Water Adsorption Isotherms and Thermodynamic Analysis of Thai Style Marinated Dried Fish (Pla Sawan)

Yongyut Chalermchat* **and Pinyo Owasit**

Department of Food Engineering, Faculty of Agro-industry, Chiang Mai University, Chiang Mai 50100, Thailand

**Corresponding author. E-mail: ychalermchat@gmail.com*

ABSTRACT

Water sorption isotherms of traditional Thai dried marinated fish (Pla Sawan) were investigated by a standard static gravimetric method. The water activity, ranging from 0.1 to 0.9, was varied using different types of saturated salt solution. The samples were placed in hermetically-sealed jars filled with saturated salt solutions and the equilibrium moisture content of the samples was determined. The experiment was conducted at temperature of 9, 26 and 50°C. Six water sorption models, namely, modified Henderson, modified Chung-Pfost, modified Oswin, modified Halsey, Brunauer-Emmet-Teller (BET) and Guggenheim-Anderson-de Boer (GAB), were fitted to the experimental data. The goodness of fit was determined using statistical criteria, i.e., coefficient of determination, root mean square error, mean relative deviation and plot of residuals. Of the models tested, GAB appeared to give the best fit to the experimental data. Monolayer water content could be estimated and compared with that estimated from BET model. It was found that the value from GAB model was higher than that from BET model. The temperature had no significant effect on the adsorption isotherms but the trend suggested that the temperature increased with decreasing moisture content. The inversion of temperature effect where the temperature positively influenced the moisture content was observed at water activity of 0.85. In addition, thermodynamic analysis was applied to gain knowledge of heat and entropy of adsorption. The best adsorption model was used to predict the equilibrium moisture contents and subsequent predicted values were used to compute thermodynamic functions, i.e., net isosteric heat of adsorption, adsorption entropy, spreading pressure and net integral enthalpy. The results showed that isosteric heat of adsorption decreased exponentially with increasing moisture content. Adsorption entropy decreased sharply with increasing moisture content. The spreading pressure increased with increasing water activity and the temperature significantly affected the spreading pressure. The integral enthalpy decreased linearly with increasing moisture content.

Keywords: Water adsorption isotherms, Dried fish, BET, GAB, Isosteric heat, Enthalpy, Entropy

INTRODUCTION

Fresh water fish is a very common main ingredient in Thai cuisine. Fish can be preserved by several means. Salting and then drying is one of the simplest methods for preservation of fish and most foods (Bellagha et al., 2005). In Thai cooking, other ingredients such as sugar, coriander root, fish sauce, cumin and garlic are added to improve the taste and organoleptic quality of dried fish products. These basic ingredients are commonly found in Thai kitchen and not only can they improve flavors and tastes of the product but they are also capable of inhibiting growth of spoilage microorganisms, leading to longer stability (Wara-Asawapati, 1997). Traditionally, Thai style marinated dried fish can be produced by thoroughly mixing fish fillet with ingredients, leaving the mix for several hours and then sun-drying for 1 day. Normally, the dried product can be either freshly consumed after frying or stored for later consumption. The fried fish can be regarded as low moisture product where they have moisture content less than 7% (wet basis). Moisture in foods can cause deteriorative reactions such as lipid oxidation, color change and microbial growth to occur during long-term storage (Wara-Asawapati, 1997). Therefore, the shelf-life of the product depends upon the moisture content of the finished product and its storage condition. Influence of moisture on the reactions has been described in terms of water activity, a_w (Arslam and Togrul, 2005). Thus, moisture content in the products and their water activity are strongly related. In order to be able to assess and predict the stability of low moisture products, water sorption data thus are of great importance. This approach is now well established in controlling reactions and predicting food stability (Togrul and Arslam, 2007). The water activity in foods is related to equilibrium moisture content via a phenomenon called water sorption isotherms. The isotherms are the greatly important tools for process/equipment design in drying, packaging and storage, for predicting shelf-life and for evaluating the water activity that is the safest for food acceptability (Hossain et al., 2001; Kaymak-Ertekin and Gedik, 2004; Togrul and Arslam, 2007; Goula et al., 2008;). Therefore, knowing water sorption isotherms of traditional Thai dried marinated fish product is of great significance to be helpful for evaluating the keeping quality and packaging requirements at changing humidity storage conditions, for designing of drying process and for extending shelf-life period.

