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Adsorption isotherms and heat of sorption of fresh and preosmosed oven-dried bananas

K.O.Falade* and O.O. Awoyele
Department of Food Technology, University of Ibadan,. P. O. Box 9508 U I Post Office Ibadan, Nigeria.
**e-mail; kolawolefalade@yahoo.com.*

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Abstract

Three banana varieties (Omini Red, Cavendish and Cooking banana) were transversely cut into 10 mm slices, pretreated in sucrose solution of 52, 60 and 68°B and maintained at 25°C for 12 hours. Both fresh and preosmosed banana slices were subsequently oven-dried at 60°C for 72 hours. Adsorption isotherms of fresh and preosmosed oven-dried banana slices were determined at 20 and 40°C using gravimetric–static method. Suitability of eight sorption models in describing the adsorption data was tested. Moreover, isosteric heat of sorption of both fresh and preosmosed oven-dried bananas was determined using Clausius–Clapeyron equation. Adsorption isotherms of fresh and preosmosed oven-dried banana slices gave type I (J–shaped) isotherms. Isotherms were affected by temperature and pretreatment sucrose solution concentration. Crossing of isotherms occurred at a_w~0.55-0.70. Among the eight models, tested, Guggenheim-Anderson-de Boer (GAB) model gave the best fit. Calculated GAB monolayer moisture (M_m) content (9.80–20.8% d.b.) decreased with increase in temperature. Generally GAB M_m content increased with increase in total solids (%) content of preosmosed banana slices. Isosteric heat of sorption increased with decreased moisture content in banana slices.

Key words: Banana, osmotic dehydration, heat of sorption, *Musa sapientum*.

Introduction

Banana (*Musa sapientum*) is one of the world's most important fruit crops. The combined effects of high rate of metabolism, tropical humid conditions, inadequate postharvest handling systems and poor marketing conditions have resulted in postharvest losses of bananas [1]. It is, therefore, necessary to adopt cost effective methods to reduce the losses and ensure steady availability of banana and its products. Osmotic dehydration with subsequent air-drying has been applied to 'Cavendish' banana [2]. Same dehydration procedure may be applied to other economically important varieties of banana.

Osmotic dehydration is the partial dehydration of fruits by immersing fruit or vegetable in a hypertonic sugar or salt solution for a given period of time [2-6]. The process has been successfully applied to a variety of fruits including pineapple, apple and coconut [7-9]. Osmotic dehydration improves the drying process and ensures production of a sweeter flavour in the fruit products. Preosmosed oven- or vacuum-dried products are pleasant to eat as snack items with relatively good shelf stability.

Temperature has a significant effect on sorption isotherms, and its knowledge is essential for the efficient design and operation of several processing operations and storage[10]. Information on isotherms may be used to select appropriate storage conditions and packaging systems that optimize retention of aroma, colour, texture, nutrient and biological stability[11-13].

The application of the Clausius–Clapeyron equation on sorption isotherms at different temperatures is a widely used procedure for the calculation of the isosteric heat of sorption [14]. The isosteric heat of sorption is a differential molar quantity derived from temperature dependence of the isotherms[15, 16]. Isosteric heat of sorption is a measure of intermolecular bonding between water molecules and absorbing surfaces [17]. Heat of sorption data is also useful when assessing energy requirements for drying [18]. The purpose of this work was to investigate the adsorption isotherms of fresh and preosmosed oven-dried banana varieties at 20 and 40°C, to fit the experimental data into eight different models and to evaluate the isosteric heat of sorption.

Materials and Methods

Three banana varieties, Omini Red, Cavendish and Cooking banana, were purchased from Oje market in Ibadan, at unripe stage. The bananas were kept at 25°C until they reached stage 5 [19] on the banana ripening chart. Sucrose (table sugar) was used in preparing the osmotic solutions at different concentration of 52, 60 and 68°Brix. Sodium metabisulphite was added at 0.25% to each of the sucrose solution maintained at 25°C.

