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SHORT COMMUNICATION

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Lecithin organogels with *n*-alkyl-D-glucosides and *n*-alkly-D-lactobionamide

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Abstract Jelly-like phases formed by mixtures of soybean lecithin with pure *n*-dodecyl-β-D-glucopyranoside (DDPG), commercial alkylpolyglucoside (APG) or *n*-dodecyl-β-D-lactobionamide (DLBA) in decane in the presence of small amounts of water were studied by oscillating rheology and FT-IR-spectroscopy. It was established that the sugar derivatives can modify the rheological properties of lecithin organogels in different ways. The viscosities, the structural relaxation times and the shear moduli decrease with increasing content of DDPG, while the same parameters increase for DLBA. For APG the modulus is increasing while the viscosity and the structural relaxation time are decreasing. By means of FT-IR spectroscopy and examination of the Cole–Cole-plots of the loss modulus vs. the storage modulus it was shown that the sugar derivatives influence both the strength of the hydrogen bonds between the molecules in the polymer-like micelles and the micellar dynamics.

Key words Lecithin – alkylglucoside – organogel – polymer-like micelles – hydrogen bonds

Introduction

Lecithin organogels consist of extended cylindrical – often called polymer-like or worm-like – lecithin micelles in an organic nonpolar solvent. If the phospholipid alone is dissolved in the nonpolar media, it forms spherical reverse micelles [1]. The sphere-to-cylinder transformation is brought about by addition of small amounts of strongly polar solvents like water, glycerol, ethylene glycol or formamide [2–5]. It was established [4–6] that this transition into polymer-like micelles is due to a formation of hydrogen bonds between the phospholipid molecules and the polar additives.

It can be expected that the jellification of nonaqueous phospholipid solutions and also the properties of the organogels will be influenced by substances which are capable to participate in the formation of hydrogen bonds between the molecules in the micellar aggregates. To test the validity of this assumption, we introduced various alkyl derivatives of sugars into a jelly-like nonpolar solution of lecithin. This class of additives was selected because of their ability to form numerous hydrogen bonds [7]. Furthermore, sugar surfactants are viewed as a type of very promising surface active compounds for the use in cosmetics and pharmacology due to their nontoxicity [8, 9]. To our knowledge, lecithin jelly-like phases containing sugar surfactants have not yet been described in the literature.

We found out in our experiments that *n*-alkyl-D-glucosides and *N*-alkyl-D-lactobionamide show a pronounced effect on all the properties of lecithin organogels, especially on their rheological behavior. Some of our preliminary results are presented in this communication.

Experimental

Soybean lecithin, Epikuron 200, was used as received from Lukas Mayer AG, Hamburg. Chromatographically pure *n*-dodecyl-β-D-glucopyranoside (DDGP) was a gift of V. Adasch and G. Voß from the University of Bayreuth. Technical grade alkylpolyglucoside (APG) was obtained from Hüls AG and was used without further purification. This sugar surfactant contains an alkyl chain with 12–14 C-atoms and an average of 1,3 glucoside units per molecule. *N*-Dodecyl-4-0-β-D-galactropyranosyl-D-gluconamide) was prepared by U. Krämer from the University of Bayreuth. *n*-decane was received in "puriss" quality from Fluka. Doubly distilled water was prepared in the usual manner. The jelly-like phases were made by dissolution of weighed amounts of lecithin, sugar surfactant and water in *n*-decane according to a procedure described previously [4, 5]. In all samples the total concentration of lecithin and sugar surfactant was 35 mg/ml. The content of sugar surfactant was given in wt% of the total amount of both compounds. The organogels contained 0.25 wt% water.

The rheological parameter of the lecithin organogels were measured in the frequency range from 0.001 to 10 s^{-1} using a Bohlin CS-10 stress-controlled rheometer which was equipped with a cone-plate measuring system as described elsewhere [10]. The experiments were carried out at (25 ± 0.1) °C.

Absorbance IR spectra were determined with a Polaris FT-IR spectrometer from Matson. The resolution was 0.5 cm^{-1}. The thickness of the sample cell with NaCl windows was equal to 0.25 mm.

