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Effects of Water on Aggregation and Stability of Monoglycerides in Hydrophobic Solutions

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We apply a set of different techniques to analyze the physical properties and phase transitions of monoglyceride (MG)−oil−water ternary systems. The effect of MGs on water absorption in food-grade hazelnut oil and in pure hydrocarbon oil (decane) is reported. Comparison between decane and hazelnut oil backgrounds indicates that the effect of water absorption is significant and universal in different MG ternary systems. Adding small amounts of cosurfactant (stearic acid) is necessary to stabilize the MGs in oil−water combinations by enhancing the swelling capacity of lamellar layers; as a result, the structures become sensitive to the pH of the aqueous phase used. The dramatic changes on increasing the aqueous content are recorded by the calorimetry. In samples with small quantities of water, the phase behavior is almost independent of the pH. Once the proportion of water increases, the effect of pH is prominent. At low pH, the solubility of MG in water is limited, and the ternary system retains key features of the oil-dominated environment, such as the sequence of two transitions on cooling, with the low-temperature sub-α crystalline phase. At high pH and a sufficient amount of water, the MG layers remain properly swollen, and the crystalline phase disappears from the phase diagram. We spend considerable effort identifying the inverse lamellar phase of MGs in an oil-dominated environment with the so-called α-gel phase that is well-established in water-dominated systems, and distinguishing "demixing" from water and from oil. The rheology is examined in different fluid and gel phases; the storage modulus generally decreased on increasing the water proportion, but a gel-like response is found in the high-temperature lamellar phase over a wide range of water dilution. We then focus on aging phenomena in the inverse lamellar (or α-gel) phase and show that the rearranging of hydrogen bonds is slowed down and disrupted by the presence of water, giving the lamellar gel longer life times.

1. Introduction

Monoglycerides (MGs) are lipid molecules consisting of a single fatty acid esterified with a hydroxy-glycerol group. They are distinguished by the length of the carbon chain. In this paper we focus on a particularly common surfactant C18 (monostearin). It exists as two chiral isomers, *D* and *L*.[1,2] Concentrated mixtures of MGs in solvents form a variety of cream-like materials which are widely used in both personal products and food industry.[3,4] Beyond their use in various applications, in general, aggregated surfactant solutions form a particular class of materials that develop a network of morphological features to retain the solvents.[5,6] The phase behavior of MG−water systems is well studied.[1,7−9] Long-chain saturated 1-MGs, such as C18, form a highly hydrated lamellar phase in the presence of water above a certain critical temperature.[8,10] Usually, when talking about hydrated MG gels, the literature reports concentrations of around

15 wt % of water.[11,12] No more than 25 wt % of water can be dispersed in MG; there are a few reports claiming that gels with up to 45 wt % water could be dispersed by vigorous mechanical mixing, but in all cases these are highly unstable systems.[12] Therefore mixing low concentration of cosurfactant (most commonly stearic acid or diacetyl tartaric acid) is necessary to stabilize the MG in water.[10,13−16] Because of these additional acidic cosurfactants, the swelling capacity of lamellar bilayers becomes dependent on the pH of the aqueous phase used. At pH below 6, only limited swelling occurs, while at pH of 7 and above, the optimal swelling takes place, forming a translucent weak-gel dispersion.[13] At high pH, the acid cosurfactant is ionized, which ensures the effective repulsion between the bilayers and enhanced stability of lamellar gels.

When the MG−water mixture is cooled below the critical temperature, which is known as the Krafft demixing point for MGs in water, a strong gel phase appears, which is often called the "α-gel". This phase is often mistakenly identified as crystalline because of the presence of hexagonal order characterized by a single wide-angle X-ray reflection at 4.18 Å.[13,17] We shall spend considerable time later in the paper discussing this phase; here it is

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just worth mentioning that only a single wide-angle X-ray reflection cannot represent a long-range crystalline order. We shall show that this spacing in fact represents the dense packing between MG heads in lamellar bilayers that are flattened after demixing between MGs and water, while the carbon chains in this α-gel phase are still melted, as opposed to the real Bragg series of wide-angle X-ray peaks when these aliphatic tails crystallize in certain conditions. The initial α-gel phase is in fact metastable and gradually transforms into an anhydrous MG crystalline phase, identified as β-crystal with triclinic packing of aliphatic chains; this phase is also frequently called "coagel".[1,3,13,17] This β-crystal phase has a higher melting point and is characterized by a series of wide-angle X-ray reflections representing the dimensions of the unit cell with the strongest lines corresponding to 4.5–4.6 Å.[13,17,18] The coagel state of MGs in water is due to hydrogen bonds establishing within head groups in bilayers, which in turn lead to a further crystallization of aliphatic tails.[1] On a long time scale of aging, the *D*- and *L*- isomers of MGs gradually separate within crystalline bilayers, leading to a more dense packing and expulsion of water.[1,19−21] Sedimentation of solids in this phase then takes places.

MGs in hydrophobic solutions follow different hydrogen bonding patterns, and show phase behavior that is very different from that of aqueous systems.[22−27] First of all, the high-temperature phase here is an isotropic fluid with some inverted micelles taking up the MG excess above the critical micelle concentration. Below the mesomorphic transition temperature, an inverse lamellar phase is formed, as expected in a hydrophobic system. The inverted lamellar bilayers have a very definite hexagonal ordering, which arises from a two-dimensional (2D) dense packing of glycerol heads compressed in the middle of each bilayer.[22] The wide-angle X-ray reflection at 4.17 Å corresponds to the closest distance of approach of glycerol groups in the bilayer plane.[13,17,22] The second, "twin" peak at 4.11 Å, which is only seen in completely water-free systems, is the characteristic distance between the neighboring heads in two planes of the bilayers.[22] This inverse lamellar phase has a pronounced gel-like rheology. Cooling it further down, below the crystallization point of the surfactant, which can be called the Krafft demixing temperature of MGs from oil, a lower-temperature crystalline phase emerges. The simple planar hexagonal packing with molten aliphatic tails transforms into a structure analogous to the sub-α crystalline phase of pure MGs, with orthorhombic chain packing in the unit cell, characterized by strong X-ray reflection at 4.17 Å and several reflections between 4.06 to 3.6 Å.[13,22,23] In both inverse-lamellar and sub-α crystalline phases, MG molecules eventually lose their emulsifying ability through the gradual change in hydrogen bonding patterns. Upon aging, the recombination of hydrogen bonds between glycerol groups causes the segregation of chiral isomers within the bilayers.[1,23] Therefore, all structures are eventually forced to reorder into the thermodynamically stable β-crystalline state.[23] The highly ordered packing of aged structures leads to the collapse of the percolating gel network of lamellar domains and sedimentation of dense solids.

A ternary system of MG−oil−water creates a special case of material that contains a mesoscopic network of lamellar domains to convert an oil−water combination into a cream-like matrix with desirable rheological features.[10,28,29] At high water content, such a system is an oil-in-water emulsion in which lamellar MG walls surround and stabilize oil droplets. At sufficient MG concentration, these walls are continuous from one droplet to the next, forming a continuous solid network to retain the solvents inside.[14−16,30] The gel formed by MG−oil−water is sensitive to factors such as MG concentration, the pH, the type and amount of cosurfactants used, storage time, and temperature. Several previous studies assumed the phase behavior of MG−oil−water is qualitatively similar to that of the aqueous systems.[10,14] However, obviously, the hydrogen-bonding pattern in a ternary system is much more complex than in a simple MG/water system, and the sensitivity of MG solubility in the water−oil mixtures also increases the complexity. Therefore rich phase behavior is expected.

