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# Moisture sorption isotherms and isosteric heat of sorption of leaves and stems of lemon balm (*Melissa officinalis* L.) established by dynamic vapor sorption

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ABSTRACT

The equilibrium moisture contents (MC) of leaves and stems of lemon balm (*Melissa officinalis* L.) were determined separately at temperatures of 25, 35 and 45 °C over a stepwise increase of relative humidity (RH) ranging from 3 to 90% by an automatic, gravimetric analyzer (DVS system). Equilibrium was achieved within 6 h for most of the target values of relative humidity. The equilibrium moisture content of leaves was significantly higher than that of stems ($p < 0.05$). Differences in moisture sorption capacity between the leaves and stems can be attributed to chemical composition and structure of the tissues. Five three-parameter moisture sorption models (modifications of Chung–Pfost, GAB, Halsey, Henderson and Oswin) were tested for their effectiveness to fit the experimental sorption data. The modified Oswin equation was found to be the best model to describe the adsorption isotherms of both leaves and stems of lemon balm. The recommended MC values of leaves and stems for microbial safe storage at 25 °C were 0.124 and 0.113 kg water per kg dry solids, respectively. The net isosteric heat of sorption was computed from the predicted sorption data by applying the integrated form of the Clausius–Clapeyron equation.


## 1. Introduction

Lemon balm (*Melissa officinalis* L.) is a perennial herb of the family Lamiaceae, cultivated for its characteristic lemon-scented leaves. It is implemented for several purposes in the food and pharmaceutical industries due to its active ingredients. The essential oil of *M. officinalis* is a well-known antibacterial and antifungal agent (Mimica-Dukic, Bozin, Sokovic, & Simin, 2004) while rosmarinic acid has been identified as the main compound related to its antioxidative and antiviral activity (Wang, Provan, & Helliwell, 2004).

The most common preservation method for medicinal plants is by convective hot-air drying because it not only reduces the moisture content to the microbial safe water activity for storage but also allows the quick conservation of the medicinal qualities of the plant material in an uncomplicated manner (Müller, 2007). The drying process of herbs usually includes low or high mechanization processing levels using flat-bed or conveyor belt dryers respectively (Heindl & Müller, 1997). After drying, the material is packed and kept at indoor climate conditions in the storage facilities until further processing. For the optimization of storage stability, knowledge of the equilibrium relationship between the moisture content (MC) in the plant material and the relative humidity (RH) of the surrounding air at a given temperature is required to prevent decline of quality by microbial or enzymatic activity (Karel, 1975). The moisture adsorption data can be further analyzed to provide a theoretical interpretation of food microstructure and physical interaction between water molecules and the solid matter of a foodstuff (Rizvi, 1986).

The measurement of moisture sorption isotherms usually relies on the static gravimetric method using thermally stabilized desiccators filled with saturated salt solutions as described in a study conducted by Spiess and Wolf (1987). Although this method is still commonly employed, automated humidity generating instruments have been introduced to the market for the continuous determination of sorption isotherms in a dynamic system. For instance, the Dynamic Vapor Sorption (DVS) method is designed to measure the equilibrium moisture content of a material at any desired relative humidity and selected temperatures in a short period of time. It has been applied to measure the moisture sorption properties of cellulosic reinforcement fibers (Kohler, Dück, Ausperger, & Alex, 2003), microcrystalline cellulose (Kachrimanis, Noisternig, Griesser, & Malamataris, 2006), lactose (Vollenbroek, Hebbink, Ziffels, & Steckel, 2010), wood (Hill, Norton, & Newman, 2010)

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and natural fibers (Xie et al., 2011). However, limited attempts have been performed to examine the moisture sorption behavior of foodstuffs (Desmorieux & Decaen, 2006; Roca, Broyart, Guillard, Guilbert, & Gontard, 2007; Ziegleder, Amanitis, & Hornik, 2004) and especially of agricultural products (Argyropoulos, Alex, & Müller, 2011b) using a DVS system.

Recently, comprehensive reviews on sorption characteristics of foodstuffs have been reported in the literature (Al-Muhtaseb, McMinn, & Magee, 2002; Basu, Shivhare, & Mujumdar, 2006). Among the several empirical, partially theoretical and theoretical equations for moisture sorption isotherms (van den Berg & Bruin, 1981), the modified equations of Oswin (Chen, 1988; Oswin, 1946), Halsey (Halsey, 1948; Iglesias & Chirife, 1976a,b), Henderson (Henderson, 1952; Thompson, Peart, & Foster, 1968), Chung–Pfost (Chung & Pfost, 1967a,b; Pfost, Maurer, Chung, & Milliken, 1976) and Guggenheim–Anderson–de Boer (GAB) (van den Berg, 1984; Jayas & Mazza, 1993) models have been commonly applied to fit the equilibrium MC/RH data of various agricultural products and foods.

