

Thermodynamic properties and modeling of sorption isotherms for longer storage of *Urtica urens* leaves

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Abstract: Moisture equilibrium data of *Urtica urens* leaves by desorption and adsorption were determined at 30, 40, and 50°C. The isotherms were determined by a static gravimetric method for various temperature and humidity conditions. Five mathematical models were used to fit the experimental data. A nonlinear least-squares regression program was used to evaluate the constants of the five desorption and adsorption isotherm models GAB and Modified Halsey models were adequate to describe the sorption characteristics of the samples. Isothermic heats of desorption and adsorption were calculated by applying the Clausius-Clapeyron equation to the sorption isotherms at different temperatures. It decreased with increasing moisture content. We recognized the linear relation exists between the enthalpy and entropy of the sorption reaction.

Keywords: enthalpy, entropy, hysteresis, mathematical models, sorption isotherm.

I. INTRODUCTION

The homeopathic remedy *Urtica urens* leaves is prepared using the entire herb known as annual nettle, while it is in blossom and is used to treat a number of health conditions, especially nettle rash or hives. Commonly known as dwarf nettle, annual nettle or small nettle, *Urtica urens* is a semi-woody plant belonging to genus *Urtica* that grows annually. Traditionally, people have been using this herb as a medication for skincare as well as alleviate skin inflammation or itchiness. In effect, scientists have especially studied the herb *Urtica urens* for its potential in supporting the skin when external irritants result in certain complaints [1].

The medicinal and aromatic plants have a great importance for both the pharmaceutical industry and the traditional. The stability of a dehydrated medicinal plant is influenced by its water activity. This stability is mainly a consequence of the relationship between the equilibrium moisture content and its corresponding water activity. Knowledge of the sorption properties of foods is of great importance in medicinal plant, especially in the quantitative approach to the prediction of the shelf life of dried medicinal plant. Equations for modeling water sorption isotherms are of special interest for many aspects of medicinal plant preservation by dehydration.

In this study, temperatures of 30°C, 40°C, and 50°C were chosen, to typify tropical storage conditions. Using an experimental approach, the equilibrium curves are determined by the saturated salt solution method. The experimental sorption curves are described by five different models to identify the most appropriate mathematical model for a better description of the product equilibrium state: GAB's model, modified Henderson's model, modified Halsey's model, modified Oswin's model. Then, we investigate from the experimental data the water activity optimal for the storage of *Urtica urens*.

Further analysis of sorption isotherm data by application of thermodynamic principals can provide information regarding differential enthalpy or the isosteric heat of sorption and differential entropy. Differential enthalpy of sorption gives an indication of the amount of bound water existing in the product. The differential entropy of material is proportional to the number of its available sorption sites at a specific energy level [2]. Subsequently we determine the thermodynamic functions (differential enthalpy, differential entropy). Moreover, we recognized the linear relation exists between the enthalpy and entropy of the sorption reaction.

II. MATERIALS AND METHODS

2.1 Experimental procedure

The plant *Urtica urens* used in our study was collected at Tahanouat, Marrakesh Morocco. The hygroscopic equilibrium could be achieved by a dynamic or static method. In the present work, a static method

is used [3]. The method is based on the use of saturated salt solutions to maintain a fixed relative humidity Rh. The mass transfers between the product and the ambient air are assured by natural diffusion of the water vapour. The atmosphere surrounding the product has a fixed relative humidity for every working temperature imposed on the system.

Six salts were chosen { KOH, (MgCl₂, 6H₂O), K₂CO₃, NaNO₃, KCl and (BaCl₂, 2H₂O)} so as to have a range of water activity of 0.0572-0.0898 [4]. The experimental apparatus consisted of six glass jars of 1 liter each with an insulated lid. Every glass jar was filled to quarter depth with a saturated salt solution. Duplicated samples each of 0.4 g (±0.0001g) for desorption and 0.1 g (±0.0001g) for adsorption were weighed and placed into the glass jars. The weight recording period was about 3 days. This procedure continued until the weight was constant. The equilibrium moisture content of each sample was determined in a drying oven at 105 °C for 24 h. The hygroscopic equilibrium *Urtica urens* leaves was reached in then days for desorption and eighth days for adsorption.