In this work we studied the phase sequences by systematically increasing the aqueous content in MG−oil. It was found earlier that the presence of small amounts of water (less than 3 wt %) shifts the crystallization transition to lower temperatures.[22] Once the amount of water increases further, the effects of pH become significant. We concluded that the effect of pH was related to the influence of the stearic acid cosurfactant. The presence of stearic acid ensures the repulsive force between lamellar bilayers at high pH to enhance their swelling by the aqueous phase. In effect, MG does not dissolve easily in water with too low pH. Two examples are studied here, with pH/cosurfactant combination just below and just above the swelling boundary. We show that a fully hydrated ternary system with a sufficient proportion of water does not crystallize into the sub-α phase at low temperature, as the oil-dominated systems do, while at lower pH the sub-α crystalline phase was found at any oil−water combinations. Moreover, to confirm the results and conclusions are general to different MG−oil−water ternary systems, we test two very different kinds of oil: food-grade hazelnut oil and pure hydrocarbon oil (decane). One may wonder whether the effect of pH is caused by the impurities in the hazelnut oil. We find that the structures and trends of transitions on increasing the water content are universal in complex and pure oils. Although their gelation and crystallization points are not the same, their phase behavior is very similar. We conclude that the effect from the additional acidic cosurfactant, which is necessary to stabilize MGs at high concentrations in the aqueous phase, takes the dominant role in determining the pH effects.

The rheology in different phases was recorded and linked to their molecular arrangement. The storage modulus (*G'*) generally decreases on increasing the proportion of water, but the gel-like nature of ternary systems was found under a wide range of water dilution. We then focused on the aging phenomena of the inverse lamellar (or α-gel) phase. The origin of aging is the recombination of hydrogen bonds between glyceride heads to segregate *D* and *L* isomers.[23] Free hydroxide groups disturb this recombination and increase the lifetime of MG gels. Accordingly, even a small quantity of water would increase the stability of lamellar gels. However, with the passing of time, aging inevitably takes on and

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leads to a dramatic change in physical properties. The emulsifying ability of aggregated MGs reduces, and the solvent separates from the more densely aggregated MG crystalline regions. In practice this means that the phase diagrams, such as those presented in Figure 3 below, have only a representative meaning. These diagrams, as all similar phase diagrams of MG/water or ternary systems that one finds in the literature, are obtained upon cooling from the high-temperature isotropic solutions when the corresponding phases first form, or upon subsequent heating of the system soon after. As the discussion of aging indicates, all these low-temperature phases are in fact metastable. Nevertheless, such an "apparent phase diagram" is a meaningful representation because the aging times are rather long, as we shall see below. However, when approaching such phase diagrams, one must be clear that the transition lines, and the nature of phases, do change with aging.

2. Experimental Details

Distilled saturated MG was purchased from the Palsgaard A/S (Denmark). The sample contained 97% 1-MGs, and the fatty acid chain length compositions were 93% C18 and 7% C16. The remainder consisted of 1.1% diglycerides and less than 1% triglycerides. The incorporation of stearic acid cosurfactant into the material was necessary to ensure solubility in aqueous matrix. The stearic acid was mixed with MGs in a ratio of 1:20, following refs 10, 14, and 15. The hydrophobic solvent used in the bulk of this work was hazelnut oil from Provence, France (de Provence), of a specific variety that contains approximately 80 wt % oleic and 20 wt % linoleic acids with low quantities of MGs[31] and decane (99% pure, Aldrich). This oil crystallizes at a temperature below -23 °C. The choice of hazelnut oil was partially dictated by practical applications in the food industry. The comparison with the hazelnut oil system and the pure hydrocarbon (decane) system indicates that the effect of water absorption is universal in the MG ternary systems.

The cosurfactant (stearic acids), oil, and a small amount of impurities from the MG itself cause the hydrophobic solution used to have acidic nature. For the hazelnut oil (mainly oleic acid), pH approaches 3. In the case of decane, the pH is around 4. The swelling capacity of the hydrated lamellar phase of MGs is strongly dependent on pH. When the stearic acid is present, at high pH, it is neutralized into sodium salt to introduce ionic repulsion between the lipid bilayers.[13] The effect of changing pH in the pure aqueous phase was confirmed in lamellar and α-gel phases.[34,35] At pH below 6, swelling is very limited, while at pH above 7 better swelling is obtained.[13] However, in an important study of MG aging in water,[1] Cassin et al. worked with a pH of 4.2 and yet reported good MG stability, perhaps due to a different cosurfactant (diacetyl tartaric acid). In order to compare the pH effects, two different solutions were prepared: the aqueous phase containing 20 g of 10 w/w% NaOH in 1 L of distilled water[10] (0.05 M NaOH, pH around 13) and 2.8 g of 10 wt % NaOH in 1 L of distilled water[14,15] (7 mM NaOH, pH around 12).

Fixed combinations of 10 wt % MGs in 90 wt % oil−water solvent were prepared. The oil−water mixtures were made in changing proportion, in steps of 10 wt % difference. The ratio between the acidic oil and the alkaline water (while in all cases having a constant amount of MGs and cosurfactant) determined the pH of the solutions and the resulting swelling of MGs. In MG−hazelnut oil−0.05 M NaOH water, the pH changed from 3 to 8 with the increasing of water content. In MG−decane−0.05 M NaOH water, the pH changed from 4 to 8 on increasing the

proportion of water. In both cases, below the fraction of 20 wt % 0.05 M NaOH water/80 wt % oil, the pH was below 6, resulting in only limited MG swelling. Above the fraction of 60 wt % 0.05 M NaOH water/40 wt % oil the pH was around 7, approaching the better MG swelling condition. Above 90 wt % 0.05 M NaOH water/10 wt % oil, the pH was above 7, and the proper swelling was approached. Compared with the samples containing 0.05 M NaOH water, the 7 mM NaOH water dilution could not fully neutralize the acidity from MGs and oils at any concentration (in both hazelnut oil and decane). The solutions gave a pH below 6 even at 100 wt % 7 mM NaOH water as solvent, resulting in only partial MG swelling.

The gel was produced by vigorously mixing a hot MG−oil solution with prepared water at a temperature of 80 °C. During the mixing process, the gel continuously transforms into a pastier, drier substance, and is characterized by a bright white color and a smooth texture. The stability of the gel is dependent on the pH and the amount of aqueous phase. Generally, the gel was stable for a long time if the amount of the aqueous phase was less than 5 wt %. Above a certain quantity of water in the solutions, the swelling of MGs in water becomes important for the stability of the gel. The details are discussed in the following sections. The water crystallization temperature in the solutions shifts down to -20 °C as the formation of ice is suppressed in the mixed systems.

Heat exchanges involved in a phase transition yielded exothermic or endothermic peaks that were recorded in a differential scanning calorimeter (DSC). From these measurements the transition temperatures and the latent heat could be accurately estimated. A Perkin-Elmer power-compensated Pyris 1 DSC with an intracooler 2P was used. The samples were heated to 90 °C and held for several minutes to erase their thermal history. Then to record the provisional phase diagrams, the samples were cooled to 0 °C, and the exothermic phase transitions were recorded. A significant part of our aging studies involved keeping the samples at a fixed temperature, mostly 45 °C, for a required time, after which they were heated back to 90 °C to record endothermic melting transition(s). In order to calculate the "coagel index" (CI) more accurately, we kept the mass of all samples the same, as well as the thermal history after initial annealing at 90 °C. In all cases, we used the scanning rate of 20 °C/min. The choice of this relatively high rate of temperature change was guided by the fact that we saw no qualitative differences in the transitions on testing at 10, 5, or 1 °C/min, but the sensitivity of the DSC technique decreased dramatically, and our errors in determining the CI increased.

To determine characteristics of hydrogen bonds, infrared absorption spectra were recorded employing a Nicolet IS10 FT-IR Spectrometer (Thermal Scientific). The spectrometer was continuously purged excluding CO_2 from the sample holder box. The samples were placed in an IR cell between two NaCl windows. The temperature was regulated by placing the cell in a thermally insulated holder with a temperature controller (Eurotherm, SPECAC). In order to record the aging phenomena, the samples were scanned at 45 °C once every 24 h for 16 days to monitor the aging states.