The moisture sorption isotherms of various leafy materials with medicinal and therapeutic properties have been studied by employing mainly the static gravimetric method for *Olea europaea* L. (Bahloul, Boudhrioua, & Kechaou, 2008; Nourhène, Neila, Mohammed, & Nabil, 2008), *Citrus x hystrix* DC. (Phoungchandang, Srinukroh, & Leenanon, 2008), *Citrus reticulata* B. (Jamali, Kouhila, Mohamed, Idlimam, & Lamharrar, 2006), *Citrus x aurantium* L. (AitMohamed, Kouhila, Jamali, Lahsasni, & Mahrouz, 2005), *Dysphania ambrosioides* L. (Jamali, Kouhila, Mohamed, Jaouhari et al., 2006), *Maytenus ilicifolia* Mart. Ex Reissek (Cordeiro, Raghavan, & Oliveira, 2006) and *Eucalyptus globulus* Labill. (Kouhila, Kechaou, Otmani, Fliyou, & Lahsasni, 2002). Soysal and Öztekin (1999) investigated the equilibrium moisture content of several medicinal and aromatic plants including some herbs of the mint family (Lamiaceae) such as *Origanum majorana* L., *Thymus vulgaris* L. and *Mentha x piperita* L. Additionally, the authors reported another work about the isosteric heat of sorption for selected medicinal and aromatic plants (Soysal & Öztekin, 2001) by dividing them into three major groups. It was found that the magnitude of the sorption heat was dependent on the species and type of the plant group. Moreover, the moisture sorption isotherms of *Mentha viridis* L. and *Salvia officinalis* L. (Kouhila, Belghit, Daguenet, & Boutaleb, 2001), *Mentha crispa* L. (Jin Park, Vohnikova, & Pedro Reis Brod, 2002), *Rosmarinus officinalis* L. (Timoumi & Zagrouba, 2005) have also been documented, however, limited experimental moisture sorption data for lemon balm *M. officinalis* L. can be retrieved from the literature (Argyropoulos, Alex, & Müller, 2011a).

Therefore, the objectives of the present work were (i) to investigate the moisture sorption behavior of leaves and stems of lemon balm using a dynamic vapor sorption apparatus at temperatures typically found in storage and processing of medicinal plants (ii) to find the most appropriate mathematical model to describe the experimental sorption data and (iii) to estimate the isosteric heat of sorption.

## 2. Materials and methods

### 2.1. Material

Herbs of lemon balm (*M. officinalis* L.) cultivar Citronella were collected before flowering from an organic farm in Magstadt, approximately 20 km west of Stuttgart (Germany). The material was obtained by cutting the herb manually to a height of about 20 cm above the ground. Prior to experiments, the leaves were picked manually from the stems. The samples were dried in a high precision hot-air laboratory dryer (Argyropoulos, Heindl, & Müller, 2011) at a temperature of 40 °C, maintaining 10 g/kg of specific humidity and an air velocity of 0.2 m/s (Argyropoulos & Müller, 2011) until constant mass was achieved. The dried leaves and stems were kept packed in aluminum coated polyethylene bags and stored at ambient conditions in the laboratory before the determination of moisture sorption isotherms.

### 2.2. DVS apparatus

The adsorption isotherms of the samples were determined by DVS at the Reutlingen Research Institute, Reutlingen University, Germany using a DVS-1000 gravimetric moisture sorption analyzer (Surface Measurement Systems Ltd., London, U.K.). The instrument essentially consists of a Cahn microbalance with two sample crucibles made of quartz and a humidification system in a temperature controlled chamber. One of the crucibles is used as a reference whereby the other contains the sample to be analyzed. A stream of dry and wet nitrogen gas flows along the crucibles. The relative humidity of the mixture is regulated by two electronic mass flow controllers. The apparatus is computer controlled, allowing pre-programming of stepwise variation of relative humidity at set temperature and continuous measurement of temperature, humidity and mass during the sorption process.

### 2.3. Experimental procedure

Pre-dried samples of leaves and stems with masses of 12.67 ± 1.63 and 16.11 ± 1.12 mg respectively were used for the experiments. The adsorption isotherms were determined at temperatures of 25, 35 and 45 °C by exposing the material to different values of relative humidity within the range of 3 and 90%. Each sample was first dried by exposure to dry nitrogen until a constant weight of the sample was reached. The dry reference mass was established for both tissues within 16 h. Then, the relative humidity was subsequently increased stepwise whereby the sample weight was equilibrated at each step. Mass, temperature and humidity data were recorded in 2 min time intervals. Equilibrium was considered to have been reached when the change in mass was less than 0.001 mg/min. To obtain the adsorption isotherms, the moisture content of the sample, expressed in kg water per kg dry solids, was calculated at equilibrium of each relative humidity step. Three consecutive measurements for each material and temperature were performed at a total of fourteen target values of relative humidity.

