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Thermal transitions of king fish whole muscle, fat and fat-free muscle by differential scanning calorimetry

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Abstract

Thermal transitions of whole king fish (*Scomberomorus commerson*) muscle, fat and fat-free muscle were measured by differential scanning calorimetry. Initial freezing points were measured by cooling curve method and modeled as a function of solids content with the Chen equation. The muscle showed thermal transitions. However, it was difficult to justify that it was glass transition of whole or fat-free fish muscles. The end point of freezing and corresponding solids content was estimated to be −17.4 °C and 68.8%, respectively. The unfreezable water content was estimated as 36.7%. Adsorption isotherms of fish muscle were measured at room temperature by the isopiestic method and data were modeled with BET and GAB equations. The BET monolayer values were found as 3.6 and 4.8% (dry basis) for whole and fat free muscle. The data obtained could be useful in the efficient design of freezing and drying processes and also in the evaluation of chemical and biochemical stability of fat and free fatty acids in fish muscle.

Keywords: Cooling curve; Differential scanning calorimetry; Glass transition temperature; Sorption isotherms; Water activity

1. Introduction

The concept of water activity (a_w) has been used conventionally to study the stability of food products. It has provided a reliable assessment of microbial growth, lipid oxidation, non-enzymatic and enzymatic activities, and the texture/mouthfeel of foods [1]. In recent years the concept of glass transition has also made a deep impact in the field of food science because food properties related to molecular mobility, such as texture, microbial growth, chemical reactions and shelf life, are affected strongly by the glass transition temperature (T_g) [2]. Over the last two decades, much research has been reported on the importance of glass transition for a large variety of food materials and ingredients. Maximum utility of glass transition is made in the state diagram which, in its simplest form, represents the pattern of change in the state of a material as a function of increasing solids provided the thermal history of the sample is known [3,4]. Recently, Rahman [5] reviewed the updated form of the state diagram and its applications in food processing and product stability during storage. The glass transition temperature, freezing point, end point of freezing, maximal-freeze-concentration condition and sorption isotherm are necessary to develop the state diagram of a food [5].

DSC can directly provide the transition temperature and enthalpy of transition/reaction. Glass transition temperatures can also be recorded mechanically using small amplitude dynamic oscillation) [6–9]. Knowledge of the initial freezing point is useful for the estimation of effective molecular weight, water activity, bound, free, and frozen water, enthalpy below freezing, and construction of state diagram [10]. Estimation of freezing time using Plank's equation also needs a value of the initial freezing point of the material.

The king fish (narrow-barred or Indo-Pacific Mackerel) known locally as '*kanad*' is a large pelagic fish. It is the most preferred fish species for consumption by Omani and other Arabian populations in the Gulf. There is a high demand of this fish

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Nomenclature

a_w	water activity (fraction)
B	constant related to net heat of sorption in Eq. (1)
C	constant related to first layer heat of sorption in Eq. (2)
i	ith experimental data
K	constant related heat of sorption of multi-layer in Eq. (2)
M_b	monolayer water content in BET equation (kg_w/kg_{ds})
M_{eq}	equilibrium water content (kg_w/kg_{ds})
M_g	monolayer water content in GAB equation (kg_w/kg_{ds})
M_w	water content (kg_w/kg_{ds})
T_F	initial/equilibrium freezing point (°C)
T_g	glass transition temperature (°C)
T'_g	glass transition temperature of maximally freeze concentrated sample (°C)
T_m	melting temperature (°C)
T'_m	end point of freezing (°C)
X'_s	solids fraction maximally freeze concentrated sample (g/g sample)
X_w	water content (kg_w/kg_{sample})
X'_w	unfreezable water (fraction kg H_2O/kg sample, w.b.)
ΔH	enthalpy (J/g)

Subscript

i	initial
m	mid
p	peak
e	end

in both local and international markets and hence has significant social and economic importance for the country. The king fish may contain 10–50 mg of polyunsaturated fatty acids (PUFA)/g fresh weight basis depending upon the fish size and mass [11]. Several epidemiological studies have pointed out the beneficial health effects from a fish-rich diet due to involvement of omega-3 free fatty acids (ω-3 PUFA). The fish is normally preserved at very low temperatures (i.e. frozen storage) or in the dried form such as fish sticks). In order to maximize storage stability of active compounds such as ω-3 PUFA in fish, the knowledge of glass transition temperatures and water sorption properties are important. The glass transition temperatures of high moisture tuna [12], cod [13], fish protein hydrolyzates [14] and mackerel [15] were reported due to its relevance to frozen storage techniques. Hashimoto et al. [16] measured the glass transition of boiled and dried bonito fish by differential scanning calorimetry and dynamic mechanical analysis. Freezing point, end point of freezing, unfreezable water content and glass transition of abalone [7] and tuna [6] were measured and used it for developing the state diagram. In the literature glass transition of sugar based products are readily available compared to the meat and fish products. There have been limited studies published in the literature related to thermal transitions of protein–water systems with a lower amount of water [17].

