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Investigation of moisture sorption behavior of soluble sodium caseinate

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Abstract

Casein is a potential food protein, used in a number of food applications. In this work, moisture sorption isotherms of casein were determined at 10, 20 and 30°C under different relative humidity in the range of 12 to 98% using gravimetric method. The equilibrium moisture uptake data were interpreted with the help of three well-known sorption isotherm models namely, (GAB, Halsey and Oswin models) using non-linear least square method. The experimental moisture uptake data were best interpreted by GAB model. The monolayer moisture content Xm was found to vary from 54.08 x 10-3 to 10.48 x10-3 kg kg^{-1} (db) for a temperature rise from 10 to 30°C, thus indicating negative temperature dependence. The Clausius-Clapeyron equation was used to determine the isosteric heat of sorption (qst). The uptake data was also used to determine isokinetic temperature Tβ (315.9 K) and harmonic mean temperature Thm (292.8 K). The enthalpy-entropy compensation theory indicated that moisture sorption process was enthalpy driven.

Key words: GAB model, Beta casein, Isosteric heat of sorption, Oswin, Enthalpy

Introduction

Casein is a major milk protein and it accounts for almost 80% of the total protein contents of milk (Silva et al., 2005). This major protein product is used as a food additive in dairy, dietary and baby foods (Aneja et al., 2002). Because of a wide range of applications, last two decades have witnessed sincere efforts in manufacturing of food and pharmaceutical grade casein. In fact, production of dried casein powder has been recognized as a significant part of dairy industry.

It has been reported that by the year 2011 the annual casein/cheese production in India might have reached to 1.23 billion US$ by the year 2011, (Gupta, 2007). Such a large scale production of casein has imposed serious challenges on the manufacturing units for its safe and moisture–free production as well as storage, particularly in the seasons when there is enough moisture in the environment. The presence of a large number of polar groups, in casein also acts as a driving force for absorption of water vapors. In general, dehydrated protein powders have atendency to absorb moisture at moderate and high water activities thus resulting in protein insolubility and enhanced flavor deterioration. Thus, it is necessary to predict the exchange of moisture between food materials and surroundings because it affects the physicochemical properties, drying process, storage capacity and microbial safety (Rangel-Marron et al., 2011). The adsorption of moisture by foods can be defined as a process in which there is reversible and progressive combination of water with the food solids via a number of sorptive processes such as chemisorptions, physical adsorption, and multilayer condensation The term Equilibrium Moisture Content (EMC) is usually regarded as the water content of food stuff when its vapor pressure equals that of the surroundings. The quantitative relation between EMC and the water activities at any temperature is quantified in the form of moisture sorption isotherms. A correlation between EMC and corresponding water activities has been described by a number of isotherm models (Van Den Berg et al., 1981). Some of the models also consider the effect of temperature. In addition to applications in food engineering, the sorption isotherms of a food product play significant role in are product and process

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development (Delgando et al., 2002). The water activities greately influence the deteriorative mechanisms in food system and therefore for longer storage stability it is desirable to make water activity modifications. The storage and packaging problems can be better handled by evaluating thermodynamic parameters of water sorbed (Maltini, 2003; Acosta-Esquijarosa et al., 2011). In addition, these parameters are also helpful in appraising the shelf life of food product under varying product, package and environment interactions.

In spite of the fact that casein has potential applications in field of food and nutrition, its hydrophilicity and stickiness create problems during its production, drying and storage and applications. This also affects its shelf life storage capacity. However, there are a few studies that have attempted to investigate its moisture absorption behavior. In a study (Mauer et al., 2000), β-casein was isolated and its sorption isotherms were determined at +4°C and +22.5°C. The isotherms were further determined after 9 months of storage at -29°C and +22.5°C. The results indicated that storage temperature had varying effect on moisture sorption isotherms.; however, at any aw differences in moisture content were small (< 0.03g H2O/g solids at high aw). β-casein stored at -29°C had lower mo . The production of casein and its associated products from buffalo milk has been adopted as very popular small scale industry in most of the parts of India where there is huge production of milk. Therefore it is required to study the moisture absorption tendency of casein under the Indian climatic conditions so as to provide some useful basic information to the manufacturers.

With these objectives this work was undertaken to study the water vapor sorption behavior of casein at different temperatures and to make a quantitative interpretation of the data using suitable isotherm models. The sorption data has been used to determine various thermodynamic parameters also.

Experimental

Materials

The milk protein casein (in soluble form as sodium caseinate, product code No. 4-2628, mol. wt 23000) was purchased from Hi Media Chemicals, Mumbai, India. The relative constant humidity environments were created by using saturated solutions of various salts i.e. KOH, CH_3COOK, K_2CO_3, $Mg(NO_3)_2$, NaCl, KCl and K_2SO_4. These salts were purchased from Merck Chemicals, Mumbai, India and were analytical grade. The whole study was carried out with double distilled water.

