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PAPER

Microemulsions from silicone oil with an anionic/nonionic surfactant mixture†

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Microemulsion phases have been prepared for the first time from the silicone oil "M_2" (hexamethyldisiloxane) and a surfactant mixture of a nonionic surfactant "IT 3" (isotridecyltriethyleneglycolether) and an ionic surfactant $Ca(DS)_2$ (calciumdodecylsulfate). For such a surfactant mixture the hydrophilicity of the system can be tuned by the mixing ratio of the two components. With increasing IT 3 content, the surfactant mixtures show a L_1-phase, a wide L_α-region and a narrow L_3 sponge phase. For constant temperature, two single phase channels exist in the microemulsion system. The lower channel (low IT 3 content) ends in the middle of the phase diagram with equal amounts of water and oil, the upper channel begins with the L_3-phase and passes all the way to the oil phase. Conductivity data show that the upper channel has a bi-continuous morphology up to 40% oil while the lower channel consists of oil droplets in water. In contrast to previous studies on nonionic systems, the two single phase channels are not connected and microemulsions with equal amount of oil and water do not have a bicontinuous structure.

Introduction

Microemulsions (ME) are thermodynamically stable fluids that consist of oil, water and a few percent of surfactant.[1] They usually are low viscous, more or less transparent and optically isotropic liquids. Microemulsions are used in many applications because of their fascinating properties. One of the reasons for their usefulness is that both polar and apolar compounds can be dissolved in microemulsions. They are therefore used for agrochemical, cosmetic, pharmaceutical and other industrial formulations where it is necessary to bring two components in a fluid together which normally are not miscible. Detailed investigations on microemulsions over the last 40 years have shown that the components of the fluids are not dispersed with each other on a molecular level like in miscible solvent mixtures but the fluids are highly structured on a scale of 1–100 nm. Domains of oil and water, with well defined interfaces from surfactants, alternate with each other. These domains are in equilibrium with each other and are very dynamic in behaviour. They constantly change their shape and size on a time scale of micro- to milliseconds. Today, the basic behaviour of nonionic microemulsions is well understood on the basis of theoretical models in which the mean curvature of interfaces,[1] the bending constants of surfactant monolayers[2] and the interfacial tension between oil and water[3] play a central role. Depending on the composition of the fluids the structures in the fluids can be oil swollen micelles (o/w-microemulsions), bicontinuous structures or water swollen inverse micelles (w/o-microemulsions).

Microemulsions can be prepared either from nonionic or from ionic surfactants.[2–6]

The single phase regions in systems that consist of oil, water and surfactants are usually plotted in triangular phase diagrams.

The isotropic phase regions (microemulsions) in these triangle presentations are very different for ionic surfactants and for nonionic surfactants.[7,8] Systems with ionic surfactants, which have been studied usually, contain large isotropic regions in the middle of the triangle while phase diagrams with nonionic surfactants are very different and contain narrow isotropic channels.[9] For constant surfactant concentration, these channels usually pass from the aqueous side without crossing a phase boundary continuously to the oil side of the phase diagram.

Detailed phase diagrams with many different systems in which the oil and the surfactants were varied have shown that two channels exist in microemulsions with nonionic surfactants and with variable temperature.[10] The two channels are connected with each other in the middle of the phase diagram and the phase region in between the channels contains an L_α-phase. Small angle neutron scattering measurements have

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shown that the micellar structures in the low temperature channel evolve from globular o/w structures, transform to bicontinuous structures in the cross-over region and change continuously to globular w/o structures in the high temperature channel.[11] The structures in the upper channel are of a bicontinuous nature right from the aqueous side.[12]

The goal of this investigation was to prepare microemulsions from the highly volatile silicone oil hexamethyldisiloxane (M_2), water and a nonionic/anionic surfactant mixture.

Microemulsions from several silicone oils and nonionic surfactants have already been published.[13] But as far as we know, a phase diagram with the silicone oil M_2 had not yet been prepared and investigated in detail. It was known however that M_2 behaves similarly in solubilisation experiments as decane.[14] Viscoelastic solutions with wormlike micelles are transformed to low viscous micellar solutions with the same molar amount of decane or of M_2. The saturation concentration for both oils is also about the same. It could therefore be expected that microemulsions from M_2 can be formed and the phase diagram with M_2 should look similar for decane for the same surfactant system. To achieve our goal, a mixed nonionic/anionic surfactant system was used. This system had to be optimized for the temperature region at which the microemulsion was to be prepared.

Surfactants for the formation of microemulsions can be optimized by interfacial tension measurements.[15] Maximum solubilisation occurs when the interfacial tension of a dilute surfactant solution has its lowest interfacial tension against the oil phase.[16] Furthermore it is known that low interfacial tensions are observed for surfactant systems which form liquid crystalline L_α-phases or L_3-phases at low surfactant concentrations of a few percent.[17] Ideal surfactant systems for the formation of microemulsions can therefore be recognised based on their phase behaviour.[18]

Ionic surfactants like sodiumdodecylsulfate are very hydrophilic and do not give L_α-phases when mixed with water soluble nonionic surfactants. The situation is improved when Na^+-ions are replaced by bivalent Ca^{2+}-ions. Previous investigations had shown that in mixtures of SDS and tetradecyldimethylaminoxide the L_1-phase could be transformed to a L_α-phase simply by substituting the Na^+-ions by Ca^{2+}-ions.[19] Solutions of $Ca(DS)_2$ on their own are still L_1-phases in which wormlike micelles are present.[20] If such solutions are mixed with nonionic compounds that are generally used as co-surfactants one obtains L_α-phases in a wide composition region. As a co-surfactant the nonionic surfactant IT 3 (isotridecyltriethyleneglycolether) was used. It is commercially produced and is worldwide available under the name "Marlipal O13/30" as other well-known nonionic surfactants like "Triton X 100".[21] The compound is a highly branched isotridecanol, etherified with average 3 EO-groups. Despite its polydispersity, it acts mostly like a pure surfactant for the observed phases.

