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THE SEGMENTAL MOBILITY OF UNHYDRATED AND HYDRATED LIPID MULTILAYERS ACCORDING TO THE DATA OF MOSSBAUER SPECTROSCOPY

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Abstract Using the hydrophilic and hydrophobic Mossbauer molecular labels (ferrocene ^{57}Fe and its derivatives) the influence of cholesterol and hydration on rigidity and intra- and intermolecular mobilities of lecithin multilayer matrix has been studied. For cholesterol containing systems, at least, two nonequivalent equilibrium states of labels were registered showing on the heterophase behavior of these systems.The model, connects the observed effects with the change of internal friction (microviscosity) of the lipid matrix in the regions of localizing of the labels,was suggested.

INTRODUCTION

Different modern physical methods are widely used for structural and dynamical investigations of biological membranes and their models (in particular - lipid systems).
Conformable to these objects the diffraction techniques based on the interaction with a substance under investigation of X-Rays, electrons, neutrons allow to get the information on the type and periodicity of mesophases, on the thickness of lipid bilayer, on average distances between aliphatic chains of lipids and so on. Thus these methods are the most informative for high ordered structures.
On the other hand, the resonance techniques, such as nuclear magnetic resonance, electron spin resonance, are the most effective for study of motions in "liquid" bi- and multilauers, but more less effective for study of lipid systems and biomembranes at comparatively low temperatures (under the liquid crystalline transition).

The optical methods are very effective for study of separate bilayers and their local regions at room and more high temperatures, but they are also of little value for investigation of lipid multilayers and suspensions.

Mossbauer spectroscopy engages its own niche in tis complex of techniques. It is particularly effective for solids. In variant of atomic or molecular label this technique is now effectively used also for study of liquid crystals [1-3]. It was shown that the use of label with a different affinity to a definite microregions of liquid crystalline (LC) matrix makes it possible to localize that label in these microregions and to study the dynamics of these individual parts in such heterogenic systems [4]. This circumstance seems promising also for study of lipid systems on molecular level.

In our papers [5-7] the results of investigation of multilayers of phospholipids: cephalin and egg lecithin (L)with tin tetrachloride and ferrocene derivatives as a labels have been published.

The recording of low-temperature (T<210 K) "defreezing" of the mobilities of molecular fragments of cephalin,chemically bonded with $SnCl_4$ label,in an anhydrous lipid matrix can be considered as the main result, obtained in [5]. However,because of temperature limitations of ^{119}Sn Mossbauer effect registration, we can not achieve in [5] the physiological temperatures. The use as a label ferrocene and its derivatives allows to raise the temperature range under investigation up to 320 - 340 K[6-7].

By comparing the isomer shift (IS) and quadrupole splitting (QS) in the Mossbauer spectra of the individual labels and the corresponding parameters of these labels in lipid system, the presence or absence of chemical interaction between the label and lipid molecules and the preferrent points of label localization may be established. In particular, for lecithin multilayers it was found that ferrocene (F) does not react with lipid molecules. Thus, the preferred point of localization for F is in hydrophobic regions of L matrices (close to hydrocarbon tails of L molecules - Fig.2a).The

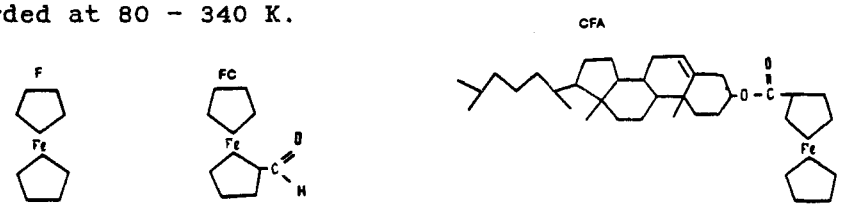
presence of chemical reaction the other label- ferrocene carbaldehyde (FC) -with L matrix suggests that FC molecules are localized in hydrophilic regions of L matrices (close to polar heads of L molecules) [6].