2.2 Modelling equations

The relationship between equilibrium moisture content, water activity, and temperature for *Urtica urens* leaves was predicted in literature by several mathematical models [5]. In our study five models have been applied: GAB's model, modified Henderson's model, modified Chung-Pfost model, modified Halsey model, and modified Oswin's model. The equations expressing those models are given below in table 1. X_{eq} represents equilibrium moisture content (%MS); a_w water activity; A, B, and C coefficients, dependant to the temperature or not, to determine by smoothing the experimental curves of sorption and θ the temperature in °C. The correlation coefficient (r) was one of the primary criteria for selecting the best equation to fit the four models to the experimental data. In addition to r, the statistical parameters mean relative error (MRE) as a percentage was used to determine the quality of the fit [6]. Levenberg-Marquardt nonlinear optimization method using appropriate software is used for the calculation of model coefficients that describe the equilibrium curves and their statistical parameters: the correlation coefficient (r) and mean relative error (MRE).

$$r = \sqrt{\frac{\sum_{i=1}^N (X_{eq_{i,pred}} - \overline{X_{eq_{i,exp}}})^2}{\sum_{i=1}^N (X_{eq_{i,exp}} - \overline{X_{eq_{i,exp}}})^2}} \quad (1)$$

$$MRE = \frac{100}{N} \sum_{i=1}^N \left| \frac{X_{eq_{i,exp}} - X_{eq_{i,pred}}}{X_{eq_{i,exp}}} \right| \quad (2)$$

Where:

X_{eq_{i,exp}} ith Experimental moisture content (%d.b)

X_{eq_{i,pred}} ith Predicted moisture content (%d.b)

N number of data points.

d.b dry basis

Table 1: Mathematical models used in our study

Model's name	Expression of the model	References
GAB	$X_{eq} = \frac{A B C a_w}{[1 - B a_w] [1 - B a_w + B C a_w]}$	[7]
Modified Henderson	$X_{eq} = \left[\frac{-\ln(1 - a_w)}{A(\theta + B)} \right]^{1/c}$	[8]
Modified Chung-Pfost	$a_w = \exp \left[\frac{-A}{\theta + B} \exp(-C X_{eq}) \right]$	[9]
Modified Halsey	$X_{eq} = \left[\frac{(-\exp(A + B.\theta))^{(1/c)}}{\ln(a_w)} \right]$	[10]
Modified Oswin	$X_{eq} = (A + B.\theta) \left[\frac{a_w}{1 - a_w} \right]^C$	[11]

2.3 Determination of the optimum conditions for storage

The study of the sorption isotherms enables us to know the optimal relative equilibrium moisture for the conservation of a product as well as the water content of equilibrium to reach at the end of the drying. Also, it affords users with accurate information on how to handle a product during storage and conservation [12]. For this purpose, the optimal water activities of conservation (a_{wop}) were dogged. The whole of the experimental points is gathered on the same graph. Then, we model the isotherm of sorption by a polynomial equation of the third degree. The part closes to horizontality corresponds to the zone of better stability of the product. This process of calculation consists in making a polynomial decomposition of the equilibrium moisture content X_{eq} , for the whole of the experimental results, according to the water activity. This makes it possible to calculate the value for which the derivative second of X_{eq} is cancelled “inflection point” and consequently optimal relative humidity for conservation.

2.4 Differential enthalpy and differential entropy of sorption

The differential enthalpy or isosteric heat of sorption (ΔH_d) indicates the state of absorbed water by the solid material. The net isosteric heat of sorption (Δh_d) represents the quantity of energy exceeding the heat of vaporization of water (ΔH_{vap}) associated with the sorption process.

$$\Delta h_d = \Delta H_d - \Delta H_{vap} \quad (3)$$

The net isosteric heat of sorption can be calculated from the experimental data using the Clausius-Clapeyron equation [13]:

$$\left[\frac{d(\ln a_w)}{d(1/T)} \right]_{X_{eq}} = \frac{-\Delta h_d}{R} \quad (4)$$

This relation requires determining the isotherms at various temperatures in order to calculate the variation logarithmic curve of the water activity according to the reverse of the temperature, for a water content fixed. However, starting from the modified equations, it is possible to obtain the analytical expression of the heat of sorption Δh_d . This approach assumes that isosteric heat ΔH_d does not vary with the temperature [14]. The relationship between the net isosteric heat Δh_d and the differential entropy ΔS_d of sorption is given by:

$$(-\ln a_w)_{X_{eq}} = \frac{\Delta h_d}{R.T} - \frac{\Delta S_d}{R} \quad (5)$$

The experimental sorption isotherm data was plotting in the form of $\ln(a_w)$ versus $\frac{1}{T}$ for specific moisture content (X_{eq}). We determined Δh_d from the slope $\left(\frac{\Delta h_d}{R} \right)$ and ΔS_d from the intercept $\left(\frac{\Delta S_d}{R} \right)$. Applying this at different moisture contents allowed determining the dependence on Δh_d and ΔS_d .

