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Water sorption isotherms of non-fermented cocoa beans (*Theobroma cacao*)

A.J. Sandoval *, J.A. Barreiro

Dept. Tecnología de Procesos Biológicos y Bioquímicos, Universidad Simón Bolívar, Apdo. 89000, Caracas 1080-A, Venezuela

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Abstract

The water sorption isotherms of non-fermented (Venezuelan fine second grade) cocoa beans (*Theobroma cacao*) were determined at three temperatures typically found during storage in tropical countries (25°C, 30°C and 35°C). For this purpose the grounded samples were equilibrated in desiccators containing 17 saturated salt solutions of known a_w at the temperatures studied, covering a range of a_w from 0.08 to 0.94. The desiccators with the samples were kept in temperature-controlled incubators at the temperatures indicated above (±0.5°C). When equilibrium was reached, the moisture content and the a_w of the samples were measured at the temperature of the experiment. The data obtained were adjusted to several regression models in order to determine the best fit. No statistical differences ($\alpha = 0.01$) were found among the isotherms of 25°C, 30°C and 35°C, being all data adjusted to a single isotherm in this temperature range. The BET equation showed the best fit for $a_w < 0.50$ ($r = 0.986$) and the Harkins–Jura model for $a_w \geqslant 0.50$ ($r = -0.986$). The adjusted equations showed constants of 0.0149 for the intercept and 0.324 for the slope of the linearized BET equation and −0.0468 and −16.711 for the intercept and slope of the linearized equation of Harkins–Jura, respectively. In both cases the regression analysis showed a linear adjustment ($P < 0.001$). Mean values for water content of the monolayer of 2.94/100 g were determined with the BET model and 2.18/100 g with the GAB model ($r = 0.970$). An average sorption enthalpy value of 1.81 ± 0.10 kcal/gmol was obtained for the temperature range studied (25–35°C).

Keywords: Sorption isotherms; Water activity; Cocoa beans

1. Introduction

Cocoa beans have been an important trade commodity in the world. Two types are usually marketed: non-fermented and fermented beans. Different grades could be given to these products depending on specific quality parameters.

Many problems of cocoa bean stability during storage and sea transportation are related to the moisture content and the water activity of the beans. Among them, the most important are the microbiological stability and water-transfer phenomena that can take place during transportation within the stow in dry containers or ship holds, or while storage of the beans in warehouses subjected to fluctuating external temperatures. Fluctuating temperature could lead to water migration resulting in condensation or sweat problems and inducing rapid deterioration of the beans.

The moisture content of the beans is affected by temperature and relative humidity of the ambient air. Since cocoa beans are usually packaged in permeable jute bags, the product is exposed to the external atmosphere during storage, gaining or loosing moisture depending on the conditions of the air. The knowledge of the water sorption isotherms is of prime importance to perform engineering calculations in order to predict the stability of the beans during storage and transportation.

Few research works have been found in the literature on water sorption isotherms of cocoa beans. Gane (1950) presented data of sorption isotherms of cocoa for water activities below 0.70, using the static jar method with sulfuric acid solutions at temperatures of 15°C and 37°C. Equilibrium moisture data for cocoa powder at 20°C were published previously (Anonymous, 1970). Moisture desorption isotherms for cocoa beans at 33.3°C, 41.8°C and 52.4°C were determined by Mercier, Tusa, and Guaíquirian (1982) using a gravimetric method. The monolayer water content and the average sorption enthalpy were calculated using the BET equation. More recently Talib, Daud, and Ibrahim (1995)

* Corresponding author. Tel.: +5812-906-3970/3976; fax: +5812-906-3971.

E-mail address: asandova@usb.ve (A.J. Sandoval).

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Notation

A	regression constant for the isotherm models (Table 1)
a_w	water activity (dimensionless)
B	regression constant for the isotherm models (Table 1)
C	constant of the BET equation (dimensionless)
C'	constant of the GAB model (dimensionless)
ΔH_T	total heat requirement (kcal/gmol)
ΔH_v	latent heat of vaporization (kcal/gmol)
K	constant of the GAB model (dimensionless)
Q_s	sorption enthalpy (kcal/gmol)
R	universal gas constant (kcal/K mol)
r	correlation coefficient
T	absolute temperature (K)
V	moisture content-dry basis (g water/100 g dry solids)
V_m	water content of the monolayer (g water /100 g dry solids)

determined moisture desorption isotherms for cocoa beans for external air relative humidities ranging from 30% to 90% and temperatures from 20°C to 70°C. The data were adjusted to the modified Hasley, Henderson, and Chung and Pfost equations, finding that these equations could be used to represent the desorption isotherms, particularly for temperatures from 50°C to 70°C.

