Application of optical and positron spectroscopy to structure transformation study in milk fat and its simple purified fractions

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Structure transformations from amorphous to crystalline state in milk fat as well as its simple purified fractions have been studied using optical and positron spectroscopy. The crystallization of amorphous fat results in appearance of a high-intensity peak in its luminescence spectrum. Transmission and luminescence excitation spectra have been also studied at different temperatures.

Методами оптической и позитронной спектроскопии исследованы структурные переходы молочного жира и его простых фракций из аморфного в кристаллическое состояние. Кристаллизация аморфного жира приводит к появлению интенсивного пика в спектре его люминесценции. Исследованы спектры пропускания и возбуждения люминесценции жира и его фракций при различных температурах.

Long chain compounds, such as milk fat (MF), contain various fractions, which can occurred in different crystal forms, a phenomenon is known as polymorphism. The polymorphic forms of these fractions differ in a number of properties, including melting points and stability. The crystal size and shape in a fat is related to its polymorphic state [1].

The triglyceride MF molecule is formed by three molecules of different fat acids connected to glycerol one and looks like a tuning fork manifesting an anisotropy in physical properties. These molecules have methyl groups at the ends of fat acid chains and exhibit strong interatomic bonds inside the molecules and relatively weak Van der Waals type bonds between them. Between the nearest terminating CH_3 groups, the crystalline structure defects, i. e. pores, can exist in MF due to different lengths of the acid chains. Most data on the polymorphism of long chain compounds has been obtained by studying simple purified substances. The natural fat often contains a wide variety of glycerides differing in chain length and unsaturation degrees of their fatty acid components. The polymorphic behaviour of such complex mixtures is often not easy explained in terms of one or more of their major components.

The method used most widely to study lipid polymorphism is X-ray diffraction. There are other well-known methods, such as low-temperature infrared spectroscopy, differential scanning calorimetry, microscopy, and thermal analysis, are also employed. Photoluminescence spectroscopy is a rather sensitive tool for studying the optical properties of solids which depend on

their electron structure. On the other hand, the electron structure of solids correlates with peculiarities of their crystalline (atomic) structure. Furthermore, the positron spectroscopy is an effective technique to study various defects of solid crystal structure. It is also well known that defects of alkali halide crystals, as vacancies, are responsible for their absorption and luminescence.

Therefore, the purpose of this work was to use experimental photoluminescence and positron spectroscopy method to obtain an additional information on the influence of the structure transformations in milk fat and their simple purified fractions on their physical properties.

Metastable amorphous phase in MF samples was obtained by quenching the melted MF from 340 K in liquid nitrogen. The structural relaxation of amorphous phase to more equilibrium crystalline one was obtained by aging the amorphous samples at different (273 and 293 K) temperatures during 90 days. Microphotography was used for the qualitative structural analyses of the prepared samples. It is known that MF can be separated into several (at least 6) simple purified fractions (SPF). Besides MF, two of these SPF were also investigated. SPF were extracted from MF using fractional crystallization from its acetone solution and separation of so-called "high-melting-point" (HM) and "low-melting-point" (LM) fractions at 286 and 273 K, respectively. It is known that the structure of various SPF of MF differ in chain length of the fat acids connected to the glycerol "core".

The luminescence and its excitation spectra of the samples were measured at room and elevated temperatures by photoelectric method in the 300–700 nm (4.13–1.77 eV) and 200–500 nm (6.2–2.48 eV) spectral ranges. respectively. The transmission spectra of 30 μm thick samples were measured in 200–500 nm (6.2–2.48 eV) spectral range at 293 K and 330 K. The absorption of was calculated as $A = \ln(1/T)$, where T is transmission. The angular distribution of the annihilation photons (ADAP) was measured using a long-slit spectrometer with angular resolution of about 1 mrad. The ^{22}Na isotope of 1 mCi activity was used as the positron source. Experimental ADAP curves were presented as the sum of three Gaussian curves. The main contribution to ADAP is provided by positrons annihilating with electrons of triglyceride molecules localized
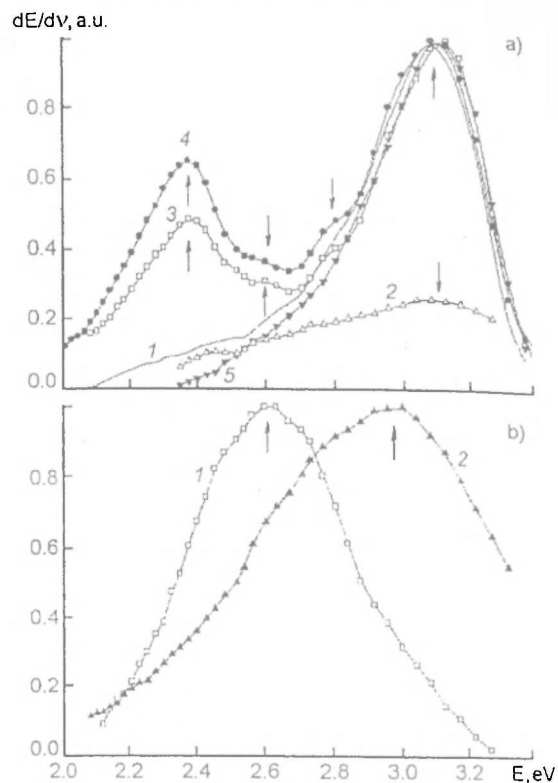