2.5 Enthalpy-Entropy Compensation Theory

According to the theory of compensation, the linear relationship between the enthalpy Δh_d and the entropy ΔS_d for a specific reaction are given by:

$$\Delta h_d = T_\beta \cdot \Delta S_d + \Delta G_\beta \quad (6)$$

The isokinetic temperature (T_β) is a characteristic property of the food surface whose dimension is absolute temperature. It represents the temperature to which all the reactions of the series proceed to the same rate. The free energy (ΔG_β) provides a criterion to evaluate if the process of the water sorption is spontaneous ($-\Delta G_\beta$) or not ($+\Delta G_\beta$). This process is repeated for several values of equilibrium relative humidity with an aim of underlining the relation between the differential entropy of sorption and the equilibrium moisture content of the studied product. The isokinetic temperature (T_β) and constant (ΔG_β)

were calculated using linear regression. The isokinetic temperature T_β represents the slope of the linear function between the differential entropy and the differential enthalpy of sorption [2].

III. RESULTAS AND DISCUSSION

3.1 Adsorption and desorption isotherms

The equilibrium moisture content increases with decreasing temperature at constant water activity (Fig 1). The sorption isotherms present the characteristic S-shaped curve (Type II), typical of sorption isotherms of many plants and food materials [3, 4, 5].

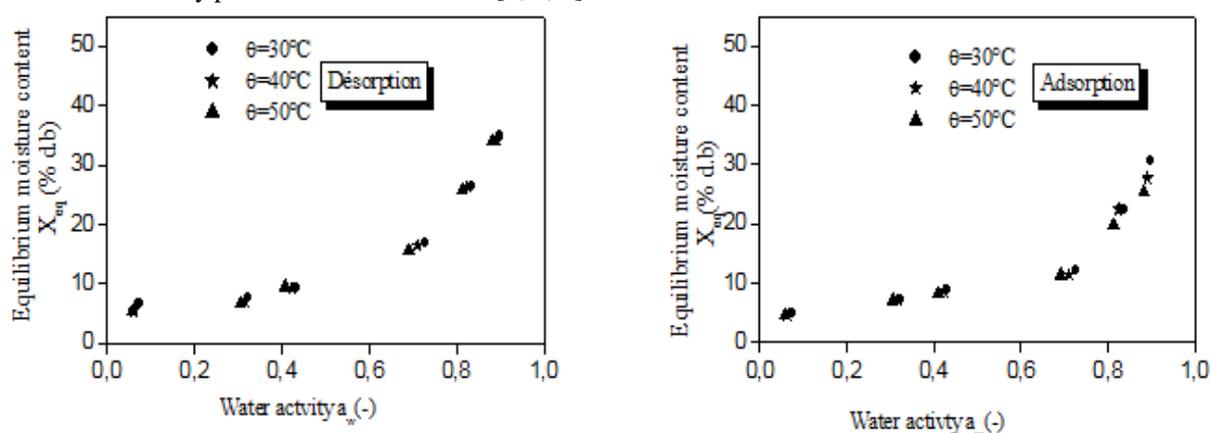


Fig. 1: Sorption isotherms of *Urtica urens* leaves at 30, 40 and 50°C

The presentation of adsorption and desorption experimental data in the same plot show that the plant does not have the same hygroscopic equilibrium behaviour (fig 2). The phenomenon of desorption-adsorption is irreversible. For the same constant relative moisture, the water content of desorption is higher than that of adsorption. Indeed, there exists a phenomenon of hysteresis. This characteristic is visible for *Urtica urens* plant.

