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# Predicting Sorption Isotherms and Net Isosteric Heats of Sorption of Maize Grains at Different Temperatures 


#### Abstract

In Sub-Saharan Africa, drying maize on their stem was the traditional technique frequently used; this technique must be improved to avoid contaminations and to increase the quality of drying. However, the method of storage is accountable for the most significant losses after harvest, because mildew develops when the conditions of storage (too high temperature and moisture of the air) do not tally with the final content of the dried product. Sorption isotherms of products are most important to model moisture uptake during storage and distribution. Sorption isotherms of intermediate moisture content maize grains were determined using the gravimetric static method of saturated salt solutions at $30^{\circ} \mathrm{C}, 40^{\circ} \mathrm{C}, 50^{\circ} \mathrm{C}$, and $60^{\circ} \mathrm{C}$, and GAB equation was applied to discuss the results. This model correctly describes the evolutions of maize sorption isotherms, with maximum deviation of 0.0080 kg water $/ \mathrm{kg} \mathrm{db}$. The net isosteric heat of sorption was determined also, using the Clausius-Clapeyron equation, and it was varied from $463 \mathrm{~kJ} / \mathrm{kg}$ to $1,264 \mathrm{~kJ} / \mathrm{kg}$, decreasing with increasing moisture content. This effect was well described by an exponential function with a regression coefficient $R^{2}>97 \%$. The monolayer moisture content was found to decrease with increasing temperature. These results can be used to predict the potential changes in the stability of maize grains and later for the development of a system of suitable drying.


Keywords: maize grains, sorption isotherm, net isosteric heat of sorption, GAB model, monolayer values, specific area

[^0]
## 1 Introduction

In 2007, maize was the first crop in the world, before rice and wheat (FAOSTAT, 2010; http://faostat.fao.org). At the
time of harvest, maize has a moisture content too high to be stored (between $30 \%$ and $40 \% \mathrm{~kg} / \mathrm{kg} \mathrm{wb}$ ) and has to be dried. As most microorganisms would not grow in foods with $a_{\mathrm{w}}$ below 0.6, $a_{\mathrm{w}}$ of food products would need to keep less than 0.6 to extend product shelf life [1]. Therefore, it is essential for dried or intermediate moisture content products to know the sorption characteristics of these products in this range of water activity (0-0.6). Sorption isotherms of foodstuffs are essential for design, modeling and optimization of many processes such as drying, aeration, and storage [2, 3]. Knowledge of sorption isotherms is also important for predicting stability and quality changes during packaging, storage, and distribution of dried foods.

Water sorption isotherms are curves describing the relation between the food water activity $\left(a_{w}\right)$ and its correspondent equilibrium moisture content $\left(X_{\text {eq }}\right)$ at a given temperature. Through the experimental determination of isotherms at different temperatures, it is possible to analyze the optimal process and storage conditions of food materials avoiding undesirable modifications and enhancing the product shelf time. The water sorption in foods is a very complex phenomenon, consisting of several different mechanisms that depend on the material structure and composition. As a consequence, hundreds of models trying to represent the water sorption behavior in food matrices have been proposed [4-7].

These models are generally classified into three categories: empirical, semi-empirical, and theoretical [8]. As empirical two-parameter models Oswin [9], Smith [10], and Henderson [11] equations can be cited among many others. As a semi-empirical example, the Peleg [12] model of four parameters can be cited. And finally, derived from the Langmuir isotherm, two theoretical expressions can be cited: Brunauer, Emmett, and Teller (BET) equation [13] and Guggenheim, Anderson, and den Boer (GAB) equation [14], which are considered the most used models to describe water sorption in food materials [15]. The main advantage of theoretical models over the empirical and semi-empirical ones is the fact that their parameters have physical meaning. As a consequence, the inclusion of temperature dependency into the equation is possible, improving its fitting capability and
most importantly, the parameters can provide essential information about the water state in the food. As an example, the BET and the GAB equations include the monolayer moisture content [16], $X_{\mathrm{m}}$. This parameter constitutes a very important information since is it directly related to the shelf life and stability of foods [17, 18]. The theoretical models have been adopted as standard equations by the American Society of Agricultural Engineers for describing sorption isotherms [19]. Particularly, the equations of BET and GAB can be considered to be the most useful ones for determining the optimum moisture conditions for good storage stability, especially for dehydrated foods [20]. But the BET equation is valid only from $10 \%$ to $50 \%$ relative humidity $[3,21]$. It is shown that the GAB values are more general and have more physical meaning and that the two BET parameters can be calculated in terms of the three GAB parameters [22].

