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Lecithin Organogels Containing Poly(ethylene glycol) Monolaurate

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Abstract—The effect of added poly(ethylene glycol) monolaurate (PEGML) on the formation and properties of lecithin organogels composed of polymer-like micelles was studied by the methods of dynamic rheology and the Fourier transform IR spectroscopy. It was established that the addition of even small amounts of PEGML causes a significant decrease in viscosity, whereas the elastic properties of organogels remained almost unchanged. The analysis of the scaling dependences indicated that the formation mechanism of polymer-like lecithin micelles remained also unchanged. Spectral studies revealed that the PEGML molecules affect intermolecular hydrogen bonding during their incorporation into micelles, thus stabilizing micellar structure. This effect is caused by the partial dehydration of the lecithin polar region. This leads to a decrease in the number of hydrogen bonds or their weakening and, as a result, to the disintegration of polymer-like lecithin micelles into shorter micellar aggregates.

INTRODUCTION

Lecithin organogels are optically transparent viscous liquids formed in the absence of polymers upon addition of small amounts of water to lecithin solution in apolar solvent. Lecithin is present in the initial solution in the form of spherical micelles. Upon addition of polar substance, they are rearranged into extremely long cylindrical micelles whose entanglement in the bulk (like polymer molecules) leads to the formation of three-dimensional network structure, which is responsible for the increased organogel viscosity [1–4]. Due to the similarity of their properties with polymers, such micelles are often called polymer-like micelles.

Formation and properties of lecithin organogels are markedly affected by the nature of organic solvent [1, 5], polar additive [6–8], lecithin fatty acid composition [9], as well as by the presence of other phospholipids and surfactants. For example, close structural analog of lecithin (phosphatidylethanolamine) causes abrupt lowering of viscosity and the degradation of gel structure at a concentration equal to several percents of the lecithin content [10]. It was found [11] that admixtures of β-carotene that are present in natural lecithin give rise to the similar effect. Out of all surfactants, substances containing saccharase residues have been studied in detail [12, 13]. It was shown that their effect is determined by the saccharase residue and the length of alkyl radical. Surfactants can either destruct or stabilize the gel structure. As was established recently [14], they also can change the formation mechanism of lecithin polymer-like micelles.

The effect of surfactants on the formation and properties of organogels is complex [14]. Intermolecular interactions are among the main factors affected by surfactants. According to the molecular model proposed in [6, 15], the binding of lecithin molecules into polymer-like micelles is ensured by phosphate groups via the hydrogen bonds with water molecules acting as bridges. Surfactants with functional groups capable of hydrogen binding influence the formation of polymer-like micelles. As was demonstrated using IR spectroscopy [12, 13], this is caused by the changes in the intermolecular interactions.

The selection of acyl derivative of poly(ethylene glycol) to be incorporated into lecithin organogels is explained by a noticeable effect of a polymer residue on the lecithin polar fragment. For example, poly(ethylene glycols) cause coagulation and coalescence of phospholipid vesicles in aqueous solutions. This effect is associated with the dehydration of the phospholipid polar region [16]. The study of mixtures with acyl derivatives of poly(ethylene glycol) demonstrated [17] that the polymer fragment forms a kind of solvate shell around the polar region of lecithin. In our experiments with ethylene glycol, it was established [6, 7] that it is capable, like water, of inducing gelation in nonaqueous lecithin solutions. Up to now, the effect of poly(ethylene glycol)s, as well as their acyl derivatives, on lecithin organogels was not considered in the published literature.

The aim of this work is to study the mixtures of lecithin with poly(ethylene glycol) monolaurate (PEGML) by the methods of dynamic rheology and the

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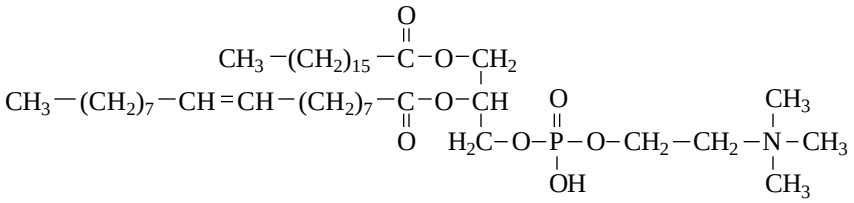

(b)

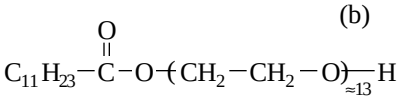

Fig. 1. Structural formulas of the studied substances. (a) Lecithin (1-palmitoyl-2-oleyl-*sn*-glycero-3-phosphatidylcholine, which is one of the main components of natural lecithin); (b) poly(ethylene glycol) monolaurate-600.

