

## Experimental Determination of the Sorption Isotherms of “Beta” Lactose, New Water Absorbent and Sodium Bicarbonate

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**Abstract:** The sorption isotherms of “beta” lactose, sodium bicarbonate and new water absorbent in powdered form were determined within the range of 11-100% relative humidity at 4°C, using saturated salt solutions method. The comparison between the sorption isotherms of “beta” lactose, sodium bicarbonate and new generation of water absorbent is studied. The new water absorbent was the most hygroscopic and had sigmoid shaped, type II isotherms according to Brunauer-Emmet-Teller (BET) classification. The “beta” lactose and sodium bicarbonate exhibited type III behaviour. The goodness of fit of the GAB model to experimental results was determined. All of the products tested, the new water absorbent gave good fit while the “beta” lactose and the sodium bicarbonate gave a less good fit.

**Key words:** Sorption isotherms, water activity, GAB equation, modelling

### INTRODUCTION

A knowledge and understanding of water sorption isotherms of foods or food ingredients is of greatest importance in food science and technology for many reasons, such as the design and optimisation of processing or shelf life stability predictions (Abramovic and Klofutar, 2002). That guarantees food safety, quality and stability which are a major challenge for food industry (Baucour and Daudin, 2000). Knowledge of the sorption properties of foods is important for calculating food stability during storage, which depends mainly on the water activity of the product. The sorption isotherm can also affect the drying kinetics, changing the boundary conditions or altering the value of the diffusion coefficient (Viollaz and Rovedo, 1999). In recent years, there have been important contributions in the field of sorption. Sorption isotherms for foodstuffs were summarized by Van den Berg and Bruin (1981), Van den Berg (1985) and Chirife (1983).

Many empirical relations describing the sorption characteristics of food or food ingredients have been proposed in literature (Abramovic and Klofutar, 2002). In the last years, the Guggenheim, Anderson and de Boer (GAB) isotherm equation has been widely utilized to describe the sorption behaviour of foods (Maroulis *et al.*, 1988; Bizot, 1983; Weisser, 1985). Having a reasonably small number of parameters (3), the GAB equation has

been found to adequately represent the experimental data in the range of water activity of most foods. The use of the GAB equation in foods was formally proposed by Van den Berg (1985). Since then the GAB model has been utilized and recommended by the European project group, COST 90, on physical properties of foods (Wolf *et al.*, 1985) and is now almost universally used by laboratories around the world. Early, Boquet *et al.* (1979) reported on the excellent fitting abilities of Hailwood and Horrobin (1946) equation, which is mathematically identical to the GAB equation (Boquet *et al.*, 1980).

The objectives of this research were to determine the water sorption isotherms at 4°C for “beta” lactose, sodium bicarbonate and a new water absorbent and to evaluate the suitability the GAB model for the description of equilibrium moisture content data of this products; and calculate the monolayer moisture content and to select the best product for describing the GAB model based on statistical analysis.

### ISOTHERM EQUATION AND FITTING METHODS

**Experimental procedures:** “Beta” lactose, sodium bicarbonate and new water absorbent (Nalco 1181, Nalco Chemical Company) from a commercial source were used throughout this work. The water sorption isotherms were determined by gravimetric technique, in which the weight was monitored discontinuously within a standard static

system of thermally stabilized desiccators. This method was recommended by the COST 90 project (Wolf *et al.*, 1985).  $2 \pm 0.001$  g of samples were placed in a petri-dish inside desiccators. Saturated salt solutions were used to maintain the specified relative humidity inside the desiccators. The prepared desiccators were then placed in temperature controlled at  $4^\circ\text{C}$ . The samples were weighed interval 24 h, the samples were allowed to equilibrate until there was no discernible weight change, as evidence by constant weight values ( $\pm 0.001$  g). The total time required for removal, weighing and replacing the samples in desiccators was approximately 25 sec. This minimized the degree of atmospheric moisture sorption during weighing. Each experiment was carried out in triplicate. The bone dry mass was determined gravimetrically by drying in a convectional oven at  $105^\circ\text{C}$  for 8-10 h (AOAC, 1980).