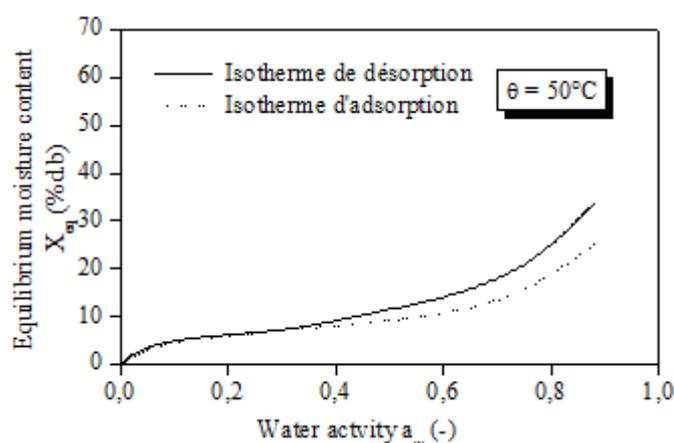


Fig.2: Sorption hysteresis phenomenon of *Urtica urens* leaves

Several hypotheses have been put to explain hysteresis. One of it is an analogy with a sponge. When the pores do not contain any more water, adsorption does not make it possible to recover the totality of initial water since this one imprisons air in the pores. Another hypothesis states that hysteresis in the sorption isotherm is a consequence of variation in the fraction of bound water present in the adsorption and desorption processes. The bound fraction being always larger on desorption than on adsorption [15].

3.2 Modelling of sorption experimental data

The results of non linear regression analysis of fitting the sorption equations to experimental data of *Urtica urens* leaves was at three temperatures are presented in Tables 2 and 3. For all the models tested, parameters A, B and C are found to be temperature dependent. For desorption isotherms, GAB model is found

to be the best estimator for predicting the equilibrium moisture of the *Urtica urens* leaves. This model gives the highest correlation coefficient (r) of 0.9989 and mean relative error MRE (2.7865 %) at $\theta = 40^\circ\text{C}$. For adsorption isotherms, modified Halsey model is found to be the best estimator for predicting the equilibrium moisture of *Urtica urens* leaves. This models gives the highest (r) of 0.9918 and the MRE (2.8321 %) at $\theta = 50^\circ\text{C}$.

Table 2: Estimated model coefficients, r, MRE of five equation model fitted to desorption isotherm of *Urtica urens* leaves

Model's name	θ ($^\circ\text{C}$)	A	B	C	r	MRE (%)
GAB	30 $^\circ\text{C}$	0.9365	151.7891	5.5773	0.9986	2.1527
	40$^\circ\text{C}$	0.9803	46.7567	7.3417	0.9989	2.7865
	50 $^\circ\text{C}$	0.9485	112.8598	5.6501	0.9975	3.0121
Modified Henderson	30 $^\circ\text{C}$	0.0039	-17.4841	1.1021	0.9697	4.3719
	40 $^\circ\text{C}$	0.0023	-15.9677	1.0599	0.9791	6.7184
	50 $^\circ\text{C}$	0.0018	-19.4031	1.0534	0.9775	5.6338
Modified Chung-Pfost	30 $^\circ\text{C}$	124.4991	8.49	0.1105	0.9472	8.7143
	40 $^\circ\text{C}$	124.0871	9.6501	0.0633	0.9411	15.2637
	50 $^\circ\text{C}$	146.5175	-3.1678	0.1068	0.9492	13.6218
Modified Halsey	30 $^\circ\text{C}$	2.6725	0.0274	1.6101	0.9955	3.3821
	40 $^\circ\text{C}$	2.3441	0.0241	1.5388	0.9966	3.2581
	50 $^\circ\text{C}$	1.1786	0.0206	1.4927	0.9965	4.8321
Oswin Modifié	30 $^\circ\text{C}$	4.2552	0.2352	1.9592	0.9872	5.3127
	40 $^\circ\text{C}$	1.0984	0.2525	1.8779	0.9915	4.1287
	50 $^\circ\text{C}$	0.2431	0.2211	1.8358	0.9905	7.7385

Table 3: Estimated model coefficients, r, MRE of five equation model fitted to adsorption isotherm of *Urtica urens* leaves

