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Sorption Isotherms and Isosteric Heats for Algerian Dates Deglet Nour

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ABSTRACT
The stability of organoleptic quality of dates Deglet Nour during storage is affected by the water activity (aw). The purpose of this study is to determine the optimal moisture in order to preserve the quality of dates using the technique of sorption isotherms. Moisture sorption isotherms of the date "Deglet Nour" were determined at 25, 30 and 40°C by balancing the atmosphere with relative humidity fixed by dilute solutions of sulphuric acid. The isotherms were fitted to Guggenheim-Andderson-Boer (GAB) and BET sorption equations. The GAB and BET equations provided a good fit to experimental data (<6% RMS). Monolayer moisture contents for date Deglet Nour was 10.07%. The enthalpy of sorption of the monolayer at 25°C was 113.03 kJ mol^{-1}. Heat of desorption estimated using the Clausius-Clapeyron equation was 75 kJ mol^{-1}.

Key words: Dates, sorption isotherm, water activity, GAB equation, BET equation, Clausius-Clapeyron equation

INTRODUCTION
The date palm constitutes the fundamental element of the oases ecosystem. It is a crucial role on the economic view point through the production of dates and sub-products (pasta, flour, syrup, vinegar, yeast, alcohol, confectionery). These products represent the bases of human and animal food of the Saharan regions. The date palm also ensures the stability of the Saharan population which is estimated at 2.8 million inhabitants. Algeria is the fifth largest in the world with an annual production of 430,000 tons (FAO, 2003). The date is a valuable energy food. It is very much appreciated on the national as well as international plan, especially the Deglet Nour variety. The search for the quality of this variety is discovered by technology. This one covers all the operations which, from harvest to marketing, are meant to protect the nutritional value of this fruit (Dowson and Aten, 1963). The sensitivity of Deglet Nour date variety to the alteration and bad storage in the production places raises major problems for the national operators. FAO has estimated that the losses of the Deglet Nour variety exceeding 6%; tells us that the production of 430,000 tons (equivalent 25 800 tons of loss) with a price of 90 Da for 1 kg leads to a loss of 2322 million Da. This alteration is more important as much as stocking and storage conditions are not adequate. Several theoretical and empirical equations have been suggested in the literature (Van den Berg and Burin, 1981; Maskan and Gogus, 1997; Al-Muhtaseb *et al.*, 2002). Many studies have been done on the conservation of dates by several authors (Kechaou *et al.*, 1996; Myhara *et al.*, 1998; Belarbi *et al.*, 2000). The aim of the present study was to determine the moisture sorption isotherms of date Deglet Nour at three temperatures 25, 30 and 40°C. We also

tested the fit of sorption data to GAB and BET equations to determine important parameters such monolayer moisture content. Equation of Clausius-Clapeyron was used to calculate the value of isosteric heat.

MATERIALS AND METHODS

Vegetable material: The sample of Deglet Nour date variety is from an oases area. The choice of this variety is justified by its abundance in the domestic mark and its appreciated tasty quality by the consumer. Fruit characteristics: average length: 4.33 and 2.4 cm $kernel^{-1}$, average width: 2.2 cm $pulp^{-1}$ and 0.6 cm $kernel^{-1}$, average weight of the date: 11.70 g, average weight of the pulp: 10.9 g, average weight-kernel: 0.8 g, kernel/fruit ratio: 0.07. In order to preserve the initial characteristics and avoid any alterations may lead to change of properties of our sample; the latter is stored at a temperature of +4°C.

Experimental protocol

Material: The dates Deglet Nour variety has to adsorb or desorb in chamber which maintain in constant temperature and relative humidity, for a required period to reach equilibrium. Ten hygrostats (vat in glass) of a 1 L are used. Each hygrostat contains a solution of sulphuric acid (H_2SO_4) in a concentration determined to prevent a defined constant relative humidity (Van den Berg and Burin, 1981).