**Model for the data analysis:** The moisture sorption isotherm of foods can be described by numerous mathematical models with two or more parameters (Van den Berg and Bruin, 1981). However, models with more than three parameters are too complex for straightforward interpretation or use. Several isotherm equations have been proposed for the correlation of the equilibrium moisture content with the water activity ( $a_w$ ) of food products. Among the most efficient equations for the prediction of the experimental data, the GAB can be mentioned. The major advantages of the GAB model are its viable theoretical background, need for only three parameters (with physical meaning) and its capacity to describe the sorption of water vapour in foods up to water activity 0.9 by just multiplying the activity by a constant less than unity (Bizot, 1983; Van den Berg, 1985; Lomauro *et al.*, 1985a, 1985b). The GAB equation is normally written in following form (Iglesias and Chirife, 1995):

$$M = \frac{M_o C K a_w}{[(1 - K a_w)(1 - K a_w + C K a_w)]} \quad (1)$$

where,  $M$  is the moisture content of material on a dry basis (kg water/kg dry solids),  $C$  is the Guggenheim constant related to heat of sorption,  $a_w$  water activity,  $K$  is the constant related to multilayer molecules properties and  $M_o$  is the moisture content of monolayer in BET theory (kg water/kg dry solids).

After transformation, the GAB equation has an equivalent form to the Hailwood and Horrobin (1946) equation:

$$a_w / M = (b_3 a_w^2 + b_2 a_w + b_1) \quad (2)$$

From the parameters  $b_1$ ,  $b_2$ ,  $b_3$  the values of  $K$ ,  $C$  and  $M_o$  were calculated through the following relations:

$$K = \frac{\sqrt{b_2^2 - 4b_1b_3} - 2}{2b_1} \quad (3)$$

$$C = \frac{b_2}{b_1 K} + 2 \quad (4)$$

$$M_o = \frac{b_2}{b_1 K C} \quad (5)$$

The isotherm fitting were obtained by extrapolation using the single-hydrate sorption model (Hailwood and Horrobin, 1946). The data were transformed by dividing the water activity ( $a_w$ ) with the equilibrium moisture contents ( $M$ ) earlier. A quadratic curve of polynomial function was obtained from these data points. A graphical illustration of the ratio  $a_w/M$  against activity water ( $a_w$ ), using the parabolic equation, is shown and was deduced the values  $b_1$ ,  $b_2$ ,  $b_3$  (Table 2) and  $R^2$  obtained. The statistical proportion of variation,  $R^2$ , is used to explain the regression line whereby higher or lower  $R^2$  would indicate the goodness of fit to regression line.

The goodness of fit for each isotherm was quantified through three standards: the correlation coefficient  $R^2$ , the standard error of the estimate SEE and the mean relative deviation  $E$  (%).

The standard error estimate SEE is the conditional standard deviation of the dependent variable and has the form:

$$SEE = \sqrt{\frac{\sum [(M_{exp} - M_{pr}) / M_{exp}]^2}{df}} \times 100 \quad (6)$$

where,  $M_{exp}$  and  $M_{pr}$  are the experimental and predicted values, respectively and 'df' is the degrees of freedom of the fitting equation. The number of degrees of freedom as follows  $N - n_p$  where  $N$  is the number of data points and  $n_p$  is the number of parameters (Maroulis *et al.*, 1988).

$$SEE = \sqrt{\frac{\sum [(M_{exp} - M_{pr}) / M_{exp}]^2}{N - n_p}} \times 100 \quad (7)$$

De Jong *et al.* (1996) proposed that a sorption isotherm is useful when the SEE is lower than 4%.

The mean relative deviation  $E$  (%) is an absolute value that was used because it gives a clear idea of the mean divergence of the estimated data from the measured data:

$$E (\%) = \left[ \sum_{n=1}^n \frac{|M_{\text{exp}} - M_{\text{pr}}|}{M_{\text{exp}}} \right] \times \frac{100}{N} \quad (8)$$

The mean relative percentage deviation modulus (E) is widely adopted throughout the literature, with a modulus value below 10% indicative of a good fit for practical purposes (Lomauro *et al.*, 1985a).

In general terms, high values of  $R^2$ , low values of SEE and E (%) mean that the model is able to explain the variation in the experimental data (Pagano and Mascheroni, 2005).

## RESULTS AND DISCUSSION

**Adsorption isotherms:** The adsorption isotherms of the products were determined at 4°C in several relative humidities (Table 1). The main disadvantage of this method is the longer time to stabilize the samples, about 2-4 weeks dependently of the product. The profile of a sorption isotherm is characteristic of the hygroscopicity of a product. Highly hygroscopic products exhibit a steep sorption isotherm, while sparingly hygroscopic products exhibit flat sorption isotherms.

