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WATER SORPTION ISOTHERMS OF LIBYAN DATE PASTE

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ABSTRACT

Water sorption and desorption isotherms of destined and ground *saidyJalu*variety dates were obtained at 30 ºC, 40 ºC and 50 ºC, using the gravimetric method. Data were analysed by applying the GAB, BET, Smith, Iglesias &Chirife, Helsey, Henderson and Oswin Models. Isosteric heat of sorption value was calculated using the Clausius-Clapeyron Equation and tried to be expressed as a function of moisture content of dates. It was found that the experimental data fitted well to Smith, lgesias and Chirife, Halsey, Hendreson and Oswin equations, which are suitable for high sugar foods. In BET model, the constant C, related to the heat of sorption was negative which is physically impossible. Isosteric heat of sorption for dates varied from 0.9 to – 1.84 KJ/mol as moisture content changed from 11.0 to 18.0%.

Keywords: Dates, Isotherms, Sorption, Water activity, GAB, BET

NOMENCLATURE

Ab   constant in the Smith model, (cm^3)
A'   constant in the Smith model, (cm^3)
c   dimensionless constant of the BET model related to the enthalpy of sorption
H   equilibrium RH, P/P°
K   constant in the GAB model related to temperature effect
k   characteristic constant for the material in the Henderson model
M   Equilibrium moisture content (g.H_2O/g.dry solid)
M_o Monolayer coverage (Kg water/ Kg solid)
M_o monolayer moisture content (g.H_2O/g. dry solid
M_o GAB monolayer moisture (Kg water/ Kg solid)
n   Exponent, constant of the material in the Henderson model
P / P°   Relative humidity
P (1)   monolayer of absorbed water
P (2)   constant correcting of the multilayer molecules with respect to the bulk liquid
Q   net isosteric heat of sorption (cal/g)
R   gas constant
RH   relative humidity
T   absolute temperature (K)
C   constant in the GAB model related to temperature

Subscripts:
a Adsorption
d Desorption
o Mono-layer value

INTRODUCTION

Date palm (*phoenix dactylifera L.*) is one of commercial crop in Arabian countries, Middle East and Asia. The world-wide production of dates is about 9.0 million ton per year [1]. In Libya, there are about 8.5 million of date trees spread throughout regions of the country. The annual production is about 161.000 tons [1]. Dry dates are known in Arabic as *Tamr,* are sugar-rich and have low moisture (on the average of the sugar content 80g/100 g d.b). [2]. There are variety of date products like date paste, date jam, date syrup, date honey anddate vinegar [8]. The date paste is produced in factories where the date is steamed, destined , macerated and converted to a semi-solid form known as date pastes , and its moisture content 20-23% and water activity (a_w) is below 0.6 [3].

Water activity (a_w) is defined as the ratio of the vapour pressure of water in the food to the vapour pressure of pure water at the same temperature. The biochemical and microbial stabilities of a food product such as the date paste need a control of water content and water activity during transportation, storage and marketing [4]. The relationship between moisture content and water activity of food at constant temperature could be represented graphically form known as the moisture sorption isotherm (MSI) [4]. The sorption isotherms reveal information about sorption mechanisms and interaction of food biopolymers with water and they are useful in design and optimization of unit operations such as preservation, drying, mixing, storing and packaging [5]. Determination of the moisture sorption behavior of dates can be used directly to solve food processing design problems, predict energy requirements, and determine proper storage conditions and aid in new food product formulations [6].

The objectives of this study were to determine the water sorption isotherms of Libyan dates "saidyJalu" at different temperature 30 ℃ 40 ℃ and 50º C , and the correlate experiment sorption date with seven well-known high sugar foods sorption isotherms equations, namely BTE , GAB, Smith, Iglesias &Chirife, Halsey ,Henderson and Oswin equations.

MATERIALS AND METHODS

In this study, an experimental set-up was constructed on the basis of the gravimetric method with modified static

Setup proposed by Bosin and Easthouse [7], and it was modified to work at different temperature conditions by Dinçer and Esin [8].

