Unusually sluggish microemulsion system with water, toluene and a technical branched alkyl polyethoxylate

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SCIENTIFIC PAPER

UNUSUALLY SLUGGISH MICROEMULSION SYSTEM WITH WATER, TOLUENE AND A TECHNICAL BRANCHED ALKYL POLYETHOXYLATE

Article Highlights
- A ternary system of water, toluene and a branched technical alkyl polyethoxylate was investigated
- The "fish-diagram" shows divergence of the phase boundaries near optimum solubilization
- Long-lasting metastable states were observed
- The destruction and formation of liquid crystals are slow processes
- Mini-emulsions were found for unusual composition near optimum solubilization

Abstract

Microemulsion systems with water, toluene and nonionic surfactants are interesting for application due to the excellent solvent properties of aromatic hydrocarbons. In this study, the pseudo-binary phase diagram ("fish-diagram") of such a ternary system was investigated using a branched technical alkyl polyethoxylate. Lutensol ON 50 (i-$C_{10}E_5$) was considered a suitable surfactant. The system with technical branched i-$C_{10}E_5$ exhibits very long, and for compositions near optimum solubilization, i.e., the minimum content of surfactant needed for a bicontinuous microemulsion, extremely long times for equilibration. In addition to visual observation, qualitative measurements of turbidity were performed with a UV-Vis spectrometer for characterizing the behavior of this unusually sluggish system. Isothermal phase diagrams at 20, 25 and 30 °C yielded inconsistent results after the change of temperature and the application of mechanical stress for different treatment of the samples. Ternary mixtures of water, toluene, and lutensol ON 50 seem to form long-living metastable states. The sluggishness and the ambiguous phase behavior of the system are discussed. Inconsistent results are attributed to the slow kinetics of the formation and destruction of liquid crystals and the ability of the system to form mini-emulsions within an unusual concentration range.

Keywords: microemulsion, toluene, oxoalcohol ethoxylate, thermodynamic stability, ternary phase diagrams, "fish" diagrams.

Microemulsions are interesting for scientific [1-6] as well as for practical reasons [1,7-10]. According to a widely accepted definition, they are thermodynamically stable non-liquid-crystalline dispersions of two immiscible liquids and at least one amphiphilic

compound that stabilizes the dispersion. The liquids may be water, ionic liquids [11] and different types of organic solvents, but also mixtures or solutions comprising electrolytes or other gaseous, liquid or solid components. The amphiphilic components can be selected from various types of ionic [12], zwitterionic [6,13] or nonionic surfactants [4,12], polymers [14], or mixtures of several of such compounds [3,12,13] allowing adaption of the microemulsion to the desired purpose. Once a base system has been found, further components modifying the properties of the surfactants (co-surfactants, linkers) can be used to opti-

mize the system regarding stability and structure [12,15]. Microemulsions may contain oil droplets in water (o/w microemulsions), water droplets in oil (w/o microemulsions) or both water and oil as continuous constituents (bicontinuous microemulsions) [4].

Three main properties delineate microemulsions from other systems comprising the same components. Microemulsions are dispersions and thermodynamically stable, and they exhibit no long-range order, in contrast to any kind of liquid crystals or similar systems [16,17]. Microemulsions are said to be clear or at least translucent liquids. They are optically isotropic and exhibit relatively low viscosity. In addition, bicontinuous microemulsions usually exhibit Newtonian flow behavior up to high shear rates [18], which is a consequence of the fast dynamic exchange of the components between the interface and the two micro-phases, *i.e.*, the water-rich and oil-rich domains, on a time scale of microseconds or less. This rapid exchange of material usually makes phase transition and phase separation fast when destabilizing a bicontinuous microemulsion [19,20].

Due to the unique properties of aromatic hydrocarbons as solvents for syntheses and for enhanced extraction efficiency [8,9], microemulsions with toluene or other aromatic solvents [14] are particularly interesting. They can be used as reaction media that exhibit improved compatibility with reactive agents [21] and products [22]. The solvent properties are particularly important for particle synthesis with metal alkoxides. Most of the microemulsions with toluene, however, either contain ionic surfactants [21,22], which may disturb reactions and contaminate products (*e.g.*, with sulfur, phosphor or halogens), or very expensive pure nonionic surfactants [23]. Other components frequently used in microemulsions like short- and medium-chain alcohols may also disturb reactions [21]. Therefore, ternary mixtures seemed most preferable. So-called detergentless microemulsions containing surface-active components of small molecular size [24] are not suitable because there is a gradual decrease of polarity contrast with decreasing molecular size of the surface-active compound [25] and well-developed structures may only be achieved with surfactants of sufficient chain length. The ternary mixture containing water, toluene and triton X-100 exhibits only a comparatively narrow single-phase region with very high surfactant content near the oil surfactant edge [5] and may be applicable only in special cases. This lack of suitable microemulsions with aromatic solvents for technical application was the motivation to start the studies presented in this paper.

Lutensol ON 50, which is technical branched pentaoxyethylene (isodecyl) ether (i-$C_{10}E_5$), was chosen as the amphiphilic component, because similar surfactants were successfully applied for making microemulsions with heterocyclic aromatic hydrocarbons [26,27]. Gotch *et al.* [28] had already qualitatively observed strong time dependence for water/toluene/ /technical alkyl polyethoxylate systems. In this paper, we give a quantitative idea on the time scale within which this type of sluggish microemulsion will respond to changes of temperature and mechanical stress (stirring or shaking). The pseudo-binary "fish- diagrams" and isothermal ternary phase diagrams at 20, 25 and 30 °C were investigated. Some samples were also investigated by additional measurements with UV-Vis absorbance and dynamic light scattering.

EXPERIMENTAL

Materials

Toluene (purity 99% GC) was purchased from Merck Schuchardt (Germany). Lutensol ON 50 (C_{10} oxoalcohol polyethoxylate with an average of 5 ethylene oxide units; CAS number 61827-42-7) is a commercial nonionic surfactant of BASF AG, Ludwigshafen (Germany). It has a hydrophilic-lipophilic balance (HLB) of 11.5 according to the producer (technical information sheet of BASF). Since the product was inhomogeneous, it was heated to 30 °C before use. Water was deionized and distilled twice.

