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EFFECT OF κ-CARRAGEENAN AND NaCl ON INITIAL FREEZING POINT OF EGG AND SURIMI

D. KOVAČEVIĆ[a] and Ž. KURTANJEK[b]

[a] Faculty of Food Technology, University of Osijek, F. Kuhača 18, HR-31000 Osijek. Croatia
[b] Faculty of Food Technology and Biotechnology, University of Zagreb, Pierottijeva 6, HR-10000 Zagreb. Croatia

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Initial freezing points T_i of egg samples (melange of egg yolk and white, egg yolk, egg white) and surimi mixed with different mass fractions of κ-carrageenan (w = 1–10%), NaCl (w = 1–10%), and mixtures of NaCl and κ-carrageenan in mass ratio of 4:1 (w = 1–10%) were determined by use of differential thermal analysis (DTA). Samples of surimi were prepeared in laboratory conditions from *Sardina pilchardus*. Water content in surimi was 81.50%, in egg yolk 47.65%, in egg white 88.1%, and in melange it was 64.41% before mixing with the added substances.

Relations between decrease of the initial freezing point T_i as function of mass fractions w of the added substances were determined by linear regression. Coefficients of determination in range of R^2 = 0.94–0.98 for samples of surimi, and R^2 = 0.92–0.98 for samples of egg were obtained. The largest effect of cryoscopic depression on initial freezing point T_i were exhibited by the samples of surimi with added: a) NaCl in the temperature range from –0.19 to –11.11 °C, b) mixtures of NaCl and κ-carrageenan (from –0.19 to –9.08 °C), and c) κ-carrageenan (from –0.19 to –0.72 °C). For the samples with pure NaCl the largest decrease of T_i was obtained for: a) egg yolk (from –0.59 to –20.77 °C), b) melange (from –0.59 to –8.74 °C), and c) egg white (from –0.50 to –7.37 °C). The results are compared and discussed with Chang-Tao model for prediction of T_i for meat.

Keywords: initial freezing point, DTA, surimi, egg, NaCl, κ-carrageenan

Thermal properties of food are important for determination of process parameters, design of process units and technology development and for effective performance of unit operations with heat transfer. In the preservation of food by freezing, a minimal mass fraction of 50% of water is, in the temperature-range below T_i, transformed to ice. The significant difference of thermal properties of water and ice results in a significant change in thermal properties of food during freezing (for example thermal conductivity is k (ice) = 2.210 W m^{-1} K^{-1}, while k (water) = 0.5815 W m^{-1} K^{-1}, specific heat capacities at constant pressure are c_p (water) = 4.187 kJ kg^{-1} K^{-1} and apparent c_p (ice) = 2.098 kJ kg^{-1} K^{-1}, and thermal diffusivities are α (water) = 5.2 10^{-4} m^2 h^{-1},

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apparent α (ice) = 4 10^{-3} m^2 h^{-1} (GRUDA & POSTOLSKI, 1980). Most of the mathematical models for prediction of thermal properties of frozen food are based on the equation for cryoscopic depression of initial freezing point T_i (HELDMAN, 1982; SCHWARTZBERG, 1976; 1983; CHANG & TAO, 1981; CHEN, 1985; 1986), $\Delta T = K_k \cdot \gamma$ (ΔT is temperature decrease, K_k is cryoscopic constant, γ is molality). The experimental methods most frequently used for determination of T_i, are differential scanning calorimetry (DSC) and differential thermal analysis (DTA) which are according to "ICTA" (Nomenclature Committee of the International Confederation for Thermal Analysis) the methods which are based on the change of apparent enthalpy (FINDLAY & BARBUT, 1990). The methods for measurement have to account for time delay of temperature sensors (large time constant), lack of standardisation of measurement methods and conditions, problem with sample homogenisation and preparation and specifically the problem with small samples (SWEAT & HAUGH, 1974; 1976). The advantages of DTA method are: negligible thermal gradient in samples, rate of temperature change does not effect the accuracy of measurement of T_i and enables the use of larger samples of food with solid particles.

