



Analysis of adsorption–desorption moisture isotherms of rosemary leaves



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ABSTRACT

The moisture sorption isotherms data of rosemary leaves were investigated via the gravimetric static method at three different temperatures (30, 40 and 50 °C). The sorption isotherms obtained were of sigmoid shape and of type II of Brunauer classification. From various mathematical models used for our experimental data, The GAB model best described the experimental data. The sorption data were analyzed for determination of monolayer moisture content (3.4–9.7%), and properties of sorbed water. Analysis of sorption isotherm by the model of the Yanniotis and Blahovec shows that the contribution of surface adsorption in relation to solution water at each water activity was higher in desorption than in adsorption. The net isosteric heat of desorption and adsorption of the rosemary leaves ranged respectively from 1.77 to 47.37 kJ/mol and from 0.85 to 26.86 kJ/mol. The enthalpy–entropy compensation suggested that the sorption mechanism involved was enthalpy driven. The net integral enthalpy of adsorption and desorption decreased with increasing equilibrium moisture content. The integral entropy increased with moisture content, but was of negative value.

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1. Introduction

In recent years, rosemary (*Rosmarinus officinalis* L.) has been extensively studied as a source among natural bioactive compounds due to its powerful antioxidant and anti-inflammatory activity, antibacterial and antimutagenic properties, and as a chemopreventive agent (Bubonja-Sonje et al., 2011; Tai et al., 2012). Antioxidant activity of rosemary justifies its use in a broad range of applications, including food preservation (Hamre et al., 2010), cosmetics (Lee et al., 2011), nutraceuticals and phytomedicines (Ibarra et al., 2010). Consequently, there is a high interest among the scientific community in attaining bioactive extracts from rosemary. The use of fresh rosemary is limited, and in the food industry the dry form of rosemary is commonly used. Fresh herbs (especially Lamiaceae) usually contain 75–80% water, and water levels need to be lowered to less than 15% for their preservation (Díaz-Maroto et al., 2002). Due to their high moisture content and vulnerability to micro organisms, it is very important to provide optimum drying and storage conditions in order to prevent quality. The drying increases the shelf life of plants by slowing micro organism growth and by preventing biochemical reactions that can alter organolep-

tic characteristics (Hamrouni-Sellami et al., 2009). Nevertheless, during storage and drying of biological materials, physical, chemical and microbiological transformation can happen. The knowledge of the sorption isotherms allows to select the appropriate final point of a drying operation and storage stability. Also, knowledge of physico-chemical nature of water bounded to the solid matrix is fundamental to understand the effect of water content and storage conditions on food stability. Properties such as enthalpy, entropy and Gibbs free energy are useful to explain reactions and phenomena at molecular level in materials. These properties represent the amount of energy, the order or excited state and the chemical equilibrium of the water molecules inside the material, respectively (Brovchenko and Oleinikova, 2008). Moisture sorption characteristic of a food is influenced by the surface area and number of surface binding sites i.e., physical stability like porosity and microstructure (Choudhury et al., 2011). Therefore, the influence of temperature on monolayer moisture content, number of sorbed monolayers, density of sorbed water, surface area of sorbent and percent bound water are required to be studied.

Models available in the literature to describe moisture sorption isotherm can be divided into several categories (Siripatrawan and Jantawat, 2006): kinetic models based on a mono-layer (Mod-BET model), kinetic models based on a multi-layer and condensed film (GAB model), semi-empirical (Henderson and Halsey models) and empirical models (Peleg and Oswin models).

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Numerous mathematical equations have been proposed to correlate the sorption isotherms values of aromatic and medicinal plants (Argyropoulos et al., 2012; Bahloul et al., 2008; Cordeiro et al., 2006; Kouhila et al., 2002). Timoumi and Zagrouba (2005) conducted an experimental study about modeling of desorption isotherm of rosemary leaves. They found the GAB model as the best fit model to their desorption isotherm data. Chenarbon et al. (2012) determined the moisture sorption of rosemary flowers, and stated that the Halsey and GAB models provided the best fit for sorption isotherm. The GAB model is considered to be the most versatile sorption model available in the literature.

Literature survey revealed that monolayer moisture content, the properties of sorbed water and the thermodynamic properties of rosemary leaves have not been reported.

The objectives of this paper were: (1) to determine experimentally the adsorption and the desorption isotherms of rosemary leaves at 30, 40 and 50 °C, (2) to mathematically model the experimental data, (3) to calculate the properties of sorber water and (4) to determine the thermodynamic functions (differential enthalpy, integral enthalpy, differential entropy and integral entropy) for the adsorption and desorption isotherms of rosemary leaves.

2. Material and methods

2.1. Sample preparation

Rosemary leaves were collected from plants growing in the garden of the university located 15 km east of Algiers (Algeria). The rosemary leaves were dried in an oven at 40 °C until a constant weight was reached (m). The dry mass (m_d) was determined by drying rosemary in oven at 105 °C for 24 h. The difference of the mass (m) and the mass (m_d) allows the determination of the products moisture content on dry weight basis. The mean moisture content of dried rosemary leaves was 0.035 kg/kg (dry basis), and the moisture content of fresh rosemary was 0.764 kg/kg (wet basis).