X-ray scattering patterns were recorded using a copper rotating anode generator (Rigaku-MSC Ltd.) equipped with X-ray optics by Osmic, Ltd. The distance between the detector and the sample was set to 300 mm, giving a maximum resolution of 3.36 Å at the edge of the diffraction pattern. Samples were held between a mica sheet of 0.1 mm (Goodfellow, Cambridge, UK) and an aluminum plate. A metal substrate plate was used deliberately, to ensure accurate heat transfer to the sample. The temperature was controlled by a homemade chamber and verified by a thermocouple.[32]

Rheological measurements were staged on a strain-controlled rheometer (PHYSICA MCR501, Anton Paar) connected to a water-bath temperature control, an acceptable source since our working range was between 90 and 20 °C. A cone−plane sensor with a relatively large gap of 0.3 mm was utilized in all experiments to ensure a constant shear rate and no jamming. All tests were

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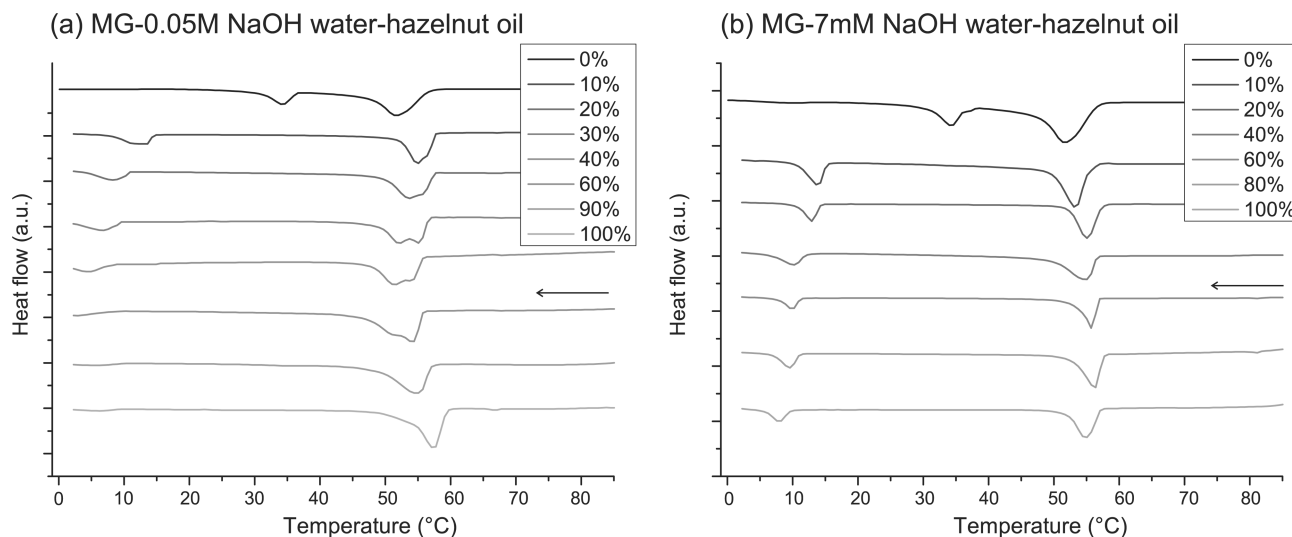(35) Larsson, K.; Krog, N. *Chem. Phys. Lipids* **1973**, *10*, 177–180.

Figure 1. DSC scans indicate the effect of adding water to MG−hazelnut oil mixtures for two different pH levels (a,b). For 0.05 M NaOH water, at low concentrations of water, the gelation transition and the crystallization transition are observed. At higher proportion of 0.05 M NaOH water, the strong interaction between MG and water allows the formation of the hydrated lamellar phase at high temperature and disturbs the crystallization of MG at low temperatures. Therefore only one transition is observed. For MG−hazelnut oil−7 mM NaOH water, the gelation transition and the crystallization transition are observed at all oil−water combinations. The percentage values in the plots represent the concentration of water in the mixture with oil.

carried out using fresh samples, which were presheared in the rheometer with a stress of 10 Pa while being kept in the fluid phase at 90 °C for 30 min. To prevent atmospheric moisture absorption, the cell perimeter was coated with low-viscosity silicone oil. The temperature ramp test involved observing the rheological transformations at the boundaries of phase transitions.[33] Measurements were performed under low amplitude oscillatory shear at a low frequency of 1 rad/s with an initial applied strain amplitude 0.05%. These test conditions were well within the linear viscoelastic range, as determined by separate stress sweeps at 90 and 20 °C. Samples were steadily cooled from 90 to 20 °C at a rate of 2.0 °C/min while the evolution of the storage modulus was monitored.

3. Phase Behavior

All our samples contained a fixed 10 wt % MG in the 90 wt % of the solvent with different oil−water ratios. First we focus on studying MG−hazelnut oil−water (using the MG−decane−water system as a comparison, to indicate the generality of results). By checking the effect of very small amounts of water added to a completely dry MG−hazelnut oil mixture, the boundary of the water content was established previously.[22] Below 0.5 wt % of water in hazelnut oil, there were no significant changes in the DSC cooling scans, and the hydrophobic mixture may therefore be regarded as "dry". Above 0.5 wt % water, the effect of water becomes increasingly significant. The lower-temperature phase transition into sub-α crystal quickly shifts from 36 to 18 °C, and the shape of the exothermic peaks becomes sharper. This could be rationalized by calculating the mol concentrations of components: 10 wt % MGs corresponded to 0.2793 M (mol/L), and 0.5 wt % water is approximately 0.277 M (mol/L). So one concludes that the changes in phase behavior become significant when the molecular number of water and MGs is just about equal, that is, approximately one molecule of water hydrating one molecule of MG. Water has a strong affinity to glycerol groups and will thus form a thin layer inside the inverse lamellar bilayer. This layer disturbs the packing of MGs and shifts the crystallization temperature to a lower value.

Once the proportion of water increases, the effect of pH becomes significant. The DSC cooling scans of the samples with changing proportion of hazelnut oil and water are given in

Figure 1. In the case of more alkaline 0.05 M NaOH water, when the concentration of water is below 20 wt %, the pH of the solutions remains below 6, which causes only a partial swelling of MGs. Two transitions are then observed in DSC cooling scans, similar to the purely hydrophobic system.[22] The high-temperature transition corresponds to the gelation point that occurs on formation of inverse lamellar phase from the initially isotropic fluid solution. The second (low-temperature) transition represents the Krafft point of MG demixing from the dominant hazelnut oil component in the solution, T_{Ko}, which is accompanied by MG crystallization to form the sub-α crystals. Evidently, as soon as the glycerol in the midplane of inverse lamellar bilayers becomes hydrated, the effective miscibility of MG in oil enhances, and the crystallization point T_{Ko} shifts to lower values and eventually disappears altogether above 40−50 wt % of water in the solution.

When the fraction of the aqueous phase is above 20 wt %, we find an additional high-temperature phase transition emerging at 52 °C. By examining the DSC cooling curves in Figure 1a, and extensive literature reports on MG in various aqueous phases, we conclude that this is the emerging Krafft point of demixing of MG from water, T_{Kw}, which is the only transition remaining in water-dominated systems.[7,8] On increasing the amount of water continuously, the intensity of this additional peak enhances, in contrast to the low-temperature crystallization transition at T_{Ko} that in turn becomes weaker. Above 50 wt % of water in solution, the full swelling is reached. In this case, MG is dissolved in the aqueous phase and shows the clear lamellar (L_α) ordering in the high-temperature region. Note the difference: at low water content, the high-temperature phase was an isotropic fluid (see the subsequent discussion of gelation rheology). The association of water molecules with glycerol heads of MG disturbs the crystallization of aliphatic tails and suppresses the crystallization transition (however, on aging, the equilibrium β-crystalline phase gradually emerges in all cases; see below).