By investigation of the temperature dependence of the logarithm of the area under the Mossbauer lines (ln S) for F and FC, localized in various microregions of L matrix, judgments regarding the dynamics of these microregions may be made. Thus, the sharp deviation of ln S(T) from linearity for lecithin-ferrocene (L-F) system at 160 - 180 K and for L-FC system at 180 -240 K indicates the appearance of additional molecular motions in the regions of label localization.The segmental mobility appears at 160 -180 K in the region of the hydrocarbon chains, while the intensive vibrations extended over the whole hydrocarbon chain at 180 - 240 K. The appearance of reorientational motion of various fragments of L molecules can be associated with the onset of an extended phase transition in L multilayers, leading ultimately to melting of the hydrocarbon chains of L (to transition from a gel to liquid crystalline state)[7].

In this paper, using the same hydrophobic (F) and hydrophilic (FC) mossbauer labels, we studied the influence of cholesterol content and the hydration of lipid systems on their segmental mobility and rigidity.

EXPERIMENTAL

Mossbauer spectra of monolipid systems cholesterol-ferrocene (C-F), C-FC, individual cholesterol ferrocene acetate (CFA),and bilipid systems L-C-F, L-C-FC and L-CFA were recorded at 80 - 340 K.



The content of X in bilipid systems was 0,03; 0,10 and 1,00 mol.% (equimolar L-C systems have been studied in [7]). The

content of labels in the systems was 2 - 6 wt.%.The sample preparation and instrumentation details were described earlier [6].

RESULTS AND DISCUSSION

Unhydrated monolipid cholesterol systems

In contrast to phospholipid systems the ln S (T) dependence in Mossbauer spectra cholesterol systems is linear for all labels over the whole experimental temperature range (Fig.1). It is not astonish, because of cholesterol at these temperatures is in a solid phase.

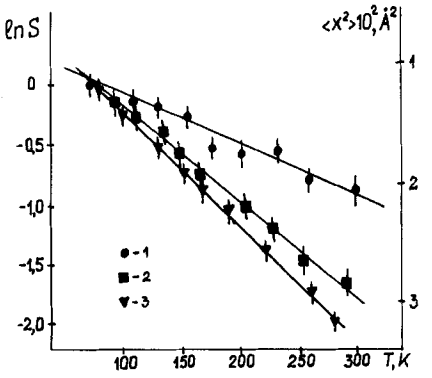


FIGURE 1 The ln S(T) and $\langle x^2 \rangle$(T) dependences for monolipid cholesterol systems: 1) C-F(3 wt.%); 2) C-FC(1:1); 3) individual CFA.

Such a linear dependence is characteristic of the molecular crystals, where Fe atom participates in intramolecular (valence and deformational) and, together with the molecule, in intermolecular translational vibrations. In the present case, S is proportional to the probability of a Mossbauer effect f' ($f' = \exp -(\langle x^2 \rangle / \lambda^2)$, where $\langle x^2 \rangle$ - mean-square amplitude of Fe atom vibrations in the direction of gamma-quantum propagation, λ - gamma-quantum wavelength); for molecular crystals: $f' = f'_a \cdot f'_m$, where f'_a is determined by intramolecular vibrations and depends weakly on the temperature, while f'_m is characterized by intermolecular vibrations. f'_a and

f_m' are sufficiently well described by Einstein and Debye models of solid, respectively [8] Therefore, in the harmonic approximation, ln S~ T. Such linearity should be observed until new degrees of freedom are exited in the system (for example, reorientational motion of molecules - see above).

It can see from Fig.1, that dependences of ln S (T) for C-FC and CFA are close enough. CFA can considered as a model compound, where ferrocene ester fragment is chemically bonded with cholesterol fragment.This fact indicates that the FC molecules in C matrix are localized near the polar heads of sterine molecules (Fig.2b). For C-F and CFA systems the slopes of ln S(T)dependence,so as IS and QS values, are essentially different. Consequently, the preferrent point of F and FC localization in C matrix are different. Apparently, F molecules localized in the region of hydrocarbon tails of C molecules - see Fig.2b.

