

Studies on equilibrium moisture absorption of kappa carrageenan

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Abstract

This study describes investigation of moisture sorption behavior of Carrageenan at 10, 20 and 30°C under different relative humidity, in the range of 23 to 96 percent using gravimetric method. The equilibrium moisture uptake data, thus obtained, were fitted to three well known three sorption isotherm models, namely GAB, Halsey and Oswin models using non-linear least square method. The well-known GAB model best interpreted the equilibrium data in a satisfactory manner. The monolayer moisture content X_m , as determined from GAB model, was found to be 31.72×10^{-3} , 43.60×10^{-3} and 17.41×10^{-3} kg kg⁻¹, db at 10, 20, and 30°C. The isothermic heat of sorption (q_{st}) was determined using Clausius-Clapeyron type equation. The uptake data was also used to determine isokinetic temperature T_β (301.7 K) and harmonic mean temperature T_{hm} (292.82 K). The enthalpy-entropy compensation theory indicated that moisture sorption process was enthalpy driven.

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Introduction

Kappa carrageenan, a sulphonated galactan extracted from many species of red algae (Figure 1) is extensively used in the food industry as a gelling agent. (Funami *et al.*, 2007). It has a special property of forming gels in the presence of potassium and calcium ions (Popa *et al.*, 2011). Carrageenan is a high molecular weight linear polysaccharide comprising repeating galactose units and 3,6-anhydrogalactose (3,6 AG), sulfated and non-sulfated, joined by alternating α -(1,3) and β -(1,4) glycosidic links. An almost continuous spectrum of carrageenans exists but the work of Anderson and co-workers. (Anderson *et al.*, 1965) was able to distinguish and attribute definite chemical structures to a small number of idealized polysaccharides. The main carrageenan types, lambda, kappa and iota, can be prepared in pure form by selective extraction techniques. The synergy of kappa carrageenan is used in water dessert gels and glazes, cooked, sliced hams and poultry products, canned meats and pet foods, air fragrance gels and similar very firmly gelled products (Campo *et al.*, 2009).

Other applications, which utilize the stabilizing properties of this reversible gel networking, include soymilks and sterilized milk drinks. Higher concentrations of this carrageenan give soft elastic gels suited to gravies for canned meats and pet foods and for various toothpastes. Extremely low levels



Figure. 1. Photograph of carrageenan

of carrageenan, around 100–200 ppm, are used to stabilize and prevent whey separation in a number of dairy products (Hoffmann *et al.*, 1996).

These include milk shake and ice cream mixes, chocolate milks, and pasteurized and sterilized creams. In these applications, carrageenan interacts with the dairy proteins to form a stabilizing network, which is able to suspend particulates such as cocoa in chocolate milks. The network prevents protein-protein interaction and aggregation during storage. This avoids whey separation in fluid products and reduces shrinkage in ice cream. In milk products where gelation or structural viscosity is required, carrageenan is normally preferred of function and economic reasons. In gelled milk desserts kappa carrageenan is the most economical gelling agent to obtain a certain firmness, and is widely used in powder preparations for making flans. Kappa-carrageenan has been found to be a suitable carrier for yeast immobilization for continuous fermentation systems due to its unique properties. Brewing lager

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yeast immobilized in kappa-carrageenan beads was studied both in batch and in a continuously fermenting gas lift bioreactor (Pilkington *et al.*, 1999). Recently, there have been several reports, describing the formation of bi-polymeric polyelectrolyte gels for various applications (Zhang, and Zhang, 2012). Most recently, the potential use of κ -carrageenan hydrogels for the delivery of stem cells obtained from adipose tissue in the treatment of cartilage tissue defects has also been reported (Mihaila *et al.*, 2012; Popa *et al.*, 2013).

The tendency of Carrageenans to hydrate at low temperatures presents problems for its efficient use. Any lumps which are produced when the carrageenan is dispersed in water or milk greatly reduce the rate of hydration and may limit the development of full viscosity or gel strength. However, a survey of the literature reveals that there are hardly any studies related with moisture absorption capacity of this useful polysaccharide. So the present work is an attempt to investigate moisture absorption tendency of this polymer so that there may be some standards set during its production, storage and uses.

