

## Seed equilibrium moisture curves, water binding and its relationship with thermodynamic magnitudes

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Received October 12, 2009; accepted February 5, 2010

**A b s t r a c t.** Seed equilibrium moisture content values for soybean cv. Incasoy-24, drybean cv. CC25-9 negro, maize cv. P-7928), cabbage cv. Georgia L-9, tomato cv. Cambell 28-V, lettuce cv. GR-30, carrot cv. P-29 and pepper cv. Chay L-3 were obtained using saturated salt solutions in desiccators. Data were fitted through three hygroscopic models: D'Arcy-Watt (DAW), Socorro (SOC) and Henderson-Thompson (HTH). The parameters of the SOC and DAW equations were obtained at a temperature range between 10 to 45°C using the association with HTH model. From these data, the enthalpy and Gibbs free energy were also calculated. Results demonstrated that the three models shown may be used for fitting seed moisture content curves with high dependability. The simulation by HTH model showed an incidence of seed moisture content on Gibbs free energy more than temperature, which could be related to the dependence of viability with these non-biotic factors during gene bank conservation.

**Key words:** moisture, seed, isotherms, simulation, sorption

### INTRODUCTION

Seed hygroscopic properties are determined by the binding formed by biological macromolecules in the seed-atmosphere system and the available water vapour molecules (Probert *et al.*, 2003; Vertucci and Leopold 1987a,b). The sorption isotherm curve represents the capacity of the seed tissue and the bound water to adhere more water molecules due to external relative vapour pressure. When the Gibbs free energy difference 'G' of the seed and the atmosphere are equal, water exchange ceases and the system arrives at the equilibrium state represented by a sigmoid shaped isotherm curve (Alsadon 2001; Vega *et al.*, 2005) (Fig. 1). The isothermal sorption is represented by the AC segment. When the system changes from state A to state B the pressure value is

constant, therefore this route is called isobaric, while the BC segment relates to a state change where values of equilibrium moisture content are constant.

The equilibrium isotherms have been represented by more than 23 mathematical models for seed or other materials, like maize and soybean flour (Eslava, 1999, 2000; Hay *et al.*, 2003; Jimenes *et al.*, 1995; Ospina and Cruz 1989; Resende *et al.*, 2006; Socorro *et al.*, 2007). The equations (1)-(3) represent three of these models: (1)-D'Arcy-Watt model (DAW), (2)-Henderson-Thompson Model (HTH) and (3)-Socorro's *et al.* Model:

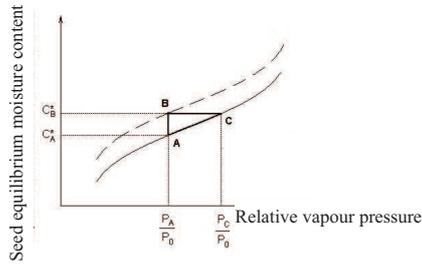
$$\text{DAW } C^* = \frac{KK'(RH)}{1+K(RH)} + c(RH) + \frac{kk'(RH)}{1-k(RH)}, \quad (1)$$

$$\text{HTH } C^* = \left[ \frac{\ln(1-RH)}{-D_1(T+D_2)} \right]^{1/d}, \quad (2)$$

$$\text{SOC } C^* = C_{50} - \frac{1}{\lambda} \left[ \frac{1}{RH} - 1 \right]. \quad (3)$$

The magnitudes  $K$ ,  $K'$ ,  $c$ ,  $k$ ,  $k'$ ,  $D_1$ ,  $D_2$ ,  $d$ ,  $C_{50}$  and  $\lambda$  are coefficients which are obtained through fitting of the experimental curves, while  $C^*$  and  $RH$  are the equilibrium moisture content and relative humidity, respectively. Several models like the HTH have the temperature  $T$  (°C) in explicit form. That is the reason why it is possible to obtain hygroscopic curves for each cultivar- $T$  independently. However, since the DAW and SOC models do not include temperature, their coefficients must be calculated experimentally for each  $T$  value. The DAW model (Eq. (1)) can, nevertheless, describe

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**Fig. 1.** Two isotherm curves for seed equilibrium moisture content at temperatures  $T_1$  (dashed line) and  $T_2$  (solid lines) where  $T_2 > T_1$ . Segments represent different phase changes: AB (isobaric), BC (to constant equilibrium moisture content) and AC (isotherm path).

sites where individual water molecules bind strongly (first term), sites where water binds weakly (second term), and sites where water condenses as a collection of molecules (multimolecular sorption sites) (third term) (Vertucci and Leopold, 1987a).