Fourier transform IR spectroscopy. The first method allowed us to elucidate the character of changes in the structure of polymer-like micelles after the addition of PEGML, while the second allowed us to disclose changes in the intermolecular interactions. The mechanism of PEGML effect on lecithin organogels was proposed based on the set of data obtained.

EXPERIMENTAL

Soybean lecithin, Epikuron 200 grade, was supplied by Lukas Meyer (Germany) and PEGML, by Ferak (Germany), *n*-decane was qualified as pure grade. Distilled water was prepared by the standard procedure. Molecular mass of poly(ethylene glycol) fragment was equal to 600. Structural formulas of both substances are shown in Fig. 1.

Organogels were prepared by the dissolution of calculated amounts of lecithin, PEGML, and water in *n*-decane. The samples were mixed with a magnetic stirrer for 3–5 h until the homogeneous optically transparent mixture was obtained and then stored for 1–3 days. As was elucidated at the initial stages of the study of lecithin organogels, this time is long enough to establish an equilibrium in mixtures.

Series of organogels with various lecithin concentrations and given molar lecithin : PEGML : water ratio were prepared by the addition of calculated amounts of *n*-decane. After dilution, the samples were mixed with a magnetic stirrer for 3–5 h and left to stand for 1–3 days until the equilibrium was established.

Rheological characteristics of organogels were measured in the regime of low-amplitude oscillations within 25–0.006 Hz frequency range at 25 ± 0.5°C on a Rotovisco RT 20 rheometer (Haake, Germany) with controlled shear loading. Measuring cell consists of a plate and a cone. In the case of low-viscosity mixtures, we used cell with the double clearance.

Absorption spectra of the samples were recorded on a Fourier transform Nicolet Protégé 460 IR spectrometer (USA) within 650–4000 cm^{-1} region (resolution is 1 cm^{-1}). The cell with measuring chamber 0.25 mm thick has windows made of NaCl. Residue factor was determined using absorption band of *n*-decane at a frequency of 894 cm^{-1}. Software OMNIC to IR spectrometer was used for data processing.

CALCULATIONS AND THE DETERMINATION OF RHEOLOGICAL PARAMETERS

The determination of the majority of rheological parameters is based on the dependence of complex viscosity $|\eta^*|$, storage modulus G', and loss modulus G'' on the frequency f of mechanical oscillations. Figure 2 illustrates corresponding dependences for organogel containing lecithin (295. 5 mg ml^{-1}), PEGML (4.5 mg ml^{-1}, 1.5 wt %), and three molecules of water per lecithin molecule ($n_w = 3$). As is seen, $|\eta^*|$ in the low-frequency range is independent of f. This allows us to equate $|\eta^*|$ to the static viscosity η_0. In the same region, the values

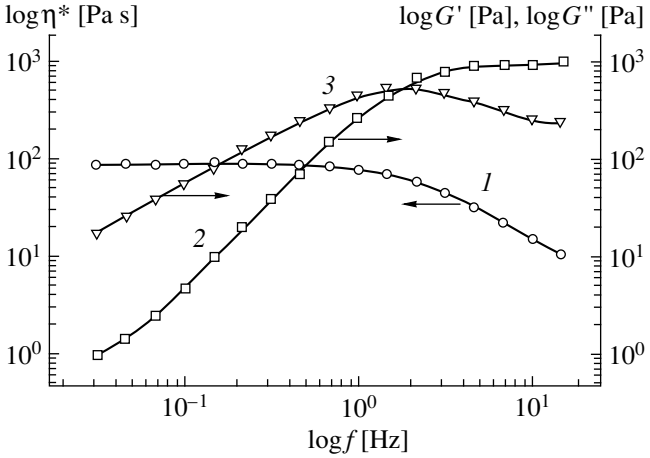

Fig. 2. Bilogarithmic dependences of (*1*) complex viscosity η^*, (*2*) storage modulus G', and (*3*) loss modulus G'' on the vibration frequency f for organogel containing lecithin (295.5 mg), PEGML (4.5 mg), and water (21 mg, $n_w = 3$) in 1 ml of decane.