Banana fingers were peeled and transversely cut into 10 mm slices. The fruit pieces were packed into perforated wire meshes and immersed in the sucrose solution. A fruit:solution ratio of 1:20 was maintained to minimize any change in solution concentrations. After 12 hours of immersion banana slices were removed, drained free of syrup arranged on stainless steel trays and oven–dried at 60°C in a Gallenkamp (Model OV–160) cross-flow cabinet oven for 72 hours. Experiment was conducted in triplicate.

Determination of moisture sorption isotherm of fresh and preosmosed oven-dried banana slices: Adsorption isotherms of fresh and preosmosed oven-dried banana slices were determined using gravimetric–static method. Solutions of sulphuric acid were prepared to give different constant relative humidities of 10–90% at 20 and 40°C [20]. Fresh and preosmosed oven-dried banana slices were weighed on plates and placed in the desiccators. The desiccators were kept in a constant temperature cabinet incubator (illuminated cooled Griffin incubator) until equilibrium was reached in about 14-17 days. Moisture contents of equilibrated banana slices were determined according to the method of Sankat et al.[2]. Triplicate determinations were made on the equilibrium moisture contents of each sample at each temperature. Average of the triplicate determination was computed. Adsorption isotherms were obtained by plotting the equilibrium moisture content (EMC) against water activity (a_w) i.e (equilibrium relative humidity/100). The net isosteric heat of sorption, Qst, was determined from the following expression derived from Clausius–Clapeyron equation [18, 21].

$$Qst = -R\left(\frac{\partial(l_n a_w}{\partial(1/T)}\right)$$

R is the universal gas constant (8.314 J/mol K). Integrated form of the above equation at fixed equilibrium moisture content is

$$In\left(\frac{a_{w1}}{a_{w2}}\right) = -\frac{Qst}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

where a_{w1} and a_{w2} are water activities at temperatures T_1 and T_2 respectively. Qst (J/mol) is the total molar enthalpy change during the phase transition.

Results and Discussion

Moisture contents increased with an increase in water activity. Adsorption isotherms of fresh and preosmosed oven-dried 'Omini Red', 'Cavendish' and 'Cooking' bananas at 40°C are shown in Figs 1-3. Generally, preosmosed oven-dried banana slices sorbed more moisture than the fresh oven-dried samples. Preosmosed oven-dried banana slices sorbed more water as pretreatment solution concentration increased. Osmotic dehydration of banana slices in higher sucrose solution concentration, prior to oven–drying depressed water activity in the adsorption isotherms. Lowering of water activity in banana slices preosmosed in higher sucrose solution concentration may be due to higher solids gain in the resulting oven-dried products.

In general, adsorption isotherms followed the type I classification scheme of Brunauer et al.[22]. Such isotherms are usual for high sugar foods [21, 23, 24]. Moisture contents were minimal at low and intermediate water activities but increased rapidly at high water activities. At low and intermediate water activities (0.10–0.50), retention of moisture by the dried banana products indicated physical sorption on the strongly active sites of the biopolymers[21, 23, 25]. Rapid increases in equilibrium moisture contents at high a_w (0.60–0.90) may be due to dissolution of the inherent sugars in the plantain and the sucrose infused during osmotic dehydration. Equilibrium moisture content of a food product increases considerably when placed in an atmosphere with water activity above the vapour pressure of saturated solution of its soluble solids[24, 26, 27].