Phase diagrams

The determination of the pseudo-binary phase diagrams was carried out in a thermostated transparent water bath with temperature control of 0.1 K. Systematic deviations were controlled by a high precision digital thermometer GMH 3710 (Greisinger Electronic, 1/10 DIN, 0-100 °C) and corrected by using linear calibration. The samples (5 g for isothermal phase diagrams and initially 10 g for the "fish-diagram") were prepared by weighing on 0.1 mg precision scales. Surfactant, toluene and water were added in succession one after the other in order to avoid or at least suppress intermediate formation of liquid crystals. The tubes were sealed with glass stoppers. The mass fractions, $\alpha = m_o/(m_w+m_o)$, $\gamma = m_s/(m_w+m_o+m_s)$ and $w_i = m_i/(m_w+m_o+m_s)$ are defined to characterize the composition. The indices "w", "o" and "s" refer to the components water, oil, and surfactant respectively. Index "i" represents any of the two components water or oil. All investigations for the "fish-diagram" were carried out at a constant water to oil mass ratio corresponding to $\alpha = 0.50$. These pseudo-

-binary phase diagrams were recorded adding successively equal quantities of toluene and water to the initial water-oil-surfactant mixture to lower the surfactant concentration.

In a thermostated water bath, the mixtures of water, toluene and lutensol ON 50 were investigated visually. The transmission of light was observed at constant sample composition and varying temperature for each surfactant concentration. The presence of anisotropic liquid crystalline phases was detected using crossed polarizers. Formation of the microemulsion was judged by the classical criteria of an optically clear and isotropic, stable single-phase solution. For obviously multiple phase systems, an appropriate time for phase separation was chosen prior to determination. For 25 and 30 °C, up to 120 h were needed. At room temperature phase separation was achieved after 4 weeks and at 20 °C after 2 months. Isothermal phase diagrams were determined throughout the Gibbs triangle for all compositions in steps of mass fractions of 0.10 except the binary mixtures of toluene and water. The mutual solubility of water and toluene can be calculated from the literature [29]. At 20-30 °C the mole fraction of water soluble in toluene is between 2.4×10^{-3} and 3.3×10^{-3}. The mole fraction of toluene soluble in water is about 1.1×10^{-4} in this temperature range. These values correspond to mass fractions of 4.7×10^{-4}-6.4×10^{-4} of water in toluene and 5.7×10^{-4} of toluene in water. Whereas the pure components water and toluene are liquids, the technical grade surfactant lutensol ON 50 is a mixture of liquid and solid components at 25 °C. Details of these experiments are described under Results and Discussion because they are important for the interpretation of the data.

UV-Vis measurements

UV-Vis measurements were carried out with a UV-1601 visible spectrophotometer (Shimadzu). The spectrophotometer is PC controlled by software (Kinetics Program Pack). Samples were placed in quartz cuvettes (10 mm path length) and equilibrated for at least 5 min. The spectrophotometer has a thermo-electrically temperature controlled cell with a precision of ±0.1 °C. Wavelength dependence was determined between 350 and 700 nm. Temperature and time dependence were measured at 400 nm.

Dynamic light scattering

Dynamic light scattering was measured on a Malvern Zetasizer Nano S at wavelength $\lambda = 633$ nm and scattering angle $\theta = 173°$. The temperature was 30.0±0.1 °C. The intensity correlation function $g^{(2)}$ exported from the software as $g^{(2)}$-1 was fitted to a single stretched exponential decay function $g^{(1)}$ yielding a decay time, τ_0, according to:

$$g^{(1)} = g^{(2)} - 1 = A(e^{-(\tau/\tau_0)^{\beta_i}})^2 \tag{1}$$

The effective diffusion coefficients, $D_{\text{eff,i}}$, assuming a dilute dispersion of oil in water (i = w) and water in oil (i = o) were determined from this decay time τ_0 according to Eq. (2). The refractive indices, n_i, of water and toluene were used for calculating the scattering vectors $q_i = 4\pi n_i \sin(\theta/2)/\lambda$:

$$D_{\text{eff,i}} = \frac{1}{\tau_0 q_i^2} \tag{2}$$

The corresponding hydrodynamic radii, $r_{\text{h,i}}$, were determined according to the Einstein-Stokes Equation (3) applying the according viscosity, η_i, of water and toluene:

$$r_{\text{h,i}} = \frac{kT}{6\pi \eta_i D_{\text{eff,i}}} \tag{3}$$

RESULTS AND DISCUSSION

Pseudo-binary phase diagrams

The pseudo-binary phase diagram of the ternary system water/toluene/lutensol ON 50 (technical branched i-$C_{10}E_5$) was determined at equal mass fractions of water and toluene ($\alpha = 0.5$) in order to find the composition and temperature of optimum solubilization. A single homogeneous phase (1ϕ) is found at high surfactant content in a temperature range that widens with increasing γ (Figure 1). The shape of the "fishtail" is not symmetrical with respect to the temperature. This behavior is typical for technical surfactants with a distribution of more or less hydrophobic components due to different degree of ethoxylation [20,30,31].

No liquid crystals are found within the region of the bicontinuous microemulsion (1ϕ) in contrast to the system with linear $C_{10}E_8$ described in the literature [23]. This behavior can be attributed to a less rigid structure of the surfactant layer at the interface between the oil and the water micro-phases due to the presence of different components and the branched alkyl chain in particular. Approaching the composition of optimum solubilization of equal masses of water and toluene, samples with the branched technical surfactant need very long and sometimes extremely long times for equilibration after agitation or temperature changes. They show very slow or even delayed visible phase separation. The phase boundaries between the bicontinuous microemulsion (1ϕ) and the two-phase regions with a coexisting oil phase
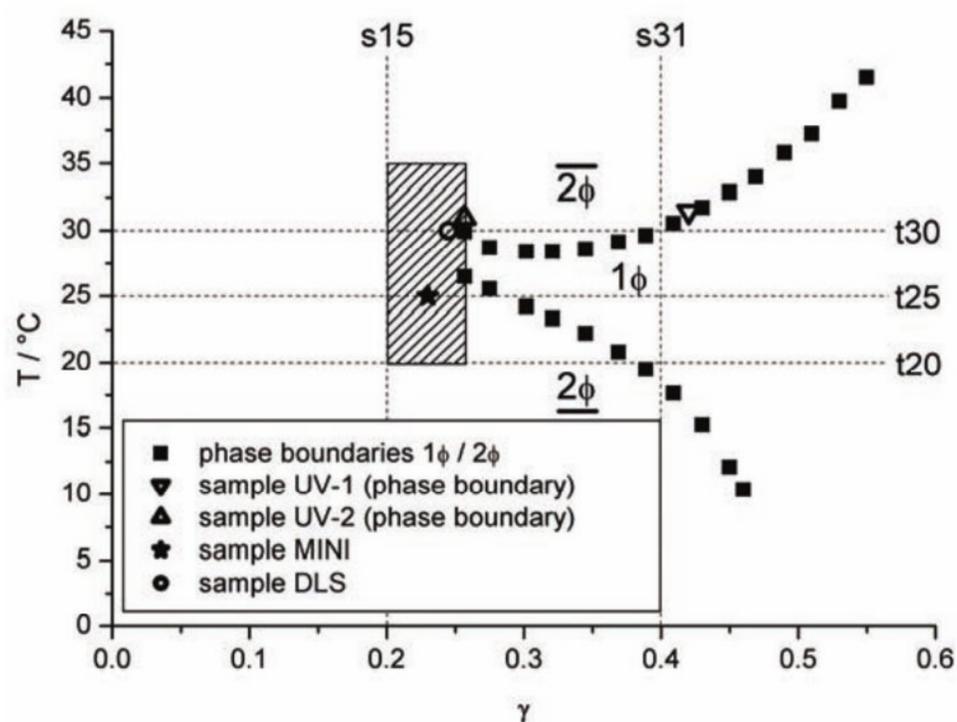
Figure 1. Pseudobinary phase diagram of ternary mixtures of water, toluene and lutensol ON 50 for equal mass fractions of water and oil (α = 0.5). UV-1 and UV-2 are phase boundaries determined by UV-Vis measurements. MINI is a miniemulsion and DLS means a sample that was investigated by dynamic light scattering. Lines t20, t25 and t30 signify temperatures chosen for the isothermal phase diagrams. Lines s15 and s31 signify compositions that were investigated in the isothermal phase diagrams.

