Sorption isotherms and their fitted equations for dried chips of cassava roots (Manihot Esculenta Crantz; Tme-7 variety) and the resulting isosteric heats of sorption

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Abstract

Cassava roots are susceptible to deterioration with 24 hrs of harvest; it needs processing into a more stable material such as dried cassava chips to extend its shelf life for long storage. However, improper knowledge of the effect of atmospheric relative humidity on these dried chips during storage makes it mouldy and unacceptable. This work aimed at studying the effect of sorption isotherms on the dried cassava chips. In this study, adsorption and desorption isotherm were carried out using static gravimetric method and data for equilibrium moisture content (EMC) were generated at five (5) temperatures (53, 60, 70, 80, 86°C). These were fitted into four (4) isotherm-models [Oswin, Peleg, the Modified Oswin and GAB]. The statistical criteria to test the models were coefficient of determination (R²), reduced chi-square (χ²), root mean square error (RMSE) and mean bias error (MBE). The values of EMC ranged from 7.21-12.44% wb. The values of R² ranged from 0.95-0.99; χ² ranged from 0.008-0.14; RMSE values ranged from 0.06-0.254 while MBE values ranged from -0.0004-1.1E-5. The values of isosteric heat of sorption calculated from the isosteres recorded a range from 6.579 to 67.829 kJ/mole. The Peleg-model gave the best fit in the relative humidity range of 10 to 80%. The values of EMC show that the chips can have a stable shelf life without spoilage.

1. Introduction

Nigeria is the world’s largest producer of cassava (FAO-STAT, 2012; MAFAP, 2013) and has a defined national policy to aggressively expand its production and processing for the economic development of the country. The production and processing are crucial due to its perishable nature after harvest. Therefore, it is quickly processed into domestic food materials such as ‘gari’, ‘lafun’ and ‘fufu’. However, in international trade, cassava chip is a major way by which cassava is being sold. It is a semi-raw material for the production of alcohol, citric acid and starch. The local demand for chips is at an alarming rate because feed composers have discovered that cassava chips provide an excellent source of carbohydrate. The European animal feed industries are demanding for cassava chips in large quantities of more than 7 million tonnes in 2000. By 2012, China alone demanded more than 1 million tonnes (NIRSAL and FMARD, 2012). The life span of cassava chips is adjudged to be six months and the long-distance covered during exportation of these chips is a crucial factor as a large part of the export turns mouldy on the high sea. This is because cassava chip is hygroscopic and gains moisture over time. This causes losses to the quality of chips more than any other means as it induces microbial and chemical reactions in the chips which affect colour and downgrade the chips. Therefore it is important to consider and study the water activity of the chips. This is a determinant factor of stability of the chips in long term storage because there is a possibility that the chips experience increase in moisture (adsorption) or decrease in moisture (desorption) due to fluctuations in relative humidity. Therefore study of adsorption and desorption isotherm or their models which define the relationship between water activity and equilibrium moisture content (EMC) at different temperatures are important for three reasons: (a) to define the extent of free water removable in hot air drying of the chips which is all the moisture above the EMC, (b) to define the water activity at EMC and ensure it is low enough to ensure long term stability in storage and (c), to provide a basis for calculating the energy (isosteric heat) profile required for drying in a
piece of equipment to be designed and operated for the purpose. These reasons form the basis of the study.

2. Materials and methods

2.1 Material

Mature cassava roots (Manihot esculenta Crantz) TME 7 variety that was free from defects were used. They were obtained from the Ladoke Akintola University of Technology Teaching and Research Farm Ogbomoso, Nigeria. The moisture content of the roots determined using AOAC (2005) method was 75% (wet basis).

2.1.1 Water and reagents

Concentrated sulphuric acids (Tetraoxosulphate VI acid) of analytical grade was formulated at predetermined concentrations by dilution with distilled water establish relative humidity values (RH- 10, 20, 30, 40, 50, 60, 70 and 80%) employed in the experiments

2.1.2 Equipment

Chips dices were made manually with a sharp stainless steel knife and were loaded into the moisture test pan as samples. Glass desiccators with their lids sealed carefully by applying a film of Vaseline fat were used to hold the samples in the test pans over the solution of sulphuric acid which at each constant temperature generated the predetermined environmental RH% required. A Genalb (England) incubator Model (M75CPD) was used to hold the desiccators and content at each predetermined constant temperature at a time. Colour Instrument (colour tech PCM, made in US, patent 5137364) was used to determine the colour of the chips. A laboratory tunnel dryer in the pilot plant of the Department of Food Science and Engineering, LAUTECH was used to dry the chips