Materials and Method

The polysaccharide carrageenan (RM-1576) was purchased from Hi Media Chemicals, Mumbai, India. The salts KOH, CH₃COOK, K₂CO₃, Mg(NO₃)₂, NaCl, KCl and K₂SO₄ whose saturated solutions were prepared to obtain constant relative humidity environments were obtained from Merck Chemicals, Mumbai, India and were analytical grade. The double distilled water was used throughout the investigations. Water activities (a_w) of saturated solutions of the above salts at 10, 20 and 30°C were adopted from the data provided by Labuja (1984) and are listed in Table 1.

Determination of moisture sorption isotherm

The moisture adsorption isotherms of samples were obtained using gravimetric static method described in detail elsewhere (Labuja, 1984; Ayranci and Duman, 2005). Before the moisture adsorption isotherm experiments, samples were dried in a vacuum oven (Tempstar, India) at 40°C for two days. Saturated solutions of various salts, given in Table 1, were prepared and transferred into separate jars. Excess salts were present on the bottom of jars at 10, 20 and 30°C. A polypropylene chamber was placed in each jar. Then samples (about 1 g) were weighed into small crucibles of aluminum foils and placed on polypropylene chamber in the jars, which were then tightly closed. Jars were maintained in a Sanyo MIR 152 incubator at 10, 20, and 30°C for the equilibration

Table 1. The water activities (a_w) of saturated salt solutions at 10, 20 and 30°C

Salt	Water activity (a_w) at		
	10°C	20°C	30°C
KOH	0.1234	0.0932	0.0738
CH ₃ COOK	0.2338	0.2311	0.2161
K ₂ CO ₃	0.4313	0.4316	0.4317
Mg(NO ₃) ₂	0.5736	0.5438	0.5140
NaCl	0.7567	0.7647	0.7509
KCl	0.8677	0.8511	0.8362
K ₂ SO ₄	0.9818	0.9759	0.9700

Table 2. Various isotherm models used in this study

Name of model	Equation	Reference
GAB (Guggenheim-Anderson-de Boer)	$M = \frac{M_0 C k a_w}{(1 - k a_w)(1 - k a_w + c k a_w)}$	(Anderson, 1946)
Halsey	$a_w = \exp\left(\frac{-A1}{M^{A2}}\right)$	(Halsey, 1948)
Linearized	$\ln M = \ln A_1 + A_2 \ln(-\ln a_w)$	
Oswin	$M = A \left(\frac{a_w}{1 - a_w}\right)^B$	(Oswin, 1946)
(Linearized)	$\ln M = \ln A + B \ln \frac{a_w}{1 - a_w}$	

of samples. The equilibration took about 3 weeks. The moisture content of the equilibrated samples was determined using the vacuum oven method (Kaymak-Ertekin and Gedik, 2004). The equilibrium moisture contents of samples were expressed as kg/kg dry solids. All the moisture adsorption experiments were replicated three times. The percentage difference in the equilibrium moisture contents between triplicate samples was, on the average, less than 1% of the mean of the three values (Ashaye, 2013). The average values were used in the determination of the moisture adsorption isotherms.

Fitting of isotherm models to equilibrium sorption data

In the present work, the equilibrium moisture content (EMC) data was analyzed using two 'two parameters models' i.e. the Oswin, and the Halsey models, and one three parameters model i.e. GAB model (see Table-II), which is considered to have a theoretical background. (Adawiyah *et al.*, 2012; Halsey, 1948; Oswin, 1946).

The GAB equation could be re-arranged into a second degree polynomial equation.

$$a_w/M = \alpha a_w^2 + \beta a_w + \gamma \quad \dots \quad (1)$$

where

$$\alpha = K/M_0 [1/C-1] \quad \dots (2)$$

$$\beta = 1/M_0 [1-2/C] \quad \dots (3)$$

and

$$\gamma = 1/M_0 CK \quad \dots (4)$$

A non-linear regression analysis of a_w/M as a_w yields a polynomial of second order. The coefficients α , β and γ were thus obtained from this polynomial equation and substituted one by one to obtain GAB constants M_0 , C and K , where M_0 is the moisture content corresponding to saturation of all primary sites by single water molecule, C is the Guggenheim constant and K is the factor comparing the properties of multilayer molecules with respect to the bulk liquid. The Halsey and the Oswin models were applied using linear equations as given in Table-II.