A conventional method to study the moisture sorption isotherms is to equilibrate the samples in the controlled relative humidity environment. This can be conducted by placing the samples over saturated salt solutions filled in insulated sealed jars at a constant temperature. The equilibrium moisture content at the relative humidity ranging 10%-90% is obtained and its correlation with relative humidity (or water activity) is represented in terms of various mathematical equations. These equations are theoretical, semi-empirical and empirical and used to predict the water activity of the foods (Basu et al., 2006). The most widely used equations are modified Henderson equation, modified Chung-Pfost equation, modified Oswin equation, modified Halsey equation, Brunauer-Emmet-Teller (BET) equation and Guggenheim-Anderson-de Boer (GAB) equation (Al-Muhtaseb et al., 2002). Non-linear curve fitting is normally applied to experimental data to estimate the model parameters. Sorption isotherm data can be analyzed using thermodynamic functions including heat of sorption and entropy of sorption. This approach provides knowledge of the energy required in dehydration process as well as the information regarding water properties and sorption kinetics (Al-Muhtaseb et al., 2004a; Shama et al., 2009). The relevant thermodynamic functions are isosteric (or differential) heat of sorption, entropy of sorption and equilibrium (or integral) heat of sorption. Net isosteric heat of sorption represents a measure of the physical, chemical and microbiological stability of food during storage. The net integral enthalpy represents water-solid binding strength. Differential entropy is proportional to the number of available sites at a specific energy level (Arslam and Togrul, 2005). These parameters essentially provide the end-point to which a given amount of water must be removed from foods in order to produce stable products with theoretical minimum energy required (Aviara et al., 2002; Arslam and Togrul, 2005). They also provide a micro-structural view of food and physical interpretation of food-water interactions. Very few papers on the sorption isotherms of fish products have been published. For instance, Bellagha et al., (2005) reported their results on the modeling of sorption isotherms of salted sardine at 40°C. They found that GAB, Oswin and Ratti model were the best to represent the experimental data. Hadrich et al., (2008) investigated the desorption of Tunisian sardine at temperatures of 25, 35 and 50°C. They found that Oswin equation was the best model to fit to the experimental data. Iglesias and Chirife (1995) used GAB and other model equations to fit to the experimental data of food products reported in published papers. The food products included eggs, whey proteins, corns, starches, grains, beef, fish, fruits, vegetables, milk and coffee. They found that GAB exhibited the best model to predict the sorption isotherms.

The objective of this research was to provide new data of the water activity-moisture content relationship in terms of adsorption isotherms in traditional Thai dried, marinated fish product by exploring the appropriate mathematical description. In addition, an effort was made to apply thermodynamic approach to interpret the experimental adsorption data to gain knowledge of the dependence of equilibrium moisture content on heat and entropy of adsorption. This investigation will be useful for the assessment of product stability and dehydration processing design.

MATERIALS AND METHODS

Mathematical models for moisture sorption isotherms

Moisture sorption isotherm is a relationship representing the equilibrium between water activity (or relative humidity of the surrounding) and moisture content of a material at a specified temperature and pressure. According to Brunauer et al., (1940), the sorption isotherms can be categorized into 6 types which almost all of foods fall in type II and III. In these categories, the relationship is generally sigmoid and nonlinear. The six well-known mathematical expressions to describe sorption behavior are summarized in the following section.

Brunauer-Emmet-Teller (BET) equation

The isotherm proposed by BET has been widely used to describe the sorption behavior and gives the best fit for various types of foods over the value of water activity in the range of 0.05-0.45. This two-parameter equation is proposed based on the monolayer adsorption on the surface. The BET model is expressed as

$$\frac{M}{M_0} = \frac{Ca_w}{(1-a_w)[1+(C-1)a_w]} \tag{1}$$

where M is equilibrium moisture content in dry basis (kg water/kg dry solids), M_0 is monolayer moisture content on the internal surface (kg water/kg dry solids), a_w is water activity and C is a parameter related to heat of sorption of monolayer domain.

Modified Oswin equation

Oswin proposed sorption isotherm in the mathematical model as a series of expansion for a sigmoid curve and it is expressed as

$$a_w = \left[\left(\frac{M}{A+BT}\right)^{-C} + 1\right]^{-1} \tag{2}$$

where A, B and C are constants.

Modified Halsey equation

This model describes the condensation of multilayer with the assumption that the potential energy of a molecule varies inversely as the C^{th} power of its distance from the surface. The model was first proposed by Halsey in the exponential form with parameter A and C. Later, the parameter A was analyzed and found to be related to the absolute temperature by empirical exponential function (Basu et al., 2006). The new equation was proposed as

$$a_w = \exp\left[\frac{-\exp(A+BT)}{M^C}\right] \tag{3}$$

where A, B and C are constants. T is absolute temperature (K)

Modified Henderson equation

This equation, first developed by Henderson and later modified by Thomson (Basu et al., 2006), can be applied to many food systems and expressed as

$$a_w = 1-\exp\left[-A(T+B)M^C\right] \tag{4}$$

where A, B and C are constants.

Modified Chung-Pfost equation

This equation was developed based on the relationship between the moisture content of a material and the change in free energy for sorption. It can be expressed as

$$a_w = \exp\left[\frac{-A}{T+C}\exp(-BM)\right] \tag{5}$$

where A, B and C are constants. T is absolute temperature (K).