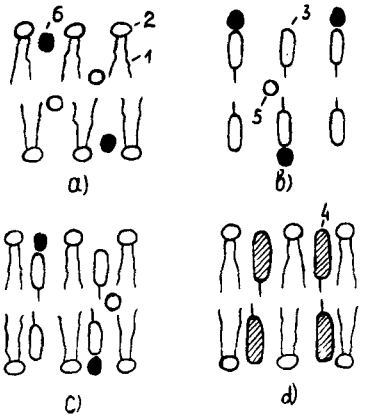


FIGURE 2 Scheme of preferrential localization of different mossbauer labels in lipid matrices: a) L, b) C, c) L-C, d) L-CFA; 1 - hydrophobic part of L molecule, 2 - hydrophilic part of L molecule, 3 - molecule of C, 4 - molecule of CFA, 5 - molecule of F, 6 - molecule of FC..

A greater slope of ln S(T) line for C-F system in comparison with corresponding line for C-F system indicates on less "rigidity" (lower frequencies of intermolecular vibrations) of hydrophilic microregions C matrix as compared to its hyd-

rophobic microregions.

Unhydrated bilipid (lecithin-cholesterol) systems

It is known that cholesterol orders the phospholipid layers in membranes, regulating and dumping the mobility of lipid frame [9]. There are indications for formation 1:1 complex between L and C molecules owing to Van der-Vaals interaction[10]. Fig.3 shows the temperature dependences of ln S for L-C-F systems with low C content. It is seen, that with the increasing of C content the L-C system becomes more rigid (the slope of linear parts of ln S (T) dependences become lower), and the lecithin aliphatic chain mobilities defreezing points change to higher temperatures.

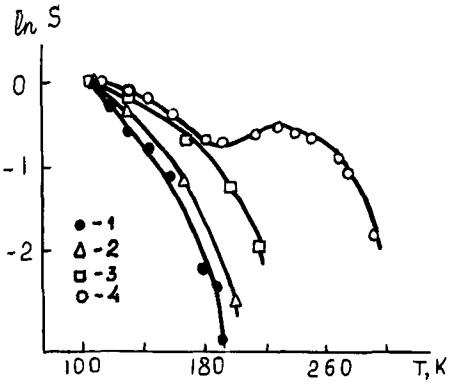


FIGURE 3 Temperature dependences of ln S for systems: 1) L-F(2,5 wt.%), 2) L-C(0,03 mol.%)-F, 3) L-C(0,10 mol.%)-F, 4) L-C(1,00 mol.%)-F.

For L-C-F system at C content equal 1 mol.% an other anomaly of ln S dependence in the range 180 - 230 K arises. The last anomaly becomes more prominent for equimolar L-C-F system, but it is absent for L-C-FC and for L-CFA systems [6-7]. It means that it reflects the molecular dynamics namely of terminal hydrocarbon fragments of L and C molecules in bilipid multilayers (Fig.2c).

For the explanation of this anomaly we suggest the model described in [7]. According to our model in such microheterogenic system there are exist several nonequivalent equilibrium energy states of label molecules, reflecting the phase

nonequivalency of bilipid matrix in its hydrophobic microregions. Such phase nonequivalency follows from X-Ray [10], so as from radio spectroscopical ^{13}C and ESR investigations[11] of L-C multilayers.

Hydrated lipid systems

Lecithin systems with the labels F, FC and CFA are investigated to study the influence of hydration (W = 20 - 86 %)on the dynamics of lipid matrix.

