

Isorption Isotherms of Some Nigerian Dry Condiment Powders

¹V.N. Enujiugha, ¹S.O. Iyiola, ¹M.O. Oluwamukomi, ²S. Gbadamosi, ¹I.B. Oluwalana and ²L.O. Lalude

¹Department of Food Science and Technology, Federal University of Technology, Akure, Nigeria

²Department of Food Science and Technology, Obafemi Awolowo University, Ile-Ife

Abstract: The moisture sorption isotherms of dehydrated flours of four commonly consumed Nigerian condiments (namely, ugba, okpeye, ogiri and iru) were determined. The dry milled products were kept at three separate temperatures (10, 30 and 40°C) and at four different relative humidities using saturated salt solutions (RH 20, 30, 50, and 70%) for a period of 21 days. Both the initial and equilibrium moisture contents were determined on the products and the data obtained were used to construct moisture sorption isotherm curves. The results reveal that higher storage temperature gave lower sorption capacities for the condiment powders. Also, the rate of moisture absorption increased at the monolayer at all the storage temperatures considered. At ambient and higher storage temperatures, ogiri had the relatively longest shelf life, followed by okpeye, then iru and finally ugba.

Key words: Sorption isotherms, condiment powders, monolayer

INTRODUCTION

Moisture sorption isotherm describes the relationship between the water activity (a_w) and the equilibrium moisture content for a food product at a constant pressure and temperature Kaymak-Ertekin and Sultanoglu^[1]. The knowledge and understanding of moisture sorption isotherms for food is of great importance in Food Science and Technology. It is usually applied for solving many problems such as the design and optimization of processing as for instance in drying, for assessing packaging problems, for modeling moisture changes which occur during drying, for predicting shelf life stability and for ingredient mixing predictions, among others Spiess and Wolf^[2].

Sorption isotherms can also be used to investigate structural features of a food product, such as specific surface area, pore volume, pore size distribution and crystallinity. Such data can be used for selecting appropriate storage conditions and packaging systems that optimize or maximize retention of aroma, colour, texture, nutrient and biological stability^[3-5].

There are several wild and uncultivated or subsistently-cultivated trees in Nigeria which are less well known but yield fruits of nutritional and dietary importance. Included in this category are African oil bean seed (*Pentaclethra macrophylla* Benth), African locust beans (*Parkia filicoidea*), castor oil seed (*Ricinus communis*) and Mesquite seed (*Prosopis africana*).

The seeds of the African oil bean (*Pentaclethra macrophylla* Benth) are highly nutritious and serve as a good source of edible protein and calories (Enujiugha and Agbede^[6]). They are usually consumed in parts of West tropical Africa in the fermented form or alternatively, cooked and roasted as a nutritious snack (Enujiugha and Olagundoye^[7]). It can also be used as a condiment in soup mixes and local porridges. The fermented seed product is known as ugba.

The African locust beans seed is rich in plant protein and essential fatty acids Antai and Ibrahim^[8]. Dawadawa and iru are the traditional names for the fermented locust bean. The fermented seed products are used as food condiments in some parts of Nigeria Antai and Ibrahim^[8].

The castor oil seed is fermented to produce an oily paste called ogiri which is used as flavouring condiment in soups and sauces and also contribute to the protein and essential fatty acid intake in West Africa^[9,10]. Ogiri from castor oil seeds is consumed in the eastern and midwestern parts of Nigeria by about 5 million people Anosike and Egwuatu^[11].

Okpeye is a condiment widely consumed in Eastern Nigeria. Mesquite seed (*Prosopis africana*) is one of the lesser-known legume seedcrops growing wild in Nigeria. The use of the dry seed as human food is limited due to its poor cooking quality. However, they are consumed as condiment after fermentation Obeta and Ugwuanyi^[12].

With urbanization, the production and consumption of these condiments are decreasing. More so, the condiments preparation is still a traditional family art done in homes, with a variable flavour and short shelf life. It is on the basis of these shortcomings that the present study was undertaken to obtain information on the sorption isotherms of the dry condiment powders (ugba, iru, ogiri and okpeye) at three temperatures and fit the data to an established sorption model equation.

