

# Microemulsions with a HIPME (High Internal Phase Microemulsion) Structure

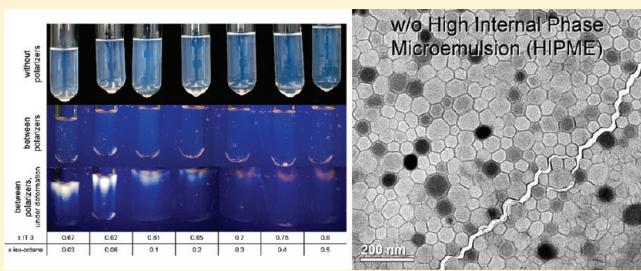
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**ABSTRACT:** We report a phase diagram for a novel microemulsion that consists of oil and water and of 15% of a surfactant mixture of an anionic and a nonionic surfactant. The phase diagram shows an optically isotropic channel that passes from the water-rich side to the oil-rich side. In contrast to the isotropic channel in microemulsions of nonionic surfactants, the reported system undergoes an abrupt transition of the structure in the isotropic channel with increasing oil content. The structural transition is reflected in the conductivity and the viscosity of the channel. Between the L<sub>3</sub> phase and the sample with 6% of oil the conductivity decreases 3 orders of magnitude. Thus, the bicontinuous structure at the origin of the channel transforms already with 6% of oil to a w/o structure. The viscosity shows a strong maximum at the transition. The w/o structures with low oil content were successful directly imaged by cryo-TEM. It can be seen that water is contained inside a polyhedral foam-like structure, where the polyhedral film is formed of the oil and the surfactant. The dimensions of the polyhedra are in the range of 20–100 nm. We call this structure “high internal phase microemulsion” (HIPME).



## INTRODUCTION

Microemulsions are thermodynamically stable, optically isotropic liquids made of water, oil, and surfactants.<sup>1</sup> They are structured in water-rich and oil-rich domains. Microemulsions produced from ionic surfactants contain a large single phase region in the phase triangle.<sup>2,3</sup> The structures in this region are well-known and have been studied by SAXS and SANS.<sup>4–7</sup> Microemulsions of equal amounts of oil and water and a few percent of an ionic surfactant like AOT or DDAB mostly contain a water-in-oil droplet structure, in which globular water droplets are surrounded by a palisade layer of the ionic surfactants.<sup>8</sup> The dimensions of the aggregates are well understood on the basis of theoretical models.<sup>9</sup> In contrast, microemulsions of nonionic surfactants contain bicontinuous structures at equal amounts of oil and water.<sup>10</sup> The bicontinuous structures had first been assumed on the basis of experimental results from diffusion and conductivity measurements,<sup>11</sup> and were later proven by results from scattering techniques and directly by classical freeze fracture electron microscopy (FF-TEM) and by the freeze fracture direct imaging technique (FFDI).<sup>12,13</sup> The development of the micellar structures and properties in both systems as a function of their composition has been studied by many groups, and can be considered to be theoretically well understood.<sup>14</sup> Nonionic microemulsions have an interesting feature in their phase behavior, namely, the single phase channels in “ $\chi$ -cut phase diagrams”. Along these channels it is possible for systems with a constant surfactant concentration to pass from the mainly aqueous phase to the oil-rich side without crossing a phase boundary. Some

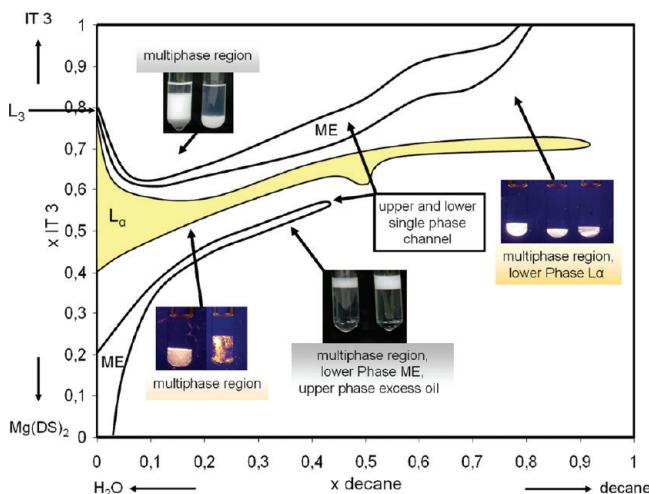
measurements have already been carried out on the influence of ionic surfactants on the phase behavior of nonionic surfactants.<sup>15</sup> A systematic study of a microemulsion system that consists of a surfactant mixture of a hydrophilic ionic and a lipophilic nonionic surfactant has been carried out recently.<sup>16</sup> With such a mixture, it is possible to change the interfacial curvature of the surfactant film by adjusting the surfactant/cosurfactant ratio. The phase diagram has novel features as compared to the phase diagrams of nonionic and ionic surfactants. It shows only one continuous isotropic single-phase channel, while microemulsions of nonionic surfactants usually show two isotropic channels connected with each other. Furthermore, there was evidence for abrupt changes in the morphology for continuous changes in the composition of the system in that channel. No bicontinuous phase could be found for systems with equal amounts of water and oil. Surprisingly, the conductivity in the isotropic channel broke down when the system had only a few percent of oil.