Model's name	θ ($^\circ\text{C}$)	A	B	C	r	MRE(%)
GAB	30 $^\circ\text{C}$	0.9538	756.4351	4.3744	0.9912	3.1829
	40 $^\circ\text{C}$	0.9351	134.8204	4.7111	0.9866	3.1815
	50 $^\circ\text{C}$	0.9237	282.8957	4.7116	0.9915	2.1923
Modified Henderson	30 $^\circ\text{C}$	0.0034	-10.9261	1.0657	0.9520	6.8457
	40 $^\circ\text{C}$	0.0019	-12.1797	1.1341	0.9594	8.1745
	50 $^\circ\text{C}$	0.0006	-9.0857	1.2814	0.9605	5.7332
Modified Chung-Pfost	30 $^\circ\text{C}$	112.5638	5.186	0.13	0.9302	13.7184
	40 $^\circ\text{C}$	136.1907	1.0462	0.1357	0.9402	12.9637
	50 $^\circ\text{C}$	153.7906	-9.9718	0.1523	0.9481	15.6013
Modified Halsey	30 $^\circ\text{C}$	2.2536	0.0193	1.5443	0.9881	3.0821
	40 $^\circ\text{C}$	2.4539	0.0178	1.5964	0.9847	3.3586
	50$^\circ\text{C}$	2.46	0.0182	1.6861	0.9918	2.8321
Modified Oswin	30 $^\circ\text{C}$	1.9962	0.2422	1.8809	0.9769	4.3167
	40 $^\circ\text{C}$	0.8772	0.2146	1.9685	0.9774	6.6218
	50 $^\circ\text{C}$	0.7391	0.177	2.1286	0.9819	8.6253

3.3 Measurement of optimal water activity of *Urtica urens* leaves

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 ($a_{w\text{op}}$) 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 (fig 3).

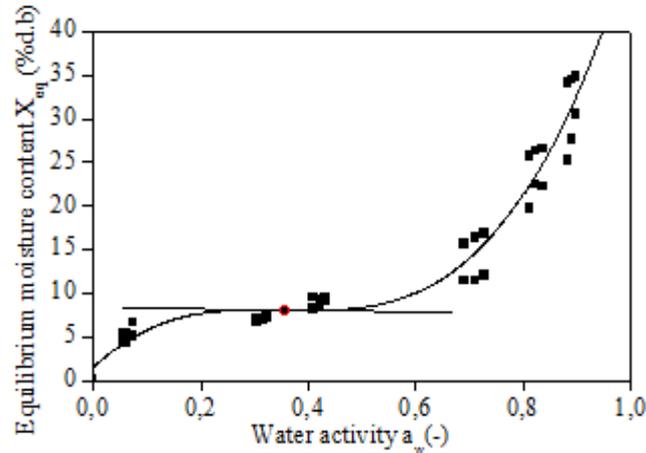


Fig.3: Determination of optimal water activity for conservation of *Urtica urens* leaves

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 (equation 7). The values of the optimal water activity conservation of *Urtica urens* leaves ($a_{w,op} = 0.3532$) are in perfect agreement with the results obtained for other products [16, 17]. The optimal water activities are ranged in (0.3-0.4).

$$X_{eq} = 1.6442 + 57.7527a_w - 167.6854a_w^2 + 157.38322a_w^3 \quad (7)$$

3.4 Enthalpy and entropy of sorption

The net isosteric heat of sorption (Δh_d) values are calculated from the equilibrium moisture data at different temperatures using Clausius-clapeyron equation (4). The variation of the heats sorption of *Urtica urens* leaves with equilibrium moisture content is shown in figure 4.

The net isosteric heat of desorption and adsorption of *Urtica urens* leaves can be expressed mathematically as a polynomial function of equilibrium moisture content:

$$\text{Desorption : } \Delta h_s = 11.753 - 1.2126 X_{eq} + 0.0436 X_{eq}^2 - 0.0005 X_{eq}^3 \quad (8)$$

$$\text{Adsorption : } \Delta h_s = 19.8186 - 3.5446 X_{eq} + 0.2116 X_{eq}^2 + 0.004 X_{eq}^3 \quad (9)$$

The differential entropy (ΔS_d) is plotted as a function of moisture content in figure 4. Once again, the entropy data display a strong dependence on moisture content. The experimental desorption and adsorption data, respectively, conform to polynomial relation as represented by the equations:

$$\text{Desorption : } \Delta S_d = 40.0995 - 4.2976 X_{eq} + 0.1727 X_{eq}^2 - 0.0023 X_{eq}^3 \quad (10)$$

$$\text{Adsorption : } \Delta S_d = 62.5820 - 10.9222 X_{eq} + 0.6521 X_{eq}^2 - 0.0125 X_{eq}^3 \quad (11)$$