Guggenheim-Anderson-de Boer (GAB) equation

$$\frac{M}{M_0} = \frac{CKa_w}{(1-Ka_w)(1-Ka_w+CKa_w)} \tag{6}$$

Rearranging Eq. (6) gives

$$\frac{M}{M_0} = \frac{(C-1)Ka_w}{(1-Ka_w+CKa_w)} + \frac{Ka_w}{(1-Ka_w)} \tag{7}$$

where C and K are constants.

Statistical tests

Since all isotherm equations are highly non-linear, the optimal procedure for obtaining the parameters must be performed through nonlinear regression analysis. Three following statistical tests are used to determine the best fitted model: the mean relative deviation (MRD), the root mean square error (RMSE) and the plot of residuals. In general, the low value of MRD and RMSE and random residual plots indicate that the model is acceptable. The definition of the aforementioned statistical quantities can be expressed in the following equations:

$$MRD = \frac{100}{n}\sum_{i=1}^{n}\frac{|M - M_{Cal}|}{M} \tag{8}$$

$$RMSE = \sqrt{\frac{1}{n}\sum_{i=1}^{n}(M - M_{Cal})^2} \tag{9}$$

where M is the experimental value, M_{Cal} is the predicted value, df is the degree of freedom and n is the number of experimental data.

The residuals, defined as ($M - M_{cal}$), will be plotted against the independent variables. This plot reflects the error distribution of the data. Therefore, the correct model is obtained when the distribution of the error around a zero mean is random.

Thermodynamic analysis of sorption isotherm data

Isosteric heat of sorption

The net isosteric heat of sorption (q_{st}) represents the difference between isosteric heat of sorption (Q_{st}) and heat of vaporization of pure water (λ_{vap}) and can be derived from Clausius-Clapeyron equation as

$$-\left[\frac{d\ln a_w}{d(1/T)}\right]_M = \frac{q_{st}}{R} \qquad (10)$$

and

$$q_{st} = Q_{st} - \lambda_{vap} \qquad (11)$$

where R is the universal gas constant. The relationship was established based on two assumptions; (1) heat of vaporization of pure water and excess heat of sorption are independent on the absolute temperature and (2) moisture content of the system is constant. From eq. (11), isosteric heat of sorption can be regarded as the amount of energy required to change unit mass of a product from liquid to vapor at a particular temperature and water activity (Togrul and Arslan, 2007). q_{st} can be determined experimentally by plotting ln a_w against 1/T for a particular value of moisture content. The slope of the regression line thus provides the net isosteric heat of sorption which can be computed directly when the heat of vaporization of pure water at mean temperature is known. This approach requires the measurement of sorption isotherm at more than two temperatures. An empirical expression relating the isosteric heat of sorption to moisture content has been proposed in the form of exponential decay (Goula et al., 2008):

$$q_{st} = q_0 e^{-M/M_c} \qquad (12)$$

where q_o is the net isosteric heat of sorption of the first molecule of water in the food (J/mol), and M_c is the characteristic moisture content of the food (kg/kg dry solids) at which q_{st} reduces by 63%. The values of q_o and M_c can be obtained by fitting Eq. (12) to the q_{st} VS moisture content data.

Sorption entropy

Sorption entropy is proportional to the number of available sorption sites at a specific energy level (Goula et al., 2008). Thermodynamically, heat of sorption is related to the entropy by

$$-\ln a_w = \frac{Q_{st}}{RT} - \frac{\Delta S}{R} \qquad (13)$$

Plotting ln a_w versus $1/T$ and fitting this equation to the data points yields the intercept which is equal to $\Delta S/R$.

Integral enthalpy

The integral enthalpy (q_{eq}) is defined the same way as the net isosteric heat of sorption but at a constant spreading pressure (ϕ) and represents the total energy available to do work,

$$-\left[\frac{d\ln a_w}{d(1/T)}\right]_\phi = \frac{q_{eq}}{R} \tag{14}$$

Spreading pressure

Spreading pressure is the force applied in the plane of the surface that must be exerted perpendicular to each unit length of edge to keep the surface from spreading (Moreira et al., 2008). According to Togrul and Arslan (2007) and Al-Muhtaseb et al., (2004b), the spreading pressure (ϕ) can be calculated from the combination of the Dent model and the integral function described by Iglesias et al., (1976) and can be written as

$$\phi = \frac{K_B T}{A_m}\ln\left[\frac{1+b_0 a_w - b a_w}{1-b a_w}\right] \tag{15}$$

where b_0 and b are constants. K_B is the Boltzman's constant (1.38×10^{-23} J/K) and A_m is the area of the water molecule (1.06×10^{-19} m^2). The values of b_0 and b can be obtained from Dent sorption isotherm,

$$\frac{a_w}{M} = \frac{1}{b_0 M_0} + \frac{b_0 - 2b}{b_0 M_0} a_w - \frac{b(b_0 - b)}{b_0 M_0} a_w^2 \tag{16}$$

using non-linear regression analysis with M_0 obtained from GAB equation. Using b_0 and b from different temperatures, the values of spreading pressure is evaluated.

