

Ice cream phase composition study using low temperature ^1H NMR spectroscopy

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ABSTRACT

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The low temperature ^1H NMR spectroscopy was used to study the aqueous phase of ice cream while its temperature was increasing from $-60\text{ }^{\circ}\text{C}$ to $0\text{ }^{\circ}\text{C}$. It is an established fact that virtually no releasable water is present in low fat ice cream of typical chemical composition, whilst bound water is observed in a form of two fractions: strongly and weakly bound. The first fraction consists mostly of water as part of hydrated sugars, and the second one is generated through adsorptive action of bio-polymeric mix components.

Radial distribution of ice crystals formed within mixtures is calculated through approximated view on the crystallization of water and sugars as separate substances. It was established that the gauges of crystals so formed are within the range of 1 to 16.6 nm, with two characteristic peaks conditioned by the different water binding energies.

The difference in phase composition between ice creams containing wheat flour and stabilization systems was proved to be negligible. It was further established that gelatinized flour, 5 times exceeding in quantity the stabilization system, virtually equals the latter in water binding.

The results of undertaken studies can be used to calculate the actual sucrose and lactose concentrations in mixtures and ice cream through a wide range of low temperatures.

Introduction

Ice cream is a dispersed heterogenic system [1] consisting of biopolymer molecules and water-emulsified fat droplets. Different concentration water solutions of sugars are used as such system's dispersive medium. Water contained in solutions may be incorporated into hydrate coating of carbohydrate molecules or have the form of molecular poly-associates held in a grid with hydrogen bounds [2, 3]. A part of water is bound through hydrogen binds with biopolymer molecules, forming their hydrate coating into which low-molecular organic compounds can penetrate. Generally speaking, all of water contained in ice cream can be divided into free (not making part of any hydrate compounds) and bound water. Water is

regarded as bound if its free energy, compared to bulk water, is reduced either by adsorption action of macromolecules or hydrate interaction with organic molecules.

Bound water in nanostructured systems is not homogenous either, dividing into strongly and weakly bound. Such differentiation can be based on the criterion of freezing temperature depression due to reduction of Gibbs free energy. Water can be considered as weakly bound if its free energy (ΔG) is reduced by no more than 0.5 kJ/mole, corresponding to the freezing temperature depression $\Delta T = 15$ K [4-6]. Freezing and thawing processes modify the phase composition of the mix since the free and a part of the bound water transfers to hexagonal ice phase, sugars crystallize and re-crystallize, and fat crystals are formed.

Y.A. Olenov et al., [7] studying the condition of water in the cream ice, proved that it is actively bound by hydro-colloids, sugars, and mineral substances of milk. Yet the phase composition of low fat ice containing up to 70% water received little attention so far. Moisture binding capacity provided by the classical stabilizing agent (wheat flour) compared to modern stabilization systems containing hydrocolloid complexes and surface-active additives, has not been studied. Additional studies of milk ice physical condition at low temperatures will be required to exclude uncontrolled ice crystallization in it.

This work purports to research the phase breakdown changes in the course of defrosting the milk ice containing traditional and modern stabilization systems. ^1H NMR spectroscopy and NMR cryometry, widely applied for solid-phase heterogenic systems and biopolymers [4-6], were used in this research.

Material and methods

Two samples were studied:

Mix №1. Milk ice containing the Cremodan stabilization system (by Danisco, Denmark).

Chemical composition, %: milk fat: 3.5; sugar: 15.5; dry skimmed milk solids: 10; water: 70; stabilization system: 0.6 % (fat acid mono- and diglycerides, guar gum, carrageenan, polysorbate).

Mix №2. Milk ice containing wheat flour.

The chemical composition of mix 2 is identical to that of mix 1, except for a slightly reduced water content, down to 68.26 %, and stabilizing system replaced with 3% of wheat flour.

NMR Spectroscopy. NMR specters were obtained using the 400 MHz Varian Mercury high-resolution NMR spectroscope. 90° probing impulse of 3 μs was used. The temperature was controlled with a thermal module Bruker VT-1000 at $\pm 1^\circ$ tolerance. The intensity of signals was determined by measuring the surface of peaks using (if needed) signal decomposition into components, on the assumption of Gaussian line form, and optimizing its zero line and phase with a tolerance which, for well resolved signals, was 5% or lower, and for overlaying signals, ± 10 %. To prevent liquid subcooling effects for the surveyed items, concentrations were measured in the course of heating the samples, previously cooled to 210 K [4-6].