### 2.4. Mathematical description of sorption isotherms

The five three-parameter moisture sorption equations tested for their accuracy to fit the experimental sorption data are listed below. The models are presented in terms of moisture content, $X_e$ dry basis (kg/kg d.b.), water activity $a_w$ (equilibrium RH/100), temperature $T$ (°C) and $a$, $b$, $c$ as model constants.

Modified Chung–Pfost

$$X_e = \frac{-1}{a}\ln\left[-\frac{(T+b)}{c}\ln(a_w)\right] \quad (1)$$

Modified Oswin

$$X_e = (a+b\cdot T)\left[\frac{a_w}{1-a_w}\right]^{1/c} \quad (2)$$

Modified Halsey

$$X_e = \left[\frac{-\exp(a + b \cdot T)}{\ln(a_w)}\right]^{1/c} \tag{3}$$

Modified Henderson

$$X_e = \left[-\frac{1}{a(T+b)}\ln(1-a_w)\right]^{1/c} \tag{4}$$

Modified GAB

$$X_e = \frac{a\left(\frac{c}{T}\right)ba_w}{(1-ba_w)\left[1-ba_w+\left(\frac{c}{T}\right)ba_w\right]} \tag{5}$$

### 2.5. Determination of the isosteric heat of sorption

The net isosteric heat of sorption was calculated from the moisture sorption data at temperatures of 25–45 °C using the best-fitting model and the integrated form of the Clausius–Clapeyron equation (Iglesias & Chirife, 1976c,d).

$$\left[\frac{d\ln(a_w)}{d(T)}\right]_X = \frac{q_{st}^n}{RT^2} \tag{6}$$

$$q_{st}^n = R\left[\frac{T_1T_2}{T_2-T_1}\ln\frac{a_{w_2}}{a_{w_1}}\right] \tag{7}$$

where $a_w$ is the water activity (–), $T$ is the absolute temperature (K), $q_{st}^n$ is the net isosteric heat of sorption (kJ/kg) and $R$ is the universal gas constant (8.314 J/mol·K).

The isosteric heat of adsorption is defined as the sum of the net isosteric heat of adsorption and the latent heat of condensation for pure water vapor at the system's temperature. Furthermore, an empirical function (Mulet, García-Pascual, Sanjuan, & García-Reverter, 2002; Mulet, García-Reverter, Sanjuán, & Bon, 1999) was used to model the interaction between the isosteric heat of sorption and the equilibrium moisture content of each plant organ by applying the following equation to the experimental data:

$$Q_{st} = q_{st}^n + L_r = d \cdot \exp(-g \cdot X_e) + L_r \tag{8}$$

where $Q_{st}$ is the isosteric heat of sorption (kJ/kg water), $X_e$ is the equilibrium moisture content (kg/kg d.b.), $d$ and $g$ are constants and $L_r$ is the latent heat of condensation of pure water vapor at 35 °C (43.53 kJ/mol or 2416.32 kJ/kg), as the average of the three temperatures considered in this work.

### 2.6. Statistical analysis

The values of the parameters were determined by fitting the models to the experimental data using the non-linear least squares procedure (Matlab v. R2010b, Mathworks, Inc.). The accuracy of fit was evaluated by the $R$-squared ($R^2$), the Sum of Squared Error (SSE) and the Root Mean Squared Error (RMSE). Two-way analysis of variance (ANOVA) followed by Tukey's test for multiply comparisons were performed on the experimental sorption data by OriginLab (OriginPro v. 8.0 SR2).

## 3. Results and discussion

### 3.1. Moisture sorption profiles

The temporal profile of moisture contents of lemon balm leaves and stems, using a dynamic vapor sorption instrument is shown exemplarily for 25 °C in Fig. 1. Absorption of moisture after increasing relative humidity can be observed as an increase in mass. It took up to 6 h for the samples to reach equilibrium. Exceptions were observed for the stems equilibrated at values of relative humidity of 85 and 90% where constant weights of the sample were achieved at longer periods. The mean values of the equilibrium moisture content ($X_e$, kg/kg d.b.) at each relative humidity step obtained from a triplicate experiment for leaves and stems are listed in Table 1. The standard deviations of these measurements varied from 0.001 to 0.025 kg/kg for the leaves, and varied from 0.001 to 0.027 kg/kg for the stems. In general, adequate precision was observed for all target values of relative humidity up to 90%, nevertheless greater stability was documented at lower values of relative humidity.