Two criteria namely, mean relative deviation modulus (P) and the standard error of estimate (SE) were used to evaluate the well fitting of sorption models to the experimental data.

$$P = 100/N \sum | M_{\text{exp}} - M_{\text{pr}} / M_{\text{exp}} | \quad \dots (5)$$

$$SE = \sqrt{\frac{\sum_{i=1}^N (M_{\text{ex}} - M_{\text{pr}})^2}{N - n}} \quad \dots (6)$$

where M_{ex} and M_{pr} were the experimental and predicted moisture content values, respectively; N and n were the number of observations and the number of constants in each model respectively. A model is considered acceptable if it has a P value less than 10 percent (Kaya and Kahyaoglu, 2005). The model with lowest SE and P and highest regression coefficient (R^2) was supposed to be the most fitted one.

Results and Discussion

Sorption isotherms

A typical moisture adsorption isotherm for fuzzy cottonseed at 10, 20, and 30°C are shown in Figure 2. All the moisture adsorption isotherms obtained are type II sigmoidal according to the B.E.T. (Brunauer *et al.*, 1938). The sigmoidal shape of the sorption isotherms has been reported numerous times for food materials in the literature (Ramesh, 2003). Type II isotherm is divided into three regions. First region ($a_w < 0.2$) represents the adsorption of the first layer of water molecules strongly and water molecules in this region are un-freezable and are not available for chemical reactions. In the second region ($0.2 < a_w < 0.6$), water molecules are less firmly bound as a

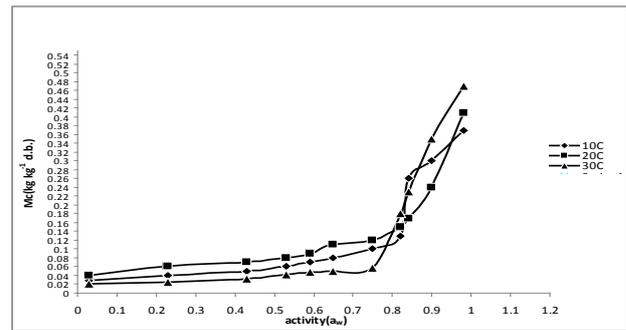


Figure 2. Moisture uptake as a function of water activity at different temperatures

multilayer above monolayer and they are available as a solvent for low-molecular-weight solutes and for some biochemical reactions. In the last region ($a_w > 0.6$), excess water is present in capillaries and this exhibits nearly all the properties of bulk water, and thus is capable of acting as a solvent. Microbial growth becomes a major deteriorative reaction in this region (Al -muhtaseb *et al.*, 2002).

It can clearly be seen from Figure 2 that for all isotherms, EMC increased as the a_w value increased, being more evident when a_w values were higher than 0.55, as mentioned. This is a common pattern in food adsorption processes. A close look also reveals that for the first two regions of isotherm plots (i.e. Region-I and II) the equilibrium moisture content (EMC) of carrageenan decreases as the temperature increase from 10 to 30°C. This trend is very common and may be explained by considering excitation states of molecules. As the temperature increases, the kinetic energy of water vapor molecules increase and this discourages their binding on the active sorption sites available on substrate (Chen, 2006).