In a general sense the optimum condition for microemulsions for a particular temperature can be adjusted by mixing a hydrophilic surfactant that forms a L_1-phase and a lipophilic surfactant that is not soluble in the aqueous phase but forms its own L_2-phase.[22] The used surfactant mixture in our study thus consists of an ionic surfactant that is just a bit too hydrophilic to form a L_α-phase and a co-surfactant that is a bit too lipophilic to form a L_α-phase on its own. The combination of the two surfactants forms a L_α-phase over a wide surfactant composition. For the aim of this project, we used this surfactant-system which could form L_α-phases and hopefully would form microemulsions of silicone oils.

It should be noted that some results on the influence of ionic surfactants on phase diagrams of nonionic microemulsions have already been published.[23]

It was observed that the isotropic channels were widened by the influence of ionic surfactants. There was however no information on the structures of the isotropic channel. As far as we know, our investigations on the described microemulsion results are really the first with a detailed phase diagram that had been established with a nonionic/ionic surfactant mixture. Some of the results turned out to be surprising and could not have been expected on the basis of previous results. The main novel features are: an L_3-phase with an anionic/nonionic surfactant mixture, a microemulsion with equal amounts of oil and water that cannot have a bicontinuous structure and two isotropic channels that are not connected.

Results and discussion

The surfactant mixtures

In Fig. 1, samples of mixtures of two surfactants are shown that fulfil the criteria described in the Introduction. The surfactants are Ca- or Mg-dodecyl sulfate ($Ca(DS)_2$, or $Mg(DS)_2$) and isotridecyltriethyleneglycolether IT 3. The Ca- or Mg-salts can be easily prepared from sodiumdodecylsulfate, and IT 3 is commercially available. $Ca(DS)_2$ has a high Krafft-temperature of K_T = 50 °C and can therefore only be used at higher temperatures or at room temperature, when the Krafft-temperature has been reduced by the second component to room temperature.[24] $Mg(DS)_2$ has a lower Krafft-temperature of K_T = 25 °C. Fig. 1 shows three rows of samples of the surfactant mixtures.

The first two rows contain samples of $Ca(DS)_2$ with increasing mass fraction of IT 3. The total concentration is constant at 15% (w/w) and temperature is at 40 °C. The lower row of the two shows the same samples between crossed polarizers and a third row shows samples with $Mg(DS)_2$ and IT 3 again with polarizers.

The $Ca(DS)_2$/IT 3 mixtures contain crystalline precipitates up to a mass fraction of x IT 3 = 0.4. The samples from x IT 3 = 0.5 to 0.75 are birefringent and contain a highly swollen L_α-phase. The sample with x IT 3 = 0.8 is optically isotropic and has a low viscosity. It is a L_3-phase. The L_3-phase can be recognised based on its microstructure from cryo-TEM measurements.[25] Surprisingly, the samples with an even higher mass ratio of IT 3 contain two phases with a L_α-phase as the larger volume fraction. For normal behaviour of hydrophilic and lipophilic mixtures one would have expected to find multiphase regions without an L_α-phase.[26] It is conceivable that the two components are no longer miscible in bilayers and phases are formed with different mixing ratios. It is noteworthy to mention that in the combination of $Ca(DS)_2$ and IT 3 a sample with a two phase L_α/L_3-situation could not

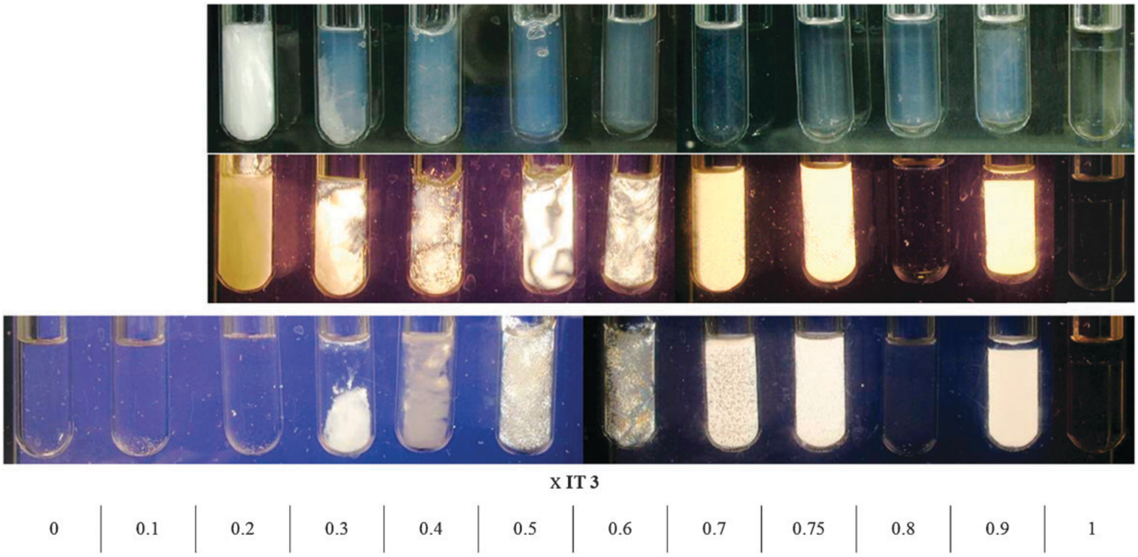


Fig. 1 Surfactant mixtures of $Ca(DS)_2$ (two upper rows) or $Mg(DS)_2$ (lower row) with increasing mass fraction x of IT 3. First row shows surfactant mixtures with $Ca(DS)_2$ in direct light. Second and third rows show samples with $Ca(DS)_2$ and $Mg(DS)_2$ between crossed polarizers. Samples prepared with a total surfactant concentration of 15% (w/w), phases observed at T = 40 °C.