Effect of temperature on adsorption isotherms of fresh and preosmosed oven-dried bananas: The effect of equilibrium temperature on the adsorption isotherms of fresh and preosmosed oven-dried 'Omini Red' banana are shown in Fig. 4a-b, respectively. Moisture content decreased with increasing temperature at low and intermediate water activity (a_w) range (0.10–0.65). However, at high a_w (>0.55) there was an inversion of the usual trend. Crossing of the isotherms occurred at a_w~0.55. Similar trend was noted in fresh and preosmosed oven-dried 'Cavendish' and 'Cooking' bananas (Figs 5a-b, 6a-b), inversion was between 0.55–0.70. This is consistent with findings on high sugar foods. Reports on foods containing high sugar content such as quince jam[10], dried apricot, fig, prunes and raisins[21, 23, 28] and blueberries[18] showed that an increase in temperature usually causes increase in the moisture sorbed at high a_w range (0.6–0.88). This leads to the inversion of the isotherms. Inversion of isotherms at about a_w~0.55–0.70, as shown in fresh and preosmosed oven-dried bananas, was due to increase in endothermic dissolution of sugars in water. This is supported by Ayranci et al.[21] and Tsami et al.[23]. At higher temperatures more sugar dissolved and thus more water was held by the banana products. Consequently, at higher temperature and a_w (>0.65) fresh dried bananas are more susceptible to mould growth.

Calculated model parameters and GAB monolayer moisture (Mm) content: The suitability of eight sorption models in describing the adsorption data of fresh and preosmosed oven-dried bananas was examined. The models include Brunauer–Emmet–Teller (BET) equation [22], Oswin [29], Halsey [30], Henderson [31], Chung–Pfost [32], Chen [33], Smith [34] and Guggenheim-Anderson-deBoer (GAB) equation [35] (Table 1). Tables 2-4 show the parameters of the models applied to the sorption data of 'Omini Red', 'Cooking' and 'Cavendish' banana, respectively, preosmosed in 60°B sucrose solution prior to oven-drying at 60°C. Among the eight models, the GAB model described the sorption data with low mean deviations and high correlation coefficient. The number of points for which deviation (Nd) is greater than 5% was also low. Therefore, GAB model described best the adsorption data.

Calculated GAB monolayer moisture (M_m) contents for fresh and preosmosed oven-dried bananas are shown in Table 5. GAB monolayer moisture content decreased with an increase in temperature. Sopade et al.[36] and Ayranci et al.[21] showed that GAB monolayer moisture contents decreased with increased temperature for dawadawa (fermented African locust bean) and dried fruits, respectively. The temperature dependence of the monolayer value has been linked [37] to a reduction in sorption active sites as a result of physicochemical changes induced by temperature[36].

Generally, GAB monolayer moisture content increased with an increase in total solids content of banana slices (Table 4). Higher pretreatment sucrose solution concentration resulted in increased total solids (TS) in banana slices during osmotic dehydration. Moreover, fresh oven-dried bananas generally gave lower monolayer moisture content than preosmosed oven-dried bananas. Monolayer moisture contents of fresh and preosmosed oven-dried bananas varied from 9.80–20.83% d.b. This falls within the range of M_m values of high sugar fruits reported in literature. Tsami et al.[23] estimated the M_m values of raisins, currants, figs, prunes and apricots to be 14.0, 17.3, 9.7, 12.6 and 11.6% d.b., respectively. Monolayer moisture content of blueberries was estimated to 17.4% d.b.[18].

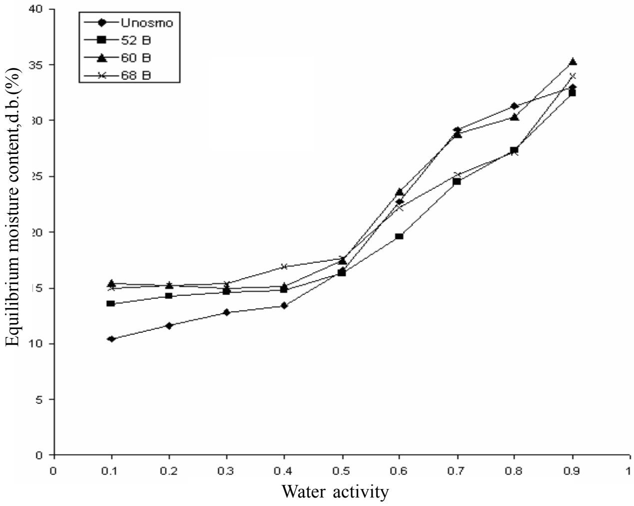

Figure 1. Effect of osmotic concentration on adsorption isotherm of oven-dried osmotically pretreated 'Omini Red' banana at 40°C.