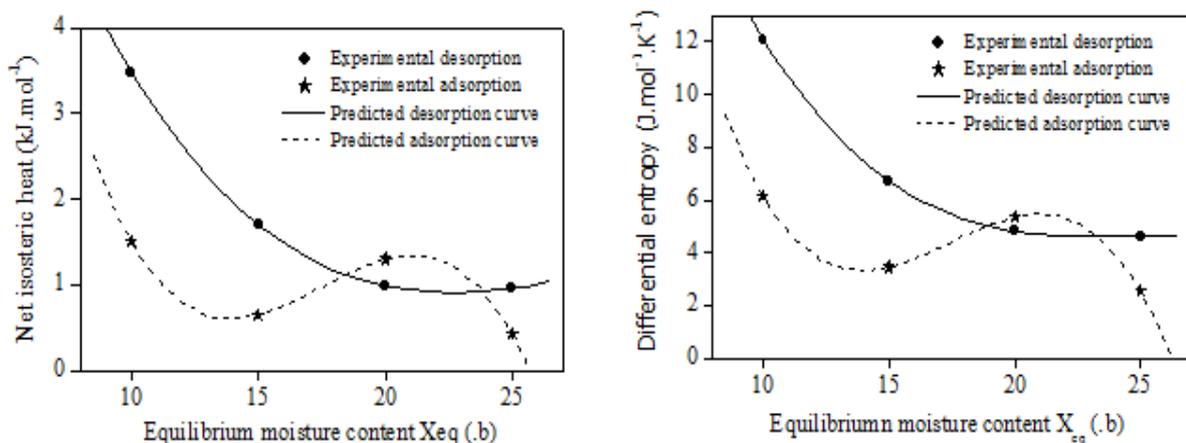


Fig.4: Net isosteric heat and differential entropy of sorption of *Urtica urens* leaves as a function of equilibrium moisture content

3.5 Enthalpy-entropy compensation theory

The Δh_d and ΔS_d values for adsorption and desorption, at given moisture contents, were calculated by linear regression equation using equation 5. It was assumed that, at specific moisture content, Δh_d and ΔS_d did not vary with temperature. Figure 5, shows a linear relation, with a correlation of determination ($r = 1$). This indicates that the compensation exists. The parameters T_β and ΔG_β (Equation 6) were calculated from the data by linear regression, and the values are detailed in table 4

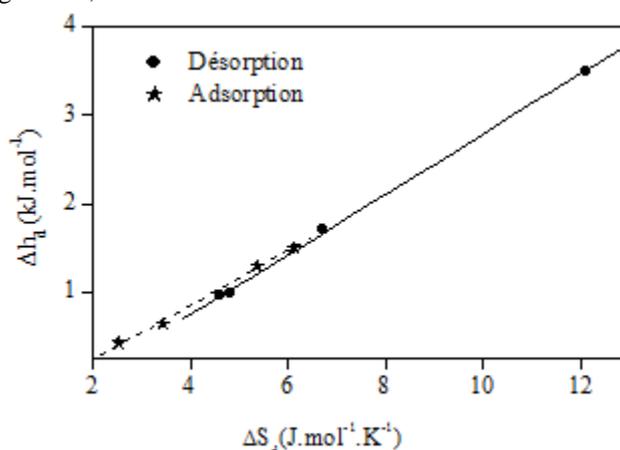


Fig.5: Compensation theory of enthalpy/entropy

Table 4: Characteristic parameters for $\Delta h_d / \Delta S_d$ Relationship

	T_β (K)	ΔG_β (J.mol ⁻¹)
desorption	340.96	-623.62
adsorption	308.08	374.35

IV. CONCLUSION

It's now widely accepted that sorption data provide valuable information for industrial drying in order to preserve and store the seasonal plants and make them available to consumers all year round. The sorption data may be used not only for the identification of the optimum residual moisture content of the final product, but also for the calculation of the drying time of hygroscopic substances.

The moisture sorption curves of *Urtica urens* leaves were experimentally investigated at three temperatures 30, 40 and 50 °C. The isotherms have a sigmoid shape (Type II) which is common for many hygroscopic products. The hysteresis phenomenon was distinctly observed. Among the sorption models chosen, the GAB model was the best model describing the equilibrium moisture data for desorption, and the modified Halsey model was the most suitable to estimate adsorption isotherms. The optimal water activities of conservation were determined. Net isosteric heat of sorption and differential entropy values of *Urtica urens* leaves were found to be a polynomial function of moisture content for desorption and adsorption. Enthalpy-entropy compensation theory could be successfully applied to the moisture sorption behaviour of *Urtica urens* leaves.

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