Raw materials for producing Thai style marinated dried fish

Giant snake head fish was purchased from local market and delivered in frozen state. Prior to processing, the fish was thawed with tab water. Subsequently, its skin and bones were removed, only its fillet was used. The fillet was sliced into strips with a dimension of 2.5 cm in width, 10 cm in length and 3 mm in thickness. The marinated mix was prepared according to a conventional recipe, i.e., 55g fish sauce, 47.5g sesame oil, 46g coconut sugar, 44g crushed garlic, 33.5g dark soy sauce, 30g white sesame, 25g soy sauce, 7g ground coriander seed, 4g ground white pepper and 1.5g ground cumin seed. A kilogram of the fillet was then mixed thoroughly with the marinated sauce for 1 hour. Subsequently the marinated fish was sun-dried for one day and deep-fried in vegetable oil at 180°C until cooked (approximately 4 min).

Experimental setup for adsorption isotherm determination

Sample preparation

The fried marinated dried fish were cut into small pieces and then ground using a blender. Ground samples were spread on a tray and dried at 50°C in a convective oven. The sample layer was stirred periodically to ensure the uniformity of the moisture content. Prior to final moisture content determination, the dried sample was kept in a desiccator for 48 h to allow the moisture to uniformly distribute throughout the sample.

Adsorption isotherm determination

A standard static gravimetric method of sorption isotherm determination was applied at three temperatures, i.e., 9, 26 and 50°C. Five saturated salt solutions were used to generate a controlled relative humidity ranging from 10 to 90% in a hermetically sealed sorption jar. Triplicate samples each of 5 g (±0.001 g) were weighed into small glass bottles and placed on a stand inside a sorption container filled with a saturated salt solution. Small amount of toluene was added to prevent fungal growth during experiment. The saturated salt solutions were prepared according to Bellagha et al., (2005) and are shown in Table 1. The sorption jars were kept in temperature-controlled cabinets whose temperatures were set at 9±1, 26±1 and 50±1°C. Change in sample weight was monitored every week until the equilibrium was reached, i.e., two successive measurements were less than 0.01 g different. The equilibrium moisture content was determined using vacuum oven at 70°C for 6 h.

Table 1. Water activity for selected saturated salt solutions at different temperatures.

Salts	Ratio		aw		
	Sal t (kg)	Water (kg)	50°C	26°C	9°C
LiCl	0.1120	0.0630	0.1124	0.1127	0.1129
$MgCl_2$	0.1000	0.0125	0.3137	0.3257	0.3357
$Mg(NO_3)_2$	0.2250	0.0340	0.4647	0.5242	0.5780
NaCl	0.3000	0.0750	0.7489	0.7532	0.7567
BaCl2	0.3750	0.1050	0.8876	0.9030	0.9157

Parameter estimation by non-linear regression

Model equations were fitted using non-linear regression algorithm performed by a commercial software (Sigmaplot 8.0), employing residual sum of square minimization approach. The best model was selected by considering the values of R^2, RMSE, MRD and the plots of residuals.

RESULTS AND DISCUSSION

Adsorption isotherms of traditional Thai dried marinated fish

The experimental data for adsorption behavior of the dried fish samples at the temperatures of 9, 26 and 50°C are illustrated in Figure 1. In the range of water activity of 0.1 to 0.9, the samples reached equilibrium moisture content ranging from 5 to 55% (dry basis). The isotherms exhibited type III pattern, indicating that the samples held small amount of water at low water activity and large amount of water at high water activity (García-Pérez et al., 2008).

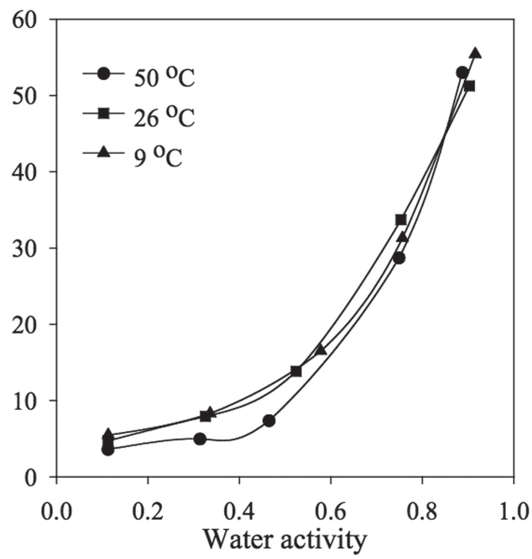

Figure 1. Adsorption isotherms of traditional Thai marinated dried fish at the temperatures of 9, 26 and 50°C.