Results and discussion

Figure 1 shows a Cole–Cole plot of the loss modulus G'' against the storage modulus G' for lecithin organogels with added DDPG (A), APG (B) and DLBA (C), respectively. The solid curves represent semicircles according to Eq. (1)

$$(G' - G_0/2)^2 + G''^2 = G_0^2/4 \tag{1}$$

which is valid for viscoelastic fluids with one single structural relaxation time τ_t and the ideal behavior of a Maxwell element. G_0 is the shear modulus characterizing the elastic properties of the samples [11] which is represented by the plateau value of G' at higher frequencies. It should be noted that the curves in Fig. 1 were normalized by dividing G'' and G' by G_0. The figure shows that the experimental point coincides nicely with the ideal solid curves in the low-frequency range. The corresponding relaxation processes are characterized by one single relaxation time τ_t (relaxation time) [11] which is given in the case of polymer-like micelles by Eq. (2) [12–14]

$$\tau_t = (\tau_b \tau_{rept})^{1/2} \ . \tag{2}$$

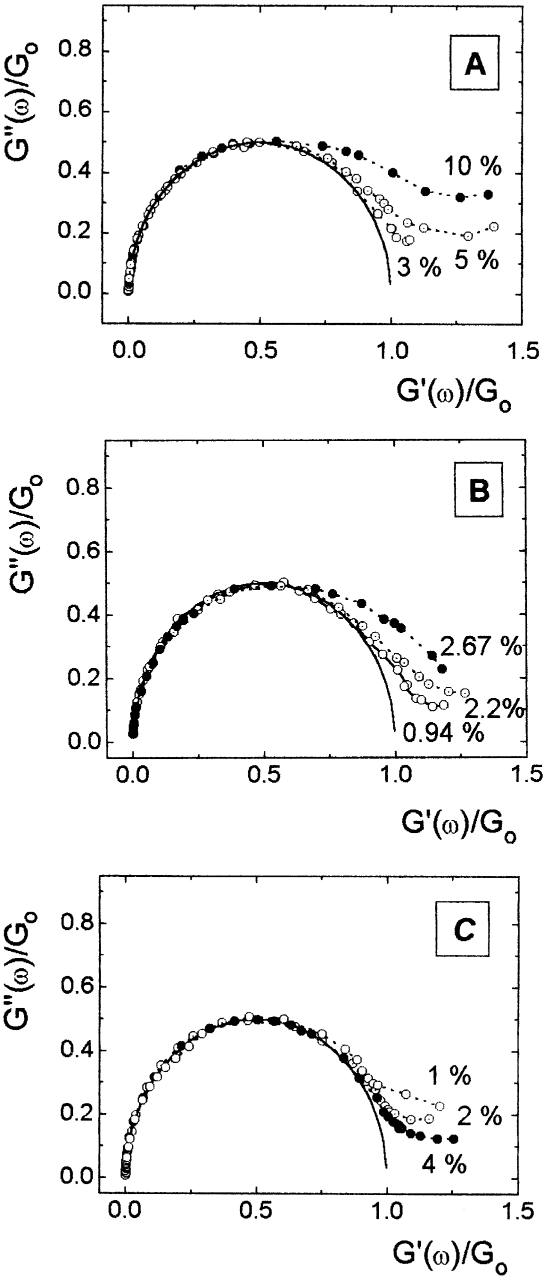

Fig. 1 Normalized Cole–Cole plots of the loss modulus G'' vs the storage modulus G'. The semicircle solid lines are the best fits corresponding to an ideal Maxwell element with a single relaxation time (Eq. (1)). (A) DDGP-containing organogels. (B) APG-containing organogels. (C) DLBA-containing organogels. The total concentration of lecithin + sugar surfactant is 35 mg/ml, the temperature (25.0 ± 0.1)°C. The additive concentrations are shown adjacent to the corresponding curves

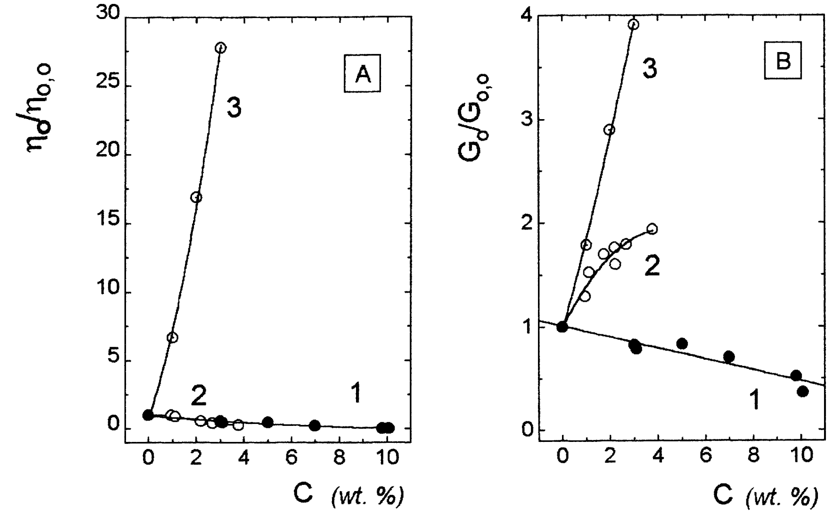

Fig. 2 The zero shear viscosity η_0 (A) and the shear modulus G_0 (B) as a function of the concentration of DDGP (1), APG (2) and DLBA (3) in the jelly-like phases. The rheological parameters were normalized by dividing both η_0 and G_0 by the corresponding quantities of the pure lecithin organogel without additives

Here τ_b and τ_{rept} are the time constants for the reversible breaking (scission) of micellar aggregates and for the movement by a reptation mechanism, respectively. The semicircle shape of the Cole–Cole plots in Fig. 1 indicates that τ_b is much shorter than τ_{rept} [15, 16].

