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Heat of Sorption of Water in Date Pastes

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ABSTRACT

The isosteric heats of sorption of water in pastes of three date cultivars (Khudari, Khlass, and Ruziz) were determined from water sorption isotherms data using Clausius-Clapeyron equation in the temperature range 5-40 °C. Based on the equilibrium moisture content range 0.04 to 0.4 kg water/kg dry matter, values of the net isosteric heat of sorption (q_{st}) varied in the ranges -6.75 to 18.43, -8.01 to 14.01, and –5.29 to 47.98 kJ/mol for the pastes of the three date cultivars, Khudari, Khlass, and Ruziz, respectively. Experimental data were fitted to a proposed empirical model which adequately correlated q_{st} with moisture content (dry basis) of date pastes, M.

Key words: Clausius-Clapeyron, Dates, Fruit, Heat, Sorption.

INTRODUCTION

The heat of sorption of water in intermediate - moisture high sugar foods is valuable in various food processes including dehydration, food packaging, and storage stability. It provides important information on the state of water in food products (Rizvi 1995, Tsami et al. 1990a). A knowledge of the temperature dependence of sorption phenomenon provides important information about the changes related to energetics of the system. Several investigators determined the heat of sorption of water in high sugar fruits such as sultana raisins, figs, prunes, apricot, apples, and whole dates, using Clausius-Clapeyron equation (Bolin, 1980; Saravacos et al., 1986; Maroulis et al., 1988; Tsami et al., 1990; Ayaranci et al., 1990; Tsami, 1991; Hassan, 1991; Hamdi and Jendoubi, 1994). Most of the published values of the heat of sorption of water in foods were determined experimentally from moisture sorption data. Theoretical prediction of the heat of sorption of water in food systems is not feasible due to the complexity of physicochemical structure of foods (Tsami et al., 1990).

In recent years, the date industry in Saudi Arabia consistently increased quantities of produced date pastes. The major users of date pastes are household consumers, the bakery sector, and confectionery and biscuits factories. The paste is produced from clean-pitted dates by mixing/mincing in large-scale electrical mincers with simultaneous addition of water or steam to soften the paste. The produced paste is packaged in solid or flexible plastic packages made from high or low-density polyethylene, polypropylene, or other plastic materials. A major problem facing, this product is partial dehydration of the paste, which renders it difficult to handle and utilize with ease (Hassan, 1991; Alhamdan and Hassan,1998).

The purpose of this investigation was to determine the heats of sorption of water in pastes of different date cultivars utilizing equilibrium sorption data, and to empirically correlate the isosteric heat of sorption to moisture content.

MATERIALS AND METHODS

Samples of commercial pastes of three date cultivar, Khudari, Khlass, and Ruziz, were provided by a local date factory. They were primarily wrapped with flexible low-density polyethylene films and contained inside carton packages. The water sorption isotherms data were obtained, as detailed in Alhamdan and Hassan (1998), using the gravimetric method described by Gal (1981). Samples of about 40 g were transferred into pettri dishes and placed inside glass dessicators containing saturated salt solutions. Ten saturated salt solutions in the water activity range 0.113 to 0.985 were used in this study. Table 1 shows the values of water activities of the saturated salt solutions at 5, 25, and 40 °C.

The glass dessicators containing the date paste samples above the saturated salt solutions were kept in temperature controlled rooms at 5, 25, and 40 °C (± 0.5 °C). Three replicates of each of the paste samples of the three date cultivars were contained in each glass dessicator for the three tested temperatures, totaling 270 samples. The date pastes samples were weighed periodically using a standard balance with a 0.1 mg accuracy (model 204, Mettler -Toledo, Switzerland)untill mass difference between two successive measurements were less than 1%. Attainment of equilibrium required up to five months due to the relatively large quantities of date paste samples. Moisture content of the date pastes samples were determined by a standard vacuum oven method (AOAC,1984).