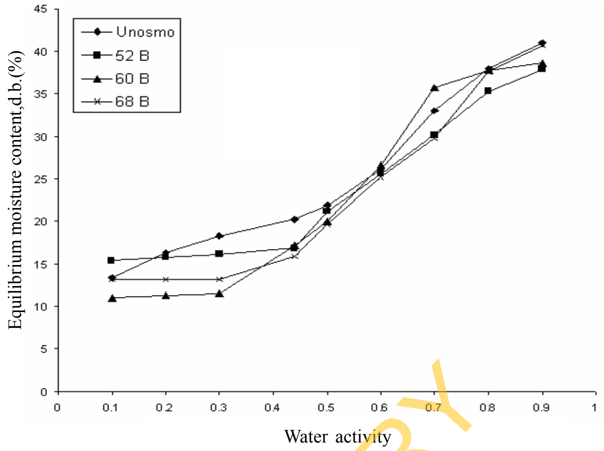

Figure 2. Effect of osmotic solution concentration on adsorption isotherm of oven-dried osmotically pretreated 'Cavendish' banana slices at 40°C.

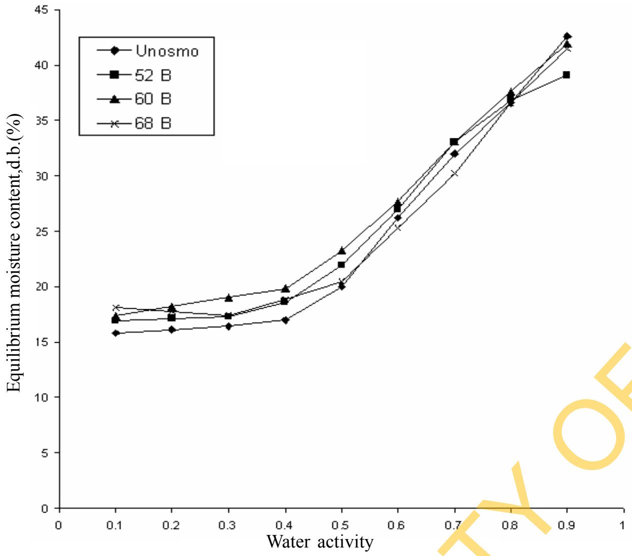

Figure 3. Effect of sucrose solution concentration on adsorption isotherm of oven-dried osmotically pretreated 'Cooking' banana at 40°C.

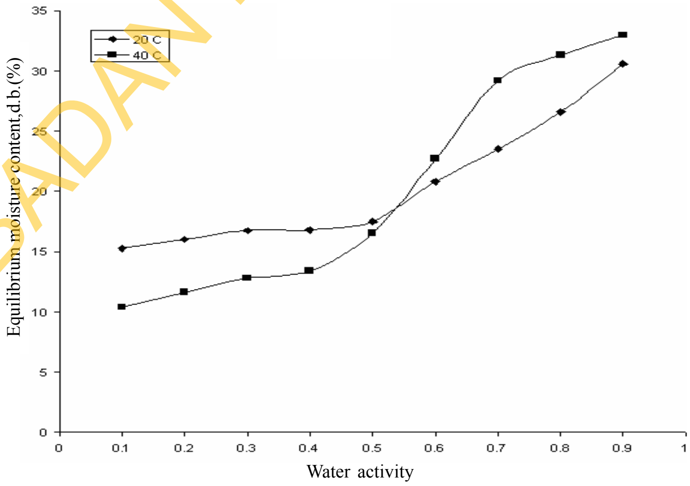

Figure 4a. Effect of temperature on the adsorption isotherm of oven-dried fresh 'Omini Red' banana.