In the present investigation we examined by cryo-TEM the nanostructures in this isotropic channel. We therefore had to replace the *n*-decane of the original microemulsion system by iso-octane as a branched hydrocarbon does not crystallize upon cooling and can be vitrified in liquid nitrogen.<sup>17</sup> The cryogen of choice, liquid ethane at its freezing point dissolves most hydrocarbons.

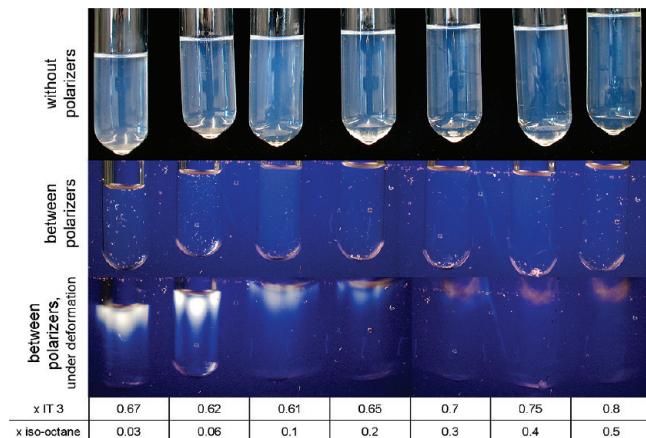
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**Figure 1.** Phase diagram of system  $\text{Mg}(\text{DS})_2/\text{IT } 3-\text{H}_2\text{O}/\text{decan}$  at 15% w/w surfactant and 25 °C, 20% glycerol in  $\text{H}_2\text{O}$ .  $x \text{ IT } 3$  = mass fraction of IT 3 in the surfactant mixture,  $x \text{ decane}$  = mass fraction of decane in the solvent mixture. “ME” indicates isotropic microemulsion area.

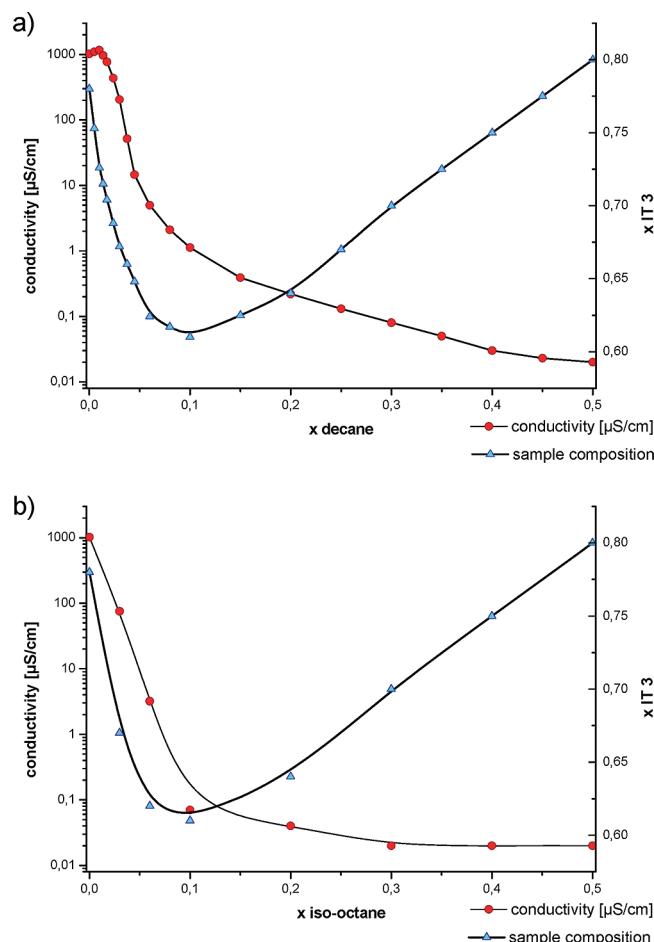


**Figure 2.** Samples with 15% (w/w) surfactant mixture  $\text{Mg}(\text{DS})_2/\text{IT } 3$  at 25 °C and increasing mass fraction  $x$  of IT 3 and isoctane, shown without polarizers and in between crossed polarizers. Samples containing low oil content show strong shear induced birefringence.