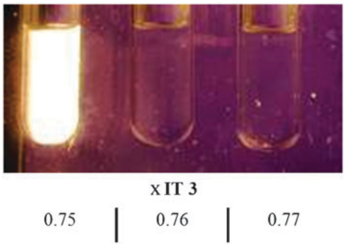


Fig. 2 Surfactant mixture $Ca(DS)_2$/IT 3 with x IT 3 0.75–0.77, 15% surfactant (w/w), shown at 40°C between crossed polarizers.

be observed when the composition of the samples was varied in small steps. This is shown in Fig. 2. Even for the condition when the composition was varied stepwise one percent by one percent the samples were within the single L_α-phase region or in the single L_3-phase region. The samples with the $Mg(DS)_2$/IT 3 mixtures form more or less the same phases as the $Ca(DS)_2$ mixtures.

The mixtures with x IT 3 = 0.1 and 0.2 are viscous single phase regions of an optically isotropic L_1-phase and the sample with x IT 3 = 0.3 is a L_1/L_α two phase sample. The samples with x IT 3 = 0.8 show again a L_3-phase, and the sample with x IT 3 = 0.9 contains a two phase region with one phase being a L_α-phase. It is remarkable that the mixtures with ionic surfactants form a L_3-phase.[27] Many investigations have shown that neutral L_3-phases are transformed to L_α-phases when small fractions of the surfactants are replaced by ionic surfactants.[28] The existence of the L_3-phase in the investigated system is probably linked to the fact that the bi-valent metal-ions bind strongly to the dodecylsulfate and the surfactants show only weak dissociation. These surfactants behave therefore very similar like nonionic surfactants.

While the existence of the L_3-phase in the used system at x IT 3 = 0.76 is unexpected, it is noteworthy that such a phase had also been observed in the phase diagram of $Ca(DS)_2$ with octanol or lower chain length alcohols.[24] In this investigation it was furthermore shown that the L_3-phase disappeared when 10% of the $Ca(DS)_2$ was replaced by SDS. What was even more surprising was the appearance of a L_α-phase for co-surfactant ratios well above the existence region of the L_3-phase. These observations show that the observed sequence of phases for the present system cannot be due to the fact that the used co-surfactant IT 3 is not a pure and single component but must be caused by the bivalent counter-ions. The experimental behaviour furthermore points out that the theoretical understanding of multicomponent systems leaves much to be desired. More experimental results in combination with theoretical models are necessary to come to a better understanding of such complex systems.

Surface and interfacial tension measurements

The samples with the highest solubilisation capacity should be samples with the lowest surface or interfacial tension values. These parameters were therefore measured for a 0.5% surfactant solution as a function of the mixing parameter. Plots of the surface tension measurements are shown in Fig. 3A for the $Ca(DS)_2$/IT 3 system, and in Fig. 3B for the interfacial tension values for the $Mg(DS)_2$/IT 3 system against the silicone-oil hexamethyldisiloxane.

The lowest surface tension ($\sigma \approx 26.4$ mN m^{-1}) is obtained at x IT 3 = 0.55 while the lowest interfacial tension is obtained at x IT 3 = 0.4 with $\gamma \approx 4$ mN m^{-1}. These measurements confirm that the samples, that have a composition in the range of a L_α-phase, have indeed low σ and γ values. It should be noted however that the interfacial tension between the oil and water phases in the presence of nonionic surfactants, that results in the formation of microemulsions, is usually in the range of 1×10^{-3} mN m^{-1}.[29] That is three orders of magnitude lower. It is conceivable that this difference comes from the fact that the used surfactant mixture contains an

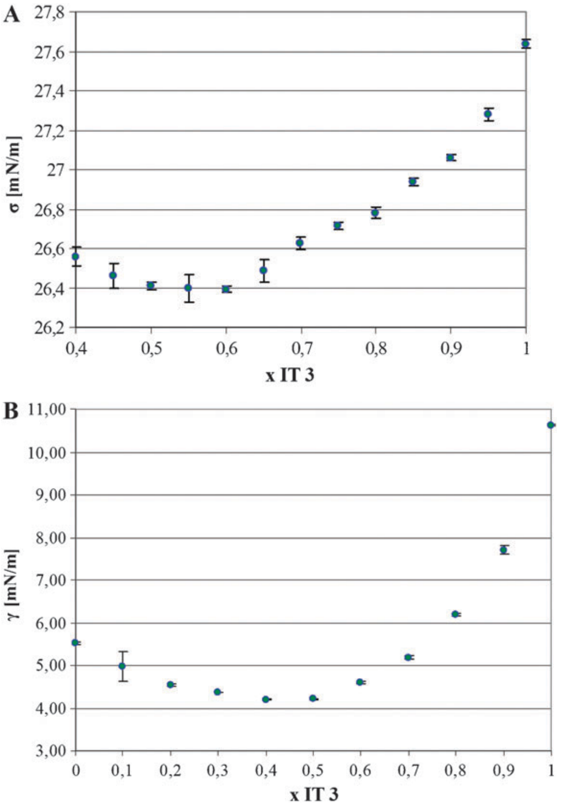


Fig. 3 Surface tension of the surfactant system Ca(DS)$_2$/IT 3 (A) and interfacial tension of the surfactant system Mg(DS)$_2$/IT 3 against silicone oil hexamethyldisiloxane (B), measured at 25 °C, surfactant concentration 0.5% (w/w).

ionic surfactant and the charges were not shielded by excess salt. Surfactant phases with an ionic surfactant and excess salt can have extremely low interfacial tension against the oil phase as observed by C. A. Miller *et al.*[30] The interfacial tension of double chain surfactants, which have been used for the preparation of microemulsions, against oil is also in the range of 0.1–1 mN m^{-1}.[31] It is conceivable that the higher interfacial tensions of the charged surfactant systems are the reason for the different behaviour of the investigated system from microemulsions with nonionic surfactants.