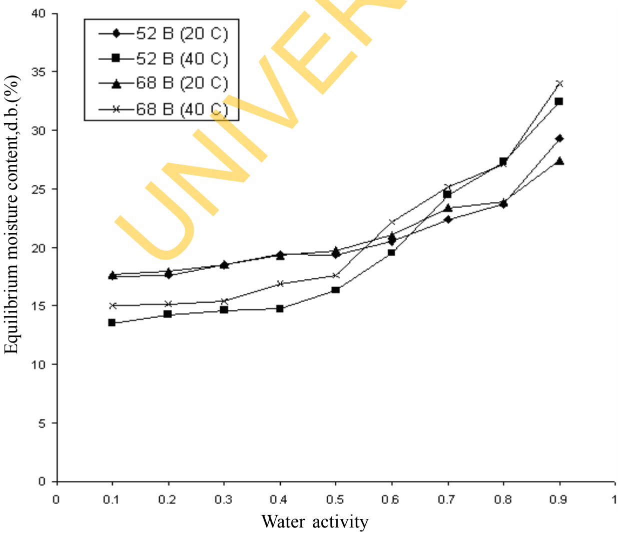

Figure 4b. Effect of temperature on the adsorption isotherms of oven-dried osmotically pretreated 'Omini Red' banana slices.

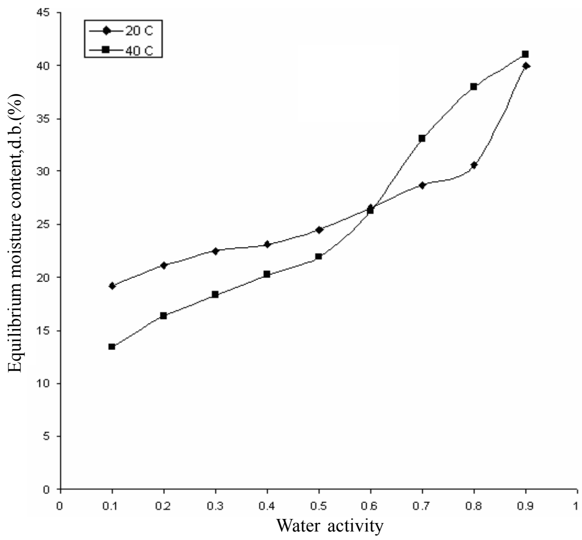

Figure 5a. Effect of temperature on the adsorption isotherms of oven-dried fresh 'Cavendish' banana slices.

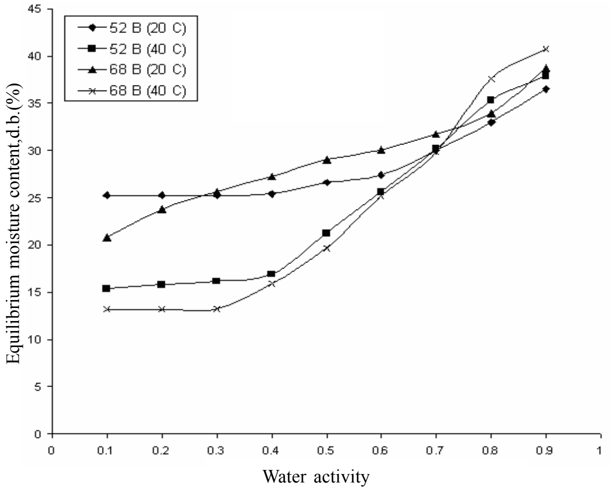

Figure 5b. Effect of temperature on the adsorption isotherms of oven-dried osmotically pretreated 'Cavendish' banana slices.

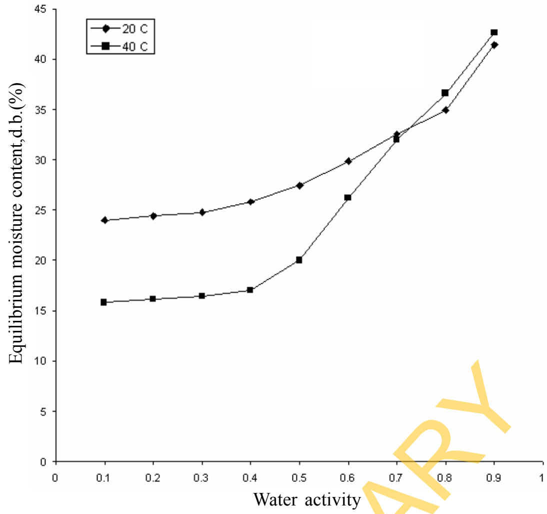

Figure 6a. Effect of temperature on the adsorption isotherms of oven-dried fresh 'Cooking' banana slices.

