

# Water Sorption Isotherms of NPK 10–20–20/4 Muriate of Potash Fertilizer

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Water sorption isotherms of NPK 10–20–20/4 muriate of potash (MOP) fertilizer were determined using a gravimetric method for temperatures ranging from 15 to 35 °C. It was found that the sorption behavior of the fertilizer assimilated to a type-III isotherm characteristic of crystalline solids. The sorption data could be represented by a single isotherm in the temperature range studied. The equilibrium data obtained were fitted to two-parameter linearized and nonlinear three- and four-parameter models. Among the models studied, the nonlinear three-parameter Guggenheim–Anderson–De Boer (GAB) model was selected. This equation allowed the calculation of a monolayer water content of 0.852 g of water/100 g of dry solids, and monolayer and multilayer water sorption enthalpy values of  $H_N = 43.3$  kJ/gmol and  $H_M = 44.2$  kJ/gmol, respectively.

## Introduction

Granulated composite fertilizers such as those based on nitrogen, phosphorus, and potassium (NPK) are widely used in modern agriculture. Caking during storage is one of the most important problems experienced with this type of fertilizers. When caking takes place, the fertilizer loses its granular properties, causing agricultural machinery to clog during application which leads to work stoppage and economic loss. Furthermore, agglomerated product is more difficult to dissolve in water in order to make the nutrients available in the soil, and rupture of agglomerated fertilizer results in the formation of dust that can be lost in the wind during application, reducing yields. Additionally, reduced size dust particles present greater surface area, which increase moisture adsorption from air, enhancing further caking. Fertilizer moisture content is one of the most important factors affecting caking, along with other factors such as storage pressure, time, particle form and size, chemical composition, temperature, and use of anticaking agents. The theory of caking and the factors affecting it have been extensively described in the technical literature.<sup>1–5</sup>

The moisture content of a stored fertilizer is affected by external factors such as temperature and relative humidity of ambient air, besides other factors such as the nature and characteristics of the packaging material and storage patterns used. Because for retail sales NPK fertilizers are frequently packaged in polyethylene bags with characteristic moisture permeability, the product can gain or lose moisture depending on the conditions of the external air. The same applies during bulk storage in warehouses, ship holds, and land transportation units. Moisture sorption by the fertilizer can take place according to a physical–chemical relationship given by the equilibrium water sorption isotherm, relating product moisture content (dry basis) with the equilibrium relative humidity of ambient air. Water activity ( $a_w$ ) at the temperature of the study is defined as the percent equilibrium relative humidity divided by 100. The knowledge of the sorption isotherm for various storage temperatures is of prime importance to predict moisture content of the fertilizer in equilibrium with the ambient relative humidity

and to make engineering calculations to study the caking of fertilizers during storage and transportation.

A large number of water sorption isotherm models have been proposed in the literature for different products. They include those derived theoretically based on thermodynamic considerations such as the BET (Brunauer, Emmett, and Teller)<sup>6</sup> and GAB (Guggenheim–Anderson–De Boer)<sup>7</sup> models and semiempirical and empirical models (e.g., Peleg,<sup>8</sup> Viollaz and Rovedo<sup>9</sup>). Other empirical two-parameter isotherm models have been proposed for different  $a_w$  ranges (Freundlich,<sup>10</sup> Smith,<sup>11</sup> Hasley,<sup>12</sup> Henderson,<sup>13</sup> Chung and Pfof,<sup>14</sup> and Khun<sup>15</sup>). Although at present there is not a unique model to accurately represent moisture sorption data in the whole range of water activity mainly because of the complex sorption mechanisms involved, the GAB equation has been recognized as the most versatile sorption model. More recently, Viollaz and Rovedo<sup>9</sup> proposed an extension of the GAB model to correlate sorption data for  $a_w$  values that include the range above 0.9 not considered in the original GAB model.

The monolayer water content represents valuable additional information that can be obtained from sorption isotherm data, using the BET and GAB models along with the sorption enthalpies. The monolayer water content gives information about the minimal water content conferring product stability including fertilizer caking, while the sorption enthalpies measure the energy of intermolecular bonding between water molecules and adsorbing surfaces.<sup>16</sup>

NPK 10–20–20/4 muriate of potash (MOP) is a granulated composite fertilizer extensively used in Venezuela, manufactured and marketed by a local petrochemical industry (Pequiven). This fertilizer contains around 4% sulfur, muriate of potash (MOP) being the main potassium source. No research work was found in the scientific literature reviewed on water sorption isotherms of NPK fertilizers and particularly for NPK 10–20–20/4 MOP.