2.2 Methods

2.2.1 Drying of cassava chips

The chips were produced from cassava roots using the method of FIIRO (2006). The cassava roots were peeled and diced with stainless steel knives into dimensions: 5 cm x 1 cm x 0.1 cm. The chips were dried down to a moisture content of 14% using the tunnel dryer (Ashaye et al., 2005). The chips were thereafter cooled and packaged into polythene bags and stored under moisture-tight conditions until they were used for the generation of adsorption and desorption isotherms.

(a) Determination of sorption isotherms

The static gravimetric method was used (Paulo et al., 2010). Three replicates of each sample of the cassava chips (10 g) were weighed into moisture test pans in desiccators at each humidity point and temperature level (Ajibola, 1986). Each desiccator was maintained at one relative humidity (rh) value between 10 and 80%. The desiccators were then placed in the Genalb incubator to maintain the required temperature level (53, 60, 70, 80 and 86°C). Samples for adsorption and desorption were monitored till equilibration by cooling and weighing at intervals until a constant weight was attained. The time taken for the experiments was four weeks. Equilibrium moisture content (EMC) values were found by calculation (Igbeka et al., 1975; Oyelade et al., 2001; Falade et al., 2003).

(b) Determination of isosteric heat of sorption

Isosteric heat of sorption ($Q_o$) for experimental temperature range explored was calculated from the Clausius-Clayperon Equation as written in Equation1

$$\frac{Q_o}{R} = \frac{T_1 - T_2}{T_1T_2}\ln(a_w)$$

where: $T_1$ and $T_2$ are the absolute temperature range of study ($^{\circ}$K), $a_w$ is the water activity and $R$ is the universal gas constant (8.314 J/mol K).

(c) Isotherm equations and modeling

Four widely tested model equations were fitted to the experimental data. The models are Guggenheim and Anderson and de Boer (GAB), Oswin, modified Oswin and Peleg. The experimental data were fitted into each of the models and the model that best described the isotherm data was selected. The models were evaluated using four parameters namely: the coefficient of determination ($R^2$), reduced chi-square ($\chi^2$), root mean square error (RMSE) and mean bias error (MBE). Mathematical expressions of the models are as shown in Table 1.

(d) Statistical analysis

Subscripted constants for each model were estimated using a non-linear regression analysis performed using Statistical Package for the Social Scientist (SPSS-15.0 versions) software. Statistical criteria viz; the coefficient of determination ($R^2$), reduced chi-square ($\chi^2$), root mean square error (RMSE) and mean bias error (MBE) were applied to test the reliability of each model. A good fit is said to occur between experimental and predicted values of a model when $R^2$ is high; and $\chi^2$, RMSE and MBE are low (Demir et al., 2004). The RMSE represent the deviation between the predicted and experimental values and it is required to approach zero (Gökhan et al., 2009). The comparison criteria calculated using equations 2, 3 and 4:
Table 1. Mathematical sorption models

| Models       | Equation                                                                 | References                      |
|--------------|---------------------------------------------------------------------------|---------------------------------|
| Oswin        | \( X_c = k_1 (a_w/(1-a_w))^c \)                                          | Maroulis and Saravacos (2002)   |
| Peleg        | \( X_c = a_2 * a_w^{b_1} + c * a_w^{d_1} \)                             | Jirawadee et al. (2011)         |
| Modified Oswin | \( X_c = (a_4 + b_4 T) (a_w/(1-a_w))^c \)                                | Maroulis and Saravacos (2002)   |
| GAB          | \( X_c = \frac{a_1 b_1 c a_w}{(1-c_4 a_w)(1-c_4 a_w + b_4 c a_w)} \)    | Cáceres-Huambo and Menegalli (2009) |

GAB= Guggenheim, Anderson and De Boer; \( a_{n},b_{n},c_{n}, d_{n} \) and \( k_{n} \) are subscripted constants for each equation, \( X_{c} \)= equilibrium moisture content (db); \( a_{w} \)= water activity

\[
\chi^2 = \sum_{i=1}^{N} \left( \frac{EMC_{(exp,i)} - EMC_{(pre,i)}}{N}\right)^2 \tag{2}
\]

\[
MBE = \frac{1}{N} \sum_{i=1}^{N} \left( EMC_{(pre,i)} - EMC_{(exp,i)} \right) \tag{3}
\]

\[
RMSE = \left[ \frac{1}{N} \sum_{i=1}^{N} (EMC_{(pre,i)} - EMC_{(exp,i)})^2 \right]^{1/2} \tag{4}
\]