Many authors have published results about sorption isotherms studies of foodstuffs [23-26], but very little information is available about properties and drying kinetics of maize grains [27-29] or desorption isotherms for shelled maize [30]. Other authors worked on sorption data for corn [23, 31]. Moreover, according to our knowledge, no information is available about sorption isotherms of maize grains of Sub-Saharan Africa.

Moreover, knowledge of the net isosteric heat of sorption is important in understanding the mechanism of sorption. It is a valuable tool in designing equipment for drying [32-34]. Iglesias and Chirife [33] calculated and constructed heat curves from sorption isotherms of several foods, including fruits, protein foods, vegetables, and spices. They found that, with a few exceptions, the heat curves showed a regular decrease with increasing moisture content. So this study was undertaken to determine sorption isotherms to fit the experimental data to the isotherm models and to calculate the net isosteric heat of sorption of maize grains.

Therefore, the goal of this work is to determine the sorption isotherms and net isosteric heat of sorption maize grains, especially sweet corn.

## 2 Mathematical models

### 2.1 Modeling of sorption isotherms using GAB equation

The GAB model was accepted as the best to represent the sorption isotherms at the International Symposium on the Properties of Water (ISOPOW) in 1983 [8] and is
recommended by the European Project Group COST 90 on Physical Properties of Food [35]. The GAB equation is given by:

$$
\begin{equation*}
X_{\mathrm{eq}}=\frac{X_{\mathrm{m}} C K a_{\mathrm{w}}}{\left(1-K a_{\mathrm{w}}\right)\left[1+(C-1) K a_{\mathrm{w}}\right]} \tag{1}
\end{equation*}
$$

where $X_{\text {eq }}$ is the amount of water and $X_{\mathrm{m}}$ is the monolayer moisture content, both generally expressed in dry basis ( kg water/ kg db ), $C$ is an energetic constant also called as Guggenheim constant [36], and $K$ is a parameter that takes into account the difference of chemical potential between the multilayer and bulk water in the food [18, 22]. $C$ and $K$ are given by the following equations:

$$
\begin{align*}
& C=C_{0} \exp \left(\frac{H_{\mathrm{m}}-H_{\mathrm{w}}}{R T}\right)  \tag{2}\\
& K=K_{0} \exp \left(\frac{H_{\mathrm{q}}-H_{\mathrm{w}}}{R T}\right) \tag{3}
\end{align*}
$$

where $H_{\mathrm{w}}, H_{\mathrm{m}}$, and $H_{\mathrm{q}}$, are, respectively, the condensation heat of pure water, the total sorption heat of the monolayer, and the total sorption heat of other layers $(\mathrm{J} / \mathrm{mol}), T$ is the absolute temperature $(K), C_{0}$ the constant, $K_{0}$ the constant, and $R$ the universal gas constant [8.314 J/(mol K)].

Generally, the GAB model is used independently for each temperature, generating a set of values for $C, X_{\mathrm{m}}$, and $K$ estimated from experimental data for each temperature condition - e.g. Yanniotis and Zarmboutis [37], McLaughlin and Magee [38], Cassini et al. [39], Samapundo et al. [23], Lee and Lee [40], and Talla [25].