Methods: Thin slices of dates (approximately 1 to 2 mm of thickness) are cut from a representative sample in order to facilitate the exchange with the surrounding environment. In the case of preparation of the adsorption, samples of about 50 g were placed in weighing pots and deposit in a hermetic chamber containing sulphuric acid (H_2SO_4) at a concentration of 96% for 15 days in an ambient temperature. Four applications of samples (hydrated or dried) will be placed in each of the 09 hygrostats (4 capsules/hygrostat) and balanced with adsorption or desorption of water steam at a relative humidity and a constant temperature. An oven was used to maintain the selected temperature (25, 30 and 40°C). The equilibrium is reached in 15 days or more (when the mass difference between three consecutive weighed less than 2%, the period between weighing is 24 h). In elevated aw (a_w>0.7), thymol crystals were placed in the hygrostats to prevent fungal growth. The total time to remove, replace and weigh the samples was limited about 30 sec recommended by COST 90 (Spiess and Wolf, 1987). The balanced moisture rate was determined by the infrared moisture meter.

MATHEMATICAL REPRESENTATION OF SORPTION ISOTHERMS

Theoretical models of isotherms: Many mathematical modelling tests were tempted, two directions have been explored, the first one is to construct theoretical equations incorporating characteristic properties of adsorption and the second track more useful in practice would be to add to the experimental results empirical equation.

BET model: Among these thermal models one of those that have been applied mostly to food is the model BET of Brunaeur *et al.* (1938). This equation gives the value of moisture content of the superficial layers (monolayer) which is an important parameter in the study of the deterioration of food.

The BET model is represented by the following equation:

$$Xeq = \frac{X_m \times C \times a_w}{(1 - a_w)(1 - a_w + C \times a_w)} \quad (1)$$

C : Constant of BET
Xeq : Water content of the product at equilibrium (g/100 g dry basis)
X_m : Water content corresponding to the monolayer (g/100 g dry basis)

The BET model is known to be used for a_w until about 0.5 (Iglesias *et al*., 1989). The application of data sorption with the BET equation even in this area of low a_w is not always applicable.

GAB model: In recent years the model usually used for sorption isotherms has been the GAB model (Guggenheim Anderson and Boer) (Labuza *et al*., 1985; Lomauro *et al*., 1985; Maroulis *et al*., 1988; Chen and Morey, 1989; Maskan and Gogus, 1997). This model is the best model for foods. The GAB equation is:

$$Xeq = \frac{Xm \times C \times K \times a_w}{(1 - k \times a_w)(1 - k \times a_w + C \times k \times a_w)} \quad (2)$$

where, Xeq is equilibrium moisture content, Xm is the monolayer moisture content, a_w is water activity, C is a constant related to the first layer heat of sorption and K is a factor related to a heat of sorption of the multilayer:

$$C = C' \times e\left(\frac{\Delta H1}{RT}\right)$$
$$K = K' \times e\left(\frac{\Delta H2}{RT}\right) \quad (3)$$

Both C and K are defined in Eq. 4, where T is absolute temperature (°K), R is the universal gas constant (8.314 J mol^{-1} K^{-1}), ΔH_1 and ΔH_2 are heat of sorption functions:

$$\Delta H1 = (H_m\text{-}H_q);\ \Delta H2 = (HL\text{-}H_q) \quad (4)$$

HL is latent heat of vaporization of the liquid water (43 kJ mol^{-1}). H_m is total heat sorption of the monolayer (J mol^{-1}). H_q is total heat sorption of the multilayer (J mol^{-1}).