Water activities (a_w) of saturated solutions of the above salts at 10, 20 and 30°C were adopted from Labuza (1984) and are given in Table 1 (Ramesh, 2003).

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

Salt	aw at 10°C	aw at 20°C	aw at 30°C
KOH	0.1234	0.0932	0.0738
CH_3COOK	0.2338	0.2311	0.2161
K_2CO_3	0.4314	0.4316	0.4317
$Mg(NO_3)_2$	0.5736	0.5438	0.5140
NaCl	0.7567	0.7547	0.7509
KCl	0.8677	0.8511	0.8362
K_2SO_4	0.9818	0.9759	0.9700

Study of moisture sorption isotherms

The accurately pre-weighed casein samples, in triplicate, were weighed in small crucibles of aluminium foils and then placed in the desiccators. This desiccator had various saturated salt solution to provide the required relative humidity environment. The desiccators were placed in temperature-controlled cabinets maintained at 10, 20 and 30°C (±1°C). The reason for selection of the given temperature was that the room temperature normally falls between 20 and 30°C in Asia subcontinent countries like India. In addition, the preservation of casein under low temperature conditions justifies 10°C as the lower temperature selected. The pre-weighed casein powder samples were placed in different desiccators till they all attained equilibrium weight which was indicated by the fact that there was no measurable weight change (±0.001g). The equilibrium moisture absorption was attained in almost twelve days. The weight gain was recorded every day. It took almost 30 s to remove, weigh, and then put back the samples into desiccators finally, the moisture content of each sample was determined by hot air oven drying method (AOAC, 1984). All measurements were made in triplicate and the average values were used in the analysis.

Sorption isotherm models

In this study, the EMC data was analyzed using four ‘two parameters models’ i.e. the Oswin, the Henderson, the Cauri, Halsey models and one ‘three parameters model’ namely the GAB model. All these models along with related parameters are given in the Table 2. The two parameter models, viz., Halsey Henderson, Cauri and Oswin, in their linear form, were used for the determination of related constants with the help of linear regression program. However, a non-linear least square procedure was applied to determine constants for three-parameter GAB model. It is often more convenient to re-arrange GAB equation into a second degree polynomial equation.

$$\frac{\mathbf{a}_w}{\mathbf{M}} = \alpha \mathbf{a}_w^2 + \beta \mathbf{a}_w + \gamma \qquad .....(1)$$

where

$$\alpha = \frac{k}{M_o}\left[\frac{1}{C-1}\right] \qquad ....(2)$$

$$\beta = \frac{1}{M_o}\left[1 - \frac{2}{C}\right] \qquad ....(3)$$

And $$\gamma = \frac{1}{M_o Ck} \qquad ...(4)$$

A non-linear regression analysis of a_w/M versus a_w gives a second order polynomial. The coefficients α, β and γ were thus obtained from this polynomial equation and substituted one by one to obtain GAB constants M_o, C and k, where M_o is the moisture content when all primary sites are occupied by single water molecules, C is the Guggenheim constant and k is the factor comparing the properties of multilayer water molecules as compared to the bulk liquid.

The mean relative deviation modulus (P) and the standard error of estimate (SE) were used as error functions to access the accuracy of fitness of different models.

Modeling isotherm models

The equilibrium moisture uptake data of Casein samples, at three temperatures, namely 10, 20 and 30°C, were fitted to various isotherm models displayed in Table II. The parameters of the GAB sorption model were calculated using non-linear regression analysis whereas other models were applied in linearized forms to evaluate associated parameters. Two criteria namely mean relative deviation modulus (P) and the standard error of estimate (SE) were used to evaluate the fitness of sorption models to the experimental data.

$$P = \frac{100}{N}\sum_{i=1}^{N}\frac{|M_{ex} - M_{pr}|}{M_{ex}} \qquad ...(5)$$

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

Table 2. Sorption isotherm models used in this study.

Name of model	Equation	Reference
GAB (Guggenheim-Anderson-de Boer)	$M = \frac{M_0Ck.a_w}{(1-ka_w)(1-ka_w+cka_w)}$	(Anderson, 1946)
Halsey (Linearized)	$a_w = \exp\left(\frac{-A1}{M^{A2}}\right)$ $\text{In } M = \text{In}A_1 + A_2 \text{ In } (-\text{In } a_w)$	(Halsey, 1948)
Oswin (linearized)	$M = A\left(\frac{a_w}{1-a_w}\right)^B$ $\text{In } M = \text{In } A + B \text{ In } \frac{a_w}{1-a_w}$	(Oswin, 1946)
Henderson (Linearized)	$\text{Log } [-\text{In } (1-a_w)] = n \log M_c + \log K$	(Henderson, 1952)
Caurie	$\ln\frac{1}{m} = -\ln(CM_0) + \frac{2C}{M_0}\ln\frac{1-a_w}{a_w}$	(Caurie, 1970)

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. The P value of less than 10 percent indicates acceptability of the model (Arslan et al., 2006). A model is said to be best fit if SE and P exhibit lowest values for it while the regression coefficient (R^2) has highest value.

