpful thermodynamic property that seeks to analyze the degree of randomness or order of the state of the water molecules. What's more, the sorption entropy (differential entropy) is bound to the repulsive force attraction that exists in the food system [16]. The sorption entropy is demonstrated by the following equation:

$$\ln\left(a_{W}\right) = \frac{-\Delta h_{a}}{RT} + \frac{\Delta S}{R}$$
(8)

In which R stands for the universal gas constant (8.314 J.mol<sup>-1</sup>.K<sup>-1</sup>).

## 2.7 Theory of enthalpy-entropy compensation

The theory of enthalpy-entropy compensation proposes a linear relationship between enthalpy and entropy given by the following relation (9):

$$\Delta h_a = T_\beta \Delta S + \Delta G_\beta \tag{9}$$

T $\beta$  is the isokinetic temperature at which all reactions in the series proceed at the same rate of progress.  $\Delta G\beta$  is the free energy at the temperature T $\beta$  [9,19]. The sign of free energy ( $\Delta G\beta$ ) provides a criterion for evaluating whether the process of desorption is spontaneous (- $\Delta G\beta$ ) or not (+  $\Delta G\beta$ ). The harmonic temperature (T<sub>hm</sub>) is given by the following relation (10):

$$T_{\rm hm} = \frac{n}{\sum_{1}^{n} \left(\frac{1}{T({\rm K})}\right)}$$
(10)

Where n is the number of isotherms, T(K) in the oven temperatures in Kelvin.

## **3. Results and discussion**

#### 3.1 Moisture adsorption of the powder of Taraxacum Officinale

Table 2 summarizes the values of Guggenheim Anderson-Boer parameters. We can note from this table that GAB model is suitable to fit the experimental data of moisture adsorption of *Taraxacum Officinale*'s powder at three temperatures 30,40 50 °C, with a correlation coefficient (r = 0.9984, r = 0.9985, r = 0.9988), and the standard error of estimate (SEH = 1.8786, SEH = 1.6797, SEH = 1.4255) respectively. what's more the table displays that the equilibrium water content at the saturation level of the monolayer is between 7.6767 and 8.0019 (%d.b).

<b>TABLE 2.</b> The values of Guggenheim Anderson-Boer parameters					
GAB	Adsorption				
parameters	30 °C	40 °C	50 °C		
А	8.0019	7.8700	7.6767		
В	0.9880	0.9920	0.9985		
С	7.8600	5.6600	2.7500		
r	0.9984	0.9985	0.9988		
SEH	1.8786	1.6797	1.4225		

The hygroscopic equilibrium is reached for the Taraxacum Officinale powder after 14 days for the adsorption process. Figure 3 presents the adsorption curves modeled by the GAB model, it shows that for a constant relative humidity, the water content at 30  $^{\circ}$  C is higher than that at 40  $^{\circ}$  C. The curves also show that the sorption isotherms have a sigmoidal appearance, similar to those commonly presented by other aromatic and medicinal products [10,14,19].

## 3.2 The determination of the specific surface area of adsorption

Using equation (4) the values of the specific surface area values of adsorption were calculated. The M0, which refers to the GAB monolayer moisture, is obtained from the GAB model. On one hand, the adsorption surface area of Taraxacum officinale' powder at 30 °C, 40°C and 50 °C temperatures take the values of 284,067 m<sup>2</sup>.g<sup>-1</sup>, 279,24



 $m^2$ .g<sup>-1</sup>, 272,52  $m^2$ .g<sup>-1</sup> respectively. We can conclude that the temperature affects the interaction between the water and solid surface area, it decreases with the increase of the temperature[10,20].

FIGURE 3. Comparison between experimental sorption data and that predicted by the GAB model

#### 3.3 The Calculation of the net isosteric heat of adsorption

The values of  $\Delta$ ha are obtained from the slope of the evolution of -ln (aw) as a function of (1/T) for a fixed equilibrium moisture content. A graphical representation of this equation is given in figure 4. The net heat of adsorption equals the slope of each isostere (an isosteric curve corresponds to the set of points with the same EMC). This calculation method is currently the most used one in thermophysical studies. As it is shown in figure 4, the slope of the isostere of EMC= 16 is above that of EMC=14, and it descends along with the decrease of the equilibrium water content [14].