The objectives of the present study are to measure the water sorption properties and thermal transition behavior of whole king fish muscle, fat and fat-free muscle. The stability criteria based on sorption isotherm and glass transition are discussed.

2. Materials and methods

2.1. Sample preparation

Fresh king fish (*Scomberomorus commerson*) was obtained from the local fish market, iced and brought chilled into the laboratory. The average mass and size of the fish were 4.0 kg and 85 cm long, respectively. The fish was washed and filleted after removing the skin. The fillets were diced and frozen at −40 °C for at least 24 h and placed in an automatically controlled freeze drier (VirTis SP Industries Company, New York, USA). The plate temperature was set at −20 °C with a vacuum of 800 mTorr (108 Pa) in the chamber while the condensing plate temperature was set at −65 °C. The variables selection was based on past experiences with other fish tissues considering plate temperature lower than end point of freezing (T'_m). At the end of 72 h drying, the water content was about 6.2% (wet basis). If allowed to dry further, some remaining water could also be removed. However, the focus of the paper was not on drying kinetics but to acquire a material of reasonably low water content so that thermal transitions and water adsorption properties could be studied.

The freeze-dried fish was ground in a laboratory scale grinder (600 W Jaipan, Mumbai, India) to form powder. Samples were stored in sealed container at 4 °C. The water content and total solids of fresh fish were measured gravimetrically by drying samples in air convection drier at 105 °C for at least 20 h. Protein, fat, and ash were measured according to AOAC [18]. Crude carbohydrate was estimated by difference. Five replicates were used for composition analysis. Compositions were expressed on a wet basis (g/100 g sample).

2.2. Extraction of fat from king fish powder

Fat free fish muscle powder was prepared according to the procedure described in AOAC [18]. Hundred millilitre of petroleum ether was used to extract fat for 8 h through the open end of the condenser. The Soxhlet flasks containing the solvent and fat were kept in an oven at 75 °C for 30 min to evaporate solvent. The fish-fat was collected in small bottles and then used for calorimetric study. The thimbles with fat-free muscle were also dried in oven to obtain fat-free muscle fraction. These samples were then equilibrated in different jars maintained at constant water activities by saturated salt solutions.

2.3. Measurement and modeling of water activity

The water sorption isotherm was determined at room temperature (23 °C) by an isopiestic method [19–21]. Freeze-dried

samples were placed in open weighing bottles and stored in air-sealed glass jars while maintaining equilibrium relative humidity with saturated salt solutions (with a crystal layer visible at the bottom of jars). The salts were: LiCl, CH_3COOK, $MgCl_2$, K_2CO_3, NaBr, $SrCl_2$ and KCl (BDH, Laboratory Supplies, Poole, England). Relative humidity values for these solutions were obtained from Greenspan [22], and Spiess and Wolf [19]. Thymol was used in high water activity jars to avoid microbial growth in the sample during equilibration.

The water activity and water content data were modeled with BET [23] and GAB equations [24]. The BET equation is:

$$M_w = \frac{M_b B a_w}{(1 - a_w)[1 + (B - 1)a_w]} \quad (1)$$

where M_b is the BET monolayer water content (dry basis) and B is a constant related to the net heat of sorption. The BET isotherm holds well between water activities of 0.05 and 0.45, an adequate range for the calculation of parameters M_b and B [25]. The GAB equation is:

$$M_w = \frac{M_g C K a_w}{[(1 - K a_w)(1 - K a_w + C K a_w)]} \quad (2)$$

where M_g is the GAB monolayer water content (dry basis). C is a constant related to the monolayer heat of sorption and K is a factor related to the heat of sorption of the multilayer. The GAB isotherm equation is an extension of the BET model taking into account the modified properties of the sorbate in the multilayer region and the bulk liquid water properties through the introduction of a third constant K. In theory, both methods should provide the same monolayer value. However, estimation of three parameters in GAB using two variables (i.e. water content and water activity) leads to a non-linear optimization. The BET monolayer value is more acceptable although the GAB model provides accurate prediction over the water activity range up to 0.9. These aspects of acceptability of BET monolayer were clearly discussed by Rahman and Al-Belushi [26]. Fitting of the models was carried out using direct non-linear regression analysis.

2.4. Initial freezing point

The freezing points of freeze-dried fish at different water contents were measured by the cooling curve method [10]. Freeze-dried powder and a predetermined amount of distilled water were equilibrated for 24 h in sealed containers in refrigerator (4 °C). The samples were filled in a stainless steel cylinder (internal diameter, 2.2 cm; height, 4.5 cm; wall thickness, 1 mm), insulated at the top and bottom with polystyrene foam and placed in a freezer set at −60 °C [27]. The temperature change at the geometric center of the cylinder was recorded with a K-type thermocouple. The initial freezing point and the end point of freezing (maximal-freeze-concentration) T'_m were determined from the cooling curve method as developed by Rahman et al. [27]. The initial cooling rate was maintained at or below 1.5 °C/min as recommended earlier [6].

