Applicability of the BET and GAB models to the moisture adsorption isotherm data of some Ghanaian food flours

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SUMMARY

The static gravimetric method was used to determine the moisture adsorption isotherm data, at 30 °C, of the food flours of cassava-starch, cocoyam, plantain, fermented maize meal, and blends of cocoyam, plantain, and cassava-starch for the a_w range 0.1 to 0.9. The adsorption data obtained were fitted to the Brunauer-Emmett-Tetter (BET) and Guggenheim-Anderson-de Boer (GAB) models, by regression analysis, to estimate and compare the monolayer moisture contents of the food flours. The moisture adsorption isotherms were a mixture of Types I and II, according to the BET classification. The monolayer moisture content values, as predicted from the BET and GAB models, were comparable ranging from 4.13 to 7.61 per cent dry solids. The quality of the fitted models, as estimated by the relative percentage deviation modulus, clearly showed that both models can be used adequately to predict the monolayer moisture contents of the food flours.

Original scientific paper. Received 12 Sep 97; revised 20 Jul 98.

RÉSUMÉ

JOHNSON, P-N. T.: *L' applicabilité de modèles de BET et GAB aux données isothermes de l'adsorption d'humidité de quelques farines alimentaires ghanéennes.* La méthode gravimétrique statique était employée pour déterminer les données isothermes de l'adsorption d'humidité, à 30 °C, de farines alimentaires de féculent-manioc, de taro, de plantain, de farine de maïs fermentée et les taros mêlés, de féculents de plantain et manoic, pour les écarts a de 0.1 à 0.9. Les données d'adsorption obtenues étaient fixées sur les modéles de Brunauer-Emmett-Tetter (BET) et Guggenheim- Anderson-de Boer (GAB), par l'analyse de régression, pour estimer et comparer les contenus d'humidité monocouche des farines alimentaires. Les isothermes de l'adsorption d'humidité étaient un mélange de genres I et II, selon la classification de BET. Les valeurs du contenu d'humidité monocouche, comme prédit de modèles BET et GAB, étaient comparable variant de 4.13 à 7.61 pour cent de solides secs. La qualité de modèles fixés, comme estimé par le module de deviation du pourcentage relatif, montraient nettement que les deux modèles pourraient être employer d'une façon adéquate à prédire les contenus d'humidité monoc.

Introduction

Cassava (*Manihot utilissima*), cocoyam (*Xanthosoma mafaffa*), maize (*Zea mays*), and plantain (*Musa paradisiaca*) are some of the important staple food crops in Ghana. The high level of post-harvest losses of these crops is, however, a matter of great national concern (Dapaah, 1990). The Food Research Institute of Ghana has, over the years, been developing staple food products from these crops. These food products are mainly in the form of food flours. Commercial processing of these flours can contribute to help arrest the perennial wastage of surpluses of these crops at the end of the harvesting season in Ghana. The main processing technique used for these food products is dehydration.

Dehydration is appropriate, considering its cost-effectiveness, for preserving tropical foods (Brennan *et al.*, 1990). During dehydration, enough water is removed from the food to lower its water activity. This prevents deterioration due to microbes and other adverse biochemical reactions. The lower the moisture content of the dehydrated food, the lower is its water activity. The lowest achievable moisture content during dehydration that can prevent microbial deterioration and other adverse biochemical reactions is the monolayer moisture content of the dehydrated food (Labuza, 1984).

The monolayer moisture content is considered to be a single layer of water molecules which coats the surface of solid food particles (Iglesias & Chirife, 1976a). It represents the portion of the total water content of a food which is strongly bound to specific sites in its particle. Iglesias & Chirife (1976b) explained that several aspects of physical and chemical deterioration in a dehydrated food were related to changes in its moisture content during storage. This is mainly for moisture contents higher than the monolayer moisture content. Thus, the monolayer moisture content is considered to be the most stable moisture for storing dehydrated foods. The monolayer moisture content is also useful information for determining the packaging of the dehydrated foods (Labuza, 1984).

The monolayer moisture content of a dehydrated food is estimated from experimentally determined moisture adsorption data of the dehydrated food and then fitted to either the BET or GAB equations (Rizvi, 1995). The BET model is generally expressed in the following form:

$$\frac{a_w}{(1-a_w)M} = \frac{1}{M_oC} + \frac{C-1}{M_oC} a_w$$

where M is the moisture content at any water activity (a_w), M_o is the monolayer moisture content, and C is a constant. The BET model gives a good fit to the moisture sorption data from a variety of foods, in the range of $0.05<a_w<0.45$ (Iglesias & Chirife, 1978). The GAB model for the sorption of water vapour is mathematically expressed as follows:

$$\frac{M}{M_o} = \frac{CKa_w}{(1-Ka_w)(1-Ka_w+CKa_w)}$$

where C and K are constants related to the energies of interaction between the first and distant sorbed molecules at the individual sorption sites. The three-parameter GAB equation, derived independently by Guggenheim (1966), Anderson (1946), and de Boer (1953) is now regarded as the most versatile sorption model available. It is applicable to the whole range of the a_w, from 0.05 to 0.95. Estimation of the monolayer moisture contents, as well as other constants, from the two models, is by regression analysis.