### 3.2. Adsorption isotherms

Fig. 2 shows the experimental results (points) of the sorption data and curves (solid lines) predicted by the selected models at temperatures of 25, 35 and 45 °C for the leaves. Similarly the adsorption isotherms of the stems are shown in Fig. 3. The data resemble the characteristic sigmoid shape of the type II pattern isotherm according to Brunauer's classification (Brunauer, 1943) which is frequently found for biological and food materials (Blahovec, 2004). This means, the plant material absorbed small amounts of water at low values of water activity, followed by a gradual higher moisture uptake as water activity increased and exhibited an asymptotic trend at the upper end of the sorption isotherm. As expected, the equilibrium moisture contents of leaves and stems increased with water activity at a constant temperature. Moreover, at a constant water activity the equilibrium moisture contents decreased with an increase of temperature, however

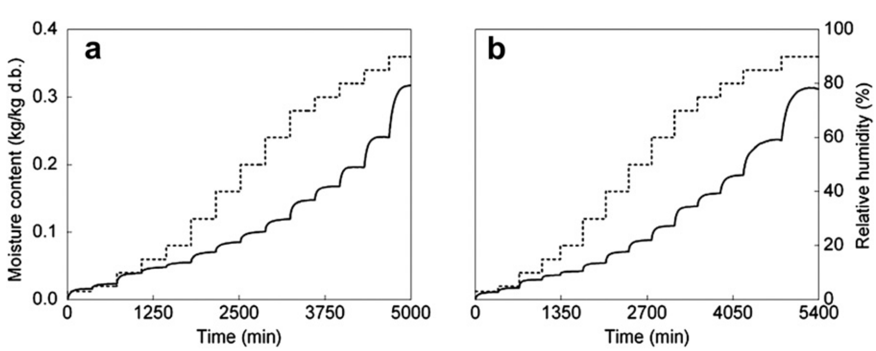


**Fig. 1.** Temporal moisture adsorption profiles for (a) leaves and (b) stems of lemon balm exposed to stepwise increase of relative humidity at 25 °C (— EMC, - - - Target RH).

**Table 1**
Equilibrium moisture content ($X_e$, kg/kg d.b.) of leaves and stems of lemon balm for adsorption by stepwise increase of relative humidity ($a_w$ = RH/100) at 25, 35 and 45 °C.

| $a_w$ | Leaves | | | Stems | | |
|---|---|---|---|---|---|---|
| | 25 | 35 | 45 | 25 | 35 | 45 |
| 0.03 | 0.016 ± 0.002 | 0.016 ± 0.002 | 0.016 ± 0.001 | 0.011 ± 0.001 | 0.011 ± 0 | 0.012 ± 0.002 |
| 0.05 | 0.024 ± 0.002 | 0.022 ± 0.002 | 0.022 ± 0 | 0.017 ± 0.001 | 0.017 ± 0.001 | 0.016 ± 0.002 |
| 0.10 | 0.039 ± 0.002 | 0.034 ± 0.003 | 0.034 ± 0 | 0.030 ± 0 | 0.028 ± 0.002 | 0.026 ± 0.002 |
| 0.15 | 0.048 ± 0.002 | 0.043 ± 0.003 | 0.043 ± 0 | 0.037 ± 0.001 | 0.036 ± 0.001 | 0.034 ± 0.003 |
| 0.20 | 0.056 ± 0.003 | 0.050 ± 0.003 | 0.051 ± 0.001 | 0.043 ± 0.001 | 0.043 ± 0.001 | 0.040 ± 0.003 |
| 0.30 | 0.070 ± 0.003 | 0.065 ± 0.004 | 0.066 ± 0.001 | 0.055 ± 0.001 | 0.056 ± 0.002 | 0.054 ± 0.003 |
| 0.40 | 0.085 ± 0.004 | 0.079 ± 0.004 | 0.081 ± 0 | 0.070 ± 0.002 | 0.070 ± 0.002 | 0.069 ± 0.002 |
| 0.50 | 0.101 ± 0.006 | 0.095 ± 0.002 | 0.096 ± 0.002 | 0.088 ± 0 | 0.086 ± 0.003 | 0.085 ± 0.004 |
| 0.60 | 0.119 ± 0.008 | 0.116 ± 0.001 | 0.112 ± 0.002 | 0.112 ± 0.003 | 0.106 ± 0.003 | 0.107 ± 0.004 |
| 0.70 | 0.147 ± 0.007 | 0.145 ± 0.003 | 0.138 ± 0.004 | 0.143 ± 0.005 | 0.133 ± 0.004 | 0.134 ± 0.005 |
| 0.75 | 0.168 ± 0.009 | 0.165 ± 0.007 | 0.154 ± 0.007 | 0.163 ± 0.006 | 0.151 ± 0.005 | 0.151 ± 0.005 |
| 0.80 | 0.196 ± 0.011 | 0.198 ± 0.010 | 0.178 ± 0.009 | 0.192 ± 0.010 | 0.177 ± 0.007 | 0.178 ± 0.006 |
| 0.85 | 0.240 ± 0.016 | 0.248 ± 0.017 | 0.219 ± 0.015 | 0.244 ± 0.010 | 0.217 ± 0.011 | 0.217 ± 0.012 |
| 0.90 | 0.317 ± 0.025 | 0.346 ± 0.022 | 0.278 ± 0.023 | 0.324 ± 0.017 | 0.291 ± 0.027 | 0.279 ± 0.020 |