In this work laboratory design of DTA apparatus was applied for determining T_i of samples of egg (melange of egg yolk and white, egg yolk, egg white) and surimi mixed with different mass fractions of κ-carrageenan (w = 1–10%), NaCl (w = 1–10%), and mixtures of NaCl and κ-carrageenan in mass ratio of 4:1 (w = 1–10%). Application of linear regression was examined for determination of functional relationship between mass fraction of added substances w and initial freezing point T_i.

1. Materials and methods

1.1. Materials

Samples of surimi were prepared in laboratory from Adriatic pilchard (*Sardina pilchardus*) according to technique by LEE (1984) with details given by SYCH and co-workers (1990). Samples were divided into three groups and each was mixed respectively with: a) κ-carrageenan; b) NaCl; c) NaCl and κ-carrageenan in mass ratio of 4:1. Mass fractions were in the range of 0 to 10% determined as percent of total mass. Moisture content was 81.50% determined by the A.O.A.C. method (1980) for meat products before addition of the added components. Total protein mass fraction was 16.30% determined with 1 g samples by Kjeldahl method; (Kjeltec System, model 1002 Distilling Unit). Samples were packaged in polyethylene bags and quickly frozen in liquid nitrogen and stored at –25 °C. Average storage time was 1 week before experimental treatment.

Samples of egg were prepared from three days old chicken eggs produced at an industrial farm. The samples were divided into three groups: egg yolk, egg white, melange of egg yolk and white, and were mixed with NaCl in different mass ratios. The mass fractions of NaCl in egg yolk were $w = 1, 4, 6, 8$, and 10%, in egg white $w = 2, 4, 6, 8$, and 10%, and in the melange $w = 1, 3, 6, 8$, and 10%. Water content was determined by A.O.A.C. method (1980) for egg and egg products, and was for egg yolk samples 47.65%, in egg white 88.01%, and in melange 64.41%. Total protein mass fraction was determined with 1 g samples by Kjeldahl method; (Kjeltec System, model 1002 Distilling Unit), and obtained to be 17.80% for egg yolk, 10.71% for egg white, and 12.02% for melange. Samples were packaged in polyethylene bags and quickly frozen in liquid nitrogen and stored at –25 °C. Average storage time was 1 day before experimental treatment.

1.2. Methods

DTA apparatus was constructed in the laboratory (KOVAČEVIĆ & KURTANJEK, 1993) and was used for measurement of inital freezing point T_i. Thermocouples were made from Alumel-Chromel wires with a diameter of 0.07 mm. The standard error in calibration was 50 mK with sensitivity of 10 mK. The instruments were interfaced with a standard PC and sampling rate of 3.5 kHz was used. All data were prefiltered with 3s rule for noise rejection prior to data analysis. Aqueous solution of $CaCl_2$, $w(CaCl_2) = 30\%$, was used as reference substance for DTA measurement. Distilled water was used as calibration substance for the static correction of the initial freezing point.

2. Results

DTA measurements of samples of surimi, melange, egg white, and egg yolk mixed with the added substances (total 49 samples) were conducted in temperature range from –25 to 5 °C. In Fig. 1 the results of DTA for surimi samples mixed with κ-carrageenan are presented, and in Fig. 2 results of DTA for samples of melange mixed with NaCl are presented.

The DTA curves have a low level of measurement noise, which is a result of statistical data filtering and rejection of outliers by $\pm 3\sigma$ rule, and is due to high frequency of data sampling. Drift from the base line in the temperature range from 0 to 0.2 °C is due to difference of thermal properties of samples and the reference substance.

From DTA diagrams the peak points were read off as the initial freezing points. Data for the initial freezing points T_i are given in Table 1.

