

Measuring and Modeling Grain Sorption Equilibria of Amaranth Grains

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ABSTRACT

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Water activity (a_w) of *Amaranthus cruentus* were measured at 35, 45, and 65°C at different moisture contents by means of an electronic water activity meter. Experimental curves were fitted to one three-parameter equation (GAB equation). The equilibrium values and temperature shifts were modeled with a three-parameter equation in the approximate a_w

range of 0.03–0.88. An analytical expression to calculate the isosteric heat of sorption and its moisture content dependence was used, and the results were compared with the isosteric heat calculated from the experimental equilibrium data by means of the Clausius-Clapeyron equation.

Grain amaranth has been identified as a promising source of food and feed (Teutonio and Knorr 1985). It is cultivated in Central and South America and parts of Asia and Africa. It has ≈12–18% lysine-rich protein and 5–8% fat that contains a relatively high level of squalene (Becker et al 1991). The main constituent is, however, starch at 48–62%, concentrated in the perispema (Becker et al 1991). This constituent has been projected to have many food and nonfood applications (Breene 1991, Ahamed et al 1996).

Reports in the literature have focused mainly on aspects such as agronomic potential, nature of the starch in the seed, and processes for isolating this constituent from the grain (Betschart et al 1981, Becker et al 1991, Uriyapongson and Rayas-Duarte 1994).

Other aspects related with drying and storing of amaranth seed have received less attention. In particular, the equilibrium relationships between amaranth seeds and the surrounding water-air mixture required to interpret adequately the mechanisms that contribute to the kinetics of dehydration operations, and for the selection of the moisture and temperature conditions most suitable for storage of the dehydrated product, are not available. The need for this information has been very well established by different investigators who have demonstrated the relationship between chemical and physical stability of food materials and modes of water binding (Labuza et al 1970, Karel 1975). In addition, moisture sorption isotherms constitute an essential part of the theory of drying and provide useful information in the design of drying equipment and in the study of storage of dehydrated products. A thermodynamic parameter such as isosteric heat is frequently evaluated from equilibrium data at different temperatures (Iglesias and Chirife 1976). The isosteric heat, defined as the total heat of sorption in the food minus the heat of vaporization of water at the system temperature, is needed both for design work and for qualitative understanding of the state of water on the food surface. Consequently, the objectives of this study were to: 1) provide reliable experimental data for the sorption characteristics of amaranth grains, 2) suggest simple mathematical models to describe their sorption behavior, 3) calculate the isosteric heat for different moisture levels, and 4) model the dependence of the isosteric heat on moisture content.

The water vapor pressure in equilibrium with several common seeds has been the subject of much experimental work by different methods. One of them is the static gravimetric method, which consists of equilibration of the specimen's moisture content to constant water activity (a_w) at selected temperatures. A detailed description of the method was given by Haynes (1961). Moisture

sorption data for various grains and seeds published in the literature have been obtained at various a_w values and temperatures (Chung and Pfof 1967, Pixton and Warburton 1971, Aguerre et al 1983, Tolaba and Suárez 1990, Rovedo et al 1993).

Several isotherm equations have been proposed for the correlation of the equilibrium moisture content with the a_w of food products. One of the most popular is the so called Guggenheim-Anderson-de Boer (GAB) equation, as outlined by Bizot (1983):

$$\frac{m}{m_m} = \frac{C a_w}{(1 - k a_w)[1 + (C - k) a_w]} \quad (1)$$

where m is the moisture content; m_m is the moisture content needed to cover the entire surface with a unimolecular layer (equivalent to the BET monolayer) (Bruanuer et al 1983); C is the Guggenheim constant [$C' \exp(H_1 - H_m)/(RT)$]; H_1 is the total heat of sorption of the first layer in primary sites; H_m is the total heat of sorption of the multilayer (which differs from the heat of condensation of pure water); k is a factor correcting properties of the multilayer molecules with respect to the bulk liquid.