With the hypothesis of an initial homogeneous monolayer filling of the product surface, one can calculate its area. Supposing that monolayer is recovered with aligned water molecules, it could easily be shown that its area can be calculated by formula [13]:

$$
\begin{equation*}
S_{\mathrm{m}}=\frac{\sqrt{3} \sqrt[3]{2}}{2}\left(\frac{N}{M \rho_{\mathrm{w}}^{2}}\right)^{1 / 3} \rho_{\mathrm{db}} X_{\mathrm{m}} \tag{4}
\end{equation*}
$$

where $S_{\mathrm{m}}$ is the monolayer area or specific area $\left(\mathrm{m}^{2} / \mathrm{m}^{3}\right)$, $N$ is the Avogadro number ( $N=6.022 \times 10^{23} / \mathrm{mol}$ ), $M$ is the absorbing material molecular mass ( $\mathrm{kg} / \mathrm{mol}$ ), $\rho_{\mathrm{w}}$ is the water density $\left(\mathrm{kg} / \mathrm{m}^{3}\right), \rho_{\mathrm{db}}$ is the solid matrix density ( $\mathrm{kg} \mathrm{db} / \mathrm{m}^{3}$ ), and $X_{\mathrm{m}}$ is the monolayer moisture content.

The value of the specific area of a product may give information about its rehydration and its internal structure.

### 2.2 Parameter estimation and evaluation of fitting and prediction accuracy

For each temperature, the parameters are estimated by minimizing the sum of the quadratic errors between the experimental equilibrium water contents $X_{\text {eq }}$ and the values calculated with eq. (1).

For the parameter estimation the same function $S$ used in Talla et al. [25] was considered; the sum of the quadratic errors between the experimental equilibrium water contents $X_{\text {eq }}$ and the values calculated with eq. (1) was minimized:

$$
\begin{equation*}
S=\sum_{k=0}^{n}\left(\frac{X_{\mathrm{eq}}-X_{\mathrm{mod}}}{X_{\mathrm{eq}}}\right)_{i}^{2} \tag{5}
\end{equation*}
$$

where $n$ is the number of measurements for a temperature (nine in the present case).

Fit and prediction quality were analyzed by the regression coefficient ( $R^{2}$ ), the mean relative deviation (MRD), the standard error (SE) and the residual of estimate $\left(e_{i}\right)$, calculated as follows:

$$
\begin{gather*}
R^{2}=1-\frac{\sum_{i=1}^{n}\left(X_{\mathrm{eq}_{i}}-X_{\mathrm{mod} i}\right)^{2}}{\sum_{i=1}^{n}\left(X_{\mathrm{eq}_{i}}-\bar{X}\right)^{2}}  \tag{6}\\
\operatorname{MRD}(\%)=\frac{100}{n} \sum_{i=1}^{n}\left|1-\frac{X_{\bmod i}}{X_{\mathrm{eq}_{i}}}\right|  \tag{7}\\
\mathrm{SE}=\sqrt{\frac{\sum_{i=1}^{n}\left(X_{\mathrm{eq}_{i}}-X_{\mathrm{mod} i}\right)^{2}}{n}}  \tag{8}\\
e_{i}=X_{\mathrm{eq}_{i}}-X_{\mathrm{mod} i} \tag{9}
\end{gather*}
$$

with $\bar{X}=\frac{\sum_{i=1}^{n} X_{i}}{n}, n$ being the number of experiments.

### 2.3 Sensitivity of GAB model parameters

The sensitivity of the GAB model parameters $X_{\mathrm{m}}, C$, and $K$ is deduced from eqs (10)-(12), respectively.

$$
\begin{gather*}
\frac{\varepsilon}{100} X_{\mathrm{m}} \frac{\partial X_{\mathrm{eq}}}{\partial X_{\mathrm{m}}}=\frac{\varepsilon}{100} X_{\mathrm{eq}}  \tag{10}\\
\frac{\varepsilon}{100} C \frac{\partial X_{\mathrm{eq}}}{\partial C}=\frac{\varepsilon}{100} X_{\mathrm{eq}}\left[1-\frac{C K a_{\mathrm{w}}}{1+(C-1) K a_{\mathrm{w}}}\right]  \tag{11}\\
\frac{\varepsilon}{100} K \frac{\partial X_{\mathrm{eq}}}{\partial K}=\frac{\varepsilon}{100} X_{\mathrm{eq}}\left[\frac{K a_{\mathrm{w}}}{1-K a_{\mathrm{w}}}+\frac{1}{1+(C-1) K a_{\mathrm{w}}}\right] \tag{12}
\end{gather*}
$$

These three formulas represent the variation of the estimated value of $X_{\text {eq }}$ indices by a relative variation of $\varepsilon \%$ of respectively the parameters $X_{\mathrm{m}}, C$, and $K$ from their nominal values.