The Gibbs free energy per mol  $G$  is related to the system variables: pressure, temperature, entropy and volume (Matveev, 1985). If the AC path is assumed (isotherm Fig. 1),  $dT=0$  and volume per mol is substituted by  $RT/P$  (considering the vapour behaviour similar to an ideal gas), then a relationship between  $G$  and  $RH$  is obtained:

$$G = RT \ln(RH), \quad (4)$$

where  $R = 8.31 \text{ J K}^{-1} \text{ mol}^{-1}$ . Starting from the integrated Clausius-Clapeyron equation (Iguaz and Virseda 2007; Tolaba *et al.*, 2004; Vega *et al.*, 2006, and ), the isosteric heat of sorption can be obtained, a magnitude which is related to enthalpy. If two isotherms  $T_1$  and  $T_2$  and the BC segment is considered (Fig. 1), a mathematical expression to describe the enthalpy per mol variation is obtained through a state change  $\Delta H$  (from 1 until 2) (Vertucci and Leopold, 1987a):

$$\Delta H = R \frac{T_1 T_2}{T_2 - T_1} \ln \left[ \frac{RH_1}{RH_2} \right], \quad (5)$$

where  $(T_1, RH_1)$  and  $(T_2, RH_2)$  are the temperature and relative humidity for states 1 and 2, respectively.

It is very common that the moisture and temperature in storage chambers differ from the experimental optimum values, which prevents the possibility of the seed managers to predict the germination of their seeds. For this reason the present paper has the following purposes:

- to obtain seed moisture content values with respect to relative humidity for several species for one temperature value,
- to use the association with the Herdenson-Thompson model (whose equation depends on  $T$ ) for predicting the isotherm behaviour on other models like D'Arcy-Watt and Socorro for a wide range of temperature values (10–45°C),

- to calculate the thermodynamic potentials using data from the simulation of the moisture equilibrium curve, and to relate them with the hygroscopic properties of agricultural seeds.

## MATERIALS AND METHODS

Moisture content measurements of whole seeds (testa + cotyledon + embryo) were made for soybean (*Glycine Max* Merrill (L) cv. Incasoy-24), drybean (*Phaseolus vulgaris* L. cv. CC25-9negro), maize (*Zea mays* L. cv. P-7928), cabbage (*Brassica oleracea* L. cv. Georgia L-9), tomato (*Solanum lycopersicum* L. cv. Cambell 28-V), lettuce (*Lactuca sativa* L. cv. GR-30) carrot (*Daucus carota* L. cv. P-29) and pepper (*Capsicum annun* L. cv. Chay L-3). Seeds reached equilibrium at  $26.50 \pm 0.16^\circ\text{C}$  (drybean),  $27.50.5^\circ\text{C}$  (soybean),  $29.37 \pm 0.15^\circ\text{C}$  (maize) and  $26.8 \pm 0.1^\circ\text{C}$  (for the rest of the species), using different saturated salt solutions (Hall, 1980) for each humidity value (Ellis and Hong, 2006; Vega *et al.*, 2005). The temperature and humidity values were measured using a digital thermometer-hygrometer (Oregon Scientific EM 913) for each salt solution selected. Equilibrium moisture content data were collected and processed starting from the dry basis method (grams of water per grams of dry mass) ( $\text{Wg g}^{-1} \text{ d.m.}$ ) (Ellis *et al.*, 1985), while the relative humidity values were represented by decimal units (between 0 and 1).

Mathematical models of water sorption DAW, SOC and HTH were used for fitting the data, using the 'Least Squares Method' function within the 'Curve Expert' program (version 1.3). These models were chosen according to the following aspects: HTH has the temperature included in the equation explicitly so that if its coefficients  $D_1$ ,  $D_2$  and  $d$  are obtained for determined  $T$  value, these coefficients values are valid for the same cultivar with other temperature values. Among the several models that are  $T$ -dependent, HTH is one of the most frequently used (Vega-León, 2008) and has showed higher precision of data fitting in this study. The DAW model is not a  $T$ -dependent model and has many parameters (five), but these parameters represent physical-chemistry properties related with seed sorption and water binding (Vertucci and Leopold, 1987a). Finally, the SOC is a model developed to describe the equilibrium curve by a mathematically simple form (only two coefficients), where  $C_{50}$  represents the moisture content at  $RH=0.5$  (50%) while is related with the increment kinetics of water activity with respect to moisture increase (Socorro *et al.*, 2007).