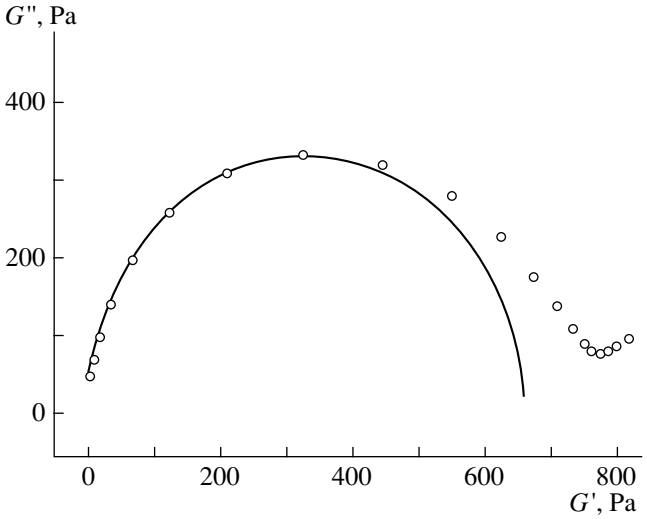

Fig. 3. Dependence of loss modulus G'' on storage modulus G' for organogel containing lecithin (250 mg) and water (17.5 mg, $n_w = 3$) in 1 ml of decane. Solid line is calculated by expression (3) at the value of the plateau modulus G_0 equal to 660 Pa.

of G' are proportional to f^2, and G'' values, to f. As the oscillation frequency increases, the curves referred to storage and loss moduluses become closer and then intersect each other. The value of f corresponding to this event is equal to the reciprocal value of maximum relaxation time τ_t of a system, in accordance with the equation:

$$\tau_t = 1/(2\pi f). \quad (1)$$

Once the curves are intersected, the loss modulus decreases, and the curve of the storage modulus reaches the plateau that characterizes the elastic properties of a system. Corresponding parameter is referred to as the plateau modulus G_0. In the theory of rubber elasticity, its value is determined by the number ν of the intersections of polymer chains with the surrounding molecules in a three-dimensional network [18]:

$$G_0 = \nu ART, \quad (2)$$

where A is the constant, which is equal approximately to unity, R is the gas constant, and T is the temperature.

The plateau modulus G_0 is determined from the graph shown in Fig. 2 with an inadequate accuracy due to effect of the Rouse processes (displacements of micelle parts between the intersection points in a network structure). For more exact determination of G_0, we used the dependence of the loss modulus on storage modulus (the Cole–Cole plot) whose values were measured at different frequencies. Corresponding graph is presented in Fig. 3. It has a shape of semi-circle described by the equation [18]

$$(G' - G_0/2)^2 + G''^2 = G_0^2/4. \quad (3)$$

The plateau modulus is found by fitting the calculated dependence to the experimental data by varying G_0 values. The results of this calculation is shown in Fig. 3 by the solid line.

Relaxation time in micellar systems characterizes not only the process of micelle displacements by the reptation mechanism but also, according to Cates [19, 20], their dissociation. This time is determined as a square root from the product of relaxation times for both processes. The values of maximal relaxation time τ_t are found for all the samples studied from the equation relating static viscosity and the plateau modulus:

$$\eta_0 = \tau_t G_0. \quad (4)$$

EXPERIMENTAL

Rheological Studies

The effect of PEGML on the rheological parameters of lecithin organogel is shown in Fig. 4 as dependences of η_0, G_0, and τ_t on the surfactant concentration in a mixture. As can be seen, the addition of PEGML to organogel considerably affects the static viscosity and maximum relaxation time. For example, after the addition of PEGML (3 wt %), the value of η_0 decreases by 72 times; τ_t, by 57 times. At the same time, the plateau modulus remained almost unchanged. The deviations of its value from G_0 did not exceed 30% for the initial organogel.

The effect of PEGML of the formation mechanism of polymer-like lecithin micelles was determined from the analysis of the scaling dependences of rheological parameters. Organogel containing 1.5 wt % of surfactant and two molecules of water per lipid molecule was used as an example. The values of η_0 and G_0 as functions of lecithin molar fraction are shown in Fig. 5. Straight lines in the graph are plotted by the experimental points using the least-squares method. The exponents of concentration dependences of η_0 and G_0 are determined from the slopes of theses dependences. The results of these calculations and the values of theoretical exponents obtained for the models of linear and branched polymer-like micelles are listed in table. Comparison of experimental and theoretical values shows that, in the case of organogels with $n_w = 2$, experimental exponents approach theoretical values for the first model, whereas for organogels with $n_w = 3$, they become closer to the values for the second model. This means that, at a low content of water, the systems studied contain predominantly linear micelles, at higher water contents, branched micelles. This agrees with data reported in [14, 21] where the organogels unmodified with surfactants were studied. Similar differences in the scaling dependences upon addition of 1.5 wt % of PEGML (table) implies that this surfactant does not

change significantly the formation mechanism of polymer-like lecithin micelles.