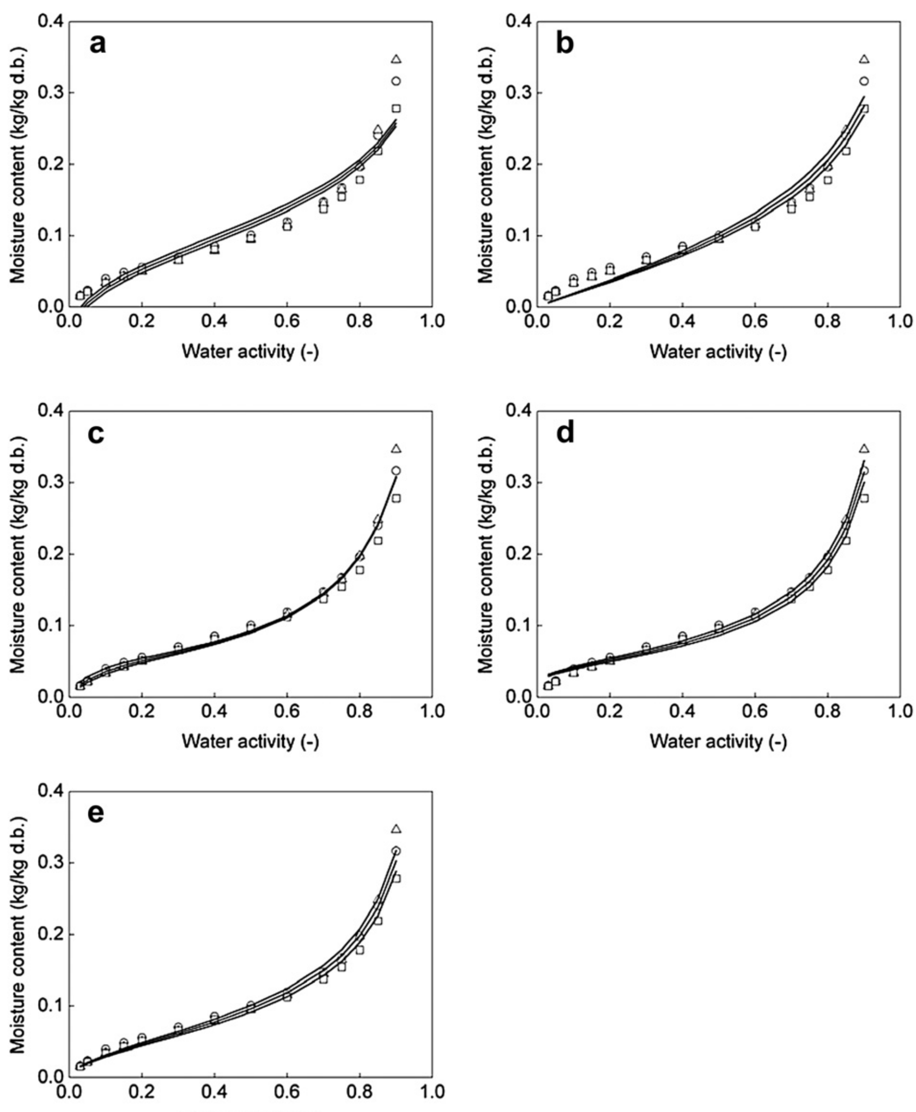


**Fig. 2.** Adsorption isotherms of lemon balm leaves at (○) 25, (△) 35 and (□) 45 °C fitted by the modified (a) Chung–Pfost, (b) Henderson, (c) GAB, (d) Halsey and (e) Oswin equation.