Fig.1. Luminescence spectra of MF (a) and SPF (b). Excitation energy 3.67 eV. Quenched MF, spectrum taken at 293 K (*1*); the same, at 340 K (*2*); MF aged for 90 days at 273 K (*3*) and 293 K (*4*); MF aged for 90 days and then re-melted (*5*).

near the pores. The positron spectroscopy allows to determine the localization radius of the positronium wavefunction near sub-nanopores as well as the annihilation probability of electrons with positrons, S. The minimum transversal pore radius, R_p, where electron-positron annihilation occurs from the positronium state (e^+e^-) was calculated as $R_p = 16.6/\sigma_{1/2}$-1.66 (in Å), where $\sigma_{1/2}$ is the FWHM of the most narrow Gaussian curve (in mrad) [2].

The luminescence spectrum of as-quenched amorphous MF is characterized by an intense band with a maximum at 3.1 eV and weak peaks on its low-energy shoulder located at 2.6 and 2.8 eV (see Fig.1). The aging of amorphous MF at 273 K as well as at room temperatures during 90 days resulted in appearance of an additional intense luminescence band with a maximum at 2.38 eV. It should be mentioned here that the relative intensity (with respect to main band) of this additional band as well as that of weak peaks on the low-energy shoulder of main band is higher at elevated

ng temperature. It can be supposed that ch a transformation of the MF lumines-cence spectrum due to aging reflects the structural relaxation of amorphous phase towards the crystalline one or crystal-lization of MF (see Fig.1). In fact, the structure study of MF using microphotogra-phy as well as results of the positron anni-hilation confirm this assumption.

The observed changes in the lumines-cence spectra are reversible, i. e. heating of the MF aged during 90 days to the liquid state (up to 340 K) restores completely the primary luminescence spectrum measured at 293 K. On the other hand, it should be mentioned here that the luminescence inten-sity in the liquid state (measured at 340 K) is much lower than in the solid state. This intensity decrease can be explained by sev-eral mechanisms, for example, temperature quenching. Even without an additional band at 2.38 eV, the MF luminescence spectrum exhibits a rather complex structure and contains at least 3 components. These bands can be supposed to be related to different SPF of MF. In fact, the luminescence maxi-mum of the HM SPF coincides with a weak peculiarity on the low-energy shoulder of the main MF band [compare Fig.1 (a) and (b)]. The low intensity of this band in the MF luminescence spectrum can be explained by relatively low content of this SPF in MF.

