

MICROEMULSIONS AS TEMPLATES FOR NEW MATERIALS

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ABSTRACT

Microemulsions are increasingly gaining importance as reaction media and templates since a great deal is known about how to tune the structure and the size of the domains. However, the 1:1 replication of the bicontinuous structure has not yet been achieved. The aim of this project is to develop a route for the synthesis of a bicontinuous solid sponge whose surface properties can be tuned. One approach to the synthesis of a bicontinuous solid sponge is to create a gel-like water or oil phase and to polymerize the remaining low-viscosity phase so that the templating structure is not destroyed during the polymerisation process. In the current project we chose to take an organogel as the templating phase and to polymerize the aqueous phase. To achieve this goal a suitable gelator had to be found. Then, the phase diagrams had to be studied after each compositional change, as the addition of gelators to the oil phase as well as of polymerisable monomers to the aqueous phase significantly affect the phase behavior of the microemulsion.

1 INTRODUCTION

Microemulsions are thermodynamically stable mixtures of at least three components, namely water, oil, and surfactant with domain sizes of 5-100nm. The domains can be discrete (water-in-oil or oil-in-water droplets) or bicontinuous [1]. All of these structures can be found in the one-phase region, the starting point of which is given by the $\tilde{\chi}$ -point. This point gives us the minimal amount of surfactant $\tilde{\gamma}$ needed to solubilize equal amounts of water and oil at a certain temperature \tilde{T} and thus describes the effectiveness of a surfactant system. The main focus of this work is on the bicontinuous or so-called sponge phase. There are two main problems associated with trying to retain this structure during the polymerization process. Firstly, surfactant monolayers are not rigid enough to preserve the shape during the process. Secondly, the reaction of the monomer to the polymer changes the phase behavior and thus the structure of the microemulsion [2].

One approach to synthesizing a bicontinuous solid polymer sponge is to create a gel-like water or oil phase and to polymerize the remaining low-viscous phase. In other words, the templating phase is "arrested" [3] so that the templating structure is not destroyed during the polymerisation process. In the current project we chose to take an organogel as the templating phase and to polymerize the aqueous phase. The aim here is to create a microemulsion system the bicontinuous phase of which is gelled. In

other words, we want to create a microemulsion for which the sol-gel transition temperature of the organogel lies at higher temperatures than the phase boundary 1-2.

Gels are three dimensional networks composed of aggregated gelator molecules in which the solvent is trapped and inhibited from flowing. In organogels the solvent is an oil and a variety of different gelators exist, e.g. ABA-block-copolymers or low molecular mass organogelator molecules (LMOG) [3]. While the ABA-block-copolymers have a strong influence on the phase behaviour of microemulsions, the LMOG's should not affect the phase behavior to such a great extent. One potential candidate for the gelation of the oil phase is 12-hydroxyoctadecanoic acid (12-HOA). It is surface active and is known to gel various organic solvents such as *n*-alkanes [5]. These gels are viscoelastic solids and have a sharp sol-gel threshold. 12-HOA is a fatty acid used in various applications such as detergents and lubricants.

The polymerisable aqueous phase, on the other hand, contains the monomer N-isopropylacrylamide (NIPAm). It is a well-known, commercially available, and water soluble monomer. The great advantage of p-NIPAm (poly - N-isopropylacrylamide) is the fact that it is a stimuli responsive polymer, which undergoes a coil-globule transition in response to increasing temperature, which results in dramatic changes in the volume, and surface area. Additionally, it is extremely versatile, and can be made responsive to a variety of external stimuli, as well as being easily modifiable with a range of functional groups [6].

2 EXPERIMENTAL PART

2.1 Materials

12-Hydroxyoctadecanoic acid (12-HOA) with a purity of 99% and *n*-dodecane with a purity of ~99% were purchased from Sigma-Aldrich. The compounds were used as received. The technical surfactant LutensolAO5 was donated by BASF. N-isopropylacrylamide (NIPAm) with a purity of 99% was purchased from Acros Organics. It was recrystallized twice from *n*-hexane. The water was purified by a Milli-Q system.

