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THE INFLUENCE OF ALKYL POLYGLUCO-SIDES (AND HIGHLY ETHOXYLATED ALCOHOL BOOSTERS) ON THE PHASE BEHAVIOR OF A WATER/TOLUENE/ /TECHNICAL ALKYL POLYETHOXYLATE MICROEMULSION SYSTEM

Article Highlights
- Addition of sugar surfactant to system of water/tolune/Lutensol ON 50 was investigated
- Sugar surfactant shifts the phase behavior to lower temperature
- Microemulsion of water/tolune/Lutensol ON 50 and alcohol ethoxylate $C_{18}E_{100}$ was investigated
- Strongly hydrophilic $C_{18}E_{100}$ shifted the one phase region to higher temperature

Abstract

The influence of additives (alkyl polyglucoside, Glucopon 600 CS UP and alcohol ethoxylate $C_{18}E_{100}$) on the behavior of the water/toluene/Lutensol ON 50 (technical oxoalcohol, $i\text{-}C_{10}E_5$) microemulsion system as a function of temperature and composition has been investigated. The phase behavior of the microemulsions was determined by vertical sections through the Gibbs phase prism (fish-like phase diagrams). Alkyl polyglucoside shifts the one phase region to lower temperatures compared with water/toluene/Lutensol ON 50 mixtures. This is contrary to the expectation, considering the extreme hydrophilic nature of the sugar headgroup. The addition of hydrophilic alcohol ethoxylate ($C_{18}E_{100}$) to the water/toluene/Lutensol ON 50 system increases the solubilization capacity of the surfactant, even if the co-surfactant is used in small quantities, and shifts the one-phase region to higher temperature by a few °C.

Keywords: microemulsion, toluene, alkyl polyglucoside, oxoalcohol ethoxylate, efficiency booster, "fish" diagrams.

Microemulsions are thermodynamically stable optically isotropic mixtures, consisting of two immiscible components, oil and water, made miscible by a third component, the surfactant. They may contain additives such as salt or alcohol. The properties of ternary nonionic surfactant/water/oil microemulsions are very interesting scientifically and technically. A convenient way to study these systems is to measure the phase behavior at constant oil/water ratios as a function of temperature, T, and surfactant mass fraction, γ.

The stability of microemulsions over a large temperature range and low surfactant concentration is required for technical applications. Some investigations [1,2] show that the use of surfactants with longer hydrophobic units reduces the amount of surfactant needed for microemulsification due to the increasing efficiency of the surfactant. Adding suitable additives such as sugar surfactants and nonionic alcohol ethoxylates received much attention in recent years. It was found that the addition of a small amount of polymer with amphiphilic properties to the microemulsion system increases the efficiency of the surfactant [3-10]. Alcohol ethoxylate surfactants are widely used for microemulsion applications. The phase behavior with respect to the length of the hydrocarbon tails and the number of ethylene oxide (EO) units depends on the purity of alcohol ethoxylates. The structure of the

hydrocarbon tail of the surfactant strongly influences the microemulsion behavior [11,12]. Technical grade alcohol ethoxylates usually contain mixtures of different alcohols and often exhibit a distribution over a large range of ethoxylation degrees.

In recent years, alkyl polyglucosides, a class of sugar surfactants, have received considerable interest as nonionic surfactants because of their excellent biodegradability, ease of manufacture from renewable resources, such as sugar and vegetable oil feedstocks [13], and potential use in a large number of industrial applications [14-19]. One potential use of sugar surfactants is in microemulsion formulations. Making microemulsions with alkyl polyglucosides is difficult owing to the low surfactant solubility in many classes of oils. Fundamentally, it is of substantial interest to form microemulsions with sugar surfactant as co-surfactant or to form sugar surfactant-based microemulsions using co-surfactant.

Alkyl polyglucosides, abbreviated as C_mG_n, represent complex mixtures [20] where m is the number of carbon atoms in the hydrocarbon chain and n is the average number of glucose units in the hydrophilic headgroup. The nonionic surfactants, *n*-alkyl polyglycol ethers (C_iE_j) are typically used. These surfactants contain i carbon atoms in the hydrophobic alkyl chain and j ethoxy units in the hydrophilic headgroup. The phase behavior of microemulsion systems containing alkyl polyglucoside has been studied by some authors [21-23].