Two key approach assumptions are used in the phase interaction theory: infinitely thin adsorption layer and Gibbs' finite thickness layer [8]. In the first case it is assumed that adsorbed substance forms nano-drops filling the cavities of the porous body. All of the excess energy due to the phase division is concentrated in the monomolecular film of adsorbed substance (e.g. water) bordering on the surface. Due to correlation between the freezing

temperature depression and the size of adsorbed substance drops, size distribution of water filled cavities can be obtained.

To determine the dimensions of inter-phase water clusters, the Gibbs-Thomson equation was used establishing connection between the radius of a spherical or cylindrical water cluster (R) and freezing temperature depression:

$$\Delta T_m = T_m(R) - T_{m,\infty} = \frac{2\sigma_{sl}T_{m,\infty}}{\Delta H_f \rho R}, \quad (1)$$

where $T_m(R)$ is melting temperature of ice localized in R radius pores, $T_{m,\infty}$ is bulk ice melting temperature, ρ is solid phase density, σ_{sl} is energy of interaction between a solid body and fluid, and ΔH_f is volumetric enthalpy of melting.

This equation may be used to calculate the water aggregate size breakdown based on the temperature dependence for the quantity of un-freezing water (C_{uw}) determined based on ^1H NMR spectroscopy with laminar water freezing when the use of other analysis methods is problematic [6]. In practice equation (1) can be used in a form of $\Delta T_m = (k/R)$, where the k constant for many water containing heterogenic systems is close to 50 [8].

For complex solutions this approach is applicable only if the components in crystallization are viewed as separate substances.

The finite layer method [8] is based on the assumption that the influence of phase dividing surface spreads several layers deep into the liquid phase: then the freezing (thawing) of inter-phase water, localized within the solid porous matrix, will occur in accordance with the changes in Gibbs' free energy. It will fall pro rata to a specific water layer's distance from the surface. At $T = 273 \text{ K}$, water will freeze if its properties are identical to bulk water, and as the temperature falls further, the layers closer to the surface will freeze sooner, and the following equation will apply to inter-phase water:

$$\Delta G_{ice} = -0,036(273,15 - T), \quad (2)$$

in which the numeric ratio represents a parameter connected with the temperature factor of changes in Gibbs free energy for ice [9]. After deducing the temperature dependence of unfrozen water concentration $C_{uw}(T)$ from the signal intensity, the method described in [5, 6, 9, 10] may be used to calculate the quantities of strongly and weakly bound water, as well as thermodynamic features of those layers.

Inter-phase energy of water, equivalent to the overall reduction of the system's free energy, which is due to presence of internal phase boundaries and solutes [4-6], can be calculated using the following formula:

$$\gamma_s = -K \int_0^{C_{uw}^{max}} \Delta G(C_{uw}) dC_{uw}, \quad (3)$$

where C_{uw}^{max} means the total quantity of unfrozen water at $T = 273 \text{ K}$.

Results and discussions

^1H NMR specters taken at different temperatures within the range $210 < T < 280 \text{ K}$ for mixes №1 and №2 are displayed on fig. 1 a, b respectively. On those specters three proton signals are observed with chemical shifts $\delta_H = 5, 3-4$ and 1 ppm which can be identified as signals of water, mono- and disaccharides and fat, respectively. Protein and polysaccharide molecules are not observed within the specters due to low mobility of their molecules. As the

temperature falls, the intensity of all signals is reduced pro rata to freezing of the components in the solution. Frozen substances are not recorded on the specters due to the short time of transverse relaxation for protons in solid bodies [11]. The relatively large width of the signals is due to reduction of molecular mobility in viscous heterogenic systems. Although the proton specter in sugars is made of several signals of hydroxyl groups, non-equivalent magnetically, but the fine structure of sugar specter is observed only for mix №1. The temperature dependence of concentration of un-frozen water, sugar, and fats for mixes №1 and №2 are shown on fig. 2.