(2ϕ) and a coexisting aqueous phase ($\overline{2\phi}$) determined by visual observation are diverging. Hence, it can be concluded that the phase boundaries found with this method are not certain already near the hatched region in Figure 1. For comparison, "fish-diagram" with all Winsor phases W I to W IV had been observed for the ternary system water/toluene/$C_{10}E_8$ by Burauer *et al.* [23].

UV-Vis measurements

Two samples with different surfactant content were investigated, one at higher γ where phase boundaries could well be visually observed, and the other at the border of the hatched region in Figure 1 where the phase boundaries 2ϕ/1ϕ and 1ϕ/$\overline{2\phi}$ are already diverging. Figure 2a and b shows the temperature dependence of the absorbance A at wavelength 400 nm near the upper phase boundary for surfactant content, γ, of 0.42 (a) and 0.257 (b). A jump of absorbance is evident for the phase boundary between the one-phase and the two-phase region ($\overline{2\phi}$) for γ = 0.42 (sample UV-1 in Figure 1) between 31.4 and 31.5 °C (Figure 2a).

This value is close to the phase boundary in Figure 1 that was obtained by visual observation in this concentration range. For the sample with γ = 0.257 (sample UV-2 in Figure 1), the turbidity is much higher and the change of absorbance is much smoother (Figure 2b). The steep increase at 30.9-31.0 °C is about 1 °C higher than the phase boundary that was visually determined with larger waiting time.
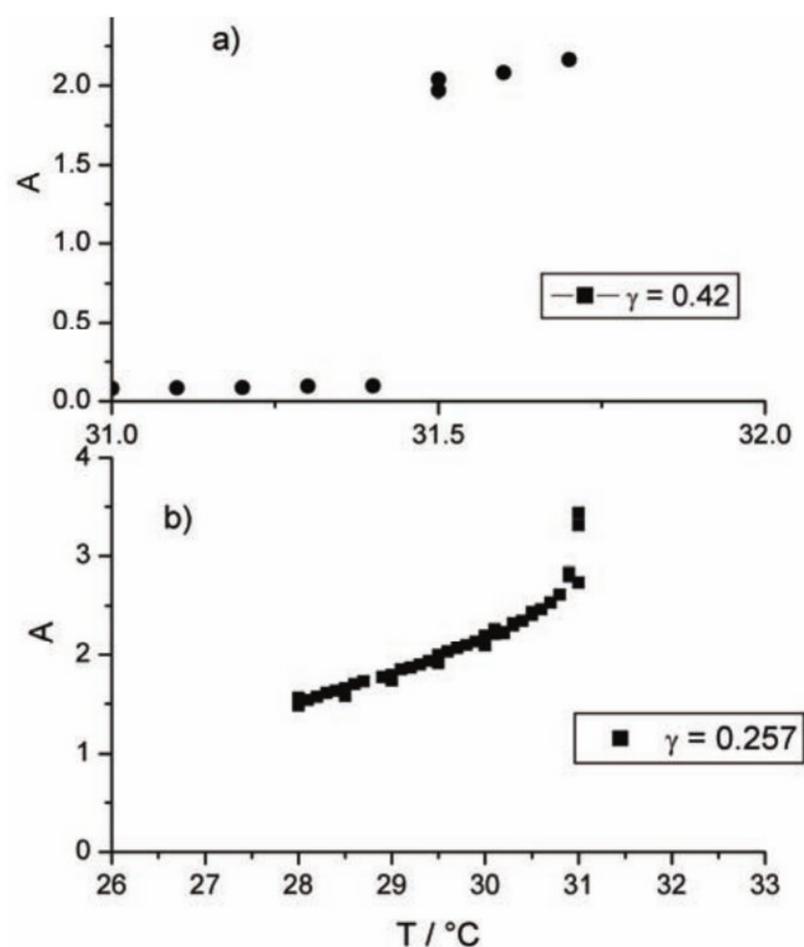

Figure 2. Temperature dependent absorbance due to scattering at 400 nm of samples a) UV-1 with γ = 0.42, and b) UV-2 with γ = 0.257 for equal mass fractions of water and oil (α = 0.5).