Several empirical and semiempirical correlations have been proposed to correlate equilibrium moisture content, temperature, and a_w in grains (Day and Nelson 1965, Chen and Clayton 1971, Iglesias et al 1986). Based on the enthalpy-entropy compensation effect for water sorption in foods, Aguerre et al (1986) derived a three-parameter equation that represents the water sorption equilibrium of foodstuffs in the entire range of moisture contents, and adequately describes the temperature dependence:

$$\psi_\tau \ln a_w = K_1 K_2^m \quad (2)$$

where $\psi_\tau = (1/T_\beta - 1/T)^{-1}$; T_β , K_1 , and K_2 are fitting parameter characteristics of each material; and T is the absolute temperature. Equation 2 was used to adequately model the effect of temperature on the sorption isotherms of several cereal grains (Falabella et al 1992).

Heat of sorption can be determined from calorimetric measurements or from moisture sorption data. The second method is more convenient, given that sorption isotherms are determined routinely. The usual procedure to evaluate isosteric heat of sorption consists in plotting the sorption isostere as in a_w versus $1/T$ and determining the slope, which is equal to Q_{st}/R , with Q_{st} being the isosteric heat, and R being the gas constant (Iglesias and Chirife 1976, Falabella et al 1989). An alternative procedure, based on Eq. 2 and the Clausius-Clapeyron equation was proposed by Falabella et al (1992):

$$Q_{st} = RK_1 K_2^m \quad (3)$$

This simple mathematical expression is in marked contrast to other formulations available in the literature for calculating heat of sorption where a large number of parameters are involved (Zuritz and Singh 1985). Equation 3 was used by Falabella et al (1992) to predict the variation of Q_{st} with moisture content for various cereal grains with satisfactory results.

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TABLE I
Desorption Equilibrium Values of Amaranth Seeds

Temperature					
35°C		45°C		65°C	
Moisture Content (% db)	Water Activity	Moisture Content (% db)	Water Activity	Moisture Content (% db)	Water Activity
3.60	0.112 ± 0.002	3.41	0.113 ± 0.003	0.76	0.029 ± 0.001
5.49	0.216 ± 0.002	4.17	0.191 ± 0.002	2.77	0.108 ± 0.002
7.13	0.290 ± 0.002	6.48	0.316 ± 0.001	4.99	0.285 ± 0.002
8.16	0.363 ± 0.001	7.78	0.389 ± 0.001	7.08	0.495 ± 0.001
9.13	0.442 ± 0.002	9.22	0.532 ± 0.001	9.53	0.666 ± 0.002
10.11	0.554 ± 0.003	10.06	0.611 ± 0.002	11.01	0.747 ± 0.002
10.94	0.605 ± 0.001	13.69	0.773 ± 0.001	13.93	0.799 ± 0.002
14.40	0.749 ± 0.001	17.09	0.836 ± 0.001
17.40	0.813 ± 0.003	19.61	0.875 ± 0.002
20.65	0.855 ± 0.002

TABLE II
Parameter Values^a and Goodness of Fit^b of Eq. 4 as Applied to the Experimental Desorption Isotherms of Amaranth Seeds

Temperature (°C)	m_m (% db)	C	k	%E
35	6.74	12.02	0.77	4.6
45	5.90	10.66	0.88	4.4
65	5.50	7.88	0.76	6.5

^a Moisture content needed to cover the entire surface with a unimolecular layer (Bruanuer et al 1938) (m_m). Guggenheim constant (C) factor correcting properties of the multilayer molecules with respect to the bulk liquid (k).

^b Relative percent deviation modulus (%E).

MATERIALS AND METHODS

A variety of amaranth (*Amaranthus cruentus*) harvested in 1997 with 9% moisture content of (kg of water/100 kg of solids) was stored at 10°C before use. To determine the desorption isotherms, a sample of ≈100 g was hydrated to ≈21% moisture (db) by exposure to water in evacuated desiccators at 4°C for two weeks; there was no mold growth. Smaller (10-g) samples were removed and partly dehydrated in vacuum desiccators with saturated NaOH, LiCl, NaI, NaBr, NaNO₃, NaCl, KCl, and MgCl₂ at 4°C for a few days before use. This procedure provided various sets of seeds with a moisture contents range of ≈0.3–21%. The a_w corresponding to the different moisture content levels was measured with a hygrometer.