## EXPERIMENTAL SECTION

**Materials.** The nonionic surfactant iso-tridecyl-triethylenglycolether, abbreviated as IT 3, was obtained from the Sasol Company, Hamburg (“Marlipal O13/30”). Sodium dodecyl sulfate (SDS, crystalline research grade) was purchased from the Serva Company, Heidelberg, Germany.  $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$  (99%, analytical grade) was purchased from the Grüssing Company, Filsum, Germany. N-Decane and isoctane (synthetic grade) were obtained from the Merck Company, Darmstadt, Germany.

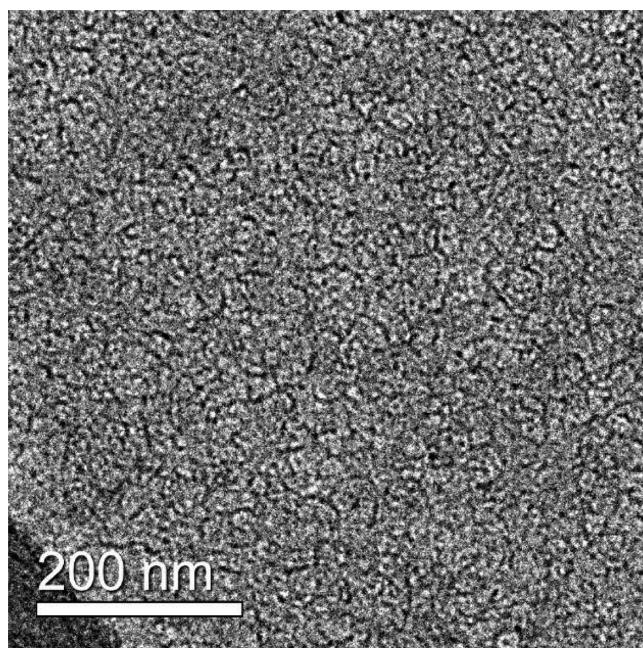
**Preparation of  $\text{Mg}(\text{DS})_2$ .** In our surfactant system, we used  $\text{Mg}(\text{DS})_2$  instead of SDS, as it leads to lower surface and interfacial tensions than SDS, and forms  $\text{L}_\alpha$  phases in a wide composition range, when mixed with nonionic surfactants.<sup>16</sup> For the preparation of  $\text{Mg}(\text{DS})_2$ , 400 mM SDS-solution was mixed with 200 mM  $\text{MgCl}_2$  solution under stirring. The bivalent counterion  $\text{Mg}^{2+}$  binds more strongly to the dodecyl sulfate than the sodium-ion, leading to precipitation of  $\text{Mg}(\text{DS})_2$  in



**Figure 3.** Plot of conductivities (red dots) and IT 3 content (blue triangles) against mass fraction of oil in the solvent mixture. Key: (a) values for system with decane; (b) values for system with isoctane.

solution below its Krafft-temperature around 25 °C. The solution was heated up above 25 °C to obtain a clear solution, and then cooled down to 20 °C. After precipitation  $\text{Mg}(\text{DS})_2$  was washed several times with deionized water to remove excess salt. The salt concentration of the washing water was checked by its conductivity. The washed  $\text{Mg}(\text{DS})_2$  was freeze-dried with the freeze-drying device Alpha 1–4, Christ Company, Osterode, Germany, and used without further purification.

**Preparation of Samples.** All samples were prepared by weighing in directly the components in test tubes with an analytical balance. The test tubes were sealed with Teflon tape, equilibrated at 25 °C in a water bath, and vortexed several times thoroughly. All samples were incubated at least 3 days at 25 °C before being investigated for their phase behavior. In general, a phase diagram was scanned with a resolution of 5% in the composition of the mass fraction of IT 3 and decane. Finer steps were investigated in the beginning of the narrow upper single-phase channel. The multiphase samples were viewed and imaged without and in between crossed polarizers to visualize the birefringence of lamellar regions. Samples for cryo-TEM investigation were prepared with isoctane instead of decane. The surfactant/cosurfactant ratio had to be adjusted slightly in order to stay in the single phase microemulsion channel when replacing decane by isoctane.