It is interesting to compare the above phase sequence with the results for the analogous systems only differing in the less alkaline (7 mM NaOH) water (Figure 1b). In this case, NaOH cannot totally neutralize the acidic MG−hazelnut oil solutions to meet
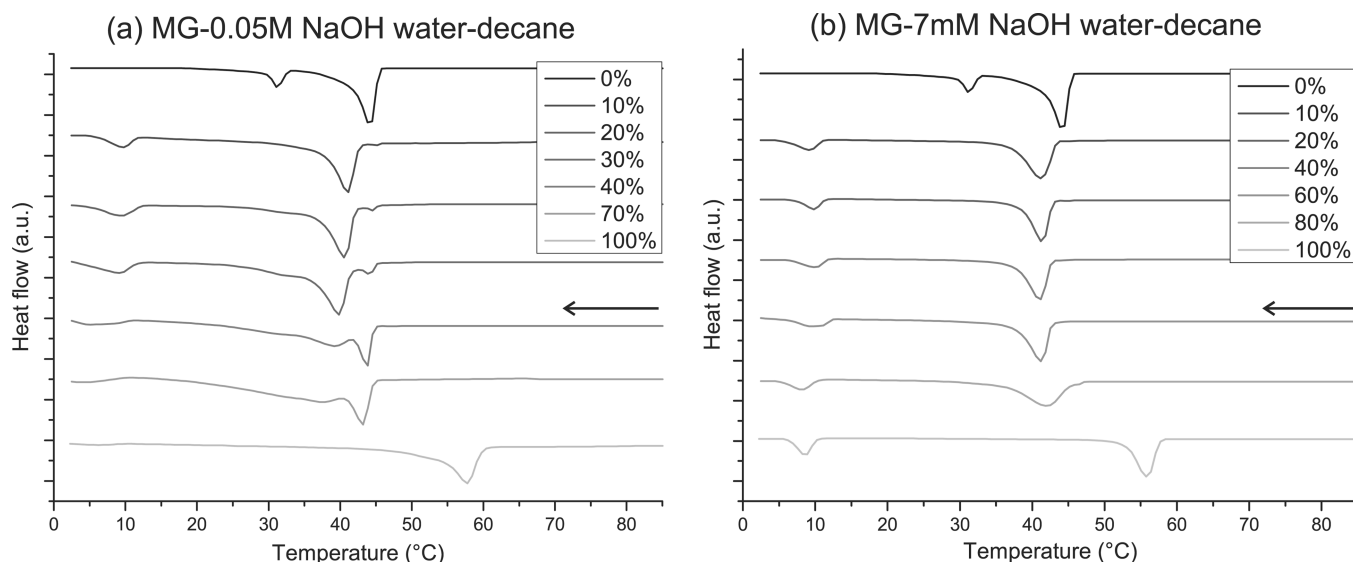
(a) MG-0.05M NaOH water-decane

(b) MG-7mM NaOH water-decane

Figure 2. DSC scans indicate the effect of adding water to MG−decane mixtures, for two different pH levels (a,b). For 0.05 M NaOH water, at low concentrations of water, the gelation and the crystallization transitions are observed. At a higher proportion of 0.05 M NaOH water, only one transition could be observed. For MG−decane−7 mM NaOH water, the gelation transition and the crystallization transition are found at all oil−water combinations. The percentage values in the figure correspond to the concentrations of aqueous phase in oil.

the required swelling conditions. The presence of water still disturbs the crystallization process by hydrating the glycerol heads in bilayers, in exactly the same fashion as in the 0.05 M NaOH water case. However, as a result of the incomplete swelling of MGs, water molecules cannot completely prevent crystallization of carbon chains, so the sub-α phase could always be observed. Two transitions, the isotropic to the inverse lamellar and the subsequent crystallization, are seen on DSC cooling scans of all oil−water combinations. These pH effects have to be linked to the content of fatty acid in the solutions, which, when neutralized into solidum salts, introduce the ionic repulsion between the bilayer aggregations in the lamellar phase and so increase the capacity of swelling in water.[36]

To generalize our results, the ternary mixture of MG−decane−water was studied in parallel. Above 0.5 wt % water, the effect of water was significant, confirming the earlier observations and molar arguments about MG hydration.[22] The crystallization point of hydrated MG shifts from 33 to 14 °C. In the sample with low proportions of water, the phase sequence is almost independent of pH of the aqueous phase. However, the same as in hazelnut oil, the effect of pH becomes significant upon increasing the water content. The DSC cooling scans of the samples with changing proportion of decane and water are given in Figure 2. For 0.05 M NaOH water, when the concentration of water is below 10 wt %, the pH of the solution is below 6, which causes the limit of MG absorption in water. Two transitions are observed in the DSC cooling scan, as in the purely hydrophobic system.[22] When the fraction of aqueous phase is above 10 wt %, an additional high-temperature transition appears at 45 °C. On increasing the amount of water, the intensity of this additional peak enhances, in contrast with the two original peaks, which in turn become weaker. Above 50 wt % of water in solution, the better swelling of MG is approached. In this case, MG is dissolved in the aqueous phase and shows clear lamellar ($L_α$) ordering in the high-temperature region. The presence of water disturbs the crystallization of MG aliphatic tails and suppresses the crystallization transition. In 100 wt % 0.05 M NaOH water, the gelation transition shifts to a higher temperature from 45 to 60 °C.

The analogous system, MG−decane−7 mM NaOH water, is studied to identify the effect of pH in the decane oil background (see Figure 2b). Again, as in the previous results in hazelnut oil, in this case, NaOH cannot fully neutralize the acidic MG−oil solutions to meet the swelling conditions. The presence of water still disturbs the crystallization process by hydrating the glycerol heads in bilayers, in exactly the same fashion as in the 0.05 M NaOH water case. However, as a result of the incomplete absorption of MG in water, water molecules cannot completely prevent crystallization of carbon chains, so the sub-α phase appears in any oil−water combinations to show two transitions are observed on DSC cooling scans.

4. Phase Diagrams

By summing up the DSC cooling scans, phase diagrams with different oil−water combinations could be obtained. MG−hazelnut oil−0.05 M NaOH water (solid line) and MG−decane−0.05 M NaOH water (dashed line) are presented in Figure 3a. MG−hazelnut oil−7 mM NaOH water (solid line) and MG−decane−7 mM NaOH water are shown separately in Figure 3b. Both hazelnut and decane oil systems show the same features in phase behavior on increasing the concentration of water. As in the discussion above, the samples with complete neutralization of natural acidity (0.05 M NaOH) show a big change in the phase sequences on increasing the water content. Below 20 wt % of water, they remain in the oil-dominated conditions, and there are three phases found upon decreasing temperature: isotropic fluid, inverse lamellar, and sub-α crystals. Above 20 wt % water, two things happen: first of all, we find that the high temperature phase is no longer an isotropic fluid but in fact a hydrated lamellar gel. Second, the principal transition splits into two, with the extra transition (at 52 °C in hazelnut oil and at 48 °C in decane) corresponding to MG−water demixing and remaining for the rest of the aqueous systems. Above 50 wt % of water, the low-temperature transition into the sub-α crystalline phase (MG−oil demixing) disappears completely in both hazelnut oil and decane oil system (see Figure 3a).

The phase sequence at high water content has been extensively discussed in the literature and includes the change from the

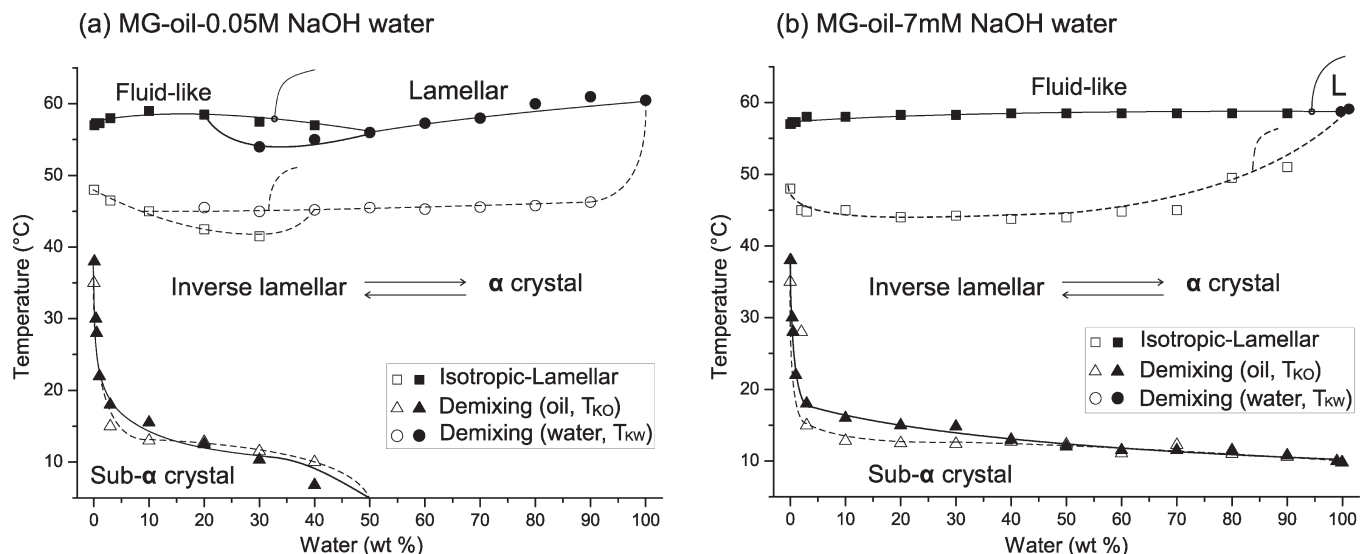(36) Krog, N.; Larsson, K. *Chem. Phys. Lipids* **1968**, *2*, 129–143.