IR Spectroscopy Study

As was established in [6, 7, 15], the lecithin organogels are formed due to hydrogen binding between the water molecules and the phosphate groups of lecithin. Therefore, to understand the nature of the effect of PEGML, it seems important to elucidate whether intermolecular interactions are changed in polymer-like micelles.

Asymmetric vibrations of PO_2^- fragment are the most sensitive to the formation of hydrogen bonds due to vibrations of phosphate group [6, 7, 22–25]. It is known that the corresponding absorption band $\nu_{as}(PO_2)$ is located at 1253 cm^{-1} in the IR spectrum of nonaqueous lecithin solution in decane. The addition of 2.6 water molecules per lecithin molecule (that is sufficient to form organogel) shifts this band to 1242 cm^{-1}. In this case, the half-width of a band increases from 39 to 46 cm^{-1}. This agrees with the results of our previous studies [6, 7, 15]. As was shown in [6, 7, 22–25], the described changes in the IR spectra observed upon addition of water are indicative of the formation of hydrogen bonds by lecithin phosphate groups.

The addition of PEGML to organogel varies the contour of $\nu_{as}(PO_2)$ band, however its maximum is not markedly shifted. In order to disclose the character of the surfactant effect on the intermolecular interactions in micelles, the $\nu_{as}(PO_2)$ band was splitted, as in [26], into two components. The result of this splitting is shown in Fig. 6. Subband with the maximum at 1228 cm^{-1} characterizes the vibrations of PO_2 group that is hydrogen-bonded with H_2O ($\nu_{as}(PO_2)_{H\text{-}b}$), while subband at 1248 cm^{-1} reflects the vibrations of nonaqueous PO_2 group $\nu_{as}(PO_2)_{n/a}$. The intensities of both subbands vary with an increase in PEGML concentration in organogel: the intensity of subband at 1228 cm^{-1} decreases, and that of the second subband at 1248 cm^{-1} increases. Figure 7 presents the dependence of the ratio of their intensities on the amount of added PEGML. As is seen, the ratio varies in favor of nonaqueous component. Hence, the addition of PEFML tends to decrease the number of H-bonded phosphate groups. Besides, upon addition of 7–10% of PEGML, the half-width of $\nu_{as}(PO_2)$ band decreases from 46 to 45 cm^{-1}, thus also indicating either a decrease in the number of hydrogen bonds between molecules of water and phosphate groups or their weakening.

RESULTS AND DISCUSSION

The performed study demonstrated that PEGML causes an unusual effect on lecithin organogel (Fig. 4) changing mainly its viscoelastic properties. The elastic properties remain practically unchanged. This fact distinguishes PEGML from other surfactants investigated