A laboratory oven (NUVE, ES 400, 0-125 ± 0.1°C, chamber dimensions 24.5x28.0x41.5cm) was used as the constant humidity chamber □ Figure 1□. A sample holder was suspended by a steel wire to a digital balance (100 ± 0.01 g) placed on one of the two openings at the top of the oven. The relative humidity probe (10-96±%2,-30/+ 80°C) was inserted through the other opening. Constant relative humidity inside the oven was maintained by the saturated salt solutions placed in the plastic cuvette. The cuvette dimensions were 17x25x6 cm providing maximum contact of the solution with the confined air to have efficient evaporation. Further, homogeneity of the humidity of the chamber air was maintained by the electrically driven fan mounted on the back wall of the oven.

Dates of 2.5- 3.0 g samples used in the experiments were *Saidy Jalu*type obtained from a local market in Benghazi Libya during the 2005 season. Average moisture content of the dates was 25% (w/w) when received. Than these were destined, macerated and converted to a paste like semi-solid form which was dried in the air-oven at 80 °C for 48 h to the moisture content of 10.5 % .The date paste was packaged in polyethylene bag and stored at 4°C in a refrigerator.
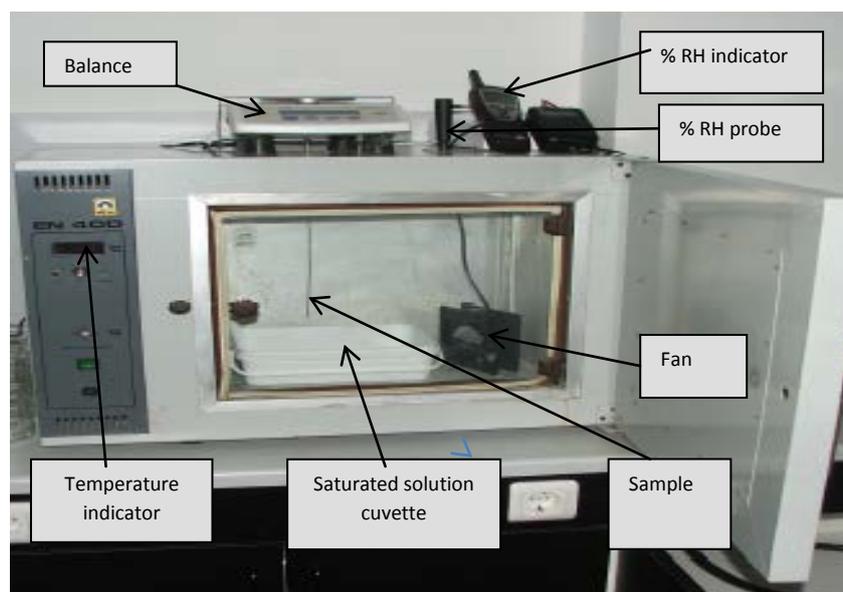
Fig.1: the front views of experimental set-up.

The moisture content determinations were done according to official methods A.O.A.C [9]. Equilibrium moisture content of the samples was measured at three temperatures 30, 40 and 50 °C and at least five or six relative humidity conditions in the range of 10-97% measured by Testo,TSTO103 (humidity/temperature measuring instrument). Constant relative humidity was sustained by using saturated salt solutions [10]. The percent relative humidities observed for the saturated salt solutions are given in Table 1, at each operating temperature and for the set-up used. For the adsorption experiments, the date paste sample about 3 g was used. The saturated salt solution, corresponding to the lowest relative humidity, was placed in the oven in the cuvette. Then, the desired temperature was adjusted and held for some time for the system to come up. Then the date paste sample was placed into the oven by attaching it to the balance. It was observed that constant relative humidity inside the chamber was maintained, at maximum, in 30 minutes. The sample was weighed intermittently until no change in weight was observed, as measured to the second decimal place [11] Usually, the time to reach equilibrium was about (75) hours. After the equilibrium was attained, the weight of the sample was recorded and equilibrium moisture content was calculated on dry basis. Upon recording the data, the dates paste sample was subjected to a higher relative humidity condition by using the next salt solution in the rank and allowed to reach equilibrium. To obtain sorption isotherm, equilibrium moisture content values of date paste were measured at the provided relative humidity conditions in increasing order. Finally, the sample was exposed to the highest relative humidity by placing pure water into the cuvette.