The equilibrium moisture content increased with an increase in water activity (Figure 1). Statistical analysis showed that the temperature had no significant effect on the equilibrium moisture content. However, the negative relationship between equilibrium moisture content and temperature was exhibited. According to BET theory, the type III isotherm could be observed when the binding energy of the first layer was lower than that between water molecules (Iglesias and Chirife, 1995). Also, the type III isotherm always appeared when salts or sugar were present in the foods. According to BET classification, the isotherm could be divided into 3 regions. The first region was represented by the monolayer water, appearing at very low value of water activity. The second region included multilayer water which was under transition to natural properties of free water (Arslan and Togrul, 2005). The water in region 3 was in free state, held in voids and capillaries (Arslan and Togrul, 2005), which could be seen when moisture content was rapidly increased at high water activity, this is so-called water condensation region. It could be noted that since the minimum value of water activity used in this experiment was 0.11, therefore, it was difficult to conclude that the experimental data followed type III isotherms. In addition, it can be seen from Figure 1 that a clear-cut inversion appeared around the water activity of 0.85 where the positive temperature effect was observed, implying higher moisture content at higher temperature of adsorption. This behavior can be explained according to Shamar et al., (2009) and Labuza and Altunakar (2007) that at low water activity, protein adsorbed more water than sugar and other soluble components whereas at higher water activity, sugars and soluble components adsorbed more water, thereby overcoming the negative temperature effect due to an increase in solubility of sugars in water.

Fitting of the sorption models to experimental adsorption data

Six sorption models were selected to fit the experimental data. Parameters in the models were estimated using non-linear regression analysis and statistical criteria were adopted in order to decide for the best model. The values of the model parameters and the statistical standards are listed in Table 2. It can be seen that GAB model gave the best fit to the experimental data for the whole range of water activity investigated in this experiment since it provided (for temperature of 9, 26 and 50°C, respectively) the highest value of R^2 (0.9955, 0.9917 and 0.9954) and lowest values in RMSE (0.0187, 0.0161 and 0.0131) and a random plot of residuals was observed. GAB model was slightly better fitted to the data than modified Halsey model. Clearly, BET isotherm was inadequate to fit the experimental data for all values of water activity, neither was the rest of the models applied. GAB and modified Halsey models could describe the adsorption behavior since they represented multilayer of water molecules adsorbed on the available active sites for adsorption.

The parameters from GAB and BET equations gave the physical insight of the adsorption, for instance, M_0, which was referred to as monolayer moisture content. From Table 2, M_0 obtained from GAB model was higher than that from BET model. However, the value of M_0 from BET model was in a good agreement with the results obtained in literature (Al-Muhtaseb et al., 2004b; Arslan and Togrul, 2005; Bellagha et al., 2005; Shamar et al., 2009) while the value from GAB model was very high. According to Arslan and Togrul (2005), the monolayer moisture content, M_0, could be viewed as the moisture content affording the longest time period with minimum quality loss at a given temperature. Therefore, deteriorative reactions, except oxidative rancidity, were minimal at the moisture content below M_0. Consequently, the safest water activity was that corresponding to M_0 or lower. By using GAB equation to predict the safest water activity in this experiment, it was found that the average value was 0.67. The comparison of adsorption isotherms between experimental results and predicted results from six adsorption isotherms models is presented in Figure 2.

Analysis of thermodynamic functions

Net isosteric heat of sorption (q_{st}) determined the state of the water held by solid material (Basu et al., 2006). When water was removed from food, heat was absorbed. Net isosteric heat of sorption is the difference between total heat of sorption in the food and heat of vaporization of pure water and can be computed

Table 2. Model parameters estimated from non-linear regression analysis and statistical standards.

Model	Temperature (K)	Parameters				R^2	MRD	RMSE	Residual plot
		A	B or K	C	M_0				
MH	323	0.0045	587.56	0.83	-	0.9441	26.7233	0.0667	random
MCP		84.01	6.39	-274.33	-	0.9029	33.6254	0.0879	random
MO		-80.32	0.25	1.29	-	0.9612	22.4364	0.0555	random
MHS		-2.14	-0.0017	0.98	-	0.9791	15.9654	0.0408	random
GAB		-	0.81	0.35	0.32	0.9954	19.7793	0.0131	random
BET		-	-	-88339.43	0.06	0.9680	46.3608	0.0353	random
MH	299	0.0049	635.20	1.01	-	0.9721	18.6394	0.0474	random
MCP		91.01	6.64	-279.48	-	0.9424	26.0357	0.0683	random
MO		-80.31	0.25	1.54	-	0.9850	12.8033	0.0349	random
MHS		-2.08	-0.0018	1.11	-	0.9914	5.1637	0.0264	random
GAB		-	0.66	0.51	0.49	0.9917	15.7305	0.0161	random
BET		-	-	8215.35	0.05	0.8923	18.5058	0.0579	patterned
MH	282	0.0056	749.27	1.14	-	0.9701	20.2749	0.0497	random
MCP		98.58	8.25	-283.63	-	0.9528	23.7530	0.0625	random
MO		-80.31	0.25	1.72	-	0.9851	13.9218	0.0351	random
MHS		-2.21	-0.0021	1.23	-	0.9917	8.3331	0.0262	random
GAB		-	0.90	4.61	0.10	0.9955	12.5375	0.0187	random
BET		-	-	62394.94	0.05	0.9152	16.4799	0.0564	patterned