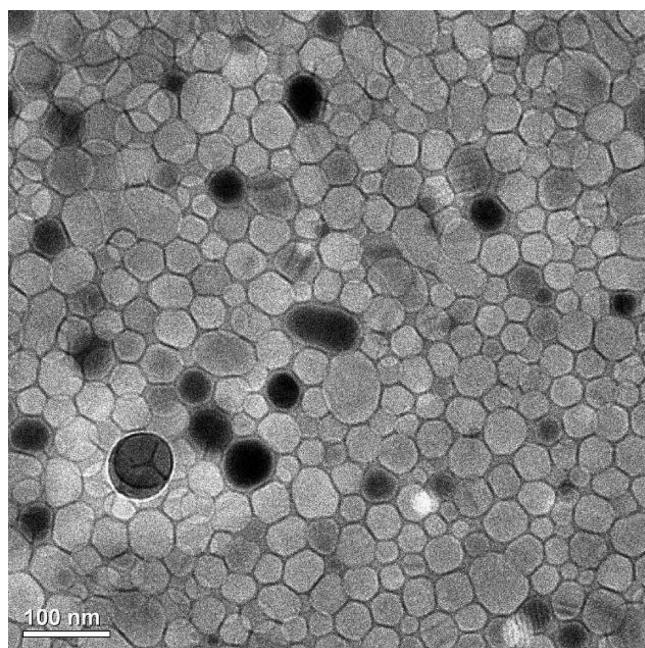
**Figure 4.** Cryo-TEM micrograph of the  $L_3$  phase with the mixed anionic/nonionic surfactant mixture  $Mg(DS)_2/IT\ 3, \chi\ IT\ 3\ 0.79, 15\%$  surfactant, at  $25\ ^\circ C$ .

**Conductivity and Rheology Measurements.** For conductivity measurements, we used a Microprocessor Conductivity Meter LF3000 from the WTW Company, Weilheim, Germany. The rheology was measured with the cone–plate rheometer RheoStress 600 from the Haake Thermo Scientific Company, Karlsruhe, Germany. All samples were investigated at  $25\ ^\circ C$ .

**Cryo-Transmission Electron Microscopy (Cryo-TEM).** The specimens for cryo-TEM were prepared in a controlled environment vitrification system (CEVS), and plunged into liquid ethane at its freezing point.<sup>18</sup> For oil continuous samples, the specimens were plunged into liquid nitrogen to avoid problems with solvent dissolution.<sup>19</sup> The CEVS was kept at  $25\ ^\circ C$  and the atmosphere either saturated with water for the samples without oil, or directly with the investigated microemulsion solution for samples containing oil. Specimens, kept below  $-178\ ^\circ C$ , were examined in an FEI TI2 G<sup>2</sup> transmission electron microscope, operated at 120 kV, using a Gatan 626 cryo-holder system. Images were recorded digitally in the minimal electron dose mode by a Gatan US1000 high-resolution CCD camera, with the DigitalMicrograph software package.

## RESULTS AND DISCUSSION

**Phase Diagram  $Mg(DS)_2/IT\ 3/H_2O$ –Oil.** The system we have studied consists of decane, water and the surfactant mixture of magnesium dodecyl sulfate  $Mg(DS)_2$  and the nonionic surfactant isotridecyl triethylene glycol ether IT 3. With such a system it is possible to adjust the amphiphilic properties of the surfactant by changing the mixing ratio of the hydrophilic surfactant and the lipophilic cosurfactant. For the ionic surfactant we chose the  $Mg^2+$ -salt of SDS, as it reduces the surface tension more effectively and is known to form liquid crystalline  $L_\alpha$  phases or even sponge like  $L_3$  phases when mixed with suited cosurfactants, what is not possible for SDS.<sup>16</sup> The phase diagram of the system with increasing oil content is shown in Figure 1.