To obtain the desorption isotherm; the same saturated solutions were used for the same sample, but in this case in decreasing relative humidity order. After the desorption procedure was completed, sample was placed in an oven at 135°C for 2 hours and the amount of dry solid present in the sample was determined. Upon completing a set of adsorption and desorption data, the temperature was readjusted to another experimental value and the entire procedure, as explained above, was repeated for all of the temperatures.

Table 1: The equilibrium relative humidity maintained in the chamber for the adsorption /desorption studies

Saturated salt solution	Temperature [°C]		
	30	40	50
LiCi	20.0/13.6	17.0/16.0	14.0/10.0
K2CO3	44.0/33.0	36.0/29.0	24.0/22.0
Mg(NO3)2.6H2O	51.0/37.0	48.0/41.0	38.0/33.0
NaCl	60.0/49.0	53.0/42.0	41.0/35.0
KNO3	68.0/52.0	62.0/48.0	5.0/40.0
H20	78.0	74.0	65.0

RESULTS AND DISCUSSIONS

The sigmoid shapes of the sorption isotherms shown in ☐ Fig. 2, 3, 4☐ indicate the characteristics of high sugar foods [12]. In the first part (low relative humidity) of the sorption isotherm curve named S-shaped , the date paste sorbed relatively lower amounts of moisture due to the water sorption of biopolymers (high molecular weight components). However, large amount of moisture was absorbed at higher relative humidities (above 45-55%) due to the dominant water sorption capacity of sugars [3].
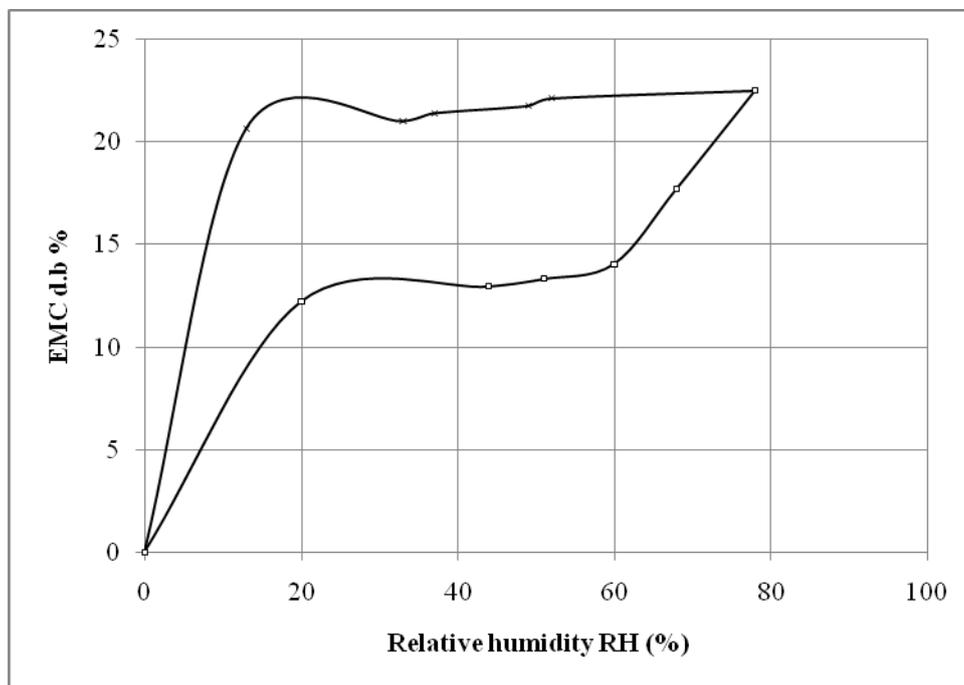
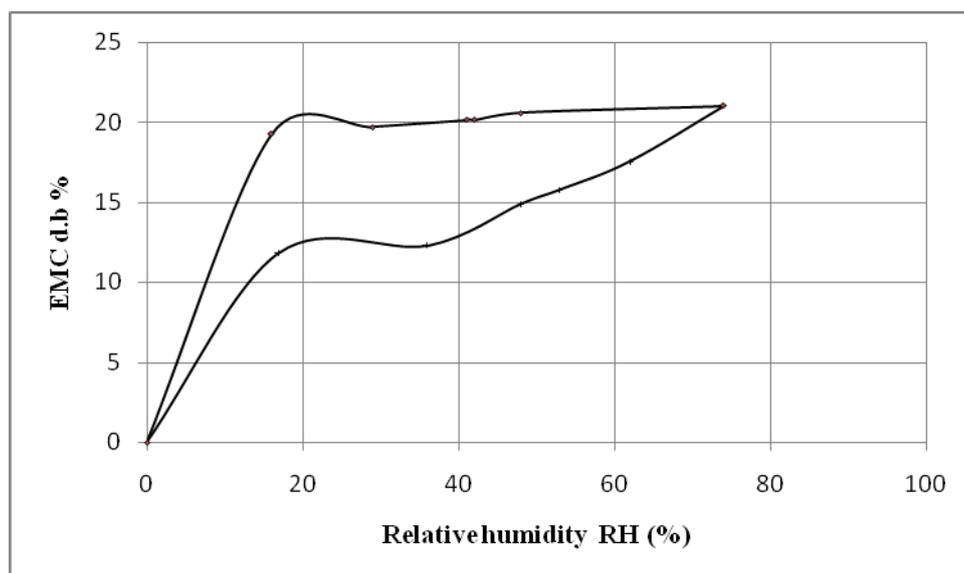Fig .2: Desorption and adsorption isotherms of date paste at 30 °C.