The temperature dependency of GAB parameters C and K can be expressed by Arrheniutype equation (Goula et al., 2008).

$$C = C_o \exp[\, \Delta H_c/RT \,] \qquad \ldots(7)$$

And

$$K = K_o \exp\left[\frac{\Delta Hk}{RT}\right] \qquad \ldots(8)$$

Here, ΔH and ΔK are functions of heat of sorption of water; and C_0 and K_0 are the adjustable constants for the temperature effect.

Monolayer moisture contents M_o, calculated using GAB isotherm model was used to calculate solid surface area S of the sample (Zareiforoush et al., 2009) using following expression.

$$s = \frac{M_0 N_A A_m}{M_{H_2o}} = 3.5\times10^3 M_o \qquad \ldots(9)$$

Where, S is the solid surface area ($m^2 g^{-1}$ dry solids); M_o is the monolayer moisture content (kg water kg^{-1} dry solid); M_{H2O} is the molecular weight of water (18 $9mol^{-1}$), N_A is Avogadro number ($6.023x10^{23}$ molecules mol^{-1}), and A_m is the area of a water molecule ($1.06x^{-19}$ m^2).

The number of adsorbed monolayer was calculated using the formula

$$S=2/N \qquad \ldots (10)$$

Where, S is cauries slope. In Cauris equation, C represents density of bound water whereas the product of monolayer moisture content M_0 and number of adsorbed monolayers N gives the percent bound or non-freezable water (Jayendra Kumar et al., 2005).

Isosteric heat of sorption and entropy of sorption

The net isosteric heat of sorption (q_{st}) is defined as the amount of energy by which the heat of vaporization of moisture in a product exceeds the latent heat of pure water (Labuza, 1968). The differential entropy of sorption (s_d) is proportional to the number of available sorption sites at a specific energy level. For a thermodynamic system, the net isosteric heat (q_{st}) and the differential entropy of sorption (s_d) are related as (Rosa et al., 2010):

$$\text{In } a_w = -\frac{q_{st}}{RT} + \frac{S_d}{R} \qquad \ldots (11)$$

Where, q_{st}, S_d, and R are expressed as $kJmol^{-1}$, $kJmol^{-1}K^{-1}$ and kJ mol^{-1} K^{-1}, respectively.

For a given range of EMC, corresponding water activities were calculated and the linear plots, obtained between In a_w and I/T were used to calculated q_{st}, and S_d, with the help of slope and intercept respectively.

Entropy – enthalpy compensation theory

According to the compensation theory, there is linear relationship between the net isosteric heat of sorption (q_{st}) and differential entropy of sorption (S_d,) for given moisture content range (Igathinathane et al., 2007):

$$q_{st} = T_\beta S_d + \alpha \qquad \ldots(12)$$

The linear regression analysis enables us to calculate isokinetic temperature T_β and constant α. The parameter T_β is obtained from the slope of linear plot between q_{st} and S_d. 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., 1996). In order to corroborate the compensation theory, Gabas et al. (2000) proposed statistical analysis test to corroborate the compensation theory. The harmonic mean temperature (T_{hm}) was given as follows:

$$T_{hm} = \frac{n}{\Sigma_1^n (1/T)} \qquad \ldots(13)$$

The compensation theory only applies $T_\beta \neq T_{hm}$. The moisture uptake process is enthalpy driven or entropy controlled as per condition that $T_\beta > T_{hm}$ or $T_\beta > T_{hm}$ (Igathinathane et al., 2007).

Results and Discussion

Moisture sorption isotherm

The moisture sorption isotherms for soluble casein (SC) at 10, 20 and 30°C are depicted in Figure 1. It is clear that the EMC increases with water activity at constant temperature. The isotherms exhibit sigmoidal shaped curves, thus indicating a Type – II isotherm (Brunauer et al., 1940), which is characteristic for most of the foods. A close look at the isotherms reveals some interesting results. Firstly, the isotherms obtained at 10 and 20^{o}C exhibit a S-shaped curve while the isotherm obtained at 30^{o}C show a little different behavior with a cross-over at the water activity of 0.8. The observed findings could be explained as below:

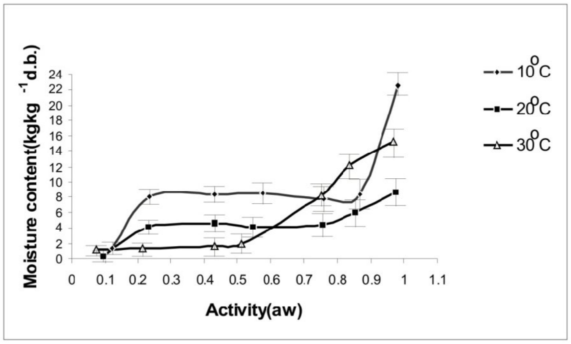

Figure 1. Moisture uptake as a function of water activity at different temperature.