The residual variance ( $S_D^2$ ) of the differences between model theoretical curve ( $y_n$ ) and reference data ( $Y_n$ ) was calculated using the sum of residual squares (Yamane, 1967):

$$S_D^2 = \frac{\sum_{n=1}^N (y_n - Y_n)^2}{N-1}, \quad (6)$$

where  $[Y_1, Y_2, \dots, Y_n, \dots, Y_N]$  is the reference group formed by  $N$  values (is the mean) which may be experimental or may correspond to another theoretical curve (model

association). The variance of reference data ( $S_R^2$ ), the relative error ( $RE$ ) and the coefficient of determination for the goodness-of-fit were respectively calculated by:

$$S_R^2 = \frac{\sum_{n=1}^N (\bar{Y} - Y_n)^2}{N-1}, \quad (7)$$

$$RE = \frac{100\%}{Y} \sqrt{\frac{S_D^2}{N}}, \quad (8)$$

$$r^2 = 1 - \frac{S_D^2}{S_R^2}. \quad (9)$$

Through the HTH coefficients for each species, curves at 10, 15, 20, 25, 30, 35, 40 and 45°C were simulated, while models DAW and SOC were fitted by curves for these temperature values by association with the HTH model. The statistical analysis for fitting also took into account the calculus of  $S_D^2$ ,  $S_R^2$ ,  $RE$  and  $r^2$ , where  $r^2 > 0.9$  and  $RE < 10\%$  were considered as valid. This method allowed the values collection of DAW and SOC parameters at 10-45°C range. These parameters were plotted with respect to  $T$ , where a correlation analysis was made. Model parameters with a high correlation coefficient ( $r_C$ ) with respect to  $T$  ( $r_C > 0.95$  for all eight species) were considered for a non linear regression analysis to determine their mathematical dependence on temperature.

Values of  $\Delta H$  were calculated by processing data between two isotherms: 10 and 11°C (low temperature) (Eq. (5)), as well as a pair of isotherms for 40 and 41°C respectively (high temperature), considering in all the cases  $C^*$  constant.

Similarly, the Gibbs free energy at which seeds are equilibrated for each relative humidity value was calculated through Eq. (4), where  $C^*$  was substituted for  $RH$  values using an inverse relationship in the hygroscopic model HTH so that  $G$  depended directly on  $C^*$ . These values of Gibbs energy were arranged in a matrix with respect to  $T$  and  $C^*$ , where values corresponding to  $T = 10; 11; 12; \dots; 45^\circ\text{C}$  comprised 36 columns and those corresponding to  $C^* = 0.01; 0.02; \dots; 0.35 \text{ Wg g}^{-1} \text{ d.m.}$  were arranged in 35 rows. This matrix was subjected to a two-factorial variance analysis to quantify the relative influence of  $T$  and  $C^*$  on  $G$ , through the Fisher coefficient of variability  $F_C^{(T)}$  and  $F_C^{(C^*)}$ , respectively.

## RESULTS

Seed sorption isotherms for the eight cultivars are presented in Fig. 2. The curves follow the expected reverse sigmoid shape and show three fundamental regions: a convex zone or 'knee' at low values of  $RH$ , a linear region (0.25-0.60 of  $RH$ ) with an inflexion point ( $C^*=C_{50}$  for  $RH=0.5$  at SOC model), and a concave region or 'sharp upswing' at high  $RH$  values. In all the cases high approximation of the models has been obtained ( $r^2 > 0.90$  and  $RE < 10\%$ ).

The values in Table 1 reflect no considerable variations in the D'Arcy-Watt coefficients  $K$ ,  $k$  and  $k'$ . Nevertheless, a high variation among species in  $K'$  and  $c$  was found. Similar results were observed in the Henderson-Thompson coefficients  $D_1$  and  $D_2$  (constant in the cases analysed), and a substantial variation for ' $d$ '. The Socorro parameters,  $C_{50}$  and  $\lambda$ , were different for each of the eight cultivars.