These condiments are very rich in terms of nutritional qualities and are consumed in the humid form. In this form, they spoil fast due to their short shelf life. However, research is on-going to increase the shelf-life and one way of increasing the shelf life could be by turning the condiment into powders. However, there has been little or no information published on sorption isotherms of the dry powders.

Theory: Sorption isotherms are graphs that provide the relationship between water activity and moisture content at constant temperature. Labuza^[13] has reviewed the various ways in which the water vapour sorption isotherms can be explained. The kinetic approach is based on the Langmuir equation which was initially developed for adsorption of gases and solids. This can be expressed in the following form.

$$A_w = \left(\frac{K}{bv_m} \right) + \frac{a_w}{V_m} \quad (1)$$

Where a_w = water activity, b = constant, $k = 1/p_0$ and p_0 = vapour pressure of water at T_0 , V = volume adsorbed, V_m = monolayer value.

When a_w/V is plotted versus a_w , the result will be a straight line with a slope equal to $1/V_m$ and the monolayer value can be calculated. In this form, the equation has not been too satisfactory for foods, because the heat of adsorption which enters into the constant b is not constant over the whole surface, because of interaction between adsorbed molecules and because maximum adsorption is greater than only a monolayer.

A form of isotherm widely used for foods is the one described by Brunauer-Emmet-Teller (BET) isotherm or equation. A form of the BET equation given by Labuza^[13] is

$$\frac{a_w}{(1-a_w)} = \frac{1}{V_m C} + a \left(\frac{C-1}{V_m C} \right) \quad (2)$$

where C = constant related to the heat of adsorption

A plot of $a_w/(1-a_w)V$ versus a_w gives a straight line. The monolayer coverage value can be calculated from the slope

$$\left(\frac{C-1}{CV_m} \right)$$

and the intercept ($1/CV_m$) of the line. The BET isotherm is only applicable between values of a_w from 0.1 to 0.5.

Other approaches have also been used to analysis the sorption isotherms in food materials.

The GAB (Guggenheim-Anderson-DeBoer) model is claimed to provide the best equation for the description of food isotherms up to a_w 0.9 (van den Berg^[14]).

The GAB model is described by the following equation.

$$\text{From } a_w = \left(\frac{P}{P^*_T} \right) \quad (3)$$

Where: P = vapour pressure of water in the substance at temperature T the substance at temperature T ; P^* = vapour pressure of pure water at temperature T .

$$a_w = 2 + \left(\frac{M_o - 1}{M} \right) C - \left\{ \left(2 + \left(\frac{M_o - 1}{M} \right) C \right)^2 - 4 + 4C^{0.5} \right\} \quad (4)$$

Where M = moisture content of food (dry basis)%
 M_o = moisture content of the monolayer, %
 and a_w = water activity.

The temperature dependencies is included in the adsorption constants C and K such that

$$C = C^1 \exp ((H_n - H_m) Rt) \quad (5)$$

Where C^1 , K^1 entropic accommodation factors
 H_n = molar sorption enthalpy of the monolayer
 H_m = molar sorption enthalpy of the multiplayer on top of the monolayer
 H_2 = molar sorption enthalpy of the bulk liquid to
 T = temperature and
 R = ideal gas constant.

The basic equation for moisture transfer through a semi-permeable membrane is derived from Fick's law in combination with Henry's law Labuza *et al.*,^[3]. The equation is

$$\frac{d_w}{d_t} = - \frac{k_w \cdot A}{x} (P_{out} - P_{in}) \quad (6)$$

Where W = mass of water transported,
 t = time,
 $\frac{k_w}{x}$ = water vapour permeability of package
 P_{out} = vapour pressure of water outside packager
 P_{in} = vapour pressure of water insider package