Rheological results

The phases with different mixing ratios of the two components have different rheological properties. The pure Mg(DS)$_2$-solution is already a viscous "shear thinning solution". The L$_\alpha$-phases are viscoelastic phases with a yield stress value. They have already a weak gel-character. The L$_3$-phase finally is a low viscous Newtonian solution. Rheograms of samples in the L$_\alpha$-region at 40 °C were measured and are shown in Fig. 4.

At a mass fraction of 0.5 (Fig. 4A), the storage modulus G' runs above the loss modulus G'' at a level of 100 Pa and is independent of the frequency f at a shear stress of τ = 5 Pa. With increasing mass fraction of IT 3, the level of G' first keeps constant at 100 Pa at x IT 3 = 0.6, and then drops to ~8 Pa at x IT 3 = 0.7 at $\tau \approx$ 0.1 Pa, but is still independent of f (Fig. 4C). The decay of the storage modulus G' with increasing mass fraction of IT 3 and the fact that G' breaks in at lower shear stress τ show that the L$_\alpha$-phase looses its gel-like character with increasing x IT 3. At x IT 3 = 0.75, measured at $\tau \approx$ 0.2 Pa (Fig. 4D), G' increases in the double

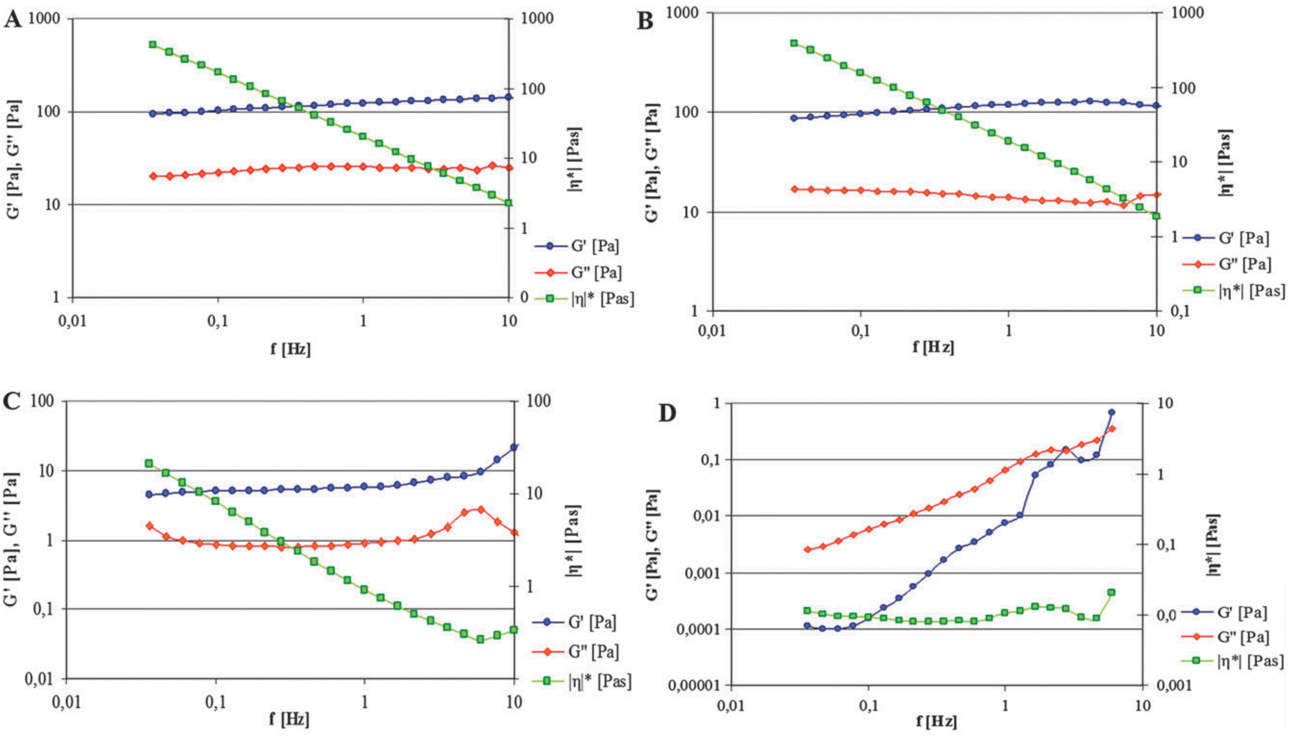


Fig. 4 Rheograms of samples in the L$_\alpha$-region, surfactant system Ca(DS)$_2$/IT 3, surfactant concentration 15% (w/w), measured at 40 °C. (A) x IT 3 = 0.5, measured at τ = 5 Pa. (B) x IT 3 = 0.6, measured at τ = 5 Pa. (C) x IT 3 = 0.7, measured at τ = 0.1 Pa. (D) x IT 3 = 0.75, measured at τ = 0.2 Pa.

log plot with a slope of 2 while G'' increases with a slope of one, indicating that the L_α-phase lost most of its gel-like character. By reason of the rheological results, we assume a structural change in the L_α-phase from multilamellar vesicles to planar lamellas with increasing x IT 3.

The change of the rheological properties from the L_α to the L_3-phase by a very small change of the binary surfactant mixture is one of the most startling effects in surfactant science. In the present situation, the difference of the properties of the two phases is especially large because one of the components is ionically charged. But even for systems with nonionic surfactants and co-surfactants the differences between the two phases are remarkable.[18] It should be mentioned that both phases consist of bilayer structures. The origin of the huge change in the rheological and other properties lies in the formation of passages between adjacent bilayers when the L_3-phase is approached.[32]

Solubilisation of hexamethyldisiloxane (M_2) in the different surfactant mixtures

The surfactant mixtures with 15% (w/w) of surfactant and at different mixing ratios were used to solubilise increasing amounts of oil. Photos of test tubes of samples between crossed polarizers can be seen in the ESI.† The phase behaviour of the samples was plotted in a phase diagram (Fig. 5). The special features of the diagram are two isotropic phase channels, a lower channel that begins at the water side at x IT 3 = 0.1 and a higher channel that begins around x IT 3 = 0.8, the mass fraction of the L_3-phase. The upper channel first decreases with increasing oil content and then increases slowly with further increase in oil content to the oil corner. The lower channel increases smoothly and seems to end in the middle phase region. In between the two channels are single phase L_α-regions or multiphase regions with one phase being a L_α-phase. The phase diagram shows that it is possible in surfactant mixtures to observe single phase channels for a constant temperature to reach from the water side to the oil side. Such channels have not yet been observed for one component surfactant systems. Under such conditions the temperature has to be changed to observe the single phase channel. While the co-surfactant content in the lower phase channel is increasing with increasing oil content, it is the other way around for the upper phase channel. In this case the co-surfactant content passes through a minimum.