Where \( EMC_{(pre,i)} \)= the i-th predicted equilibrium moisture content, \( EMC_{(exp,i)} \)= the i-th experimental equilibrium moisture content, \( N \)= number of observed experiments and \( z \)= number of constants in the models.

Water activity values corresponding to designated relative humidity values are calculated by applying Equation 5.

\[
a_{w} = \frac{RH\%}{100} \tag{5}
\]

3. Results and discussion

3.1 Evaluation of constants in the models

Table 2 shows the values of constants for all the four models tested. In all the models, the constants recorded ‘\( a_2 \)’ recorded the highest and lowest values of 12.63 and 1.00, respectively which correspond to desorption at 53 and 60°C calculated for the Peleg model; the constant \( a_4 \) in the Modified Oswin recorded the highest and lowest values of 10.61 and 8.917 corresponding to adsorption at 53°C and adsorption at 60°C respectively; also, the constant \( a_4 \) in the GAB model recorded the highest and lowest values of 6.869 and -7.44 corresponding to desorption at 80 and 53°C, respectively. The constant ‘\( b_4 \)’ recorded the highest and lowest values of 2.143 and -0.978, respectively corresponding to adsorption at 53°C and desorption at 60°C calculated for the Peleg model while constant ‘\( b_4 \)’ recorded the highest and lowest values of 1.018 and 0.945 corresponding to adsorption at 53°C and desorption at 70°C, respectively in the GAB model. The highest values recorded for constant ‘\( c_4 \)’ is 1.00 corresponding to both adsorption at 53 and 86°C and likewise, desorption at 53°C whereas the lowest value for constant \( c_1 \) is 0.121 which corresponds to desorption at 70°C calculated for the Oswin model; the highest and lowest values recorded for constant ‘\( c_2 \)’ are 8.859 and -0.996 corresponding to desorption at 53°C and desorption at 60°C calculated for Peleg model; the highest and lowest values recorded for constant ‘\( c_3 \)’ are 1.28 and 0.121 corresponding to desorption at 80°C and adsorption at 70°C, respectively; the highest and lowest values for constant ‘\( c_4 \)’ are 87863 and -4505 corresponding to desorption at 80°C and adsorption at 70°C respectively. The highest and lowest values recorded for constant ‘\( d_4 \)’ are 0.093 and -0.99 calculated for desorption at 80°C and adsorption at 60°C, respectively for the Peleg model. The highest and lowest values recorded for the constant ‘\( k_{1} \)’ are 10.28 and -0.051, corresponding to desorption at 60°C and adsorption at 86°C, respectively for the Oswin model. Values of constants presented in Table 2 show that sorption temperatures affect the constants as there are variations in recorded values for the same model. For instance, ‘\( a_2 \)’ in the Peleg model, varied from temperature to temperature between 53°C and 86°C. No discernible pattern is evident in the variations.

3.2 Model evaluation using statistical criteria

From Table 3, all values of \( R^2 \) calculated are greater than 0.96. These high values of \( R^2 \) in all cases suggest that each of the four models gave a good fit to the experimental data. A good fit occurs when \( R^2 \) is high (Ahmet et al., 2007). The highest value of \( R^2 \) calculated was 0.999 recorded for the Peleg model corresponding to desorption isotherm at 53°C. The lowest value was 0.967 calculated for the Oswin model corresponding to adsorption isotherm at 70°C. The same \( R^2 \) value of 0.967 was also recorded for the Modified Oswin model corresponding to adsorption isotherm at 70°C. The average \( R^2 \) values recorded for the models are as follows: Oswin (0.9816), Peleg (0.9966), Modified Oswin (0.9816) and GAB (0.9902). The lowest value of reduced chi-square is 0.008 corresponding to the adsorption isotherm at 60°C for the Peleg model. The highest value is 0.1489 corresponding to the adsorption isotherm at 53°C for the Modified Oswin model. The average value of the reduced chi-square was 0.0434 for all models; however, the average reduced chi-square
Table 2. Values for model constants