It is generally recognized that the microbiological stability of cocoa is attained once the water activity is below 0.70 (Anonymous, 1970). However, there are still discrepancies in relation to the moisture content to obtain microbiological stability in this product. There is insufficient data to predict the equilibrium moisture content of the beans for the whole range of water activity and for the temperatures usually found in storage.

The objectives of this research work were to determine the water sorption isotherms for non-fermented cocoa beans at temperatures usually found in storage of this commodity in tropical regions (25°C, 30°C and 35°C); to establish a sorption model capable of fitting the data in order to predict the moisture sorption isotherms in the temperature range studied; and to calculate the monolayer moisture content and the sorption enthalpy.

2. Materials and methods

2.1. Sample collection

Non-fermented cocoa beans (*Theobroma cacao*) grown in Eastern Venezuela in 1993 were collected from exportation lots. The cocoa had been graded as Venezuelan fine second grade (VFSG). A composite sample of about 25 kg of beans was collected from about 36 individual samples drawn from a similar number of lots. Sampling was done following a statistical sampling plan for bagged cocoa beans, using a grain trier to draw the samples (Anonymous, 1978a).

2.2. Physical and chemical analysis

The moisture content was determined using an atmospheric drying method at 100–102°C for 16 h, until constant weight; for protein the micro-Kjeldahl method was used, with a factor for nitrogen conversion of 6.25; crude fat, crude fiber and ash were also determined. Carbohydrates were calculated by difference. In all cases the procedures indicated in AOAC (1996) were followed. The analyses of the raw material were done by triplicate.

2.3. Water sorption isotherm

In order to determine the water sorption isotherms, the beans were grounded in a motorized mill (Wiley N°4) using a 3-mm sieve. Afterwards, they were manually grounded through a 20-mesh sieve.

A weight of about 2–3 g of the ground samples was placed in open shallow plastic containers (3.8-cm diameter), filled to a height of about 0.6 cm. The containers were placed inside desiccators, each one containing saturated salt solutions of known equilibrium relative humidity at the temperatures studied. Seventeen saturated salt solutions were used in these experiments. Three desiccators were used for each salt solution in order to obtain triplicates for the results obtained. A range of a_w from 0.08 to 0.94 was studied, with the following salts used for this purpose: KOH, LiCl, $C_2H_3KO_2$, $Zn(NO_3)_2$, K_2CO_3, $Mg(NO_3)_2$, NaBr, $CoCl_2$, $NaNO_2$, KI, NaCl, $NaNO_3$, KBr, $(NH_4)_2SO_4$, K_2CrO_4, KNO_3 and K_2SO_4 (Anonymous, 1984). The equilibrium relative humidity values in the ambient inside the desiccators was checked using an electronic relative humidity meter (Vaisala HMK 11). In this way, part of the data was obtained by adsorption (product containing final moisture equilibrium values above 6.27/100g) and the rest by desorption.

The desiccators with the samples were kept in temperature-controlled incubators (±0.5°C) at 25°C, 30°C and 35°C. After equilibrium was reached, the a_w of the samples was measured at the temperature of the experiment using a Decagon CX-1 equipment, previously calibrated, and the moisture content of the equilibrated samples determined by the oven method indicated above. Moisture determinations were done by triplicate and the averages calculated.

The data obtained were adjusted to several regression models in order to determine the best fit. The following equations for sorption isotherms were studied: Freundlich (1926), BET (Brunauer, Emmett, & Teller, 1938), Harkins and Jura (1944), Smith (1947), Hasley (1948), Henderson (1952), Chung and Pfost (1967), Kuhn (1967) and GAB model (Anderson, 1946; De Boer, 1953; Guggenheim, 1966). Linear and non-linear regression statistical analyses were done, depending on the equation, using a statistical software (Statgraphics 6.0).