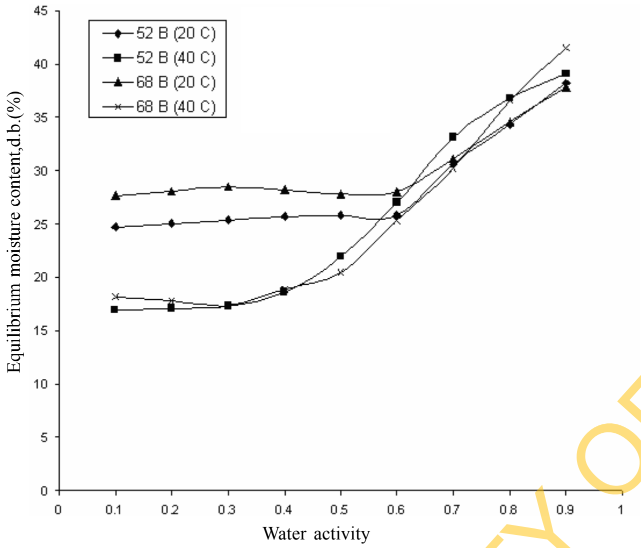

Figure 6b. Effect of temperature on the adsorption isotherms of oven-dried osmotically pretreated 'Cooking' banana slices.

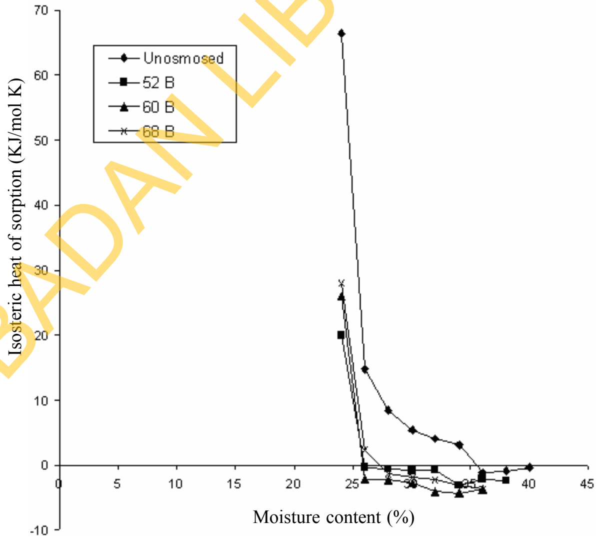

Figure 7. Isosteric heat of sorption of oven-dried fresh (unosmosed) and osmotically pretreated 'Cooking' banana slices.

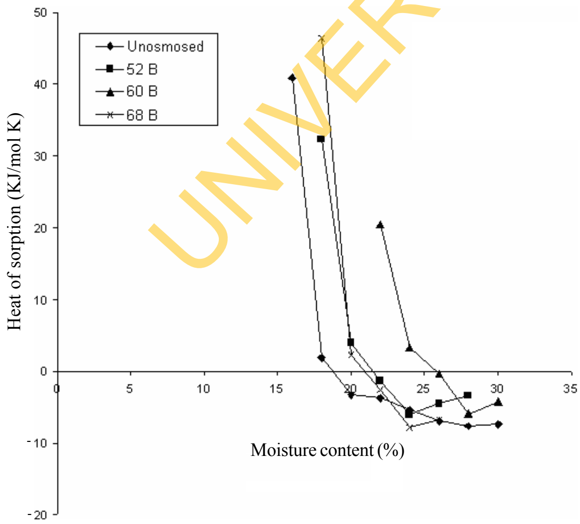

Figure 8. Isosteric heat of sorption of oven-dried fresh (unosmosed) and osmotically pretreated 'Omini Red' banana slices.