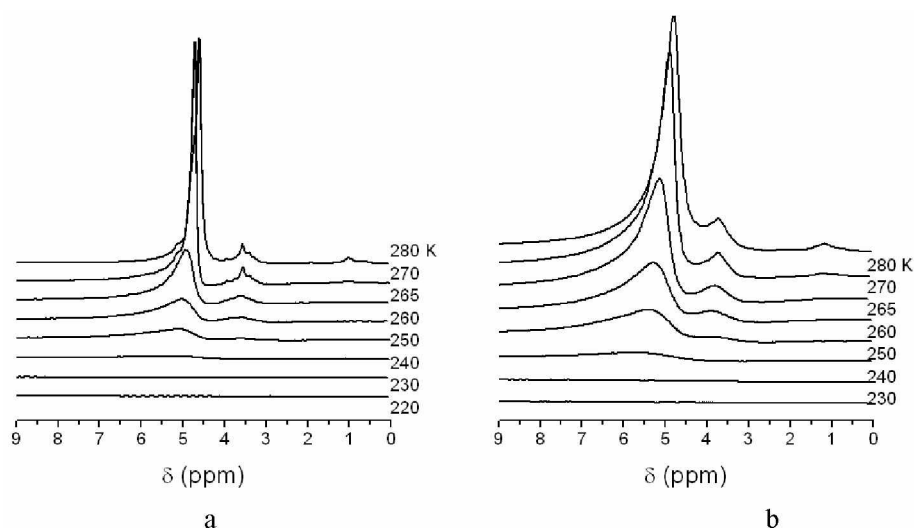


Fig. 1. ^1H NMR specters at different temperatures for mix №1 (a) and №2 (b)

According to data on fig. 2, the water thawing curves are closely shaped for mixes №1 and №2. In both cases nearly no water is freezing in close proximity to 273 K. Therefore, nearly all of it is bound with biopolymer components or engaged in hydrate coating of carbohydrate molecules. The dependence curves $C_{uw}(T)$ display an inflection point corresponding to a temperature of $T = 260$ K. For the systems in question, water freezing above that temperature can be considered as weakly bound.

Water freezing in saccharide solutions in mix 1 occurs at $T < 270$ K, and in mix 2, near $T = 280$ K.

The difference in carbohydrate freezing curves (fig. 2) signals the difference of their concentrations in the non-frozen phase, which difference can be calculated based on proportions between the quantity of un-frozen water and saccharides (fig. 3).

Those dependences have a complex shape, which differs for mixes №1 and №2. For mix 1, as long as the temperature is descending to $T = 260$ K, concentration of un-frozen phase sugars monotonously increases. For mix 2, sugar concentration growth is observed between $260 < T < 270$ K. This growth is notably lower than for mix 1. At $270 < T < 280$ K the concentration of sugars in non-frozen water is decreasing for mix 1. Both mixtures display falling sugar concentrations due to their freezing. Their signals in ^1H NMR specters are not observed under $T = 250$ K (fig. 1, 2). Whereas the temperature of $T = 260$ K is a transition point delimiting

strongly and weakly bound water, it can be assumed that weakly bound water in mixes №1 and №2 is mainly present in a form of sugar hydrates.

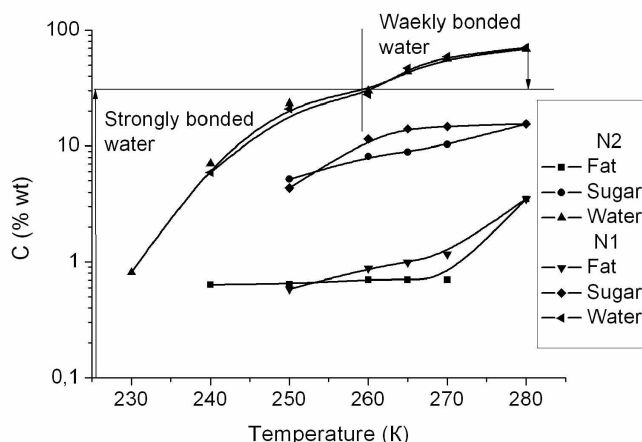


Fig. 2. Temperature dependences of concentration of un-frozen water, sugar, and fats for mixes №1 and №2.

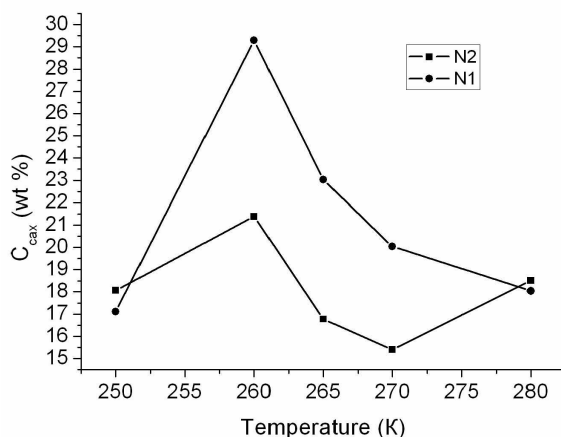


Fig. 3. Temperature dependences for concentration of un-frozen phase sugars in mixes №1 and №2.

On fig. 4 the dependences are shown for inter-phase Gibbs energy, calculated using formula (2), on the un-frozen water concentration per weight unit of aggregate concentrations of biopolymer components and sugars. The features of inter-phase water layers calculated as per method described in [4-6] are summarized in the table below.