The objectives of this research work were to determine the water sorption isotherms for NPK 10–20–20/4 MOP granulated fertilizer at temperatures usually found in storage of this commodity in tropical regions (15, 23, and 35 °C), to establish a sorption model capable of fitting the data in order to predict the equilibrium moisture sorption isotherms in the temperature

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**Table 1. Physical and Chemical Characteristics of of NPK 10-20-20/4 MOP Fertilizer As Provided by Manufacturer**

test	unit	nominal	minimum	maximum
total nitrogen (N)	% (w/w)	10	9.5	
total phosphorus (P <sub>2</sub> O <sub>5</sub> )	% (w/w)	20	19.5	
total potassium (K <sub>2</sub> O)	% (w/w)	20	19.5	
sulfur	% (w/w)	4		
moisture	% (w/w)			1.5
granulometry (Tyler)	% weight retained			
(+) 5 (PD <sup>a</sup> > 3.96 mm)				10
(+) 16 (PD <sup>a</sup> > 0.99 mm)		85		
(-) 16 (PD <sup>a</sup> < 0.99 mm)				5

<sup>a</sup> PD: Particle diameter.

range studied, and to calculate the monolayer moisture content and the monolayer and multilayer water sorption enthalpies.

## Materials and Methods

**Sample Collection and Preparation.** Samples of NPK 10–20–20/4 MOP fertilizer were obtained from a local distributor. This product was manufactured at Pequiven (Moron, Venezuela). It is usually marketed in the form of pellets packed in two-piece polypropylene/polyethylene bags of 50 kg sewn in the filling end. The physical–chemical characteristics and specifications were provided by the manufacturer<sup>17</sup> and are presented in Table 1. Additionally, the following characteristics are also indicated: reddish-brown color; slight ammonia odor; pH: 6.7–7.0; specific gravity: 1.803 (20 °C); solubility in water: 70 g/100 g (21.1 °C).

The granular fertilizer was manually ground in a mortar and sieved using a 1 mm sieve. The sieved sample was packed in hermetically sealed plastic containers with screw caps and kept in a dry place at room temperature until used.

**Moisture Analysis.** Moisture of ground samples was determined as the weight loss during drying in a vacuum oven (GCA Corp., Model 29) according to procedure Covenin 245-76,<sup>18</sup> heating under a vacuum of 500 mmHg at 50 °C for 2 h. Twelve moisture determinations were performed in order to determine the initial moisture content of the fertilizer sample used in this study.

**Water Sorption Isotherm.** Moisture sorption isotherms were determined at 15, 23, and 35 °C. A weight of about 7 g of the ground sample was placed in open shallow plastic containers (3.8 cm diameter and 1 cm height). The containers were placed over a support inside desiccators, each one containing an oversaturated salt solution of known equilibrium relative humidity at the temperatures studied. Special care was taken to avoid contact of the fertilizer with the salt solution. Twelve oversaturated salt solutions were used in these experiments. Three samples were used for each salt solution in order to obtain triplicates for the results obtained. The correspondence between the equilibrium relative humidity and water activity ( $a_w$ ) was already mentioned. At constant temperature each oversaturated solution has a corresponding equilibrium relative humidity in a closed system. Those values have been reported in the technical literature for different temperatures.<sup>19</sup> The method for obtaining sorption isotherms in agricultural products using gravimetric techniques has been described in detail elsewhere.<sup>20–22</sup> A range of  $a_w$  from 0.08 to 0.97 was studied, with the following salts of known  $a_w$  used for this purpose:<sup>19</sup> KOH, LiCl, CH<sub>3</sub>COOK, MgCl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub>, Mg(NO<sub>3</sub>)<sub>2</sub>, CoCl<sub>2</sub>, KI, NaCl, (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>, KCl, and K<sub>2</sub>SO<sub>4</sub>.