Figure 3. Phase diagrams of MG−oil−0.05 M NaOH water and MG−oil−7 mM NaOH water are presented separately (a,b). Both hazelnut oil (solid lines) and decane (dashed lines) results are plotted on the same maps, both showing the same qualitative features. (a) In the samples containing 0.05 M NaOH water, three phases appear in the oil-dominated environment: isotropic fluid-like, inverse lamellar, and sub-α crystalline phase. Above 50 wt % of water in oil, there is only one transition to show the formation of α-gel from the high-temperature lamellar phase. (b) In the samples containing 7 mM NaOH water, the gelation and crystallization transitions are observed in whole range of oil−water concentrations, except at over 99% water where the high-temperature lamellar phase is also present.

high-temperature lamellar phase to what is commonly called the α-crystal. In the later discussion, X-ray diffraction results will show that the structure of MG−oil−water in the inverse lamellar phase is identical to that in the α-crystalline state. We thus conclude that both inverse lamellar phase and α crystalline phase are are in fact the same state, and is not a real crystalline phase. The single wide-angle scattering peak at 4.17 Å that occurs at all compositions with more than 0.05 wt % water represents the 2D dense packing between MG head-groups compacted in the inverted-lamellar bilayers, but is not evidence of the crystallization of carbon chains. This 2D hexagonal order sets in before crystallization to form the inverse lamellar phase, which is the first stage of molecular ordering in the hydrophobic system.[22] In the water-dominated solutions, there is an ordinary lamellar phase at high temperatures, but the effective inversion of the bilayers occurs below the water-Krafft temperature T_{Kw} when the originally hydrated bilayers compact and effectively form the same structure.

In the oil-dominated mixtures with low water content, on continuously cooling, the carbon chains crystallize to form the three-dimensional (3D) orthorhombic packing below the second phase transition point into the phase, which is known as the "sub-α crystal" in pure MG. For the water-dominated mixtures, with more than 60 wt % of 0.05 M NaOH water in MG−oil, the strong interaction between MG head-groups and water disturbs the crystallization process to cause the absence of crystallization transition upon cooling.

In both the decane and the hazelnut oil environment, the 7 mM NaOH water was not able to neutralize the natural acid of MG−oil to achieve the full swelling. Therefore the effect of water was not strong enough to completely prevent the crystallization of aliphatic chains, and the formation of sub-α crystals was observed for all oil−water combinations (Figure 3b). Similarly, in the high-temperature region, the isotropic fluid-like state extends over almost the whole range of water content, and the ordinary hydrated lamellar phase only was found with well over 95 wt % of water in solution, as determined by the rheological measurements in the next section.

DSC experiments were also performed on samples with a fixed (low) water concentration (at 3 wt %), but different concentrations of MG. Both MG−hazelnut oil−water and MG−decane−water were tested in parallel, and the results are presented in Figure 4a,b, respectively. It is observed that, due to the small amount of MG and diglyceride in the hazelnut oil itself, the gelation temperature of hazelnut oil systems is higher (up to 60 °C in 10 wt %MG) than the gelation point of decane systems (at 45 °C). At low concentration of MG, impurities in hazelnut oil are relevant for the phase behavior. The gelation transition in the hazelnut oil shifts to the higher temperature on increasing MG concentration, but in the decane system this transition is almost independent from MG concentration. Apart from these minor differences, there are not many changes between the natural hazelnut oil, full of dopants and impurities, and the pure decane system.

These phase diagrams were obtained on cooling from the high temperature fluid-like solutions when the corresponding phases first form or on subsequently heating the system soon after. In spite of these not being true thermodynamic equilibrium phases (see the discussion of aging), similarly to Figure 3, such an "apparent phase diagram" remains a meaningful representation. At this low water content, the two transitions observed on DSC between 0 and 90 °C correspond to the gelation temperature of the inverse lamellar phase, and the oil-Krafft temperature T_{Ko}, at which the alkyl chains crystallize to form the sub-α crystals (orthorhombic packing). This comparison of the water-contained sample and the purely hydrophobic system shows that even a very small amount of water added to the MG−oil has a significant change on the topography of phases.

5. Structure and Rheology

In this section we focus on studying MG−hazelnut oil−water to indicate the structures and the mechanical features of phases. X-ray diffraction was used to analyze the molecular arrangement of MG−oil with 3 wt % water and 10 wt % MG. This composition was chosen so that (a) it is well above the "dry" oil boundary (of ca. 0.5 wt %), (b) is it far from the triple point where the three

(a) MG hazelnut oil-water
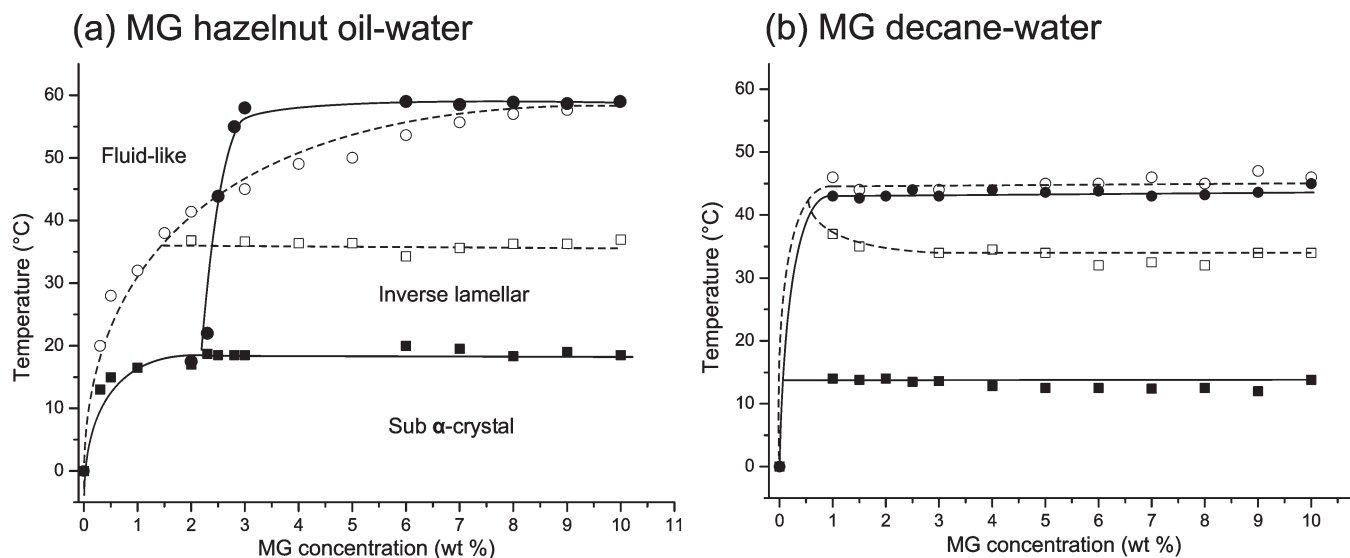

(b) MG decane-water

Figure 4. (a) The phase diagram of MG−hazelnut oil with a constant 3 wt % water (solid lines) is presented to compare with the completely dry MG−oil system (dashed lines). (b) The phase diagram of MG−decane with the same concentration of water (3 wt %, solid lines) is similarly compared with the completely water-free system (dashed lines). Both systems show the same trends upon adding a small quantity of water in the MG−oil matrix.

key phases meet at low MG concentration (see Figure 4), (c) these three phases are well formed and not obscured, and (d) the results at low water concentration complement a significant amount of existing structural studies of highly hydrated mixtures.

