INTRODUCTION
The citrus is one of the most extensively consumed fruits in the world. In this important group, lemons and limes represented about 11% (~1.4 Mt) of the citrus world production in 2009. The main producing countries of lemons and limes in 2008 were India (18.2%), Mexico (16.2%), Argentina (9.9%), Brazil (7%) and China (6.7%) (FAOSTAT 2011).

Lemons and limes production is destined for fresh fruit markets, processing juice, pectin and essential oil. The industrial processing of limes and lemons generates a large quantity of wastes that can range between 49 and 69% of the initial weight. These wastes include peel, segment membranes, seeds, and other by-products.

Some studies have reported the use of citrus seeds for production of essential oil (Waheed et al. 2009) and biofuels (Pourbafrani et al. 2010).

The oil from the lemon and lime seeds has potential use in various products and industrial applications. This oil consists mainly of unsaturated fatty acids (about 64%), where the essential fatty acid content (linoleic and linolenic) is about 40%. Lemon and lime seed oil is also an important source of tocopherols (Waheed et al. 2009).

The thermodynamic properties of water and the moisture sorption isotherms are useful tools to determine water/material interactions and to provide essential information for assessing processing operations such as drying, mixing and storage. These properties may also help to establish the final moisture content and to estimate the energy requirements on processing (Eim et al. 2011).

The main objectives of this study were: to determine the water sorption for Key lime (Citrus aurantifolia) seeds at different temperatures; to model the effect of the temperature on the water sorption; and to determine thermodynamic functions as the isosteric heat of sorption and the differential entropy.

MATERIAL AND METHODS
Experimental procedure
Lime seeds were obtained from waste material of juice processing of Key limes (Citrus aurantifolia). The seeds were separated from the pomace by hand using an 8-mm screen, dehydrated in a forced-air tray dryer until constant weight and grounded using a food processor.

The equilibrium moisture contents of the lime seed samples were determined using the static gravimetric method reported by Lopes Filho et al. (2002) at temperatures of 30, 50 and 70°C. The sample weights were controlled until the moisture content on a dry weight basis did not exceed 0.1%, at which point equilibrium was assumed.

For each essay, the initial moisture content was determined according to the AOAC method 926.12 (AOAC 1997) to determine the equilibrium moisture content from the registered weight up to equilibrium. Experiments were carried out in triplicate and an arithmetic average was used for data analysis.

Isotherm modelling
Sorption isotherms of lime seeds were modelled using the GAB theoretical model (Eq. 1). This equation has been widely applied to describe the moisture isotherms in foodstuffs (Simal et al. 2007).
The GAB model parameters $K$ and $C$ can be written as temperature-dependent functions using Arrhenius type relationships (Eq. 2).

$$C = C_0 \exp\left(\frac{H_m}{RT}\right); \quad K = K_0 \exp\left(\frac{H_a}{RT}\right)$$

The identification of GAB model parameters were performed by nonlinear regression using the ‘nlinfit’ function of the Statistic Toolbox of Matlab® 7.1 (The MathWorks Inc., Natick, MA, USA). The 95% confidence intervals of the estimated GAB parameters were determined by using the ‘nlparci’ function of the same Matlab Toolbox. The coefficient of determination ($R^2$) and the mean relative error (MRE) were used to evaluate the goodness of the estimations provided by the model (Garau et al. 2006).

**Thermodynamic properties**

The isosteric heat of sorption ($Q_s$) was computed from GAB sorption isotherm using Eq. (3) which is derived from the Clausius-Clapeyron equation (Simal et al. 2007; García-Pérez et al. 2008).

$$Q_s = \lambda - R \frac{\partial (\ln a_w)}{\partial (1/T)} = \lambda + \frac{RT^2 \partial a_w}{a_w \partial T}$$

In Eq. (3) the partial derivative of water activity with respect to temperature (Eq. 4) can be solved in an analytical way from GAB model parameters.

$$\frac{\partial a_w}{\partial T} = \frac{\beta (a_w - 1) \frac{\partial a_w}{\partial T} - a_w \frac{\partial^2 a_w}{\partial T^2}}{\alpha^2 (2a_w + \beta)}$$

where $\alpha$ and $\beta$ are written as functions of the GAB model parameters (Eq. 5) and $X_m$ is constant.

$$\alpha = (C - 1)K^2; \quad \beta = [2 - C(1 - X_m/X)]K$$

The changes in differential molar entropy ($\Delta S$) can be calculated from Gibbs-Helmholtz equation (Eq.6), where the Gibbs free energy ($\Delta G$) is calculated by Eq. (7) (Simal et al. 2007; Eim et al. 2011).

$$\Delta S = (q_s - \Delta G)/T$$

$$\Delta G = RT \ln a_w$$

**RESULTS AND DISCUSSION**

The experimental isotherms for lime seeds at temperatures of 30, 50 and 70ºC are shown in Fig. 1. As it can be observed, the equilibrium moisture content of the product increases with the water activity for a constant temperature. However, the equilibrium moisture content decreased when the temperature increased for a constant water activity, thus indicating that the lime seed is becoming less hygroscopic (Gabas et al. 2007; García-Pérez et al. 2008).
The isosteric heat of sorption was found to decrease with increase in moisture content being close to water vaporization energy for moisture content higher than 0.05 kg kg\(^{-1}\) d.b. The high isosteric heat values at low equilibrium moisture contents indicate strong interactions of water-food components, which could be explained by the existence of highly active polar sites on the material surface (García-Pérez et al. 2008; Eim et al. 2011).

The strong dependence of differential entropy on moisture content lower than 0.05 kg kg\(^{-1}\) d.b. can be observed in Fig. 3, with an exponential trend similar to the exhibited for the isosteric heat of sorption.

The differential entropy increases as the moisture content decreases (Fig. 3), since the differential entropy, that measures the ordering change, is lower when the molecular movement is more restricted (Eim et al. 2011).

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CONCLUSIONS

The moisture desorption isotherms of Key lime seed obtained for the temperature range of 30–70°C show a typical behaviour of foodstuffs. The usefulness of GAB model to simulate the desorption data of lime seeds has been evaluated. By using the GAB model, the net isosteric heat of sorption and the differential entropy have been calculated as function of both moisture content and temperature. The analysed properties were in agreement with the thermodynamic theory and were comparable with those reported in the literature for other agrofood materials.

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REFERENCES


NOMENCLATURE

\( Q_e \) isosteric heat of sorption \( \text{kJ mol}^{-1} \)

\( R \) ideal gas constant \( \text{kJ mol}^{-1} \text{K}^{-1} \)

\( T \) absolute temperature \( \text{K} \)

\( X_e \) equilibrium moisture content \( \text{kg kg}^{-1} \text{d.b.} \)

\( X_m \) moisture content of the monolayer \( \text{kg kg}^{-1} \text{d.b.} \)

\( \alpha, \beta \) dependent functions of the GAB model parameters

\( \Delta S \) differential entropy \( \text{kJ mol}^{-1} \text{K}^{-1} \)

\( \Delta G \) Gibbs free energy \( \text{kJ mol}^{-1} \)

\( \lambda \) evaporation enthalpy of water \( \text{kJ mol}^{-1} \)

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REFERENCES