The desiccators with the samples were kept in temperature-controlled ( $\pm 0.1$  °C) incubators (VELP Scientifica, model FTC

901) at 15 and 35 °C. The samples corresponding to 23 °C were kept in desiccators at room temperature. After equilibrium was achieved, as evidenced when the sample reached constant weight, the moisture content of the equilibrated samples was determined in triplicate by the vacuum oven method indicated above. In order to ensure that equilibrium was reached in each environment tested, two plastic dishes were placed in desiccators containing the salt to be used for oversaturation until constant weight was reached. When equilibrium was reached, water activity was measured using Decagon equipment (Model CX-2,  $\pm 0.001$ ).

The data obtained corresponding to  $a_w$  and moisture content at the temperatures studied were adjusted to several regression models in order to determine the best fit. The following equations for sorption isotherms (Table 2) were studied: Freundlich,<sup>10</sup> BET,<sup>6</sup> Smith,<sup>11</sup> Hasley,<sup>12</sup> Henderson,<sup>13</sup> Chung and Pfost,<sup>14</sup> Khun,<sup>15</sup> (1967), GAB model,<sup>7</sup> and modified GAB model.<sup>9</sup> Linear and nonlinear regression statistical analyses were performed, using Matlab v. 2007R-B (The MathWorks, Inc.).

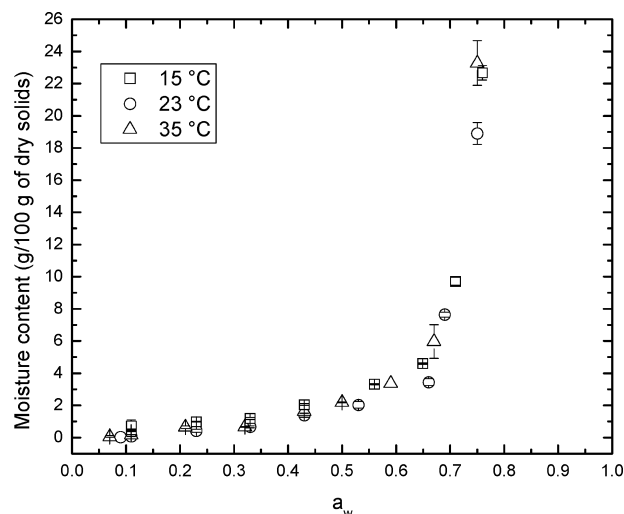
The adequacy of the regression was evaluated using the coefficient of determination ( $R^2$ ) and the root mean squared error (RMSE) defined as:

$$\text{RMSE} = \sqrt{\sum_{i=1}^n \left[ \frac{(M_i - \hat{M}_i)^2}{n - p} \right]} \quad (1)$$

where  $M_i$  and  $\hat{M}_i$  are experimentally observed and predicted by the model values of the equilibrium moisture content, respectively,  $n$  is the number of data points, and  $p$  is the number of fitted coefficients estimated from the model. The water content of the monolayer and multilayer and their associated enthalpies were determined from the GAB equation.

## Results and Discussion

The average initial moisture content of the NPK 10–20–20/4 MOP sample used in this work was 4.74 g water/100 g of dry solids, with a standard deviation of 0.30 and 95% confidence intervals of 4.53–4.96 g water/100 g of dry solids. This value corresponds to a water activity ( $a_w$ ) at 25 °C of 0.674. The moisture content obtained was higher than the tolerance of 1.50% (wet basis) or 1.52 g water/100 g of dry solids, indicating that the sample had adsorbed moisture during storage. In this way, part of the sorption data was obtained by adsorption



**Figure 1.** Sorption isotherms of NPK 10–20–20/4 MOP fertilizer for a combined temperature range between 15 and 35 °C.

**Table 2. Adjustment of the Experimental Data Obtained for the Sorption Isotherm for the Combined Temperature Range (15, 23, and 35 °C) of NPK 10-20-20/4 MOP Fertilizer to Various Sorption Models**