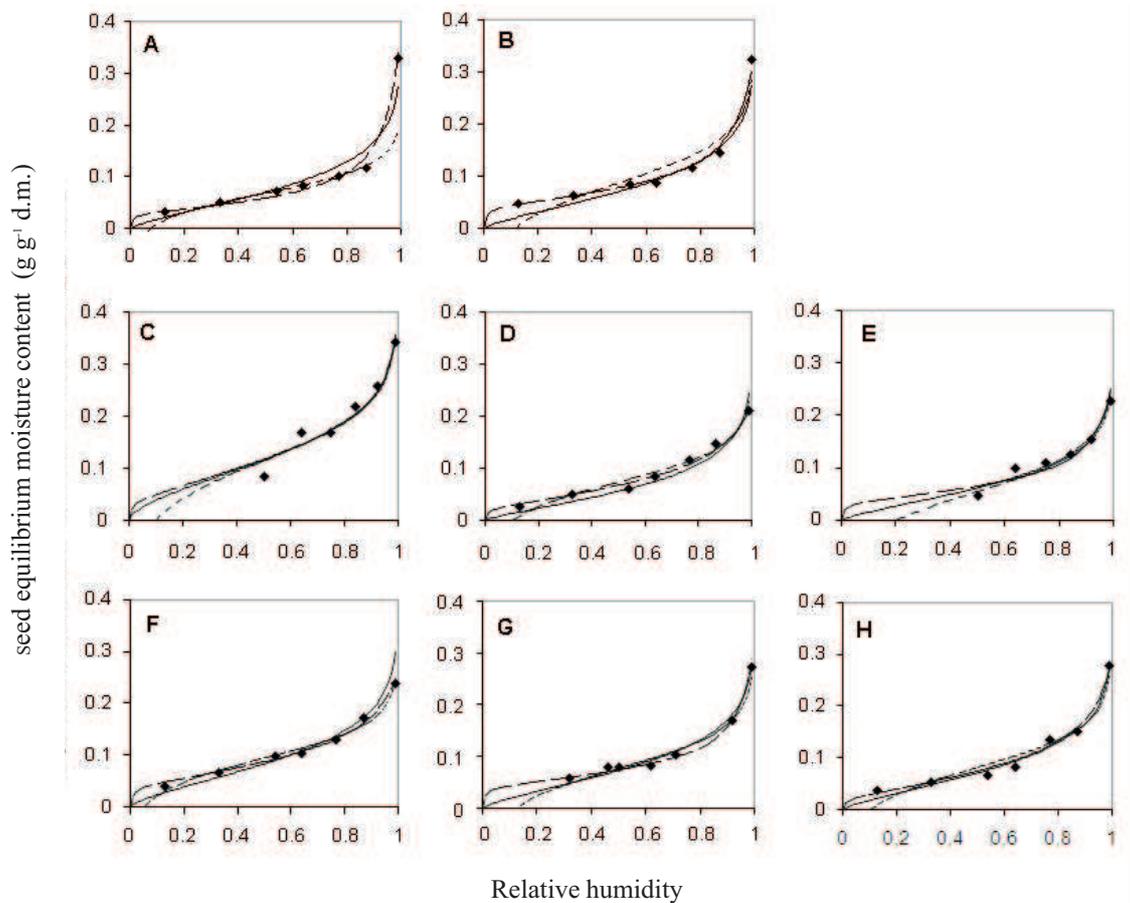
Data processing of  $K$ ,  $K'$ ,  $k$  and  $k'$  by HTH model association did not result in high variations regarding temperature (according to the correlation analysis), showing values close to those contained in Table 1 for each species. The computer analysis demonstrated a clear dependence of the rest of the parameters (high correlation) on temperature from 10 to 45°C ( $\lambda$  logarithmic,  $C_{50}$  and  $c$  exponential behaviour in Fig. 3). Table 2 contains values obtained by fitting equations for each species and their respective parameters for goodness-of-fit ( $RE < 10\%$  and  $r^2 > 0.9$  for all eight species). Figure 3 shows the behaviour for each parameter in three selected species: lettuce, drybean and maize. Lettuce has high values of  $\lambda$  and low values of  $C_{50}$  and  $c$ , while an inverse case was obtained for drybean. Maize curve values fell entirely between the other two species.

