Water Vapour Desorption of Deglet Noor and Alig Dates

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Abstract

Desorption isotherms at 5, 30 and 40°C were determined gravimetrically for Deglet Noor and Alig dates. The products have been hydrated then equilibrated over saturated salt solutions in the range of relative humidity from 11 to 92 %; 21 days were necessary to reach the thermodynamical equilibrium. Deglet Noor and Alig dates exhibited S-shaped isotherms witch departed from each other and the discrepancy got more pronounced with decreasing temperature and increasing relative humidity. The Guggenheim-Anderson-de Boer equation (GAB), regressed using indirect non-linear regression method, described the sorption behaviour satisfactorily. Estimated GAB parameters and constants were in good agreement with what the model dictates and with literature. Critical moisture content was estimated to be 28.3 and 5.5 % dry basis at 5°C for Deglet Noor and Alig dates respectively. These values are smaller than what the FAO/OMS Codex Alimentarus ONU-DF-08 imposes for commercial whole dates. Heat of desorption estimated using the Clasius–Clapeyron equation was 68.87 and 62.66 Kjmol-1 for Deglet Noor and Alig dates, respectively.

Keywords: Water activity, isotherms, model, total heat of desorption, critical moisture content

INTRODUCTION

North-African countries furnish edible date varieties, which are highly appreciated by local people and traded to Europe according to the FAO/OMS Codex Alimentarus ONU-DF 08. Knowledge of quality loss processes will be necessary condition to improve dates quality and to achieve higher export prices.

Water activity (a_W), based on the thermodynamic concept of water chemical potential in solutions (Basunia and Abe, 1999; Menkov, 2000) is an important factor in understanding the control of the deterioration of reduced moisture and dry foods, as well as the total moisture content (*RH*) since it is related to physical and physicochemical modifications, microbiological stability, and both aqueous and lipid phase chemical reactions. The relationship between water content and water activity at a given temperature is given by the water vapour sorption isotherms, which still have to be determined experimentally.

The sorption behaviour of various types of foods and the influence of temperature on equilibrium moisture content (m) have been studied and modelled extensively (Chen and Morey, 1989; Pioter, 1997). Numerous models for predicting the relationship between m, a_W, and temperature have been developed. Each of these models had relative success in reproducing equilibrium moisture content, depending on the water activity range or the type of foodstuff.

In more recent years, among sorption models, the Guggenheim-Anderson-de Boer

(GAB) equation has been applied most successfully to various foods (Belarbi et al., 2000; Barriero et al., 2003; Nguyen et al., 2004). Adequately representing the experimental data in the range of water activity of most practical interest in foods, the GAB model has been recommended by the European Project Group COST 90 on the Physical Properties of Foods as the fundamental equation for the characterisation of the water sorption of food materials. (Maroulis et al., 1988)

Concerning the date, published sorption isotherms are scattered throughout the literature of the last two decades (Belarbi et al., 2000). In this work, water vapour desorption behaviour of Deglet Noor and Alig dates is studied. The specific objectives are to determine: (1) the desorption isotherms of Deglet Noor and Alig dates over a wide range of values for a_W (0.11 to 0.92) at 5, 30 and 40 °C; (2) the suitability of the Guggenheim-Anderson-de Boer (GAB) equation in describing the sorption isotherms; (3) the effect of sugar content on desorption phenomenon and (4) the critical storage parameters.

MATERIALS AND METHODS

Desorption Experiments

Desorption experiments were conducted for Deglet Noor and Alig dates collected from Nefzaoua oasis in west south of Tunisia. A sample of every cultivar's dates was sorted out according to the FAO/OMS Codex Alimentarus ONU DF-08 concerning exportation of whole dates, then being frozen at –18°C. The samples were put in autoclave at 90°C for 30 minutes then cut into small pieces (about 5 mm long) in order to accelerate the desorption process. The sugar content of samples was determined using enzymatic Kits Sucrose/D-Glucose/D-Fructose (Boehringer Mannheim) and a spectrophotometer (Milton, Roy 401) at 340 nm.