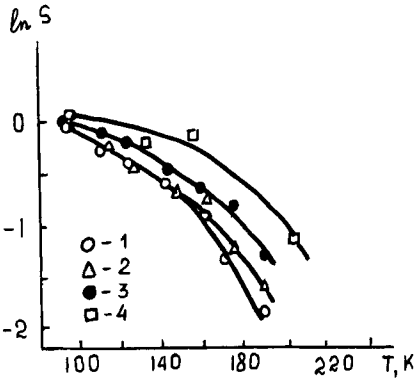


FIGURE 4 Temperature dependences of ln S(T) for hydrated systems L-F(2,5 wt.%): 1) degree of hydration W=0, 2) W=21%, 3) W= 52%, 4) W=86%.

Comparison of the linear parts of ln S(T) dependence (T <150 K) for hydrated L-F samples (Fig.4) indicates that at these temperatures the hydrophobic parts of lipid matrix becomes more rigid (its mobility decreases) with increase in the degree of hydration. This effect is directly opposite to observed at physiological (and close) temperatures.It may be explained on the basis of the specific properties of free and bound water at low temperatures.

Microviscosity of lipid systems

For interpretation of experimental sharp decrease in ln S(T) without essential broadening of lines in Mossbauer spectra of lipids we use the model of a Brownian oscillator with strong dumping.

In this model , the effects accompanying increase in temperature are associated with a sharp (near - experimental) decrease in internal friction (internal microviscosity) for

the relative and restricted motions of macromolecular chain fragments[12].

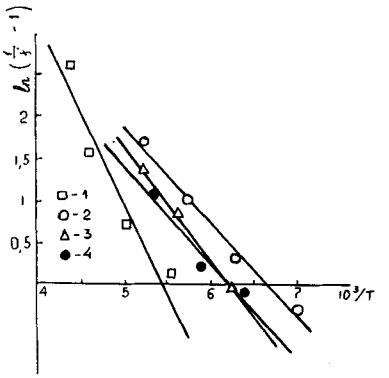


FIGURE 5 Linearization of ln S(T) dependences for hydrophilic (1) and hydrophobic (2) W=0, 3) W=21%, 4) W=52%) mossbauer labels.

With this model, the effective activation energy ε of the microviscosity ana the microviscosity η, characterizing a small local volume (~5 Å) around the label, may be estimated for hydrophobic and hydrophilic regions of lipid matrices (Fig.5).

At room temperature, ε is close to 2,5 kcal/mole for hydrophobic region of lecithin matrix, and 3,5 - 4,5 kcal/mole for its hydrophilic region - depending on the degree of hydration.The corresponding η values are 14 - 17 Pa·s (hydrophobic regions of L multilayers) and 8 - 13 Pa·s (hydrophilic regions of L multilayers).

These η values are related not to the mossbauer label molecule, but to the lipid microregions, where this label is localized.

I.e. it is a characteristic of media and may be compared with corresponding parameters, measured by other methods. Naturally, its value will be dependent as from the technique used, as from accepted approximations. For this reason, the values of η, published in literature, can be sufficiently different. Nevertheless, if these characteristics are received by the same technique and with the same (or close) labels, their comparison becomes quite grounded.

In particular, our data correlate with the results, received

also from Mossbauer label experiments for hydrophobic sections (ε = 2 kcal/mole) and for hydrophilic sections (ε = 3,4 6,0 kcal/mole) of the chromatophores [13]. But the η values for chromatophores (η = 56,0 - 68,4 pa.s)[13] are much higher than for lipid multilayers.

This difference may be explained by the complex structure of the chromatophores, in which diverse lipids and proteins appear. In any case, our estimations for L-C-F systems give ε 11 kcal/mole and η = 70 Pa·s. This value of η is closer to that for the chromatophores.

CONCLUSION

It has been shown that the use of Mossbauer labels with different affinities to the functional groups of lipids offers the possibility of obtaining original data on the dynamics of various microregions of lipid systems as model biomembranes. The method here proposed is of undoubted interest for studying of complex byopolymers and byomembrane systems, as well as lyotropic and polymer metallomesogens.

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