An interesting consequence of this behaviour is that the single L_3-phase, where the channel begins, is transformed over a multiphase region with increasing oil solubilisation into the upper phase microemulsion with 30% of oil. It is noteworthy that preliminary results with decane as oil have shown a similar behaviour. The shape of the channel for isothermal conditions is thus a consequence of the used surfactant mixture and not of the oil. Of general interest on the phase diagram is also the fact that with increasing solubilisation of the oil into the L_α-phase, the widest extension of the L_α-phase is in the middle of its existence region. At this composition the L_α-phase can solubilise more than its own weight of oil, before it

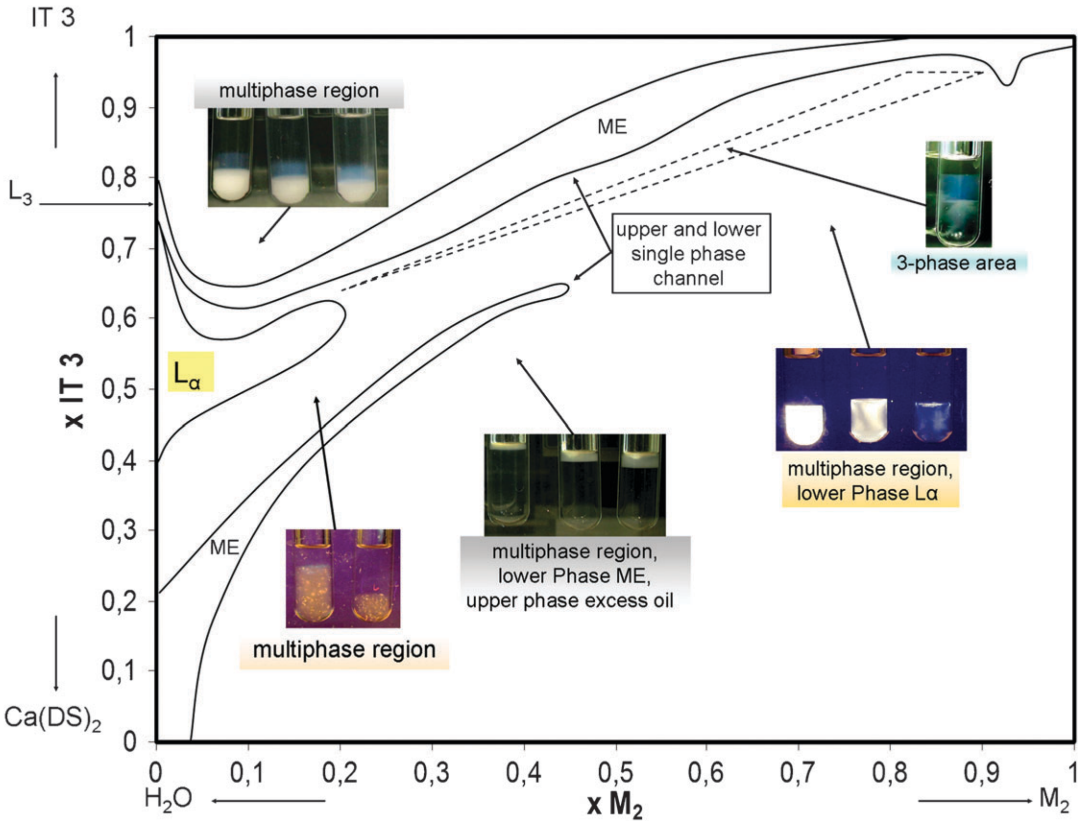


Fig. 5 Phase diagram of the system $Ca(DS)_2$/IT 3–H_2O/M_2 with 15% (w/w) surfactant and 85% (w/w) solvent. Phases observed at 40 °C. Abbreviation "ME" stands for "microemulsion" and indicates area of isotropic microemulsion channels.

breaks down. The high content of oil in a L_α-phase is however not a special feature of the used oil or the surfactant mixture. Other microemulsion phase diagrams have been reported with L_α-phases that contain more oil than surfactant and where the surfactant is a nonionic surfactant.[33] It is however interesting to note that such L_α-phases exist that consist of two monolayers of surfactant that encloses the oil in between the monolayers and the whole package is like a sandwich.

The multiphase region between the two channels

The multiphase region between the two isotropic channels is very large and dominates the phase diagram. It extends to 45% of oil on the oil axis. Other phase diagrams for microemulsions with nonionic surfactants do not have such a large multiphase region. In the surfactant composition region between x IT 3 = 0.2 and 0.55 the two phase regions are the L_α/L_1-region. The L_α-phases on the water side are transformed with increasing amount of oil into two phase regions and finally into the single phase channel. The amount of oil that is necessary to destroy the L_α-phase increases with the mass fraction of IT 3 in the surfactant mixture. It is interesting to note that the surfactant phase with x IT 3 = 0.55 can accommodate more than its own weight of oil before some of the L_α-phase is transformed to a microemulsion phase.

Close to the upper channel, the situation is more complicated.