2.5. Thermal transitions by DSC

A differential scanning calorimeter (DSC, Q10, TA Instruments, New Castle, DE) was used to perform DSC experiments. A mechanical refrigerated cooling system was used to cool the sample to −90 °C. The calorimeter was calibrated according to the instruction provided by TA instruments user manual by checking temperature and enthalpy of fusion of indium and water as standards. Freeze-dried king fish samples (5–10 mg) equilibrated at different water activities were placed in aluminum pans (capacity 30 μL) and were cooled to −90 °C at 5 °C/min, and equilibrated for 10 min. They were then scanned from −90 to 130 °C at a rate of 5 °C/min. Each thermogram was analyzed for the onset, mid and end of transition and enthalpy of melting. Three replicates were used for selected samples (water activity/water content).

A different procedure was used for samples (high water) containing freezable water. Samples of 10–20 mg (water content, 50–70%) of the powder in a sealed aluminum pan were cooled to −90 °C at 5 °C/min, and equilibrated for 10 min. It was then scanned initially from −90 to 40 °C for initial assessment of the thermogram and to locate apparent T_g, and end point of freezing (i.e. apparent T'_m). In the literature it was mentioned that annealing is necessary in order to achieve maximal-freeze-concentration condition (i.e. real T'_g and T'_m) and eliminate the exothermic peak if present. In these experiments annealing time was varied from 0 to 1 h at $T'_m - 1$ and optimum-annealing time was considered when melting thermogram showed no significant variation. The procedure was as follows: sample was cooled to −90 °C at 5 °C/min, heated at 5 °C/min to $T'_m - 1$, annealed from 0 to 1 h at $T'_m - 1$, cooled at 5 °C/min to −90 °C, and scanned from −90 °C at 5 or 2 °C/min to 50 °C in order to determine actual T'_g and T'_m. The initial or equilibrium freezing point was considered as the point of maximum slope of the endothermic peak. For the materials showing wide peak of ice melting on the DSC thermogram, the point of maximum slope corresponds well with the initial freezing point estimated from cooling curve method. [28]. The latent heat of ice melting or freezing was estimated from the area of the melting endotherm. The average values and standard deviation of three replicates were obtained for selected data point to identify the experimental variability.

3. Results and discussion

3.1. Sorption isotherm

The water, protein, fat, ash and carbohydrate contents of fresh king fish were 76.6, 21.2, 3.89, 1.29 and 1.79% (wet basis), respectively. Experimental water sorption data is plotted in Fig. 1. As expected, the equilibrium water content increased with increasing water activity. The shape of isotherm of fat free fish was similar to the whole fish muscle but water content was higher. The water content of whole fish muscle at a given water activity decreases as the fat content increases because lipids are inaccessible to water but contribute to the dry weight [29].

The constants of the BET and GAB equations are shown in Table 1. These constants can be used to predict water sorption

Table 1
BET and GAB model parameters of water adsorption isotherms of king fish muscles

Material	BET				GAB		
	M_b (g/g dry matter)	B	MRE (%)	M_g (g/g dry matter)	C	K	MRE (%)
Whole king fish muscles	0.036	3.3×10^6	3.11	0.052	9.934	0.952	11.2
Fat free fish muscles	0.048	3.823	20.5	0.086	1.848	0.832	9.20

isotherms at room temperature. The knowledge of sorption models of a given product is useful in the modeling drying processes. The values of the monolayer water content of whole king fish muscles were 3.6 and 5.2% (d.b.), as determined by BET and GAB model, respectively. For fat free muscles BET and GAB monolayer water contents were 4.8 and 8.6% (d.b.). The differences in water sorption behavior can be partially attributed to the differences in fat content [30]. The isotherm of whole fish muscle using the water content calculated based on fat free basis shifts towards the isotherm of fat-free fish muscle however they still do not overlap completely on each other. Results were in the range previously reported for fish flour (3.24–5.12% d.b.), sardines (4.94% d.b.) and abalone (2.1–6.8% d.b.) [7,20,25]. The BET monolayer is an effective method for estimating the amount of strongly bound water at the monolayer where a food product is most stable against microbial and chemical deteriorations.