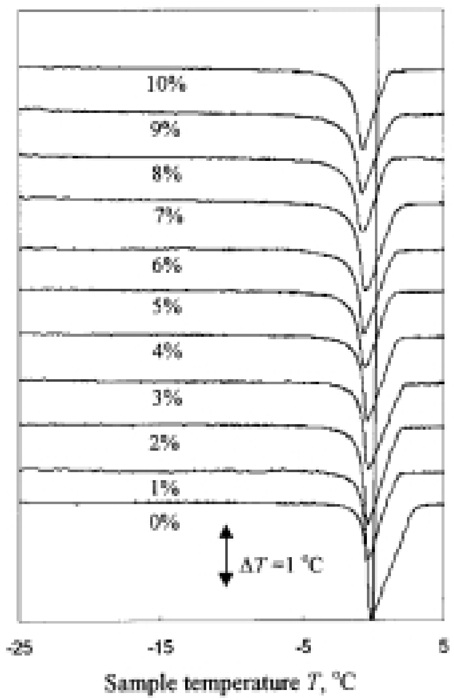

Fig. 1. DTA curves of surimi as a function of mass fraction of κ-carrageenan. ΔT is the temperature difference between sample and reference substance

In Figs 1 and 2 systematic shifts of the initial freezing points can be observed toward lower temperatures with increased concentration of added substances. Below the initial freezing points DTA diagrams for all samples show systematic increase in the temperature difference with increased level of the added substances.

Each DTA diagram is corrected only for constant error of +0.045 °C which was determined from calibration with distilled water. By the method of linear regression of T_i to mass fraction of the added substances the parameters of the regression equation were determined:

$$T_i = a + b \cdot w \tag{1}$$

a and b, standard errors $e(T)$ and coefficient of determination R^2. Parameters of the regression models (1) are given in Table 2.

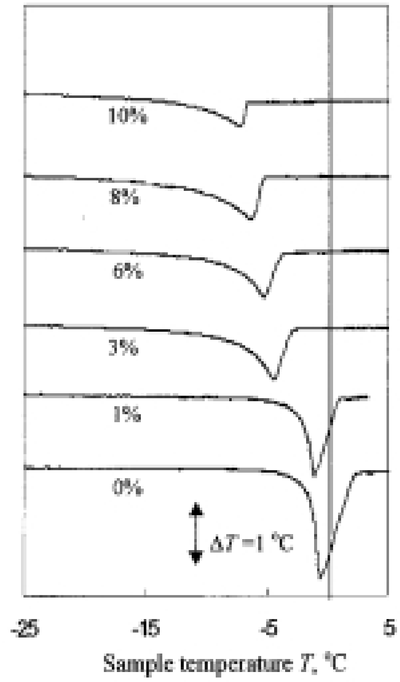

Fig. 2. DTA curves of melange as a function of mass fraction of NaCl. ΔT is the temperature difference between sample and reference substance

The difference in the slopes of linear regressions is in accordance with the equation of cryoscopic freezing point decrease which is inversely proportional to the molecular mass of dissolved substances.

The most pronounced effect of cryoscopic depression on initial freezing point T_i is exhibited by the samples of surimi with added: a) NaCl in the temperature range from –0.19 to –11.11 °C, b) mixtures of NaCl and κ-carrageenan in mass ratio of 4:1 (from –0.19 to –9.08 °C), and c) κ-carrageenan (from –0.19 to –0.72 °C). For the samples with pure NaCl the highest decrease of T_i was obtained for: a) egg yolk (from –0.59 to –20.77 °C), b) melange (from –0.59 to –8.74 °C), and c) egg white (from –0.50 to –7.37 °C).

