ELSEVIER
Materials Science and Engineering C 19 (2002) 33–35
MATERIALS SCIENCE & ENGINEERING C
www.elsevier.com/locate/msec

Identification of moisture nanoparticles in the butter sub-microstructure

T.A. Rashevskaya [a,*], I.S Gulyi [a], A.I. Ukrainets [a], M.M. Nishchenko [b], S.P. Likhtorovich [b], E.V. Buzaneva [c]

[a] *Ukrainian State University of Food Technologies, Vladimirskaya St. 69, Kiev, 01033 Ukraine*
[b] *Institute for Metal Physics, N.A.S.U., Vernadsky Blvd. 36, Kiev, 03142 Ukraine*
[c] *Kiev State University, Vladimirskaya St. 64, Kiev, 01033 Ukraine*

Abstract

Formation of sub-microstructure, including the nucleation and growth of ultradisperse water particles (with the average diameter of 46 nm) in the butter, is studied by means of electron microscopy. It is shown that addition of the red-beet cryopowder leads to the formation of water particles (3 nm in diameter) at the interfaces between monomolecular layers of the milkfat triglycerides. The larger moisture nanoparticles of 10–16-nm diameter are formed at the edges and vertices of octahedral, dodecahedral, and icosahedral crystals consisting of the high-melting milkfat fractions. © 2002 Published by Elsevier Science B.V.

Keywords: Milkfat triglycerides; Water; Monomolecular layers; Interfaces; Electron microscopy; Nanovoids

1. Introduction

Water is one of the basic components of the butter. It substantially affects the most indicators of the butter quality. State of the water (adsorbed, ultradisperse, etc.), disperseness, the size and configuration of the free water phase determine the storage limits, consistence and taste of the butter. The worsening of the butter's durability during the storage is caused by coarsening of the moisture and subsequent appearance of continuous water phase [1]. The latter accelerates the intensity of biochemical and microbiological processes. Therefore, control of the water state in the structure of the butter is of major importance. The decisive factor is the high degree of moisture disperseness and its stability in the butter. These can be achieved by the admixture of natural additives prepared from safe vegetable nutrients, which change coefficient of the surface tension at the interface between the two immiscible liquids (the milkfat and the water) and can promote the formation of such a structure of the butter that stabilizes and holds the disperse water subsystem.

We have studied by means of the electron microscopy the processes of sub-microstructure formation in the butter as well as the distribution of ultradisperse water particles (less than 100 nm in diameter) on their sizes in as-received butter and after its storage at −18 °C. We have found a stabilizing effect of beet cryopowder additive on these processes. Thermodynamical calculations were carried out to support a suggestion that the objects less than 100 nm in diameter are indeed the water-phase particles.

* Corresponding author. Tel.: +44-380-2210-740; fax: +44-380-2212-352.
E-mail address: rashevsk@usuft.kiev.ua (T.A. Rashevskaya).

2. Experiment and results

The samples for the electron microscopy studies were prepared by cleavage of the butter rapidly quenched to the temperature of −160 °C. Freezing was used to fix the structure of the butter at the given storage temperatures.

Frozen butter samples were cleaved in a deep vacuum. Cleavage surface was covered at an angle of 30° with a platinum layer 2–3-nm thick and fixed with a carbon layer 15–30-nm thick. Replica thus obtained was subsequently studied in the electron microscope. An analysis of the electron-microscope images has shown that spherical particles of 3 to 64 nm in diameter are present in the sub-microstructure of all butter samples investigated. Coalescence of these particles leads to the formation of long quasi one-dimensional chains aligned along the interfaces.

Size distribution of the particles in the reference butter samples (conserved at −18 °C) was found to obey the normal (Gaussian) distribution with the most probable r value of 23 nm (see Fig. 1). It means that the particles are in thermodynamical equilibrium with the fat phase of the butter. In order to identify the particles' water origin,

0928-4931/02/$ - see front matter © 2002 Published by Elsevier Science B.V.
PII: S0928-4931(01)00420-9

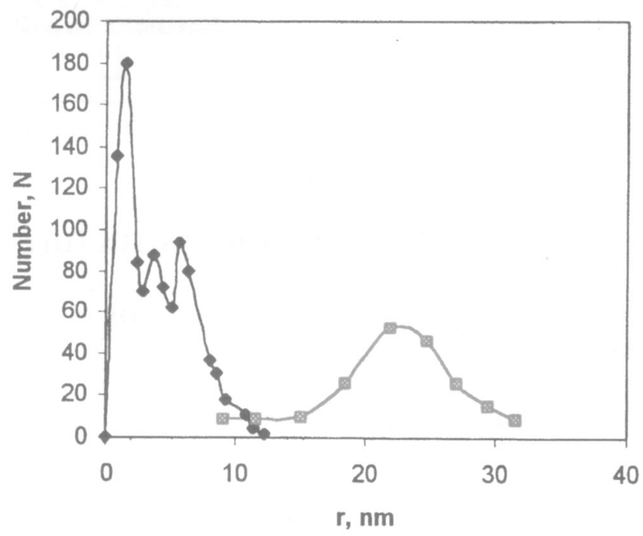

Fig. 1. Size distribution of water nanoparticles (r is the radius) in the butter with the red-beet cryopowder additive (diamonds) and in the reference butter samples without additives (squares).

thermodynamical calculations based on the known surface-tension coefficients of the milkfat and water were carried out.