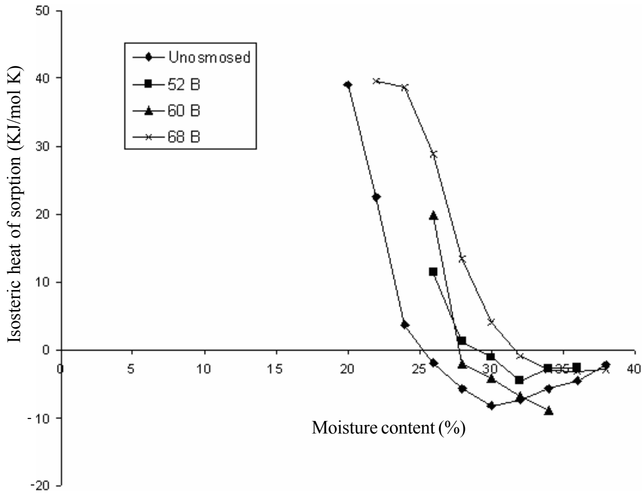

Figure 9. Isosteric heat of sorption of oven-dried fresh (unosmosed) and osmotically pretreated 'Cavendish' banana slices.

Table 1. Sorption isotherm models.

Model	Equation
BET[22]	$M = M_m Ca_w/[(C1-a_w)+ (C-1)(1-aw)^a{}_w]$
Oswin[29]	$M = C(a_w/(1 - a_w)]^k$
Halsey[30]	$a_w = \exp.(-C/RT\,\theta^k)$ where $\theta = M/M_m$
Henderson[31]	$a_w = 1 - \exp.(CTM^k)$
Chung-Pfost[32]	$\ln a_w = (-C/RT)\exp.(-KM)$
Chen[33]	$a_w = \exp.[C + k\exp.(-BM)]$
Smith[34]	$M = C - k\ \ln(I - a_w)$
GAB[35]	$M = M_m\, Cka_w/[(1-ka_w)(1 - ka_w + Cka_w)]$

Table 2. Parameters of models applied to sorption data of 'Omini Red' banana slices preosmosed in 60°B sucrose solution and oven-dried at 60°C.

Model	k	C	Mean deviation	Correlation coefficient	Nd
Bradley	-539.48	0.7587	1.657	-0.98803	0.00
BET	4.5726	-3.3384	64.640	0.84765	88.89
Oswin	24.339	0.1000	2.059	0.98144	0.00
Smith	20.321	4.8123	1.940	0.98192	11.11
Halsey	0.11904E+13	7.0848	1.500	0.98815	0.00
Henderson	0.36563E-27	7.3110	3.354	0.95758	33.33
Chun-Pfost	0.15508E+07	0.2829	1.567	0.98803	0.00
GAB	0.99665	129.8089	1.741	0.99690	0.00

C and k are model constants.
Nd Number of points for which deviation is greater than 5%.

Table 3. Parameters of models applied to sorption data of 'Cooking' banana slices preosmosed in 60°B sucrose solution and oven-dried at 60°C.

Model	k	C	Mean deviation	Correlation coefficient	Nd
Bradley	-109.87	0.8335	4.658	-0.95844	33.33
BET	5.5955	-3.5196	71.042	0.86520	100.00
Oswin	28.104	0.1158	5.007	0.93448	55.56
Smith	22.269	7.0653	2.745	0.98041	22.22
Halsey	0.76264E+11	5.9556	3.537	0.96660	33.33
Henderson	0.78593E-25	6.5023	6.505	0.88533	55.56
Chun-Pfost	0.42390E+06	0.19803	4.277	0.95844	33.33
GAB	0.98206	32.3179	4.598	0.99009	33.33

C and k are model constants.
Nd Number of points for which deviation is greater than 5%.

Table 4. Parameters of models applied to sorption data of 'Cavendish' banana slices preosmosed in 60°B sucrose solution and oven-dried at 60°C.