A measure of the hygroscopicity of a product is consequently the magnitude of the increase or decrease in its water content as a function of relative humidity at a constant temperature. Weakly hygroscopic products exhibit no or only a slight change in their water content as a consequence of variations in relative humidity. In strongly hygroscopic products, water content may vary widely.

The new water absorbent Fig. 1 show the isotherm classified as type II, sigmoid form and the most common in foods. This typical sigmoid shape is characteristic of materials with a high sugar content, which sorbs relatively small amount of water at lower activities and large amounts at high relative humidities (Samaniego-Esquerre *et al.*, 1991). The points at low values of water activity ( $a_w < 0.60$ ) represent the

adsorption bound water and so isotherm has only a gentle upward slope. As the water activity increases, the equilibrium moisture content increases sharply with  $a_w$  due capillarity. This behaviour is typical for many foods products and a large number of reports exist in the literature.

The “beta” lactose and sodium bicarbonate (Fig. 1) show isotherms type III, “J sharpe”, in classification of BET. They absorbed very little moisture over the low water activity range (0.11-1). It is only at water activities above 0.85 that the significant amounts of moisture are adsorbed. The moisture content increases exponentially above this point and adjoin an asymptote at a water activity of one. Similar results were reported by Jouppila and Ross (1994). One reason for the exponential increase in moisture content at high water activities is capillary condensation (Adamson, 1960). Capillary condensation is the process where direct condensation can occur, due to surface tension effects, in the capillaries formed at the contact points between adjacent particles. Sodium bicarbonate was most hygroscopic (moisture content in the range 107 g g<sup>-1</sup> dm) than “beta” lactose (moisture content in the range 24 g g<sup>-1</sup> dm) at high water activities ( $a_w = 1$ ) (Fig. 1).

In all cases, the graphs are exponential to a certain value of  $a_w$  above 0.95 after which point, suggesting the transition of the water sorption stage. This analysis of sorption isotherms of sample suggests that above  $a_w = 0.95$ , a change in the physical state of water occurred (Timmerman and Chirifie, 1991). For unstructured foods, this phenomenon has been explained. At low  $a_w$ , water is strongly bound to the food matrix. It remains bound (although in different stages) up to high values of  $a_w$ , but above a certain value much less bound water becomes available (liquid-like water layers).

**Mathematical modelling:** The graphical illustrations of the ratio  $a_w/M$  against water activity ( $a_w$ ), using the parabolic equation gave the values of parameters  $b_1$ ,  $b_2$ ,  $b_3$  (Table 2).

Table 1: Equilibrium moisture content  $M$ , % d.b. of “beta” lactose, new water absorbent and sodium bicarbonate obtained by adsorption at 4°C

| $a_w$ | Sodium bicarbonate |                   | β lactose |                   | New water absorbent |                   |
|-------|--------------------|-------------------|-----------|-------------------|---------------------|-------------------|
|       | $M^a$              | s.d. <sup>b</sup> | $M^a$     | s.d. <sup>b</sup> | $M^a$               | s.d. <sup>b</sup> |
| 0.11  | 0.13               | 0.02              | 0.09      | 0.01              | 6.4                 | 0.03              |
| 0.23  | 0.15               | 0.01              | 0.12      | 0.01              | 15.3                | 0.04              |
| 0.34  | 0.17               | 0.02              | 0.21      | 0.01              | 24.2                | 0.40              |
| 0.43  | 0.18               | 0.03              | 0.22      | 0.01              | 29.4                | 0.11              |
| 0.56  | 0.32               | 0.02              | 0.23      | 0.01              | 39.3                | 0.14              |
| 0.65  | 0.34               | 0.03              | 0.35      | 0.05              | 50.0                | 0.40              |
| 0.75  | 0.35               | 0.02              | 0.43      | 0.07              | 68.8                | 0.26              |
| 0.87  | 0.80               | 0.04              | 0.98      | 0.09              | 93.4                | 0.22              |
| 0.97  | 17.34              | 0.10              | 4.40      | 0.07              | 138.0               | 0.21              |
| 0.99  | 38.57              | 0.16              | 11.61     | 0.09              | 182.0               | 0.33              |
| 1.00  | 107.31             | 0.21              | 24.09     | 0.17              | 228.6               | 0.26              |

<sup>a</sup>Mean of three replications. <sup>b</sup>Standard deviation based on three replications