If it is assumed that the water transported a cross the packaging material is instantaneously adsorbed by the dry food
 Then: M = weight of dry solid closed
 Therefore

$$\frac{dw}{dt} = \frac{W_s}{100} \frac{dM}{dt} \quad (7)$$

Substituting (7) into (6) we obtain

$$\frac{W_s}{100} \frac{dM}{dt} = K_w A \left(\frac{P_{out}}{X} - P_{in} \right) \quad (8)$$

But from (1) in combination with (2)

$$P_{in} = \frac{P^* \{ 2 + (M_o/M_c - 1) c - \{ 2 + (M_o/M_c - 1) C \}^2 - 4 (1-c)^{0.5} \}}{2k (1-c)} \quad (9)$$

and

$$P_{out} = \frac{P^* \{ 2 + (M_o/M_c - 1) c - \{ 2 + (M_o/M_c - 1) C \}^2 - 4 (1-c)^{1.5} \}}{2k (1-c)} \quad (10)$$

Where M_c = moisture content of food as predicted by the isotherm equation if exposed to the external package relative humidity

Substituting (9) and (10) into (8)

$$\frac{W_s}{dt} \frac{dM}{dt} = \frac{100 k_w A P^*}{x 2k (1-C)} \left[(M_o/M_c) C - \{ [2 + (M_o/M_c) C - C]^2 - 4 + 4 \}^{0.5} - (M_o/M_c) + \{ [2 + (M_o/M_c) C - C]^2 - 4 + 4 \}^{0.5} \right] \quad (11)$$

Assuming constant T and external relative humidity, let

$$\frac{K_w P^* A 100}{(x) (2) K (1-C) W_s} = \text{constant} \quad (12)$$

$$\frac{(M_o/M_c) C - [2 + (M_o/M_c) C - C]^2 - 4 + 4 \}^{0.5}}{2 - 4 + 4C} = \text{Constant} = P \quad (13)$$

Substituting (12) and (13) into (11)

$$\frac{dM}{dt} = \Phi (\beta - M_o/M_c) C + \{ [2 + (M_o/M_c) C]^2 - 4 + 4C \}^{0.5} \quad (14)$$

Integrating between $t = 0$ to $t = t$ and M_i to M_f (initial and final moisture) we get

$$\int_{M_i}^{M_f} \frac{dM}{\beta - \left(\frac{M_o}{M} \right) C + \left[\frac{1}{M} (4M_o C - 2M_o C^2) + \left(\frac{M_o}{M} \right)^2 C^2 + C^2 \right]^{0.5}} = \Phi t \quad (15)$$

Expanding the square in the denominator and simplifying.

$$\int_{M_i}^{M_f} \frac{dM}{\beta - \left(\frac{M_o}{M} \right) C + \left[\frac{1}{M} (4M_o C - 2M_o C^2) + \left(\frac{M_o}{M} \right)^2 C^2 + C^2 \right]^{0.5}} = \Phi t \quad (16)$$

Equation (16) can be integrated only by numerical methods. However, if C is large so that $4M_o c \ll 2M_o C^2$ or $C \ll 2$ then Eq. 16 can be written as

$$\int_{M_i}^{M_f} \frac{M dM}{\beta M - M_o C + C \left(M^2 - 2M_o \frac{M}{M} + M_o^2 \right)^{0.5}} = \Phi t \quad (17)$$

But $M^2 - 2M_o M + M_o^2 = (M - M_o)^2$

Therefore Eq. 17 simplifies to

$$\int_{M_i}^{M_f} \frac{M dM}{M (\beta + C) - 2M_o C} = \Phi t \quad (18)$$

Eq. 18 can be integrated to yield

$$t = \frac{1}{(\beta + C) \Phi} \left[M_f - M_i + \frac{2M_o C}{(\beta + C)} \ln \left[\frac{(\beta + C) M_f - 2M_o C}{(\beta + C) M_i - 2M_o C} \right] \right] \quad (19)$$

Equation 19 is the time domain moisture content equation using the GAB sorption equation. This model is limited to C values greater than about 20. If C is less than 20, Eq. 16 must be used and numerical solution is required Diosady *et al.*^[15].