It is commonly observed that moisture sorption isotherm consists of three zones. Here, in the isotherms obtained at 10 and 20°C, three zones can be noted; zone – I (aw: 0.0 to 0.2), zone – II (aw; 0.2 to 0.7) and finally zone – III (aw: 0.7 to 1.0) In the region I (termed as monolayer sorption region), the EMC increases with water activity due to the fact that casein contains a large number of polar groups along the macromolecular chains. These groups act as strong binding sites for incoming water vapor molecules. In addition, according to Falade et al. (2004), there is possibility of swelling or unfolding of protein chains thus offering new active sites for binding of water molecules. The zone – II, also termed as multilayer sorption region, consists of multilayer moisture which is under transition to natural properties of free water and is available for chemical reactions. In this zone, there is linear increase in moisture content with water activity but relatively at a slower rate as compared to the rate observed in the zone-I. In this zone, sorption takes place at less active sites. Finally, in the zone – III (usually termed as capillary condensation zone) there is sharp increase in EMC which may be attributable to diffusion of moisture into voids and capillaries. The water in this zone is in the free state. A close look at the two isotherms reveals that there is more moisture uptake at the later stages of the curves. The sharp rise in EMC is also attributable to partial dissolution of casein. Here, it is also noteworthy that for a given water activity, the EMC shows negative temperature dependence. This may simply be due to the fact that as the temperature is increased from 10 to 200C, vapor molecules gain more kinetic energy and this prevents them from binding at available sorption sites.

The isotherm behavior, exhibited at 30°C, appears to be a little different. There is gradual water absorption in linear fashion till the water activity reaches a value of nearly 0.6. However, a drastic increase in EMC is observed as the water activity of the surrounding environment exceeds 0.6. In addition, a crossover is also observed. This could probably be due to dissolution of casein at 30^{o}C beyond the water activity of 0.6. Such as intersection or cross-over behavior has also been reported for moisture sorption by dry powder (Hassan, 2004), basundi mix (Sharma et al., 2009), gingerbread (Cervenka et al., 2008) etc. Overall, all the three curves showed continuity.

Fitting of isotherm models

The experimental data on moisture sorption was fitted to various isotherm models given in Table 2. The estimated parameters and various error functions for selected isotherm models in the water activity and temperature range studied are given in Table 3. A close look at the values of error functions P, and SE indicate that out of various isotherm models applied, the GAB isotherm model appears to fit best on the equilibrium moisture uptake data. The best quantitative interpretation of the moisture uptake data by the GAB model was almost expected because it is a semi-theoretical, multi molecular, localized homogenous adsorption model. It is also reported frequently that GAB is the most versatile sorption model available (Ayrarci et al., 2005).

The treatment of sorption data, according to GAB model, allows us to evaluate monolayer moisture content value M_o of foods. The M_o value represents the moisture content of a material when its entire surface is fully covered with a uni molecular layer of water vapor molecules (Sawhney et al., 2011). The significance of M_o values is that deterioration of foods is very small below M_o. because the reason is that water is strongly bound to the food below M_o and does not take part in any deteriorative reactions either as solvent or as one of the substrates. Therefore, at a given temperature the water activity level corresponding to M_o or less is the safest one. The values of M_o, in this work, were found to be 5.40, 3.34 and 1.04 g/100g solid at 10, 20 and 30^{o}C respectively. The M_o values reported for dried acid casein from buffalo skim milk are reported to be 5.60, 4.70 and 4.54 g/100g solid at 25, 35 and 45^{o}C respectively. Similarly, the moisture contents for soy protein, as reported by Cassini et al. (2006) at 10, 20 and 30^o were 7.40, 6.40 and 5.50 g/100g db respectively. The overall assessment of all these values reveals that in the temperature range of 45 to 10^{o}C, the moisture uptake of food proteins falls in the range of 1.0 to 8.0g/100g dry basis. The observed decrease in moisture content with temperature range mentioned above may be due to reduction in number of active sites for water binding because of folding of macromolecular chains , thus causing a decrease in the number of active binding sites exposed (Ariahu et al., 2006). However this reasoning does not seem to be justified in the present study as the temperature range selected was 10 to 30°C. Also, there is another possibility that as the temperature is raised, there is increase in kinetic energy of water vapor molecules and this makes them less stable, thereby, favoring their departure from the binding sites of food material (Tunc et al., 2007). Finally, this causes the monolayer moisture content to decrease. The negative temperature dependency of EMC is well known phenomenon and reported by a large number of workers.