Desorption isotherms were determined at nine a_W between 0.11 and 0.92 each at temperatures (5, 30 and 40°C), a_W were obtained using air tight glass jars containing saturated solution of LiCl, FK, MgCl2, Mg $(NO_3)_2$, NaBr, KI, NaCl, KCl, $BaCl_2$ K_2CO_3 (Multon, 1991). Each jar had the capacity for four dates samples. At high a_W (> 0.7) crystalline thymol was placed in the jar to prevent microbial spoilage of the samples. Experiments were conducted in a temperature-controlled cabinet (VWR Scientific, Low Temperature Incubator 2005, ± 0.5°C). Samples were kept at experimental temperatures for 21 days recommended by the European project COST 91 for thermal equilibrium. The dry mass of the samples was determined at 105 °C for 72 hours in a vacuum oven using an analytical balance (Mettler AE 260, Delta Range 0.0001).

Mathematical Modelling

Several empirical, semi-empirical, and theoretical isotherm models have been proposed for the correlation of equilibrium moisture content of food with relative humidity of surrounding air. Among them, theoretical Guggenheim-Anderson-de Boer (GAB) equation [(equation 1)] considering adsorbed water molecules lay on each other in layers.

$$m = m_o CKa_W / [(1 - ka_W)(1 - ka_W + Cka_W)] \quad (1)$$

Where m is the experimental equilibrium moisture content (% dry basis); m_o is the monolayer moisture content (% dry basis), C and K are model coefficients.

The dimensionless parameters C and K can be correlated with temperature using the following Arrehenius type equations:

$C = C_o \exp (qc/RT)$ (2)
$K = K_o \exp (qk/RT)$ (3)

Where C_o and K_o are constants related to C and K respectively, qc and qk are heats ($Kjmol^{-1}$) related to the monolayer and the multilayer respectively, T is the absolute temperature (°K) and R is the universal gas constant (8.314 $Kjmol^{-1}K^{-1}$). The equation was regressed using the indirect non-linear regression method using the computer programs Curve Rt-Science Plot. Three constants of the GAB equation, m_o, C and K were first estimated at each temperature using equation (1), and they were used to estimate C_o, qc, K_o and qk through equation (2) and (3).

Parameter Optimisation

The fit of the sorption model was based on the mean relative error P and the coefficient of determination D.

$P = 1/n\ [\Sigma|\ 100\ (m_i - m_{ip})/\ m_i|]$
$D^2 = [1 - \Sigma\ (m_{ji} - \overline{m_{ji}})^2/\ \Sigma\ (m_{ji} - m_j)^2]$

Where $\Sigma\ (m_{ji} - \overline{m_{ji}})^2$ is the sum of the square residue, $\Sigma\ (mji - mj)^2$ is the sum of the square gap and n is the number of observation

RESULTS AND DISCUSSION

Regression of the GAB Equation

Estimated GAB parameters along with the statistics and constants model are shown in Table 1 and Table 2 respectively. The regression gave values for D^2 very close to 1.000 and values for P less then 10 %. The equation gives a good representation of the experimental data if D^2 is superior to 0.8 (Banaszek and Siebenmorgen, 1990; Madambra et a.l., 1994) and if P *is* less then 10 % (Aguerre et al., 1989). The model may be considered satisfactory for fitting the Deglet Noor and Alig dates desorption. However, further investigation into the estimated parameters and constants would help to reach more confident conclusion on the applicability of the GAB equation on the desorption of dates. The parameter K *is* in keeping with sorption on multilayer above the first layer and the heat of vaporisation of water. Thermodynamically, K's needs to be smaller than 1.000 (Chirife et al., 1992). The sign of qk indicate that values of K are smaller than 1.000 as dictated by the GAB equation. The magnitude of qc is in respect to other foodstuffs. Generally values of m_o decrease with increasing temperature (Labuza et al., 1985; Ayranci et al., 1990).