This study was therefore carried out to construct the moisture adsorption isotherms of air-dried flours of cassava-starch, cocoyam, plantain, blends of cassava-starch, cocoyam, and plantain as well as fermented maize meal. The BET and GAB models were fitted to the moisture adsorption data obtained, and the monolayer moisture contents of these flour food products were estimated. The implications of the nature of the moisture adsorption isotherms for the packaging and shelf lives of these foods are also discussed.

Materials and methods

Materials

The cassava-starch, cocoyam, plantain, and fermented maize meal food flours, with particle size 400 - 500 μm, used for the study were prepared by the Commercial Unit of the Food Research Institute of Ghana. About 100 g of each sample was first dried, at 40 °C for 5 h, in a fan-assisted, hot air laboratory cabinet drier (Imperial IV Microprocessor Oven, Lab-line Instruments Inc.). Each sample was further dried down in a dessicator for 1 week at room temperature to a moisture content of about 3 per cent d.s.

Determination of moisture adsorption isotherms

Saturated solutions of different salts as described by Speiss & Wolf (1987) were used to establish atmospheres of different relative humidities (or water activities). For convenience, Table 1 lists the saturated solutions applied.

The set-up used for exposing the food samples to the various relative humidities was based on the principles of the Proximity Equilibrium Cells (PEC) (Lang, McCune & Steinberg, 1981). In the PEC technique, the time needed for a food sample to equilibrate to conditions created within a sorption container is reduced from several weeks

TABLE 1

Salt Solutions Used to Provide Atmospheres of Specified a_w

Saturated solution of salts	*Approximate a_w at 30 °C*
Lithium chloride	0.11
Potassium acetate	0.23
Magnesium chloride	0.33
Potassium carbonate	0.44
Magnesium nitrate	0.53
Sodium bromide	0.58
Strontium chloride	0.71
Sodium chloride	0.75
Potassium chloride	0.84
Zinc sulphate	0.89

to a few weeks by increasing the surface area of the saturated salt per unit volume of water vapour. Each saturated salt solution was held in a small sorption container (Lang, McCune & Steinberg, 1981). This consisted of a small cylindrical glass jar (90 mm long and 75 mm diameter) with a tightly fitted lid. Each sorption container was filled to about a third of its volume with saturated solutions of one of the salts (Table 1).

The weighed food material was held in a previously dried and weighed polypropylene weighing boat, 44 mm × 44 mm in size (Fisher Scientific, UK). To improve water-vapour transmission, the bottom of this boat was modified by removing a 25-mm diameter circular section and replacing it with Whatmann No. 1 filter paper. The sample in the modified boat was suspended over the saturated salt solution, with a wire string attached to the lid of the sorption container. The sorption containers with the food samples were placed inside an incubator set at 30 °C. The weight of sample used was 1.0 ± 0.050 g. Triplicate determinations were made at each a_w. The weight of each sample was monitored weekly until it was constant. Samples were equilibrated between 3 and 5 weeks. The equilibrium moisture content was determined by air-oven method at 103 °C for 24 h (AOAC, 1984). Deviations from the means of the moisture contents determined ranged from 1.0 ± 0.5 per cent at low a_w to 5.5 ± 1.0 per cent at high a_w. The mean moisture contents were used in constructing the isotherms.

Fitting of BET and GAB models

The BET and GAB models were fitted to the equilibrium moisture contents obtained by using regression programmes (MINITAB, 1994). The BET model was fitted to data obtained for the a_w range 0.1 to 0.5 whilst the GAB model was fitted to whole range of a_w from 0.1 to 0.9.

The quality of the fitting was evaluated by calculating the mean relative percentage deviation modulus, E % (Boquet, Chirife & Iglesias, 1978) as given below:

$$E\,\% = \frac{100}{N}\sum_{i=1}^{n}\frac{|m_e - m_p|}{m_e}$$

where n is the number of experimental data and m_e and m_p are the experimental and predicted values, respectively.