It has been observed that strong adsorbent – adsorbate interactions, is exothermic in nature and is favored at lower temperature. These results in an increase in parameter C when temperature is lowered (Diosady et al., 1996). This behavior is also in agreement with above equation (7) that suggests negative temperature dependency of C. A quite compatible behavior is also found in this study; increasing temperature from 10 to 30^{o}C caused by decrease in C value from 507.9 to 66.0 From a study of 30 different foods, Iglesias et al. (2008) reported that in 74% of them, C did not show negative temperature dependence. They suggested that there could be some irreversible changes associated with increasing temperature such as enzymatic reaction, protein de-naturation. However, in this study a change of temperature from 10 to 30°C is not sufficient to cause denaturation of casein in this work. Finally, as the values obtained are >2, the isotherms could be classified as type II as already mentioned earlier. Similar observations are reported elsewhere (Farahnaky et al., 2009).

The interactions between the molecules in multi layers and the adsorbent are interpreted in terms of value of K. When K is unity, the properties of multi-layer resemble with those of bulk water, and under this situation the BET isotherm model can well interpret the sorption process. However, in this study, the values of K, displayed in Table 3, are less than unity except that obtained at 30°C.

Finally, the specific surface area enables us to determine the water binding properties of particulate materials. In order to determine surface area, the monolayer moisture content values (M_o), obtained from GAB isotherm model, were put in equation (9). The values of S were found to be 189.2, 110.5 and 35.1 m^2g^{-1} for the equilibrium sorption temperatures of 10, 20 and 30°C, respectively. It is clear that specific surface area decreases with temperature, which may be attributed to the decrease in the number of active sorption sites available (Rizvi et al., 1983).

Properties of bound water

The spoilage of food stuff is usually governed by the physical state of water absorbed by them (Van den Berg et al., 1981). Hence, it is necessary to determine various characteristics of bound water such as its density, its relation to surface area of adsorbent, number of adsorbed monolayers etc. All the parameters describing the property of sorbed water are shown in Table 4. The data reveals that density of water, percent of bound or unfreezable water, monolayer moisture content and specific surface area of sorbent decrease with increase in temperature. The observed decrease is simply attributable to the increase in the kinetic energy of water molecules, thus resulting in a decrease in the percent bound water, monolayer moisture content and density of water.

Net Isosteric heat of adsorption (qst) and differential entropy (sd)

The isosteric heat of adsorption can be determined by the use of Clausius-Clapeyron equation, provided the isotherm data is available at two or more temperatures. The isosteric heat of sorption varies with the amount of water sorbed by the substrate. In this work, the In a_w versus 1/T plots were obtaining for various moisture contents using the equilibrium moisture uptake data obtained at different temperature (shown in Figure 1). The slopes and the intercepts of linear plots, as shown in Figure 2, were used to evaluate q_{st} and S_d respectively. As the slopes obtained are linear, it may be concluded that the heat of sorption is independent of temperature for different values of EMC.

Table 3. Parameters obtained for various isotherm models.

Model	Constants	Temperature (^{0}C)		
		10	20	30
GAB	Mo	5.40	3.34	1.04
	C	507.964	477.354	66.0393
	K	0.78613	0.5368	1.02667
	SE	0.5213	0.4187	0.3217
	P	3.4813	4.6143	5.1305
	r^2	0.9736	0.9711	0.7884
Halsey	A1	0.07371	0.04212	0.0237
	A2	-0.22	-0.1849	-0.5847
	SE	1.6783	0.9917	2.3154
	P	8.6189	9.2785	11.5680
	r^2	0.774	0.8667	0.5311
Oswin	A	0.08579	0.0475	0.0282
	B	0.1901	0.1856	0.8666
	SE	3.6023	2.1765	1.7436
	P	7.3542	6.6076	5.2258
	r^2	0.4284	0.7054	0.8622
Henderson	N	0.0291	0.0175	0.0056
	K	0.491	0.183	0.091
	SE	3.6002	1.2487	1.6321
	P	10.6548	8.2416	9.3581
	r^2	0.827	0.727	0.870
Cauri	M_o	8.18	6.67	2.25
	C	0.560	0.964	0.973
	SE	2.3126	3.1763	1.9457
	P	9.5682	7.3785	8.1793
	r^2	0.884	0.843	0.822

Table 4. Properties of sorbed water of casein at different temperatures.

Temperature (^{0}C)	Monolayer moisture content (g/100g dry solid) M_0	Cauri slope S	No.of adsorbed monolayer N	Density of sorbed water C	Bound water %	Surface Area m^2g^{-1}
10	5.40	0.364	14.5	0.0926	0.973	186
20	3.34	0.189	6.8	0.0648	0.964	397
30	1.04	0.116	2.3	0.0590	0.560	63

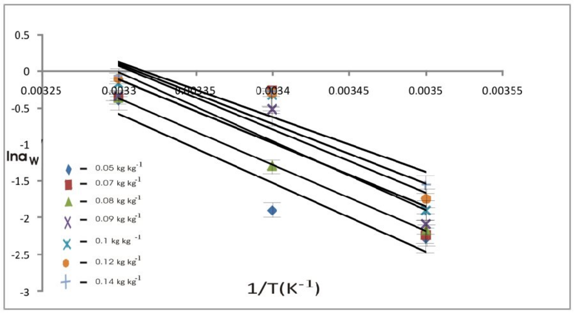

Figure 2. $\ln a_w$ versus 1/T plots for evaluation of qst.