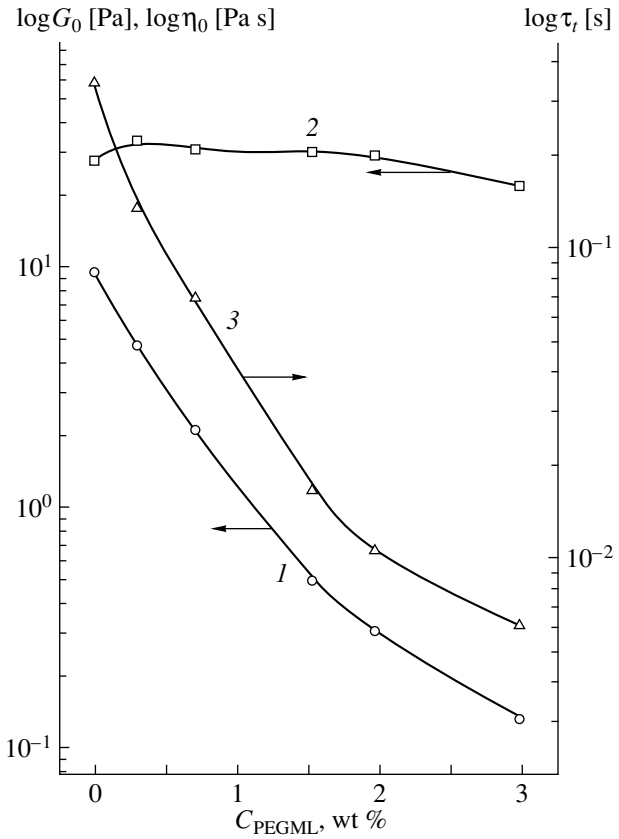

Fig. 4. Dependences of (*1*) static viscosity η_0, (*2*) plateau modulus G_0, and (*3*) maximum relaxation time τ_t on the concentration of poly(ethylene glycol) monolaurate in organogel containing lecithin (75 mg) and water (4.5 mg, $n_w = 2.6$) in 1 ml of decane.

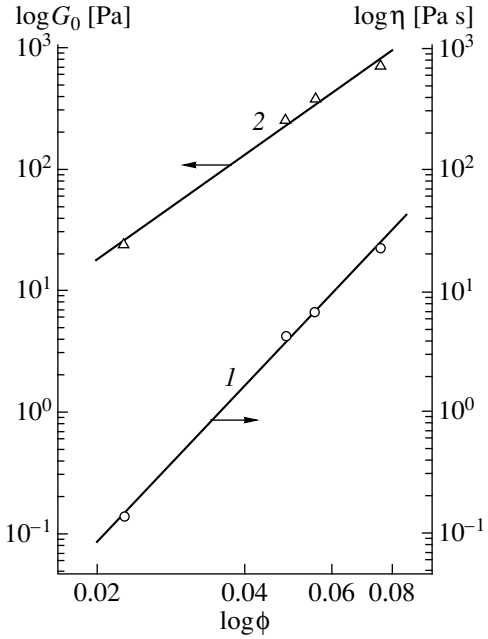

Fig. 5. Bilogarithmic dependences of (*1*) static viscosity η_0 and (*2*) plateau modulus G_0 on the lecithin molar fraction at a constant content of PEGML (1.5% of total mass of lecithin and PEGML) and water ($n_w = 2$).

Exponents of concentration dependences of rheological parameters

Model/Studied system	η_0	G_0	References
Theoretical values			
Linear micelles	3.5	2.25	[9, 20]
Branched micelles	2.5	2.25	[21]
Experimental data			
$n_w = 2$	4.0 ± 0.1	2.5 ± 0.1	This work
$n_w = 2$, 1.5 wt % of PEGML	4.2 ± 0.2	2.9 ± 0.2	"
$n_w = 3$	2.7 ± 0.3	2.2 ± 0.2	"
$n_w = 3$, 1.5 wt % of PEGML	2.1 ± 0.1	1.8 ± 0.1	"

earlier. Their addition results usually in simultaneous changes of both static viscosity and plateau modulus [12–14]. Although these rheological parameters characterize different properties of viscoelastic systems, they are interrelated with each other [18].

Significant decrease in η_0 and τ_t upon addition of PEGML (Fig. 4) indicates that micelles become shorter, because the static viscosity and relaxation time directly depend on particle linear sizes [20]. The absence of serious changes in the plateau modulus implies that, according to Eq. (2), the number of intersections of a single micelle with neighbor micelles in the network structure is not changed. This contradiction is eliminated, if we suggest that PEGML causes the disintegration of micelles into shorter aggregates, thus compensating the effect of their decreasing size. In this connection, the conservation of the character of scaling dependences upon addition of PEGML seems to be important (table). Hence, the formation mechanism and the dynamics of polymer-like micelles are not significantly changed. This fact also emphasizes the effect of PEGML. For example, surfactants with saccharas residues affect greatly the viscoelastic properties of lecithin-based organogel due to the transformation of linear micelles into branched aggregates [12–14].