Most interesting are the sequence of phases in the surfactant composition between x IT 3 = 0.6 and 0.7. With x IT 3 = 0.6, the L_α-phase is transformed with 5% of oil into the two phase L_α/ME region and with 20% of oil the system re-enters the single L_α-phase. For higher oil ratios the system approaches the lower single phase channel in a two phase L_α/ME region. With x IT 3 = 0.65, the phase diagram becomes even more complicated. With 5% oil, the L_α-phase is transformed into the upper isotropic channel. In the oil region between 20% and 40%, a two phase region with the L_α-phase and an isotropic phase exists, in which the L_α-phase first increases with the oil content and then decreases again (see tube pictures of samples in ESI†). It is likely that the isotropic phase in the two phase region first is a ME from the upper phase channel while it is a ME from the lower phase channel in the second region.

An even different situation is observed with x IT 3 = 0.7. The pure L_α-phase is again transformed with little oil into the bi-continuous channel. With more oil, multiphase regions are observed that have no L_α-region.

The search for a connection of both single phase channels

We were surprised not to find a connection between the lower and the upper single phase channel as would have been expected from known phase diagrams with nonionic surfactants. The reason for this could have been that the composition of the investigated samples was not close enough to detect the connection. To search for a possible connection between both single phase channels, more samples between both channels were investigated. Fig. 6 shows a row of samples that have been prepared by mixing directly a sample from the end of the lower single phase channel with a sample from the upper single phase channel.

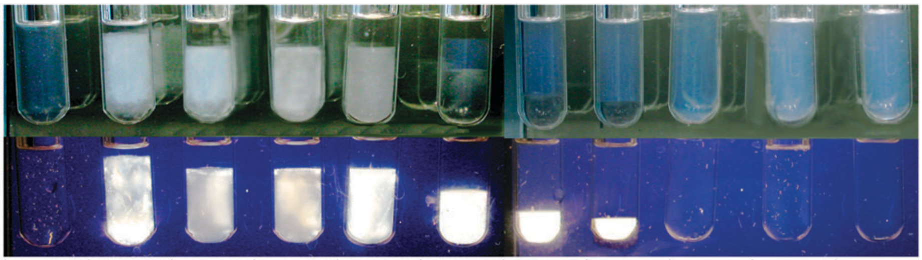
The first mixed sample with a composition of x IT 3 = 0.675 and x M_2 = 0.46 is already a two phase sample with a lower L_α-phase and an upper isotropic phase. While we did not analyse the upper phase, it looked like it consists of pure M_2.

This result is a strong indication of existing tie lines between the L_α-phase and pure M_2. It would mean that an isotropic channel cannot exist in between the lower and the upper single phase channel.

In the following samples, the volume of the L_α-phase decreases and the volume of the upper phase increases, a sign that the distance of the composition of the sample is increasing from the L_α-phase and decreasing from the upper phase. With the sixth sample with the composition x IT 3 = 0.775 and x M_2 = 0.5, the situation changes completely. The sample clearly consists now of three phases, a lower L_α-phase, a middle bluish microemulsion phase and an upper oil phase. This three-phase area is followed by a two phase area with a decreasing lower L_α-phase and an upper bluish microemulsion phase. With x IT 3 = 0.85 and x M_2 = 0.53, the sample reached the upper isotropic single phase channel. More samples with this three phase situation were found and drafted as a triangle in the phase diagram (Fig. 5). This three phase area indicates that there cannot be a connection of both single phase channels.

The properties of the samples in the single phase channels

It is evident from visual inspection of the samples that the structure of two samples with the same amount of oil but at different surfactant ratios is not the same. An overview of



x IT 3	0.65	0.675	0.7	0.725	0.75	0.775	0.8	0.825	0.85	0.875	0.9
x M_2	0.45	0.46	0.47	0.48	0.49	0.5	0.51	0.52	0.53	0.54	0.55

Fig. 6 Mixtures of a sample from the lower and upper single phase channels of the system $Ca(DS)_2$/IT 3–H_2O/M_2 with x M_2 = 0.45 and x M_2 = 0.55. Upper row shows samples without crossed polarizers, lower row shows samples in between crossed polarizers at 40 °C.

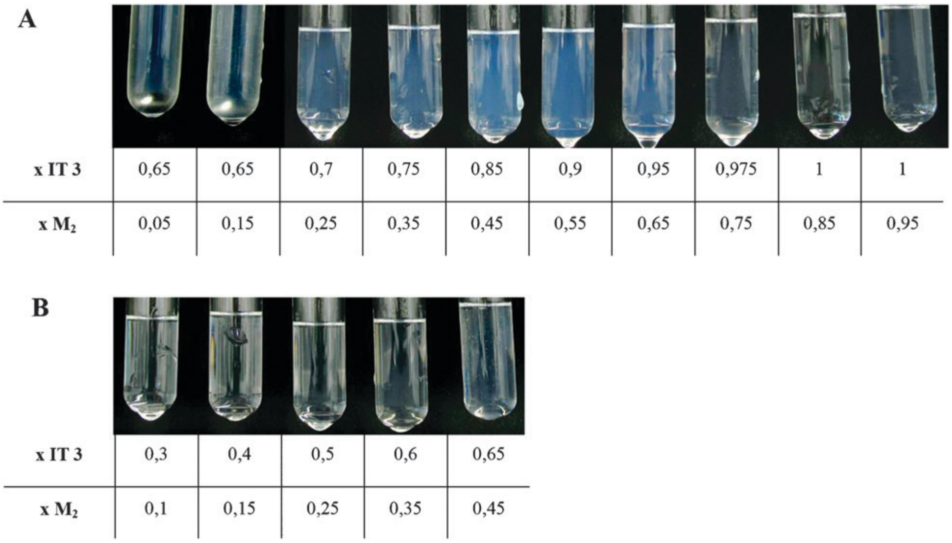


Fig. 7 Overview of selected samples in the upper (A) and lower (B) single phase channel of the system $Ca(DS)_2$/IT 3–H_2O/M_2 at 40 °C.

samples in the upper and lower single phase channels with increasing amount of oil is shown in Fig. 7.