It is clear that a gradual water absorption in linear fashion is observed till the water activity reaches a value of nearly 0.6. In this zone, molecules are mechanically entrapped in the voids, crevices, and capillaries. It is noticeable that a drastic increase in EMC is observed as the water activity of the surrounding environment exceeds 0.6. More interestingly, there is observed a crossover. This could probably be due to faster dissolution of carrageenan at 30°C beyond the water activity of 0.6. In addition, more water binding sites in the matrix may be exposed due to thermal effect. Increased water binding at higher temperature has also been reported elsewhere for food particularly rich in soluble solids and susceptible to structural orientations (Aviara *et al.*, 2004). Chowdhury and Das (2012), have also reported such an intersection or crossover behavior. Overall, all the three curves showed continuity. The equilibrium uptake data, obtained at 10, 20, and 30°C was fitted on the three isotherm models and

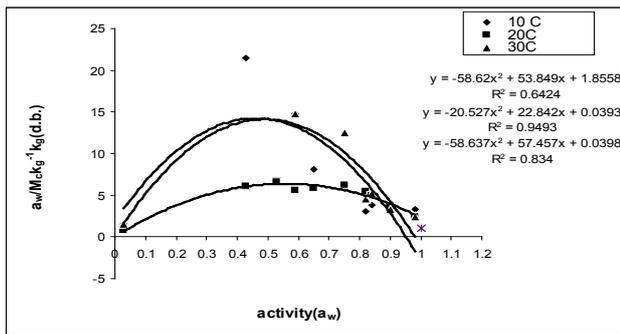


Figure 3. Polynomial plots for GAB model at different temperatures

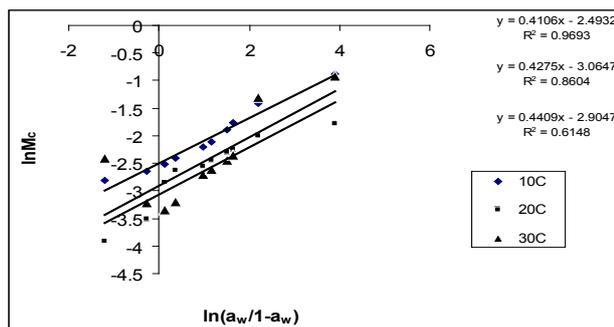


Figure 4. Oswin isotherm plots for moisture uptake at different temperatures

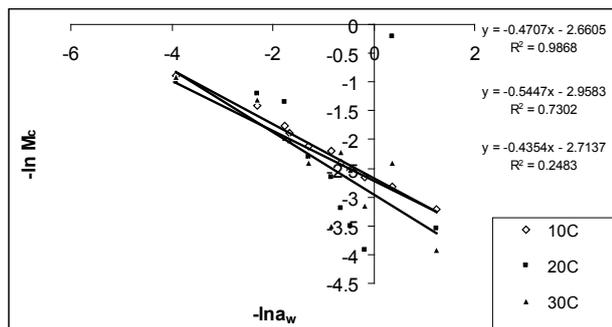


Figure 5. Halsey isotherm plots for moisture uptake at different temperatures

the corresponding curves obtained are shown in the Figures 3, 4 and 5 respectively.

The parameters obtained using various isotherm models are given in the Table-III along with respective error functions. Based on the values of various error functions obtained, namely SE, P and R^2 , the GAB equation was found to be most fitted one as compared to other two models. The best representation of the sorption data by the GAB model is expected because it is a semi-theoretical, multi molecular, localized homogenous adsorption model and has been suggested to be the most versatile sorption model available (Ariahu *et al.*, 2006).

The monolayer moisture content M_0

Modeling of sorption data using GAB equation allows the determination of monolayer moisture

content values, M_0 that are the measure of sorption possibility of the food material. This represents the moisture of a material when its entire surface is covered with an uni-molecular layer water vapor molecules (Sawhney *et al.*, 2011). The monolayer value indicates the maximum amount of water that can be adsorbed in a single layer per gram of dry substance and it is a measure of number of sorbing sites (Cassin *et al.*, 2006).