Figure 3 shows the UV-Vis absorbance (turbidity) of the two samples mentioned above over a wavelength range from 350-700 nm in a double logarithmic plot. Whereas the scattering of sample UV-1 with γ = 0.42 is nearly independent of the wavelength above the upper phase boundary at 31.5 °C,
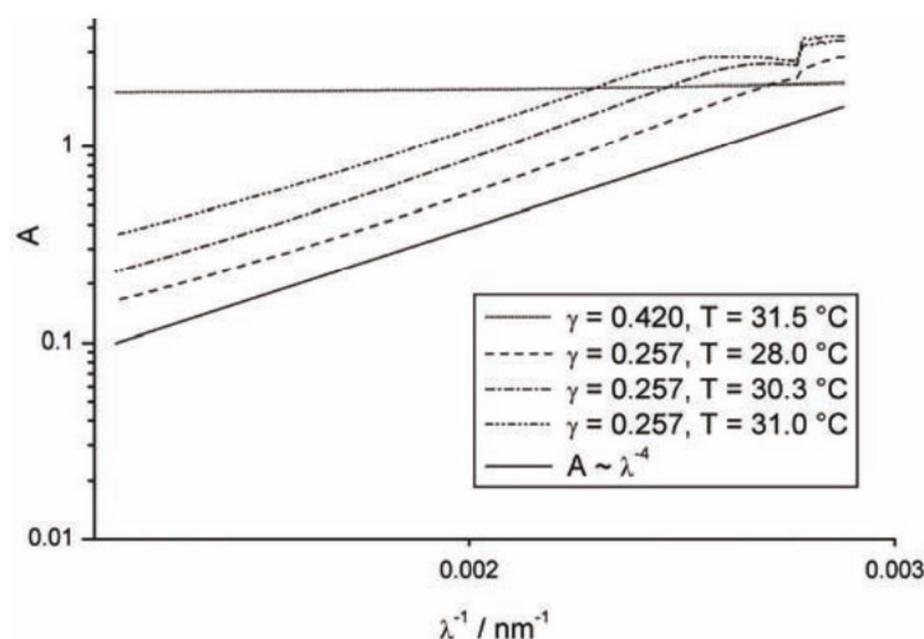
Figure 3. Wavelength dependent absorbance of samples UV-1 at 31.5 °C (2ϕ) and UV-2 at different temperatures in the single phase region (28 °C), near the phase boundary (30 °C) and above the phase boundary (31 °C), compared with the theoretical wavelength dependence for Rayleigh scattering (A ~ λ^{-4}).

scattering of sample UV-2 with $\gamma = 0.257$ is strongly dependent on the wavelength for 3 temperatures below 28 °C, near 30 °C and above 31 °C the upper phase boundary (cf. Figure 1) with $A \sim \lambda^{-4}$. This behavior is characteristic for Rayleigh scattering on particles that are considerably smaller than the wavelength. In contrast, the behavior of sample UV-1 with $\gamma = 0.42$ lutensol ON is typical for Mie scattering on large particles.

Thus, for the higher surfactant content large emulsion droplets are formed, whereas the transition near the optimum solubilization is gradual and no changes in the wavelength dependence can be observed. There is only an increase of turbidity. The turbidity of the sample with $\gamma = 0.257$ was also found to be dependent on time. The absorbance of this sample after a temperature change from 27.0 to 27.1 °C, *i.e.*, in the single phase area 1ϕ near the lower phase boundary. The system responded with a slow change of turbidity. Only a part of the slow response can be explained by the time needed for thermal equilibration that was found to be less than 5 min. Considerable changes of absorbance were found for longer times in several similar experiments. All curves were different but ended at about the same value after about 60 min. Only the curve of the first measurement showed a smooth change that started immediately after the temperature change. All others showed a delayed start and changes that were not continuous (data not shown). Strong variations of absorbance are due to inhomogeneous distribution of various scattering structures in the cuvette. Local equilibrium needs more time to be reached, because the experiments were performed without stirring.

The results of UV-Vis spectroscopy show that approaching optimum solubilization, the scattering of the samples increases strongly and the visually observable difference in the optical properties of the one-phase and the two-phase region becomes less and less pronounced. Furthermore, the time needed for equilibration becomes longer. Consequently, the phase boundaries determined by visual detection are not certain for γ smaller than about 0.26. At lower surfactant content, changes of the samples are extremely slow. This behavior may be attributed to supersaturating effects for some of the components of the technical surfactant (in particular those with low concentration and high solubility) as well as to the branching of the molecules. Both facts may lead to a slow equilibration of the interfacial surfactant monolayer.

Isothermal phase diagram

Mass fractions of water, toluene and lutensol ON 50 were varied in steps of 0.1. Samples containing surfactant ($\gamma \geq 0.1$) were consecutively numbered in Gibbs triangles with repeatedly increasing mass fraction of toluene at constant surfactant content followed by an increase of surfactant and starting at zero toluene again. They were investigated at 30 and 25 °C with different pretreatment, and additionally, after longer storage time at 20 °C and at varying room temperature. A scheme of the entire procedure is available as Supplementary Material (from the authors upon request). The surfactant obtained from the producer was inhomogeneous at room temperature and 25 °C. It visibly contained solid or liquid crystalline components that showed optical anisotropy between crossed polarizers. At 30 °C, lutensol ON 50 became a clear liquid without birefringence. Liquid

crystals or crystals were also found in samples (marked by a square in Figure 4) with high surfactant content at room temperature (sample S53) and 20 °C (samples S52 and S53), when the samples had been standing for longer time.
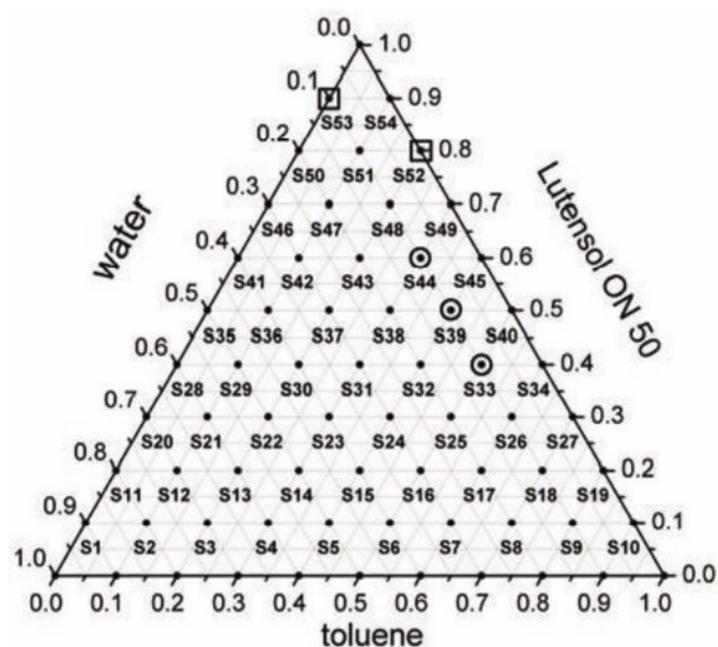

Figure 4. Numbering of samples with γ ≥ 0.1 in the Gibbs triangles; Samples with symbols surrounded by a square or a circle show inconsistent results.

Other samples with such high surfactant content, however, did not show liquid crystal formation within the observation time (samples S50, S51 and S54). These results suggest that some of the samples at high surfactant content had not yet reached thermodynamic equilibrium.