RESULTS AND DISCUSSIONS

The Clausius –Clapeyron equation is often used to predict water activity at any temperature if the isosteric heat and water activity values at one temperature are known. The equation for water vapor, in terms of isosteric heat (Q_{st}) is (Rizvi, 1995):

$$d(\ln P) = -\frac{Q_{st}}{R} d\frac{1}{T} \qquad (1)$$

Where P = pressure, Pa, Q_{st}= isosteric heat of sorption, Kj/mol, R= gas constant = 8.134 Kj/mol K, and T= absolute temperature K.

Subtracting the corresponding relation for vapors in equilibrium with pure water at the same temperature gives,

$$d(\ln p) - d(\ln Pw) = -\frac{Q_{st} - \Delta\overline{H}_{vap}}{R} d(\frac{1}{T}) \qquad (2)$$

where P_w is partial pressure of pure water, Pa, $\Delta\overline{H}_{vap}$ is the heat of condensation of water vapor, kj/mol.

Since $a_w = P/P_w$, Eq. 2 can be written as,

$$d(\ln a_w) = -\left(\frac{q_{st}}{R}\right) d\left(\frac{1}{T}\right) \qquad (3)$$

where q_{st} = net isosteric heat of sorption (also called excess heat of sorption) $= Q_{st} - \Delta\overline{H}_{vap}$.

Integration of above equation yields,

$$\ln(a_w) = -\frac{q_{st}}{RT} + const. \qquad (4)$$

Water activity values for the equilibrium moisture content range 0.04 to 0.4 kg water/kg dry matter were obtained from the experimental sorption isotherm curves of the pastes of the three date cultivars (Alhamdan and Hassan, 1998) and are given in Table 2.To confirm the applicability of Eq.(4), water activity (a_w) was plotted versus the resiprocal of the absolute temperature (1/T K) at various moisture contents for the pastes of date cultivars Khudari, Khlass, and Ruziz, as shown in Figs. 1 to 3, respectivly. The sorption isosestors for Khudari (Fig. 1) and Khlass (Fig. 2) showed smooth straight lines at the seven tested equilibrium moisture contents, indicating a good fit of the experimental data to Eq. (4). The slopes of the straight lines $\left(-\frac{q_{st}}{2.303R}\right)$ were positive for the equilibrium moisture content range 0.04 to 0.1 and negative for the range 0.2 to 0.4 kg water/kg dry matter. The sorption isosestors for the paste of Ruziz cultivar, as shown in Fig. 3, followed the same trend for the equilibrium moisture content range 0.2 to 0.4 kg water/kg dry matter. However, for the moisture content range 0.04 to 0.1kg water/kg dry matter the lines were broken at temperature 25 °C (298.15 K) as a result of the lower water activity values at 5°C (278.15 K) as compared to the pastes of Khudari and Khlass.

Values of the net isosteric heat of sorption (q_{st}) obtained from the slopes were plotted as a function of moisture content for the pastes of the three date cultivars as illustrated in Fig. 4. Net isosteric heat of sorption curves of the cultivars Khudari and Khlass were similar in shape, with values of q_{st} consistently slightly higher for the Khudari cultivar. However, the curve for Ruziz cultivar was distinctly different in shape as compared to Khudari and Khlass, with much higher values of q_{st} at lower moisture content below about 0.12 (kg water/ kg dry matter).

In the moisture content region of 0.15 to 0.3, the curve shows a platue with a minimum value of q_{st} at moisture content of about 0.23, and then levels up at moisture content beyond 0.3. Within the moisture content range of 0.04 to 0.4 kg water/ kg dry matter the ranges for values of q_{st} were -6.75 to 18.43, -8.01 to 14.01, and -5.29 to 47.98 Kj/mol for pastes of the three date cultivars Khudari, Khlass, and Ruziz; respectively. The high net isosteric heats of sorption of water at low moisture contents (< 0.12) indicates a stronger water-date paste component interaction in the dried state. As moisture content increases, the available monolayer sites for sorption of water diminishes, resulting in lower values of q_{st}. The negative values of q_{st} at high moisture contents (>0.18) may be explained by the contribution of the endothermic dissolution of sugars in the sorbed water (Saravacos et al., 1986). Sawaya et al., 1986, experimentally determined the sugar contents as 76.2, 82.9, and 73.3 (g total sugar / 100 g dry matter); 76.2, 81.0, and 72.9 (g reducing sugar (glucose and fructose) / 100 g dry matter); and zero, 1.9, and 0.4 (g sucrose/100 g dry matter), for the three date cultivars Khudari, Khlass, and Ruziz, respectivly. The variation in behavior may be related to the total amount of sugar present, and the different proportions of each individual type of sugar.