Below the gelation temperature (58 °C), an initially isotropic fluid solution of MG aggregates into an inverse lamellar phase. A series of concentric rings in a small angle region determined that the structure contained lamellar ordering with the ratio of small-angle reflection spacing following the characteristic sequence of 1, 1/2, 1/3, and 1/4. These consecutive peaks successfully represent higher order reflections from the periodic inverse lamellar structure and are in good agreement with the expected thickness of the lamellar bilayer, determined as 52 Å in MG−oil and 56 Å in MG−oil−water (see Figure 5). In the dry MG-oil system, the "twin" wide-angle X-ray diffraction peaks are observed. These two reflections represent the regular spacings of 4.17 Å and 4.11 Å.

In a hydrophobic environment (and also below the water-demixing Krafft point T_{Kw} when that exists), the glycerol heads have to pack in the midplanes of inverse lamellar bilayers. A combination of evidence suggests that there is a remarkable coincidence between the size of the glycerol group and the cross-sectional size of the C16−C18 alkyl chain when it laterally packed in a dense polymer brush.[37] Due to this matching of sizes, the dense-brush arrangement drives the alkyl chains to be aligned parallel on the outside of each bilayer and the densely packed glycerol heads to adopt a planar hexagonal packing with a periodical spacing between in-plane glycerol groups at 4.17 Å. The other regular spacing at 4.11 Å represents the distance between the two glycerol layers inside each bilayer (Figure 5a). In contrast, there is only one wide-angle X-ray diffraction peak at 4.17 Å in the MG−oil−water system (Figure 5b). This suggests that the water molecules are absorbed in the middle of inverse lamellar bilayers to disrupt the regular spacing between the two hexagonal planes. The in-plane head arrangement is also some-what disturbed by the presence of water, which shows in a much broader diffraction peak at 4.17 Å.

Rheological experiments were carried out in the linear viscoelastic region. The measurement involved observing the low-frequency

shear modulus changing as a function of temperature in samples with different water fractions and pH values, as the systems evolve from fluid-like phases to gel-like materials. The samples were heated to 90 °C and presheared at 10 Pa for 30 min to erase the thermal and mechanical history. The samples were then cooled through the transition zones at a chosen well-controlled rate (2 °C/min). The typical results for MG−hazelnut oil are shown in Figure 6 as 0% curves. Without water, the modulus at high temperature is very near 0 Pa, and there are two subsequent regions corresponding to the key phases: isotropic fluid-like, inverse lamellae gel, and sub-α crystal-line gel. When the temperature drops down below the lamellar transition point T_L, the rapid increase in mechanical rigidity is immediately expressed by the storage modulus G'. The system acquires mechanical characteristics of a gel.[33] On continuously cooling toward the crystallization temperature T_{Ko}, the sample enters the sub-α crystalline phase, and the storage modulus continuously increases to reach the saturated level.

In a ternary MG−hazelnut oil−water system, the two cases of MG−hazelnut oil−0.05 M NaOH and MG−hazelnut oil−7 mM NaOH have to be discussed separately. Cooling down from the isotropic fluid phase, the MGs aggregate under the gelation temperature, which occurs on formation of lamellar domains, and the mechanical rigidity immediately increases to a certain level. The subsequent crystallization transitions could be observed in the rheological signature of MG−oil with low concentration of both 0.05 M NaOH water and 7 mM NaOH water, labeled by vertical arrows on plots. Above 50 wt % 0.05 M NaOH water, the lower-temperature change in the storage modulus G' is not associated with any phase change in α crystals (since we have verified by X-ray and DSC that the microscopic structure remains the same). The most likely reason for this remaining feature in $G'(T)$ is that the kinetic effect due to the stress-relaxation rate of lamellar domains becomes close, and then exceeds the applied rate of cooling in the rheometer.

The rheological measurements at room temperature indicate that the samples are gel-like over a wide range of water dilution, with the relatively high storage modulus G', although there is a systematic decrease in the modulus on increasing water concentration. The high-temperature region is sensitive to pH and the amount of the aqueous phase in the mixture. Above 30 wt % of

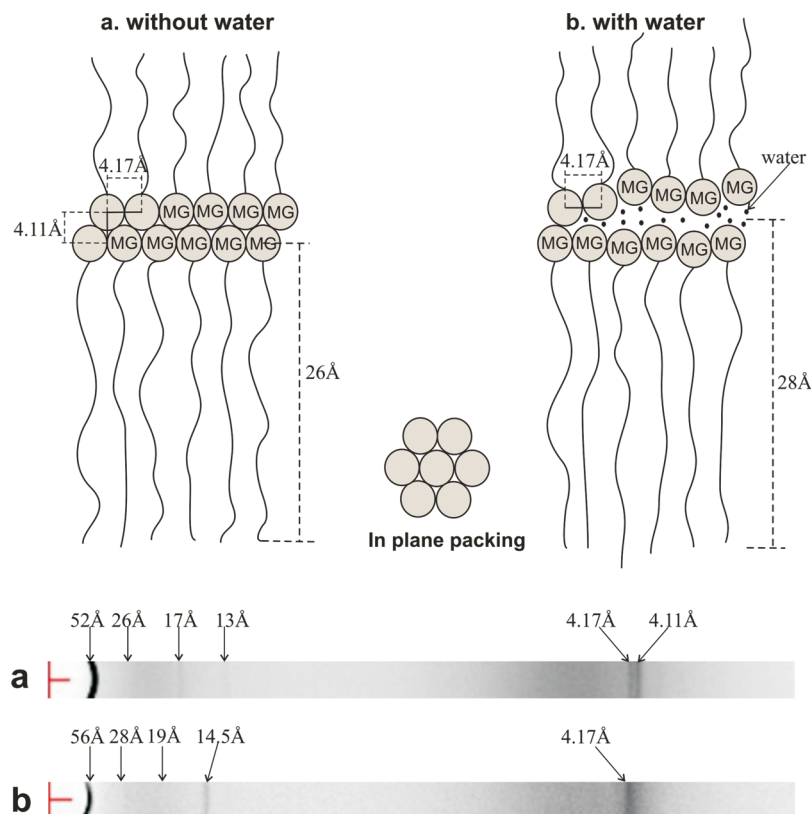(37) Milner, S. T. *Science* **1991**, *251*, 905–914.

Figure 5. Structures of (a) dry MG−hazelnut oil and (b) MG−hazelnut oil−water are described by X-ray diffraction patterns. The small-angle peaks identify the lamellar ordering. The evidence shows the thickness of inverse lamellar bilayers increases from 52 Å to 56 Å on adding 3 wt % of water. The wide-angle scattering shows that the existence of water disturbs the head dense packing between layers, so the periodical spacing in 4.11 Å is absent in MG−oil−water.
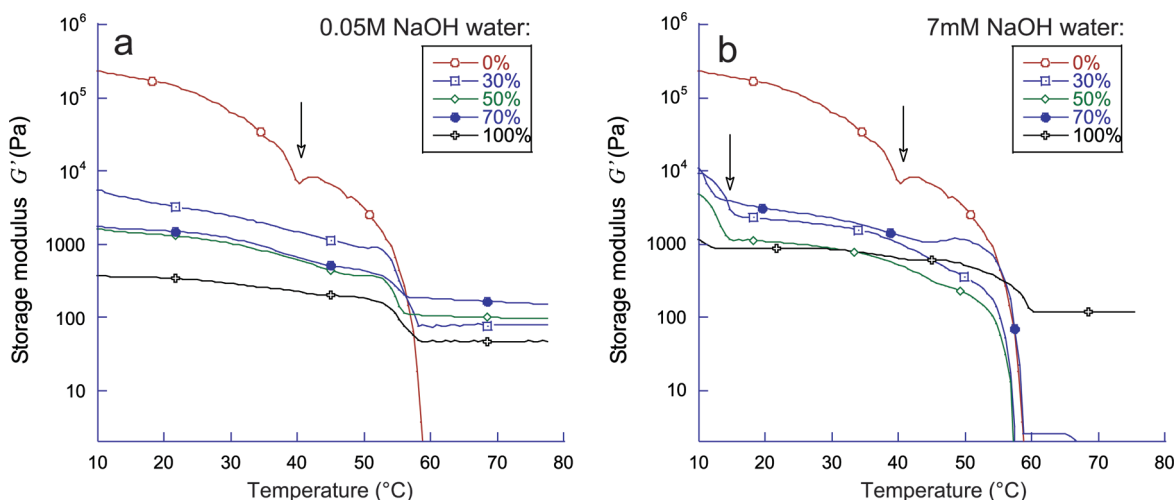