This order for the species curves was also obtained for the thermodynamic potentials. The enthalpy calculated by Eq. (5) (Fig. 4) shows a state change between 10-11°C (cool system or low temperature), and 40-41°C (hot system or high temperature). In this case the species lettuce (lower curve) and drybean (upper curve) represent the extremes of each group. Maize has intermediate values (marked with dots in Fig. 4). The simulation curves of enthalpy and Gibbs free energy followed an exponential behaviour, where their values tend to zero for high equilibrium moisture content. The variance analysis demonstrated that seed moisture content has a greater influence on Gibbs free energy than temperature does, for all eight species. The Fisher parameters for each species are listed in Table 3.

## DISCUSSION

The  $r^2$  and  $RE$  values resulting from fitting the three models to the experimental data indicate reasonably high confidence in the models whose curves did not differ substantially from each other. Nevertheless, the convex zone of the isotherms (low values of  $RH$ ) showed small differences in some cases, which could influence the model choice for hygroscopic studies within that range of  $RH$ . This isotherm interval ( $RH < 0.4$ ) is generally used to evaluate the tolerance of seed tissue to desiccation, and to predict the effect of equilibrium moisture content on viability during storage (Tang *et al.*, 2000; Socorro, 2008).

Variations of the models' parameters across the species were observed, although  $K$ ,  $D_1$  and  $D_2$  did not show such differences.  $K'$  is related to the number of sorption sites where strong binding predominates, whereas  $K$  is associated



**Fig. 2.** Curves of equilibrium sorption isotherms for eight cultivars fitted by three hygroscopic models: D'Arcy-Watt (DAW) (long dashed line), Socorro (SOC) (small dashed line) and Henderson-Thompson (HTH) (solid line). Experimental values of equilibrium moisture content are represented with dots. A – cabbage, B – carrot, C – drybean, D – lettuce, E – maize, F – pepper, G – soybean, H – tomato.

with the attraction intensity of these bindings (approximately equal to 118 in the eight species). For these two parameters, minimal variation regarding temperature was observed. Neither the intensity nor the number of multi-molecular sorption sites ( $k$  and  $k'$ ) depended on  $T$  significantly due to low correlation values in most of the species. For the number and the affinity of weak binding sites (parameter  $c$  in DAW model), temperature dependence followed an exponential curve whose fit constants are shown in Table 2 with a high degree of accuracy. This result allows us to modify the D'Arcy-Watt equation for temperature dependence for the interval 10–45°C, specifically for the second term (Eq. (1)) related with sorption sites (weak binding predomination). Although a mathematical expression for  $c$  regarding  $T$  was obtained with a high accuracy, this result of regression analysis should be verified for other species.

In this paper it was assumed that the hydration process follows a general path with only small parameter changes between species with similar biophysical characteristics.

Furthermore, we believe that all sorption sites do not influence the vapour-seed system with equal intensity. For example, it has been found that sorption sites where weak bindings predominate are most likely to show variations with respect to temperature. This is particularly important because such bindings predominate among biological macromolecules.

Water molecules at low temperatures have lower kinetic energy, insufficient to overcome the corresponding adsorption energy. They can also be linked with other organic molecules like carbohydrates, protein and lipids at the atmosphere-seed interface. This binding is based on hydrogen links that require exothermic reactions which decrease as  $T$  increases (Vega *et al.*, 2006). This relationship between increased lipid content and fewer sorption sites is shown in Fig. 5. Temperature and seed fat content (SFC) caused a decrease of the number and intensity of sorption sites with weak binding. Therefore, it is reasonable to believe that each species has a different number of sorption sites where weak binding is dominant, and that the intensity of these interactions also varies due to morphological characteristics.

**Table 1.** Values of coefficients of the three models for the eight cultivars (Fig. 2). The statistical parameters calculated by Eqs (6)-(9) are also shown. All the coefficients have no units, except  $D_1$  ( $^{\circ}\text{C}^{-1}$ ),  $T$  and  $D_2$  ( $^{\circ}\text{C}$ )