Results and discussion

General patterns of the moisture adsorption isotherms

The moisture adsorption isotherms of the four individual food flours (Fig. 1) were a mixture of Types I and II isotherms (Labuza, 1984). The isotherms of cassava-starch and cocoyam were similar and different from those of plantain and fermented maize meal. At low a_w, the cassava-

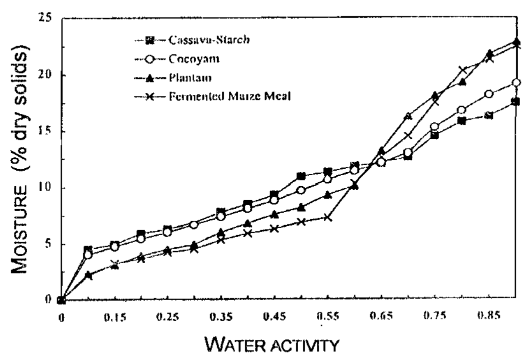

Fig.1. Moisture adsorption isotherms of cassava-starch, cocoyam, plantain and fermented maize meal at 30 °C.

starch and cocoyam flours adsorbed more moisture than the plantain and fermented maize meal. However, above a_w = 0.55, the plantain and fermented maize meal showed greater tendency to adsorb moisture than cassava-starch and cocoyam.

There could be several reasons for the observed trends. At a_w 0.05 to 0.4 range, usually referred to as Zone 1, water molecules are mainly adsorbed onto hydrophilic, charged and polar groups of proteins and polysaccharides (Kapsalis, 1987). In all food flours, the main constituents are carbohydrates. The carbohydrates of these foods are mainly starch and sugars. Wooton & Bamunuarachi (1978) have explained that the main water-binding sites in starch are the hydroxyl groups and inter-glucose atoms. During gelatinization, the water-binding sites are increased as the heat disrupts the intragranular bonds. In the process of making the four flours, the four food products were air-dried between 65 and 70 °C. At this temperature range, some of the starch was found to be 60 - 66 °C (Johnson, 1996). This means the differences noted between the moisture adsorption abilities of cassava-starch, cocoyam, plantain, and fermented maize meal reflect differences in the contents of starch as well as differences in the extent of gelatinization of the starch granules of the four different food flours during their processing.

The cassava-starch did not have any effect on the moisture adsorption ability of the cocoyam flour (Fig. 2). This is in contrast with plantain (Fig. 3) which seems to have been affected when mixed with the cassava-starch. Here two effects are evident. In the monolayer zone (i.e., at a_w < 0.4), there is an increased ability of the plantain flour, when mixed with cassava-starch, to equilibrate to a relatively high moisture content than in the plantain flour alone. This supports the relatively higher monolayer moisture contents obtained for the blends of plantain and cassava-starch (Table 2).

However, in the Zone 3 (i.e., a_w > 0.7), where water molecules are mechanically entrapped in the voids, crevices and capillaries, the cassava-starch reduced the amount of moisture the plantain flour would normally have adsorbed. On its own, the plantain flour showed a relatively high tendency to absorb moisture at above a_w = 0.55. This observation may be related to the fact that more starch molecules are hydrolyzed to sugar in plantain than in either cassava or cocoyam (Chan, 1983).

Foods with relatively high sugar content show the tendency of adsorbing a lot of water at high relative humidities. This is because the sugars in such foods, which are mainly in the amorphous state at low relative humidity (a_w < 0.55), are transformed into the crystalline state at a_w > 0.55 (Labuza, 1984). The transformation is accompa-

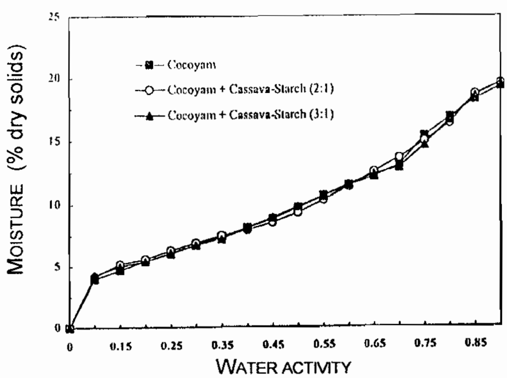

Fig. 2. Moisture adsorption isotherms of cocoyam and blends of cocoyam and cassava-starch flours at 30 °C.

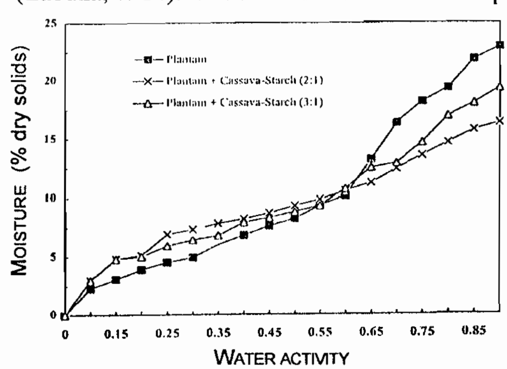

Fig. 3. Moisture adsorption isotherms of plantain and blends of plantain and cassava-starch flours at 30 °C.