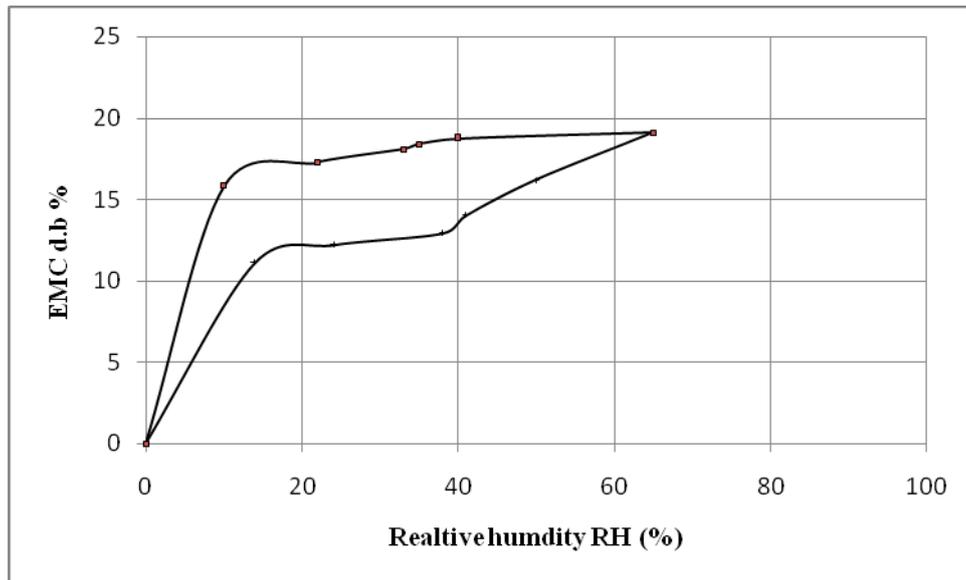Fig. 3: Desorption and adsorption isotherms of date paste at 40 °C.

Fig 4: Desorption and adsorption isotherms of date paste at 50 °C.

Water is more strongly bound at lower temperatures with a concomitant increase in a_w as temperature increases. This trend, evident in this study at lower a_w levels, is due to water sorption onto primary sites of hydrophilic compounds present in the dates [5]. At higher a_w levels a reversal of this occurs where a_w levels are lower at constant M, as temperature increases. The result is a crossing of moisture sorption isotherms conducted at differing temperatures.