isotherm	model	range of $a_w$	constant values	$R^2$ (RMSE)
Freundlich (1926)	$M = Aa_w^{1/B}$	$a_w < 0.90$	$A = 13.47$ $B = 0.490$	0.924 (1.88)
BET (1938)	$M = ABa_w/(1 - a_w)(1 + (B - 1)a_w)$	$a_w < 0.50$	$A = 1.37$ $B = -2.44$	0.432 (1.86)
Smith (1947)	$M = A + B \ln(1 - a_w)$	$0.50 < a_w < 0.95$	$A = -23.7$ $B = -29.2$	0.691 (4.76)
Hasley (1948)	$M = (-A/(\ln a_w))^{1/B}$	$0.10 < a_w < 0.80$	$A = 0.590$ $B = 0.241$	0.934 (1.79)
Henderson (1952)	$M = (-\ln(1 - a_w)/A)^{1/B}$	$0.50 < a_w < 0.95$	$A = 0.882$ $B = 0.151$	0.903 (2.68)
Chung-Pfost (1967)	$M = A + B \ln(-\ln a_w)$	$0.20 < a_w < 0.90$	$A = 1.22$ $B = -9.42$	0.591 (4.71)
Khun (1967)	$M = A/\ln a_w + B$	$a_w < 0.50$	$A = -1.85$ $B = -0.579$	0.846 (1.28)
GAB (Van den Berg and Bruin, 1981)	$M = (ABCa_w)/((1 - Ca_w)(1 - Ca_w + BCa_w))$	$a_w < 0.95$	$A = 0.852$ $B = 2.72$ $C = 1.27$	0.953 (1.50)
modified GAB (Viollaz and Rovedo, 1999)	$M = (ABCa_w)/((1 - Ca_w)(1 - Ca_w + BCa_w)) + (ABCDa_w^2)/((1 - Ca_w)(1 - a_w))$	$0.00 < a_w < 1.00$	$A = 0.612$ $B = 8.27$ $C = 1.27$ $D = 0.025$	0.954 (1.52)

(product containing final moisture equilibrium values above 4.74 g/100 g) and the rest by desorption.

In a previous study it was experimentally shown that equilibrium in all environments was reached within a maximum of 21 days for salts with  $a_w < 0.692$ . In the case of sodium chloride solution, a period of 35 days was required to reach equilibrium. For this reason, a period of 35 days was used in all cases, in order to ensure that equilibrium was reached during the experiments.

The experimental data obtained relating the moisture content (dry basis) of the fertilizer with  $a_w$  for the temperatures studied (15, 23, and 35 °C) are presented in Figure 1. The isotherms obtained had the typical shape of type III isotherms characteristic of porous and crystalline solids, according to the Brunauer et al.<sup>6</sup> classification. This type of isotherm can be explained by the fact that NPK fertilizers are composed of chlorides, sulfur, phosphates, sulfates, carbonates, nitrates, and oxides as well as cations such as calcium, potassium, and ammonia, among others. These compounds have defined crystalline structures in their solid form.<sup>1</sup> The isotherms obtained are qualitatively similar to those of potash presented by Bookey and Raistrick<sup>2</sup> and Chen,<sup>23</sup> which is one of the main components of this fertilizer.

It has to be pointed out that moisture values increased dramatically for  $a_w > 0.50$ . As visually assessed during experimentation, at water activity values greater than 0.756, the solid fertilizer liquefied, losing its physical integrity and forming a slurry. Sample liquefaction corresponded with a huge increase in moisture content as an asymptote was approached for  $a_w > 0.756$ . This behavior could be explained by the mobility of ions of crystalline species within the fertilizer and their solubilization in the adsorbed water. During this process, mass transfer from the solid fertilizer to the water adsorbed in its surface takes place, forming a solution. The ionized salt components in this solution are able to adsorb additional water or even undergo chemical reaction between them to form new compounds that were originally not present in the fertilizer. This mechanism is similar to that presented by Sauchelli<sup>1</sup> to explain caking of fertilizers during storage. For this reason, salts with high water activity ( $a_w > 0.756$ ) should be discarded because the sample moisture exceeded the expected equilibrium value, as evidenced by water activity measurements using Decagon CX-2 water activity equipment.