### 2.4 Determination of the net isosteric heat of sorption

The isosteric heat of sorption is defined as the total heat of sorption of water from the material minus the heat of vaporization of the water [38]. The Clausius-Clapeyron equation is applied for food materials to represent the relation of $a_{\mathrm{w}}$ with $T$ as a function of the net isosteric heat of sorption $Q_{\text {sorp }}(\mathrm{kJ} / \mathrm{mol})$ :

$$
\begin{equation*}
\frac{d \ln a_{\mathrm{w}}}{d T}=\frac{Q_{\mathrm{sorp}}}{R T^{2}} \tag{13}
\end{equation*}
$$

which can be conveniently rearranged to express the water activity temperature dependence:

$$
\begin{equation*}
\frac{d a_{\mathrm{w}}}{d T}=a_{\mathrm{w}} \frac{Q_{\text {sorp }}}{R T^{2}} \tag{14}
\end{equation*}
$$

Solving the Clausius-Clapeyron equation [eq. (14)], for $Q_{\text {sorp }}$, a relation between $Q_{\text {sorp }}$ and $a_{\mathrm{w}}$ is obtained:

$$
\begin{equation*}
Q_{\text {sorp }}=\frac{R T_{\text {ref }} T}{T-T_{\text {ref }}} \ln \frac{a_{\mathrm{w}}}{a_{\text {wref }}} \tag{15}
\end{equation*}
$$

where $R$ is the universal gas constant $\left[8.31410^{-3} \mathrm{~kJ} /(\mathrm{mol}\right.$ K)] and $a_{\mathrm{w}}$ and $a_{\text {wref }}$ are the water activity values at temperatures $T$ and $T_{\text {ref }}$, respectively. The $a_{\mathrm{w}}$ values at various moisture content levels were calculated using the GAB model.

In a two-dimensional diagram where $\ln \left(a_{\mathrm{w}}\right)$ is represented as a function of $1 / T$, the sorption isosters are straight lines according to the relation:

$$
\begin{equation*}
\left[\frac{\partial \ln \left(a_{\mathrm{w}}\right)}{\partial\left(\frac{1}{T}\right)}\right]_{X=\mathrm{constant}}=-\frac{Q_{\text {sorp }}}{R} \tag{16}
\end{equation*}
$$

The isosteric sorption heat can be deduced from the slope of sorption isosters representing $\ln \left(a_{\mathrm{w}}\right)$ as a function of $1 / T$ for each product water content $X$, and then the curve $Q_{\text {sorp }}=f(X)$ can be plotted. It is an important parameter whose values show at the end of the drying it cannot be neglected in energy balance since it has the same order of magnitude as the vaporization latent heat.

## 3 Materials and methods

### 3.1 Sorption method

The static method of the saturated salts solutions has been used for sorption isotherms determination. It is a method where diffusion is the only way of mass transfer between the tested product and the surrounding air. The relative air humidity is fixed by contact with saturated salts solution whose water vapor pressure at a given temperature is perfectly known. This method is commonly used for product sorption isotherms determination [23, 26, 41-44]. The time necessary to reach equilibrium is quite long compared to the dynamic method since the diffusion rate is limiting factor.