In the last decades, a lot of papers were published concerning many aspects of polymers in microemulsions, such as solubilization efficiency boosting by amphiphilic polymers in microemulsions [24-26]. The influence of various polymers on the phase equilibrium of microemulsions containing nonionic surfactant, water and oil, has also been studied. It was found that water-soluble polymers expelled into the coexistent water phase cause the coexistence of the lamellar phase with water, which does not appear in the absence of polymer [27].

In this work, we studied the phase behavior of Lutensol ON 50-based microemulsions after addition of alkyl polyglucoside Glucopon 600 CS UP as a co-surfactant or a hydrophilic alcohol ethoxylate ($C_{18}E_{100}$) as an efficiency booster [28].

MATERIALS AND METHODS

Toluene (purity 99% by GC) was purchased from Merck Schuchardt (Germany). Octaethylene glycol decylether ($C_{10}E_8$, octaethyleneoxide decylether) with purity higher than 98% (GC) was purchased from Fluka (Germany). It has a hydrophilic-lipophilic bal-

ance (HLB) of 13.8, according to Griffin [29]. Lutensol ON 50 (C_{10} oxoalcohol polyethoxylate with an average of 5 ethylene oxide units, i-$C_{10}E_5$) is a commercial nonionic surfactant of BASF AG, Ludwigshafen (Germany). It has a HLB of 11.5 (technical information sheet of BASF).

Glucopon 600 CS UP alkyl polyglucoside (alkyl chain containing 10 to 16 carbon atoms, and an average number of glucose units of 1.4) is a commercial nonionic sugar surfactant containing 51% active matter and 49 mass% water (technical information sheet of Cognis, Monheim, Germany). The alcohol ethoxylate $C_{18}E_{100}$ was synthesized under argon using a high vacuum line by Frank *et al.* [28] in the laboratory of JCNS-1 at Forschungszentrum, Jülich. Water was deionized and twice distilled.

Phase diagram determination

Kahlweit *et al.* [30,31] introduced a way of studying the phase behavior of ternary or quaternary mixtures. A procedure to obtain an overview of the phases is to draw the phase diagram at a constant oil/water ratio as a function of temperature, T, and surfactant mass fraction, γ. The phase boundaries resemble the shape of a fish. Typically, temperature-composition phase diagrams obtained for a 1/1 mass ratio of oil and water show a one-phase microemulsion at relatively high surfactant concentration. At lower surfactant concentration a three-phase body exists consisting of a middle-phase microemulsion in equilibrium with excess phases of oil and water, surrounded by two-phase regions illustrated as $\underline{2\overline{\Phi}}$ and $\overline{2\Phi}$. When a surfactant is mainly dissolved in water and two phases consist of a surfactant-rich water (lower) phase in equilibrium with an excess oil phase, the region is denoted as $\underline{2\phi}$. At high temperature a nonionic surfactant is more soluble in oil and forms a surfactant-rich oil (upper) phase in equilibrium with an excess water phase denoted $\overline{2\Phi}$ (Figure 1).
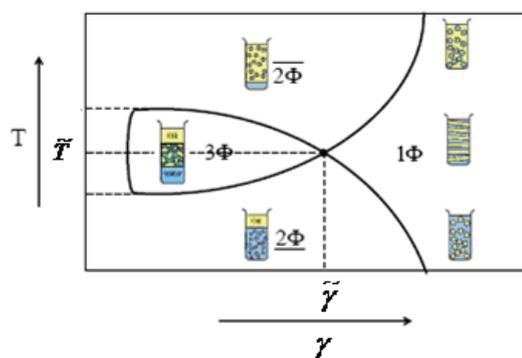

Figure 1. Schematic "fish cut" phase diagram of a nonionic microemulsion with equal water to oil proportions as a function of surfactant concentration.

The convenient variables are the temperature and the following composition variables (pressure is always kept constant) - the mass fraction of oil in the mixture of water and oil:

$$\alpha = m_B/(m_A + m_B) \tag{1}$$

The mass fraction of surfactant in the mixture of all three components in ternary mixtures:

$$\gamma = m_C/(m_A + m_B + m_C) \tag{2}$$

or:

$$\gamma = (m_C + m_D)/(m_A + m_B + m_C + m_D) \tag{3}$$

when two surfactants or mixtures of surfactant and co-surfactant are used. In this case, the mass fraction of one of the surface-active components (δ) in the mixture is defined as:

$$\delta = m_C/(m_C + m_D) \tag{4}$$

where the capital indices A, B, C, D refer to the components, water, oil, surfactant and co-surfactant, respectively.