The three GAB constants depend on product characteristics and temperature, they are determined from experimental results. Labuza *et al*. (1985) found that the moisture content of the monolayer obtained by the GAB equation is not far than that obtained by the BET equation to a level of 95% of meaning for each temperature. In fact, the tests of Ayranci *et al*. (1990), shows that the Xm value obtained by the two models decreases with increasing temperature. The GAB model has the advantage to describe correctly the sorption isotherms of food products for the water activity values no more 0.90. The use of the BET model is limited to the water activities not exceeding 0.50

(Do Amaral Sobral *et al.*, 1999; Belarbi *et al.*, 2000). The adjustment of the experimental values by the GAB model and estimation of its parameters are realized using the STATISTICA software whose estimation method used is of Quasi-Newton. The adjustment quality of these models (BET and GAB) was checked determined by calculating the relative mean square root of the error (RMS%):

$$RMS\% = 100\sqrt{\frac{\sum\left[\frac{(X_{exp} - X_{cal})}{X_{exp}}\right]^2}{N}} \tag{5}$$

where, X_{exp} and X_{cal} are the experimental and calculated moisture contents and N is the number of experimental points.

Isosteric heat of sorption: The most common method for determining the heat of sorption (ΔHb), resulting from the Clausius-Clapeyron equation (Rizvi and Benado, 1984; Iglesias *et al.*, 1989; Ayranci *et al.*, 1990; Do Amaral Sobral *et al.*, 1999):

$$\ln\frac{a_{w1}}{a_{w2}} = -\frac{\Delta Hb}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right] \tag{6}$$

ΔH_b is net isosteric heat of sorption (kJ mol^{-1}), a_{w1} and a_{w2} is water activities at temperatures T_1 and T_2, respectively and R is a perfect gas constant. The isosteric heat (Qst) is then calculated by the equation:

$$Qst = \Delta Hb + \Delta Ho$$

where, ΔHo is the heat of pure water vaporization.

RESULTS AND DISCUSSION

Moisture sorption data for Deglet Nour dates at 25, 30 and 40°C are shown in Table 1. Moisture sorption isotherms for Deglet Nour at 25, 30 and 40°C are presented in Fig. 4-8. All the isotherms have a sigmoidal shape, typical of food materials containing a high sugar content (Tsami *et al.*, 1990; Iglesias and Chirife, 1976; Iglesias and Chirife, 1982). The experimental points and the fitted isotherms were compared (Fig. 4-8). For all isotherms the RMS% values were between 3 and 6 indicating good fit. In this study it was found that for date Deglet Nour the monolayer moisture level (Xm = 10.01%) determined by GAB equation is equivalent to that BET equation. A suitable long term storage should be possible at this moisture level (Maroulis *et al.*, 1988).

The hysteresis phenomenon: The Fig. 1 shown that the hysteresis presents itself in dates, yielding thermodynamics functions for adsorption which are quite different from those obtained for adsorption. The hysteresis between adsorption and desorption isotherm of the dates is significant at temperature 25°C (Fig. 1, 2) and 40°C (Fig. 2) and the RSM values of different iso-therms are presented in Table 2.

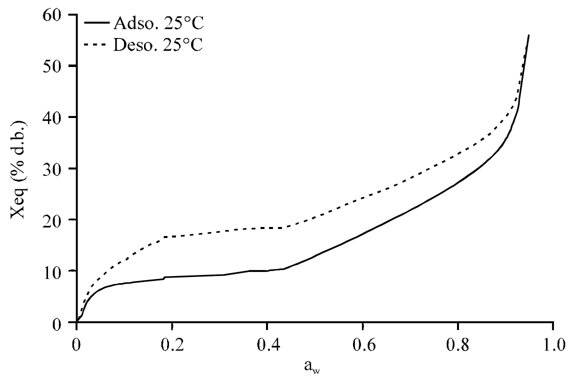

Fig. 1: Hysteresis of Deglet Nour dates at 25°C

Table 1: The moisture content at the equilibrium Xeq (g water/100 g dry basis) for the adsorption isotherm of the dates