The empirical exponential relationship proposed by Tsami et al. (1990) for dried fruits ($q_{st} = q_o \exp (M/M_o)$, where q_o and M_o are empirical parameters), and the empirical power type relationship proposed by Manuel and Sereno(1993) for quince jam ($q_{st} = a M^b - c$, where a, b, and c are empirical constants) were both inadequate in fitting the experimental data of date pastes.

The following empirical model was found adequate in correlating the experimental values of the net isosteric heat of sorption (q_{st} kj/mol) and moisture content (M kg water/kg dry matter) for the pastes of the three date cultivars:

$$q_{st} = C_o + \frac{C_1}{M} + \frac{C_2}{M^2} \qquad (5)$$

whereC_o, C_1, and C_2, are constant parameters. A statistical software (JMP, SAS Institute Inc.,SAS Campus Drive,Cary,NC 27513) was used in an Apple Macintosh PC to fit the data to the empirical model , and the results of the statistical analysis is shown in Table 3.

CONCLUSION

The energetics of sorption behavior of the tested pastes of the three date cultivars, adequately followed the Clausius-Clapeyron relationship. The date cultivar, structure, and composition, may impose a significant effect on variation of the net isosteric heat of sorption (q_{st}) with moisture content (M). A second order empirical equation successfully described q_{st} as a function of M.

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REFERENCES

Alhamdan, A.M and Hassan, B. H. 1998. Water sorption isotherms of date pastes as influenced by date cultivar and storage temperature. Accepted by J. Food Eng.

AOAC. 1984. Official methods of analysis. The Association of Official Analytical Chemists, 14th Ed. Arlington,VA

Ayranci, E, Ayranci, G. and Dogantan, Z. 1990. Moisture sorption isotherms of dried apricot, figs, and raisin at 20 °C and 30 °C. J. Food Sci, 55: 1591- 1593, 1625.

Bolin,H.R. 1980.Relation of moisture to water activity in Prunes and Raisins. J. Food Sci: 45: 1190- 1193.

Gal,S.1981.Recent developments in techniques for obtaining complete sorption isotherms. In: Water Activity: Influences on Food Quality,(L.B.Rockland and G.F. Stewart, eds.) pp 89-110, New York:Academic Press.

Greenspan,L.1977. Humidity fixed points of binary saturated aqueous solutions.J.Res.Natl.Bur. Std.A : Phys. Chem. 80 A (1) : 89 – 96.

Hamdi, S.and Jendoubi,M.1994. Adsorption of water vapor by Tunisian dates. Proceedings of the second Saudi Symposium on Food and Nutrition, 7–10 Nov. College of Agric, King Saud Univ., Riyadh, Saudi Arabia.

Hassan,B.H.1991. Water sorption Isotherm of dried dates. Bulletin of Faculty of Agriculture, University of Cairo. 42 (4): 1213 – 1224.

Labuza, T.P, Kaauane, A., and Chen, J. Y. 1985. Effect of temperature on the moisture sorption isotherms and water activity shift of two dehydrated foods. J. Food Sci. 50: 385–391.

Manuel,M.SA., and Sereno,A.M.1993.Effect of temperature on sorption isotherms and heats of sorption of quince jam. International J. Food Sci.Technol.28: 241-248.

Maroulis,Z.B; Tsami,E; Marinos-Kouris,D and Saravacos,G.D.1988. Application of the GAB model to the moisture sorption isotherms of dried fruits. J.Food Eng. 7:63-78.

Rizvi,S.S.1995.Thermodynamics properties of Foods in Dehydration. In: " Engineering properties of Food ". Editors: M. A. Rao and S. S. Rizvi. Marcel Dekker, Inc., New York.

Saravacos,G.D, Tsiogrras, D. A and Tsami, E. 1986. Effect of temperature on the water adsorptions isotherms of Sultana Raisins. J. Food Sci, 5 : 381 – 383, 387.