| Model      | Water Activity | Constants | C_1 | K_1 |
|------------|----------------|-----------|-----|-----|
| Oswin      | Adsorption at 53°C | 1         |     | -0.032 |
|            | Adsorption at 60°C | 0.128     | 9.86 |
|            | Adsorption at 70°C | 0.131     | 9.505 |
|            | Adsorption at 80°C | 0.135     | 9.143 |
|            | Adsorption at 86°C | 1         | -0.051 |
|            | Desorption at 53°C | 1         | -0.03 |
|            | Desorption at 60°C | 0.129     | 10.28 |
|            | Desorption at 70°C | 0.121     | 9.846 |
|            | Desorption at 80°C | 0.122     | -0.014 |
|            | Desorption at 86°C | 0.127     | 9.263 |
| Peleg      | Adsorption at 53°C | 5.769     | 2.143 | 8.859 | 0.045 |
|            | Adsorption at 60°C | 5.045     | 1.919 | 8.715 | 0.054 |
|            | Adsorption at 70°C | 6.266     | 1.546 | 7.904 | -0.02 |
|            | Adsorption at 80°C | 5.707     | 1.552 | 7.104 | 0.005 |
|            | Adsorption at 86°C | 5.475     | 2.066 | 7.646 | 0.043 |
|            | Desorption at 53°C | 12.63     | 0.419 | 0.878 | -0.57 |
|            | Desorption at 60°C | 1         | -0.978 | -0.996 | -0.99 |
|            | Desorption at 70°C | 5.852     | 0.873 | 6.673 | -0.01 |
|            | Desorption at 80°C | 3.47      | 1.068 | 8.566 | 0.093 |
|            | Desorption at 86°C | 4.812     | 0.958 | 7.064 | 0.038 |
| Modified Oswin | Adsorption at 53°C | 10.1      | 0     | 0.131 |
|            | Adsorption at 60°C | 9.86      | 0     | 1.28 |
|            | Adsorption at 70°C | 9.505     | 0     | 0.131 |
|            | Adsorption at 80°C | 9.143     | 0     | 0.135 |
|            | Adsorption at 86°C | 8.917     | 0     | 0.14 |
|            | Desorption at 53°C | 10.61     | 0     | 0.13 |
|            | Desorption at 60°C | 10.27     | 0     | 0.129 |
|            | Desorption at 70°C | 9.846     | 0     | 0.121 |
|            | Desorption at 80°C | 9.562     | 0     | 0.122 |
|            | Desorption at 86°C | 9.236     | 0     | 0.127 |
| GAB        | Adsorption at 53°C | -6.02     | 1.018 | 64.81 |
|            | Adsorption at 60°C | 6.277     | 1.011 | 96.01 |
|            | Adsorption at 70°C | 6.695     | 1     | 4505 |
|            | Adsorption at 80°C | 1         | 0.974 | -0.943 |
|            | Adsorption at 86°C | 1         | 0.977 | -0.943 |
|            | Desorption at 53°C | 7.44      | 1     | 20692 |
|            | Desorption at 60°C | 1         | 0.948 | -0.947 |
|            | Desorption at 70°C | 1         | 0.945 | -0.944 |
|            | Desorption at 80°C | 6.869     | 1     | 87863 |
|            | Desorption at 86°C | 6.555     | 1     | 21410 |

Figure 1. Hysteresis plot of dried cassava chips at 53°C

Figure 2. Hysteresis plot of dried cassava chips at 60°C
Figure 3. Hysteresis plot of dried cassava chips at 70°C