Evaluation of the Desorption Isotherms

The behaviour of date isotherms is presented in Fig. 1 and Fig. 2 for the temperature worked. Desorption isotherms of Deglet Noor and Alig dates are type II according to BET classification (Brunauer et al., 1938) and cross each other at about 0,8 a_W that is typical for materials with high sugar content (Tsami et al., 1990). The first bent part of a curve is related to tightly bound water on polymers such as pectin, cellulose and proteins. When water activity is increased beyond 0.50 the water content is dramatically raised. After elimination of available surrounding water, crystallized sugar turns into amorphous state more hygroscopic (Chinacoti and Steinberg, 1986).

Generally, at constant a_W, an increase in temperature will result in decreased equilibrium moisture content (Jayas and Mazza, 1991). However increasing temperature increases the number of the carbohydrate amorphous sites at the expense of the crystalline sites and reduces the principal effect of temperature in food rich in carbohydrates (Sarvacos et al., 1986; Ayranci et al., 1990). The effect of temperature is less marked in 5-30°C rang for Alig dates and 30-40°C for Deglet Noor dates. The spectrophotometric study show that Alig dates are invert sugar variety (32.62 % fructose, 29.8 %glucose and 6.16 % sucrose) and Deglet Noor is can sugar variety (52.9 % sucrose, 13.25 % glucose and 11.86 % fructose). The small molecular weight of glucose and fructose increase the specific area and water affinity at molecular level with increasing temperature.

Water vapour isotherms for the temperature extremes worked (Fig. 3) show that isotherms departed from each other and the discrepancy got more pronounced with increasing a_W and decreasing temperature. Deglet Noor dates exhibited lower m values than Alig dates under the same conditions.

The multilayer desorption region is in the range of 0.2-0.55 a_W at all temperatures for both dates. The upper limit of the region allows predicting 28.3 and 35.5 % (db) as critical moisture content at 5°C for Deglet Noor and Alig dates, respectively. These values are smaller than what the FAO/OMS Codex Alimentarus ONU-DF-08 imposes for commercial whole dates.

The Monolayer Moisture Content

The monolayer moisture content (m_o) is recognised as the moisture content affording the longest time period with minimum quality loss (Labuza, 1968). At m_o each polar group had adsorbed one water molecule, so the reaction rates in aqueous phase are minimal (Labuza, 1980). The a_W and m safest values for both samples were presented in table 3. Alig dates had m_o and a_W higher values than Deglet Noor dates at all temperatures.

Heat of Desorption

The survey of the a_W variation with the temperature at stationary moisture content gives access to iso-steric heat of sorption (Qs). Clasius–Clapeyron equation had been widely used for calculating Qs of food and agricultural materials during water vapour sorption process (Iglesias and chirife, 1976).

$$d(\ln a_W)/d(1/T) = -Qs/R \qquad (4)$$

The thermodynamic parameter Qs is not in fact the measure of the entirety of the energizing transition that comes with water vapour desorption; the total iso-steric heat considered for the energising balances Q, includes the latent heat of vaporisation of water hV.

$$Q = Qs + hV \qquad (5)$$

The variation of total heat of desorption with moisture content are provided in fig. 4 for both dates. It decreased from 69.2 Kjmol^{-1} and 65 KJmol^{-1} for Deglet Noor and Alig dates, respectively, with increasing m and approached to hV. Using Clasius-Clapeyron equation for average m_o, Q was calculated to be 68.87 and 62.66 Kjmol^{-1} for Deglet Noor and Alig dates, respectively. For most food, Q varies between 52 and 86 Kjmol^{-1} for $m < m_o$ (Labuza, 1968).