### 3.2 Experimental process

The experiment was conducted at the Laboratory of Energizing, Water and Environment, in the National Advanced School of Engineering, University of Yaounde I, Cameroon, during the period of June-September, 2013. The gravimetric static method was used to measure the sorption equilibrium moisture content of maize grains. Nine airtight cylindrical plastic containers, 115 mm diameter and 135 mm height, containing saturated salt solutions were placed in an electric oven to provide constant temperature and relative humidity environments. The digital temperature controller, on control panel of electric oven, provided the desired temperature (accuracy $0.1^{\circ} \mathrm{C}$ ). A mini fan of $60 \mathrm{~mm}(3 \mathrm{~V}, 0.25 \mathrm{~A})$ was fitted inside the plastic container to provide continuous stirring of the air inside the container. The values for water activity of the saturated salt solutions were obtained from Greenspan
[45] and these are listed in Table 1. The critical water activity for shelf life of dried product is 0.6 [1], therefore, the water activity range of $0.058-0.982$ were selected for this study.

Three dried samples (about 10 g each) from maize grains, especially sweet corn, were placed inside nine airtight cylindrical plastic boxes each, and suspended over the saturated salt solutions in each container. They were characterized by a high sugar rate in the range of 9-16\% (WIKIPEDIA, 2013; http://fr.wikipedia.org/wiki/ Maïs_doux). The use of three samples in each container aims at making sure that the results obtained could be reproduced with each experiment. The containers were then placed in the oven at a desired constant temperature and allowed to equilibrate with the environment inside the containers. Figure 1 shows the schematic diagram of the experimental apparatus [44]. The selected temperatures were $30^{\circ} \mathrm{C}, 40^{\circ} \mathrm{C}, 50^{\circ} \mathrm{C}$ and $60^{\circ} \mathrm{C}$ with an accuracy of $0.1^{\circ} \mathrm{C}$ variation. The weight of each sample was recorded at 24 h intervals by taking out the sample from the container very fast and then replacing the sample in the container. The weight recording period was about $15-20$ s for each sample. This procedure was continued until the weight was constant; their mass variation became less than 1 mg . The equilibrium moisture content $X_{\text {eq }}$ of each sample was then determined by the ovendrying method at $102^{\circ} \mathrm{C}$ for 24 h .

The equilibrium moisture content is given by the following formula:

$$
\begin{equation*}
X_{\mathrm{eq}}=\frac{m_{\mathrm{eq}}}{m_{\mathrm{db}}}-1 \tag{17}
\end{equation*}
$$

where
$m_{\text {eq: }}$ : sample equilibrium mass (kg); and $m_{\mathrm{db}}$ : sample oven dry mass (kg db).

Table 1 Water activity of saturated salt solutions from $10-40^{\circ} \mathrm{C}$

| Solution | Water activity at various temperatures |  |  |  |  |  |  |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  | 10 | 15 | 20 | 25 | 30 | 35 | 40 |
| Lithium bromide ( LiBr ) | 0.071 | 0.069 | 0.066 | 0.064 | 0.062 | 0.060 | 0.058 |
| Potassium acetate ( $\mathrm{KCH}_{3} \mathrm{CO}_{2}$ ) | 0.234 | 0.234 | 0.231 | 0.225 | 0.216 |  |  |
| Magnesium chloride ( $\mathrm{MgCl}_{2}$ ) | 0.335 | 0.333 | 0.331 | 0.328 | 0.324 | 0.321 | 0.316 |
| Potassium carbonate ( $\mathrm{K}_{2} \mathrm{CO}_{3}$ ) | 0.432 | 0.432 | 0.432 | 0.432 | 0.432 |  |  |
| Sodium bromide ( NaBr ) | 0.622 | 0.607 | 0.591 | 0.576 | 0.560 | 0.546 | 0.532 |
| Potassium iodide (KI) | 0.721 | 0.710 | 0.699 | 0.689 | 0.679 | 0.670 | 0.661 |
| Sodium chloride ( NaCl ) | 0.757 | 0.756 | 0.755 | 0.753 | 0.751 | 0.749 | 0.747 |
| Potassium chloride ( KCl ) | 0.868 | 0.859 | 0.851 | 0.843 | 0.836 | 0.830 | 0.823 |
| Potassium sulfate ( $\left.\mathrm{K}_{2} \mathrm{SO}_{4}\right)$ | 0.982 | 0.979 | 0.976 | 0.973 | 0.970 | 0.967 | 0.964 |

[^1]