The water content of the monolayer was determined from the BET and GAB equations, and the sorption enthalpy from the BET equation.

3. Results and discussion

3.1. Physical and chemical characteristics

The physical–chemical analyses for the raw cocoa beans used in this work showed the following results (g/100 g ± S.D.): Moisture = 6.27 ± 0.09; protein content = 12.51 ± 0.04; crude fat = 41.87 ± 0.12; crude fiber = 4.28 ± 0.05; ash = 3.31 ± 0.01; carbohydrates = 31.76 (by difference).

3.2. Water sorption isotherms

The experimental data obtained relating the moisture content of the beans with their a_w for the temperatures studied (25°C, 30°C and 35°C) are presented in Fig. 1. The isotherms obtained for the three temperatures studied were practically coincident and overlapped (not shown in Fig. 1) over all the a_w range. For this reason all the experimental values were adjusted to a single isotherm, as

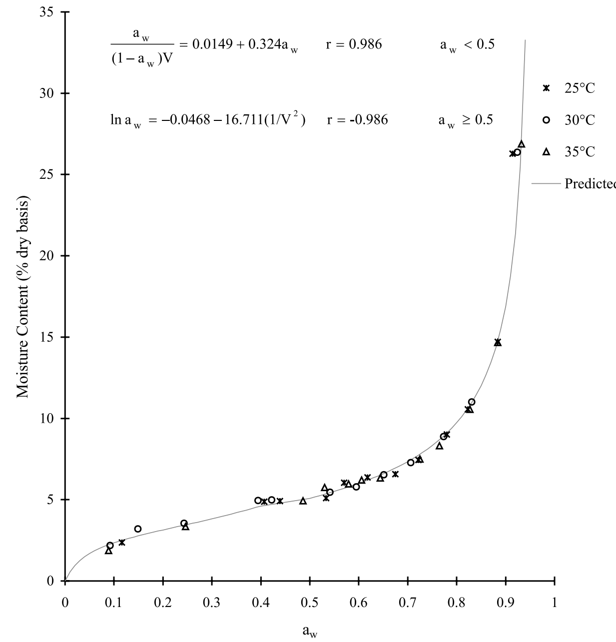

Fig. 1. Sorption isotherm of non-fermented cocoa beans for a temperature range from 25°C to 35°C. The solid line represents the results of the equations BET and Harkins–Jura in the a_w ranges indicated.

discussed below. The data obtained were adjusted to various sorption models, in order to determine the best model to predict the sorption isotherm for the product studied. The results obtained are presented in Table 1.

The best fittings were obtained for the BET equation for $a_w < 0.50$ ($r = 0.986$) and for the Harkins–Jura equation for $a_w \geqslant 0.50$ ($r = -0.986$). In this way, the water sorption isotherm in the temperature range from

Table 1
Adjustment of the experimental data obtained for the sorption isotherm (25–35°C) of non-fermented cocoa beans to various sorption models

Isotherm	Model	Range of a_w	Constants	r
Freundlich (1926)	$V = A(a_w)^{1/B}$	$a_w < 0.90$	$A = 10.2$ $B = 1.30$	0.944
BET (1938)	$a_w/[(1-a_w)V] = A + Ba_w$	$a_w < 0.50$	$A = 0.0149$ $B = 0.324$	0.986
Harkins and Jura (1944)	$\ln a_w = A + B(1/V^2)$	$a_w > 0.5$	$A = -0.0468$ $B = -16.7$	−0.986
Smith (1947)	$V = A + B\ln(1-a_w)$	$0.5 < a_w < 0.95$	$A = -4.84$ $B = -10.7$	−0.934
Hasley (1948)	$a_w = \exp[A(1/V)^B]$	$0.10 < a_w < 0.80$	$A = -13.6$ $B = 1.82$	0.982
Henderson (1952)	$(1-a_w) = \exp(AV^B)$	$0.5 < a_w < 0.95$	$A = -0.256$ $B = 0.748$	0.946
Chung and Pfost (1967)	$\ln a_w = A\exp(BV)$	$0.20 < a_w < 0.90$	$A = -2.29$ $B = -0.234$	−0.952
Kuhn (1967)	$V = A/\ln a_w + B$	$a_w < 0.5$	$A = -3.58$ $B = -0.753$	0.960
GAB	$V = V_m C'Ka_w/[(1-Ka_w)(1-Ka_w+C'Ka_w)]$	$a_w < 0.95$	$V_m = 2.18$ $C' = -76.8$ $K = 0.990$	0.970