The so-called $\tilde{\gamma}$-point, where the three-phase body meets the one-phase region, defines the minimum mass fraction of surfactant needed to solubilize water and oil and is a measure for the efficiency of the surfactant. The corresponding temperature, $\tilde{T}$, is a measure for the phase inversion temperature (*PIT*).

The phase diagrams were recorded by successively adding water and oil to the initial water-oil-surfactant mixture. The samples were prepared by weighing appropriate amounts of components (1:1 ratio of oil to water) on 0.1 mg precision scales in the order surfactant, toluene, water to suppress intermediate formation of liquid crystals. The mass fraction of the surfactant (or surfactant/additive) is calculated with Eqs. (2) or (3) and the mass fraction of the additive in the surfactant /additive mixture with Eq. (4).

Samples were weighed into test tubes, which were immediately sealed (glass stoppers) and put into a thermostated water bath with temperature control up to 0.2 °C. In the thermostated bath, the mixtures were stirred with small magnetic stirrers to ensure complete mixing of the components at the given temperature. After equilibrium was established, the occurring phases were characterized by visual inspection between crossed polarizers.

RESULTS AND DISCUSSION

The pseudo-binary phase diagrams of microemulsion systems were determined at equal mass fractions of water and toluene ($\alpha = 0.5$) for two nonionic surfactants, pure linear $C_{10}E_8$ and technical branched i-$C_{10}E_5$ (Lutensol ON 50) in order to find the composition and temperature of optimum solubilization (Figure 2).
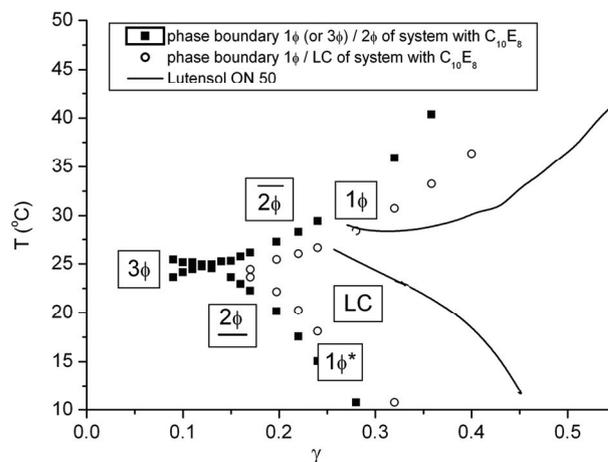

Figure 2. Phase diagrams of water/toluene/$C_{10}E_8$ and water/toluene/Lutensol ON 50 at equal mass fractions of water and toluene ($\alpha = 0.5$).

The phase boundaries of the system with $C_{10}E_8$ meet at $\tilde{\gamma} = 0.123$, $\tilde{T} = 24.9$ °C. Beyond that point, a single homogeneous phase appears, when the mass fraction of surfactant γ is further increased. Thus, this point where the three-phase (3ϕ) and one-phase regions (1ϕ) meet represents the lowest surfactant concentration needed to solubilize equal masses of the two immiscible components, water and toluene. At lower temperatures the microemulsion coexists with excess oil (denoted by $2\underline{\Phi}$). At higher temperatures the microemulsion coexists with excess water ($\overline{2\Phi}$). This system exhibits a strong tendency to form liquid crystals. Its phase diagram shows a large area of liquid crystals (LC) surrounded by microemulsion (regions 1ϕ and $1\phi^*$). These results are very similar to those reported for the same system with equal volume fraction ϕ of water and toluene, *i.e.*, lower mass fraction α of oil ($\alpha \approx 0.465$). In that case, the "fishtail point" was found at $\tilde{\gamma} = 0.114$ and $\tilde{T} = 24.34$ °C [32]. Owing to the lower density difference of toluene and water compared to alkane systems, the samples exhibit somewhat slower phase separation. The bicontinuous microemulsion containing water, toluene and $C_{10}E_8$ also shows some unusual behavior at low temperatures. Shear-induced birefringence was observed between crossed polarizers in the region denoted $1\phi^*$ while stirring the sample.