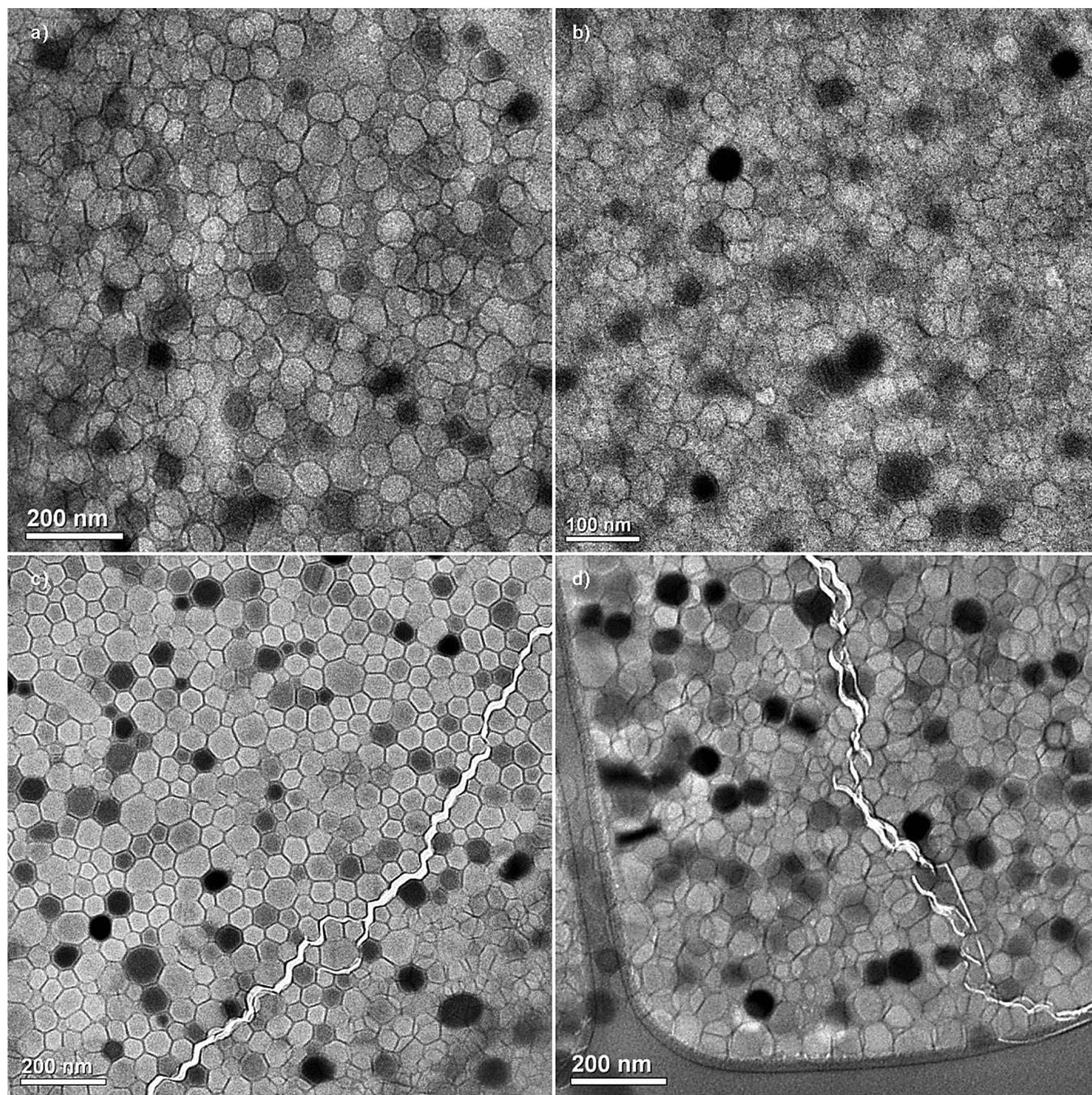


**Figure 5.** Cryo-TEM micrograph of a microemulsion with 15% of the anionic/nonionic surfactant mixture  $Mg(DS)_2/IT\ 3, \chi\ IT\ 3\ 0.7, \chi$  isoctane 0.3 (water:oil = 7:3), quenched from  $25\ ^\circ C$ .

The special features of the phase diagram are two isotropic channels above and below a liquid crystalline channel that passes from the aqueous side to the oil side. It should be noted that the channels are isothermal channels. In order to stay in the channel, one has to adjust the ratio of surfactant and cosurfactant. The upper isotropic phase channel above the liquid crystalline channel begins at the water side with an  $L_3$  phase, the lower channel begins at the  $L_1/L_\alpha$  phase boundary at the aqueous side. The upper channel passes through a steep minimum at around 6% oil from the aqueous to the oil-rich side with increasing mass fraction of the cosurfactant. The lower channel is bent upward, ending in the middle of the phase diagram, while the  $L_\alpha$ -channel does not change much its surfactant composition with the oil content. It is noteworthy that such large liquid crystalline channels have not previously been observed in classical microemulsion systems with single nonionic surfactant. We would like to emphasize that the  $L_\alpha$  phases in the liquid crystalline channel have a high tolerance to temperature variation.<sup>20</sup> While nonionic surfactants become more lipophilic with rising temperature, ionic surfactants become more hydrophilic.<sup>21</sup> Thus, these two effects are compensating each other in our system.

It is important to note that in all phase-diagrams of microemulsions of nonionic systems the  $L_\alpha$  phases are also present, but the isotropic channels are connected in the middle of the phase diagram, and are not separated by a liquid crystalline channel. The reason for this difference between the two types of microemulsions lies, probably, in the different persistence length of the bilayers. It is likely that the persistence length of charged bilayers is much longer than the persistence length of the uncharged bilayers, which is connected to the stiffness of the bilayer. As a consequence the charged bilayers can accommodate more oil than the neutral bilayers, before they fold back or form other structures.