Dates contain large quantities of fructose and glucose, which at low temperature and equilibrium moisture contents may at least partly be present in crystalline form. The crossing phenomenon described above is due to the increased solubility of sugars as temperature is increased. The increased quantity of sugar in solution binds large amounts of water thus, decreasing water activity. Similar results have been obtained for other high sugar fruits [5]. As glucose concentration increases, this crossing shall be expected to move down the curve to lower a_w values. Lower relative humidities, below 10%, could not be studied as this necessitates the room air humidity be at least below 10 % from the trend of isotherms. Hence behaviour of the isotherms in the monolayer region could not be detected. Nevertheless it can be stated the monolayer is completed at relative humidities above of 10% and up to 20%. There was a marked hysteresis in the sorption isotherms for all temperatures .As expected, for most biological materials, hysteresis decreased at low and high relative humidities and the maximum hysteresis was at the intermediate RH values.

The effect of temperature on adsorption and desorption isotherms are given in □ Fig 5, 6□. For most food products it is widely accepted that an increase in temperature increases the water activity [4].This was valid for this study also but up to a water activity range of 0.45-0.55. In this range crossing of sorption isotherms curves of the different temperatures were observed. Above this range, it was found that increase in temperature resulted in a decrease of water activity for high sugar foods due to dissolution of sugars [14].
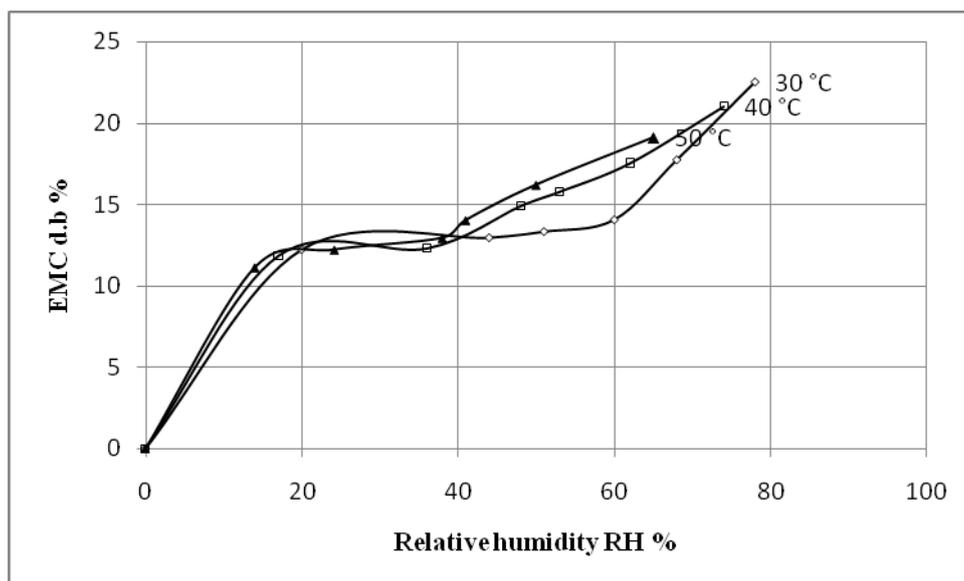
Fig 5: the effect of temperature on Adsorption isotherms of date paste
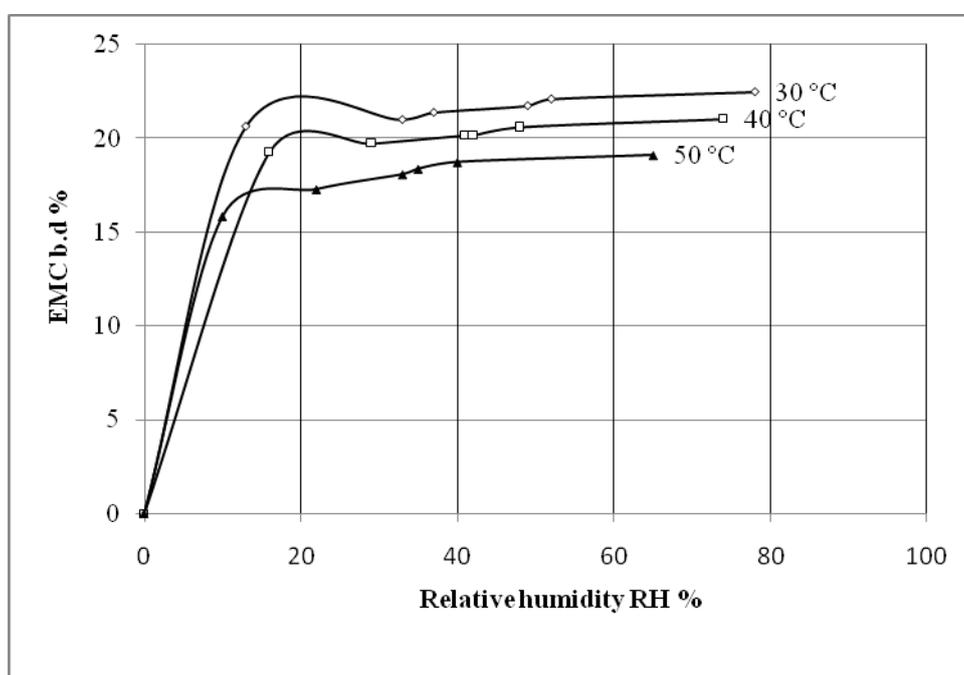◊ 30°C; □40 °C ▲50 °C.