Figure 1 Schematic diagram of the experimental apparatus [44]

## 4 Results and discussion

### 4.1 Sorption isotherms

Sorption isotherms of maize grains at temperatures of $30^{\circ} \mathrm{C}, 40^{\circ} \mathrm{C}, 50^{\circ} \mathrm{C}$, and $60^{\circ} \mathrm{C}$ in the water activity range of 0.058-0.982 are presented in Figure 2. Isotherm curves were found to be sigmoid in shape, and all curves followed similar patterns. Higher equilibrium moisture contents were found at the lower temperature at the same water activity or $a_{\mathrm{w}}$ are seen to increase with temperature at the same equilibrium moisture content. This indicates that the maize grains become less hygroscopic when temperature is increased. The reason may be that with the increase in temperature, water molecules get


Figure 2 Experimental and calculated isotherms for dried maize grains with GAB model
activated due to their energy level, causing them to become less stable and to break away from the waterbinding site of the food materials, thus decreasing the monolayer moisture content [3, 38, 46, 47]. Talla [25], Yan et al. [26], and Samapundo et al. [23] have presented similar results. Whereas Mazza and LeMaguer [48] suggested that increase in temperature induces physical and/or chemical changes in the product that can reduce the number of active sites for water binding. The temperature dependence of the equilibrium moisture content has an important practical bearing on chemical and microbiological reactions associated with spoilage [49]. At the same moisture content, higher temperatures entail a higher $a_{\mathrm{w}}$ and consequently faster rates of deterioration [50].

Tables 2 and 3 show the parameters of the GAB model fitted to the experimental sorption data of maize grains and the values of the regression coefficient $\left(R^{2}\right)$, the mean relative deviation (MRD), and the standard error (SE). The mean MRD values obtained were very small (MRD 2.87\%), the coefficients ( $R^{2}$ ) for the calculated curves were always higher than 0.989 and the standard errors SE were smaller than 0.0042 .

Moreover, the specific area is directly proportional to the water content at the saturation of monolayer. The decreasing of the specific area $S_{\mathrm{m}}$ with temperature increasing can be explained by the decrease of porosity as an effect of the thermal expansion of the solid matrix leading to pores shrinkage. Table 2 also indicates the values of $X_{0} \rho_{\mathrm{db}} / S_{\mathrm{m}}$, which represents, at the initial state, the water content filling the pores by unit of specific area and so has the dimension of a water thickness. The density of solid phase of maize grains measured by Chung et al. [27] is in range $1,230-1,300 \mathrm{~kg} / \mathrm{m}^{3}$. The average value of this product used in this work was $1,265 \mathrm{~kg} / \mathrm{m}^{3}$. The water content filling the pores by unit of specific area increases when the temperature rises and may indicate that maize grains will be easier to dry on high temperature. This prediction is in agreement with the results of Talla et al. [44] for tropical fruits.

In Figure 3 the residual plots for maize grains are depicted with higher deviation for high values of water activities. In accordance with the previous comments about the results of fitting and prediction of isotherms, the better are the statistical results shown in Table 3, the more random is the pattern presented by the residual plot. The maximum deviation for this product is lower than $0.80 \%$ for a water activity of 0.753 .

The mean relative deviation of the GAB model using the values of Table 2, compared to all the experimental points, is $2.87 \%$ for this product. Nevertheless, the

Table 2 Estimated parameters of the GAB model for the sorption isotherm of maize grains at different temperatures