Table 1

Experimental data of initial freezing point T_i

Mass fraction of added substances w, %	Initial freezing point T_i, °C					
	Surimi + κ–carrageenan	Surimi + NaCl	Surimi + mixture of NaCl and κ–carrageenan in mass ratio of 4:1	Egg white + NaCl	Egg yolk + NaCl	Melange + NaCl
0	−0.19	−0.19	−0.19	−0.50	−0.59	−0.59
1	−0.30	−1.02	−0.81		−1.00	−1.94
2	−0.33	−2.01	−1.85	−2.00		
3	−0.33	−2.52	−2.78			−4.50
4	−0.37	−3.48	−3.43	−4.10	−6.80	
5	−0.52	−4.08	−3.58			
6	−0.58	−5.45	−5.15	−4.85	−7.65	−5.30
7	−0.53	−6.40	−5.07			
8	−0.73	−7.05	−6.69	−5.87	−12.01	−7.22
9	−0.75	−8.68	−7.10			
10	−0.72	−11.11	−9.08	−7.37	−20.77	−8.74

Table 2

Parameters of the regression models (1) for initial freezing point T_i

Samples	Added substances (w = 1–10%)	b	a	$e(T)$	R^2
Surimi	NaCl	−1.0007	0.27250	0.0590	0.97
	κ–carrageenan	−0.0571	−0.20616	0.0048	0.94
	mixture of NaCl and κ–carrageenan in mass ratio of 4:1	−0.8219	−0.05168	0.0426	0.98
Egg white	NaCl	−0.6608	−0.82570	0.0439	0.98
Egg yolk	NaCl	−1.8470	0.79084	0.2698	0.92
Melange	NaCl	−0.7611	−1.16324	0.0715	0.97

If T_i of surimi and egg samples with the same mass fraction of NaCl are compared, the highest cryoscopic depression is observed in the following order: egg yolk, surimi, melange and egg white. The results confirm the assumption that T_i is not a function of the mass fraction of water only. It can be assumed that T_i is determined by the mass fraction and type of proteins and intensity of interaction between water and NaCl and proteins.

In Figs 3 and 4 T_i by Chang-Tao model is presented (CHANG & TAO, 1981), given by the linear regression equation with respect to mass fraction of water w_{wo}:

$$T_i = 1.47 \cdot w_{wo} - 1.97 \tag{2}$$

The experimental value for T_i and results by the Chang-Tao model (2) show large deviations. The most important differences for T_i were exhibited for samples with large mass fraction of dry matter. It can be concluded that for complex polydispersed systems, the effect of mass fraction is not the only parameter, but also specific components are important, which require experimental determination.

In Fig. 5 a comparison of dependencies of T_i is presented for melange, egg white, egg yolk, and water solution of NaCl on mass fraction of w NaCl calculated on total mass of water. The good agreement for T_i can be attributed to the assumption of weak interaction between water and NaCl and dry matter of egg.

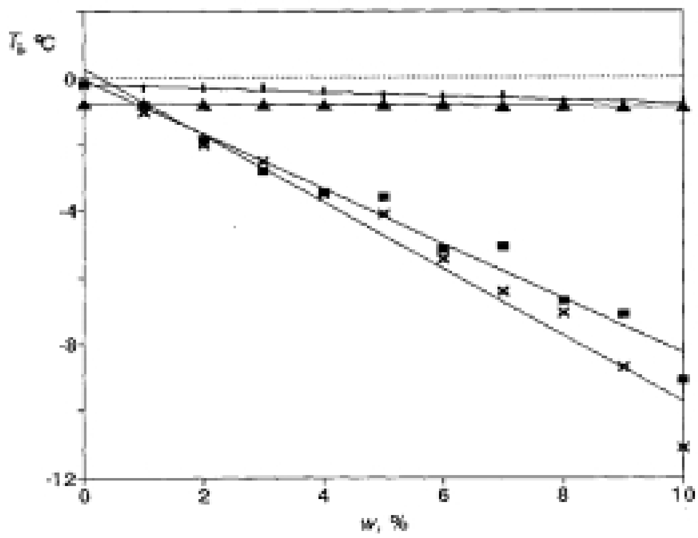

Fig. 3. Initial freezing points T_i of surimi as functions of mass fractions w of the added substances. ····: κ-carrageenan; ×: NaCl; ■: κ-carrageenan + NaCl; ▲: Chang-Tao model; —: linear regression