25°C to 35°C can be predicted with the following equations:

$$a_w < 0.50: \quad a_w/(1-a_w)/V = 0.0149 + 0.324a_w, \qquad (1)$$

$$a_w \geqslant 0.50: \quad \ln a_w = -0.0468 - 16.711(1/V^2). \qquad (2)$$

The analysis of variance showed for both equations a highly significant linear regression ($\alpha = 0.01$) to a single isotherm ($P < 0.001$) in the temperature range studied. The graphical representation of the isotherm obtained with these equations is shown in Fig. 1, along with the experimental data.

The water content (dry basis) corresponding to a water activity of 0.70, considered as safe for microbiological stability, according to Eq. (2) was 7.34 g water/100 g dry solids (25–35°C). Values estimated from the data presented by other authors for the same water activity value were 10.1% and 10.7% (dry basis) for cocoa at 15°C and 37°C, respectively (Gane, 1950). A calculated value of 10.4% (basis not specified) for cocoa powder (fat content unknown) at 20°C was reported (Anonymous, 1970). From the data showed by Talib et al. (1995) for fermented cocoa beans, values of the equilibrium moisture content (dry basis) of 40.63 (20°C), 26.56 (30°C), 18.52 (40°C), 14.06 (50°C), 11.09 (60°C) and 9.22 (70°C) were estimated for a water activity of 0.70. It is obvious that the values reported by these authors lack practical meaning since the moisture content of the beans was excessive, not being in the normal range usually found for cacao beans. Some authors indicated a moisture content of 8% (wet basis) or 8.7% (dry basis) for safe storage of this product (Braudeau, 1970; Anonymous, 1978b).

The water content of the monolayer was calculated from the linearized BET equation and the non-linear GAB model presented in Table 1. For the BET equation presented in Table 1, the intercept $A = 1/(V_m C) = 0.0149$ and the slope $B = (C-1)/(V_m C) = 0.324$. It was found by solving these equations that the water content associated to the monolayer was $V_m = 2.94$/100 g dry solids and the constant $C = 22.78$. The sorption enthalpy (Q_s) was calculated by the equation presented by Chirife, Suárez, and Iglesias (1986) that relates the constant C with this parameter and the absolute temperature (T).

$$Q_s = RT \ln C. \qquad (3)$$

Values from 1.67 to 1.90 kcal/gmol, with an average sorption enthalpy of 1.81 ± 0.10 kcal/gmol were obtained for the temperature range studied (25–35°C). In the same way, the total heat requirement in this process (ΔH_T) was calculated with the following equation (Labuza, Kaanane, & Chen, 1985):

$$\Delta H_T = Q_s + \Delta H_v. \qquad (4)$$

The calculated values ranged from 12.2 to 12.3 kcal/gmol with an average value of 12.3 ± 0.05 kcal/gmol. Similar results were obtained by Mercier et al. (1982), using the BET equation working with non-graded cocoa beans: 3.07/100 g dry solids for the water content associated with the monolayer and 1.1 kcal/gmol for the adsorption enthalpy, for a range of temperature from 33.3°C to 52.4°C.

The data were adjusted to the non-linear GAB model, with the following constants obtained: $V_m = 2.18$/100 g dry solids, $C' = -76.8$, $K = 0.990$ for the temperature range studied. The value obtained for the monolayer water content using the GAB model (2.18/100 g dry solids) was slightly smaller than that determined from the BET equation (2.94/100 g dry solids).

4. Conclusions

Sorption isotherms for non-fermented cocoa beans (Venezuelan fine second grade) were determined for three temperatures (25°C, 30°C and 35°C). The proximate analyses of the beans were presented. The data obtained for the isotherm were adjusted to various models, with the best fittings found for the BET ($a_w < 0.50$) and Harkins–Jura ($a_w \geqslant 0.50$) models. The analysis of variance showed for both equations a highly significant regression to a single isotherm in the temperature range studied.