3.2. Initial freezing point and T'_m by cooling curve

Cooling below the initial freezing point of a sample without formation of ice is defined as supercooling. At this stage, the critical mass of nuclei is attained which marks the onset of ice crystallization (point (a) at −4.8 °C in Fig. 2). This is accompanied by release of the latent heat of fusion which is faster than the amount of heat removed from the system, hence causing a small increase in temperature to the equilibrium freezing point (b). Freezing point data of whole muscle as a function of solids content are given in Table 2 and plotted in Fig. 3. The data was used to fit prediction model for initial freezing point. The standard deviation of the freezing point increased with increasing solids content suggesting a higher variability in experimental measurements due to their higher tendency of supercooling.

The depression in freezing points with increased amounts of solids was modeled by the Clausius-Clapeyron equation in conjunction with an improved model based on the concept of

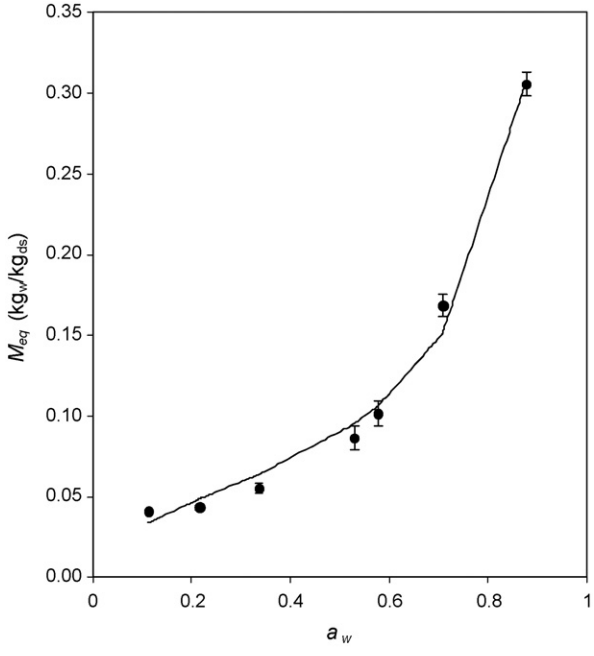

Fig. 1. Experimental data for freeze-dried king fish and predicted sorption isotherm using the GAB equation.

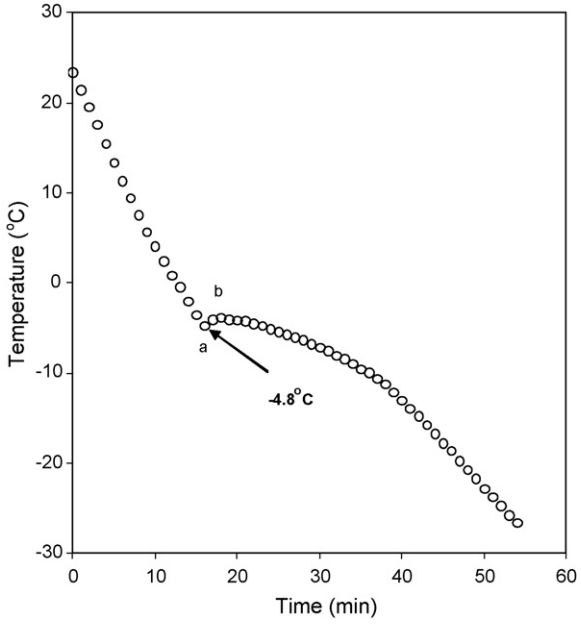

Fig. 2. Cooling curve of king fish at 50% water content indicating the onset of ice crystallization (a) and the equilibrium freezing point (b).

Table 2
Freezing point (T_F), and end point of freezing (T'_m) of king fish muscles as a function of solid content (X_s) as measured by cooling curve method

X_s (fraction)	T_F (°C)	T'_m (°C)
0.2	−0.68 (0.13)	−17.4 (2.1)
0.3	−1.78 (0.25)	
0.4	−2.56 (0.21)	
0.5	−3.47 (0.35)	
0.6	−7.60 (1.16)	

Note: Average of four to six readings, values in the parentheses are standard deviations.

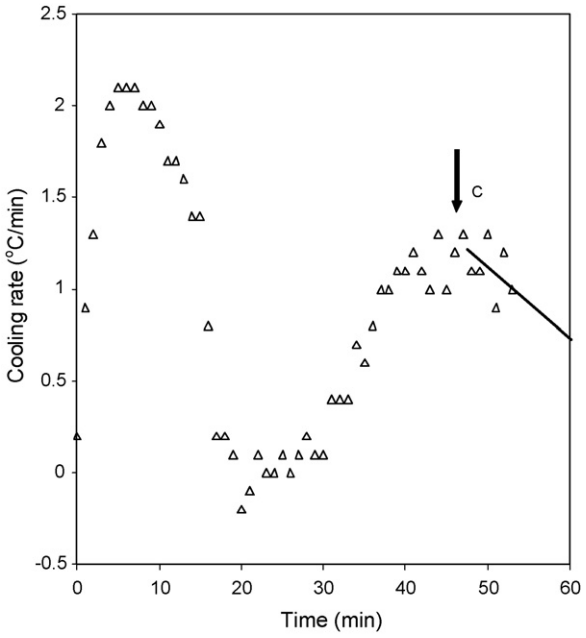

Fig. 3. Plot of cooling rate (i.e. slope) at the center of the sample as function of cooling time showing the end of freezing point at C.