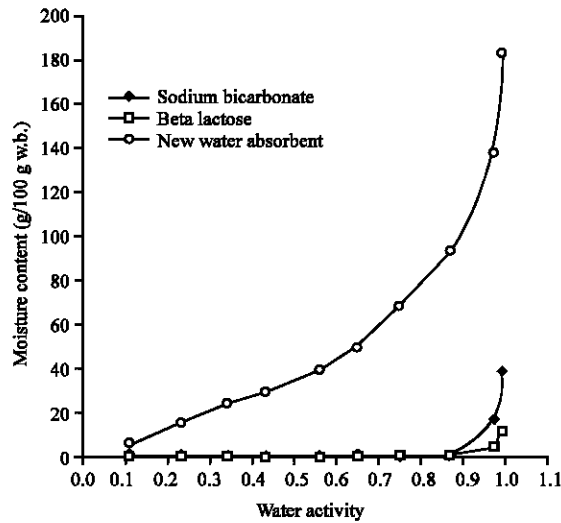


Fig. 1: Comparison of moisture sorption of “beta” lactose, sodium bicarbonate and new water absorbent at 4°C

Table 2: Values of parameters of equation for samples at a temperature of 4°C

|                     | $b_3$   | $b_2$  | $b_1$   |
|---------------------|---------|--------|---------|
| Sodium bicarbonate  | -9.1544 | 9.2044 | -0.0778 |
| Beta lactose        | -7.5385 | 7.0819 | 0.4924  |
| New water absorbent | -0.0147 | 0.0005 | 0.0156  |

Table 3: Constants and mean relative percentage deviation obtained for samples at a temperature of 4°C

|                     | $M_0$ | K    | C       | $R^2$ | E (%) | SEE (%) |
|---------------------|-------|------|---------|-------|-------|---------|
| Sodium bicarbonate  | 0.11  | 1.00 | -117.53 | 0.93  | 21.18 | 39.10   |
| Beta lactose        | 0.12  | 0.99 | 16.53   | 0.94  | 12.69 | 17.26   |
| New water absorbent | 32.79 | 0.83 | 2.36    | 0.96  | 6.08  | 8.21    |

Table 3 shows that relatively high values were found for the correlation coefficient for all products ( $R^2$ ), showing in the first analysis that the new water absorbent can be considered valid. The value of  $R^2$  is not by itself a solid or robust analysis index (Sun and Woods, 1994).

Following this concept, it can be observed in Table 1 that the equation gave higher values of SEE 39.10; 17.26 and E (%) 21.18; 12.69 and the acceptable values of  $R^2$  0.93; 0.94, respectively for sodium bicarbonate and “beta” lactose (Fig. 2). These results should suggest that this is not the most appropriate model for description of their experimental data. The new water absorbent show lower values of SEE 8.21 and E (%) 6.08, accompanying higher values of  $R^2$  0.96 compared with those corresponding to sodium bicarbonate and “beta” lactose. The mean relative percentage deviation modulus E (%) is widely adopted throughout the literature, with a modulus value below 10% indicative of a good fit for practical purposes (Lamauro *et al.*, 1985b). Therefore, SEE and E (%) criteria do not always provide the same ranking for all