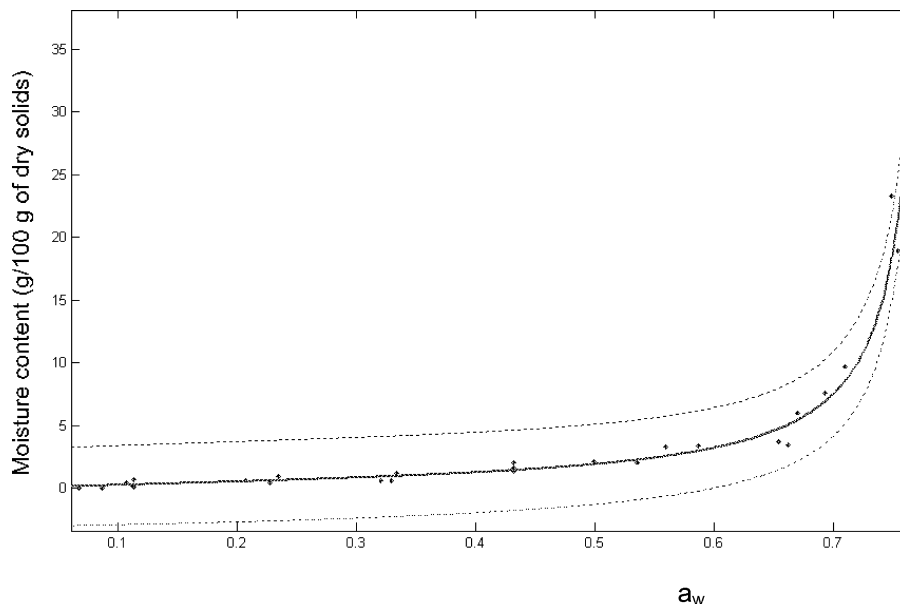
Figure 1 also shows that sorption data for the three studied temperatures (15, 23, and 35 °C) were practically coincident and overlapped over the entire  $a_w$  range considered. For this reason, all the experimental values were adjusted to a single isotherm, as discussed below. As shown later in this paper, practically all data collected was contained within the 95% confidence interval of the experimental values obtained, evidencing a limited effect of temperature, in the range studied on sorption data. This behavior has been found in previous research work in foods,<sup>20–22</sup> and crystalline solids such as lactose.<sup>24</sup>

The data obtained were adjusted to various sorption models, in order to determine the best model to predict the sorption isotherm for the product studied. The classical linearizable two-parameter nonlinear models, as well as the nonlinear GAB and modified GAB models, were used. The results obtained are presented in Table 2. Evaluation of the goodness of model fitting was carried out through the determination of relative ( $R^2$ ) and absolute (root-mean-square error, RMSE) error measurements, and the corresponding values are also shown in Table 2.

The better fittings to the experimental data, as indicated by the generally high  $R^2$  and low RMSE values obtained, were obtained for the Hasley isotherm ( $R^2 = 0.934$  and  $RMSE = 1.79$ ) for the two-parameter linearized models, and for the GAB ( $R^2 = 0.953$  and  $RMSE = 1.50$ ) and modified GAB ( $R^2 = 0.954$  and  $RMSE = 1.52$ ) for the nonlinear models. These models are suitable for the  $a_w$  range studied of (0.100–0.756). Among the nonlinear models, the three-parameter GAB model was preferred based on the parsimony concept and considering that the modified-GAB model is an empirical model developed to correlate sorption data that include  $a_w$  values higher than 0.90.<sup>9</sup> It should be pointed out that the Hasley equation is not able to predict important parameters such as the monolayer water adsorbed and sorption enthalpies associated to the mono- and multilayer adsorbed water. These parameters can be estimated using the GAB model<sup>25</sup> that was preferred in this research work.

The following equations are associated to the three-parameter GAB model:<sup>25</sup>

$$M = \frac{ABCa_w}{(1 - Ca_w)(1 - Ca_w + BCa_w)} \quad (2)$$



**Figure 2.** Adjusted GAB model for the sorption isotherms of NPK 10–20–20/4 MOP fertilizer for a combined temperature range between 15 and 35 °C. Dotted lines represent the 95% confidence interval bounds.

In eq 2,  $A$  is the GAB monolayer moisture (g/100 g of dry solids), and  $B$  and  $C$  are constants related to the temperature effect, as indicated by eqs 3 and 4 below:

$$B = B_0 e^{\Delta H_B/RT} \quad (3)$$

$$C = C_0 e^{\Delta H_C/RT} \quad (4)$$

where  $B_0$  and  $C_0$  represent entropic accommodation factors,  $R$  the universal gas constant, and  $T$  the absolute temperature. The sorption enthalpies  $\Delta H_B$ ,  $\Delta H_C$ , can be written as:

$$\Delta H_B = H_M - H_N \quad (5)$$

$$\Delta H_C = \lambda - H_N \quad (6)$$

where  $H_M$ ,  $H_N$ , and  $\lambda$  are, respectively, the sorption enthalpies of the monolayer, multilayer, and latent enthalpy of pure water.