MH: modified Henderson; MCP: modified Chung-Pfost; MO: modified Oswin;
MHS: modified Halsey; GAB: Guggenhein-Anderson-de Boer; BET: Brunauer-Emmet-Teller

from experimental sorption data by using Eq. (10). GAB model was employed to estimate the values of water activity at a given equilibrium moisture content. Then, ln aw was plotted against 1/T (Figure 3.). The slope of the plot was determined and thus converted into the net isosteric heat of adsorption. As seen from Figure 3, linear correlations were exhibited for all values of moisture content. Additionally, the slope of the straight lines decreased to zero when moisture content increased. This behavior indicates that the interactions of water with the surface for adsorption are decreased, suggesting that the binding energy is decreased and that the behavior becomes more like pure water (Labuza and Altunakar, 2007).

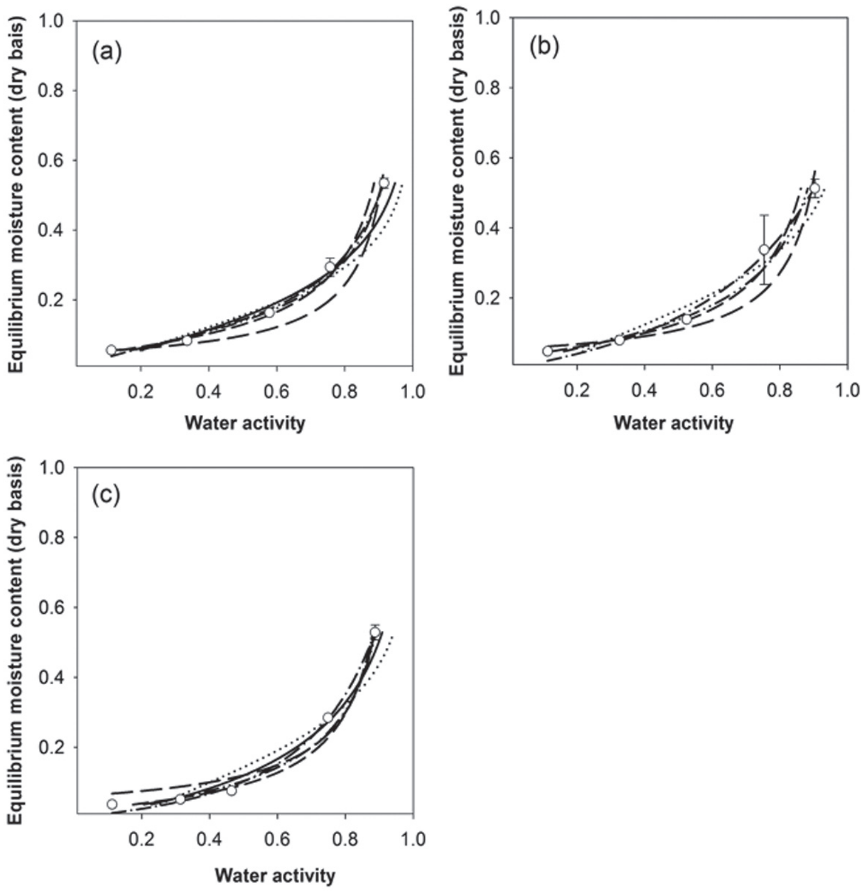

Figure 2. Comparison of adsorption isotherms between experimental results and predicted results from six adsorption isotherms models at (a) 9°C, (b) 26°C and (c) 50°C. Solid line: MH; medium dash line: MHS; dotted line: MCP; dash-dot line: GAB; dash-dot-dot line: MO; long dash line: BET.