Model	k	C	Mean deviation	Correlation coefficient	Nd
Bradley	-413.98	0.7972	5.123	-0.91895	33.33
BET	5.3181	-3.3480	64.375	0.84429	88.89
Oswin	28.524	0.0852	5.115	0.88466	44.44
Smith	24.157	5.2248	3.717	0.94064	33.33
Halsey	0.91186E+14	8.0442	4.058	0.92093	44.44
Henderson	0.41572E-33	8.8850	6.232	0.83379	66.67
Chun-Pfost	0.33496E+07	0.2683	4.325	0.91895	44.44
GAB	0.98535	34.2620	4.779	0.99767	33.33

C and k are model constants.
Nd Number of points for which deviation is greater than 5%.

Table 5. GAB monolayer moisture and total solids content of fresh- and osmo-oven-dried bananas.

Banana variety	Equilibrium temp. (K)	Fresh-oven- dried	Osmo-oven dried Sucrose solution concentration			
			52°B	60°B	68°B	
Omini Red	293	26.71	39.88	43.37	46.46	TS%
		11.910	14.1705	18.4798	15.668	
Cooking	293	22.79	46.40	47.44	52.56	TS%
		19.0419	17.9281	17.9671	20.3103	
Cavendish	293	20.50	41.85	46.97	55.85	TS%
		16.1511	19.1439	19.4078	20.8288	
Omini Red	313	26.71	39.88	43.37	46.46	TS%
		11.4264	9.8010	11.5281	11.7190	
Cooking	313	22.79	46.40	47.44	52.56	TS%
		12.8905	13.3949	13.7165	15.1535	
Cavendish	313	20.50	41.85	46.97	55.85	TS%
		13.3050	14.0103	13.5355	15.1495	

TS Total solids content (%)of banana slices

Isosteric heat of sorption of fresh and preosmosed oven-dried banana slices: Heat of sorption values vs moisture content (%) obtained from isotherms at 20 and 40°C for fresh and preosmosed oven-dried bananas are shown in Figs 7-9. For both 'Cavendish' and 'Omini Red' slices, isosteric heat of sorption increased with increasing sucrose solution concentration prior to oven–drying. However, in the case of 'Cooking' banana, isosteric heat of sorption (Qst) decreased with increasing sucrose solution concentration prior to oven-drying. The Qst values of 'Cooking' banana slices were lower compared to those of 'Cavendish' and 'Omini Red' slices.

Generally, heat of sorption increased with decreased moisture content in banana slices. Isosteric heat of sorption was large and positive at low moisture contents (11.46–66.41 kJ/mol) but decreased sharply to lower and negative values, especially for 'Cavendish' and 'Omini Red'. The results are in agreement with reports on raisins, figs, prunes and apricots [23], sultana raisins [28] and apple [38]. Large endothermic values of isosteric heat of sorption at a low moisture contents, noted especially in fresh and preosmosed oven-dried 'Cavendish' and 'Omini Red' banana slices, indicated weaker interactions between water vapour and the absorbent. These interactions become stronger as moisture content increases [23]. Moreover, the observed positive values of the net isosteric heat of sorption at low moisture contents are supposedly due to physical sorption of water molecules forming a monomolecular layer [39]. On the other hand, negative values of Qst at high moisture contents have been explained to be the contribution of the endothermic dissolution of sugars in the sorbed water [28].

Conclusions

Adsorption isotherms of fresh and preosmosed oven-dried banana slices followed the type I (J–shaped) isotherms. Crossing of 20 and 40°C isotherms occurred between a_w~0.55-0.70. Inversion point was affected by varietal difference. GAB model best described the sorption data of fresh and preosmosed oven-dried banana slices. GAB monolayer of the banana products was in the range of 9.80–20.80% d.b. Isosteric heat of sorption of fresh and preosmosed oven-dried banana slices was in the range of -8.89 - 66.41 kJ/mol, and was influenced by pretreatment sucrose solution concentration, moisture contents and varietal differences.

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