The variation in net isosteric heat of sorption q_{st} with moisture contents is well depicted in Figure 3. It is obvious that q_{st} shows a negative dependence on EMC. This decrease is attributable to the fact that when moisture content is quite low, the water vapors are adsorbed at the most active sites, thus producing highest interaction energy. This results in higher values of q_{st} at fairly low moisture contents. However, with the increase in the moisture content, the number of active sites available for water vapor sorption decreases, and this finally results in lower q_{st} values (Paulo et al., 2010). When the isosteric heat of sorption approaches towards zero, the interaction between the adsorbent and the adsorbed molecules becomes negligible i.e. these water molecules are termed as 'free water' which is available to microorganisms. The energy required for removal of water during the drying process can be estimated form the heat of sorption (i.e.Q_{st}) data.

Finally, the S_d values obtained at the three experimental temperature were plotted against respective moisture content experimental temperature and the results, as shown by the net isosteric heat of sorption (q_{st}) as depicted in Figure 4. Similar types of results have also been shown elsewhere (Goula et al., 2008).

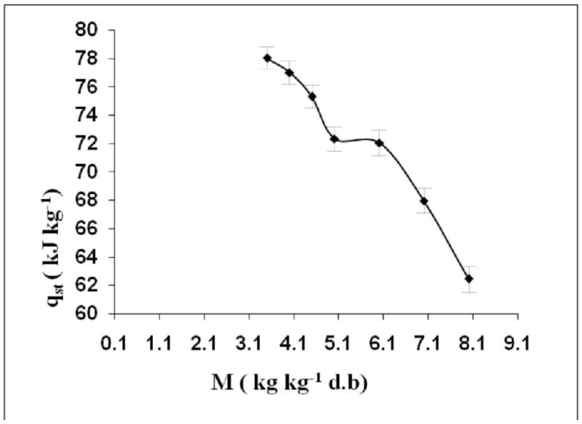

Figure 3. Variation of q_{st} with moisture content.

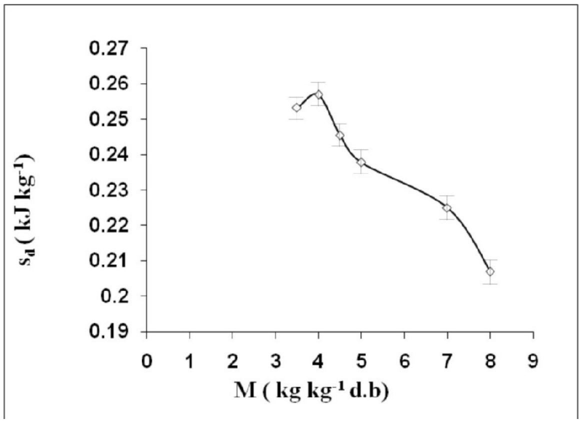

Figure 4. Variation of differential entropy absorption sd with moisture content.

Entropy – Enthalpy compensation theory

The plot of q_{st} versus S_d was observed to exhibit a linear relationship for casein as shown in Figure 5. The value of isokinetic temperature $T_\beta$and constant α were calculated from the linear regression analysis and were found to be 315.9 K and 2.893, respectively ($r^2 = 0.983$). According to Gabas et al. (2000), in order to apply the compensation theory, it is necessary that calculated harmonic mean temperature T_{hm} should differ significantly from T_β. In this work, the value of T_{hm}, obtained using eq. (12) was found to be 292.8 K, which is finitely different from the T_β value.

Finally, as $T_\beta > T_{hm}$, the water vapor sorption onto casein could be said to be enthalpy driven process.

Conclusions

Casein exhibited typical Type-II adsorption isotherms with sigmoidal shape. For a given water activity, the equilibrium moisture content was found to decrease with temperature. The EMC data was best interpreted in terms of GAB isothermal model. The q_{st} and S_d were calculated using Clausius – Clapeyran equation and showed negative dependence on moisture contents. The enthalpy-entropy compensation theory was successfully applied on moisture sorption data obtained for casein. The moisture uptake process was found to be enthalpy driven.