bound water. The Clausius-Clapeyron equation is expressed as:

$$\delta = -\frac{\beta}{\lambda_w}\ln\left[\frac{1-X_s}{1-X_s+EX_s}\right] \quad (3)$$

where δ is the freezing point depression ($T_w - T_F$), T_F the freezing point of food (°C), T_w the freezing point of water (°C), β the molar freezing point constant of water (1860 kg K/kg mol), λ_w the molecular mass of water, X_s the solids mass fraction, and E is the molecular mass ratio of water to solids (λ_w/λ_s).

The Clausius-Clapeyron equation is limited to an ideal solution, which is equivalent to a very dilute solution. The theoretical approach can be extended to our samples by introducing parameters for non-ideal behavior. The latter refers to the part of water that remains in the amorphous phase of the matrix of the food thus being unavailable for freezing. Chen [31] introduced the ratio of unfreezable water to the total solids content (B) and modified Eq. (3) as follows:

$$\delta = -\frac{\beta}{\lambda_w}\ln\left[\frac{1-X_s-BX_s}{1-X_s-BX_s+EX_s}\right] \quad (4)$$

Parameters E and B were estimated using SAS non-linear regression and found to be 0.0275 and 0.303, which corresponds to conditions of 76.7% solids and 23.3% unfreezable water. In case of squid mantle meat the values of E and B were found as 0.067 and 0.12 [32]. Similarly the value of B, 0.307, corresponds to 76.5% solids and 23.5% unfreezable water in case of abalone [7]. It is important to mention here that the above equation is accurate for predicting the freezing point of foods; this method for estimating unfreezable water content however may not be reliable. Rahman [28] demonstrated this by measuring amount of unfreezable water content in date flesh using four different methods.

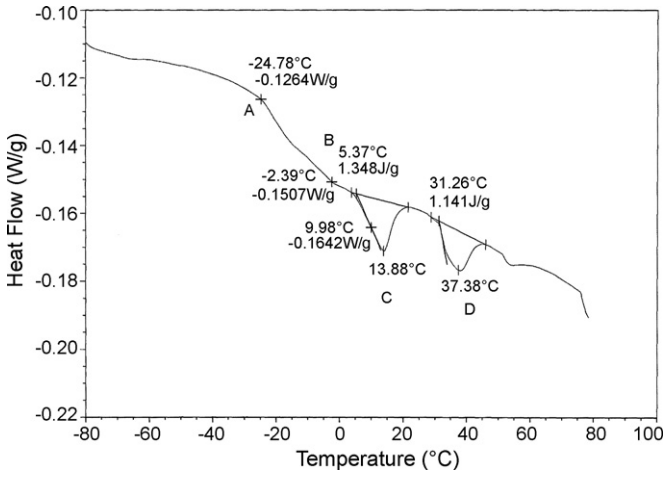

Fig. 4. DSC thermogram of king fish muscle containing unfrozen water showing a thermal transition and two endothermic peaks related to fat melting (water content 3.9% w.b., scan rate 5 °C/min).

The end point of freezing (T'_m) calculated by the cooling method was −17.4 °C (Table 3). Fig. 3 shows the cooling rate (i.e. slope) at the center of the sample versus cooling time plot showing the end point of freezing (T'_m) marked as point C when slope reached a maximum after a minimum value. The value of T'_m was measured at the solids content of 50%. Rahman and Driscoll [32] found that the T'_m estimated from cooling curve methods match closely with the DSC method around solids content of 41.5%. The freezing curve (T_F and X_s) was modeled with the Chen equation and then the solids content (X'_s) at the T'_m was estimated as 68.8% (X'_w: 31.2%) by extrapolating the freezing curve up to T'_m of −17.4 °C. For abalone T'_m was found as −18.1 °C at solids content 68.0% [7], for tuna T'_m was −13.3 °C at solids content 61.0% [6], respectively. This technique was also used by Rahman et al. [33] for garlic and compared with the T'_m measured by DSC method.