For cryo-TEM investigation of the upper isotropic channel, samples with oil were prepared with isoctane instead of decane,



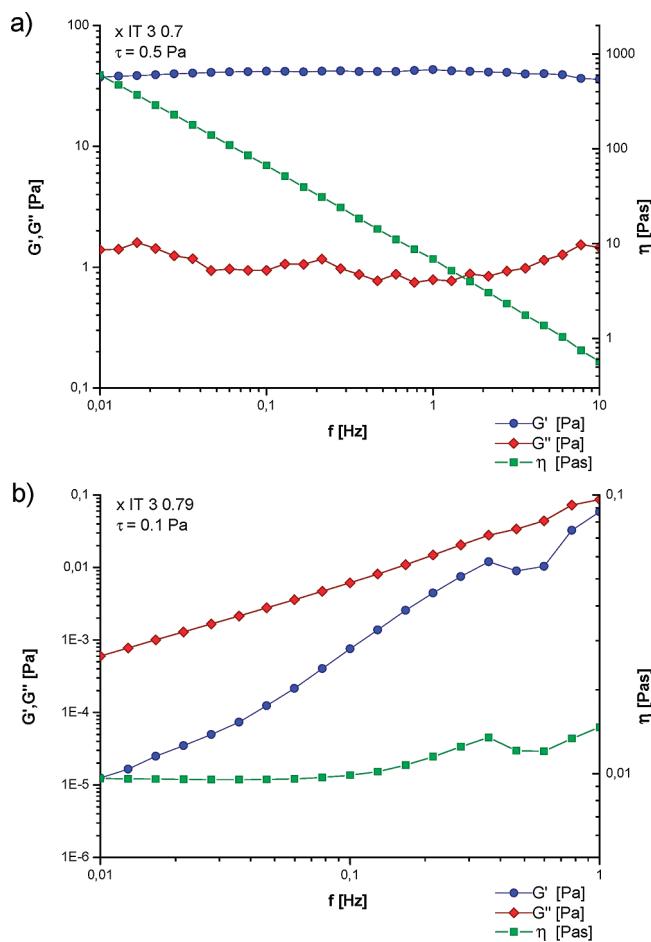
**Figure 6.** Cryo-TEM micrographs of microemulsions with a HIPME-structure with (a) 6% isoctane, (b) 20% isoctane, (c) 40% isoctane, and (d) 50% isoctane in the solvent-mixture.

because it is known that decane, like other normal linear hydrocarbons, crystallizes when quenched in liquid nitrogen during cryo-TEM specimen preparation.<sup>19</sup> We have to use liquid nitrogen for cryo-specimen preparation, not the better cryogen liquid ethane at its freezing point, as the latter dissolves hydrocarbons. The original microemulsion system with decane was prepared with 20% glycerol in the aqueous phase to avoid freezing artifacts in FF-TEM experiments that were performed.<sup>20</sup> Unlike the decane system, we prepared the microemulsions containing isoctane without glycerol in the aqueous phase, as it would have shifted the single phase channel too much toward lower  $\alpha$  IT 3 values. Without glycerol, the sample

compositions with respect to the surfactant/cosurfactant ratio, as well as the properties of the phases are similar to the decane-system. The various domains are only slightly shifted by going from decane to isoctane. Microemulsions with isoctane of the upper single-phase channel are shown in Figure 2.

The prepared microemulsions are slightly bluish; they do not show stationary birefringence between crossed polarizers. However, samples with low oil content around 6% isoctane show strong flow induced birefringence.

**Conductivities in the Upper Isotropic Channel.** The conductivities in the upper isotropic channel were investigated with



**Figure 7.** Rheograms of the binary surfactant mixtures at constant 15% surfactant (w/w) with increasing mass fraction  $x \text{ IT 3}$  at 25 °C. Key: (a) rheogram of  $L_{\alpha}$  phase at  $x \text{ IT 3 } 0.7$ ; (b) rheogram of  $L_3$  phase at  $x \text{ IT 3 } 0.79$ .

decane as the oil (Figure 3a), and compared to the conductivities when decane was replaced by isoctane for cryo-TEM investigations (Figure 3b). The conductivity in the upper isotropic channel begins at the water side in the  $L_3$  phase with a value of around  $1000 \mu\text{S}/\text{cm}$ . The conductivity of the  $L_3$  phase decreases, however, dramatically with the solubilization of small amounts of oil, and disappears practically for 10% of decane. The same abrupt transition in the properties is found for samples with isoctane. No doubt, the  $L_3$  phase changes into a different phase.

This result is in strong contrast to conductivity measurements of microemulsions in the isotropic channel with nonionic surfactants.<sup>22</sup> In those systems, the conductivity from added electrolyte usually decreases slowly with increasing oil content. Such a modest decrease can be expected on the basis of the theoretical model for the structures in the channel. The bicontinuous structure of the  $L_3$  phase continues in the channel. The surfactant bilayers just swell with increasing oil content, as concluded from SANS measurements.<sup>23</sup> The conductivity results are therefore a first indication that the continuous aqueous domains disappear completely in the isotropic channel, and that the  $L_3$  structure is replaced by another structure, in which the water is present as discrete domains, completely surrounded by oil.