Temperature (°C)	a_w	Xeq (%)
25	0.74	42.95
	0.66	32.11
	0.56	19.30
	0.45	13.10
	0.35	11.50
	0.25	9.90
	0.16	9.10
	0.09	8.50
	0.04	6.06
30	0.94	50.01
	0.87	30.05
	0.74	19.00
	0.67	14.40
	0.47	10.05
	0.26	8.76
	0.17	8.70
	0.09	8.11
	0.04	6.27
40	0.95	54.51
	0.87	28.86
	0.75	19.50
	0.67	14.30
	0.47	8.61
	0.36	8.27
	0.26	8.05
	0.17	7.09
	0.04	6.52

EFFECT OF TEMPERATURE ON THE MOISTURE SORPTION ISOTHERMS

Effect of temperature on the desorption isotherm: The Fig. 2 shows that when temperature increases, the water content in the equilibrium decreases. This figure shows that around the a_w of 0.8 there is no crossing and at the a_w values exceed 0.8 when the increase in the temperature leads to a reduction of the content water at the equilibrium. These results are comparable to those of Kechaou *et al.* (1996).

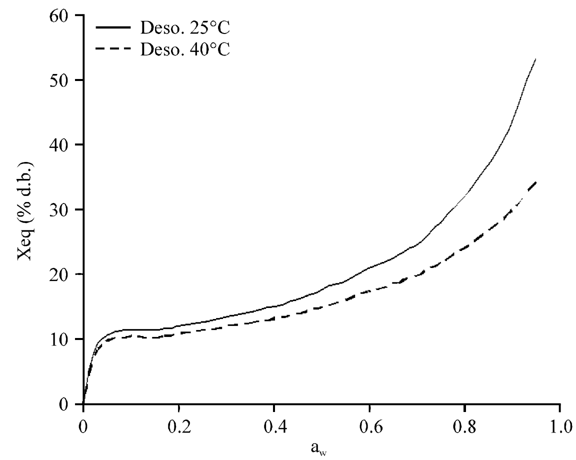

Fig. 2: Moisture desorption isotherm of the dates Deglet Nour at 25 and 40°C

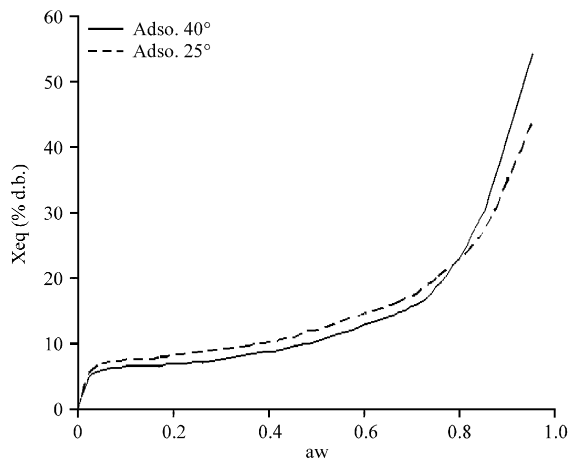

Fig. 3: Moisture adsorption isotherm of the dates Deglet Nour at 25 and 40°C

Table 2: The RMS (%) value of different isotherms

Isotherm (°C)	RMS (%)
Desorption in 25	6.32
Adsorption in 25	5.86
Adsorption in 30	4.41
Desorption in 40	4.68
Adsorption in 40	3.60

Effect of temperature on the adsorption isotherm: The Fig. 3 presents the curves of the adsorption isotherms determined at 25 and 40°C. We notice that the moisture content in the equilibrium decreases when the temperature increases for the same value of the water activity. This is observed for the water activity lower than 0.8. However, for the water activity values superior than 0.8 the opposite effect is observed namely the moisture content in equilibrium increases when the temperature increases. The crossing of both curves of isotherms is observed around the water activity of 0.8.

Fitting of sorption models to experimental data: The results of the analysis of the nonlinear regression of the adjustment of GAB and BET equation in the experimental values are respectively presented on the Table 3 and 4. The relative average values of the deviation percentage of deviation RMS (%) are given in the Table 2. The values of the percentage RMS (%) are between 3.6 and 6.32 for five adsorption and desorption isotherms. The values of RMS (%) are less than 10% and this allows us to conclude that the equations GAB and BET can be used to predict the value of moisture in the equilibrium and other parameters such as the moisture content of the mono-molecular layer and enthalpy of link to the monolayer and multilayer.