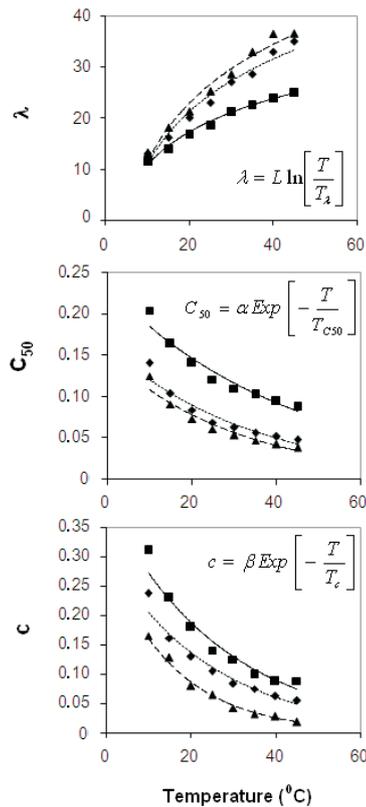
Model	Parameters	Species							
		Cabbage	Carrot	Drybean	Lettuce	Maize	Pepper	Soybean	Tomato
SOC	$\lambda$	36.71	22.89	18.94	29.35	24.63	29.79	25.77	25.91
	$C_{50}$	0.068	0.087	0.115	0.073	0.055	0.095	0.077	0.082
	$S_D^2$	0.00004	0.00070	0.00040	0.00020	0.00013	0.00009	0.00010	0.00030
	$S_R^2$	0.0099	0.00875	0.008	0.004	0.004	0.005	0.006	0.007
	RE (%)	2.1	8.3	3.5	5.2	3.4	2.9	3.1	5.8
	$r^2$	0.99	0.92	0.95	0.95	0.97	0.98	0.98	0.96
DAW	$K$	118	118	118	118	118	118	118	118
	$K'$	0.028	0.040	0.037	0.022	0.032	0.040	0.041	0.021
	$c$	0.029	0.044	0.140	0.060	0.045	0.067	0.044	0.077
	$k$	0.95	0.93	0.94	0.88	0.94	0.89	0.95	0.91
	$k'$	0.018	0.019	0.013	0.019	0.013	0.019	0.013	0.019
	$S_D^2$	0.00012	0.00010	0.00035	0.00003	0.00024	0.00005	0.00005	0.00007
	$S_R^2$	0.0099	0.00875	0.008	0.004	0.004	0.005	0.006	0.007
	RE (%)	3.7	3.0	3.4	2.0	4.6	2.1	2.2	2.7
$r^2$	0.99	0.99	0.96	0.99	0.93	0.99	0.99	0.99	
HTH	$D_1$	0.997	0.997	0.997	0.997	0.997	0.997	0.997	0.997
	$D_2$	0.912	0.912	0.912	0.912	0.912	0.912	0.912	0.912
	$D$	1.389	1.443	1.708	1.269	1.357	1.489	1.419	1.393
	$T$	26.8	26.8	26.5	26.8	29.37	26.8	27.5	26.8
	$S_D^2$	0.00078	0.00044	0.00033	0.00035	0.00018	0.00005	0.00008	0.00007
	$S_R^2$	0.0099	0.00875	0.008	0.004	0.004	0.005	0.006	0.007
	RE (%)	9.5	6.4	3.3	7.2	4.0	2.1	2.8	2.8
	$r^2$	0.92	0.95	0.96	0.91	0.95	0.99	0.99	0.99

The biochemical composition, therefore, has a significant influence on water binding in seeds, where hydration levels are determined by a variety of chemical linkages between dry matters components and water molecules. The molecular monolayer (seed-atmosphere interface) is linked to several strongly-polarized molecular groups like hydroxyls (OH-) (Marques and Manal, 1991). These covalent bindings are predominant in this monolayer region and form weak bindings. For this reason, we believe that morphological variations may affect this type of weak binding more than they affect strong bindings. Therefore, sorption sites where weak binding predominates, will be most subject to variation, as these results indicate. For example, seed fat content (SFC) is inversely related to moisture content at equilibrium (Walters and Hill, 1998). The values of the  $c$  parameter tend to decrease with increasing SFC (Fig. 5). Lipids are hydrophobic substances whose presence can obstruct the diffusion of water vapour molecules at the seed-

atmosphere interface, thus reducing the sorption capacity. This may be related to a decrease in both the quantity and attraction intensity of the weakly-linked sites.

With regard to the Henderson-Thompson model (Eq. (2)), no differences were obtained for  $D_1$  and  $D_2$  coefficients. This result contrasts with research for other species, including soybean, where variations were found in these parameters (Vega-León, 2008). Values for  $D_2$  near  $0.912^{\circ}\text{C}$  do not substantially affect the term  $T+D_2$  because such values of  $D_2$  are much smaller than the temperature values. Mathematically, the effect of the quotient  $D_1/(T+D_2)$  on the functional relationship between  $C^*$  and  $RH$  will be less than that of the exponential coefficient  $d$ .