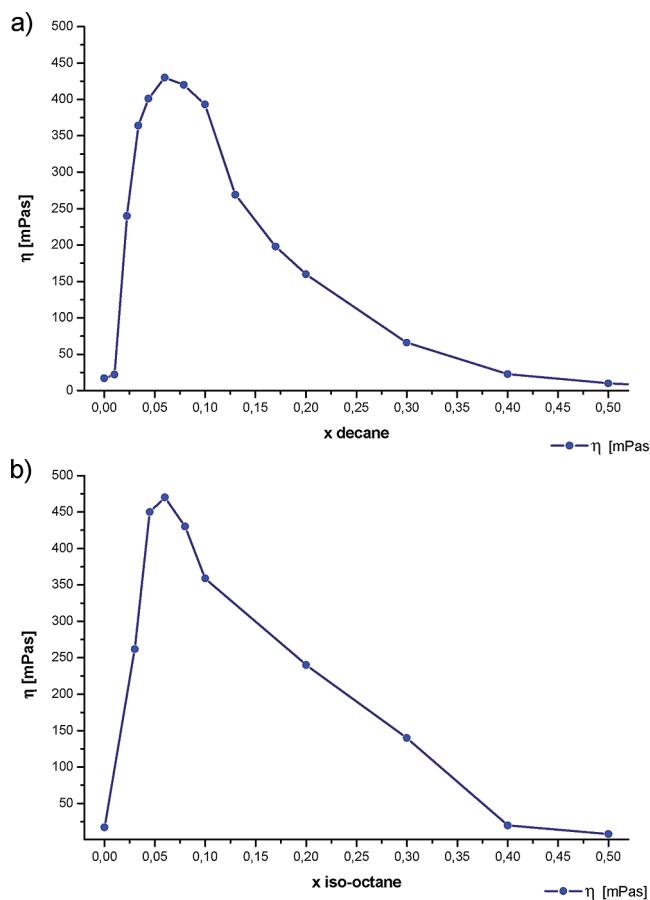
**Cryo-TEM of the Isotropic Channel.** The nanoscopic structures in the isotropic channels of microemulsions with nonionic

surfactants have been well documented by NMR, SANS and SAXS. At the water side, the channel begins with the  $L_3$  phase, which has a bicontinuous sponge-like structure. The bicontinuous structure of  $L_3$  phases of ternary surfactant systems and microemulsions with nonionic surfactant has already been directly shown by FF-TEM.<sup>24,25</sup> The FF-TEM micrographs show a two-dimensional micrograph of the fracture plane in which the fracture runs through both water and oil domains. The water areas and the hydrocarbon areas are well differentiated by their different graininess and gray shades. The typical dimensions between the bilayers on the micrograph are in agreement with the dimension that is evaluated by SANS.<sup>26</sup> In Figure 4, we show a direct-imaging cryo-TEM micrograph of the  $L_3$  phase of our investigated system without oil.

In cryo-TEM micrographs, the imaged vitrified film is usually thicker than the typical correlation length in the sponge phase. Several bilayers are therefore usually on top of each other in the thin film, all projected on the detector. The structure therefore looks more like a network of thread-like micelles than a sponge structure. As part of a separate study, which we plan to publish soon, we studied the sponge structure of a bicontinuous microemulsion with a single nonionic surfactant and oil by cryo-TEM. The sample was prepared with  $C_{12}E_5$ , isoctane,  $H_2O$  and had a water/oil ratio (w/w) of 7:3. The micrographs clearly show a sponge structure with typical dimensions of water and oil domains around  $0.2 \mu\text{m}$ . In Figure 5 we show a cryo-TEM micrograph of a microemulsion of the present system, which also has a water/oil ratio of 7:3 (w/w), but was prepared with 15% of the mixed anionic/nonionic surfactant system. In this micrograph one sees a nanostructure that is very different from what one would expect of a bicontinuous microemulsion. Now the system consists of a densely packed w/o-droplet structure, which resembles a “polyhedral foam” with thin films with a thickness of about 3 nm.