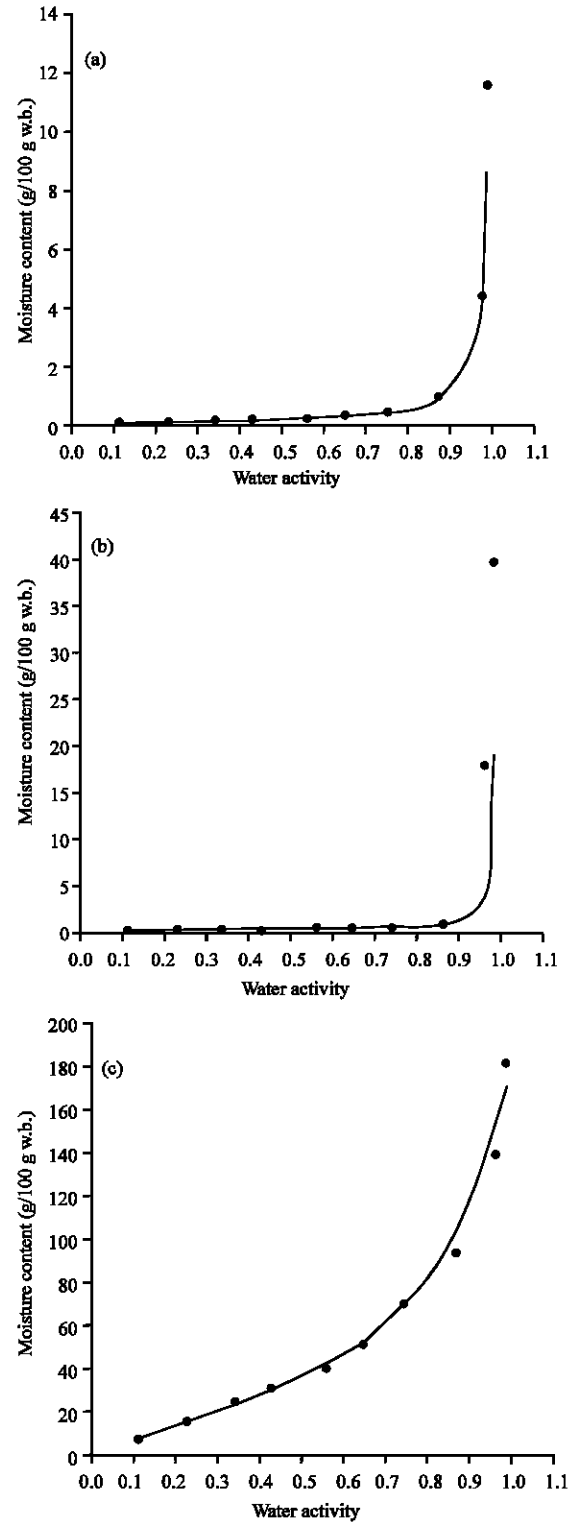


Fig. 2: Water sorption isotherm at 4 °C: experimental data (symbols) and GAB prediction (continuous curve) f “beta” lactose (a), sodium bicarbonate (b) and new water absorbent ©

EMC-ERH models (Chen and Morey, 1989). Finally, it is obvious that a single statistical parameter can not be used to select the best model and the assessment of model must always be made based on multiple statistical criteria (Jayas and Mazza, 1993). When the coefficients  $R^2$ , an error E (%) are analyzed, it is verified that the new water absorbent that best represents the model, showing the highest values of  $R^2$  equal to 0.96 and lower E (%) 6.08 (less than 10%).

The results indicate that the GAB equation is accurate for the prediction of the new water absorbent. It is noteworthy that the merits of this equation should be judged considering that its fitting abilities cover the range of water activity (0.11-1) and has a reasonably small number of parameters (three) to be determined (Iglesias and Chirifíe, 1995).

At high  $a_w$  the standard GAB sorption theory no longer holds (Timmermann and Chirifíe, 1991). The fact that the GAB isotherm still deviates from the experimental observations means that sorption in structured cellular foods above 0.95  $a_w$  is even more complex than in unstructured foods. This also means that the three-parameter GAB model can predict well the experimental data for  $a_w$  up to 0.95. It has been noted that the validity of a sorption model cannot be proven just by its ability to fit the observed data and a physico-chemical basis is also needed (Chirifíe *et al.*, 1992).

The values of mono-layer moisture content for new water absorbent, "beta" lactose and sodium bicarbonate were, respectively 32.79; 0.124; 0.109 g 100 g solids.

For the new water absorbent, "beta" lactose and sodium bicarbonate, the value of mono-layer moisture content determined by GAB correspond, respectively to water activity of around 0.43; 0.23; 0.11 at 4°C. For most dry foods, the rate of quality loss due the chemical reactions is negligible below the monolayer value (Bell and Labuza, 2000). These values are particularly important in storage of the product, since level the water does not act as a solvent, being biologically inert (Arévalo-Pinedo *et al.*, 2004).

According to Chirifíe *et al.* (1992), a value of K is physical unsound. But K of sodium bicarbonate was similar to dried apricots (0.94-1.02) (Samaniego-Esguerra *et al.*, 1991).

## CONCLUSION

"Beta" lactose and sodium bicarbonate exhibited type III isotherms. However the new water absorbent exhibited type II. The adsorption of sodium bicarbonate was higher than "beta" lactose adsorption. The new water absorbent was the most hygroscopic of the 3 products.

The proposed equation satisfactorily correlates the experimental sorption data for new water absorbent for a wide range of water activities. The functional nature of the proposed equation allows performing the fitting process with some problems at high water activities.

The GAB model can be used to predict the sorption behaviour of the three products. This model was found to best represent the experimental data of the new water absorbent.

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