CONCLUSION

The desorption isotherms of Deglet Noor and Alig dates are type II according to the BET classification. The GAB model correlates satisfactorily the experimental results and five parameters were used, involving monolayer moisture content and heats of sorption. The lower hygroscopicity of Deglet Noor dates shows its potentially higher stability than Alig dates at the practically encountered *RH* conditions.

The effect of temperature on equilibrium desorption is function of carbohydrates transition from the crystalline state to the amorphous state. The analysis of total isosteric heat of desorption shows the presence at the monolayer moisture content of strongly bound water particularly the monolayer moisture content. The quality standard for exporting whole dates and the critical moisture content could be reviewed.

Using this work, other sorption models and the effect of some factors such storing period are being investigated.

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Literature

Aguerre, R.J. Suarez, C and Viollaz, P.E. 1989. New BET type multilayer sorption isotherms: Part II. Modelling water sorption in foods. Lebensm. Wiss. Technol. 22: 192−195.

Ayranci, E. Ayranci, G. and Dogantan, Z. 1990. Moisture sorption isotherms of dried apricot, fig and raisin at 20°C and 30°C. J. Food. Sci. 55: 1591-1593.

Barriero, J.A. Fernandez, S.and Sandoval, A.J. 2003. Water sorption characteristics of six barley malt (*Hordeum vulgare*). Lebensm. Wiss. Technol. 36: 37−42.

Banaszec, M.M. and Siebenmorgen, T.J. 1990. Adsorption equilibrium moisture contents of long-grain rough rice. Trans. Agri. 33: 247-252.

Basunia, M.A. and Abe, T. 1999. Moisture sorption isotherm of rough rice. J. Food. Eng. 42: 235–242.

Belarbi, A. Aymard, C. Meot, J.M. Thermelin, A. and Reynes, M. 2000. Water desorption isotherms for eleven varieties of dates. J. food. Eng. 43: 103-107.

Brunauer, S. Emett, P. and Teller, E. 1938. Adsorption of gases in multimolecular layers. J. American. Chem. Soc. 60: 309-319.

Chen, C.C. and Morey, R.V. 1989. Equilibrium relative humidity relationships of yellow dent corn. Trans. ASAE. 32: 999-1006

Chinacoti, P. and Steinberg, M.P. 1986. Moisture hysteresis is due to amorphous sugar. J. food. Sci. 51: 453-455.

Chirife, J. Timmermann, E.O. Iglesias, H.A and Boquet R. 1992. Some features of the parameter k of the GAB equation as applied to sorption isotherms of selected food materials. J. Food. Eng. 15: 75−82.

Iglesias H.A and Chirife J., 1976. Isosteric heats of water vapour sorption on dehydrated foods. Part I. Analysis of the differential heat curves. Lebensm. Wiss. Technol. 9: 116−122.

Jayas D.S., and Mazza G., 1991. Equilibrium moisture characteristics of safflower seeds. Trans. ASAE. 34: 2009-2103.

Labuza, T P. 1968. Sorption phenomena in foods. *J Food Technol*. 22: 263−272.

Labuza, T P. 1980. The effect of water activity on reaction kinetics of food deterioration. J. Food. Technol. 34: 36-41.

Labuza, T.P. 1985. Application of chemical Kinetics to deterioration of food. J. Chemistry. 61: 348-358.