The diameter of the water domains is about 50 nm. The thin film was obviously made of the surfactants with the hydrocarbon in between the two monolayers, and the water inside the polyhedra. It seems that the micrograph does not reflect exactly the 3:7 oil-to-water ratio, in the sense of the projected area of the different domains. Some of the isoctane may have evaporated. The structures look very much like the structures found in high internal phase emulsions (HIPE). HIPEs are concentrated systems with a large volume of the dispersed phase. Those high volume fractions result in the deformation of droplets into polyhedra, which are separated by thin films of the continuous phase. In such situations the size of the structures are usually in the range of several  $\mu\text{m}$  and can easily be seen by light microscopy. Both o/w and w/o-systems of HIPEs are known.<sup>27</sup> Similarly to dilute emulsions, HIPEs are thermodynamically unstable.<sup>28</sup>

On the basis of that, we call the newly found microemulsion structure HIPME (high internal phase microemulsion). To the best of our knowledge, such structures have so far only been observed in real emulsions. In the microemulsion sample with the HIPME structure, the water domains are not connected with each other. This can be concluded from the fact that the ice crystals in dark have the same size as the ice crystals in gray. The crystals with the dark color are a result of a particular orientation with respect to the electron beam, which satisfies Bragg's law. At higher oil content, the polyhedra might have been round water domains in the liquid phase. Quenching by liquid nitrogen vitrifies the isoctane but freezes the water. That is manifested by the crystalline contrast causing some polyhedra to appear very



**Figure 8.** Zero shear viscosity,  $\eta$ , against the mass fraction of oil of samples from the upper single phase channel: (a) viscosity with increasing mass fraction of decane; (b) viscosity with increasing mass fraction of iso-octane.

dark. The polyhedral appearance may have been promoted by the crystallization, too.

In Figure 6 we show cryo-TEM micrographs of microemulsions along the upper isotropic channel from 6% to 50% iso-octane in the solvent mixture. Obviously, the HIPME structures are present all along the upper isotropic channel.

The shown HIPME structures are the first HIPE-like structures observed in microemulsions with mixed anionic/nonionic surfactant systems. The results thus show that HIPME structures can also be new dynamically stable structures. As conductivity data already indicated, HIPME structures might also occur in systems with single ionic surfactants, like DDAB, oil and water.<sup>29</sup> The latter system is now investigated by cryo-SEM (scanning electron microscopy). We expect to report the results soon.<sup>30</sup>

**Rheological Results.** Bicontinuous microemulsions can be visualized as  $L_3$  phases that have oil solubilized between the surfactant monolayers. The rheological behavior of microemulsions with nonionic surfactants is therefore similar to the rheological behavior of the  $L_3$  phase without oil. One of the most startling properties of the  $L_3$  phase is its extremely low viscosity, although the phase consists of a three-dimensional network of bilayers. Most remarkable is that the rheological properties of the neighboring  $L_\alpha$  phase are so different from the rheological properties of the  $L_3$  phase, although both phases consist of bilayers. In the present system the differences between the two phases are even more

dramatic, because the  $L_\alpha$  phase of the system without oil, like any other ionically charged  $L_\alpha$  phase without excess salt, has a rheological yield stress, and thus behaves like a soft gel.<sup>31</sup> A rheogram of this is given in Figure 7a. The  $L_3$  phase, which is next to the  $L_\alpha$  phase, differs only from the  $L_\alpha$  phase by a small difference in the composition. It is a low-viscosity fluid with a viscosity that is only about 10 times higher than water viscosity (Figure 7b). Rheologically speaking, the transition from the  $L_\alpha$  to the  $L_3$  phase can be compared to a melting transition.

Microemulsions are usually low viscosity liquids.<sup>32</sup> The low viscosity behavior can be understood on the basis of the high deformability of the existing structures with droplets or bicontinuous shapes. This behavior is already indicated in the viscosity of the  $L_3$  phase.<sup>33</sup> Viscosities in the isotropic channels have already been measured.<sup>34</sup> A modest viscosity maximum is usually observed with increasing oil content.

The viscosities in the upper channel of the presently investigated system are shown in Figure 8. The results show a high maximum at around 6% oil. At higher oil content the viscosities decrease slowly toward the oil side of the microemulsion. The abrupt maximum of the viscosity can be taken as an indication of a structural transition in the channel. The viscosity maximum is reached at about the same oil concentration where the conductivity disappeared. Obviously the transition of the structure is also expressed in the viscosity of the system.

## CONCLUSIONS

We showed that w/o-HIPME structures with dimensions of about 20–100 nm can be thermodynamically stable structures in microemulsions. These structures occur in microemulsions formed from surfactant mixtures of anionic and nonionic surfactants. They are observed in the isotropic channel of microemulsions, when small amounts of oil are solubilized into aqueous  $L_3$  phases. In spite of their small oil content, the HIPME phases have a conductivity that is about 3–4 orders of magnitude lower than the conductivity of the  $L_3$  phase. These results thus demonstrate that very thin surfactant films with little oil can practically be impenetrable for the transport of ions. It can be concluded from the measurements that structural transitions can occur in micellar phases, in which bicontinuous structures of nonionic surfactants and oil are transformed into foam-like structures, when the surfactant layers are charged by ionic surfactants. It is likely that such transitions can also be produced, when the electric double-layer in ionically charged systems is shielded by excess salt.

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