2.2 Phase Behavior

Various amounts of water, *n*-dodecane, 12-HOA, LutensolAO5, and NIPAm were weighed into test tubes and sealed with polyethylene stoppers. The samples were placed in a water bath and the phase boundaries were determined with a precision of ± 0.5 K. All samples were prepared at a 1:1 water-to-oil weight ratio, *i.e.* at $\alpha = 0.5$. The mass fraction ψ of the monomer in the aqueous phase was kept at a constant value of 0.07. The phase behavior of the multicomponent system water / NIPAm – *n*-dodecane / 12-HOA – LutensolAO5 was studied as a function of the temperature T and the total surfactant concentration γ . The parameters α , ψ , and γ specify the composition and are defined as follows:

$$\alpha = \frac{m_{\text{oil}}}{m_{\text{water}} + m_{\text{oil}}}$$

$$\psi = \frac{m_{\text{NIPAm}}}{m_{\text{water}} + m_{\text{NIPAm}}}$$

$$\gamma = \frac{m_{\text{surfactant}}}{m_{\text{water}} + m_{\text{oil}} + m_{\text{surfactant}}}$$

2.3 Gelation Point Measurements

The sol-gel temperature of the binary system *n*-dodecane – 12-HOA was determined in a water bath with a precision of ± 1 K. As the sol-gel temperature depends on the gelator concentration a dilution series was carried out.

3 RESULTS

The effect of NIPAm on the microemulsion water / NIPAm – *n*-dodecane – LutensolAO5 at equal mass of water and oil is presented in Figure 1. As can be seen in Figure 1, the addition of NIPAm to the aqueous phase shifts the one-phase region about 10 K towards higher temperatures. Consequently, the coordinates of the “fish-tail” are also affected. In the presence of 7% NIPAm the minimum weight fraction of LutensolAO5

required to solubilize equal amounts of water and oil is $\tilde{\gamma} = 0.129$ at $\tilde{T} = 54.9^\circ\text{C}$, while it was $\tilde{\gamma} = 0.083$ at $\tilde{T} = 55.4^\circ\text{C}$ for the NIPAm-free system. Thus the surfactant efficiency slightly decreases, while the so-called mean temperature \tilde{T} remains almost the same.

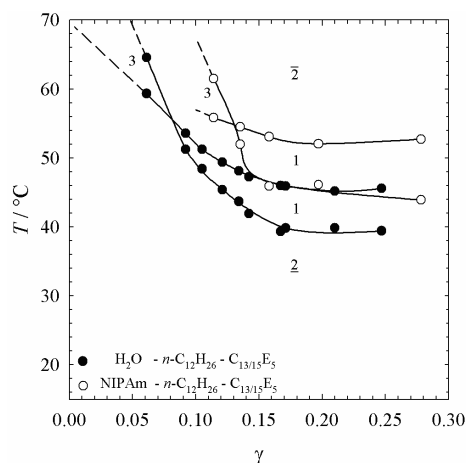


Figure 1: Phase diagrams of the ternary base system water – *n*-dodecane – LutensolAO5 (black) and of the system containing 7 wt.-% ($\psi = 0.07$) NIPAm (white), respectively, plotted as a function of the surfactant mass fraction γ and the temperature T at $\alpha = 0.5$.

The next step was to add the gelator to the system water / NIPAm – *n*-dodecane – LutensolAO5. In order to have a rough idea about the amount of gelator necessary to achieve our goal we first determined the sol-gel transition temperatures of the binary system 12-HOA / *n*-dodecane as a function of the gelator mass fraction β (see Figure 2).