The GAB model parameters  $A$ ,  $B_0$ ,  $C_0$ ,  $\Delta H_B$ , and  $\Delta H_C$  were obtained by direct nonlinear regression, by substituting eqs 3 and 4 into eq 2, using the same statistic weight for all experimental values.<sup>25</sup> For this purpose, the nonlinear regression adjustment was performed using software Matlab v. 2007-RB. A one-way analysis of variance was carried out to establish statistical differences in sorption data between treatments (temperatures of 15, 23, and 35 °C) with 2 and 24 degrees of freedom. An  $F = 0.076$ , lower than the critical value ( $F_{2,24,0.05} = 3.40$ ), was obtained, accepting the null hypothesis that there were not significant differences ( $\alpha = 0.05$ ) between treatments, and a combined temperature range could be used from the statistical point of view. Curve fitting to the GAB model was performed using the combined values for the three temperatures studied (15, 23, and 35 °C). An average interval temperature of 24.3 °C (297.45 K) was used. Figure 2 shows the adjusted GAB model including the 95% confidence interval bounds. Most of the sorption values were contained within those bounds.

Values of  $B = 2.72$  and  $C = 1.27$  were obtained by substituting the values of  $B_0$ ,  $C_0$ ,  $\Delta H_B$ , and  $\Delta H_C$  into eqs 3 and 4, with  $A = 0.852$  given in Table 3. It has to be pointed out that at the average temperature (24.3 °C) of the interval studied (15 to 35 °C), the value of the exponential terms in eqs 3 and 4 is practically 1. For this reason, the values of  $B$  and  $C$  are basically the same as  $B_0$  and  $C_0$ , indicating that the effect of

**Table 3. Nonlinear Regression Parameters for the GAB Model ( $a_w < 0.756$ ) in the Combined Temperature Range from 15 to 35 °C for NPK 10-20-20/4 MOP Fertilizer**

GAB parameter	estimated value <sup>a</sup>
$A$ (g/100 g)	0.852
$B_0$ (dimensionless)	2.72
$C_0$ (dimensionless)	1.27
$\Delta H_B$ (kJ/gmol)	0.932
$\Delta H_C$ (kJ/gmol)	0.696

<sup>a</sup> Sum of squares error (SSE) = 54.19; RMSE = 1.569; sum of residuals = -0.39;  $R^2 = 0.953$ .

temperature on those parameters was negligible. The residuals plot is presented in Figure 3. As can be observed in this figure, the residuals for the GAB model appear to be randomly distributed, indicating that this model (eq 2) describes the sorption data adequately, with a sum of residuals of -0.39. Deviations observed for high water activities close to the asymptote obtained for values around  $a_w = 0.75$  could be explained by water adsorption exceeding the monolayer value that resulted in the beginning of liquefaction of the fertilizer as already discussed.

In general, for the GAB equation,  $0 < C \leq 1$  and  $B > 0$ . For  $B \leq 2$ , a type III isotherm results.<sup>25,26</sup> For the fertilizer NPK10–20–20/4 MOP, a type III isotherm typical of crystalline solids was obtained ( $B = 2.72$ ). In the same way, a value of  $C$  greater than one (1.27) was obtained, indicating that water sorption tends to infinite at a water activity value less than 1. In this case an asymptote was found for a water activity value close to 0.756. The observed behavior could be due to the mobility of ions and the liquefaction process already mentioned and described by other authors to explain fertilizer caking.<sup>1,3,4</sup>

The following equation represents the three-parameter GAB equation for the fertilizer NPK10–20–20/4 MOP for the temperature range (15 to 35 °C) studied in this work. This equation was obtained by substituting constants  $A$ ,  $B$ , and  $C$  into eq 2.

$$M = \frac{2.94a_w}{[1 + 0.914a_w - 2.77a_w^2]} \quad \text{with } a_w \leq 0.756 \quad (7)$$

As pointed out by Rhaman,<sup>25</sup> the monolayer value in the GAB equation is given by parameter  $A$  in eq 2. In this case  $A = 0.852$