The Fig. 4-8 representing the adsorption and the desorption isotherms of the dates of the Deglet Nour variety, show that the curves of the experimental and calculated points are closely matched and this is confirmed by the low values of RMS (%).

GAB AND BET PARAMETERS

The parameters of the GAB equation (X_m, C and K) and BET (X_m, C) are determined from the experimental results by using nonlinear regression. The values of the moisture mono-molecular layer X_m determined by the equations of GAB and BET is showed on the Table 3 and 4. The X_m values determined by the BET equation are slightly higher than those determined by the equation

Table 3: Estimated GAB parameters for Deglet Nour dates

Parameter isotherm (°C)	X_m	C	K	R^2
Adsorption in 25	6.525	377.655	1.207	0.9936
Desorption in 25	10.071	1228.635	1.665	0.9551
Adsorption in 40	5.29	1854.669	1.625	0.9982
Desorption in 40	9.388	2680.387	1.662	0.9438
Adsorption in 30	5.779	1796.135	1.263	0.9989

Table 4: Estimated BET parameters for Deglet Nour dates.

Parameter isotherm (°C)	X_m	C	R^2
Adsorption in 25	6.451	342.942	0.9601
Desorption in 25	11.921	790.382	0.9917
Adsorption in 40	5.343	376.592	0.9408
Desorption in 40	9.673	362.725	0.9592
Adsorption in 30	5.857	885.202	0.9777