| $\boldsymbol{\theta}\left({ }^{\circ} \mathrm{C}\right)$ | $\boldsymbol{X}_{\mathrm{m}}(\mathrm{kg}$ water $/ \mathrm{kg} \mathrm{db})$ | $\boldsymbol{C}$ | $\boldsymbol{K}$ | $\boldsymbol{S}_{\mathrm{m}}\left(\mathrm{m}^{\mathbf{2}} / \mathrm{m}^{\mathbf{3}}\right)$ | $\boldsymbol{X}_{\mathbf{0}} \rho_{\mathrm{db}} / \boldsymbol{S}_{\mathrm{m}}\left(\mathrm{kg}\right.$ water $\left./ \mathrm{m}^{2}\right)$ |
| :--- | ---: | ---: | ---: | ---: | ---: |
| 30 | 0.146 | 12.649 | 0.510 | $6.523 \times 10^{+10}$ | $1.047 \times 10^{-8}$ |
| 40 | 0.124 | 12.357 | 0.562 | $5.496 \times 10^{+10}$ | $1.243 \times 10^{-8}$ |
| 50 | 0.103 | 12.172 | 0.606 | $4.562 \times 10^{+10}$ | $1.497 \times 10^{-8}$ |
| 60 | 0.083 | 13.651 | 0.649 | $3,690 \times 10^{+10}$ | $1.851 \times 10^{-8}$ |

Table 3 Results for isotherm predictions with the GAB model compared with experimental data

| $\boldsymbol{\theta}\left({ }^{\circ} \mathrm{C}\right)$ | MRD (\%) | $\boldsymbol{R}^{\mathbf{2}}$ | $\mathbf{S E}$ |
| :--- | :---: | :---: | :---: |
| 30 | 2.87 | 0.989 | 0.0042 |
| 40 | 1.96 | 0.992 | 0.0030 |
| 50 | 1.11 | 0.998 | 0.0025 |
| 60 | 1.65 | 0.995 | 0.0030 |



Water activity $a_{\text {w }}$
Figure 3 Residual plots of isotherm predictions for maize grains
deviation is quite low (maximum 0.42\%) for water activities lower than 0.35 and is thus interesting for drying modeling since final water content around 0.15 kg water/kg db is generally recommended. The relatively low deviations lead to the conclusion that the GAB model, with parameters of Table 2, can therefore be surely used to relate moisture content and water activity for maize grains in the whole range of practical application. It is worth mentioning that, for the case studied, the error in prediction did not increase with temperature. This indicates that the temperature was not the cause of the deviations between experimental and calculated curves. Formulas (9)-(11) represent the variation of the estimated value of $X_{\text {eq }}$ indices by a relative variation of $\varepsilon \%$ of respectively the parameters $X_{\mathrm{m}}, C$, and $K$ from their nominal values. For example,


Figure 4 Residual variation of $X_{\text {eq }}$ induced by a relative variation of $10 \%$ of each parameter at $50^{\circ} \mathrm{C}$

Figure 4 represents this sensitivity at $50^{\circ} \mathrm{C}$ and shows that the GAB model is quite insensitive to parameter $C$ : a relative variation of $10 \%$ on the parameter $C$ has no effect on the simulated values of $X_{\text {eq }}$. This confirms, as pointed out by Rouquerol et al. [51], that the simplified theoretical expression of the parameter $C$ given by formula (2) cannot lead to reliable estimation of the total sorption heat $H_{\mathrm{m}}$ of monolayer.

The parameters $C_{0}$ and $H_{\mathrm{w}}-H_{\mathrm{m}}$ have not been estimated since it will not be reliable as previously pointed out. The values of estimated parameters of $K$ calculation were $K_{0}=7$ and $H_{\mathrm{q}}-H_{\mathrm{w}}=0.806 \mathrm{~kJ} / \mathrm{mol}$ with $H_{\mathrm{w}}=$ $44.643 \mathrm{~kJ} / \mathrm{mol}$ and $H_{\mathrm{q}}=37.934 \mathrm{~kJ} / \mathrm{mol}$. The value of $H_{\mathrm{q}}-H_{\mathrm{w}}$ represents the mean value of sorption heat of the studied maize, which is lower than the vaporization heat of water.