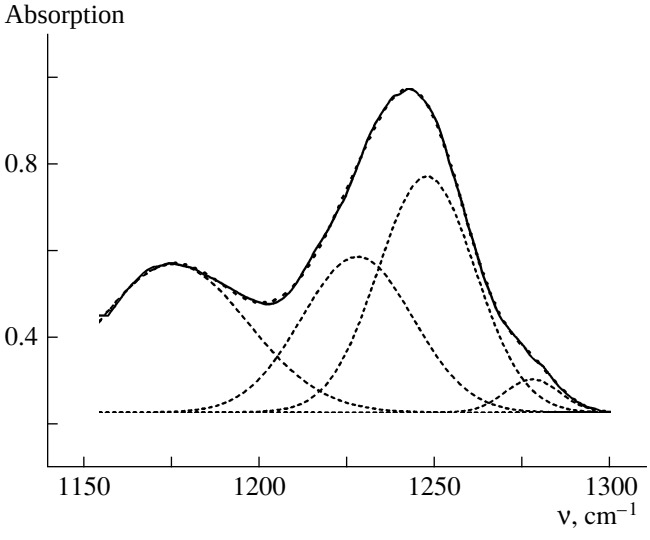

Fig. 6. Absorption band $\nu_{as}(PO_2)$ in the IR spectrum of organogel containing lecithin (53 mg) and water (3 mg, $n_w = 2.6$) in 1 ml of decane. Spectrum fragment is represented by the solid line; subband $\nu_{as}(PO_2)_{n/a}$ and $\nu_{as}(PO_2)_{H\text{-}b}$ obtained by the spectrum splitting are denoted by the dashed lines; the integral band is shown by the solid dashed line.

We believe that possible reason for the disintegration of micellar aggregates can be indicated by the results of spectral studies, in particular, by an increase in the intensity of the subband of $\nu_{as}(PO_2)$ band that characterizes the vibrations of nonaqueous PO_2 group. The intensity of subband for H-bonded PO_2 group decreases simultaneously. This means that the poly(ethylene glycol) fragment exerts the dehydration effect. This conclusion well agrees with the published data. As was already mentioned in the introduction, poly(ethylene glycol)s in aqueous solutions result in the coagulation and coalescence of phospholipid vesicles due to dehydration of polar region [16]. During the study of mixture of lecithin with Triton X-100 by the IR spectroscopy [27], it was shown that the surfactant containing poly(ethylene glycol) fragment affects hydrogen bonding in the polar region of phospholipid while incorporating this fragment into vesicles. We established similar effect for the reverse polymer-like micelles upon addition of PEGML. Because the stability of aggregates is explained, within the framework of proposed molecular model [6, 7, 15], by hydrogen bonding, the weakening or rupture of hydrogen bonds leads to the deterioration of stability and the disintegration of micellar aggregates. Indeed, such an effect is observed upon addition of PEGML (Fig. 4). In this case, surfactant causes probably dual effect. On the one hand, the dehydration occurs due to the binding of water molecules with the poly(ethylene glycol) fragment. On the other hand, as was shown in [17], poly(ethylene glycol)s themselves are capable of forming the solvation shell around the lecithin polar region, thus competing with water molecules. However, in contrast to water, PEGML acts only as a proton acceptor during the formation of hydrogen bonds (Fig. 1). This fact is of crucial significance, because poly(ethylene glycol) fragment cannot serve as a binding bridge between neighbor lecithin molecules and stabilize the micellar structure.

Thus, the possible mechanism of the effect of PEGML on polymer-like lecithin micelles is in the partial dehydration of phospholipid polar region. A decrease in the number of water molecules binding neighbor lecithin molecules by H-bonds causes the destabilizing effect. Micelles are disintegrats into shorter aggregates, thus lowering the organogel viscosity.

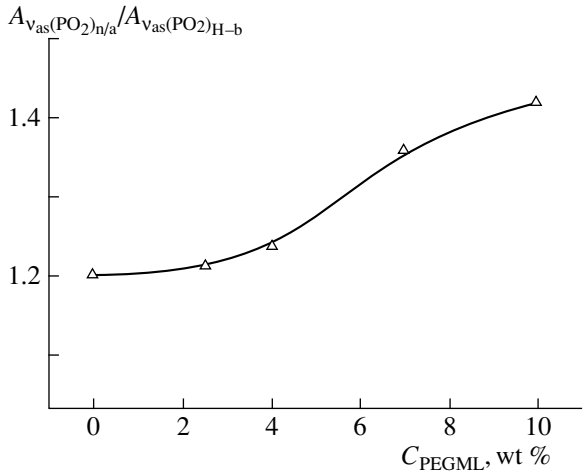

Fig. 7. Ratio of the intensities of subbands $\nu_{as}(PO_2)_{n/a}$ and $\nu_{as}(PO_2)_{H\text{-}b}$ corresponding to free and bonded phosphate groups, respectively, as a function of the amount of added PEGML (in % of total mass of lecithin and PEGML equal to 50 mg per ml of decane).

ACKNOWLEDGMENTS

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