Madambra, P.S. Driscoll, R.H. and Buckle, K.A. 1994. Predicting the sorption behaviour of garlic slices. Drying Technol. 12: 669-683.
Maroulis, Z.B. Tsami, E. Marinos-Kouris, D. and Saravacos, G.D. 1988. Application of the GAB model to the moisture sorption isotherms for dried fruits. J. Food. Eng. 7: 63−78.
Menkov, N.D. 2000. Moisture sorption isotherms of lentil seeds at several temperatures. J. Food. Eng. 44: 205–211.
Multon,J.L. 1991. In: Lavoisier (eds.), Analyse des constituants alimentaires. p. 32-35. Vol. 4, Techniques d'analyse et de contrôle dans les Industries Agroalimentaires. Paris, France.
Nguyen, T.A. Verboven, P. Daudin, J.D. and Nicolai, B.M. 2004. Measurement and modelling of water pear flesh tissue in the high humidity range. Post. Harvest. Biol. Techol. 33: 229-241.
Pioter, P.L. 1997. A three-parameter equation for food moisture sorption isotherms. J. Food. Process. Eng. 21: 127-144.
Saravacos, G.D.Tsiourvas, D.A. and Tsami E. 1986. Effect of temperature on the water adsorption isotherms of sultana raisins. J. Food. Sci. 51: 381-383.
Tsami, E. Marinos-Kouris, D. and Maroulis, Z.B. 1990. Water sorption isotherms of raisins, currants, figs, prunes and apricots. J. food. Sci. 55: 1594−1597.

Tables

Table 1.GAB model parameters with regression coefficients for Deglet Noor and Aligdates at 5, 30 and 40 °C.

GAB Parameters	Deglet Noor dates			Alig dates		
	5°C	30°C	40°C	5°C	30°C	40°C
m_o % (db)	17.44	11.43	9.95	20.30	18.01	11.18
Cg	28.710	23.470	21.622	23.979	22.336	16.246
K	0.751	0.900	0.950	0.754	0.813	0.966
Regression coefficients						
P %	2.015	2.015	6.715	1.611	2.433	6.251
R^2	0.996	0.996	0.975	0.995	0.995	0.963

Table 2. GAB model constants

GAB constants	Deglet Noor dates	Alig dates
C_o	2.324	1.351
Qc (Kj mol^{-1})	1.384	1.602
K_o (Kj mol^{-1})	6.241	5.124

Table 3. Monolayer moisture content *m* and safest a_w values for Deglet Noor and Alig dates

T (°C)	Deglet Noor dates		Alig dates	
	m_o %(db)	a_w	m_o %(db)	a_w
5	17.44	0.209	20.30	0.225
30	11.18	0.189	18.01	0.215

40	9.95	0.186	11.18	0.206

Figures

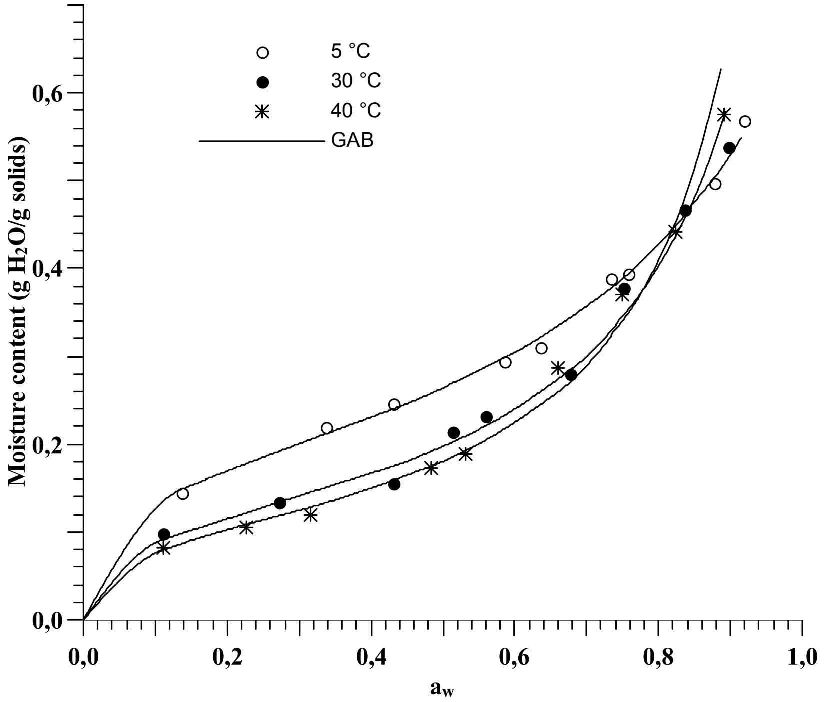

Fig. 1. Desorption isotherms, at 5, 30 and 40°C of Deglet Noor dates and GAB model