The SOC model parameters showed good fit with respect to temperature: a logarithmic increment for  $\lambda$  and an exponential decrease for  $C_{50}$ .  $\lambda$  is related to the vapour flow kinetics of water molecules in the surrounding atmosphere (Socorro *et al.*, 2007), which are directly proportional to  $T$ . Temperature increase also causes a greater evaporation rate



**Fig. 3.** Regression parameters of  $\lambda$ ,  $C_{50}$  and  $c$  with respect to temperature and their respective equations for three selected species: lettuce (triangles with dashed line), maize (rhombus with dots) and drybean (squares with solid line). The values of regression coefficients are shown at Table 4 for all eight species used.

of molecules located in the external region of the seed-atmosphere interface, which reduces the capacity to hold these molecules and therefore is associated with low values of  $C_{50}$ .

A decrease in  $C^*$  while  $T$  increases at the monolayer could be caused by a low number of active sites in the water-polymer bindings. The water molecules with higher kinetic energy have a lower probability to be ‘trapped’ within the system.

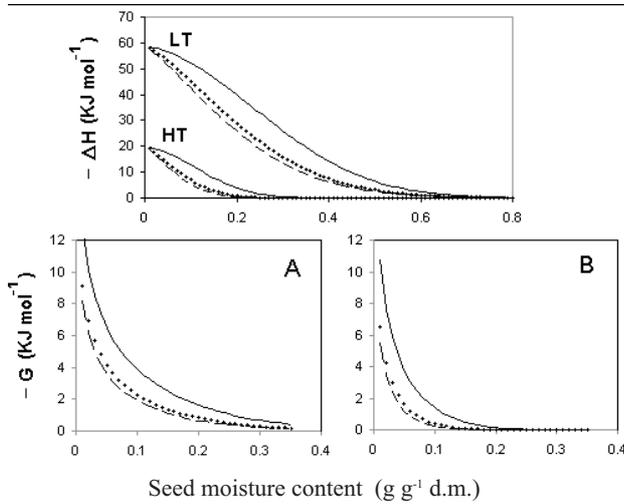
Drybean and lettuce produced the extreme values in Fig. 5, as well as the extreme enthalpy and Gibbs curves in Fig. 4. The activation energy necessary to create or break water binding in the seed is related to the amount of heat released at the change of phase with  $C^*$  constant. The adsorption heat may be obtained from enthalpy. The exponential behaviour of  $\Delta H$  and  $G$  with respect to  $C^*$  was similar to the Tsami *et al.* (1990) model for the isosteric heat of sorption for seed moisture content. At low values of  $C^*$ , adsorption energy values are highest. The inverse proportional dependence of enthalpy with respect to  $T$  and  $C^*$  is found in many of orthodox seed species.

Analysis of variance (Table 3) confirmed that the influence of  $C^*$  on  $G$  is much greater than the influence of temperature. A similar relationship is found when studying the preservation of seed viability during storage. Experience has demonstrated that high humidity is the principal non-biotic factor affecting the phylogenetic resource conservation, while the effect of temperature is not significant (Pérez *et al.*, 2007). It is plausible that seeds are better preserved when the energy sorption barrier that water molecules need to overcome to adhere to the seed-atmosphere interface is high enough to incur low levels of sorption without damaging the embryo tissue. Further research based on thermodynamic potentials will lead to improved understanding of the quantitative effects of non-biotic factors on seed conservation.

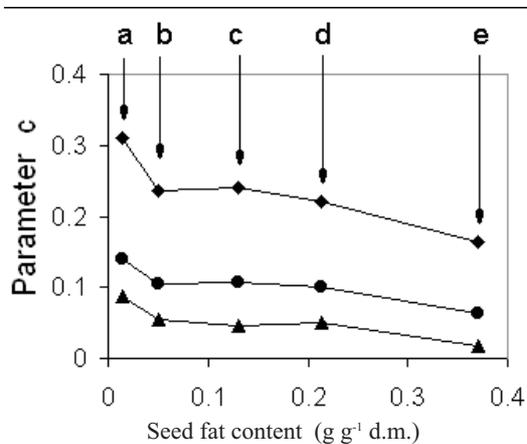
**Table 2.** Values fitted for dependence of  $\lambda$ ,  $C_{50}$  and  $c$  with respect to  $T$ , obtained from association with the HTH model (Fig. 3)