Figure 6. Rheological responses of MG-hazelnut oil-0.05 M NaOH water and MG-hazelnut oil-7 mM NaOH water are illustrated in plots a and b, respectively. Generally, the samples lost their gel-like character on increasing the concentration of water. The nonzero modulus at high temperature indicates the lamellar phase. (a) In the sample with 0.05 M NaOH water, the high-temperature lamellar phase appeared once the water concentration was above 30 wt %. (b) In the sample with 7 mM NaOH water, the lamellar phase was formed only in the nearly-100 wt % aqueous environment.

0.05 M NaOH water in MG−oil, the storage modulus at high temperature is no longer zero, indicating that the lamellar structure exists well above 70 °C (see Figure 6a). Since this structure is most prominent at higher water fraction, and we do not find any wide-angle X-ray reflections here, one has to conclude that this is an ordinary (hydrated) lamellar phase which then transforms into the inverted lamellar (or α-crystal) phase below the water-demixing line T_{Kw}, just below 60 °C. Unfortunately, since water

evaporation is involved, we could not establish the upper-temperature phase boundary of this L_α lamellar phase (see phase diagrams in Figure 3).

The mechanical strength of this high-temperature lamellar phase varies: in the sample with 50 wt % 0.05 M NaOH water, the storage modulus at high temperature was around 100 Pa, and at 70 wt % water it was up to 300 Pa. In a 100% MG−0.05 M NaOH water system, the storage modulus at high temperature

Figure 7. Restructuring during the aging of the inverse lamellar phase of MG−oil−water is monitored by X-ray scattering. In the fresh lamellar phase, the wide-angle peaks show the packing of glycerol groups in a 2D hexagonal manner. During aging, the wide-angle structure breaks into two series of peaks, which indicate the formation of the β-crystals.[13,14,22]

decreased to 50 Pa, and matches that of the less alkaline 100% MG−7 mM NaOH water system (see Figure 6b). Unlike the alkaline sample containing 0.05 M NaOH water, in 7 mM NaOH water systems with any nonvanishing amount of oil, the storage modulus at high temperature always remained around zero, indicating that an isotropic fluid phase has transformed into the inverted lamellar (or α-crystal) phase directly below the gelation line.

6. Aging

We now focus on studying the aging behavior of 10 wt % MG in the matrix with 3 wt % water and 97 wt % hazelnut oil, the same system that we have presented in the X-ray studies. The freshly prepared samples were cooled and kept at 45 °C to monitor aging in the inverse lamellar phase. After 16 days, the aged structures changed, with their X-ray diffraction signature shown in Figure 7. As always, there is a series of concentric rings in the small-angle region to show the existence of lamellar ordering. The difference of the aged samples is revealed by a series of wide-angle diffraction peaks. As mention before, the fresh sample shows periodical spacing at 4.17 Å in the wide angle diffraction region. On aging, the wide-angle scattering pattern develops two series of peaks, which is identical with the β-crystals known in pure MG, with triclinic alkyl chain packing in the unit cell.[13] This result is similar to the earlier work by Batte et al.,[14] which concludes that the α-crystalline phase in MG−oil−water was metastable and eventually transferred to the β-crystalline state, same as in the purely hydrophobic system that ages into the β-crystal both from the inverse-lamellar and the sub-α crystalline states.[23]

The aging of MG−oil−water was recorded by infrared spectroscopy, focusing on the change in the hydrogen bonding patterns. To study hydrogen bonds, we focus on the low-energy region from 3000 to 4000 (1/cm).[39] In our recent study of hydrophobic MG−oil systems, we have established that the vibration mode of 2-OH bonds is at 3250 (1/cm), while the 3-OH stretching bond vibration is at 3300 (1/cm) (see Figure.8a).[23,39,40] 3-OH hydrogen bonding is not a stable intermolecular link and only plays a subsidiary role in MG structuring. The 2-OH hydrogen bonds form and force MG to rearrange in a more ordered way. *D* and *L* isomers contain different orientations of hydroxide in the glycerol groups. The 2-OH hydrogen bonds between glycerol groups prefer to link the isomers that matched chirality. Therefore, *D* and *L* isomers spontaneously select the same type of isomers, and this eventually promotes the separation of *D* and *L* layers. This slow reordering process is the key to the aging phenomena we observed on the macroscopic scale.

The same behavior was also obtained in MG−oil−water. However, due to the presence of water, the process of rearranging

hydrogen bonds is disturbed by the free hydroxide groups available in the solution, which causes the longer lifetime of inverse-lamellar gels. To understand the relationship between aging and the formation of the hydrogen bonding in MG−oil−water, the time-evolution of IR spectrum of 10 wt % MG, 3 wt % water in oils was conducted at 45 °C (at this temperature, both the dry and the aqueous systems are in the same inverse lamellar phase, which allows fair comparison).

Generally, the strong molecular bonds correspond to high frequency (high wavenumbers) of absorption. However, in these measurements we detect not the hydrogen bond directly, but the O−H vibration frequency. Once the strong H bond appears between O−H and C=O (2-OH) groups, the O−H vibration shifts to a lower frequency (wavenumber) band. The free O−H bond shows higher wavenumber absorption at around 3500 (1/cm). It does not mean the free O−H state gives higher energy hydrogen bonding, it merely shows that free O−H vibrations (both in 3-OH and 2-OH positions) are not constrained by any hydrogen bonding, so they absorb the higher frequency infrared radiation. The O−H bonding bands of MGs and other compounds are in agreement with the relevant literature data.[39,43] Compared with the dry MG−oil sample, after heating, there is a broad peak at 3400 (1/cm) to show the bonding between MG and water.[41−43] It suggests that most MGs prefer to form the hydrogen bond with the water molecules rather than with each other in the initial state. During aging, the absorption band splits into three. The new emerging peak is attributed to the hydrogen bonding 2-OH (3250 1/cm) and 3-OH (3300 1/cm), respectively. After one week, the lower-frequency bands become sharper and increase their intensity (see Figure 8b). Over 16 days, the 2-OH bonding becomes dominant, which can only occur is *D* and *L* isomers were separated, as required for the formation of anhydrous β-crystals.[38−40]

The aging process could be followed thermodynamically by introducing a dimensionless number called the coagel index (CI), which is the ratio of total latent heat of the transition in fresh and aged materials: CI = ΔH(aged)/ΔH(fresh).[1,23] As in the original study of Cassin et al.[1] for 5 wt % MG on water, we find that the aged structure of aggregated MG contains the β-crystals with a highly regular arrangement achieved through segregated molecular chirality. This causes the latent heat of the aged material to be higher than that of the freshly ordered system. Therefore the CI could be used to monitor the fraction of the aged part in the sample by comparing the heat flow used to melt the freshly ordered and the aged material. The result of our DSC study shows that CI increases gradually with time, and eventually reaches a saturation state. To focus on observing the time evolution of CI in the inverse lamellar (or, equivalently, α-crystal) phase, the samples in these experiments were stored at a fixed temperature (45 °C) after initial quenching. The melting enthalpy of aged β-crystalline samples was about two times the value obtained from melting the fresh samples. This difference, and the evolution of CI on aging, is shown in Figure 9. The initial value of CI = 1 indicates the sample melting from the fresh inverse lamellar state, while a saturation value of 2 suggests better-ordered β-crystals with a higher melting entropy.[1,23] The time-evolution of CI shows that the inverse lamellar phase is metastable and is ready to transform into a more stable β-crystalline arrangement.