Figure 4. Hysteresis plot of dried cassava chips at 80°C

Figure 5. Hysteresis plot of dried cassava chips at 86°C

Table 3. Values of the statistical criteria calculate for the models

| Model        | Water Act. | R²   | χ² | RMSE   | MBE    |
|--------------|------------|------|----|--------|--------|
| Oswin        | Adsorption at 53°C | 0.969 | 0.0815 | 0.2472 | -0.0015 |
|              | Adsorption at 60°C | 0.984 | 0.0429 | 0.1794 | -0.0016 |
|              | Adsorption at 70°C | 0.967 | 0.0854 | 0.2532 | -0.0024 |
|              | Adsorption at 80°C | 0.977 | 0.0592 | 0.2104 | -0.0022 |
|              | Adsorption at 86°C | 0.973 | 0.0749 | 0.2371 | -0.0029 |
|              | Desorption at 53°C | 0.99 | 0.0246 | 0.1696 | -0.0198 |
|              | Desorption at 60°C | 0.982 | 0.0159 | 0.1328 | 0.0267 |
|              | Desorption at 70°C | 0.993 | 0.0156 | 0.1904 | -0.0931 |
|              | Desorption at 80°C | 0.989 | 0.0228 | 0.1584 | -0.0223 |
|              | Desorption at 86°C | 0.992 | 0.0172 | 0.1182 | -0.0502 |
| Peleg        | Adsorption at 53°C | 0.995 | 0.0222 | 0.1055 | -0.0003 |
|              | Adsorption at 60°C | 0.998 | 0.0081 | 0.0639 | -0.0016 |
|              | Adsorption at 70°C | 0.998 | 0.0095 | 0.0689 | 1.10E-05 |
|              | Adsorption at 80°C | 0.995 | 0.0199 | 0.0998 | -0.001 |
|              | Adsorption at 86°C | 0.998 | 0.0087 | 0.0666 | 0.0021 |
|              | Desorption at 53°C | 0.999 | 0.0169 | 0.1956 | -0.0198 |
|              | Desorption at 60°C | 0.997 | 0.0463 | 0.1791 | 0.0267 |
|              | Desorption at 70°C | 0.995 | 0.0155 | 0.1988 | -0.0956 |
|              | Desorption at 80°C | 0.995 | 0.0165 | 0.1909 | -0.0223 |
|              | Desorption at 86°C | 0.996 | 0.0115 | 0.1291 | 0.0514 |
| Modified Oswin | Adsorption at 53°C | 0.969 | 0.1489 | 0.2729 | -0.0015 |
|              | Adsorption at 60°C | 0.984 | 0.0643 | 0.1794 | -0.0016 |
|              | Adsorption at 70°C | 0.967 | 0.0128 | 0.2532 | -0.0024 |
|              | Adsorption at 80°C | 0.977 | 0.0889 | 0.2108 | -0.0022 |
|              | Adsorption at 86°C | 0.973 | 0.1124 | 0.2371 | -0.0029 |
|              | Desorption at 53°C | 0.99 | 0.0369 | 0.1696 | -0.0198 |
|              | Desorption at 60°C | 0.982 | 0.0233 | 0.1328 | 0.0267 |
|              | Desorption at 70°C | 0.993 | 0.0233 | 0.1904 | -0.0931 |
|              | Desorption at 80°C | 0.989 | 0.0342 | 0.1584 | -0.0223 |
|              | Desorption at 86°C | 0.992 | 0.0258 | 0.1182 | 0.0502 |
| GAB          | Adsorption at 53°C | 0.987 | 0.0595 | 0.1929 | -0.0015 |
|              | Adsorption at 60°C | 0.994 | 0.0265 | 0.1287 | 0.0008 |
|              | Adsorption at 70°C | 0.973 | 0.1034 | 0.2542 | 1.10E-05 |
|              | Adsorption at 80°C | 0.993 | 0.0277 | 0.1317 | -0.001 |
|              | Adsorption at 86°C | 0.99 | 0.0394 | 0.1571 | -0.0004 |
|              | Desorption at 53°C | 0.997 | 0.06 | 0.1565 | -0.0211 |
|              | Desorption at 60°C | 0.992 | 0.0787 | 0.0948 | 0.0229 |
|              | Desorption at 70°C | 0.994 | 0.0683 | 0.1813 | -0.0956 |
|              | Desorption at 80°C | 0.988 | 0.0158 | 0.1558 | -0.0236 |
|              | Desorption at 86°C | 0.994 | 0.0729 | 0.096 | 0.0527 |
value recorded for each model is as follows: Oswin (0.0440), Peleg (0.0175), Modified Oswin (0.0171) and GAB (0.0552). The lowest value of the root mean square error (RMSE) recorded is 0.0639 corresponding to the adsorption isotherm at 60°C in the Peleg model. The highest value recorded occurred in Modified Oswin model with a value of 0.2729 (adsorption at 53°C). The overall average value of RMSE in all models is 0.1666; while the average in each model for Oswin, Peleg, Modified Oswin and GAB are 0.1897, 0.1298, 0.1923 and 0.1549, respectively. The average value of mean bias error (MBE) for the four models is recorded as -0.00913. The lowest value of MBE recorded is -0.0956 found at 70°C for desorption for the Peleg model, while the highest MBE value recorded is 0.0527 corresponding to 86°C for desorption in the GAB model. The average MBE value recorded for each of the models is as follows: Oswin (-0.0169), Peleg (-0.0060), Modified Oswin (-0.0068) and GAB (-0.0067).