TABLE 2

Estimated Monolayer Moisture Contents and Other Constants from the BET and GAB models

Sample	BET			GAB			
	M_o	C	r	M_o	C	K	E %
Cassava-Starch	7.13	13.4	0.97	7.61	6.66	1.73	9.15
Cocoyam	5.18	12.8	0.95	5.22	13.7	0.83	4.59
Plantain	4.13	12.2	0.95	4.68	13.4	0.82	6.74
Cocoyam + Cassava - Starch (2:1)	5.45	13.6	0.96	5.62	21.2	0.86	5.69
Cocoyam + Cassava - Starch (3:1)	5.80	7.84	0.86	6.12	8.89	0.82	6.23
Cocoyam + Plantain (2:1)	6.42	8.56	0.89	6.33	12.5	0.84	8.71
Cocoyam + Plantain (3:1)	4.89	5.12	0.92	4.91	21.8	0.89	11.5
Plantain + Cassava - Starch (2:1)	6.29	4.56	0.85	6.63	15.1	0.87	8.05
Plantain + Cassava - Starch (3:1)	6.21	4.87	0.89	6.11	15.6	0.85	9.23
Cocoyam + Plantain + Cassava - Starch (2:1:1)	6.23	5.23	0.92	6.23	14.9	0.86	12.5
Fermented Maize Meal	4.53	6.10	0.99	4.72	11.6	0.87	8.91

M_o = Monolayer moisture content (in % d.s), C and K are constants in the BET and GAB models
r = Correlation coefficient, and E % = Mean percentage deviation modulus

nied by an increased adsorption of moisture (Johnson, 1996). This behaviour of plantain flours usually leads to plasticization (Karel, 1992) during storage in packages as noted by Dei-Tutu (1975) in his work on a plantain product called *Tatale mix*.

The suppressing effect of cassava-starch on moisture adsorption, at high relative humidity, has positive practical implication for packaging and shelf-life of plantain flour. This observation means that a blend of plantain flour and cassava-starch may have a longer shelf life than ordinary plantain flour.

The estimated monolayer moisture content, M_o

The estimated monolayer moisture contents for all the food flours studied (Table 2) fell within ranges found for other foods (Iglesias & Chirife, 1976b). The estimated monolayer moisture contents from the BET model were usually slightly less than those obtained from the GAB model. This observation agrees with results obtained by Wang & Brennan (1991).

Iglesias & Chirife (1976b) explained that the accuracy of the estimated monolayer moisture content from the BET model is diminished as the value of the C approaches unity. In such situations, the direct use of the BET equation in the conventional manner is not recommended for isotherms with C values less than 4. Since all the C values obtained are higher than 4 (Table 2), it can be concluded that the estimated monolayer values from the BET model are reliable.

The mean relative percentage modulus (E %) values are mostly less than 10 (Table 2). This, together with the coefficients of correlation, indicates that the two models fitted the moisture adsorption data of all the food flours studied reasonably well (Boquet, Chirife & Iglesias, 1978).

The estimated C values from the two models (Table 2) are not comparable. This may be explained by considering the original theories behind the BET and GAB models. In both theories, the magnitude of the constant C is related to the energy of sorption of the adsorbed monolayer water molecules. However, Iglesias &. Chirife (1976b), after applying the BET model to a wide range of foods, concluded that the constant C in the BET model cannot be used adequately to represent the heat of sorption of the monolayer water molecules.

Conclusion

It can be concluded from the study that the moisture adsorption isotherms of flours of cassava-starch, cocoyam, plantain, and fermented maize meal as well as of blends of cassava-starch, cocoyam, and/or plantain (Fig. 4) resemble a mixture of Types I and II, according to the BET classification. Both the BET and GAB models can be

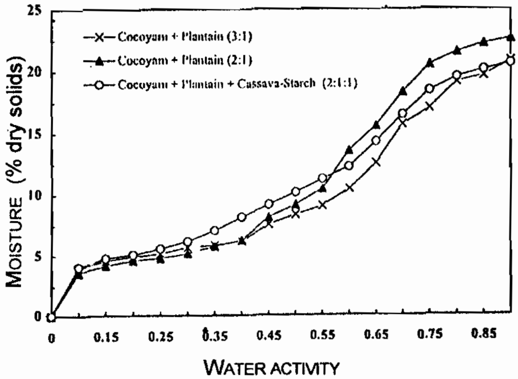

Fig. 4. Moisture adsorption isotherms of blends of cassava-starch, cocoyam and plantain flours at 30 °C.

used adequately to determine the monolayer moisture contents of the food flours from cassava, cocoyam, plantain, and fermented maize meal.

When plantain is mixed with cassava-starch, the ability of the plantain to absorb moisture at high water activities is reduced.

The study also showed that manufacturers of these food flours must ensure that the moisture contents for safe storage of their products do not exceed 7.61 per cent d.s.

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