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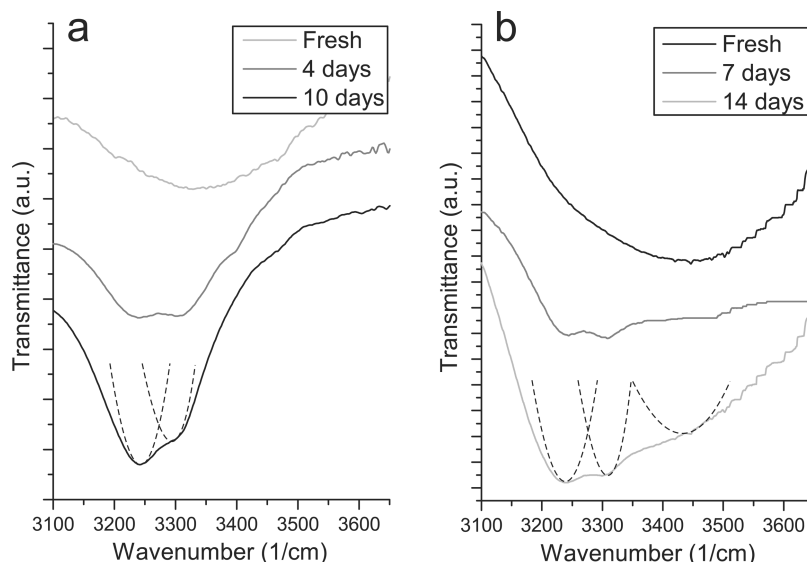
Figure 8. (a) During aging, the hydrogen-bonding absorption peak of the water-free MG−oil system gradually splits into two. The upper wavenumber line corresponds to 3-OH hydrogen bonds, while the lower wavenumber is related to the 2-OH hydrogen bonds. After 5 days of aging, the ordered 2-OH hydrogen bonds continuously grow and finally dominate. (b) In the MG−oil−water system, the hydrogen bonds between MG and water give an additional broad weak peak at 3450 (1/cm) in the initial state. During aging, this broad peak at 3450 (1/cm) is weakened and splits into three. After 16 days, 2-OH hydrogen bonding eventually begins to dominate the IR absorption.
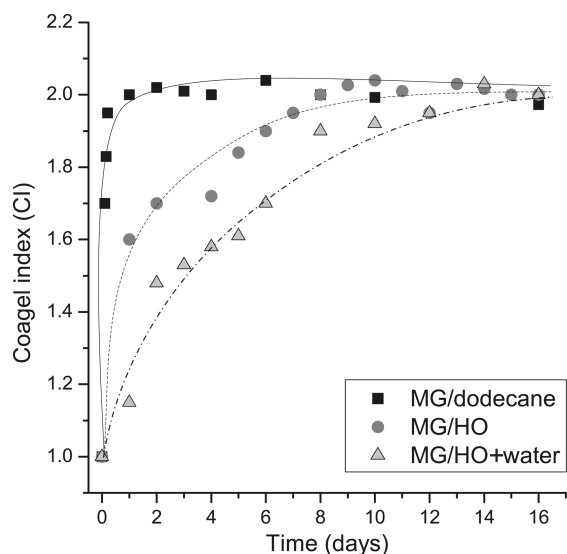

Figure 9. Time evolutions of the CI in different environment solutions are shown above. The results briefly demonstrate the stability of the gel was enhanced by increasing the concentration of free hydroxide groups. As a result of the small molecular weight of water, adding a small quantity of water is an effective method to increase the lifetime of lamellar gels.

To test our understanding of the effects of adding water to the hydrophobic solutions of MGs, we compare the time evolutions of CI in a different kind of background solution: pure dodecane. Figure 9 shows that aging into β-crystals is very fast in this case. Within about 4 h, the MG−dodecane mixture has lost its gel phase and completely transformed into the β-crystalline state. The hazelnut oil provides a more stable environmental condition for the inverse lamellar phase, and the aging process takes around 3 days to complete. By adding water, the lifetime of MG−oil−water increases up to around 16 days. The results show the stability of MG gel is dependent on the concentration of free hydroxide groups (OH) in the solutions. Dodecane does not maintain any free hydroxide groups, so MGs rearrange into the

optimal hydrogen-bonding pattern in a short time. Hazelnut oil contains 80 wt % oleic acid and 20 wt % linoleic acid, which provide free hydroxide groups in the solutions. These free hydroxide groups disturb the recombination process of hydrogen bonds and increase the lifetime of the gel. Because of the small molecular weight of water, adding even a small amount (3 wt %) of water increases the number of free hydroxide groups significantly to significantly slow the aging process.

7. Conclusions

In conclusion, this work provides a systematic framework to understand the effects of water on MG−oil mixtures. First of all, the phase diagrams of MG−oil−water were established to provide the background for the discussion. MG−hazelnut oil−water and MG−decane−water were tested for comparison, confirming qualitatively that the phase sequence and structures are universal. We found that the solubility of pure MG in water is very limited naturally (no more than 25 wt %). To enhance the stability of MG gel, it is important to mix an appropriate cosurfactant in the solutions, in our case stearic acid, which makes the phase ordering of MG highly dependent on the pH.

In both hazelnut oil and decane systems, two series of samples were compared: MG−oil−0.05 M NaOH water and MG−oil− 7 mM NaOH water. For more alkaline solutions containing 0.05 M NaOH water, two distinct regions could be identified on increasing the fraction of water. In the oil-dominated environment, there are two ordered phases: inverse lamellar and sub-α crystals. When the fraction of aqueous phase is over 20 wt %, demixing between MG and water is observed. Above 50 wt % water, the crystallization of the carbon chains is disturbed by the water, so the sub-α crystalline phase becomes weaker. In contrast, in the less alkaline MG−oil−7 mM NaOH system, the aqueous phase cannot neutralize the acids from MG−oil to achieve the proper swelling, so the presence of water does not to stop the crystallization of carbon chains. In this case, the two transitions are observed in any oil−water combinations.

After the phase diagrams were established in both hazelnut oil and decane systems, we focused on studying the structures,

rheological features, and aging in MG−hazelnut oil−water mixtures. The structure of MG−hazelnut oil−3 wt % water was studied by X-ray diffraction. It was confirmed that the structure of the inverse lamellar phase was changed by adding a small quantity of water. In the dry oil environment, the twin wide-angle X-ray diffraction peaks at 4.11 and 4.17 Å suggest the dense packing of glycerol heads in the hexagonal bilayer. In the samples with 3 wt % water, because of the strong affinity of water to glycerol head groups, water molecules are absorbed inside the inverse lamellar bilayers and cause less irregular packing between the layers, shown by the absence of the 4.11 Å layer−layer spacing. The mechanical response in a wide range of conditions was characterized by rheological measurements. The samples remain gel-like over a wide range of water dilutions, with a high storage modulus. Generally, a decrease in the storage modulus on increasing water concentration was found. The retention of storage modulus at high temperature indicated the presence of ordinary hydrated lamellar structure under the proper swelling conditions.

With the clear phase diagram and the structure description, we especially focus on studying the aging phenomena in inverse lamellar phase in the low-water samples (3 wt %). The inverse lamellar phase is metastable and evolves into β-crystals characterized by a series of wide-angle diffraction peaks from 3.56 to 4.6 Å. The hydrogen bonding pattern is also changed by the presence of water. A broad weak absorption in the infrared spectrum at 3450 (1/cm) indicates that, after heating, MG molecules prefer forming hydrogen bonds with water rather than with each other. This broad peak gradually splits to three distinct peaks at 3400, 3300, and 3250 (1/cm), which suggests that the D and L isomers start to segregate, and aged thermodynamically stable structures appear. The absorption peak at 3250 (1/cm) eventually comes to dominate the spectrum to confirm the formation of β-crystals.[23] The CI quantifies the aging processes of MG gels in different background solutions. The results demonstrate that the lifetime of the inverse lamellar phase increases by the presence of free hydroxide groups in the solutions. The existence of these free hydroxide groups disturbs the aging process and enhances the stability of the MG gel. We conclude that, by adding a small quantity of water, lamellar gels with longer lifetimes can be obtained.