Sawaya,W.N.; Miski,A.M.; and Al-Mashhadi, A.S.1986. Physical and chemical characteristics of major Saudi Arabian date cultivars. In: Dates of Saudi Arabia, Wajih N. Sawaya (Editor). Safir Press, Riyadh, Saudi Arabia.

Tsami, E,Marinos -Konris, D.and Maroulis, Z.B.1990. Water sorption isotherms of Raisins, Currants, Figs, Prunes, and Apricots. J. Food Sci, 55 : 1594 – 1597, 1625.

Table1.Water activity of saturated salt solutions at 5, 25, and 40 °C

(Adapted from Greenspan, 1977 and Labuza et al., 1985).

Saturated Salt Solution	Water activity (a_w)		
	5 °C	25 °C	40 °C
Lithium chloride	0.113	0.113	0.113
Potassium acetate	0.291	0.225	0.206
Magnesium chloride	0.336	0.328	0.316
Potassium carbonate	0.431	0.432	0.433
Sodium bromide	0.644	0.584	0.533
Sodium nitrate	0.731	0.658	0.614
Sodium chloride	0.757	0.753	0.747
Potassium chloride	0.877	0.843	0.823
Barium chloride	0.936	0.934	0.907
Potassium sulphate	0.985	0.973	0.964

Table2.Equilibrium water activity (a_w) obtained by interpolation from experimental isotherms (Alhamdan and Hassan,1998).

Date cultivar	Temperature °C	Equilibrium moisture content (kg water/kg dry matter)						
		0.04	0.06	0.08	0.1	0.2	0.3	0.4
	5	0.070	0.100	0.150	0.190	0.520	0.805	0.984
Khudari	25	0.100	0.145	0.215	0.260	0.520	0.700	0.864
	40	0.175	0.245	0.310	0.360	0.510	0.615	0.684
	5	0.070	0.110	0.140	0.190	0.520	0.870	0.990
Khlass	25	0.094	0.144	0.190	0.240	0.490	0.720	0.900
	40	0.140	0.230	0.256	0.300	0.482	0.610	0.690
	5	0.020	0.030	0.050	0.080	0.640	0.756	0.960
Ruziz	25	0.090	0.140	0.200	0.260	0.545	0.692	0.809
	40	0.200	0.250	0.290	0.320	0.468	0.580	0.706

Table3. Values of empirical parameters of Eq.(5) for the pastes of the three date cultivars.*

Date cultivar	C_o	C_1	C_2	R^2
Khudari	-15.587	3.566	-0.089	0.996
	[0.376]	[0.154]	[0.009]	
Khlass	-17.001	3.439	-0.088	0.998
	[0.201]	[0.095]	[0.005]	
Ruziz	-29.943	7.377	-0.170	0.985
	[1.304]	[0.642]	[0.039]	

* Values between brackets are standard deviations.

C_0, C_1, and C_2 are constant parameters.

R^2 is the coefficient of determination.