2.2. Sorption isotherms measurements

The equilibrium moisture contents of rosemary leaves were determined by a gravimetric technique. Six saturated salts solutions (KOH, MgCl₂·6H₂O, K₂CO₃, NaNO₃, KCl, BaCl₂) were used to provide constant water activities ranging from 0.05 to 0.90 (Kouhila et al., 2001). The experimental apparatus used consists of six glass jars of one liter with insulated lid. The leaves were placed on a perforated tray at 100 mm from the base of the vessel to avoid any contact between the saturated salts solution and the sample of rosemary leaves. The initial leaf mass used was of about 0.5 ± 0.001 g for desorption experiments and 0.15 ± 0.001 g for adsorption experiments. The vessel was then placed in an oven at controlled temperature of 30, 40 and 50 °C. The rosemary leaves samples were weighed every 2 days using an analytical balance (±0.0001 g). The equilibrium moisture content (X_{eq}) was determined when consecutive weight measurements showed a difference of less than 0.001 g (after 12–15 days). The dry matter content of equilibrated samples was determined by using drying oven, which its temperature was fixed at 105 °C for 24 h. All moisture sorption experiments were done in triplicate and the average values were used for further data analysis.

2.3. Data analysis

2.3.1. Modelling of sorption isotherms

The experimental adsorption and desorption data of rosemary leaves at three different temperatures were fitted to eleven sorption equations, however, only the best models are summarized in Table 1. Precision of fit of the experimental data to all models was

evaluated using the coefficient of determination (R^2), root mean square error (RMSE), Chi-square (χ^2) statistics and average absolute deviation (AAD). The statistical evaluations were made on the predictions of equilibrium moisture content by sorption isotherms. A model is considered acceptable if it has an AAD value less than 10% (Lomauro et al., 1985). The model with lowest RMSE, and χ^2 and highest coefficient of determination (R^2) was selected.

In the GAB model, C_G is a constant related to the first layer heat of sorption and k is a factor related to the heat of sorption of the multi-layer. The influence of temperature on the GAB parameters C_G and k can be expressed with an Arrhenius equation (Arslan and Toğrul, 2006).

$$C_G = c_0 \exp \left[\frac{H_1 - H_m}{RT} \right] \quad (1)$$

$$k = k_0 \exp \left[\frac{H_L - H_m}{RT} \right] \quad (2)$$

where c_0 and k_0 are pre-exponential factors; H_1 , H_m and H_L (kJ mol⁻¹) are respectively, molar sorption enthalpies of the mono-molecular layer, of the multi-layer and the bulk liquid water. R is the universal gas constant in kJ mol⁻¹ K⁻¹; and T is the temperature in K. ΔH_c ($H_1 - H_m$) and ΔH_k ($H_L - H_m$) represent the difference in enthalpy between mono-layer and multilayer sorption and the difference between the heat of condensation of water and the heat of sorption of the multi-layer, respectively.

Evaluation of the parameters c_0 , k_0 , H_1 and H_m is carried out using non-linear regression analysis, with Eqs. (1) and (2) being substituted into the GAB equation in Table 1.

The monolayer moisture content X_0 , can be determined from the equilibrium sorption isotherm data by fitting BET, GAB and Caurie expressions. The prediction of X_0 has a significant importance for physical and chemical stability of foods. Below X_0 values, food deterioration is expected to be extremely small, because water is strongly bound to the food and water is not involved in any deteriorative reaction (Dalgıç et al., 2012). Treatment of sorption data to Caurie equation allows the evaluation of the number of binding sites, the influence of temperature on monolayer, density of sorbed water, surface area of adsorbent and percent non-freezable or bound water. The number of adsorbed monolayers (N) (Rao et al., 2006) was calculated using;

$$N = \frac{X_c}{C_c} \quad (3)$$

where X_c is the monolayer moisture content from Caurie's equation and C_c is Caurie's constant. Assuming that the magnitude of C_c equals the density of adsorbed water in the monolayer, the surface area of adsorbent (A) was calculated as:

$$A = \frac{X_c}{c_c d 10^8} \quad (4)$$

where d is the diameter of water molecule ($d = 3.673 \times 10^{-10}$ m).

2.3.2. Isosteric heat of sorption and entropy of sorption

The net isosteric heat of sorption (q_n) is the amount of energy above the heat of vaporization of water (H_L) associated with the sorption process, and it is calculated from the experimental data using the Clausius–Clapeyron equation (Tsami, 1991).

$$q_n = -R \left[\frac{d \ln(a_w)}{d(1/T)} \right]_x \quad (5)$$

where q_n is the net isosteric heat of sorption (kJ/mol), a_w the water activity (dimensionless), T the absolute temperature (K), R the universal gas constant (kJ/mol K) and X the moisture content (kg/kg).

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