The hygrometer (Thermoconstanter Humidat TH2, Novasina AB, Zurich, Switzerland) had a temperature controller with a conductivity cell containing a hygroscopic electrolyte mounted in a metal cap that covered each of the samples in a holder in a disposable dish. Calibration followed Falabella et al (1989) using saturated LiCl, Mg(NO₃) and KCl, with activity values at 35, 45, and 65°C from Greenspan (1977) confirming good linear response and stability. The rate of approach to equilibrium was rapid and practically reached within 45 min for all samples, depending on temperature and moisture level tested. To be certain, a time of 60 min was adopted.

Moisture contents were measured gravimetrically after vacuum drying over magnesium perchlorate at 70°C and 6.7 kPa until constant weight.

RESULTS AND DISCUSSION

The measured desorption isotherms were fitted to the GAB equation by using the least square method for minimizing the absolute differences between measured and calculated a_w values. Estimates of the GAB constants (m_m , C , and k) were obtained by transforming Eq. 1 to the quadratic form:

$$\frac{a_w}{m} = C_1 + C_2 a_w + C_3 a_w^2 \quad (4)$$

where $C_1 = 1/m_m$, $C_2 = (1 - 1/C)/m_m$; and $C_3 = (1/C - 1)k/m_m$.

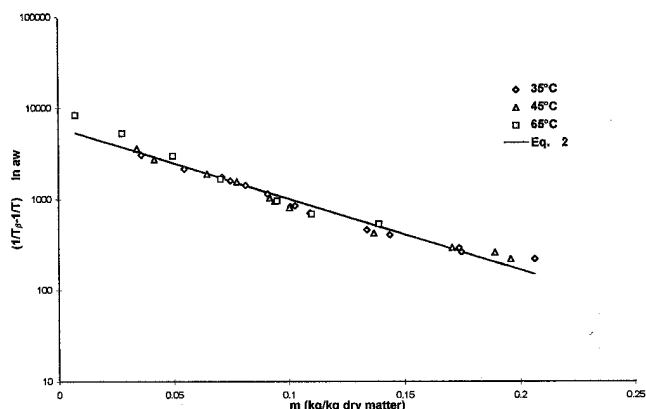


Fig. 1. Equilibrium data of amaranth seeds at different temperatures plotted according to Eq. 2 (—).

The quality of the fit of the GAB model was judged from the value of the relative percent deviation modulus (%E)

$$\%E = \frac{100 \sum |a_{wi} - a_{wi}^*|}{n a_{wi}} \quad (5)$$

where n is the number of experimental points, a_{wi} is the measured water activity; and a_{wi}^* is the calculated water activity.

Table I gives the equilibrium values for the three temperatures investigated. The a_w values reported in Table I are the mean of three replicates; the maximum relative error in equilibrium values was 0.3%. Estimations of the GAB constants (m_m , C , and k) were obtained by fitting the equilibrium data from Table I to Eq. 4. The values of these parameters and relative percent deviation modulus (%E) for each temperature are given in Table II. The values of E were in all cases <6%, which reflects the good fit of the isotherm used, according to Lomauro et al (1985). The monolayer moisture content, which varies slightly with temperature as usual, occurs for most biological materials. It must also be noticed that the k constant is lower than unity, ≈0.7–0.8, as is usual in many food materials, showing a little dependence on temperature (Weisser 1986).

Once the moisture content at the monolayer (m_m) was known, the sorption surface area of amaranth grain was determined (Gregg and Sing 1982):

$$A = \frac{m_m N a_{H_2O}}{M} = 3.5 \times 10^6 m_m \quad (6)$$

where A is the surface area of the adsorbent; N is the Avogadro's number (6×10^{26} molecules/kmole); M is the molecular weight of H₂O (18 kg mole); a_{H_2O} is the area of a water molecule (10.6×10^{-20} m²). The values of A from Eq. 6 were 236, 207, and 193 m²/g for the equilibrium temperatures of 35, 45, and 60°C, respectively, which are comparable with those reported in the literature for other starchy materials (Aguerre et al 1989).