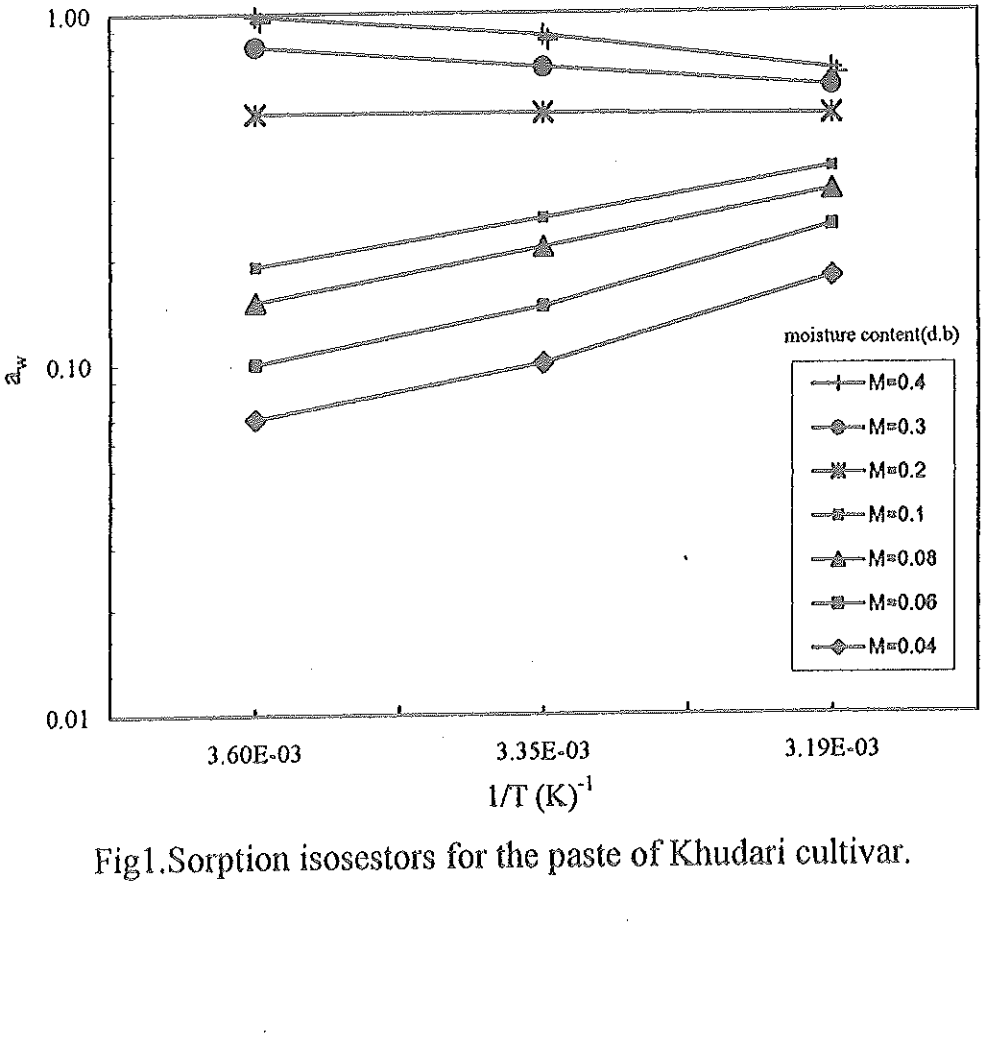

Fig1.Sorption isosestors for the paste of Khudari cultivar.