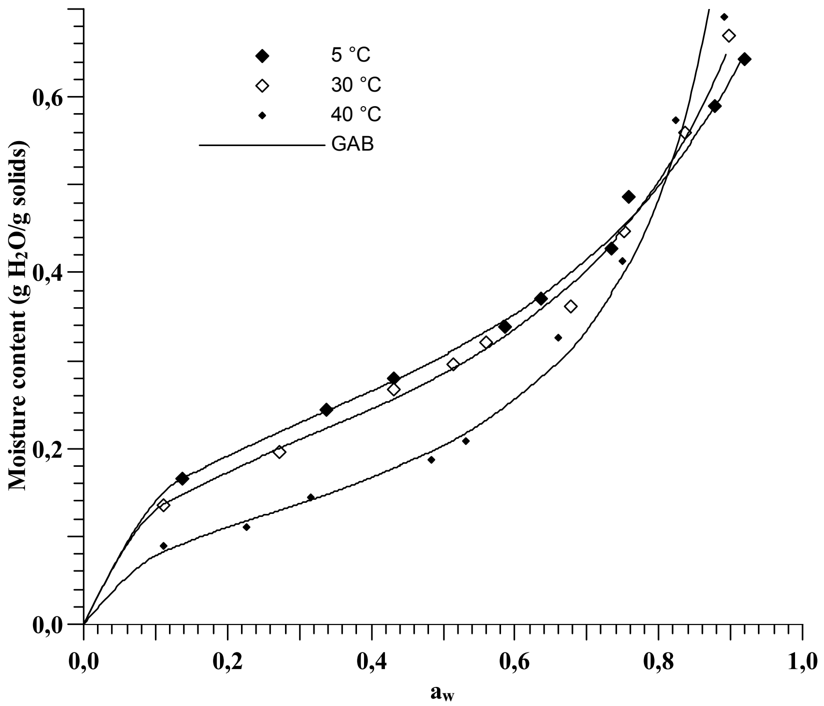

Fig. 2. Desorption isotherms, at 5, 30 and 40 °C of Alig dates and GAB model.

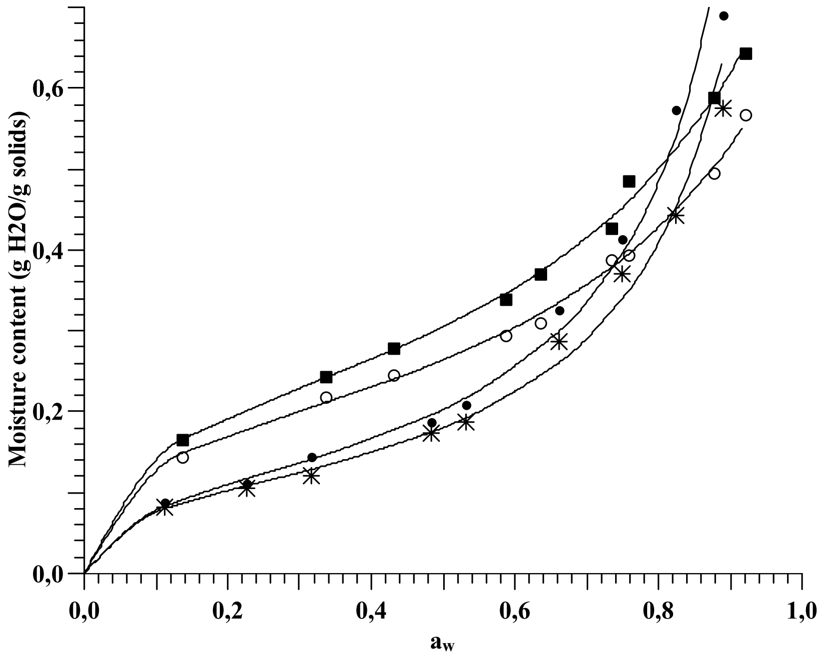

Fig. 3. Desorption isotherms at 5 and 40 °C and GAB model; ——— GAB
⁎ Deglet Noor Dates at 40 °C; • Alig dates at 40 °C
○ Deglet Noor at 5 °C; ◆ Alig dates at 5 °C