Samples from the upper phase channel (Fig. 7A) are somewhat bluish and the scattering intensity of the samples increases from the water corner to samples with 65% of oil. Samples with larger oil content scatter less. All samples from the lower phase channel scatter much less (Fig. 7B). Samples from the upper channel show flow birefringence up to 40% oil, while the samples from the lower channel do not show flow birefringence. These features are a first indication that the upper channel has a bi-continuous structure while the lower channel consists of oil droplets in a continuous water phase. The structures of the microemulsions in the channels are now already reported[36] and the physicochemical properties like their rheology and their structural relaxation times will be given in another manuscript. It also will be shown that the obtained phase diagram changes only little if M_2 is replaced by decane. The obtained results are thus typical for microemulsion phase diagrams with mixed nonionic/ionic surfactant mixtures. The temperature stability of the samples in both channels hasn't been investigated in detail, but it was observed that the samples in the lower single phase channel were less sensitive to temperature changes than the samples in the upper single phase channel, especially close to the L_3-phase. This can be explained by the higher mass fraction of a temperature sensitive nonionic surfactant in the upper channel. Nevertheless, all samples are stable in a wider temperature range than samples with nonionic surfactant mixtures that are only stable within around ±1 °C.

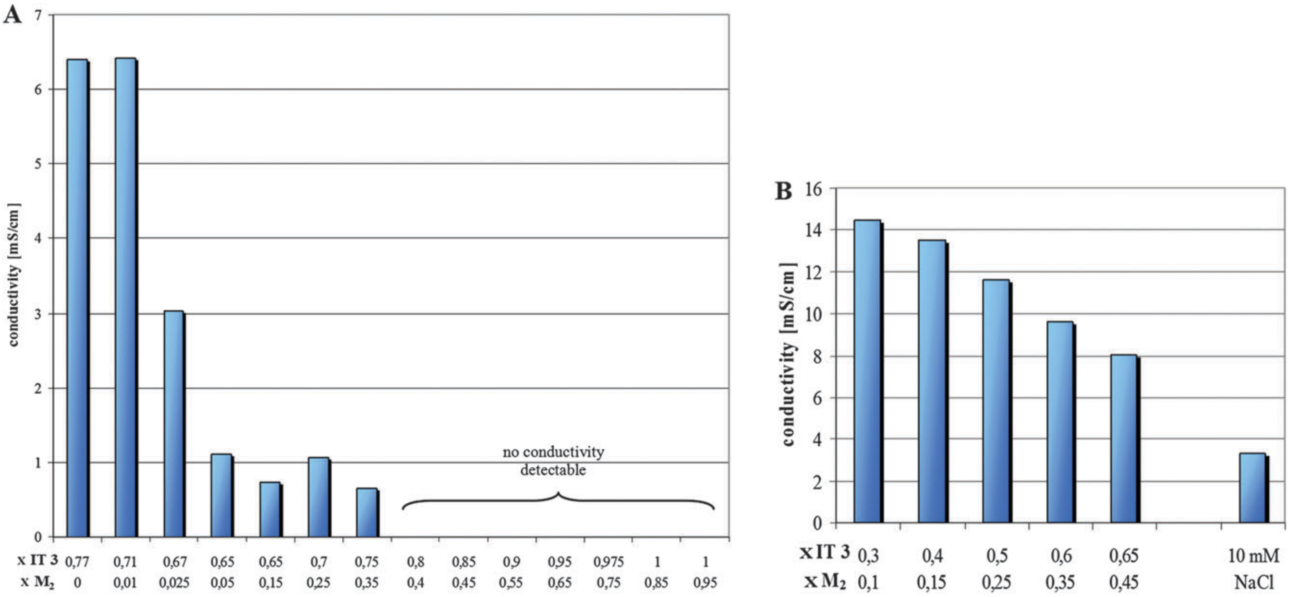


Fig. 8 Conductivity measurements in the upper (A) and lower (B) single phase channel of the system $Ca(DS)_2$/IT 3–H_2O/M_2 at 40 °C.

Conductivity measurements

For conductivity measurements, all samples have been prepared with 10 mM NaCl. A plot of the conductivity in the two channels against the weight fraction of oil is given in Fig. 8. Note that the conductivities in the lower channel (Fig. 8B) are much higher at the water corner than those in the upper channel (Fig. 8A). The reason for this is that the $Ca(DS)_2$ concentration is much higher in the lower channel. If the conductivities are normalized to the same $Ca(DS)_2$ concentration they are about the same. The conductivities decrease linearly with the oil content to the middle of the phase diagram, which is where the channel ends. The reason for the decrease is mainly the decreasing mass fraction of $Ca(DS)_2$. The conductivities therefore indicate that the microstructure in the lower channel does not change and that the channel consists of a continuous water phase in which oil droplets are dispersed.

The situation is different in the upper channel. In this channel the conductivity drops for a few percent of oil (5%) to only about 18% of its value in the L_3-phase even though the fraction of $Ca(DS)_2$ is increasing from 23% to 35%. For higher mass fraction of oil the conductivities remain about constant and drop to zero for x M_2 = 0.4. The conductivities thus indicate a dramatic change in the microstructure of the bi-continuous channel with solubilisation of small amounts of oil into the L_3-phase. Obviously the constraints in the microemulsion for the transport of the ions must be much larger than those in the L_3-phase. This means that the water channels in the ME-phase must be much smaller than those in the L_3-phase where the conductivity is only about 2/3 of the value of the normal aqueous phase without a surfactant. The complete break-down of the conductivity for oil fractions larger than 0.4 means that the system changes from a bi-continuous structure to a w/o-structure. Conductivities in the isotropic channels of microemulsions from nonionic surfactants have been reported in the literature.[34] In the upper channel the reported conductivities decrease continuously with increasing oil content. These measurements have helped to establish the view which we have today from the structures in the upper channel. With increasing oil content the bicontinuous L_3-phase swells with the solubilised oil between the bilayers and is finally transformed at high oil content to a w/o system. With equal amount of oil and water both SAXS-data and conductivities show that this phase is still a bicontinuous phase.[35] Our conductivity measurements unambiguously show that the structures in the upper channel of the investigated system are different from the structures of known systems with nonionic surfactants. We find a rather abrupt transition from the L_3-structure to another bicontinuous structure with swollen aqueous channels at around 10% of oil and another abrupt transition at 40% of oil to a w/o structure.