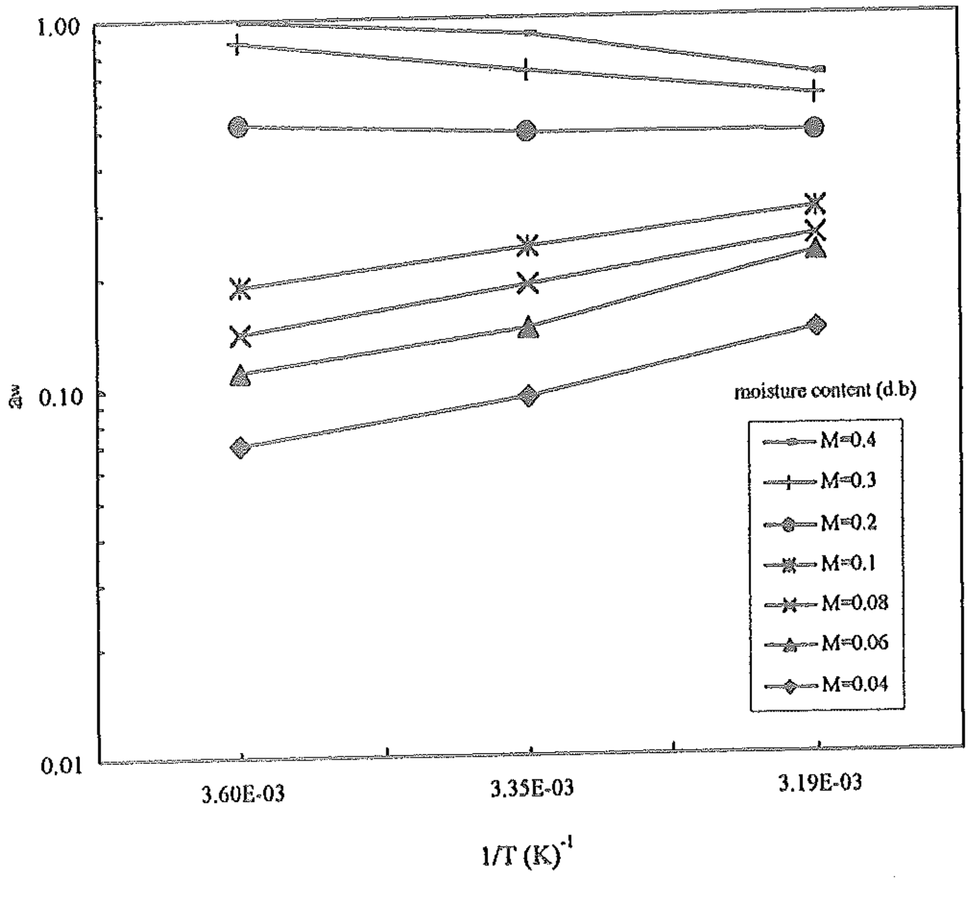

Fig2.Sorption isosestors for the paste of Khlass cultivar .