For the water/toluene/Lutensol ON 50 system, the determination of the point of optimum solubilization of equal masses of water and toluene failed. At high γ values, a single homogeneous phase (1ϕ) was

found in a temperature range similar to that of the $C_{10}E_8$ system, but with considerably higher surfactant content needed for mutual solubilization of both water and toluene. The shape of the "fishtail" is also not symmetrical with respect to temperature. This behavior is typical for technical surfactants with a distribution of more or less hydrophobic components due to different degrees of ethoxylation [10]. In contrast to the system with linear $C_{10}E_8$, no liquid crystals are found within the region of the bicontinuous microemulsion (1ϕ) indicating a less rigid structure of the surfactant layer at the interface between the oil and the water micro--phases. Approaching the composition of optimum soulubilization of equal masses of water and toluene, samples with the branched technical surfactant needed very long and sometimes extremely long times for equilibration after agitation or temperature changes. They show delayed visible phase separation and the phase boundaries to the two-phase regions determined visually are diverging.

Using the ternary mixtures water/toluene/Lutensol ON 50 as a base case, the role of added substances, sugar surfactant and hydrophilic alcohol ethoxylate on the phase behavior is explored.

Effect of alkyl polyglucoside (Glucopon 600 CS UP): Phase behavior as a function of δ

Figure 3 shows the temperature-composition phase diagram at mass fraction α = 0.5 for the quaternary system water/toluene/Lutensol ON 50/Glucopon 600 CS UP for varying fractions of sugar surfactant, δ (0.05, 0.10 or 0.20).

The water/toluene/Lutensol ON 50 "fish" (δ = 0) is shown for reference in Figure 3. As can be seen, with the addition of C_mG_n, the homogeneous micro-emulsion region ("fish tail" with the phase sequence $\overline{2\Phi}$-1-$\overline{2\Phi}$) becomes wider and the efficiency of the surfactant mixture increases slightly.

With increasing δ, the "fish tail" unexpectedly moves downward on the temperature scale despite the hydrophilic nature of the sugar surfactant. The efficiency of the surfactant mixture increases with increasing δ. In these quaternary systems the location of $\tilde{\gamma}$ is not determined because, in contradiction to many other microemulsion systems, equilibration for the system water/toluene/Lutensol ON 50 was particularly slow near the point of optimum solubilization for the investigated ternary mixture (see Figure 1).

Effect of hydrophilic alcohol ethoxylate

The effect of small amounts of hydrophilic alcohol ethoxylate $C_{18}E_{100}$, on the location and width of the one-phase region was investigated.

Figure 4 shows phase diagrams for the water/toluene/Lutensol ON 50 system with and without addition of $C_{18}E_{100}$. In this presentation the oil mass fraction is α = 0.5 and the mass fraction of additive is δ = 0.01. Compared with the system without additive, the one-phase region with additive is shifted to higher temperature. This effect can be explained by the large hydrophilic moiety of $C_{18}E_{100}$.

For higher content of $C_{18}E_{100}$, formation of liquid crystals was observed, which makes the system unsuitable for many applications (data not shown).
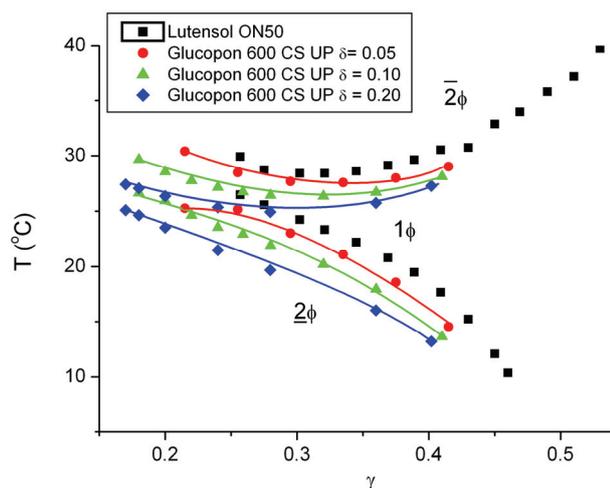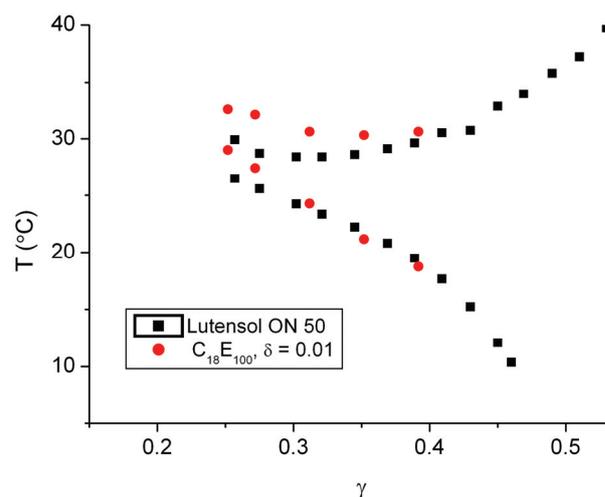