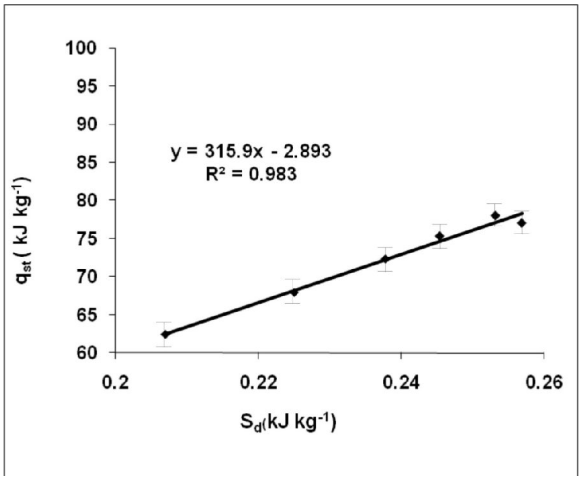

Figure 5. Sd versus q_{st} plot to test the compensation theory.

References

Acosta-Esquijarosa, J., A. Álvarez-Reyes and J. A. González-Lavaut. 2011. Behavior and modelling of humidity isotherms of *Erythroxylum minutifolium* Griseb. leaves. Emir. J. Food Agric. 23(6):511-516.

Al-Muhtaseb, A. H., W. A. M. McMinn and T. R. A. Magee. 2002. Moisture sorption characteristics of food products. Trans J. Chem. E. 80:118-128.

Aneja, R. P., B. N. Mathur, R. C. Chandan and A. K. Banerjee. 2002. Technology of Indian Milk Products, New Delhi, Dairy India Year book Publishers.

AOAC, 1984. Official Methods of Analysis. 10th Edn., Association of Official Analytical Chemists, Washington DC., USA.

Arslan, N. and H. Togrul. 2006. The fitting of various models to water sorption isotherms of tea stored in a chamber under controlled temperature and humidity. J. Stored Prod. Res. 42:112-135.

Ariahu, C. C., S. A. Kaze and C. D. Achem. 2006. Moisture sorption characteristics of tropical fresh water crayfish (*Procam barus* clarkia). J. Food Eng.75:355-363.

Asbi, B. A. and I. C. Bainu. 1986. An equation for fitting moisture sorption isotherms of Food proteins. J. Agric. Food Chem. 34:494–496.

Ayrarci, E. and O. Duman. 2005. Moisture sorption isotherms of cowpea (*Vigna unguiculata* L. Walp) and its protein isolate at 10, 20 and 30°C. J. Food Eng. 70:83-91.

Brunauer, S., L. S. Deming and E. Teller. 1940. On a theory of Vander waals adsorption of gases. J. Am. Chem. Soc. 62:1723-1732.

Cassini, A. S., L. D. F. Marczak and C. P. Z. Norena. 2006. Water adsorption isotherms of texturized soy protein. J. Food Eng. 77:194-199.

Cervenka, L., S. Rezkova and J. Kralovsky. 2008. Moisture adsorption characteristics of ginger bread, a tradition bakery product in Pardubice Czech Republic. J. Food Eng. 84:601-607.

Delgando, A. E. and D. W. Sun. 2002. Desorption isotherms for cooked and cured beef and pork. J. Food Eng. 51:163–170.

Diosady, L. L., S. S. H. Rizvi, W. Cai and D. J. Jagdeo. 1996. Moisture sorption isotherms of canola meals and applications to packaging. J. Food Sci. 61C:204-208.

Falade, K. O. and O. C. Aworh. 2004. Adsorption isotherms of osmo oven dried african star apple (*Chrysophyllum albidum*) and African mango (*Irvingia gabonensis*) slices. Eur. Food Res. Technol. 218:278-283.

Farahnaky, A., S. Ansariand and I. M. Majzoob. 2009. Effect of glycerol the moisture sorption of figs. J. Food Eng. 93:468-473.

Foster, K. D., J. E. Bronlundand Peterson (Tony) A. H. J. 2005. The prediction of moisture sorption isotherms for dairy powders. Internat. Dairy J. 15:411–418.

Gabas, A. L., V. R. N. Telis, P. J. A. Sobral and J. Telis – Romero. 2007. Effect of maltodextrain and Arabic gum in water vapor thermodynamic properties of vacuum dried pineapple pulp powder. J. Food Eng. 82:246-253.

Gabas, A. L., F. C. Menegalli and J. Telis-Romero. 2000. Water sorption enthalpy-entropy compensation based on isotherms of Plumskin and pulp. J. Food Sci. 65(4):680-684.

Goula, A. M., T. D. Karapantsios, D. M. Achilias and K. G. Adamopoulos. 2008. Water sorption isotherms and glass transition temperature of spray dried tomato pulp. J. Food Eng. 85:73-93.

Gupta, S. (Ed.), 2007. Dairy India – 6th edition, New Delhi, Dairy India Year book Publishers

Hassan, B. H. 2004. Moisture sorption characteristics of dried date powder. J. King Saud. Univ. 14(2):105-112.

Igathinathane, C., A. R. Womac, S. Sokhansanj and L. O. Pordesimo. 2007. Moisture sorption thermodynamic properties of corn stover fractions. Am. Soc. Agric. Biol. Eng. 50(6):2151-2160.