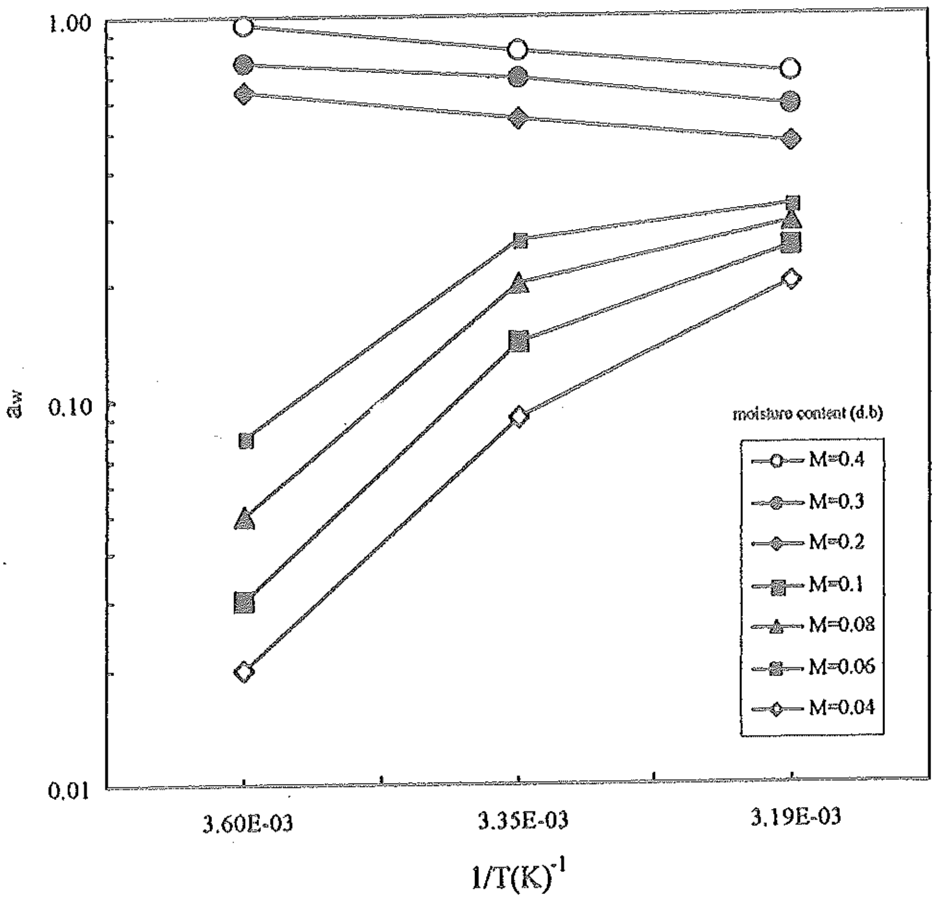

Fig3.Sorption isosestors for the paste of Ruziz cultivar

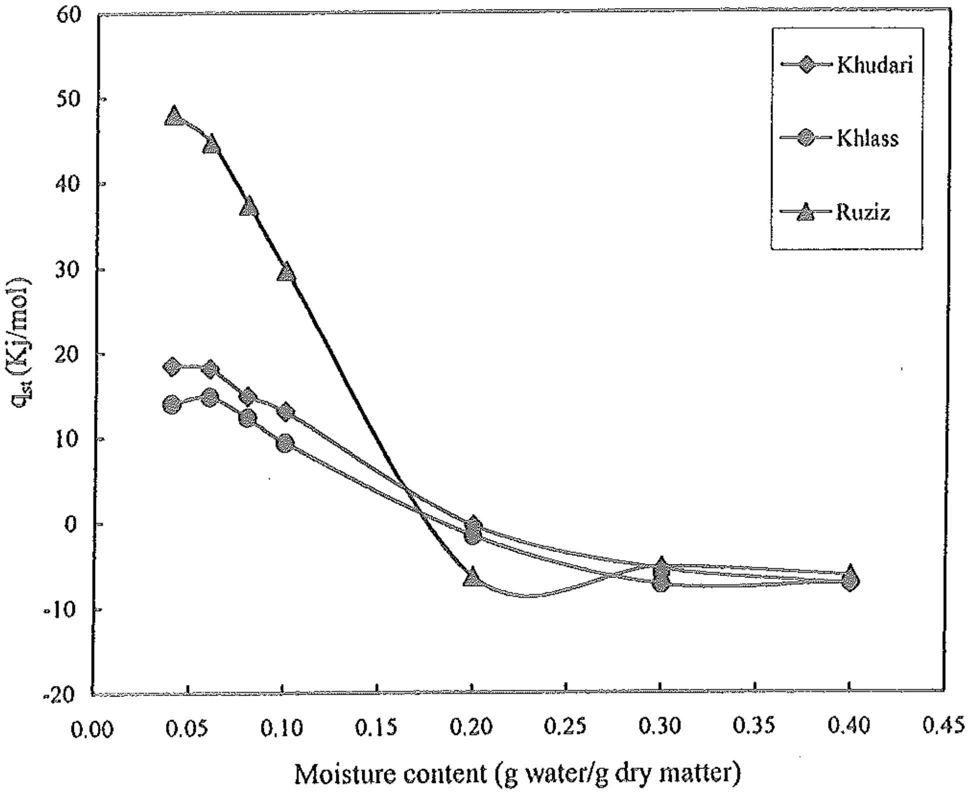

Fig4.Net isosteric heat of sorption vs. moisture content for date pastes.

مجلة الإمارات للعلوم الزراعية (١٩٩٨) ١٠ : ١-١٥

حرارة امتزاز الماء في معاجين التمور

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ملخص:

تم إيجاد حرارة امتزاز الماء ذو الجزيئات المتماثلة في التوزيع الإليكتروني (isosteric) في معاجين ثلاثة أصناف من التمور هي الخضري والخلاص والرزيز من نتائج الامتزاز المائي عند درجات حرارة ثابتة باستخدام معادلة كلوسياس وكلابيرون في حدود درجات الحرارة من ٥ إلى ٤٠ °م . واستنادا إلى قيم المحتوى المائي عند التوازن في الحدود من ٠,٠٤ آلي ٠,٤ كجم ماء/كجم مواد صلبة، فان قيم محصلة حرارة الامتزاز تفاوتت في الحدود من -٦,٧٥ إلى ١٨,٤٣، ومن -٨,٠١ آلي ١٤,٠١، ومن -٥,٢٩ إلى ٤٧,٩٨ ك جول/كجم لمعاجين أصناف التمور الثلاثة خضري وخلاص ورزيز، على الترتيب.

ولقد استخدمت النتائج التجريبية لاختبار نموذج رياضي تجريبي مقترح وإيجاد ثوابته إحصائيا . وعبر النموذج الرياضي عن العلاقة بين محصلة حرارة الامتزاز q_{st} والمحتوى المائي على أساس جاف M لمعاجين التمور بصورة وافية.

كلمات مفتاحية: كلوسياس وكلابيرون، تمور، فاكهة، حرارة، امتزاز.