MATERIALS AND METHODS

Materials collection: Samples of ugba, iru, okpeye and ogiri freshly made by local processors were used for this research work. The samples were purchased from the king's market in Akure. Care was taken to purchase all samples from a particular source to eliminate environmental and genetically generated errors.

Preparation of condiment powders: The wet samples of ugba, iru, okpeye and ogiri, were oven dried at 60°C for 5 days using air oven. The dried samples were then milled into a fine powder using a combination of hammer and pin-disc mills. The fine powder produced was kept in a cool and dry place until used.

Preparation of salt solution: Saturated aqueous salt solutions were prepared by diluting the solid salt with warm water to a slurry consistency, to ensure saturation Diosady *et al.*^[15]. The saturated salt solution was then kept in desiccators for further use. Salt used include sodium acetate, sodium bromide, sodium nitrite and calcium chloride

Determination of equilibrium moisture content: The static gravimetric method of Diosady *et al.*^[15] and Kaymak-Ertekin and Sultanoglu^[1] was adopted in determining the equilibrium moisture content

The initial moisture content was firstly determined by using oven drying method. Clean and dry petri dishes were weighed by using Mettler weighing machine

Their respective weights were recorded as W_1 . About 5 g of the sample were weighed into petri dishes (W_2), spreading as much as possible. The petri dishes containing the sample were transferred into the oven maintained at 105°C and dried for about four hours. After four hours they were transferred to the desiccators to cool and then weighed. This process was continued until constant weight (W_3) were obtained. The loss in weight during drying in percentage was taken to be the percentage moisture content.

$$\% \text{ Moisture} = \frac{\text{loss in weight due to drying}}{\text{Weight of sample taken 1}} \times 100$$

The determination of initial moisture content was followed by equilibrium moisture content determination.

Equilibrium moisture content was determined by weighing about 5g of each of the sample into petri dishes and placed on perforated plastic in desiccators containing different levels of saturated salt solutions. Some of the

desiccators containing the samples were kept inside refrigerator, some were maintained at ambient temperature of about 30°C and others were kept inside incubator maintained at 40°C. The samples were weighed periodically until they attained moisture equilibrium when a weight change of $<+0.001$ g was recorded on two consecutive weighings.

The equilibrium moisture content was calculated using the data of initial moisture content and the amount of moisture gained until equilibration.

Determination of sorption isotherm: The equilibrium moisture content on wet basis was plotted against the equilibrium relative humidity to obtain the moisture isotherm.

RESULTS AND DISCUSSION

Sorption isotherms of the condiment powders: The moisture sorption isotherms of the dehydrated and milled popular Nigerian condiments (ugba, okpeye, ogiri and iru) are shown on Figures 1- 4. The isotherms manifested the typical sigmoid curve, except for ugba, okpeye and are stored at 10°C. A general sigmoid sorption isotherm is divided into three different parts; ranges I (a_w 0-0.22}, II (a_w 0.22-0.73) and III (a_w 0.73-1.0). In ranges I and II, water molecules sorb or penetrate into newly created pores of the already swollen structure and are mechanically entrapped in the void spaces.

However, it is generally observed that there are no sharp divisions between the three regions and no definite values of relative humidity exist to delineate them.

In the present study, the isotherms were determined within the range of water activity (a_w) 0.2-0.7 and at three temperatures (10, 30 and 40°C) corresponding to refrigerated, ambient and higher temperature storage and at equilibrium moisture contents of 4-45 H₂O/100 g solids. The sudden shift in isotherm curve of dry okpeye powder at ambient storage and at 50% RH Fig. 2 could be a result of experimental error, or hysteresis effect. Kaymak-Ertekin and Sultanoglu^[1] also observed significant hysteresis with some dry peppers at a_w 70.5 and 30°C

Effect of temperature on the isotherms: It appears from the present study that the higher the storage temperature, the lower the sorption capacity. This is in agreement with the finding of Tencel^[16] that water sorption capacity decreased as temperature increased. However, the rate of absorption of moisture was of the order ugba, okpeye, ogiri, iru. It is also evident from the figures that for any constant moisture content, an increase in temperature of