The two-phase region near the toluene-surfactant edge (samples S33, S39 and S44 with $w_w = 0.1$, marked by a circle in Figure 4) is not consistent with chemical equilibrium in a ternary system. The samples contain two liquid phases that do not exhibit a considerable change of phase volumes inside this two-phase region as would be expected for real phase equilibrium in a ternary system. There is always only a small amount of non-birefringent denser phase observable. Such behavior has also been found earlier for systems with heterocyclic aromatic hydrocarbons [24,25]. Phase separation without continuous variation of phase volumes as observed in this study, might be attributed to the fact that technical surfactants are mixtures of a variety of ethoxylated species and contains certain amounts of the precursor alcohols, salt and other impurities. Another explanation may be the formation of hydrated surfactants that are insoluble in toluene but act as additional components in the system.

Figures 5-7 represent isothermal Gibbs triangles for the ternary system of water, toluene and lutensol ON 50 at different temperatures and for different

pretreatment of the samples. Figure 5a and b correspond to non-agitated and agitated treatment before storage for 72 and 120 h, respectively, at 30 °C. Figure 6a features agitation and storage for 64 h at 25 °C while Figure 6b corresponds to longer storage at room temperature, several further steps and agitation at 25 °C. Finally, Figure 7a and b shows the behavior of the samples after storage at varying room temperature of 19-24 °C for 4 weeks and at 20 °C after 2 months. During this time intervals liquid crystals formed in some of the samples between γ 0.1 and 0.4 for $\alpha \le 0.6$ (Figure 7).
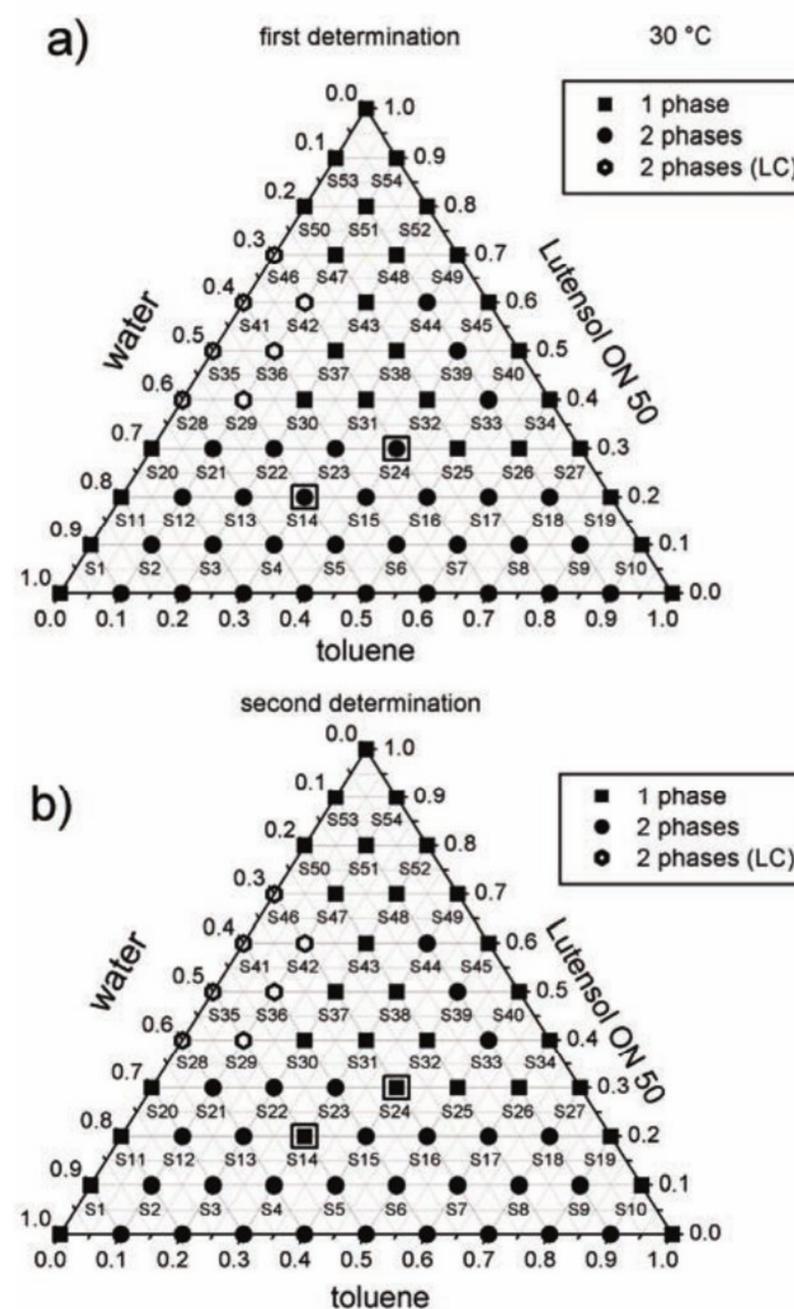

Figure 5. Isothermal phase diagrams of ternary mixtures of water, toluene and lutensol ON 50 at 30 °C; a) after equilibration for 72 h without agitation and b) after shaking and equilibration for 120 h; samples with different behavior for both determinations are emphasized by a square surrounding the symbol. LC signifies samples containing liquid crystals.

At 30 °C, most of the samples exhibited identical phase behavior for both determinations with and without agitation. Liquid crystals (open symbols) originating from the binary lutensol ON 50/water mixture