The prediction of M_0 values is important since deterioration of foods is very small below M_0 . This is because water is strongly bound to the food below M_0 and is not involved in any deteriorative reactions either as solvent or as one of the substrates. Therefore, at a given temperature the safest water activity level is that corresponding to M_0 or less. The monolayer moisture content calculated from the GAB model (Table 1) ranged between 0.0437–0.0137 g/g (dry basis) the range of temperature considered in this work. Now, taking the average of values obtained at 20 and 30°C as that for 25°C, the M_0 value was calculated to be 0.030 kg/kg (db). This is quite below the values reported for the two polysaccharides, namely, low acyl gellan gum (0.0683 g/g), and for high acyl gellan gum (0.0594 g/g) at 25°C (Abramovic and Klofutar, 2006). They also reported that Oswin model provided good descriptions of the moisture isotherms throughout the entire range of water activity. The average error in predicted moisture content was 4.3% for low acyl and 2.8% for high acyl gellan gum using the Caurriemodel, while using the Oswin model the corresponding values amounted to 3.6% and 3.4%. In a work by Siripatrawan and Jantawat (2006), the GAB model gave the best fit to the experimental sorption data for a wide range of water activity (0.10–0.95). The monolayer moisture content calculated from the GAB models ranged between 0.040–0.059 g/g (dry basis), for the temperature range of 30 to 60°C. Here, the observed increase in M_0 was also explained on the basis of the generation of new sorption sites due to increased temperature.

It is, note worthy here that the M_0 values obtained in the present work are comparable with the M_0 value of 0.035 kg / kg (db) reported for plain cassava starch (Mali *et al.*, 2005). In addition, the average M_0 values for guar seeds and guar gum splits were reported to be 0.075 and 0.072 kg/kg (db) respectively (Viswakarma *et al.*, 2012). A close look at the values obtained indicates that the M_0 value increases from 0.0317 to 0.0436 kg/kg db as the temperature is raised from 10 to 20°C, thus showing a positive temperature dependence. However, as the temperature is further increased to 30°C, the M_0 decreases to 0.0174 kg/kg db. The observed variation in moisture content with

Table 3. Parameters obtained for various isotherm models

Model	Constants	Temperature(°C)		
		10	20	30
GAB	M ₀	0.031	0.043	0.0174
	C	111.7	350.8	717.35
	K	1.038	0.897	1.0198
	SE	0.521	0.418	0.321
	P	4.351	5.814	5.568
	R ²	0.989	0.981	0.994
Halsey	A1	0.069	0.040	0.051
	A2	-0.470	-0.654	-0.544
	SE	2.998	1.971	1.918
	P	9.384	9.642	12.631
	R ²	0.874	0.896	0.853
Oswin	A	0.082	0.046	0.054
	B	0.410	0.427	0.440
	SE	2.685	2.389	1.367
	P	8.376	6.699	6.389
	R ²	0.728	0.835	0.895

temperature is attributable to the fact that increase in temperature from 10 to 20°C causes opening of new binding sites, thus allowing more and more water vapor molecules to bind, thus finally resulting in enhanced EMC. Although this variation of M₀ with temperature is unusual. However as the temperature is further increased, there occurs a decrease in the moisture uptake. This may probably be due to the fact that with the increase in temperature, the water molecules are activated to higher energy level and this makes the water molecules less stable, thereby, favoring their break away from the binding sites of food material (Palou *et al.*, 1997; Kaymak *et al.*, 2004). Similar observations have also been reported by Lim *et al.* (1995) for blue berries, and by Ruchi *et al.* (2011) for the moisture absorption by sago starch based films.

Constants C and K

It is believed that strong adsorbent – adsorbate interactions, which are exothermic, are favored at lower temperature, causing an increase in parameter C with decreasing temperature (Diosady *et al.*, 1996). However, just opposite trend was found in this study; increasing temperature from 10 to 30°C caused an increase in C value from 111 to 717. However, as the values obtained are >2, the isotherms obtained could be classified as type II as already mentioned earlier. Similar observations are reported elsewhere. (Farahnaky *et al.*, 2009). However, Iglesias and co-worker (Iglesias and Chirife, 1982) studied more than 30 different foods and found that in 74% of them, C did not decrease with increase in temperature, probably due to irreversible changes associated with increasing temperature such as enzymatic reaction, protein de-naturation.