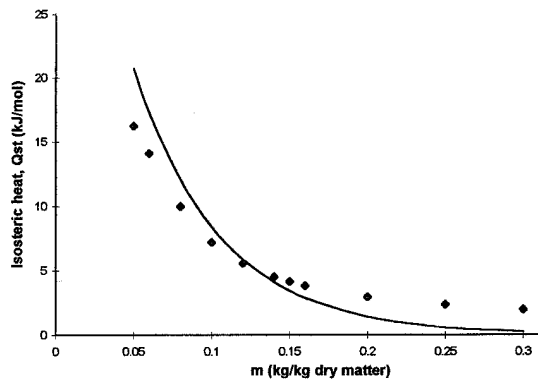


Fig. 2. Comparison of isosteric heat predicted by Eq. 3 (—) with values obtained from direct application of Clausius-Clapeyron equation to the experimental equilibrium data (◆).

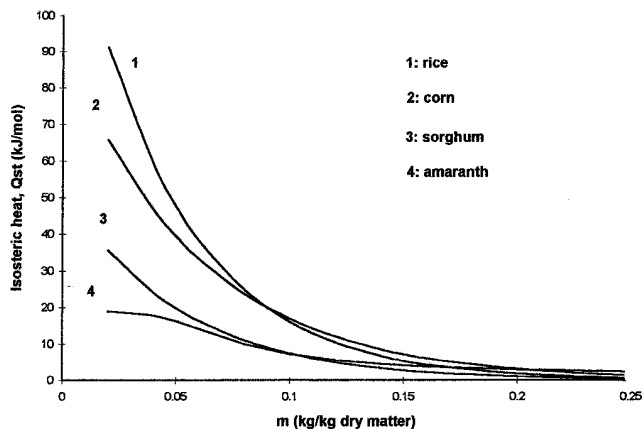


Fig. 3. Effect of moisture content on the isosteric heat of desorption of amaranth grain compared with corn, sorghum, and rice from Cenkowski et al (1992).

To test the validity of Eq. 2, the equilibrium data at the three temperatures investigated were plotted as $\ln(\psi_r \ln a_w)$ against m in Fig. 1. A good straight line can be observed for the three temperatures. The values of K_1 and K_2 calculated by linear regression are 6119.8 and 1.57×10^{-8} , respectively. The value of T_β is 394.4. K is comparable to other T_β values reported by Falabella et al (1992) for different cereal grains.

The calculation of the isosteric heat variation with moisture content was done using Eq. 3 and plotted in Fig. 2. The ability of Eq. 3 to predict isosteric heat was checked by comparison with the usual graphical method based on the Clausius-Clapeyron equation. The agreement was satisfactory. For moisture contents >0.20 (db), the isosteric heat tends to zero, which reflects the fact that there is little difference between the heat of vaporization from the seed kernels and that of free water. Below that level of moisture, the isosteric heat increases considerably.

The isosteric heat values of desorption for selected cereal grains are shown in Fig. 3. For moisture contents <0.20 (db), the heat of desorption values increase for all grains. In the case of rice and corn, the isosteric heat values decrease rapidly with moisture content, while for amaranth and sorghum, such decrease is smooth.

CONCLUSIONS

The GAB model was used to accurately describe the desorption isotherms of amaranth grains at different temperatures in the range of a_w investigated.

Calculations of the sorption areas from the monolayer moisture values obtained from the GAB equation were comparable with

other sorption areas reported in the literature for various cereal grains.

Equation 2 constitutes a convenient way to describe the effect of temperature on water sorption isotherms of amaranth grains.

Also, Eq. 3 can be used to predict net isosteric heat of sorption and its dependence on the material moisture content. Having this type of analytical expression is convenient for computational purposes related to drying and storage of amaranth grains.

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