were found at 30 °C only for toluene content w_o < 0.2. A large extension of liquid crystals up to w_o = 0.6 was observed, when the samples were left at varying room temperature for 4 weeks (Figure 7a) and after equilibration at 20 °C for 2 months (Figure 7b).
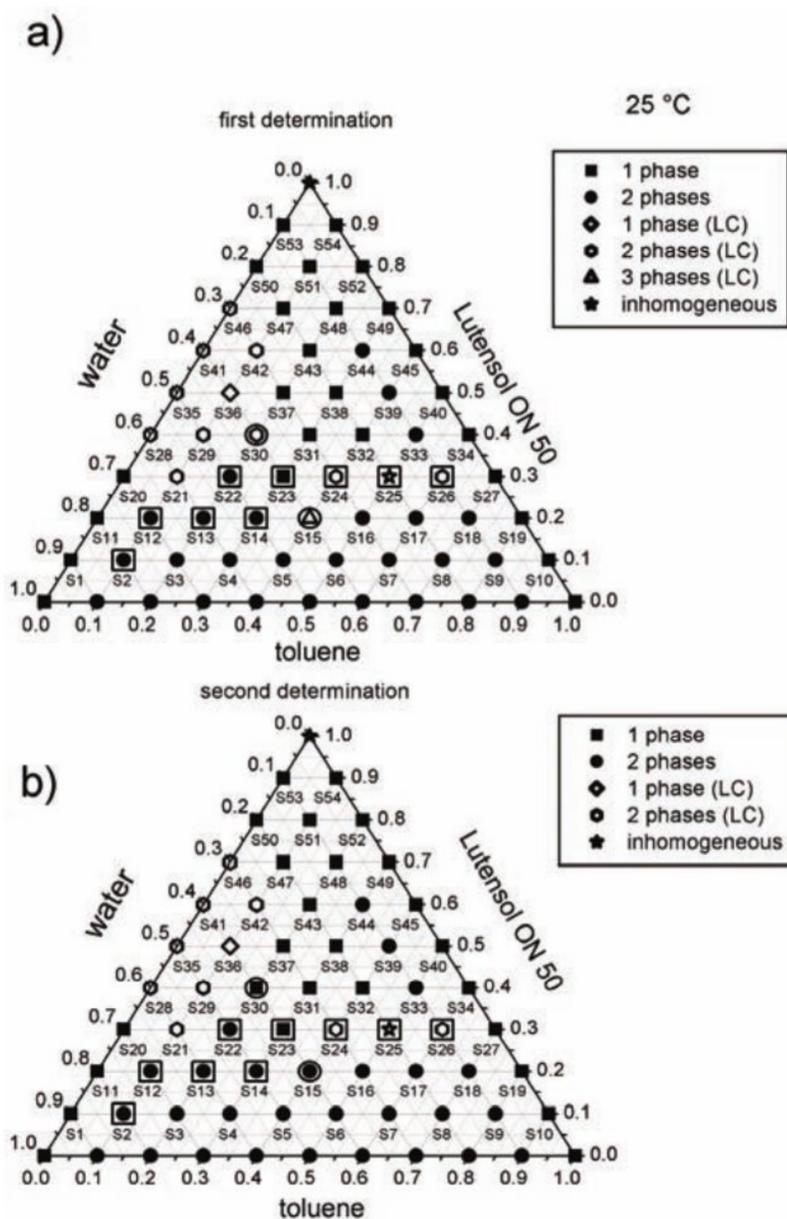

Figure 6. Isothermal phase diagrams of ternary mixtures of water, toluene and lutensol ON 50 at 25 °C. a) After preparation, shaking and equilibration for 64 h, and b) after first cooling from 30 °C without shaking followed by storage at 25 °C for 48 h and second shaking with Vortex followed by equilibration for 72 h. Samples with different behavior for both determinations are emphasized by an open circle surrounding the symbol. Open squares around the symbols indicate samples with ambiguous or inconsistent phase behavior at 25 °C. LC signifies samples containing liquid crystals.

At 25 °C, the results of the phase investigations were found to depend strongly on the pretreatment of the samples situated in the area of the Gibbs triangle which exhibited liquid crystals at 20 °C and room temperature. The samples for which ambiguous or inconsistent phase behavior was found are denoted in the phase diagrams with the numbers S2 at γ = 0.1, S12--S15 at γ = 0.2, S22-S26 at γ = 0.3 and S30 at γ = = 0.4. They are mostly situated near the surfactant

content for which determination of the "fish-diagram" became impossible (γ = 0.26) and are emphasized in the figures by circles or squares surrounding the symbol. In most of these samples (except S25, S26 and S30), liquid crystals formed between two optically isotropic phases after storage at varying room temperature (Figure 7a).
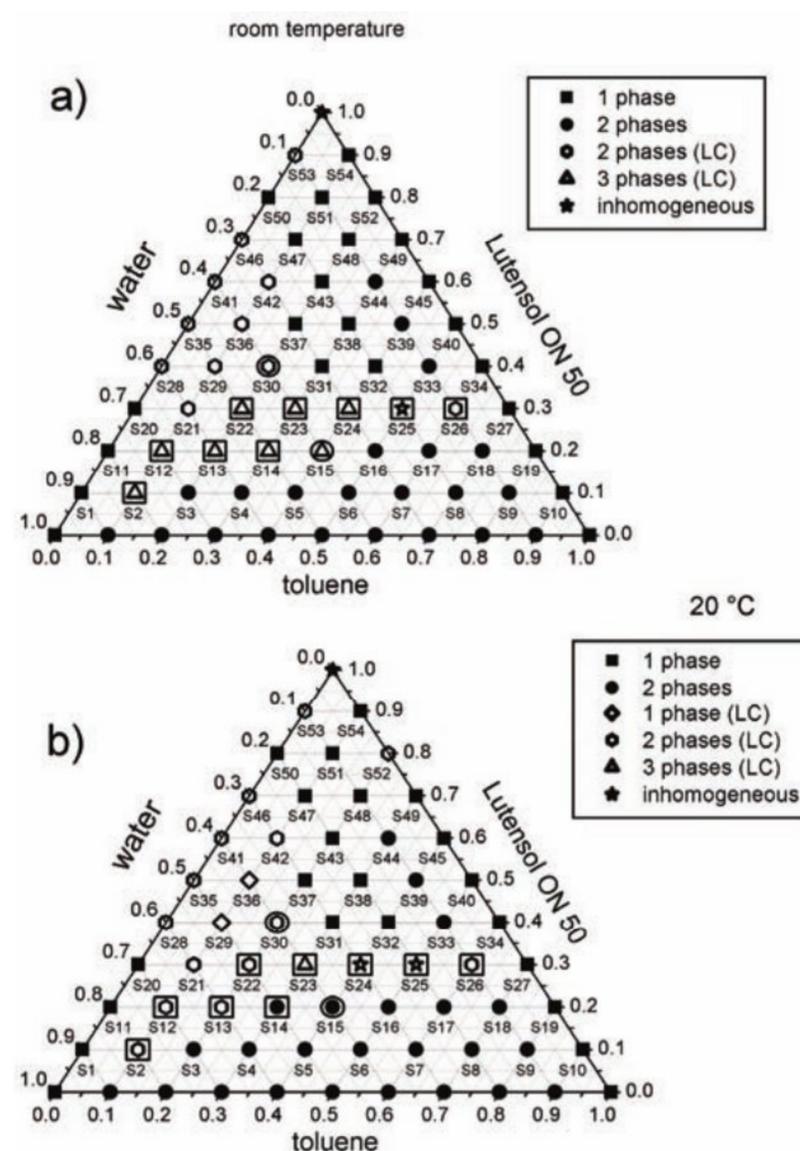

Figure 7. Isothermal phase diagrams of ternary mixtures of water, toluene and Lutensol ON 50, (a) after storage for 4 weeks without agitation at varying room temperature, and (b) at 20 °C after shaking and equilibration for 2 months. Open squares and circles indicate samples with ambiguous or inconsistent phase behavior at 25 °C. LC signifies samples containing liquid crystals.