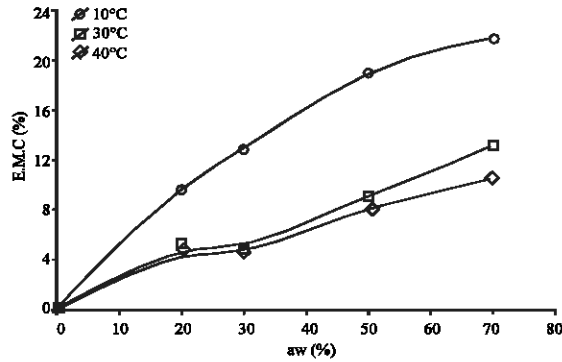


Fig. 1: Moisture sorption isotherm of 'Ugba'

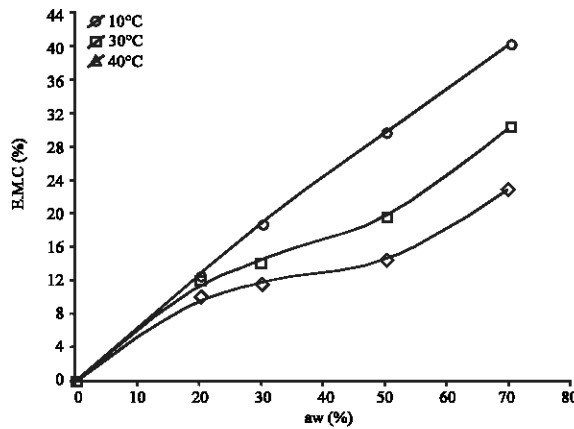


Fig. 2: Moisture sorption isotherm of 'Iru'

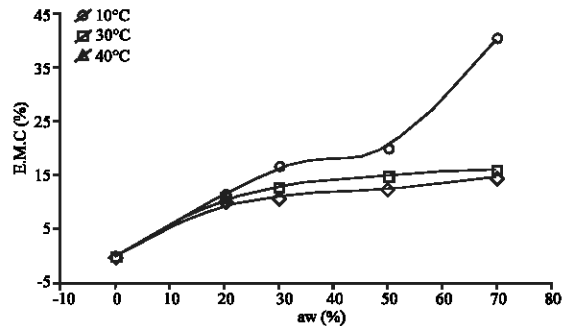


Fig. 3: Moisture sorption isotherm of 'Ogiri'

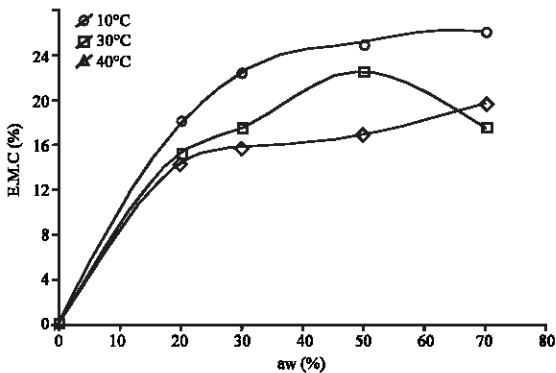


Fig. 4: Moisture sorption Isotherm of 'Okpeye'

storage significantly ($p > 0.05$) increases the a_w , resulting in decreased shelf life.

This agrees with the results obtained by Labuza *et al.*^[17] using two dehydrated foods: fish flour and corn flour.

With the exception of ogiri, low temperature (10°C) storage gave desorption curves, while higher temperature (30 and 40°C) gave adsorption curves. This implies that storage at refrigerated temperatures will obviously prolong the shelf life of the condiment powders, while the shelf life would be shortened by storage at ambient and higher temperature was increased at constant a_w , the moisture content decreased, which agrees with the work of Diosady *et al.*^[15] using canola meals. Thus the products became less hygroscopic at higher temperatures, as expected on the basis of the fundamental thermodynamic equation relating free energy (G) enthalpy (H), temperature (T) and entropy (S):

$$dG = dH - T dS \quad (20)$$

since $dG < 0$ (sorption is spontaneous) and $dS < 0$ (adsorbed molecule is less free) then $dH < 0$ therefore an increase in temperature does not favour sorption.