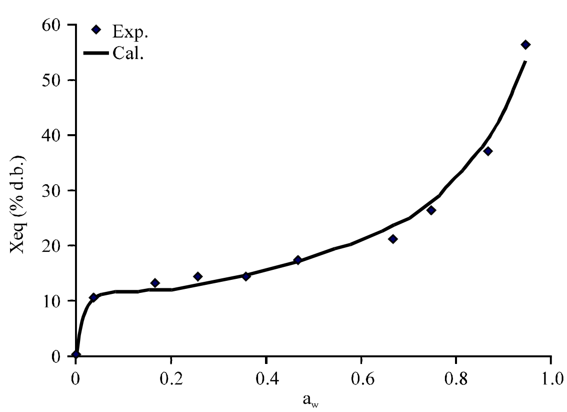

Fig. 4: Desorption isotherm of date at 25°C

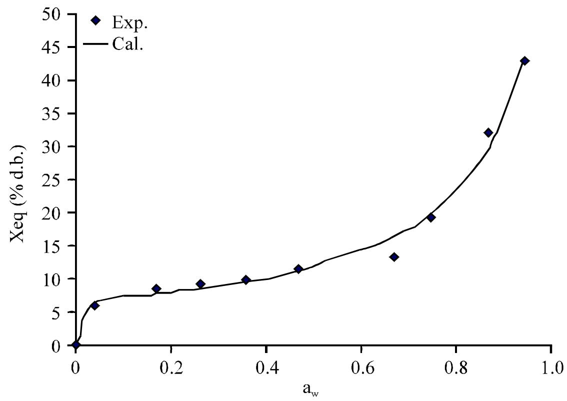

Fig. 5: Adsorption isotherm of date at 25°C

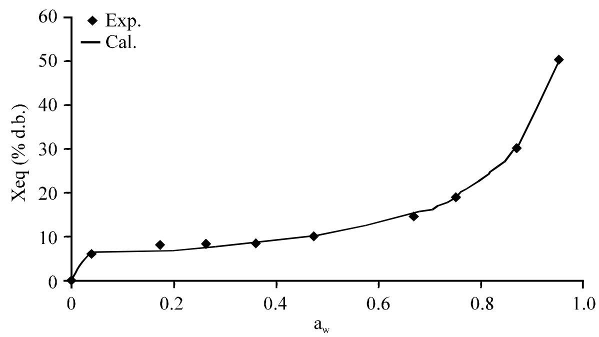

Fig. 6: Adsorption isotherm of date at 30°C

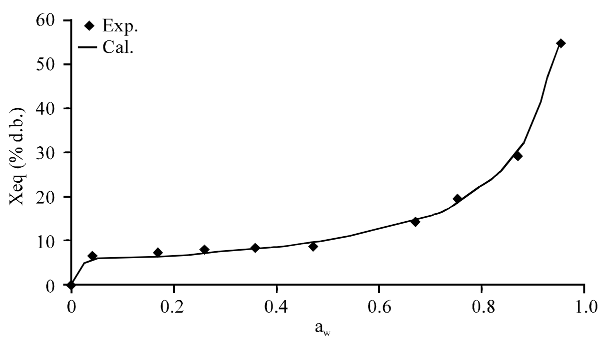

Fig. 7: Adsorption isotherm of date at 40°C

of GAB. This observation is similar to that reported by Labuza *et al*. (1985). The value of the moisture of the mono-molecular layer (Xm) estimated by the GAB equation at 25°C is 10.07%. This value is larger than that reported by Belarbi *et al*. (2000) (Table 5).

GAB thermodynamics parameters: The parameter ΔH_1 of the GAB equation represents the difference between the enthalpy of the mono-molecular layer and the multilayer. In this study the ΔH_1 value is estimated at 39.70 kJ mol^{-1} (Table 6). This value indicates that there is a strong link

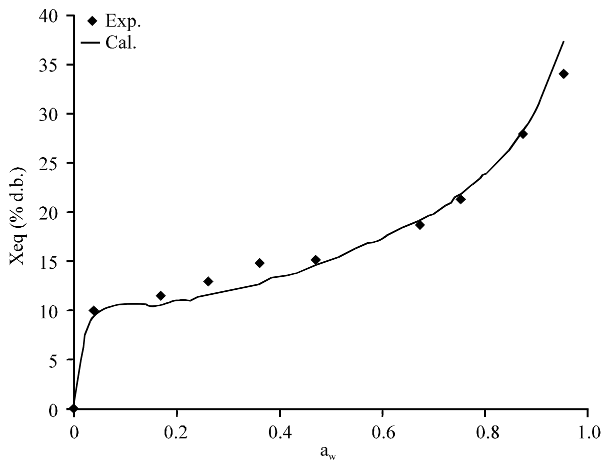

Fig. 8: Desorption isotherm of date at 40°C

Table 5: Comparison of X_m values of dates with other dried fruits

	Dates					
Product	Deglet Nour	Dates*	Apricot	Apple	Potato	Raisin
X_m (% d.b.)	10.07	8.73	9.5	7.6	6.7	11.5

*Data taken from Belarbi *et al*. (2000)

Table 6: Estimated GAB thermodynamics parameters for adsorption and desorption isotherms

Parameter isotherm (°C)	X_m	C'	K'	ΔH_1 (kJ mol^{-1})	ΔH_2 (kJ mol^{-1})	R^2
Adsorption in 25	6.525	377.655	1.207	39.76	-0.74	0.9936
Desorption in 25	10.07	1228.635	1.665	67.401	-1.657	0.9551
Adsorption in 40	5.29	1854.669	1.175	31.734	-0.554	0.9982
Desorption in 40	9.388	2680.387	1.662	52.213	-2.028	0.9438
Adsorption in 30	5.779	1796.135	1.263	23.413	-0.77	0.9989