At high frequencies there are deviations from the ideal Maxwell behavior as can be seen from Fig. 1. This implies that the dynamic behavior on this time scale should be characterized by a spectrum of relaxation times [12, 14, 17, 18]. Various relaxation mechanisms for jelly-like phases consisting of polymer-like micelles were considered in the literature [12, 14–19].

The effects of sugar surfactants on the rheological properties of lecithin organogels can be elucidated from measurements of the zero shear viscosity η_0, the shear modulus G_0 and the structural relaxation time τ_t. η_0 was determined as the plateau value of the complex viscosity $|\eta^*|$ at low frequencies where it is independent of the frequency [18]. The shear moduli were calculated by a fitting procedure using Eq. (1) with G_0 as an adjustable parameter. The values of η_0 and G_0 which are changing on addition of the sugar surfactants into the lecithin organogel are presented in Figs. 2A and B, respectively. It should be mentioned that the measurements were extend to additive concentrations at which the organogels separate into a lowly viscous solution and a compact gel or a solid precipitate.

One can see in Fig. 2 that all the sugar surfactants affect the rheological behaviour of the lecithin organogels already at small concentrations. The effects, however, vary for the different additives. Three cases can be distinguished: (i) DDGP leads to a decrease both of η_0 and of G_0; (ii) DLBA causes an increase of η_0 and G_0; (iii) APG gives opposite changes of these parameters i.e. a decrease of η_0 and an increase of G_0.

The changes of the rheological parameters, η_0 and G_0, in the case of DDPG and DLBA are consistent with each other. The decrease of η_0 comes about because the polymer-like micelles becomes smaller and the increase of η_0 is caused by a growth of the aggregates. According to the classical theory of rubber-like elasticity, the shear modulus increases linearly with the number density v of entanglement points between the aggregates according to Eq. (3) [20]:

$$G_0 = vAkT \ . \tag{3}$$

In this equation A is a numerical factor close to unity, k and T are the Boltzmann constant and the absolute temperature, respectively. Thus G_0 should change in a way similar to η_0 if τ_t is not affected by the additives.

For the system with APG the above-mentioned correlation between η_0 and G_0 does not exist. This arises the question why this additive influences the rheological behavior of lecithin organogels in a different manner in comparison to the other two additives. To our opinion, a plausible explanation can be provided if one remembers that the zero shear viscosity and shear modulus are related to each other by the fundamental equation (4) [11, 21]:

$$\eta_0 = G_0 \cdot \tau_t \ . \tag{4}$$

According to Eq. (2) the molecules of an additive which are incorporated into the lecithin micelles can change the terminal relaxation time both by changing the micellar breaking, if the additive modifies the molecular interactions between lecithin molecules within the aggregates, and by changing the micellar diffusion, if the micellar length and flexibility are varied.

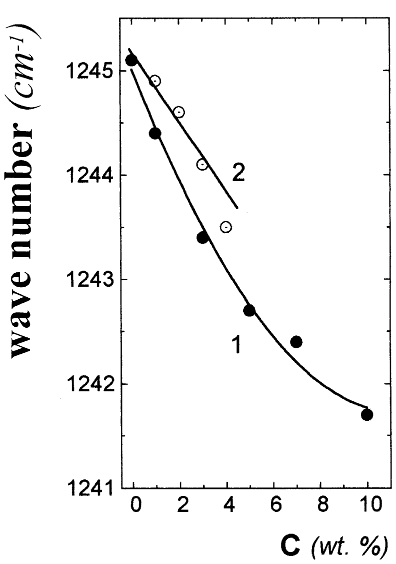

Fig. 3 The wave numbers of the P = O asymmetric stretching vibrational band as a function of the concentration of DDGP (1) and DLBA (2) in the lecithin organogel