Fig 6: the effect of temperature on Desorption isotherms of date paste
◊ 30°C; □40 °C ▲50 °C.

Analysis of experimental adsorption and desorption data for date paste with respect to the isotherm models BET, GAB, Smith, Iglesias and Chirife, Halsey, Henderson and Oswin. It was tried to correlate the data using a relevant model and to determine the physical and/or chemical parameters associated with the most acceptable one.

Table 3: Results of Regression Analysis, Adsorption/ Desorption, for the Model Equations in Table 2

Model	Parameter	Temperature [°C]		
		30	40	50
BET	M_o	50.2/10.18	5.78/10.14	6.84/10.99
	C	-5.80/-10.45	-7.02/-11.46	-12.60/-27.57
	r	0.98/0.98	0.97/0.97	0.98/0.99
GAB	M_o	8.41/20.08	9.55/18.67	21.87/15.30
	K	0.78/0.16	0.75/0.18	0.47/0.47
	r	0.97/0.93	0.99/0.99	0.94/0.99
Smith	Ab	8.40/20.45	9.30/18.70	9.46/15.27
	A'	8.30/2.38	8.79/2.81	9.07/7.03
	r	0.86/0.95	0.96/0.98	0.97/0.97
Iglesias &Chirife	b	1.07/1.17	1.06/1.19	1.06/1.52
	P	2.88/3.70	2.95/3.64	2.95/3.42
	r	0.75/0.92	0.93/0.97	0.95/0.95
Henderson	M_o	16.14/22.09	17.65/20.82	17.48/20.02
	n	0.27/0.04	0.30/0.05	0.27/0.10
	r	0.85/0.92	0.92/0.97	0.94/0.99
Halsey	M_o	12.66/21.43	13.54/20.05	13.75/18.50
	n	-0.3/-0.06	-0.35/-0.06	-0.36/-0.18
	r	0.85/0.91	0.93/0.97	0.95/0.99
Oswin	M_o	14.37/21.86	15.67/20.50	15.79/19.41
	n	0.27/0.04	0.30/0.05	0.27/0.10
	r	0.85/0.92	0.92/0.97	0.96/0.99

Table 3 summarizes the results of the regression analysis for selected models. For the BET equation, at all of the experimental temperature and for both adsorption and desorption data the *y*-axis intercepts were negative. This merely necessitates the □*c*□ term in the equation to be negative which is physically impossible [8]. The negative intercept value due to the BET equation does not fit to relative humidities higher than 20%. On the other hand, when BET plot is constructed for relative humidity below 20 %, the positive intercepts were obtained [13].

In this study, minimum relative humidity attained was 0.10 and only two points are present below 0.2 for some isotherms. So, it was not possible to check the validity of BET plot in suggested range with the obtained data results shown in Table 3 .On the other hand, they were obtained the BET model to describe the interaction between water vapour and the date paste. The values of the monolayer M_o were between 5.0 to 7.0 for adsorption and 10.0 to 11.0 for desorption which were close to the values that were reported by A. Belarbi and his colleagues in their study on water desorption isotherms for eleven varieties of dates [2].