The concentrations of strongly and weakly bound water, ΔG^s and ΔG^w , were determined in section points of curves $\Delta G(C_{unf})$ with the straight line on the level of $\Delta G = 0.5$ kJ/mole (fig. 4), and the total quantity of water in mixtures prior to freezing.

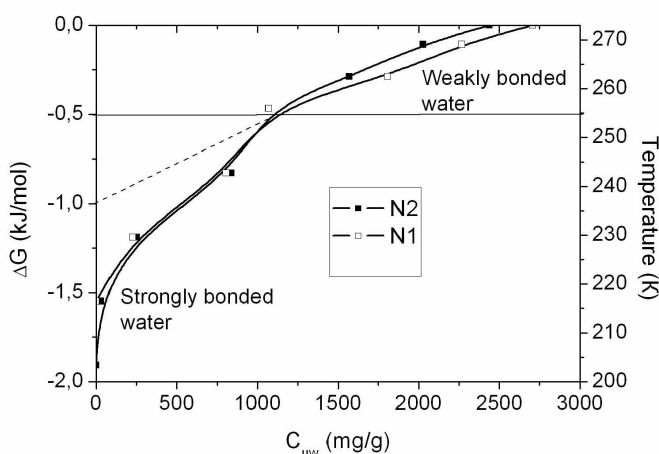


Fig. 4. The dependence of change in the inter-phase Gibbs energy on un-frozen water concentration per weight unit of biopolymers and sugars combined.

The maximal free energy drop within the layer of strongly (ΔG^s) and weakly (ΔG^w) bound water was determined in section points of the relevant curve parts $\Delta G/C_{uw}$ with the Y axis. Considering that weakly bound water is mostly presented in a form of hydrated sugars, it can be speculated that the value of ΔG^w is approximated to the free energy of sugar hydration. Strongly bound water in mixes 1 and 2 is seen as water bound to biopolymer components. The aggregate reduction of water's free energy due to presence of solutes and adsorption action of biopolymers, is expressed as γ^s . This quantity is slightly higher for mix 1, mainly due to a higher quantity of weakly bound water (see the table). Figure 5 shows the distribution of ice crystals per radius as obtained from equation (1).

Table 1. Un-frozen Water Layer Features for Mixes №1 and №2

Mix	C_{uw}^s mg/g	C_{uw}^w mg/g	ΔG^w kJ/mole	ΔG^s kJ/mole	γ^s J/g
1	1100	1600	-1	-1.6	81
2	1070	1370	-1	-1.8	78

For both mixes the dimensions of ice crystals fall within the range of 1 to 16.6 nm. There are two peaks on distribution curves. The right peak, comprising the three right bars, pertains mostly to sugars freezing out of solutions. The left peak mainly reflects crystallization of water bound by biopolymer components of the mix.

Thus, it is evident that the differences in phase composition of ice mixtures containing the traditional and modern stabilizing agents are marginal. Gelatinized flour, 5 times exceeding in quantity the stabilization system, virtually equals the latter in water binding.

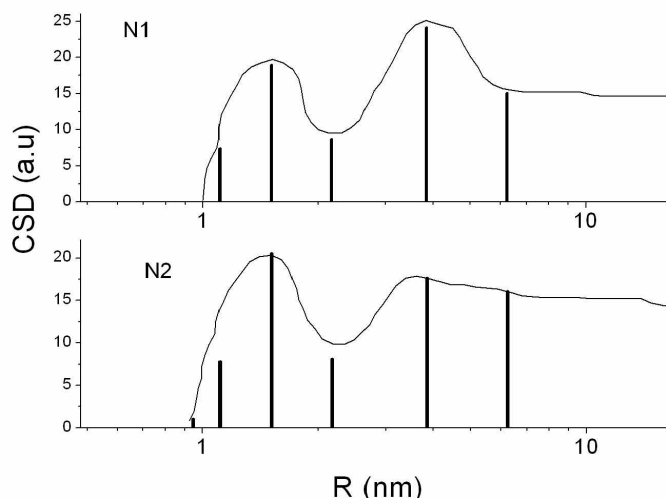


Fig. 5. Distribution of ice crystals per radius in frozen mixes.

Further studies should address the rheology of those mixes to achieve a deeper understanding of the ice cream structure formation and stabilization behavior.

Conclusions

The low temperature ^1H NMR spectroscopy enables to study the aqueous phase of ice cream while its temperature is increasing from -60°C to 0°C .

In milk ice with low free water content, free water is observed in two fractions: strongly and weakly bound.

The calculated dimensions of ice crystals built within milk ice fall within the range between 1 and 16.6 nm.

Water crystallization in mixes containing wheat flour compared to those with stabilizing system, both in quantities recommended by the manufacturer, is virtually identical.

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