Parameters	Species								
	Cabbage	Carrot	Drybean	Lettuce	Maize	Pepper	Soybean	Tomato	
$\lambda$	$L$	14.74	12.00	9.36	16.55	14.90	12.79	12.47	14.80
	$T_\lambda$	4.88	4.01	3.19	5.00	4.81	4.32	4.00	4.86
	RE (%)	2.1	2.6	0.9	1.8	2.0	1.3	1.7	2.2
	$r^2$	0.96	0.94	0.99	0.98	0.97	0.99	0.97	0.96
$C_{50}$	$\alpha$	0.171	0.177	0.234	0.150	0.162	0.192	0.181	0.173
	$T_{C50}$	34.84	37.88	42.74	30.77	34.13	37.45	33.67	34.97
	RE (%)	2.8	3.1	2.3	3.6	3.5	2.5	3.0	3.2
	$r^2$	0.96	0.94	0.96	0.95	0.93	0.96	0.95	0.95
$c$	$\beta$	0.292	0.333	0.395	0.301	0.308	0.378	0.300	0.365
	$T_c$	21.60	27.25	26.95	15.97	24.70	21.69	24.27	20.83
	RE (%)	2.8	3.6	3.6	2.5	3.9	2.7	3.0	2.0
	$r^2$	0.98	0.95	0.96	0.99	0.96	0.98	0.98	0.99

$T_\lambda, T_{C50}, T_c$  – °C.



**Fig. 4.** Values of thermodynamic potentials obtained through simulation with respect to  $C^*$  for three species: lettuce (dashed line), maize (dots) and drybean (solid line). Enthalpy per mol (top) was calculated by Eq. (5) using two curves group: *HT* – high temperature values ( $T_1 = 40^\circ\text{C}$  and  $T_2 = 41^\circ\text{C}$ ), *LT* – low temperature values ( $T_1 = 10^\circ\text{C}$  and  $T_2 = 11^\circ\text{C}$ ). Gibbs free energy (bottom) was calculated by Eq. (4) for  $T = 10^\circ\text{C}$  (A) and  $T = 45^\circ\text{C}$  (B).



**Fig. 5.** Decrease of parameter  $c$  with respect to seed fat content (SFC) for five representative species: drybean (a), maize (b), carrot (c), soybean (d) and lettuce (e) at three temperature values:  $10^\circ\text{C}$  (rhombus),  $25^\circ\text{C}$  (circles) and  $45^\circ\text{C}$  (triangles). SFC data from Jamieson (1943) and Bewley and Black (1982).

#### CONCLUSIONS

1. The isotherm curves for equilibrium moisture content of seed with respect to humidity were obtained experimentally for different cultivars using three hygroscopic models with a high accuracy level.

**Table 3.** Variance analysis for Gibbs free energy values regarding  $T$  and  $C^*$

Species	$FC^{(C^*)}$	$FC^{(T)}$	$\frac{F_C^{(C^*)}}{F_C^{(T)}}$
Cabbage	1.625.95	62.67	25.95
Carrot	1.929.60	70.83	27.24
Drybean	4.390.83	129.66	33.86
Lettuce	1.100.28	47.69	23.07
Maize	1.467.40	58.28	25.18
Pepper	2.229.24	78.61	28.36
Soybean	1.788.69	67.08	26.67
Tomato	1.646.84	63.24	26.04

2. The dependence on  $T$  for  $c$  coefficient (D'Arcy Watt parameter related with weak binding),  $C_{50}$  and  $\lambda$  (SOC model) were obtained using extrapolation and association with the Henderson-Thompson model toward an interval from 10 to  $45^\circ\text{C}$ . This result allows improving both models for the prediction of equilibrium moisture curves regarding humidity and temperature through a modification of their equations. Nevertheless, this behaviour regarding  $T$  would be valid for the species used, while for other cultivars the equations should be verified experimentally.

3. The calculation of thermodynamic potentials through the Henderson-Thompson curves showed that moisture content has an incidence on enthalpy and Gibbs free energy higher than temperature. The behaviour of these magnitudes could relate the hygroscopic parameters with the sorption energy barrier for water molecules which determines the sorption properties of seeds for storage at gene bank.

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