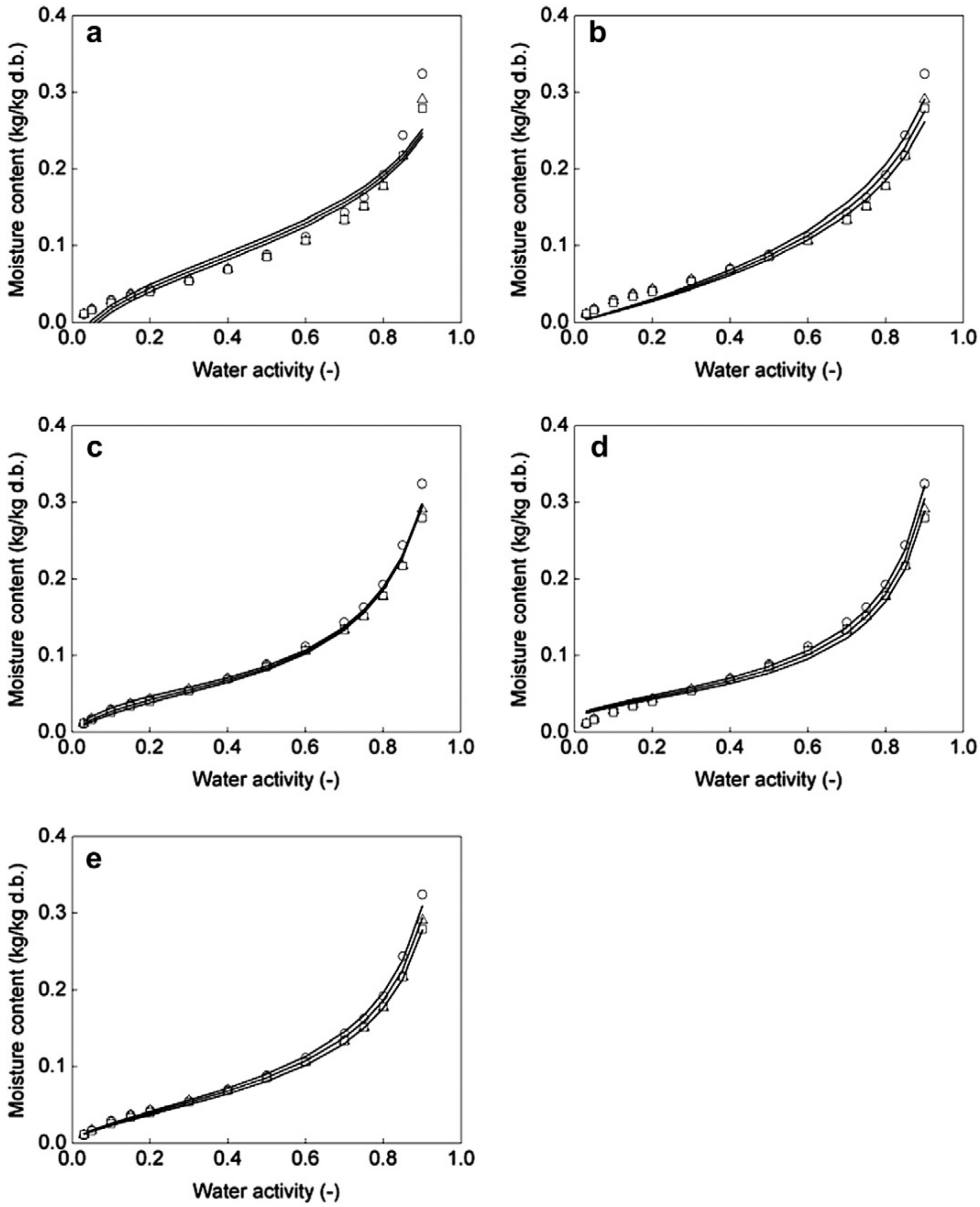


**Fig. 3.** Adsorption isotherms of lemon balm stems at (○) 25, (△) 35 and (□) 45 °C fitted by the modified (a) Chung–Pfost, (b) Henderson, (c) GAB, (d) Halsey and (e) Oswin equation.

different patterns between the adsorption isotherms of leaves and stems were observed. More specifically, there is an insignificant influence of temperature on the equilibrium moisture content of leaves in the range of 25 and 35 °C ($p > 0.05$). In contrast, the statistical analysis revealed the significant effect of temperature on the adsorption isotherm of leaves at 45 °C ($p < 0.05$). As far as the equilibrium moisture contents of stems are concerned, statistically identical values for 35 and 45 °C ($p < 0.05$) were recorded. A decrease in temperature to 25 °C indicated its significant influence on the equilibrium moisture content of stems ($p < 0.05$). The different behaviors in moisture absorption between the two plant organs at the same temperatures can be ascribed to differences in the tissue structure and chemical composition (Ashori, Hamzeh, & Amani, 2011; Dastmalchi et al., 2008) which consequently affect the diffusion of water from the surface to the interior of the material. Moreover, controversial results regarding the effect of temperature on equilibrium MC at a constant water activity have been published in the literature. Arabhosseini, Huisman, van Boxtel, and Müller (2006) found that a change in temperature between 25 and 70 °C affected the equilibrium MC of tarragon whereas Kaya and Kahyaoglu (2007) pointed out that there was no effect of temperature on the sorption isotherms of tarragon leaves between 15 and 35 °C. It can be speculated that the temperature range investigated in the latter study was not large enough to cause an increase to the excitation state of water molecules (McLaughlin & Magee, 1998). In addition, drying prior to sorption may modify the intermolecular forces between the water vapor and the solid matter of the product (Moreira, Chenlo, Vazquez, & Camean, 2005). It is worth mentioning that in the current work, according to the statistical analysis, the values of equilibrium moisture content of leaves were significantly different than those of stems ($p < 0.05$), independently of temperature. A similar result has been reported for miscanthus (Arabhosseini, Huisman, & Müller, 2010) as well as alfalfa (Arabhosseini, Huisman, & Müller, 2011) stems and leaves. In particular, the leaves indicated a higher moisture sorption capacity for $0.03 \leq a_w < 0.8$.