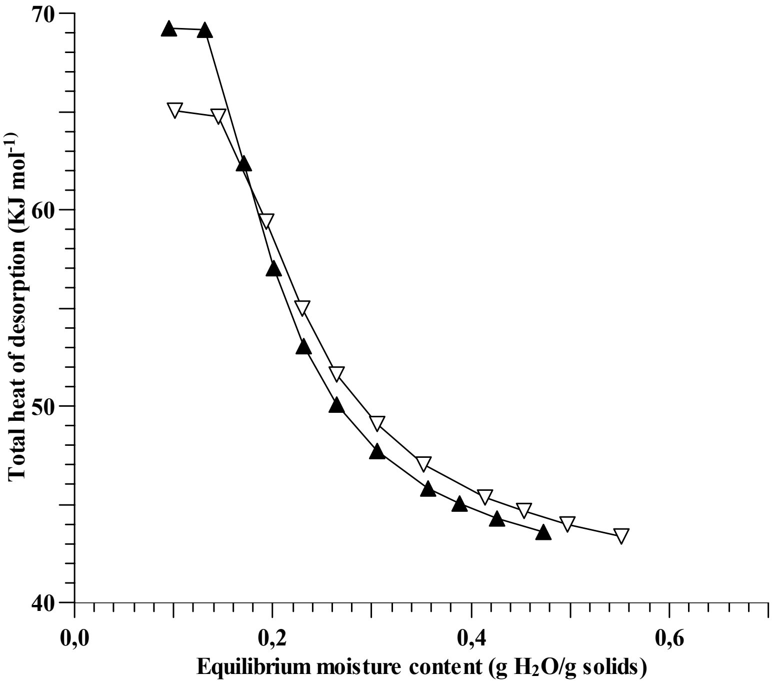

Fig. 4. Variation of total heat of desorption with moisture content;
▽ Alig Dates; ▲ Deglet Noor dates

Désorption de Vapeur d'Eau des Dattes Deglet Nour et Alig

Mots-clés : *Activité de l'eau, isothermes, modèle, chaleur de désorption, teneur critique en eau*

Résumé

Les isothermes de désorption des dattes Deglet Nour et Alig ont été déterminés par méthode gravimétrique à 5°, 30° et 40°C. Les produits ont été hydratés puis maintenus grâce à des solutions salines saturées à des humidités relatives de l'air variant de 11% à 92%. L'équilibre thermodynamique a été atteint au bout de 21 jours. Les dattes des variétés Deglet Nour et Alig on présenté des isothermes distincts en forme de S, dont les différences s'accroissent en fonction de la baisse de la température ou de l'élévation du taux d'humidité relative. L'équation Guggenheim – Anderson – de Boer (GAB) appliquée par une méthode de régression indirecte non linéaire décrit convenablement le comportement de désorption. Les paramètres de l'équation GAB et ses constantes se sont avérées conformes à ceux de la littérature. La teneur critique en eau estimée par le modèle est de 28.3% et 5.5% de matière sèche à 5°C pour les fruits de Deglet Nour et Alig , respectivement. Ces valeurs sont inférieures à celles imposées par la FAO/OMS dans le Codex Alimentarius ONU-DF-08 pour la commercialisation des dattes entières. La chaleur de désorption, calculée au moyen de l'équation de Clausius-Clapeyron, a atteint 68.87 et 62.66 kJ mol-1 pour les fruits de Deglet Nour et Alig, respectivement.