The value of K provides a measure of the interactions between the molecules in multi layers with the adsorbent, and tends to fall between the energy value of the molecules in the monolayer and

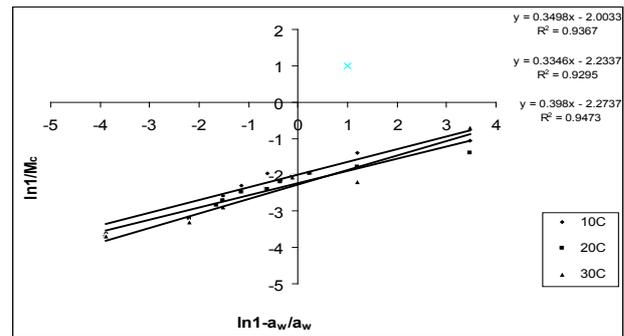


Figure 6. Caurie isotherm plots for moisture uptake at different temperatures

that of liquid water. If K is equal to 1, the multilayer have properties of bulk water, and the sorption behavior could be modeled by the BET equation. In this work the values of K did not show any particular trend but its variation showed the trend just opposite to that exhibited by M₀. In addition, it can be seen that values of K also exceeds unity at 10 and 30°C. In fact, there are various reports in which K values of particular food products have been found to be more than unity (Park *et al.*, 2002). Thus, it may be concluded that for carrageenan, GAB parameters do not show conventional temperature dependent behavior. The Halsey and the Oswin isotherm models were also applied on the equilibrium moisture uptake data, but they showed poor fitness.

Properties of bound water

The physical state of water adsorbed by foods actually determines the actual spoilage (Raji and Ojediran, 2011). It is therefore essential to generate information related to various aspects of bound water viz its density, its relation to surface area of adsorbent, number of adsorbed monolayer etc. In order to evaluate various parameters, describing the properties of sorbed water, Caurie equation was employed, as shown below (Caurie, 1970).

$$\ln 1/M = -\ln(CM_0) + 2C/M_0 \ln(1-a_w)/a_w \quad \dots (7)$$

The equilibrium moisture uptake data was applied on Eq. (9) and ln1/M values were plotted against ln(1-a_w)/a_w values to obtain linear plots as shown in Figure 6. The slopes obtained, usually called Caurie slope, were used to evaluate surface area A (m²g⁻¹) using following expression (Cervenka *et al.*, 2008).

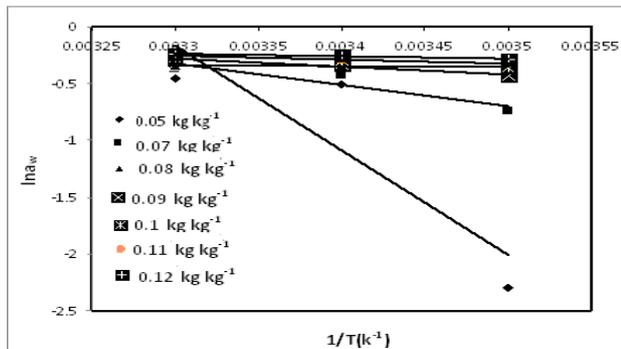
$$A = 54.45/S \quad \dots (8)$$

The number of adsorbed monolayer, N, was obtained by the formula

$$S = 2/N \quad \dots (9)$$

Table 4. Properties of sorbed water on carrageenan at different temperatures

Temperature (°C)	Monolayer moisture content (g/100 g dry Solid)	Caurislope (S)	No of adsorbed monolayer(N)	Density of adsorbed water(C)	Surface area (m ² g ⁻¹)
10	6.515	0.364	5.730	1.137	156.16
20	7.743	0.189	5.988	1.248	163.17
30	6.984	0.116	5.025	1.389	136.91

Figure 7. $\ln a_w$ versus $1/T$ plots for evaluation of q_{st}

Where S is cauries slope.

Density of bound water is represented by C in Cauries equation and percent bound water or non-freezable water is the product of monolayer moisture content M_0 and number of adsorbed monolayer N (Jayendra *et al.*, 2005). All the related parameters are given in Table-IV.