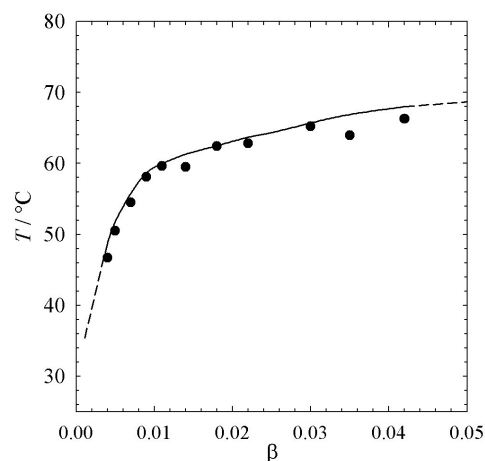


Figure 2: Sol-gel transition temperatures as a function of the gelator mass fraction $\beta = m_{\text{HOA}} / (m_{\text{oil}} + m_{\text{HOA}})$ and the temperature T . With increasing gelator concentration the sol-gel transition shifts to higher temperatures until it levels off at $\sim 68^\circ\text{C}$.

As is seen in Figure 2, the sol-gel transition temperature increases with increasing β . As our aim was to have a gel the sol-gel transition temperature at a higher temperatures than the phase boundary 1 - $\bar{2}$ we chose $\beta = 0.018$. At this gelator concentration the sol-gel transition is above 60°C and above the 1 - $\bar{2}$ phase boundary of the NIPAm containing system (see Figure1).

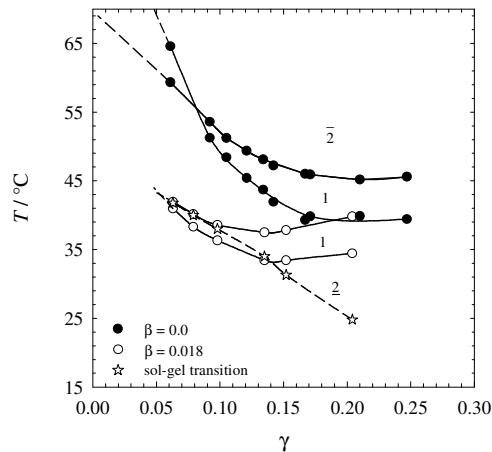


Figure 3: Phase diagrams of the ternary base system water - *n*-dodecane - LutensolAO5 (black) and of the system containing 1.8 wt.-% ($\beta = 0.018$) 12-HOA (white), respectively, plotted as a function of the surfactant mass fraction γ and the temperature T at $\alpha = 0.5$.

Having decided to use $\beta = 0.018$ we went one step further and studied the effect of 12-HOA on our base system water - *n*-dodecane - LutensolAO5. The result is shown in Figure 3. As the 12-HOA is slightly surface-active and behaves like an alcohol, the one-phase region shifts to lower temperatures [7]. Simultaneously the $\tilde{\chi}$ -point is shifted towards a lower $\tilde{\gamma}$ and a lower \tilde{T} , which are now $\tilde{\gamma} = 0.05$ and $\tilde{T} = 43^\circ\text{C}$ compared to $\tilde{\gamma} = 0.083$ and $\tilde{T} = 55.4^\circ\text{C}$ of the gelator-free system. As can be seen in Fig.3, the sol-gel transition line meets the $\underline{2}$ -1 phase boundary of the system water - *n*-dodecane / 12-HOA - LutensolAO5 at a mass fraction of approximately $\gamma \approx 0.14$ and a temperature of $T = 33^\circ\text{C}$. With decreasing γ values the sol-gel transition line approaches the 1 - $\bar{2}$ phase boundary. Thus we managed to have a gelled and clear area in the one-phase region of the system water - *n*-dodecane / 12-HOA - LutensolAO5. The next step was to replace water by the NIPAm containing aqueous phase. That is to say that except for small amounts of crosslinker and a starter for the radical polymerization all components are added to the system.

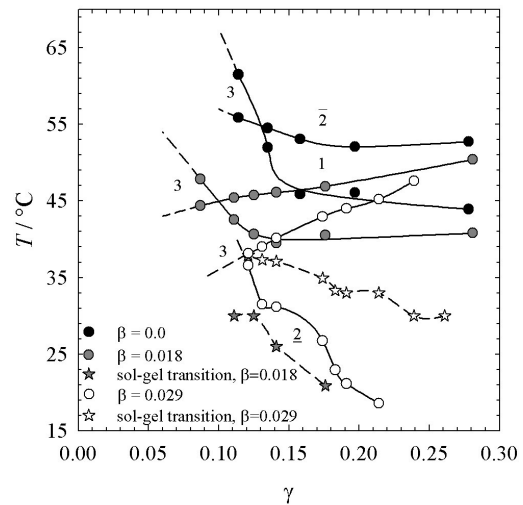


Figure 4: Phase diagrams of the system water / NIPAm - *n*-dodecane - LutensolAO5 without (black), with 1.8 wt.-% ($\beta = 0.018$) (gray), and 2.9 wt.-% ($\beta = 0.029$) (white) 12-HOA plotted as a function of the surfactant mass fraction γ and the temperature T at $\alpha = 0.5$.