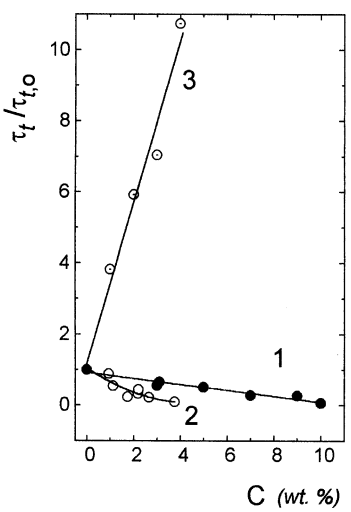

Fig. 4 The terminal relaxation time τ_1 as a function of the concentration of added DDGP (1), APG (2) and DLBA (3). Values of τ_t were normalized by dividing by the corresponding quantity of the pure lecithin organogel without additives

An influence of the sugar surfactants on the molecular interactions can be elucidated by FI-IR spectroscopy. Lecithin molecules in the polymer-like micelles in the nonpolar media are linked to each other by hydrogen bonds formed by the phosphate groups as has been shown previously [4, 5]. The bond formation can be proven by a bathochromic shift of the asymmetric stretching vibration of the P = O-band in the region from 1265 to 1220 cm^{-1} [22, 23]. Examination of the lecithin organogels containing the sugar surfactants revealed that on being incorporated into the organogel all the additives caused a further low-frequency shift of the above-mentioned band. Results for DDGP and DLBA are presented in Fig. 3. Based on the literature [22, 23] the low-frequency shift can be interpreted as the strengthening of the hydrogen bonds in the lecithin polymer-like micelles by the sugar surfactants. According to the theory of micellar kinetics [24] their strengthening would thus be expected to increase τ_b.

Evidence for a change in the micellar diffusion by the reptation mechanism on addition of sugar surfactants can be deduced from an examination of the Cole–Cole plots. It was shown by Turner and Cates [15, 16] that the character of the deviation from a single exponential relaxation in the high-frequency range is determined by a parameter ζ which is defined according Eq. (5):

$$\zeta \equiv \tau_b/\tau_{\mathrm{rept}} \; . \tag{5}$$

The larger the ratio $\tau_b/\tau_{\mathrm{rept}}$ is, the greater the deviation is, and it increases with increasing DDGP and APG concentrations (see Figs. 1A and B). The dependence of the terminal relaxation time τ_t on the additive concentrations is presented in Fig. 4. As can be seen, the values of τ_t decrease with increasing DDGP and APG content in an organogel. From the spectroscopic result shown above it follows that the increase of τ_b is due to the strengthening of the hydrogen bonds (Fig. 3), the value of τ_{rept} should decrease according to Eqs. (2) and (5). In other words, the relaxation processes due to the movement of polymer-like micelles become faster and faster, whereas the breaking kinetics of the aggregates slow down with increasing amounts of sugar surfactants.

The DLBA-containing mixtures show a quite different behavior. With increasing amounts of DLBA, the semicircular shape of the curve of G'' vs G' extends to the high-frequency range (Fig. 1C). This tendency is opposite to that observed in the case of DDGP and APG (Figs. 1A and B). The theory of Turner and Cates suggests that the extension is due to a decrease in magnitude of the parameter ζ. If the increase both of the terminal relaxation time τ_t (Fig. 4) and of the breaking relaxation time τ_b due to the strengthening of hydrogen bonds (Fig. 3) is taken into account, it becomes apparent from Eqs. (2) and (5) that the reptation relaxation time τ_{rept} should rise more rapidly than τ_b. This effect could be caused by a significant increase of the lengths of the DLBA micelles as well as by their increasing stiffness.

In general the experimental results show that the change of the viscosities is mainly determined by the changes of the structural relaxation times and not so much by a change of G_0. This actually is to be expected because the number density v of entanglements is mainly determined by the amount of material in the entangled network and not by the dynamic behavior of the network. Normal viscoelastic surfactant solutions of threadlike micelles have the same modulus for the same surfactant concentration while their structural relaxation times can vary by many orders of magnitude. This is for example the case for systems in which the chainlength of the surfactant is varied while the other parameters like total concentration or ionic strength remain constant.

On the basis of these data it is difficult, however, to explain the differences of G_0 for the different additives in the present system. For the DDGP system the modulus is decreasing while for DLBA the modulus is increasing with the concentration of the sugar surfactant. The system APG is in between these two cases. Qualitatively, the data seem to indicate that the moduli show the same tendency as the reptation times.

Thus the data presented above make it evident that the sugar surfactants can change the rheological properties and the dynamic behavior of lecithin organogels in different ways. This provides a means to adjust their properties and to develop jelly-like phases with a desired rheological behavior. Our preliminary study mainly ascertains the effects. The obtained results are not enough to suggest a proper explanation for the observed effects. To gain a better insight into the real mechanisms, it is necessary to perform further experiments on the lecithin organogels with the various sugar surfactants; such a study is now in progress.

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