Figure 3. Temperature-composition phase diagram at water to toluene mass fraction α = 0.5 for the system water/toluene/Lutensol ON 50 with added sugar surfactant, Glucopon 600 CS UP , for varying mass fractions of sugar surfactant, δ (.05, 0.10 or 0.20).

Figure 4. Temperature-composition phase diagram at water to toluene mass fraction α = 0.5 of the water/toluene/Lutensol ON 50 system with $C_{18}E_{100}$ as additive (mass fraction δ = 0.01).

CONCLUSIONS

We have studied the phase behavior of water/ /toluene/Lutensol ON 50/Glucopon 600 CS UP and water/toluene/Lutensol ON 50/$C_{18}E_{100}$ mixtures as a function of temperature and composition. Both additives lead to improved solubilization and shift the one-phase region to lower surfactant content near to the values obtained for pure $C_{10}E_8$.

The addition of the alkyl polyglucoside, Glucopon 600 CS UP, to the ternary water/toluene/Lutensol ON 50 system additionally shifts the phase behavior to lower temperature. This behavior is unexpected, because the sugar surfactant is absolutely insoluble in toluene and should act as a hydrophilic surfactant. It should rather increase the temperature for the one-phase region. No formation of liquid crystals was observed by the addition of Glucopon 600 CS UP. The microemulsion consisting of water, toluene, Lutensol ON 50 and alcohol ethoxylate $C_{18}E_{100}$ as an additive also increases the efficiency of the surfactant system, but shifts the one-phase region to higher temperature, as expected. The formation of liquid crystals at higher content of $C_{18}E_{100}$, however, makes this additive less suitable. These findings make the sugar surfactant a better choice for improving the ternary system water/ /toluene/Lutensol ON 50 with respect to applications. Alkyl polyglucosides are also preferable because of their outstanding ecological and biological properties.

Nomenclature

C_iE_j	*n*-alkyl polyglycol ethers
C_mG_n	alkyl polyglucosides
EO	ethylene oxide units
HLB	hydrophile-lipophile balance
T	temperature
$\tilde{T}$	phase inversion temperature
γ	surfactant mass fraction

Acknowledgments

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NAUČNI RAD

UTICAJ ALKILPOLIGLUKOSIDA (I ALKOHOLA VISOKOG STEPENA ETOKSILACIJE U ULOZI POJAČIVAČA) NA FAZNO PONAŠANJE MIKROEMULZIONOG SISTEMA VODA/TOLUOL/TEHNIČKI ALKIL POLIETOKSILAT

Ispitivan je uticaj aditiva (alkil poliglukosida, Glukopon 600 CS UP, i alkohol-etoksilata $C_{18}E_{100}$) na fazno ponašanje mikroemulzionog sistema voda/toluol/lutensol ON 50 (tehnički oksoalkohol, i-$C_{10}E_5$) u funkciji temperature i sastava sistema. Za određivanje faznog ponašanja u mikroemulziji korišćeni su vertikalni preseci Gibbs-ovih faznih prizmi (dijagrami oblika tela ribe). Jednofazni region sistema voda/toluol/Lutensol ON 50 dodatkom alkil poliglukozida se pomera ka nižim temperaturama. Ovakvo ponašanje je suprotno očekivanom, polazeći od izrazito hidrofilne prirode glave molekula površinski aktivnog šećera. Dodatak malih količina hidrofilnog alcohol etoksilata ($C_{18}E_{100}$) sistemu voda/toluol/Lutensol ON 50, povecava kapacitet rastvaranja površinski aktivne supstance i pomera jednofazni region sistema ka višim temperaturama.

Ključne reči: mikroemulzija, toluol, alkil poliglukozid, oksoalkohol etoksilat, aditiv-pojačivač, "riba" dijagram.