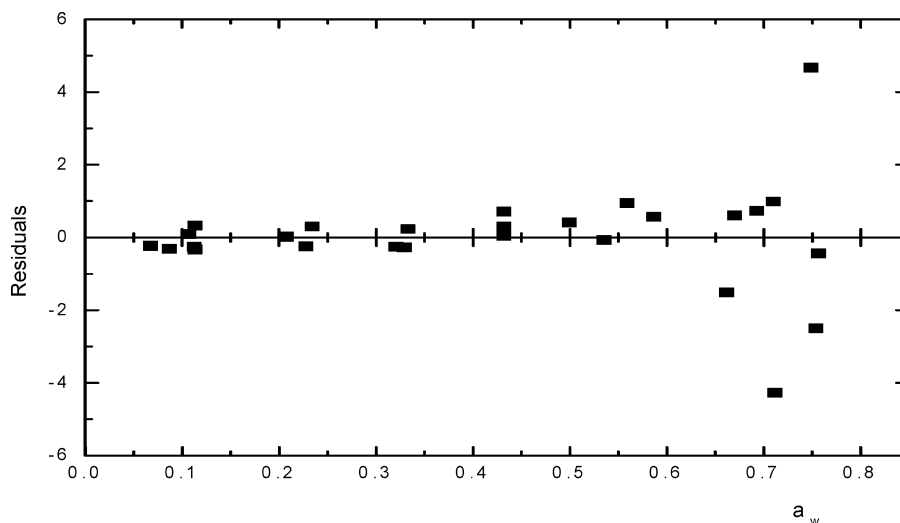


Figure 3. Residuals plot of the GAB model for NPK 10–20–20/4 MOP fertilizer.

g of water/100 g dry solids. For the monolayer value, a corresponding  $a_w = 0.299$  was obtained using eq 7. This value satisfactorily agrees with  $a_w$  values for initiation of caking (0.200–0.300) in most fertilizers.<sup>2</sup> Following this criterion, moisture contents between 0.861% and 1.27% (dry basis) or 0.854% and 1.25% (wet basis) were calculated using eq 7 for the indicated water activities. It should be realized that caking depends also on other factors such as storage pressure, fertilizer hygroscopic properties and composition, particle size, time, and temperature.<sup>3</sup> The knowledge of this parameter is particularly relevant to define the onset of caking during modeling product storage stability, taking into account mass and heat transfer through packaging laminates and within the product itself under different storage conditions including combined ambient relative humidity and temperature effects.

Values of  $\Delta H_B = 0.932$  kJ/gmol and  $\Delta H_C = 0.696$  kJ/gmol were obtained from the three-parameter GAB model and presented in Table 3. From the steam tables,<sup>27</sup> a value of  $\lambda_{24,3^\circ\text{C}} = 43.99$  kJ/gmol was estimated. When eqs 5 and 6 were solved simultaneously, values of  $H_N = 43.3$  kJ/gmol and  $H_M = 44.2$  kJ/gmol were obtained. These parameters are useful to estimate energy requirements in drying processes. Values for such parameters were not found in the literature reviewed.

## Conclusions

Water sorption isotherms of NPK 10–20–20/4 MOP fertilizer were determined for a temperature range between 15 and 35 °C using a gravimetric method. Experimental data indicated that the effect of temperature on the sorption characteristics of this material was negligible and the data collected could be represented by a single isotherm. A type III isotherm, characteristic of crystalline solids, was obtained.

Fitting of the experimental data to different sorption models at the temperatures studied (15, 23, and 35 °C) was carried out. From the two-parameter linearized models studied, the Hasley isotherm showed the best fitting ( $R^2 = 0.934$ ). Among all the models studied, the better fittings were obtained for the nonlinear three-parameter GAB ( $R^2 = 0.953$ ) and modified GAB ( $R^2 = 0.954$ ) equations. Among these two models, the first one was preferred because it is simpler and because the latter is an empirically more complex model developed to correlate sorption data for  $a_w$ , including values higher than 0.90, which was out of the range studied in this work.

The monolayer water content calculated from the GAB equation was 0.852 g of water/100 g of dry solids, corresponding to a water activity of 0.299. Fertilizer moisture content above this value would present positive risks of caking during storage. Values of monolayer and multilayer water sorption enthalpies of  $H_N = 43.3$  kJ/gmol and  $H_M = 44.2$  kJ/gmol, respectively, were obtained.

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