between the primary hydrophilic sites of the solid and the first layer of water molecules. ΔH_2 represents the difference between latent heat of condensation of pure water and heat sorption of the multilayer is estimated at -0.74 kJ mol^{-1} (Table 6). This negative value indicates that the heat of sorption of multilayer is higher than the latent heat of condensation of pure water. In order to determine the energy required for evaporation of water from dates, during drying, the desorption heat of the mono-molecular layer (H_m) and the multilayer (H_q) was obtained using respectively the parameters $\Delta H_1 = H_m - H_q$ and $\Delta H_2 = H_L - H_q$. The results shown that the heat of desorption of the mono-molecular layer (H_m = 113.03 kJ mol^{-1}) is more important than that of the multilayer (H_q = 45.637 kJ mol^{-1}). This superiority is due to a strong fixation of the molecules of water. In the monolayer, the molecules of water are strongly fixed to the polar sites hydrogen liaisons high energies. Whereas, the molecules of water in the multilayer are kept by hydrogen liaisons whose energies are less and less strong. It explains that the water of this monomolecular layer is relatively difficult to remove. These results are comparable to those found by Kaymak-Ertekin and Gedik (2004).

Sorption heat: The calculated values of ΔHb are inversely proportional to the values of moisture. The variation of the sorption heat of according to the moisture content is represented in the Fig. 9.

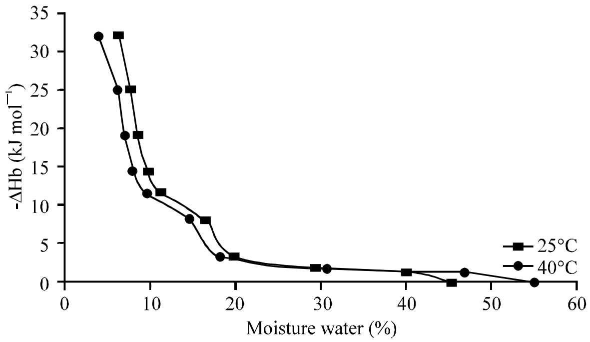

Fig. 9: Isosteric sorption for date Deglet Nour variety

These results are comparable to those found by Do Amaral Sobral *et al.* (1999). The study of the variation of sorption heat of water depending on the moisture content, showed that ΔHb increases when the water content decreases and this is explained by the strong interaction between water and adsorbents components of the dates. In high water contents, the sorption sites decrease and this leads to a decrease in the ΔHb value (Tsami *et al.*, 1990). At low water contents (<0.15) the energy of liaison (ΔHb) is negative and it shows that the interaction is exothermic. The maximum value of this energy (ΔHb) being equal to ≈32 kJ mol^{-1} and consequently Qst (Qst = ΔHb+ΔHo where, ΔHo = 43 kJ mol^{-1}) was calculated to be 75 kJ mol^{-1}. This value is similar to the value of Qst (68.87 kJ mol^{-1}), for Tunisian Deglet Nour reported by Nabili *et al.* (2005). For most food, Qst varies between 52 and 86 kJ mol^{-1} (Labuza, 1968). In high water contents, the value of the energy of liaison tends to zero, it means that the isosteric heat of sorption is equal to the heat of condensation of water (Qst = ΔHo). The Fig. 9 shows that in the area of high moisture, the heat sorption (ΔHb) is positive and this indicates that the interaction between water and the substrate is endothermic and corresponds to dissolution of sugars. The initial heat of sorption is very high in low levels of water content. This indicates that the interaction between components of the food and water is important. When the water content increases, the available sorption sites decrease and leading to a decrease in values of sorption heat.

CONCLUSION

From the results and discussion presented results above obtained, the following conclusions can be drawn: we have calculated the water content of the monolayer “Xm” by the GAB and BET equations whose values are, respectively 10.07 and 11.92% for a temperatures of 25°C. Based on the heat desorption calculated by the model GAB, we noticed that the desorption heat of the mono-molecular layer (Hm = 113.03 kJ mol^{-1}) is more important than the multilayer (Hq = 45,637 kJ mol^{-1}). This superiority is probably due to strong attachment of water molecules to the polar sites. While the sorption heat determined by the Clausius-Clapeyron equation decreases with increasing moisture content. This moisture corresponds to a water activity of less than 0.65 to slow the biochemical deterioration and prevent microbiological alteration.

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