In GAB equation, it is assumed that the number of molecular layers at the saturation pressure is finite, possibly a small number. The constant □ k□ introduced measures the strength of attractive force field of the adsorbant. A small value of □k□ implies a low attractive force field of the adsorbant and it is one of the reasons for the compensation in the BET theory caused by strong force field attributed to the adsorbant. The GAB model has been considered as versatile sorption model for various foods and earlier works on date products [3].

In Table 3 the results of the nonlinear fit using GAB model are displayed Monolayer moisture content, M_o varied from a minimum 8.41 g water/100 g dry matter at 30° C and increased with temperature to 21.87 g water/100 g dry matter. The values of Kat 30°C and 40°C are close to 1.0. In both BET and GAB, the correlation coefficient was higher than 0.94.

When Smith model was used to correlate the data of sorption and desorption isotherms, the correlation coefficients were between 0.86 to 0.98(Table 3). Smith considered the sorbed water to be of two principal classes; that which is bound to the inner and outer surface of solid sorbent and that which is normally condensed with the adsorbent[8]. In this study, a relatively low correlation coefficient at 30°C resulted which was satisfactorily high at the other temperatures.

The parameter Ab represents moisture bound to the surface and parameter were 8.40, 9.30, 9.46 at 30, 40 and 50 °C respectively for adsorption and 20.45, 18.70, 15.27 at 30,40 and 50 °C respectively for desorption.

And A' represents the moisture in a unimolecular layer of normally condensed moisture were 8.30 to 9.07 for adsorption and 2.83 to 7.03.

In Iglesias and Chirife equation for high sugar foods:

$$\ln[M + (M_2 + M_{0.5})^{1/2}] = ba_w + p$$

Where M is the equilibrium moisture content (g water/g dry matter), a_w the water activity, $M_{0.5}$ the equilibrium moisture content at $a_w = 0.5$, and b and p are constants. $M_{0.5}$ was directly determined from the experimental sorption isotherms by manually finding the values of M at $a_w = 0.5$. Results of linear regression of the Iglesias and Chirife equation using experimental sorption data are shown in Table 3. The values of the constant □ b□ consistently increased with increasing temperature, while values of □p□ consistently decreased with increasing temperature for the desorption data. The regression coefficient r was high for most of the samples at the three temperatures studied indicating a good fit of the experimental sorption data by the model as shown in Table 3. Iglesias and Chirife applied their model for sorption data of nine high sugar foods which were mostly fresh fruits with sugar precent mainly in dissolved form[4]. The date pastes are similar in sugar type since they contain predominantly reducing sugars (glucose and fructose) naturally in dissolved state[3].

Halsey equation is also one of the widely used in modelling experimental sorption data of high sugar foods. The equation can be written as follows:

$$M = M_o(-\ln(a_w))^n$$

Where M is the equilibrium moisture content (g water/g dry matter), a_w the water activity, M_o monolayer moisture content. The values of the parameters are shown in Table 3. The values of the regression coefficient indicate a good fit of the equation by the experimental data. According to the fit, values of M_o, monolayer moisture content are increasing with temperature for the adsorption .while decreased with temperature for the desorption data. The values of n are negative .which are similar to which were found by Jasim Ahmed [5].

Henderson equation is also one of the widely used equations in modelling experiments sorption data of high sugar foods. The equation is in this form:

$$M = M_o(-\ln(1-a_w))^n$$

Where M_o is the equilibrium moisture content (g water/g dry matter), a_w the water activity, M_o monolayer moisture content. The values of the parameters are shown in Table 3. The values of the regression coefficient indicate an acceptable fit of the equation to the experimental data. Again as in the other models, the values of M_o monolayer moisture content are increasing with temperature for adsorption .while decreasing with temperature for the desorption. The results and values are similar to which were found by Jasim Ahmed [5].