The relationship between net isosteric heat of adsorption and moisture content is illustrated in Figure 4. From the results, q_{st} decreased with increasing moisture content. The maximum value was 3.2 kJ/mol and this value decreased exponentially and was close to zero at the moisture content of around 35% (dry basis). This trend was in agreement with other food systems (Hossain et al., 2001; Kaymak-Ertekin and Gedik 2004; García-Pérez et al., 2008; Goula et al., 2008; Janjai et al., 2009). The decrease in q_{st} when moisture content increased could be explained by the fact that adsorption initially took place on the most active sites such as hydrophilic polar groups, leading to the occurrence of the maximum interaction energy (Kumar et al., 2005). When the moisture content increased, these active sites became unavailable and the adsorption occurred on the less active sites, requiring lower heat of adsorption. The relationship between and moisture content provided the value of M_c by fitting the Eq. (12) to the plot

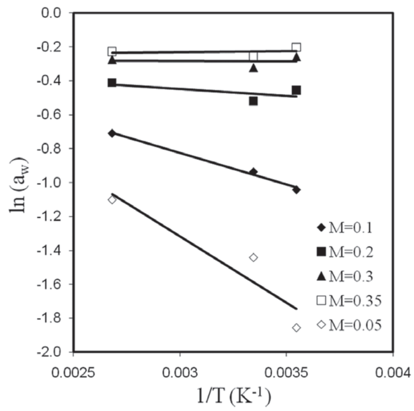

Figure 3. Relationship of Clausius-Clapeyron equation for determining net isosteric heat of adsorption.

of q_{st} and moisture content. The resulted regression equation was q_{st}. = 15117.82 exp(–15.85M). The coefficient in the exponential term led to the value of M_c of 0.063. The value of q_{st} in the present work was found to be 3 kJ/mol at moisture content of 10% (dry basis). The investigation of q_{st} in published papers shows that this value is varied among food materials. For dried tomato pulp, q_{st} was found to be 25 kJ/mol at moisture content of 10% (dry basis) (Goula et al., 2008) while it was found to be 50 kJ/mol for dried longan (Janjai et al., 2006). However, the low value of q_{st} have also been reported. For instance, Starch powder exhibited this value to be 2.5 kJ/mol at moisture content of 10% (dry basis) (Al-Muhtaseb et al., 2004), in agreement with the present work. For fresh water crayfish, it was found to be approximately 6 kJ/mol at moisture content of 10% (dry basis) (Ariahu et al., 2006), similar to that for peppers (Kaymak-Ertekin and Sultanoglu, 2001) and potato (Kaymak-Ertekin and Gedik, 2004).

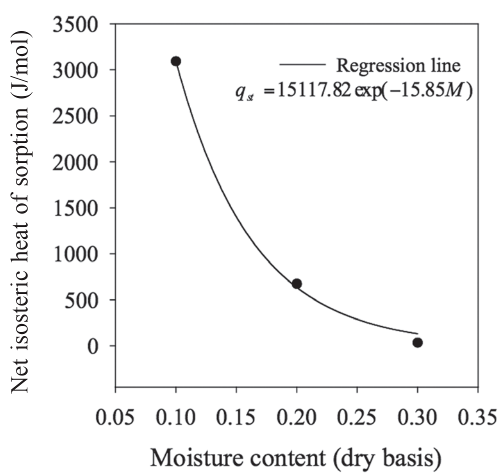

Figure 4. Net isosteric heat of sorption at different moisture contents.

Entropy of adsorption

The entropy (ΔS) of adsorption of water at each moisture content was determined from Eq. (13) by fitting to the experimental data and plotted against moisture content, as illustrated in Figure 5. The results showed that the entropy of adsorption was strongly dependent on the moisture content. This behavior was in a similar trend with the net isosteric heat of sorption. The value of entropy of adsorption was in the range of 9 J/mol.K to -2.8 J/mol.K. The entropy was maximal at low moisture content and decreased rapidly and was constant at the moisture content of 25% (dry basis).

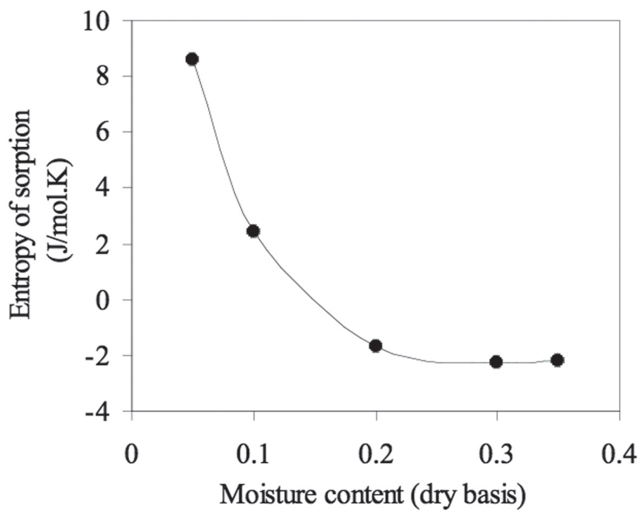

Figure 5. Entropy of adsorption at different moisture content.