We start from the following assumptions. Growth of a spherical particle with the radius r results in the decrease of the fat–fat contact area and its surface energy by $2\sigma_1\pi r^2$ and in the appearance of a hew interface with the surface energy equal to $4\pi\sigma_{12}r^2$. Here σ_1 and σ_{12} are specific surface energies for the milkfat and the milkfat–water interface, respectively. Thermodynamic stability of a spherical water particle is determined by the minimum of the net surface energy, the work A_e of elastic forces (to surpass fat's resistance to the growing particle) and the work needed to surpass atmospheric pressure, $4/3\pi r^3 P_{at}$. Thus, the change of the Gibbs free energy F can be written as:

$$\Delta F = -2\sigma_1\pi r^2 + 4\pi\sigma_{12}r^2 + 4/3\pi r^3 P_{at} + A_e.$$

The radius r_{cr} of the most stable water particles is then determined by a zero of the first derivative, $d(\Delta F)/dr = 0$:

$$r_{cr} = (\sigma_1 - 2\sigma_{12})/P_{at}.$$

In the case of the reference butter samples, with $\sigma_1 = 30.6\times10^{-3}$ N/m and $\sigma_{12} = 13.3\times10^{-3}$ N/m [1], we obtain $r_{cr} = 40$ nm, which is larger than experimental value of 23 nm for spherical water particles (see Fig. 1). This discrepancy may be caused by an assumption of ideal wetting at the fat interfaces ($\gamma_{in} = 2\sigma_1$). Thermodynamical stability of spherical particles is enhanced when they merge. In this case the increase of the particle length is accompanied by increase of their thickness. This conjecture agrees with the results of the electron microscopy studies (see Fig. 2).

Size distribution of the water particles in the butter with beet supplement differs from that in the reference samples. Shown in Fig. 1 is the size distribution of water particles in the reference samples of the butter and in the butter with the beet additives. In the first case, only spherical particles are observed with a mean radius of 23 nm. In the second case, there are three maxima at 1.5, 4, and 6 nm.

This is an evidence of the presence of three types of spherical particles. The smallest of them, with a concentration of $\sim 10^{12}$ cm^{-2}, reside in the most low-melting amorphous phase of the milkfat. They are thermodynamically unstable and grow to the radius of 6–10 nm when placed at the flat interfaces, and to 10–16 nm when they are formed at the edges or the vertices of octahedra, dodecahedra, and icosahedra consisting of the most high-melting fatty-acid triglycerides. The latter form in the centres of the cellular fat structure, while the low-melting components are forced out to the cell's boundaries. Free energy of the milkfat–water system reduces as a result of the water particle growth due to both an adsorption layer and coalescence of the particles situated along the interfaces, for example, at the cells' boundaries. The vertices and edges of the crystals consisting of the most high-melting fatty-acid triglycerides are the nucleation centres of the water particles, which are thermodynamically most stable. At flat interfaces the size of the water particles depends on the melting temperatures of adjacent phases; for the low-melting amorphous phase the water drops are smaller, whereas for the high-melting phases they are larger. It is accounted for the increase of the surface tension with increasing melting points of the milkfat components.

Substantial increase of the water drops in the butter with a beet cryopowder supplements can be achieved through a small increase in the surface tension (from $13.3\cdot10^{-3}$ to $15.1\cdot10^{-3}$ N/m) at the milkfat–water interface as a result of the beet cryopowder dissolution in the water phase.

Formation of the smallest water particles (~ 2 nm), which can still be observed in electron microscope, may be conjectured as follows. The nanovoids found in the fat phase of the butter [2] have the radii of 0.27 to 0.52 nm.

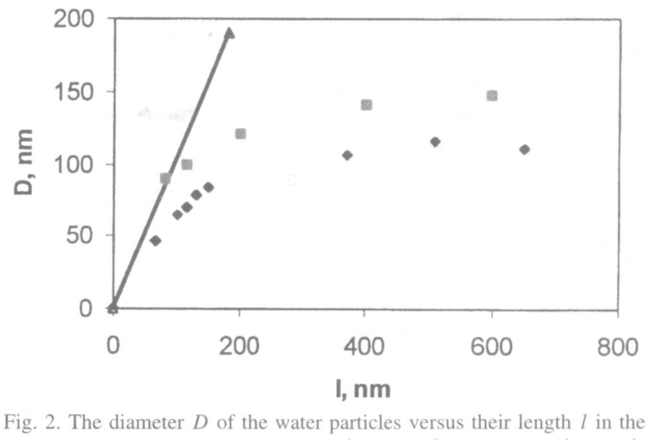

Fig. 2. The diameter D of the water particles versus their length l in the butter without additives: experiment (diamonds) and theory (squares). Straight line corresponds to the case of spherical particles.

Energetically, the most favourable process in the butter, which also contains the nanovoids, is the process of the water adsorption at the inner surfaces of the largest nanovoids. These ones are situated between the lamellae or triglycerides' monomolecular layers. The next stage is the growth of spherical water drops to the size, which can be detected by the electron microscopy.

References

[1] A.P. Byelousov, Physical and Chemical Processes in the Butter Production from Cream, Legkaya i Pischevaya Promishlennost, Moscow, 1984 (in Russian).

[2] T. Rashevskaya, I. Guly, M. Nishchenko, S. Likhtorovich, Int. Agrophys. 14 (2000) 221.