### 3.3. Fitting of sorption models to experimental data

The values of the constants for each model along with the corresponding statistical criteria selected to assess the goodness of fit are presented in Table 2. Among the various three-parameter models tested the modified Oswin equation yielded the most accurate fit to the experimental data of both leaves and stems at $25 \leq T \leq 45$ °C and $0.03 \leq a_w \leq 0.9$. Oswin equation was ranked best since it has exhibited the highest $R^2$, while indicated the lowest SEE and RMSE. The adsorption isotherms of the leaves and stems at a temperature of 25 °C fitted by the modified Oswin equation are jointly presented in Fig. 4. The modified Halsey equation could also represent the experimental sorption data for both tissues adequately, however, did not fit very well for $a_w < 0.1$. A work conducted by Soysal and Öztekin (2001) on the moisture sorption data of selected medicinal and aromatic plants proposed the modified Oswin and Halsey equations as the most appropriate to describe their adsorption isotherms. Similarly, the modified Halsey equation predicted the equilibrium moisture content of withered leaves, black and green tea adequately (Ghodake, Goswami, & Chakraverty, 2007). Although the modified GAB equation yielded relatively high $R^2$ as well as low SSE and RMSE values, this model was unable to predict the adsorption isotherms of the plant organs at different temperatures between 25 and 45 °C. Moreover, the modified Henderson and Chung–Pfost equations were considered as inappropriate models to describe the sorption isotherms of the leaves and stems of lemon balm. Consequently, the equilibrium values of moisture content for leaves and stems at the microbial safe water activity of 0.6 and a selected temperature were calculated by the modified Oswin model. The leaves and stems should be stored at a maximum moisture content of 11.0 and 10.1% w.b. (wet basis) respectively in order to prevent the growth of microorganisms or quality deterioration at 25 °C. The European Pharmacopoeia (Ph. Eur. 6.00, 2008) prescribes a value of 10% w.b. for lemon balm leaves. Since the plant is typically being dried and stored as a whole herb, the material including leaves and small stems is recommended to be dried to a moisture content of 10% w.b. when is intended to be stored at a temperature of 25 °C.

**Table 2**
Estimated coefficients and accuracy of fit for different three-parameter moisture sorption models to describe the adsorption isotherms of leaves and stems of lemon balm.

| | GAB | Halsey | Henderson | Oswin | Chung–Pfost |
|---|---|---|---|---|---|
| *Leaves* | | | | | |
| *a* | 0.05261 | −3.743 | 0.05026 | 0.1121 | 13.28 |
| *b* | 0.9236 | −0.007109 | 159.8 | −0.00046 | 121.2 |
| *c* | 575.8 | 1.509 | 1.143 | 1.911 | 506.5 |
| $R^2$ | 0.9876 | 0.988 | 0.9611 | 0.9889 | 0.9293 |
| SSE | 0.0037 | 0.0036 | 0.0118 | 0.0034 | 0.0214 |
| RMSE | 0.0098 | 0.0097 | 0.0174 | 0.0093 | 0.0234 |
| *Stems* | | | | | |
| *a* | 0.05044 | −3.674 | 0.04918 | 0.1018 | 13.49 |
| *b* | 0.9249 | −0.007792 | 143.6 | −0.0004576 | 126.5 |
| *c* | 327.5 | 1.427 | 1.038 | 1.785 | 473.8 |
| $R^2$ | 0.9937 | 0.9916 | 0.9794 | 0.9974 | 0.9353 |
| SSE | 0.0019 | 0.0025 | 0.006 | 0.00076 | 0.0189 |
| RMSE | 0.0069 | 0.0079 | 0.0124 | 0.0044 | 0.022 |

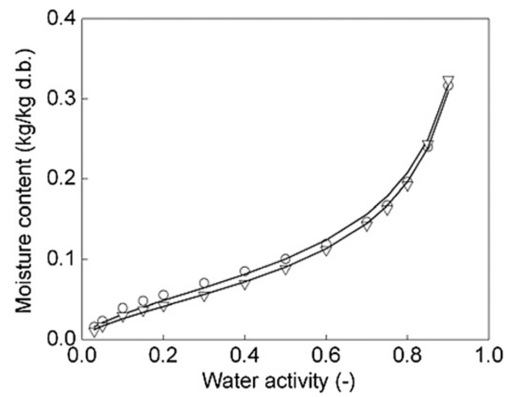


**Fig. 4.** Adsorption isotherms of (○) leaves and (▽) stems of lemon balm fitted by the modified (—) Oswin equation at 25 °C.