According to the data obtained, the moisture of the ground beans (20 mesh) corresponding to the water activity considered as safe for microbiological stability ($a_w = 0.70$) was 7.34 g water/100 g dry solids. The water content of the monolayer obtained using the BET equation was $V_m = 2.94$/100 g dry solids and the constant of that model $C = 22.78$. A value for the monolayer water content calculated using the GAB model was 2.18/100 g dry solids. The average sorption enthalpy (Q_s) and the sorption activation energy for the temperature range studied (25–35°C) showed values of 1.81 ± 0.10 and 12.3 ± 0.05 kcal/gmol, respectively.

References

Anderson, R. (1946). Modifications of the BET equation. *Journal of the American Chemical society*, *68*, 689–691.

Anonymous. (1970). Physical constants of cocoa powder and cocoa butter. Technical Bulletins. N.V. Cacaofabriek De Zaan. Holland.

Anonymous. (1978a). Granos de cacao. Toma de muestras. Comisión Venezolana de Normas Industriales. Norma COVENIN 1339. Min. de Fomento, Caracas.

Anonymous. (1978b). Granos de cacao. Comisión Venezolana de Normas Industriales. Norma COVENIN 50. Min. de Fomento, Caracas.

Anonymous. (1984). Operation manual. Decagon CX-1. Decagon Devices, Inc, USA.

A.O.A.C. (1996). *Official methods of analysis* (16th ed.). Arlington, VA, USA: Association of Official Analytical Chemists.

Braudeau, J. (1970). *El Cacao*. Barcelona, Spain: Editorial Blume.

Brunauer, S., Emmett, P., & Teller, E. (1938). Adsorption of gases in multimolecular layers. *Journal of the American Chemical Society*, *60*, 309.

Chirife, J., Suárez, C., & Iglesias, H. (1986). Technical note: the calculation of the heat of water sorption in foods on the basis of BET theory. *Journal of Food Technology*, *21*(1), 103–107.

Chung, D., & Pfost, H. (1967). Adsorption and desorption of water vapor by cereal grains and their products. Part 1: Heat and free energy changes of adsorption and desorption. *Transactions of the ASAE*, *10*(3), 549.

De Boer, J. (1953). *The dynamic character of adsorption* (2nd ed.). Oxford, UK: Clarendon Press.

Freundlich, H. (1926). *Colloid and capillary chemistry*. London, UK: Metuen.

Gane, R. (1950). The water relations of some dried fruits, vegetables and plant products. *Journal of the Science of Food and Agriculture*, *1*, 42.

Guggenheim, E. (1966). *Applications of statistical mechanics*. Oxford, UK: Clarendon Press.

Harkins, W., & Jura, G. (1944). Surfaces of solids. XIII. A vapor adsorption method for the determination of the area of a solid without the assumption of a molecular area, and the areas occupied by nitrogen and other molecules on the surface of a solid. *Journal of the American Chemical Society*, *66*, 1366.

Hasley, G. (1948). Physical adsorption in nonuniform surface. *Journal of Chemistry and Physics*, *16*, 931.

Henderson, S. (1952). A basic concept of equilibrium moisture. *Agricultural Engineering*, *33*, 29.

Kuhn, I. (1967). J. Colloid Sci. 23:563. In: Brooker, D., Bakker, F., & Hall, C. 1974. *Drying cereal grains*. Westport, Connecticut. USA: The Avi Publishing Company, INC.

Labuza, T. P., Kaanane, A., & Chen, J. Y. (1985). Effect of temperature on the moisture sorption isotherms and water activity shift of two dehydrated foods. *Journal of Food Science*, *50*(2), 385.

Mercier, P., Tusa, A., & Guaíquirian, H. (1982). Adsorción del agua en semilla de café y cacao. *Acta Científica Venezolana*, *33*(1), 398.

Smith, S. (1947). The sorption of water vapor by high polymers. *Journal of the American Chemical Society*, *69*, 646.

Talib, M., Daud, W., & Ibrahim, M. (1995). Moisture desorption isotherms of cocoa beans. *Transactions of the ASAE*, *38*(4), 1153–1155.