The microemulsion with equal amount of oil and water does not have a bicontinuous structure. In the meantime, this has been confirmed by cryo-TEM images, which show clearly a w/o-structure.[36]

Finally, at the end of the discussion we would like to draw attention to several experimental observations which have been made during this investigation and which to our knowledge are not theoretically understood and need further scouting. To mention here are the existence of the L_3-phase in the anionic nonionic surfactant mixture, the occurrence of a second L_α-region after the existence of the L_3-phase and a structural transition in the bi-continuous upper phase channel.

Conclusion

The ternary phase diagram of the silicone oil hexamethyldisiloxane M_2, water and a surfactant mixture of the ionic surfactant $Ca(DS)_2$ and the nonionic surfactant isotridecyltriethyleneglycolether IT 3 has been established as a function of the mass fraction of IT 3.

Two isotropic single phase channels occur in the system with increasing oil content x M_2. The lower channel, that is the one with the lower x IT 3 value, begins at the phase boundary of the L_1-phase toward the L_α-phase. This channel increases with increasing x M_2 and ends in the middle of the phase diagram at x IT 3 = 0.65. This channel contains oil droplets in a continuous water phase (o/w-system). The upper channel begins at the L_3-phase and passes with increasing oil content through a shallow minimum to the oil side. It has, like the L_3-phase, a bi-continuous structure until 40% oil, and then switches to a w/o structure to the oil side. The microemulsion with equal amount of water and oil does not have a bicontinuous structure. Phases of bicontinuous structure show a strong flow birefringence. Samples from the o/w and the w/o channel are transparent and show no flow birefringence.

In contrast to phase diagrams with one component, surfactant mixtures with surfactants can form channels that pass from the water to the oil side at constant temperature. The amphiphilic properties for the channels can be adjusted by changing the composition of the surfactant mixture instead of the temperature.

The upper channel and the lower channel are not connected with each other. It is likely that the non-connectivity is due to the influence of the ionic surfactant and the high interfacial tension of the surfactant system against oil, which promotes the formation of globular structures instead of a bicontinuous topology.

In total, the investigation has shown that microemulsion phase diagrams, that are established with mixtures of an anionic and a nonionic surfactants, differ from the phase diagram that can be produced with ionic or with nonionic surfactants. We propose that the situation in our system is somewhere between and of general importance.

Experimental

Materials

Sodiumdodecylsulfate (SDS, cryst. research grade) was purchased from the Serva Co., Heidelberg. The nonionic surfactant isotridecyltriethyleneglycolether, in the following text abbreviated as IT 3, was obtained from the Sasol Co., Hamburg (product name Marlipal O13/30). $MgCl_2{\cdot}6H_2O$ and $CaCl_2{\cdot}2H_2O$ were purchased from the Grüssing Co., Filsum.

The silicone oil hexamethyldisiloxane, abbreviated as M_2, was obtained as a gift from the Wacker Co., München.

Preparation of $Ca(DS)_2$ and $Mg(DS)_2$

For the preparation of $Ca(DS)_2$ and $Mg(DS)_2$, 400 mM SDS-solutions were mixed with either 200 mM $CaCl_2$ or $MgCl_2$

solution under stirring. The bi-valent counter ions Ca^{2+} and Mg^{2+} bind strongly to the dodecylsulfate than the sodium-ion, leading to a precipitation of $Ca(DS)_2$ in solution below its Krafft-temperature of 50 °C and $Mg(DS)_2$ below its Krafft-temperature of 25 °C. The solutions were heated up to 60 °C for the solution with $CaCl_2$ or warmed up above 25 °C for the solution with $MgCl_2$ to get a clear solution and then cooled down to 20 °C. After precipitation, $Ca(DS)_2$ and $Mg(DS)_2$ were washed several times with de-ionised water to remove excess salt. The purity was checked then by measuring the conductivity of the flow through. The washed $Ca(DS)_2$ and $Mg(DS)_2$ were dried several days in a cabinet dryer at 50 °C and used without further purification.

Preparation of samples

All samples were prepared by weighing in directly the components in test tubes, first surfactant and co-surfactant, H_2O, and as the last component M_2 due to its high volatility. The test tubes have been sealed with a teflon tape, tempered at 40 °C in a water bath and vortexed several times thoroughly. This temperature was necessary to prevent the crystallization of $Ca(DS)_2$ in microemulsions with a mass fraction of x IT 3 < 0.5. All samples have been incubated at least 3 days at 40 °C before being investigated for their phase behaviour. For the phase diagram, the samples below the mass fraction of x IT 3 $= 0.3$ had to be prepared with $Mg(DS)_2$ instead of $Ca(DS)_2$ to avoid problems with precipitation of $Ca(DS)_2$. The surfactant concentration of 15% (w/w) was necessary to find the single phase channels. In general, the phase diagram has been scanned with a resolution of 5% in the composition of the mass fraction of IT 3 and M_2. More detailed steps have been investigated in the beginning of the upper single phase channel and in between the two single phase channels to find a possible connection of both channels. The multiphase samples were viewed without and in between crossed polarizers.

Surface/interfacial tension measurements, conductivity and rheology

The surface and interfacial tensions were measured with the help of the volume-drop tensiometer TVT1 from the Lauda Co., Königshofen. For conductivity measurements, the Microprocessor Conductivity Meter LF2000 from the WTW Co., Weilheim was used. The rheology was measured with the cone-plate rheometer RheoStress 600 from the Haake Thermo Scientific Co., Karlsruhe.

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