In Figure 4 one can see the phase behavior of the final system water / NIPAm - *n*-dodecane / 12-HOA - LutensolAO5 with various amounts of gelator in the oil-phase. In contrast to the NIPAm-free system, the sol-gel boundary at $\beta = 0.018$ lies below the one-phase region. Thus the mass fraction of the gelator had to be increased to at least $\beta = 0.029$. With increasing mass fraction of 12-HOA the one-phase region shifts to lower temperatures while the sol-gel transition “moves up”. Like in the system without NIPAm (Figure 3) the $\tilde{\chi}$ -points shift simultaneously towards a lower \tilde{T} , namely $\tilde{T} = 48.7^\circ\text{C}$ at $\beta = 0.018$ and $\tilde{T} = 37.8^\circ\text{C}$ at $\beta = 0.029$. In the latter case, the sol-gel transition of the system water / NIPAm - *n*-dodecane / 12-HOA - LutensolAO5 and the one-phase region “meet” at a mass fraction of approximately $\gamma \approx 0.15$ and a temperature of $T = 35^\circ\text{C}$. We have to mention that at $\gamma > 0.14$ liquid crystalline (LC) phases were observed. However, for the sake of clarity, they are not shown in Figure 4. It is because of these LC phases that the one-phase, gelled region is very small in terms of its temperature (~ 30 - 35°C) and concentration (~ 0.12 - 0.14) ranges. It is in this region where we are planning to polymerize our sample.

4 CONCLUSION

The phase behavior of the complex microemulsion mixture containing organic gellator and organic monomers was investigated stepwise. First, the influence of the monomer NIPAm on the base system water - *n*-dodecane - LutensolAO5 was studied. The increase in temperature of the one-phase region by

adding NIPAm can be explained by the polarity of this monomer and thus its hydration. As molecules are used for the hydration shell, less water is left for the interface. The system becomes more hydrophobic and shifts to higher temperatures. Second, the influence of the gelator 12-HOA on the base system water – *n*-dodecane – LutensolAO5 was studied. The fatty acid is slightly surface-active and has an effect similar to that of an alcohol in a microemulsion, *i.e.* the one-phase region shifts to lower temperatures and the microemulsion system gets more effective. Simultaneously the sol-gel transition shifts to higher temperatures with increasing gelator concentration. At a mass fraction of $\beta = 0.018$ the sol-gel transition of the microemulsion gel lies within the one-phase region of the system water / *n*-dodecane / 12-HOA – LutensolAO5.

As the addition of the monomer NIPAm to the gelled system water – *n*-dodecane / 12-HOA – LutensolAO5 leads to a shift of the one-phase region towards higher temperatures, while the sol-gel transition shifts it slightly to lower temperatures, more 12-HOA had to be added to the system. At a mass fraction of at least $\beta = 0.029$ the sol-gel transition of the microemulsion gel lies within the one-phase region, which is distinctly higher than for the system without the monomer. A reason for this could be that more gelator molecules are located at the surface as the water phase becomes more hydrophilic and does not contribute to the network.

We can therefore conclude that we are able to create a clear, gelled phase that is located in the one-phase region of the microemulsion. The following questions still need to be answered: (1) What is the microstructure of this gelled phase? Do we still have a bicontinuous structure, *i.e.* did we indeed “arrest” the structure of the microemulsion? (2) What do we get if we now polymerize the NIPAm containing subphase? Do we get a bicontinuous polymer of high surface area? Is the gel rigid enough to prevent structural changes during the polymerization? Work is underway to address these issues.

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