According to Demir et al. (2004), a good fit is said to occur between experimental and predicted values of a model when R² is high; and the reduced chi-square (χ²), mean bias error (MBE) and root mean square error (RMSE) are low. Therefore the Peleg model can be considered to be the best tested in this study to represent the sorption isotherm of cassava chips.

3.3 Adsorption and desorption (hysteresis) characteristics of the cassava chips

Figures 1, 2, 3, 4 and 5 are hysteresis isotherm plots for the chips at designated isotherm temperatures from 53°C to 86°C. It is observed that each of hysteresis loop isotherms; in accordance with BET classification, conform to the characteristic behaviour of type II sigmoidal sorption isotherm in which the curves are concave upwards. It takes into account the existence of multilayers at material internal surfaces (Ertugay and Certel, 2000; Ricardo et al., 2011). From Figure 1, at 53°C the lowest EMC value of adsorption isotherms is 8.07% corresponding to 0.1 aₑ while the highest value is 12.44% corresponding to 0.8 aₑ. Also, the lowest EMC value of desorption isotherm is 8.09% at 0.1 aₑ while the highest value is 12.46% at 0.8 aₑ. Figure 2 presents the hysteresis loop of the cassava chips sample. The lowest adsorption EMC value at 60°C is 7.73% corresponding to 0.1 aₑ while the highest value is 11.2% at 0.8 aₑ. Figure 3 presents the hysteresis loop of the cassava chips sample. The lowest adsorption EMC value at 70°C is 7.63% corresponding to 0.1 aₑ while the highest value is 11.63% corresponding to 0.8 aₑ. In addition, the lowest EMC value for desorption isotherm is 7.64% corresponding to 0.1 aₑ while the highest EMC value is 7.64% corresponding to 0.8 aₑ. Figure 4 presents the isotherm properties of cassava chips samples at 80°C. The lowest adsorption EMC value is 7.21% corresponding to 0.1 aₑ while the highest value is 11.23% at 0.8 aₑ. Also, the lowest desorption EMC value is 7.21% corresponding to 0.1 aₑ while the highest value is 11.22% corresponding to 0.8 aₑ. Furthermore, the lowest EMC desorption isotherm value is 7.21% while the highest value is 11.22% corresponding to 0.1 aₑ and 0.8 aₑ, respectively. Besides, the lowest desorption EMC isotherm value recorded is 7.00% while the highest value recorded is 11.19% corresponding to 0.1 aₑ and 0.8 aₑ, respectively. The values are also comparable with those for castor bean flour which ranged from 4.77-18.91% at aₑ ranges of 0.37-0.87 (André et al., 2016).

There is a direct relationship between water activity and equilibrium moisture content of the samples as shown in Figures 1-5. At lower water activity, all the samples had lower equilibrium moisture content and conversely, at higher water activity, the samples had higher equilibrium moisture content. The reason could be that at lower water activity, the moisture is tightly bound to the active sites of the food material. The bound water includes structural water (H-bound water) and monolayer water which is absorbed by the hydrophilic and polar groups of food components (polysaccharides, protein and fat). A further reason for these patterns, according to Ricardo et al. (2011), could be that the enthalpy of vapourisation at lower water activity is considerably higher than that of pure water. As water activity increased, food nutrients especially starch molecules become more mobile in the internal phase which resulted in increased adsorption of water. This is because water-sugar interaction is sufficient to cause a dissociation of sugar inducing more active sorption as reported by Rangel–Marrón et al. (2011) and Johnson and Brennan (2000).