3.3. Thermal transitions by DSC

3.3.1. Samples containing unfreezable water

For whole muscle, the heat flow curves obtained from DSC showed three characteristic transitions (Fig. 4). A decrease in heat rate caused by a glass phase transition was observed in the thermogram from point A to B, and two endothermic peaks at C and D (Fig. 4). The glass phase transition was found consistently in samples of different water content. Kawai et al. [17] reported that two kinds of glass transitions have been observed with protein–water systems. One is known to be at low temperatures (around −113 to −73 °C) which are associated with freezing of motions of water molecules. However, the transition observed in this work was at a comparatively higher temperature which could be due to the initiation of mobility in protein and/or fat molecules. Two endothermic peaks showed the melting of fats in the whole muscle which could be due to melting of different fractions of fat in it. The increasing water had very little influence on the first transition. The effect of water on the melting temperatures (peaks 1 and 2) was negligible, whereas the enthalpy of melting of fat decreased with the increase of water

Table 3
Thermal transitions at different water content in whole fish muscle having unfrozen water

Transition 1				Endothermic peak 1				Endothermic peak 2			
M_w (gH_2O/g dry matter)	T_{gi} (°C)	T_{gp} (°C)	T_{ge} (°C)	T_{mi} (°C)	T_{mm} (°C)	T_{mp} (°C)	ΔH (J/g)	T_{mi} (°C)	T_{mm} (°C)	T_{mp} (°C)	ΔH (J/g)
0.041	−23.9 (0.7)	−16.3 (0.9)	−8.9 (0.7)	5.06 (1.1)	10.1(0.5)	13.9 (0.2)	1.11 (0.18)	30.9 (1.5)	33.5 (1.1)	37.4 (0.280)	1.01 (0.132)
0.044	−24.4	−14.0	−2.15	5.67	10.7	13.6	1.05	31.3	34.1	37.1	0.976
0.055	−23.5	−14.2	−3.34	5.91	11.4	13.9	0.984	30.3	34.3	37.4	1.03
0.087	−25.4	−15.7	−3.81	6.14	9.9	13.2	0.591	30.1	33.6	37.7	1.09
0.102	−25.9	−18.0	−9.97	5.43	11.0	13.2	0.884	30.8	32.9	37.2	1.19
0.168	−25.4	−15.0	−4.52	6.62	10.7	13.6	0.307	31.5	35.1	38.2	0.952
0.306	−23.2	−19.5	−15.0	5.34	8.7	11.5	0.156	30.7	35.5	41.1	3.46

Note: Values for sample having water content 0.041 are average of four to six readings, and values in the parentheses are standard deviations.

content (Table 3). This was due to decrease of fat content with the increasing water content based on the total mass of sample.

To investigate further the thermal characteristics in the muscle, fat in the whole muscle was separated and thermal scans were carried out with pure fat and fat-free muscle. In case of fat two clear endothermic peaks were observed corresponding to melting (Fig. 5). The locations of these two peaks (i.e. temperature range) obtained with whole king fish muscle and extracted fat was in a similar range. The peak 1 however showed a broader range in fat when compared to muscle (Fig. 4). This could be attributed to melting of different fat fractions that could become significant in fat samples. The average enthalpy values of two fractions of fat melting were 23.0 and 3.94 J/g, respectively.

The DSC curves with fat free fish muscle fraction showed two distinct glass phase transitions in the trace of thermogram and two endothermic peaks (Fig. 6). The two endothermic peaks are attributed to the presence of a small fat fraction in the muscle. Similar events were also observed with oil free date-pits [34]. There have been some reports in the literature that many foods contain free and bound lipid constituents within their structural matrix. Only the free part of the lipid phase in the muscle can be extracted by less polar solvents, e.g. light petroleum fractions and diethyl ether. Other acid treatment could be used to remove all bound fat; however this treatment may also change the protein matrix. The two glass transitions are at −11 to 0 and 70 to 105 °C, respectively. The first was within the range similar as whole fish muscle indicating the dynamics of protein water system. The second could be attributed to glass transition of protein (as usually observed with amorphous biomaterials). However, the increasing water had little influence on the change in the glass transition temperature range, i.e. plasticization effects of water on the protein was very small. Thus this shift could not be considered as glass transition. It is important to mention that for complex food systems it is difficult to find clear glass transition with thermal analysis since other changes interfere or complexity of the structure affects identifying the glass transition. In a recent study Rahman et al. [34] found similar complexity in the case of date-pits. They also could not trace the glass transition even though oil was separated from the date-pits and they performed thermal analysis with DSC and more sensitive modulated DSC for both pure oil and oil free solids. Acevedo et al. [35] also reported the difficulty in detecting the glass transition of chicken muscle in their DSC measurements. In addition, Green et al. [36] concluded from their results that hydrated proteins indeed may be classed among glass-forming systems, but due to their special structural features and to the disposition of the bound water, they showed great departures from thermo or rheological