This state was obviously a frozen metastable one, because only one of these samples, namely S23, showed the same behavior at 20 °C when the samples were shaken before storage. For some of the samples with γ ≤ 0.2 (S2, S13 and S15) a liquid crystalline phase forming between two isotropic phases was also found when cooling the samples from 30 to 25 °C without shaking (not shown). Other samples in the vicinity with γ = 0.2 (S12 and S14) formed two isotropic phases. Samples S2, S13, and S15 could also be converted into two isotropic phases by shaking and re-equilibration at 25 °C (Figure 6b). For the

first determination at 25 °C when the samples had been freshly prepared and were equilibrated for 16 plus additional 48 h, sample S15 had shown 3 phases (Figure 6a) with a liquid crystalline phase at the bottom. Sample S22 with $\gamma = 0.3$ yielded two phases, when it was cooled down from 30 to 25 °C without agitation (not shown). Vigorous shaking induced a change to a single phase. 72 h later during which the sample was held at 25 °C, the system had split into two isotropic phases again (Figure 6b). Two phases had also been observed during the first determination at 25 °C (Figure 6a) after 72 h equilibration time, *i.e.*, the results were identical for the same equilibration time.

In contrast, ambiguous results were found 25 °C for the neighboring sample with the same oil content S30 at $\gamma = 0.4$. It yielded a single phase for the second determination at 25 °C, whereas it had formed two phases including a liquid crystalline one during the first determination (Figure 6b). Sample S30 also exhibited liquid crystals when the sample was cooled down from 30 to 25 °C without agitation, but became single phase after subsequent shaking. Sample S23 was single phase for both determinations at 25 °C and exhibited 3 phases including a liquid crystalline one at varying room temperature and 20 °C. Although the results were identical at 25 °C and comparable for the lower temperatures, the results at 25 °C do not fit well to the liquid crystals found for samples S24 and S26 at this temperature, unless two different types of liquid crystals exist in the water-rich ($\alpha < 0.5$) and in the oil-rich region ($\alpha > 0.5$). Sample S24 with $\alpha = 0.571$ formed two phases at 25 °C from which the lower one was liquid crystalline. At varying room temperature, three phases were found with a liquid crystalline one in the middle. At 20 °C the sample looked inhomogeneous, but without any visible phase separation like the neighboring sample S25.

Sample S25 with $w_w = 0.2$, $w_o = 0.5$ and $\gamma = 0.3$ was visibly inhomogeneous for all determinations up to 25 °C, but phase separation could never be observed. The coexisting phases seem to have very similar density in this sample. Liquid crystals could not be identified S25 due to its extreme turbidity. At 30 °C, this sample was found to be single phase (Figure 5a and b). Sample S26 with $w_w = 0.1$, $w_o = 0.6$ and $\gamma = 0.3$ formed 2 phases with liquid crystals as the lower phase at all determinations up to 25 °C and a single phase at 30 °C. Phase separation at lower temperature needed at least three days for this sample.

The ambiguous results seem to be influenced by different effects which, however, interact, in particular near the "fishtail". Most samples with ambiguous or doubtful results were found for samples with surfactant content between 0.2 and 0.3. Liquid crystals were found for all these samples when they were left for some weeks at varying room temperature of 19-24 °C. They seem to play a decisive role in the behavior of the ternary system of water, toluene and lutensol ON 50. Liquid crystals may be intermediately formed due to gradients of composition during preparation of the samples or when material is exchanged between phases after temperature change. Their dissolution may be very slow so that long-lasting multi-phase systems can form which are not in thermodynamic equilibrium. Indeed, the differences between the phase diagrams obtained at varying room temperature by cooling down from 30 °C without agitation, and 20 °C by cooling down from 25 °C with manual shaking can be well explained with the intermediate formation of liquid crystals between the two liquid phases. Many of the samples showed three phases with a liquid crystal between the oil-rich and the water-rich phase at varying room temperature (Figure 7a), but only one (S23) at 20 °C (Figure 7b) when samples were manually shaken before storage.

However, not only the dissolution but also the formation of liquid crystals was found to be slow. Samples at very high surfactant content showed sometimes the formation of liquid crystals and sometimes not after longer time of storage. Samples at lower surfactant concentration may also be in a metastable state which needs extremely long times for equilibration and separation of a liquid crystalline phase owing to supercooling effects. Results for S22 and S30 at 25 °C could be a consequence of such behavior. The presence of liquid crystalline samples (S24 and S26) at temperatures up to 25 °C at the toluene-rich side of the Gibbs triangle isolated from the liquid crystals at the water-rich side supports this interpretation. However, it cannot be excluded, that two different types of liquid crystals exist like in the ternary system of water, toluene and Triton X-100 [5].

The ternary mixtures of toluene, water and lutensol ON 50 seem to form mini-emulsions near the "fishtail". Such metastable systems have the aspect of microemulsions, but they are not thermodynamically stable. The formation of a miniemulsion for the additional sample MINI in the hatched zone of Figure 1 is unusual, because the kinetic stability of those systems can only be achieved starting from the microemulsion or liquid crystalline state, by a considerable change of thermodynamic conditions (temperature [32] or composition [33-35]) as a rule. Metastable systems close to a single microemulsion droplet phase have already been observed and studied in

detail under gentle shear [35] and for sudden temperature changes [36] in the water-rich part of ternary systems, but not at equal masses of water and oil. The ambiguous behavior of sample S14 at 30 °C as well as findings for samples S22, S30 and sample MINI are rather a consequence of the formation of mini-emulsions, which might be relatively instable (S22) or exhibit long-lasting kinetic stability (S14 and MINI).

Dynamic light scattering

Dynamic light scattering was determined for a sample (DLS in Figure 1) with α = 0.5 and γ = 0.245 at 30 °C. This sample is situated in the hatched zone of Figure 1. The phase behavior of neighboring sample S14 (α = 0.375, γ = 0.2) was found to be dependent on the treatment in the isothermal phase diagrams (Figures 5-7). The system did not show any phase separation during the measurement. Nearly identical results were obtained for 4 consecutive measurements, averaging over all 4 measurements results in a decay time τ_0 = 203±2 μs. (data not shown). The fit with a single stretched exponential function for one of the measurements is shown in Figure 8.