Spreading pressure and integral enthalpy

The constants b and b_0 were estimated using the Dent model, Eq. (16), and then used for computing the spreading pressure in Eq. (15). The values of b were found to be 0.9717, 0.9122 and 0.8913 for temperatures of 9, 26 and 50°C, respectively, and 0.4648, 0.0799 and b_0 were 0.0904 for temperatures of 9, 26 and 50°C, respectively. The spreading pressure was then calculated for different temperatures and presented against water activity in Figure 6. The results showed that the spreading pressure increased with increasing water activity. This finding was supported by other researchers (Al-Muhtaseb et al., 2004b; Arslan and Togrul, 2005; Chen, 2006; Togrul and Arslan, 2007). The net integral enthalpy was calculated from Eq. (14) at constant spreading pressure and presented against moisture content as shown in Figure 7. As can be seen, the integral enthalpy decreased rapidly with increasing moisture content.

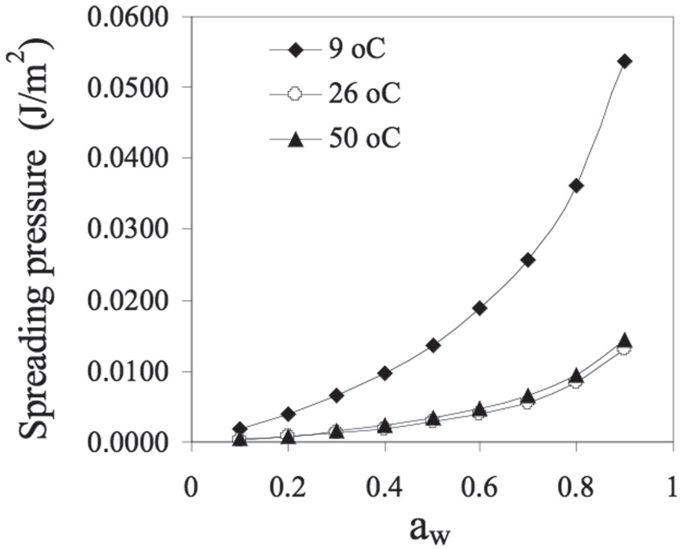

Figure 6. Calculated spreading pressure as a function of water activity (a_w).

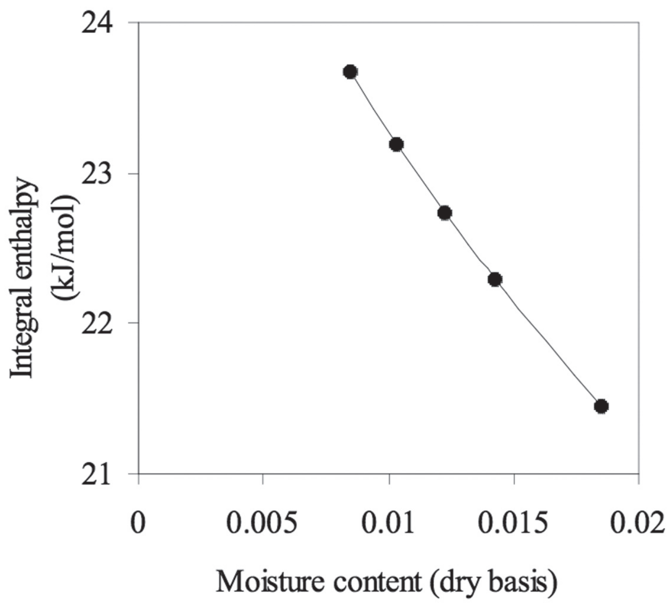

Figure 7. Integral enthalpy as a function of moisture content.

CONCLUSION

The water adsorption isotherms for traditional Thai dried marinated fish at different temperatures were studied and the thermodynamic principle was applied to analyze the water adsorption data. The obtained water adsorption isotherms were sigmoid and the temperature had no significant effect on the equilibrium moisture content. At low water activity, very small amount of water was adsorbed onto the active sites but at high water activity, much more water was adsorbed, leading to a rapid increase in equilibrium moisture content. GAB adsorption model was found to be the best model to represent the relationship between water activity and equilibrium moisture content. The equilibrium moisture content was in the range of 5-55% (dry basis) for the water activity of 0.1-0.9. It could also be concluded from thermodynamic analysis that the net isosteric heat of adsorption decreased with increasing moisture content. The decrease in net isosteric heat of adsorption continued until it reached a zero at the moisture content of 35% (dry basis) where the isosteric heat of adsorption was equal to the heat of vaporization for pure water ($Q_{st} = \lambda_{vap}$). Adsorption entropy also decreased sharply with increasing moisture content.

ACKNOWLEDGEMENTS

The authors thank Dr. Kanok-orn Pothinun and Dr. Pichaya Boonprasom Poonlarp of the Department of Food Engineering, Faculty of Agro-Industry, Chiang Mai University, Thailand for their kind support to improve the manuscript.

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