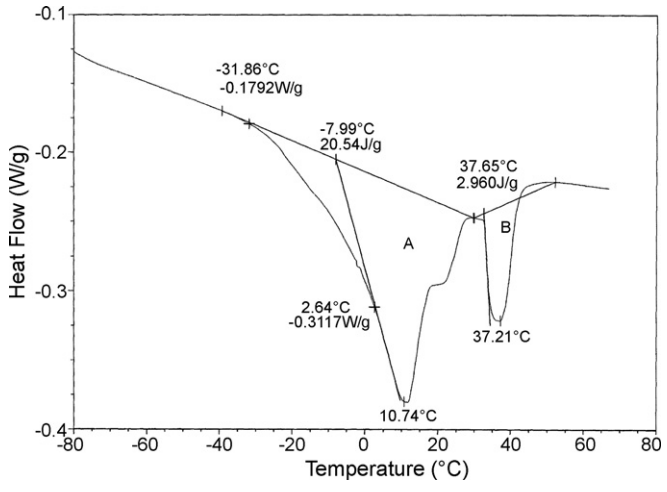

Fig. 5. DSC thermogram of king fish fat showing two melting peaks (scan rate 5 °C/min).

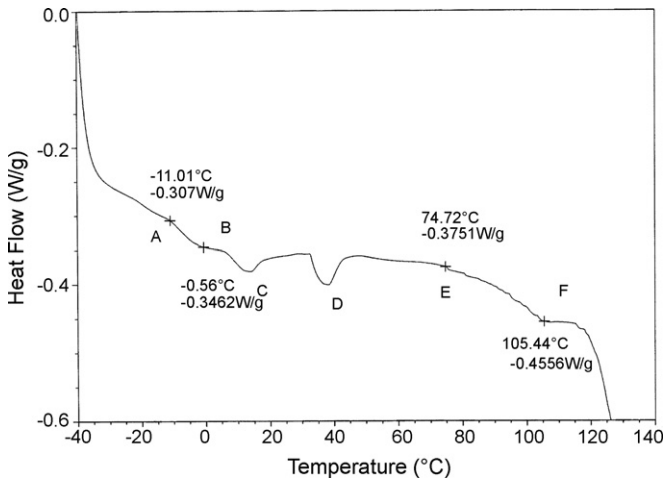

Fig. 6. DSC thermogram of oil free king fish muscle containing unfrozen water showing two thermal transition and two endothermic peaks (water content 3.5% w.b., scan rate 5 °C/min).

Table 4
Thermal transitions in whole king fish muscle at different water content (freezable water)

Ice melting						
X_w	r_c (°C/min)	T_{fi} (°C)	T_{fm} (°C)	ΔH (J/g)	T'_m	T'_g
0.50	5	−2.58 (0.63)	−6.23 (0.80)	61.9 (4.79)	−18.4 (2.61)	−21.4 (1.51)
0.50	15	1.28 (1.13)	−4.22 (1.76)	76.0 (29.9)	−15.3 (4.81)	−22.8 (3.87)
0.50	2	−4.25	−6.95	59.2	−18.7	−25.5
0.55	5	−1.44	−5.17	85.7	−18.8	
0.60	5	−1.06	−4.08	110	−16.6	
0.65	5	0.31	−2.31	128	−12.6	
0.70	5	0.78	−1.48	150	−11.3	

Note: Values for samples having 0.50 water content are average of four to six readings, values in the parentheses are standard deviations.

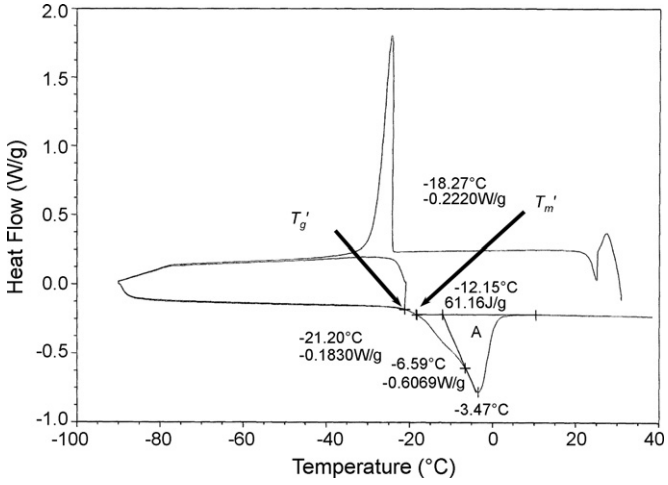

Fig. 7. DSC thermogram of whole king fish muscle showing freezing exotherm and melting endotherm, T'_m and T'_g (water content 50% w.b., scan rate 5 °C/min).

simplicity. Glass transition temperatures have been reported for some protein systems such as gelatin, tuna, abalone and shark tissues [6–8,37]. However, these studies used mechanical measurements of small amplitude dynamic oscillation. More work on thermal transition of protein foods is needed and efforts are in progress in our laboratory.