In order to understand more the nature of the luminescence spectra for the studied samples, their absorption spectra were stud-ied at room and elevated temperatures. The results obtained are shown in Fig.2. It is seen that all these spectra are characterized by absorption bands at 3.9, 4.4, and 4.6 eV as well as by a general background. The backgrounds are rather similar for all sam-ples and show a progressively increasing ab-sorption with photon energy. Transition from the solid state to the liquid one (with the temperature elevation up to 340 K) re-sults in a remarkable decrease in the back-ground without any changes in the absorp-tion bands intensity and in their arrange-ment [see Fig.2 (b)]. The luminescence excitation spectrum for MF exhibits an in-tense band at 3.9 eV and two weak peculi-arities at 4.4 and 4.6 eV [see Fig.2 (b)]. The location of components in the excitation spectrum corresponds to band locations in absorption one. As mentioned above, the main difference between various SPF is due to the length differences between the fat acid chains connected to the glycerol core. On the other hand, the absorption spectra
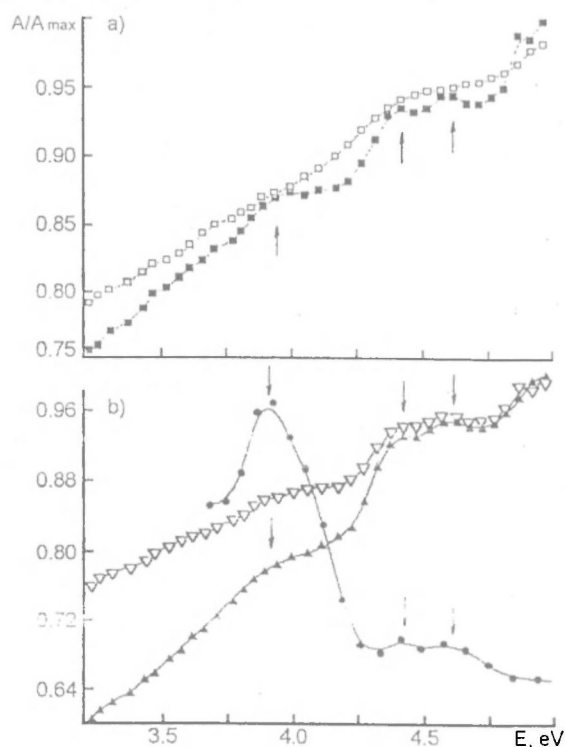

Fig.2. Absorption spectra of SPF (a), excita-tion of the luminescence spectrum (circles); MF absorption spectra measured at different temperatures (b). Curves are denoted as in Fig.1.

of all studied SPF as well as MF are rather similar to each other. Therefore, it can be supposed that the luminescence excitation mechanism for all samples studied here is the same, while non-radiative transitions to the final excited state differ for different SPF.

According to the positron spectroscopy results, the nanopore radius depends on structural state of MF or SPF triglyceride and varies from 2.2 to 3.9 Å for all sam-ples. A correlation between the average pore radius, R_p, and the positronium annihila-tion probability, S, has been established: the larger is R_p, the lower is S (see Fig.3). The maximum radius value for various structural states of different fractions var-ies in a very narrow range from 3.6 to 3.9 Å. These values are rather close to the interchain distances in fat acids for different modifications of triglyceride (α, β and β') that are 4.14, 3.78 and 3.68 Å, respectively [3]. The long-term (38 days) aging of HM SPF at room temperature results in a decrease in R_p from 3.6 to 2.2 Å. This decrease in aver-age pore radius may be caused by structure ordering (crystallization) due to aging.
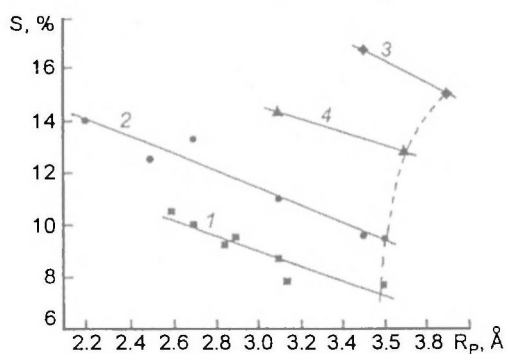
Fig.3. Dependence of the positronium annihilation probability inside the pore, S, on the pore radius, R_p: amorphous HM SPF (1); crystalline HM SPF (2); liquid HM SPF (3); liquid LM SPF (4). Dashed line connects maximum R_p values for different states and fractions.

The decrease in the mean pore radius to 2.2 Å after the long-term exposure HM SPF at RT can be accompanied by an increase in the pore length and bending of the triglyceride molecules towards the pore interior. The decrease in the pore radius R_p is accompanied by an increase in the positronium formation probability, S, inside the pore. This is due most likely to the weakening of the electron binding with CH_n groups due to their polarization in the vicinity of the pore. This reduction of the electron binding energy around the pore may be responsible for the observed shift of the luminescence spectrum towards the long-wave region after the long-term (90 days) MF exposure at 273 K.

Thus, the long-term aging of MF results in a structural relaxation of amorphous MF towards the crystalline phase. The heat treatment of the aged MF restores the amorphous phase of milk fat. The absorption spectra of MF comprise bands located at 3.9, 4.4 and 4.6 eV on the general absorption background. The correlation dependence between the average pore radius, R_p, and the probability of the positronium annihilation, S, has been established: the larger is R_p, the smaller is S.

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