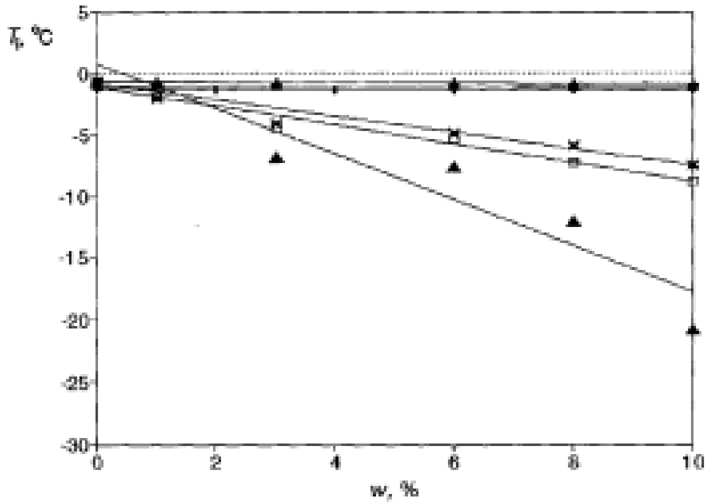

Fig. 4. Initial freezing points T_i of melange, egg white and egg yolk as functions of mass fractions w of the NaCl. +: Chang-Tao model for egg white; ■: Chang-Tao model for melange; □: melange; ····: Chang-Tao model for egg yolk; ×: egg white; ▲: egg yolk; —: linear regression

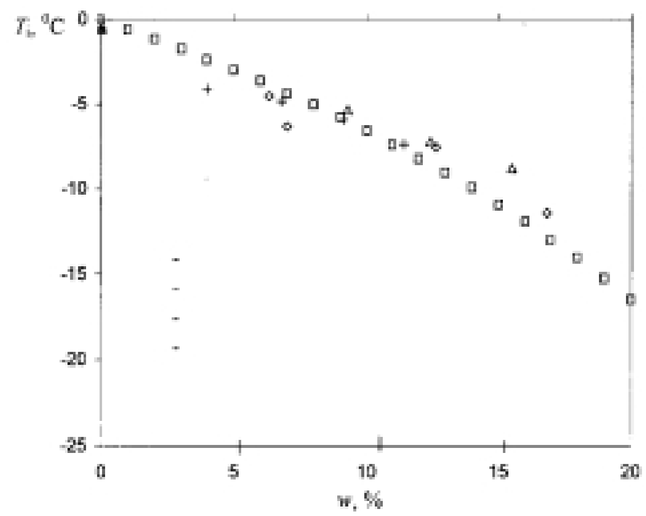

Fig. 5. Comparison of dependencies of T_i for melange, egg white, egg yolk, and water solution of NaCl on mass fraction of w NaCl calculated on total mass of water. □: Water solution of NaCl; Δ: melange; ◇: egg yolk; +: egg white

3. Conclusions

Cryoscopic depression of initial freezing point of surimi and egg (egg yolk, egg white, melange) is a linear function of the increase of mass fraction of added substances: NaCl, mixtures of NaCl and κ-carrageenan in mass ratio of 4:1, and κ-carrageenan.

Maximum decrease of the initial freezing point is observed for samples of egg yolk mixed with NaCl (from –0.59 to –20.77 °C), and the least pronounced effect for samples of surimi with κ-carrageenan (from –0.19 to –0.72 °C).

Comparison of the initial freezing points T_i for samples of egg yolk, egg white, melange and water solution of NaCl as a function of mass fraction of NaCl calculated on total mass of water in respective samples show good agreement.

This result (i.e. the observed fact) supports the assumption that in the process of the freezing the interaction of dry matter of egg and NaCl is negligible.

Chang-Tao model of T_i as a linear function of mass fraction of water is not applicable for samples of surimi with addition of NaCl, mixtures of NaCl and κ-carrageenan in mass ratio of 4:1 and κ-carrageenan.

Initial freezing point T_i of complex polydispersed systems is not only a function of dry matter, but properties of substances which compose dry matter must also be considered.

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