The Oswin equation is also one of the widely used equation in modelling experimental sorption data of high sugar foods. The equation can be written in logarithmic form which is more suitable regression analysis.

$$M = M_o(a_w/1-a_w)^n$$

$$\ln M = \ln M_o + n.\ln(a_w/1-a_w)$$

Here M is the equilibrium moisture content (g water/g dry matter), a_w the water activity , M_o monolayer moisture content. The values of the parameters are shown in Table 3. The values of the correlation coefficient □r□ indicate a good fit of the equation to the experimental data. Here again values of M_o increased with of temperature for the adsorption. While M_o decreased with increase temperature for the desorption data. The results are similar to those reported by Jasim Ahmed [5].

Isosteric moisture sorption:-

The relationship between a_w and temperature (at constant equilibrium moisture content) is described by a moisture sorption isostere. The isosteric heat of sorption (Q_{st}), is a measure of interaction between absorbate and absorbent, which can be determined from the integrated form of the Clasius-Clapeyron equation [15].

$$\ln(a_{w1}/\, a_{w2}) = -\Delta Q_{st}/R\,(1/T_1 - 1/T_2)$$

At constant equilibrium moisture content. a_{w1} and a_{w2} are water activities at temperatures T_1 and T_2. As moisture content increased for the date paste 　Fig.7　, Q_{st} decreased from 0.90KJ/mol at 11.0% moisture, to -1.84 KJ/mol at 18.0 % moisture. These trends were similar to those of date variety Fard and Khalas [16]. That indicated the weaker interactions between date solids and water, as well as the endothermic dissolution of sugars at higher equilibrium moisture contents.
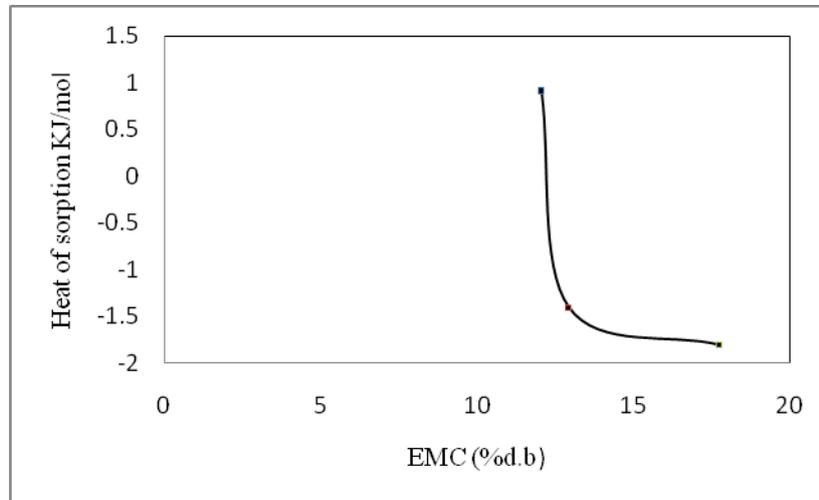

Fig 7: Isosteric heat of sorption of date paste

CONCLUSIONS

On the basis of sorption isotherms obtained experimentally for the date paste prepared from *SaidyJalu* variety and related discussion it is possible to draw the following conclusions. The Type II trends are quite common for most foods. Isotherms of the dates indicate that the well-known general shape of high sugar content materials could be observed only for the two of the three regions present in Type II isotherms namely multilayer adsorption and capillary condensation regions, where only partially with the monolayer zone.
Sorption isotherms exhibit lower moisture contents and approach each other with increasing temperature but the decrease in the heat of sorption varies nonlinearly with temperature.
Considering the simplicity of the equation as well as its ability to fit experimental equilibrium moisture isotherms in specified of relative humidity, the Smith, Iglesias & Chirife, Halsey, Henderson and Oswin models proved to be more useful for describing equilibrium moisture isotherms of the date paste.
Monolayer moisture content, M_o , values were between 8.0 to 22.0 for adsorption and between 15.0 to 22.0 for desorption. An empirical equation to relate the heat of desorption as a function of moisture content is possible.
For future research, it can be recommended that chemical composition of dates, crystalline sugar dissolution and transitions between the amorphous state and other factors can be studied to obtain a truly universal moisture content model.

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