From Figures 1-5, it is observed that temperature affected the equilibrium moisture content of the samples. The higher the temperature of a sorption isotherm, the
lower the equilibrium values of the moisture content of the sample. In both cases of adsorption and desorption, samples at 53°C exhibited the highest moisture content, while the isotherm at 86°C recorded the lowest moisture content. These results demonstrate a strong temperature dependency of sorptive behaviour with increase in temperature leading to decrease in sorption capacity. The same observation was earlier reported by Brett et al. (2009). The reason for this, according to Machhour et al. (2012) and Mennkov and Durakova (2007), is that at increased temperature, water molecules become activated to higher energy levels causing them to become less stable and to break away from the water binding sites of the food material, thus decreasing the value of the equilibrium moisture content. A further reason for this, according to Chowdhury and Das (2010), may be attributed to the reduction in the total number of binding sites for water arising from temperature-induced changes in the microstructure of the glycerol-water film matrix.

Differences between adsorption and desorption isotherms produce hysteresis loops in which the equilibrium moisture content is higher at a particular relative humidity (ERH) for desorption than for adsorption. It is observed that temperature affects the size of the hysteresis loop because as the temperature of the isotherms increased from 53 to 86°C, the monolayer moisture content decreased. The reason for this has been given previously by Chowdhury and Das (2010) and Mennkov and Durakova (2007) who suggested that higher temperatures reduce the number of water molecules binding at the microstructure of adsorbed (food materials).

3.4 Isotherm heat of sorption of the cassava chips

Figure 6 presents the isosteric heat of sorption of cassava chips. The values decreased from 67,829 J/mol to 6,579 J/mol as water activity increased from 0.1 to 0.8. The values of isosteric heat of sorption in this study are greater than those reported by Machhour et al. (2012) for peppermint tea which ranged from 40,000 J/mol to 5,000 J/mol. The values are greater than those for potato starch which ranged from 20,000 J/mol to 5,000 J/mol as reported by Chowdhury and Das (2010). However, the values are in close to those of cassava fufu (78,000 J/mol), soyfufu (72,000 J/mol) and soylafun (82,000 J/mol) as reported by Elizabeth et al. (2005). Machhour et al. (2012) suggested that high values of heat of sorption at low equilibrium moisture content may be attributed to the existence of highly active polar sites on the surface of the product, which when covered with water molecules form a mono-molecular layer. As moisture content further increased, heats of sorption tend toward the value for pure water, which indicates that the moisture exists in its form as a free water surface.

Heat of sorption is the energy released in the process of sorption of water vapour molecules on a surface of the adsorbent. It is a measure of the intensity of interactive forces between water vapour molecules and the adsorbent food material (Arslan and Toğrul, 2005). The moisture content at which the heat of sorption approaches the heat of vapourisation of pure water is often taken as an indication of the level of binding of water in food (Sibel and Osman, 2007). Knowledge of the magnitude of heat of sorption at specific moisture content levels provides an indication of the state of sorbed water and hence a measure of the physical, chemical and microbiological stability of the food material under the given storage conditions (Paul et al., 2009). In addition, variation in heat of sorption with moisture content and its magnitude relative to the latent heat of vapourisation of pure water provides valuable data for energy consumption calculations required for the design and operation of drying equipment. It elucidates and an understanding of the extent of water–solid versus water–water interactions (McMinn and Magee, 2003).

Figure 6 shows that water activity and isosteric heat of sorption are inversely related. This is because as moisture content increases, fewer active sites are available to the water molecules to bind, resulting in lower isosteric heat of sorption (Jayendra-Kumar et al., 2005). Rangel et al. (2011) observed that when moisture content increased, the available sites to suck the water are reduced, resulting in very small values of heat of sorption (Qs), giving rise to multilayer rearrangement in the structure of water and food molecules within the food sample.

Knowledge of sorption isotherms is very important not only for designing and operation of drying equipment, but also in the design of packages, prediction of quality, stability, shelf life and for calculating moisture changes that may occur during storage (Richado et al., 2011). According to Machhour et al. (2012), other applications of sorption isotherm data
abound in respect of thermodynamic principles underlying and associated with microstructure and physical phenomena in food-water relations and in sorption kinetic studies summarized the usefulness of the sorption isotherm as three fold. First, for explaining the existences of two different classes of moisture in food materials namely bound and free moisture; secondly, for defining the phase transition at boundary between bound moisture and free moisture; thirdly, for elucidating thermodynamic phenomena associated with this boundary.

4. Conclusion

The Peleg equation was identified as the best model to represent sorption isotherms of cassava chips in the temperature range of 53 to 86°C studied. Temperature affected the equilibrium moisture content of the samples; also, water activity and isosteric heat of sorption are inversely related.

Conflict of Interest

The authors declare no conflict of interest of any sort on the project.

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