3.3.2. Samples containing freezable water

Fig. 7 shows a DSC thermogram for whole muscle with freezable water. Thermogram showed one endothermic peak for melting of ice, and glass transition was unable to trace in the whole muscle. The freezing point, end point of freezing (T'_m and T'_g), and latent heat of fusion were determined from the endothermic peak, and are presented in Table 4. The values of freezing point by cooling curve and DSC methods are also plotted in Fig. 8 for a comparison. The freezing point values estimated using the cooling curve method matched closely with the values obtained using DSC method up to 65% water content. As solid content increased the difference between the values of initial freezing points obtained using both the methods increased.

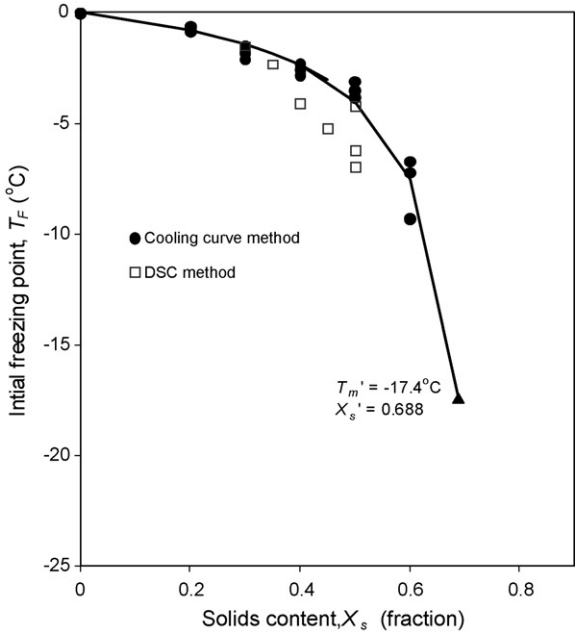

Fig. 8. Plot of initial freezing point as a function of solids content measured by cooling curve and DSC methods.

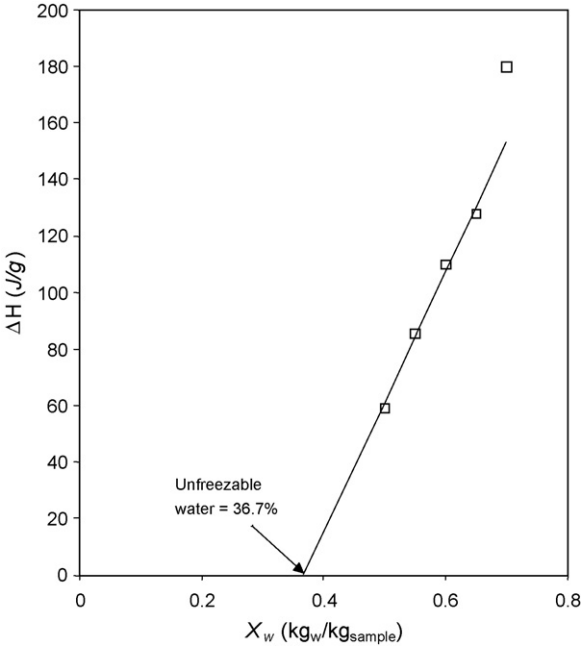

Fig. 9. Plot of the enthalpy of ice meting as a function of water content.

This has been noted earlier that the cooling curve became less sensitive as the solids content in the sample increased and the amount of possible ice formation was decreased [33]. Enthalpy of melting of ice is plotted as a function of water content in order to identify the unfreezable water content in the whole fish muscle. The value of X'_w (unfreezable water) was found as 36.7% by extending the linear line to ΔH equal to zero (Fig. 9). This value is relatively close to the value of 31.2% estimated from the freezing curve method as discussed earlier.

4. Conclusions

A methodology was presented to evaluate initial freezing point, end point of freezing and amount of unfreezable water. A cooling curve method and differential scanning calorimetry were used to obtain thermal transition parameters of whole muscle, fat free fish muscles. The end point of freezing (T'_m) and corresponding solid content (X'_s) was estimated to be $-17.4\,^\circ$C and 68.8%, respectively. The unfreezable water (X'_w) obtained from enthalpy of melting of ice data and freezing curve were 36.7 and 31.2%, respectively. Data on initial freezing temperatures as a function of solids contents can be useful in the construction of a state diagram for king fish. Samples with high water content exhibited a thermal event (-21.4 to $-25.5\,^\circ$C) attributed to glass transition, which did not show significant dependence with the initial solid contents representing the glass transition temperature of the maximally freeze concentrated phase (T'_g). The shift in thermogram trace at higher temperature was within the range of 70–105 °C. The water had a very little influence on this transition. The BET monolayer water for whole king fish and fat free muscles were 3.6 and 4.8% (d.b.), respectively. These results can be employed in the design of efficient processes and defining optimal storage conditions for frozen as well as dehydrated fish. The thermal and water sorption properties are useful for processing and utilization of fish and can also provide information for exploring and understanding the structure of fish muscles.

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