FIGURE 4. The Isosteric curves (1/T, -ln(a<sub>w</sub>)) at different EMC

62

When water vapor is adsorbed on a surface, a quantity of heat (the heat of adsorption) is released. It corresponds to the energy that must be added to the adsorbed gas to break the intermolecular force. The adsorption heats indicate binding energy or intermolecular force between molecules of water vapor and the surface of the adsorbent (wet product) [20,21].

The isosteric net of water adsorption on *Taraxacum Officinale's* powder decreases with increasing equilibrium moisture content (Figure 5). The enthalpy reaches a high value of enthalpy at low equilibrium moisture contents. This indicates a strong bond of water in the product being dried. The maximum enthalpy of adsorption reaches the value of 33.37156 kJ / mol. The equation (11) represents the relationship between the isosteric heat of adsorption data and the equilibrium moisture content. This model has been determined in order to predict the required heat of adsorption that must be added to fix a specific amount of water [20].

$$\Delta h_a = 59.28 - 4.64 EMC - 0.17 EMC^2 + 0.015 EMC^3$$

$$r = 0.9964$$
(11)



**FIGURE 5.** Variation of the net isosteric heat of moisture adsorption of *Taraxacum Officinale's* powder as a function of the EMC

## 3.4 The calculation of the differential entropy of adsorption



FIGURE 6. Variation of the differential entropy of adsorption of Taraxacum Officinale's powder as a function of the EMC

The evolution of the adsorption entropy as a function of the equilibrium moisture content of *Taraxacum Officinale's* powder is shown in Figure 6. The evolution of entropy is similar to that of the isosteric heat of adsorption. It is highly dependent on moisture content, especially for low equilibrium moisture content. The maximum adsorption entropy reaches values of 18.5793 J.mol<sup>-1</sup>.K<sup>-1</sup> at equilibrium moisture content EMC = 5. The

following equation represents the relationship between the differential entropy data and the equilibrium moisture content:

$$\Delta S = 59.28 - 4.064 EMC - 0.17 EMC^{2} + 0.015 EMC^{3}$$

$$r = 0.9996$$
(12)

#### 3.5 Application of the enthalpy-entropy compensation theory

Figure 7 presents the evolution of the net isosteric heat of adsorption as a function of the differential entropy. The thermodynamic properties released from the studied product are correlated by the following linear functions equation (13):

$$\Delta h_a = 360.68 \Delta S + 1009.91 \tag{13}$$

r = 0.9994

The isokinetic temperature  $(T\beta)$  and free energy were determined by linear regression of equation (13).

Values of isokinetic temperature (T $\beta$ ) for Taraxacum Officinale's powder in the adsorption process is 360,68 K. The harmonic temperature T<sub>hm</sub> is equal to 312,78 K( $\approx 40^{\circ}$ C)of the study. The isokinetic temperature of the studied powder is different from the harmonic one. This result confirms the existence of enthalpy-entropy compensation theory and the moisture sorption of Taraxacum Officinale's powder is an enthalpy driven process. The sign of the free energy ( $\Delta G\beta$ ) of the powder is positive, which indicates that the water adsorption is a non-spontaneous process [9,10,20].



FIGURE 7. Variation of the differential enthalpy as a function of the differential entropy of *Taraxacum* Officinale's powder

#### 4. Conclusion

This work has been devoted to the study of adsorption isotherms and the thermodynamic properties of the Taraxacum Officinale leave's powder. The desorption isotherms were determined using the gravimetric static method. The results of this study show that the adsorption isotherms of the product have a sigmoidal type II form. The water content equilibrium decreases with decreasing water activity at a constant temperature. The isosteric heat was determined by applying the Clausius-Clapeyron equation. The adsorption enthalpy is important at low moisture content as it decreases with increasing moisture content until it reaches the latent heat of evaporation from the water. Similar behaviors of the differential entropy as a function of the water content was found. For the Taraxacum Officinale leaves powder, the isokinetic temperature is different from the harmonic one, which confirms the existence of enthalpy-entropy compensation theory.

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