The effective diffusion coefficient, $D_{eff,o}$, calculated from this value with Eq. (2) assuming the oil (toluene) as the continuous phase is 5.6×10^{-12} m^2 s^{-1}. With water as the continuous phase, the diffusion coefficient, $D_{eff,w}$, is 7.1×10^{-12} m^2 s^{-1}. The hydrodynamic radii calculated from the diffusion coefficients using Eq. (3) are $r_{h,o}$ = 75 nm for water dispersed in toluene and $r_{h,w}$ = 39 nm for toluene dispersed in water. The corresponding particle size distributions are shown as inset in Figure 8. Since both liquids are

continuous and bicontinuous microemulsions are not diluted systems with spherical particles, these values can give only a rough estimation of the structure and dynamics of the sample. Both diffusion coefficients are rather small and corresponding radii large for bicontinuous microemulsions compared with values found in the literature for other systems [3,26], but they are not beyond the limits which can be obtained for bicontinuous systems approaching a critical or tricritical point [3].

CONCLUSIONS

Long-lasting metastable states were found for the ternary mixture of water, toluene and the branched technical surfactant Lutensol ON 50 (i-C$_{10}$E$_5$) in large parts of the isothermal phase diagram at 25 °C. The number and type of phases were strongly dependent on the pretreatment. Slow formation as well as slow dissolution of liquid crystals was found for several compositions below 30 °C, indicating that the structural and/or the compositional equilibration of surfactant layers seems to be very slow. The equilibration was particularly slow near the point of optimum solubilization for the investigated ternary mixture. Diverging phase boundaries were found by visual observation. The point of optimum solubilization might be situated between 25 and 30 °C for surfactant content $\gamma \approx 0.25$. A kinetically stable miniemulsion was found at 25 °C for α = 0.5 and γ = 0.23, by sample preparation with a Vortex without using rapid changes of temperature or composition. With its unusual behavior, the ternary system of water, toluene and lutensol ON 50 seems to be an interesting base system for further
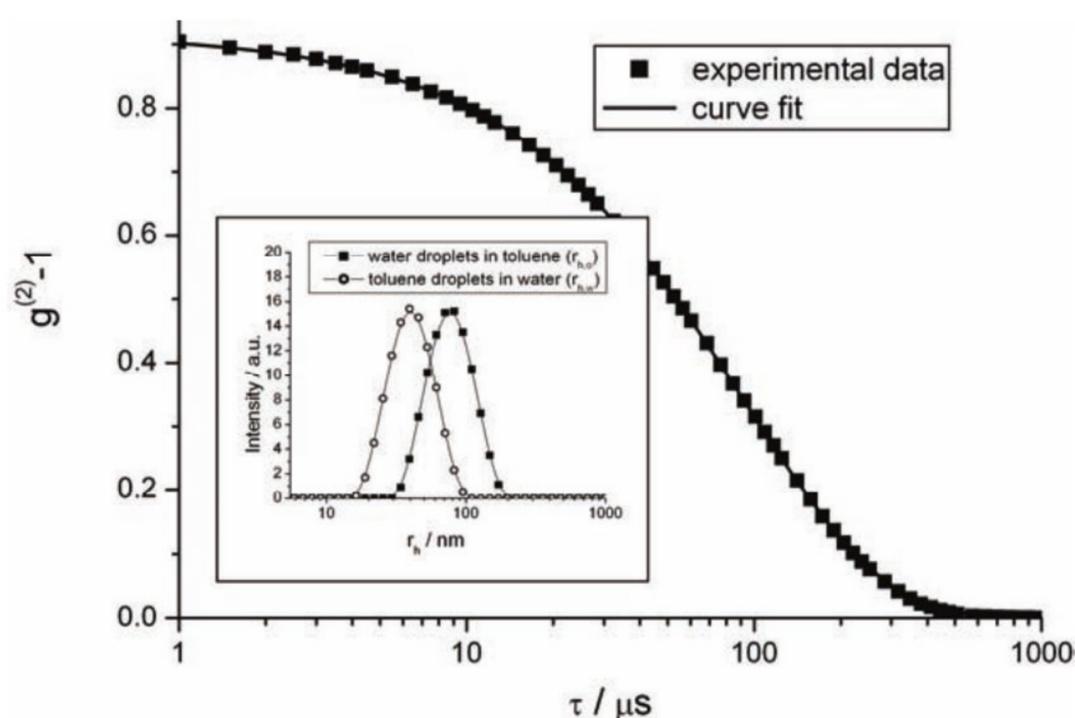

Figure 8. Correlation function $g^{(2)}$-1 of dynamic light scattering on sample DLS with γ = 0.245 at 30 °C. Inset: particle size distribution for water dispersed in toluene (■) and for toluene dispersed in water (○).

investigations that may yield new insight into the transitions between liquid crystals, microemulsions and mini-emulsions and to provide a microemulsion system for technical application.

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NAUČNI RAD

NEUOBIČAJENO SPORO USPOSTAVLJANJE RAVNOTEŽE MIKROEMULZIJA SA VODOM, TOLUENOM I TEHNIČKI RAZGRANATIM ALKIL POLIETOKSILATOM

Mikroemulzije na bazi vode, toluena i nejonskih površinski aktivnih supstanci su interesantni za primenu, zahvaljujući izvanrednim karakteristikama aromatičnih ugljovodonika kao rastvarača. U ovom radu, ispitivani su pseudo-binarni fazni dijagrami ("riba-dijagram") ternatnih sistema upotrebom tehnički razgranatog alkil polietoksilata. Kao pogodana površinski aktivna supstanca korišćen je Lutensol ON 50 (i-$C_{10}E_5$). Sistem sa tehnički razgranatim i-$C_{10}E_5$ pokazuje izuzetno dugo vreme za postizanje ravnoteže, iako sardžaj površinski aktivne supstance u sistemu odgovara optimalnoj rastvorljivosti (tj. minimalnom sadržaju površinski aktivne supstance koji je neophodan za bi-kontinualnu mikroemulziju). Pored vizuelnog posmatranja, kvalitativno merenje zmućenosti je vršeno UV-Vis spektroskopijom da bi se okarakterisalo neuobičajeno sporo uspostavljanje ravnoteže u sistemu. Izotermni fazni dijagrami na 20, 25 i 30 °C dali su rezultate nekonzistentne promeni temperature i primeni mehaničkog opterećenje za različit tretman uzoraka. Trokomponentna smeša vode, toluena i Lutensol ON 50 formira dugoživeća metastabilna stanja. Diskutovana je sporost i dvosmislenost ponašanja ovakvog sistema. Nekonzistentni rezultati su pripisani sporoj kinetici formiranja i razlaganja tečnih kristala, kao i sposobnosti sistema da formira mini mikroemulzije unutar neuobičajenog opsega koncentracija.

Ključne reči: mikroemulzija, toluen, oksoalkohol etoksilat, termodinamička stabilnost, ternarni fazni dijagrami, "riba" dijagrami.