The surface area of some polysaccharides was determined (Robitzer *et al.*, 2011); 200 m²g⁻¹ for kappa Carrageenan, 330 m²g⁻¹ for Chitosan from β -chitin, 390 m²g⁻¹ for Alginic acid, 570 m²g⁻¹ for Calcium alginate, 485 m²g⁻¹ for pectin, 320 m²g⁻¹ for Agar, etc. It can be seen the values obtained in the present study are much less, but there is little agreement with the surface area value obtained for kappa carrageenan. It is reported that large surface area of biopolymers is due to existence of intrinsic micro porous structures in the material. It appears that the kappa carrageenan does not exhibit porosity largely.

Isosteric heat of sorption and entropy of sorption

The net isosteric heat of sorption (ΔH) is the amount of energy by which the heat of vaporization of moisture in a product exceeds the latent heat of pure water (Labuja, 1984). It is related with the total heat of sorption and enthalpy of vaporization ΔH_v by following relation:

$$Q_{st} = \Delta H + \Delta H_v$$

The net isosteric heat of sorption can be determined by the Clausius-Clayperon equation (Phomkong *et al.*, 2006).

$$\partial \ln a_w / \partial T = \Delta H / RT^2 \quad \dots (10)$$

Where a_w is the water activity, T is the absolute temperature, R is gas constant (8.314 J/mol/K) and ΔH is the isosteric heat of sorption (kJ/mol). Integration of Eq. (10) with the presumption that ΔH is independent of temperature gives the Eq. (11) as below :

$$\ln a_w = -[\Delta H / R].1/T + C \quad \dots (11)$$

Where C is the intercept of Eq. (11). The value of ΔH is computed from slope of Eq. (11) and now following relationship is used (Tunc and Duman, 2007).

$$\Delta G = \Delta H - T \Delta S \quad \dots (12)$$

Where ΔG is the Gibbs free energy change (J/mol), and ΔS (J/mol/K) is differential entropy of sorption. For moisture sorption process we can write

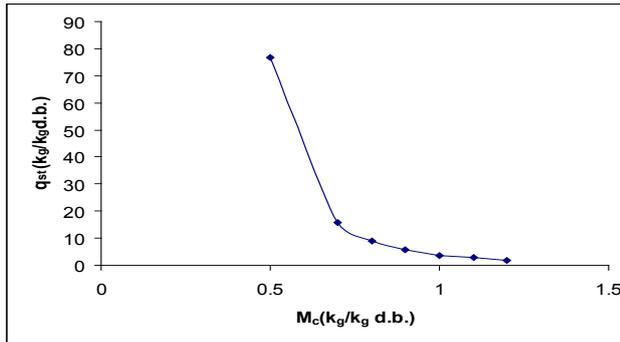
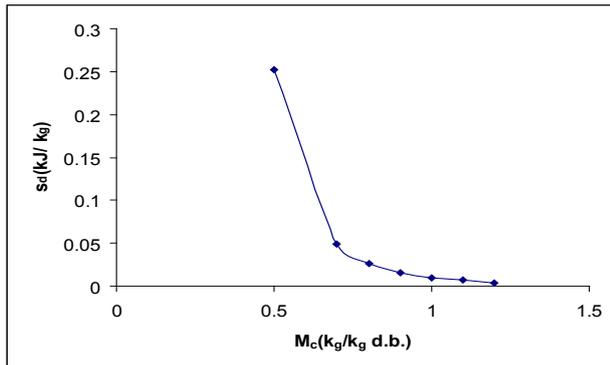
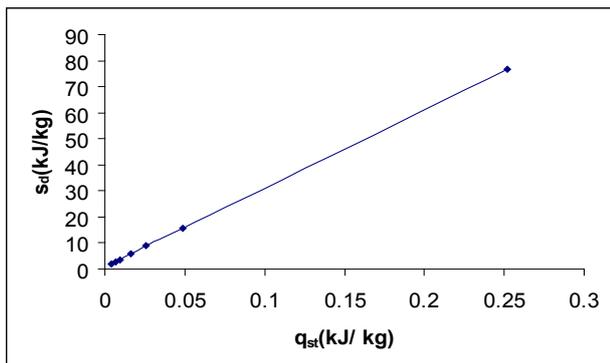
$$\Delta G = -RT (\ln a_w) \quad \dots (13)$$