Effect of relative humidity on the isotherms: The results of the present study reveal that as a_w of the storage environment increased, the rate of moisture adsorption by the condiment powders increased at all the temperatures considered. At Relative Humidities (RHs) of <30%, rate of moisture adsorption by the condiments was rapid, but rate of reaction was low. Labuza *et al.*^[17] have shown that most deteriorative reactions in food systems have the lowest rate at the Brunauer-Emmett-Teller (BET) monolayer, which usually corresponds to the 0.2-0.4 a_w range.

All the powdered condiments exhibited specific hydration rates. The equilibrium moisture content represented the water hydration capacity, which has a linear relationship with protein content. The time to reach equilibrium was different for all the samples and was strongly dependent on the a_w . The hydration rate was initially rapid and slowed as equilibrium was approached. This agrees with the observations of Elizalde *et al.*^[18] using soy protein isolate, commercial wheat flour and commercial corn starch. However, according to Jouppila and Roos^[19] time-dependent changes in the physical state that accompany water sorption must be considered in modeling isotherms. For example, water contents have been found to be lower than predicted values at high RH as a result of crystallization and other such time-dependent phenomena.

In the present study, iru absorbed more water at higher relative humidities compared to ogiri, followed by okpeye and last by ugba at low temperature storage. At higher storage temperature, ogiri absorbed the least water.

Table: 1 Equilibrium moisture contents of the condiment powders

Product	Temp (c)	Initial M.C (%)	Relative humidity (%)			
			20	30	50	70
Ugba	10	4.31	10.57	43.77	20.32	23.07
	30	4.31	5.62	5.13	8.92	4.75
	40	4.31	5.12	4.62	9.94	11.31
Okpeye	10	12.72	17.05	16.72	23.20	24.29
	30	12.72	14.16	20.25	25.95	16.26
	40	12.72	13.34	14.67	15.73	18.30
Ogiri	10	9.84	11.62	16.88	11.08	40.66
	30	9.84	10.88	11.34	14.93	14.27
	40	9.84	10.94	9.89	12.47	10.77
Iru	10	9.31	19.90	10.64	30.36	41.22
	30	9.31	14.43	13.50	18.09	31.11
	40	9.31	10.54	11.94	23.72	22.67

Effect of moisture content on sorption equilibrium: Table 1 shows the results of the equilibrium moisture contents of the condiments at constant temperature and relative humidity values, with reference to their initial moisture contents. The study was undertaken for 21 days at each a_w . At low temperature and 0.3 a_w of storage environment, ugba with very low initial moisture content absorbed significantly ($p < 0.05$) higher moisture than the other condiment. The same product absorbed relatively lower moisture than the other condiments at ambient temperature. At higher temperatures okpeye sorbed more moisture at the monolayer value than the other condiments. The results indicate that temperature and relative humidity affect equilibrium moisture values. This agrees with the observations of Onayemi and Oluwamukomi^[20] who worked with some dehydrated cassava and yam products. Overall from the moisture equilibrium data, it could be concluded that ogiri would keep longer than the other condiments, followed by okpeye, then iru and finally ugba. An earlier report has indicated that ugba deteriorates within 2 weeks of production (Enujiugha^[21]).

CONCLUSION

The storage stability of some important condiments (in powdered forms) have been investigated. However, a number of conclusions could be drawn from the results of the present study. The products gave normal sigmoid isotherms, especially at ambient and higher temperatures. The higher the storage temperature, the lower the sorption capacity of the product. Also, for any constant moisture content and increase in temperature of storage resulted in increased a_w and hence, decreased shelf life. As temperature was increased at constant a_w , the moisture content decreased, making the products less hygroscopic at higher temperatures. At relative humidities of 30% rate of moisture absorption by the condiment powders

increased at all the temperatures considered. At ambient and higher storage temperature ogiri has longer shelf life, followed by okpeye, then iru and finally ugba.

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