Iglesia, H. A., J. Chirife and J. L. Lombardi. 1975. Comparison of water vapour sorption by sugar beet root components. J. Food Technol. 10:385-388.

Jayendra Kumar, A., R. R. B. Singh, A. A. Patiland A. A. Patel. 2005. Effect of temperature on moisture desorption isotherms of kheer. LWT Food Sci. Technol. 38:303–310.

Labuza, T. P. 1984. Moisture Sorption: Practical Aspects of Isotherm Measurement and Use. 150 Seiten, 36 Abb. American Association of Cereal Chemists, St. Paul, Minnesota.

Lewicki, P. 1997. The applicability of the GAB model to food water sorption isotherms. Internat. J. Food Sci. Tech. 32:553-557.

Lomauro, C. J., A. S. Bakshi and T. P. Labuza. 1985. Evaluation of food moisture isotherm equations. Part II: Milk, coffee, tea, nuts, oilseeds, spices, and starchy foods. Lebensmittl-Wissenchaft und Technoloic. 18:118-122.

Maltini, E., D. Torreggiani, E. Venir and G. Bertolo. 2003. Water activity and preservation of plant foods. Food Chem. 82:79-86.

Madamba, P. S., R. H. Driscoll and K. A. Buckle. 1996. Enthalpy- entropy compensation models for sorption and browning of garlic. J. Food Eng. 28:109-119.

Mauer, L. J., D. E. Smith and T. P. Labuza .2000. Effect of water content, temperature and storage on the glass transition, moisture sorption characteristics and stickiness of β-casein. Internat. J. Food Prop. 3:233-248.

Mazza, G. and M. LaMeguer. 1978. Water sorption properties of yellow globe onion (*Alliun cepa* L.). Can. Inst. Food Sci. Tech. J. 11(4):189-193.

Paulo, C. C., A. L. D. Goneli, P. C. A. Junior, G. H. H. de Oliveria and D. S. M. Valente. 2010. Moisture sorption isotherms and isosteric heat of sorption of coffee in different processing levels. Int. J. Food Sci.Technol. 45:2016-2022.

Ramesh, M. N. 2003. Mosin Romans for properties of cooked rice during drying. LWT- Food Sci. Technol. 36:245-255.

Rangel Marron, M., J. Welti-Chanes, A. V. Cordova – Quiroz, J. G. Ceron- Breton, R. M. Ceron-Breton and F. Anguebes – Franseschi. 2011. Estimation of moisture saption isotherms of mango pulp freeze – dried. Int. J. Biol. Biomed. Eng. 1(5):18-23.

Rizvi, S. S. H. and A. L. Benado. 1983. Thermodynamic analysis of drying foods. Food Technol. 2:471-502.

Rosa, G. S., M. A. Moraes and L. L. A. Pinto. 2010. Moisture sorption properties of chitosan. L. W. T- Food. Sci. Technol. 43:415-420.

.Ruszkowska, M., A. Ocieczek and P. Palich. 2008. Sorption features of corn and rice crisps. Acta Agrophys. 11(1):183–193.

Sawhney, I. K., B. C. Sarkarand G. R. Patil. 2011. Moistures sorption characteristics at dried acid casein from buffalo skion milk. LWT- Food Sci. Tech. 44:502-510.

Sharma, P., R. R. B. Singh, A. K. Singh, A. A. Patel and R. R. Patil. 2009. Sorption isotherms and thermodynamics of watar sorption of ready to use Basundi mix. LWT- Food Sci. Technol. 42:445-452.

Silva, S. V. and F. X. Malcata. 2005. Casein as source of bioactive peptides. Int. Dairy J. 15:11-15.

Tsami, E. Z. B. Maroulib, D. Marinos- Kouris and G. D. Saravocas. 1990. Heat of sorption of water in dried fruits. Internat. J. Food Sci. Technol. 25:350-359.

Tunc, S. and O. Duman. 2007. Thermodynamic properties and moisture adsorption isotherms of cottonseed protein isolate and different form of cottonseed samples. J. Food Eng. 81:133-143.

Van Den Berg, C. and S. Bruin. 1981. Water activity and its estimation in food systems: Theoretical aspects. In: L. Rockland and G. F. Stervart (Eds.), pp. 1-64. Water Activity: Influence on Food Quality. Academic Press, New York, NY.

Vishwakarma, R. K., U. S. Shivhare and S. K. Nanda. 2010. Moisutre adsorption isotherms of guar (*Cyamposis tetragonoloba*) grain and guar gum splits. LWT – Food Sci. Tech. 1-7.

Zareiforoush, H., M. H. Komarizadeh and M. R. Alizadeh. 2009. Effect of moisture content on some physical properties of paddy grains. Res. J. App. Sci. Eng. Tech. 1(3):132-139.