On substituting value from Eq. (13) in Eq. (12) we may write

$$(\ln a_w) = [\Delta H / R].1/T + \Delta S / R \quad \dots (14)$$

Now plot of $\ln a_w$ against $1/T$ yields a straight line with a slope of $(\Delta H / R)$ and intercept of $\Delta S / R$. Using the slope and intercept, the values of ΔH and ΔS are evaluated. Figure 7 shows $\ln a_w$ versus $1/T$ plots for evaluation of these parameters.

Figure 8 shows the variation in net isosteric heat of sorption ΔH with moisture contents. It is obvious that ΔH shows a negative dependence on EMC. This decrease can be qualitatively explained by the fact that when moisture content is quite low, the sorption occurs at the most active sites, giving rise to the greatest interaction energy. This results in higher values of q_{st} at low moisture contents. However, as the moisture content increases, the number of active sites available for water vapor sorption decreases, thus resulting in lower ΔH values. As the isosteric heat of sorption tends to zero, the influence of the adsorbent on the adsorbed molecules becomes negligible i.e. additional sorbed water molecules represent so called

Figure 8. Variation of q_{st} with moisture contentFigure 9. Variation of differential entropy absorption S_d with moisture contentFigure 10. S_d versus q_{st} plot to test the compensation theory

'free water' available for micro organisms. The total heat of sorption (i.e. Q_{st}) is useful for estimating the energy requirement for water removal during the drying process.

Finally, the ΔS values obtained at the three experimental temperatures were plotted against respective moisture content experimental temperature and the results, as shown by the net isosteric heat of sorption (ΔH) as shown in Figure 9. Similar types of results have also been shown elsewhere (Gaula *et al.*, 2008).

Entropy – enthalpy compensation theory

The compensation theory suggests a linear relationship between the net isosteric heat of sorption (ΔH) and differential entropy of sorption (ΔS) for given range of moisture content (Moyano and

Zuniga, 2004) :

$$\Delta H = T_{\beta} \Delta S + \alpha \quad \dots (15)$$

The isokinetic temperature (T_{β}) and constant (α) were calculated using linear regressions. The parameter T_{β} represents the slope of linear function between ΔH and ΔS . T_{β} is the isokinetic temperature with an important physical meaning as it represents the temperature at which all reactions in the series proceed at the same rate and α is a constant (Madamba *et al.*, 1966). Figure 10 shows a linear plot between ΔH and ΔS with a high regression of 0.999, thus indicating suitability of the compensation theory. The slope of the linear plot yielded the isokinetic temperature T_{β} that came out to be 301.7 K.

In order to corroborate the compensation theory a statistical analysis test was proposed by Krug *et al.* (Krug *et al.*, 1976). The harmonic mean temperature (T_{hm}) was given as follows:

$$T_{hm} = n / \sum (1/T) \quad \dots (16)$$

The compensation theory only applies $T_{\beta} \neq T_{hm}$. If $T_{\beta} > T_{hm}$ the moisture sorption process is enthalpy driven, while if $T_{\beta} < T_{hm}$ the process is considered to be entropy controlled. The T_{hm} was calculated to be 292.8 K. Now, in the present work, $T_{\beta} > T_{hm}$, thus suggesting that moisture sorption process is enthalpy driven.

Conclusion

It can be concluded from this work that adsorption isotherms of carrageenan were typical Type – II sigmoidal shape. The equilibrium moisture content was found to decrease with temperature at constant water activity with a crossover behavior in the region-III of isotherm. The EMC data was best interpreted in terms of GAB isotherm model. The monolayer moisture content M_0 showed unusual trend with temperature. The ΔH and ΔS were calculated using Clausius – Clapeyron equation and showed negative dependence on moisture contents. The enthalpy-entropy compensation theory could be successfully applied on moisture sorption onto carrageenan and the process was enthalpy driven.

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