### 4.2 Net isosteric heat of sorption

Figure 5 represents, for maize grains, the sorption isosters $\ln \left(a_{\mathrm{w}}\right)$ vs $1 / T$ that must be straight lines according to formula (16). For each water content $X$, a sorption isoster has plotted and the isosteric sorption heat was calculated from its slope. The relationships between the net isosteric heat of sorption $Q_{\text {sorp }}$ and moisture content $X$ of maize grains are shown in Figure 6. When the moisture content increased, the isosteric heat of sorption of maize grains was regressed, indicating the strong link between the absorbate (water) and the adsorbent, but it is quite negligible compared to vaporization latent heat for high water content. The net isosteric heat of sorption of the maize grains ranged from $463 \mathrm{~kJ} / \mathrm{kg}$ at 0.21 kg water $/ \mathrm{kg}$ db moisture content to $1,264 \mathrm{~kJ} / \mathrm{kg}$ at 0.11 kg water $/ \mathrm{kg} \mathrm{db}$ moisture content. The net isosteric heat of sorption of


Figure 5 Sorption isosters of maize grains


Figure 6 Net isosteric heat of sorption of maize grains
water in maize grains can be expressed mathematically using an exponential function of moisture content given by relation (18):

$$
\begin{equation*}
Q=454.60 \exp \left[94.58(X-0.215)^{2}\right] \tag{18}
\end{equation*}
$$

with
the regression coefficient $R^{2}=0.974$, the mean relative deviation MRD $=0.64 \%$ and, the standard error $\mathrm{SE}=16.77 \mathrm{~kJ} / \mathrm{kg}$

This mathematical relationship may be used to calculate the heat of sorption of maize grains for various moisture contents.

## 5 Conclusions

The maize grains sample dehydrated by vacuum oven and placed on saturated solutions showed different sorption isotherms at $30^{\circ} \mathrm{C}, 40^{\circ} \mathrm{C}, 50^{\circ} \mathrm{C}$, and $60^{\circ} \mathrm{C}$. Temperature has an effect on the sorption behavior, higher water activity values being observed at the same moisture content when temperature is increased. The GAB model may be used to estimate sorption isotherms of maize grains in this range of temperature and water activity range $6.4-97.3 \%$, with a maximum mean relative deviation of $2.87 \%$. The net isosteric heat of sorption of maize grains decreased with an increase in moisture content and was found to be an exponential function of moisture content. To supplement this work, the kinetics of maize grains drying is studied in our laboratory. All this information and observations, obtained sooner or later, play an important role in the determination of suitable preservative design, including the optimal drying process and atmospheric conditions for storage.

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## Nomenclature

| $a_{\mathrm{w}}$ | Water activity |
| :--- | :--- |
| $C$ | Parameter linked to monolayer heat of sorption |
| $H_{\mathrm{w}}$ | Condensation heat of pure water $(\mathrm{J} / \mathrm{mol})$ |
| $H_{\mathrm{m}}$ | Total sorption heat of the monolayer $(\mathrm{J} / \mathrm{mol})$ |
| $H_{\mathrm{q}}$ | Total sorption heat of other layers $(\mathrm{J} / \mathrm{mol})$ |
| $K$ | Parameter linked to multilayers heat of sorption |
| $m$ | Product mass (kg) |
| $M$ | Absorbing material molecular mass $(\mathrm{kg} / \mathrm{mol})$ |


| $N$ | Avogadro number (/mol) |
| :--- | :--- |
| $Q_{\text {sorp }}$ | Sorption heat $(\mathrm{kJ} / \mathrm{kg})$ |
| $S_{\mathrm{m}}$ | Specific area $\left(\mathrm{m}^{2} / \mathrm{m}^{3}\right)$ |
| $X$ | Moisture content $(\mathrm{kg}$ water $/ \mathrm{kg} \mathrm{db})$ |
| $X_{\mathrm{m}}$ | Monolayer moisture content |
| $T$ | Absolute temperature $(\mathrm{K})$ |
| $R$ | Perfect gas constant $[\mathrm{J} /(\mathrm{mol} \mathrm{K})]$ |
| $\rho$ | Density $\left(\mathrm{kg} / \mathrm{m}^{3}\right)$ |
| $\theta$ | Temperature $\left({ }^{\circ} \mathrm{C}\right)$ |

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## Indices

0 Initial
db Dry basis
eq Equilibrium
exp Experimental
ref Reference
W Water
wb Wet basis
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[^1]:    Source: Adapted from Greenspan [45].