### 3.4. Isosteric heat of sorption

The modified Oswin equation was selected to predict the water activities at different temperatures and selected moisture content in order to estimate the net isosteric heat of sorption using the derived expressions from equation (8) for leaves and stems respectively:

$$a_w = \frac{1}{1 + \left(\frac{0.1121 - 0.00046 \cdot T}{X_e}\right)^{1.911}} \tag{9}$$

$$a_w = \frac{1}{1 + \left(\frac{0.1018 - 0.00046 \cdot T}{X_e}\right)^{1.785}} \tag{10}$$

The isosteric heat of sorption was computed for different moisture contents ranging between 0.02 and 0.30 kg/kg. Fig. 5 shows the isosteric heat of sorption as a function of the moisture content at an average temperature of 35 °C for lemon balm leaves and stems. At a moisture content of 0.02 kg water per kg dry solids the estimated isosteric heat of sorption was approximately 2800 kJ per kg water for both plant tissues. As the moisture content increased, the isosteric heat of sorption decreased sharply and reached a value of 2600 kJ/kg at a moisture content of 0.10 kg/kg. This can be explained by the fact that the available sites for moisture adsorption become occupied resulting in lower values of isosteric heat of sorption (Tsami, Maroulis, Marinos-Kouris, & Saravacos, 1990). Since there are more active polar sites on the surface of the plant tissue at low moisture content, the isosteric heat of sorption is assumed to be higher. A further decrease in the heat of sorption was recorded at higher moisture contents and both tissues approached the value of latent heat for condensation of pure water vapor at $X_e \geq 0.25$ kg/kg. The heat of adsorption provides an indication of the energy released during the sorption process by the interaction between the sorption sites and molecules of water vapor (Wang & Brennan, 1991). Therefore, the values of sorption heat reported in the present study revealed the existence of large amounts of bound water. The results are in agreement with a previous work published for green tea (Sinija & Mishra, 2008). On the other hand, the values of the isosteric heat of adsorption for lemon balm leaves at $X_e < 0.10$ kg/kg were lower than the values computed by Soysal and Öztekin (2001) for peppermint and marjoram. In general, a similar behavior between the leaves and

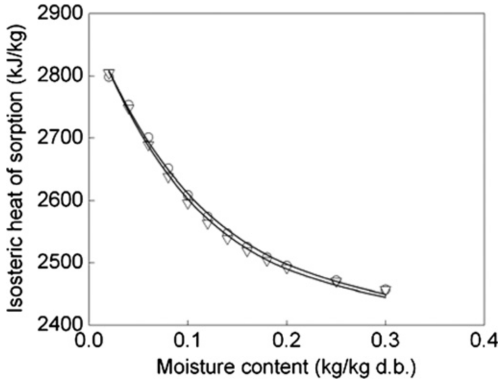


**Fig. 5.** Isosteric heat of sorption as a function of moisture content for (○) leaves and (▽) stems of lemon balm, (—) model.

stems was observed although slightly higher values of the isosteric heat of sorption were predicted by the model for the leaves at $0.1 \le X_e \le 0.3$ kg/kg. The mathematical expressions below can be used to calculate the isosteric heat of sorption at different moisture content for:

Leaves

$$Q_{st} = 467.5\exp(-8.802X_e) + L_r \quad (R^2 = 0.9970)$$

Stems

$$Q_{st} = 471.3\exp(-9.348X_e) + L_r \quad (R^2 = 0.9973)$$

## 4. Conclusions

The moisture sorption isotherms of *M. officinalis* were established using an automated DVS system at three temperatures (25, 35 and 45 °C) and fourteen values of relative humidity within the range of 3–90%. The small required sample size significantly reduced the time to reach equilibrium. The influence of temperature on the sorption capacity was considered significant for leaves at $35 < T < 45$ °C and for stems at $25 < T < 35$ °C. The equilibrium moisture contents of leaves were significantly higher than those of stems for $0.03 \le a_w < 0.8$. The different moisture sorption behavior of leaves and stems can be attributed to different composition and structure of the tissues. The modified Oswin equation was found to be the best model to describe the experimental sorption data for both leaves and stems of lemon balm at $25 \le T \le 45$ °C. The recommended values of moisture content for leaves and stems at the threshold $a_w$ of 0.6 for storage at a temperature of 25 °C were 11.0 and 10.1% w.b. respectively. The sorption isosteric heat of *M. officinalis* decreased as moisture content increased and equations were developed to predict the sorption isosteric heats of leaves and stems at different moisture contents.

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