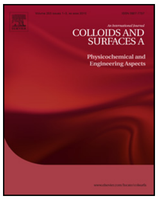
Colloids and Surfaces A: Physicochem. Eng. Aspects 494 (2016) 139–146

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa



Alcohol as tuning parameter in an IL-containing microemulsion: The quaternary system EAN–*n*-octane–$C_{12}E_3$–1-octanol

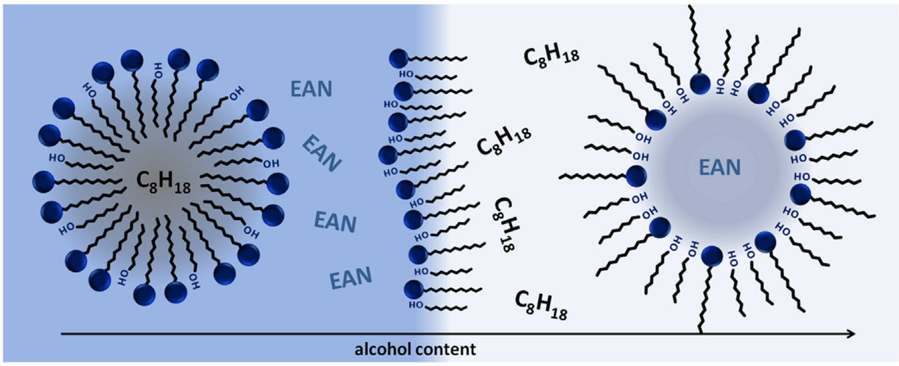
Jan C. Thater, Thomas Sottmann, Cosima Stubenrauch*

Universität Stuttgart, Institut für Physikalische Chemie, Pfaffenwaldring 55, 70569 Stuttgart, Germany

HIGHLIGHTS

- Alcohol as tuning parameter for the curvature in an IL-containing microemulsion.
- General patterns of IL- and water-containing microemulsions: similarities and differences.
- Discussion of monomeric solubilities of both surfactant and alcohol.
- First values for the saddle-splay and the bending rigidity of an IL-containing microemulsion.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 21 October 2015
Received in revised form
16 December 2015
Accepted 18 December 2015
Available online 24 December 2015

Keywords:
Microemulsions with ionic liquids
Phase behavior
Interfacial tension
Self-diffusion NMR
Alcohol as tuning parameter

ABSTRACT

With an appropriate tuning parameter a microemulsion can be forced to undergo a phase inversion, *i.e.* to invert the curvature of the amphiphilic film. In microemulsions consisting of water, an *n*-alkane and a nonionic alkyl polyglycolether (C_iE_j) temperature is an appropriate parameter since the surfactant head groups dehydrate with increasing temperature. Recently we were able to show that this also holds true for ethylammonium nitrate (EAN)–*n*-alkane–C_iE_j systems. However, the temperature sensitivity is weaker which is why we decided to use a hydrophobic cosurfactant to induce a phase inversion in the EAN-containing microemulsion. We studied the quaternary system EAN–*n*-octane–$C_{12}E_3$ – 1-octanol as a function of the alcohol concentration at $T = 15\,^{\circ}\mathrm{C}$ and found the same trends as for the aqueous counterparts. (1) Studying the phase behavior as a function of the alcohol content (δ) and of the total surfactant concentration (γ), one finds that the phase boundaries resemble the shape of a fish. (2) Measuring the interfacial tension σ between the IL- and oil-rich phase, one observes a minimum in the center of the three-phase region. (3) NMR self-diffusion measurements reveal a transition from an oil-in-EAN microemulsion to a bicontinuous microemulsion and finally to an EAN-in-oil microemulsion.

1. Introduction

The properties of ternary microemulsions composed of water, an alkane, and a nonionic surfactant of the alkyl polyglycolether (C_iE_j) type are known to be temperature sensitive [1–3]. With increasing temperature a phase inversion is observed, *i.e.* that the curvature of the amphiphilic film changes from being curved around the oil to being curved around the water [4]. This observation can be explained by the fact that the size of the hydration shell surrounding the polar head group of the surfactant shrinks with increasing temperature, whereas the size of the hydrophobic chain increases due to an increasing number of chain conforma-

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* Corresponding author. Fax: +49 711 68564443.
E-mail address: cosima.stubenrauch@ipc.uni-stuttgart.de (C. Stubenrauch).

http://dx.doi.org/10.1016/j.colsurfa.2015.12.021

tions and the increasing penetration of oil molecules. This change of the interfacial curvature results in a change of the microemulsion's microstructure [4,5]. Furthermore, it has been shown that the curvature of the amphiphilic film is the most relevant parameter for other important properties of microemulsions such as the phase behavior [6] and the interfacial tension [4,7–9].

In the 1980s, Evans et al. observed micelle formation of TX-100 in the protic ionic liquid (IL) ethylammonium nitrate (EAN) and postulated the existence of networks of hydrogen bonds in the IL [10]. It is not surprising that a solvent which forms hydrogen bonds and in which micelles are formed [10,11] makes the formulation of microemulsions possible. Thus, non-aqueous microemulsions were formulated with the aforementioned protic ionic liquid EAN [12,13]. It was shown that both nonionic surfactants [12] and ionic surfactants [13] can be used to stabilize microemulsions with EAN. Atkin and Warr found a temperature sensitive phase behavior for microemulsions consisting of EAN, an *n*-alkane, and a nonionic surfactant which mirrors the behavior known from water–*n*-alkane–C_iE_j systems discussed above [12]. Recently we were able to show that the systems investigated by Atkin and Warr also possess other characteristic properties known from the aqueous counterparts [14]. Firstly, the ionic liquid/oil interfacial tension runs through a minimum in the range of the phase inversion temperature. Secondly, NMR self-diffusion measurements reveal a structure of oil droplets in a continuous EAN phase at temperatures below the phase inversion temperature. Around the phase inversion temperature the microemulsion is bicontinuous and at temperatures above the phase inversion temperature a continuous oil phase was found. We found that – other than in the aqueous counterparts – the amount of EAN dispersed in the oil phase is very small. Although the exact reason for this behavior remains unclear, the most likely explanation is based on the fact that EAN by itself exhibits a sponge-like microstructure similar to the structure of bicontinuous microemulsions but with a smaller domain size of 1 nm [15]. A confinement of this structure in nanosized droplets is unfavorable, which is why EAN prefers to form an excess phase rather than nanosized droplets.

For possible applications of IL-containing microemulsions temperature may not be a suitable tuning parameter, which is primarily due to the fact that the temperature sensitivity is not as pronounced as in the case of microemulsions containing H_2O. Furthermore, for microemulsions with aprotic ionic liquids, where a formation of hydrogen bonds between the IL and the surfactant's head group is impossible, temperature may not be a relevant tuning parameter at all [16]. In the case of aqueous microemulsions the cosurfactant/surfactant-ratio was used as an alternative tuning parameter for the film curvature [17,18]. Penders and Strey were able to show that the addition of 1-octanol to a microemulsion consisting of water, *n*-octane, and the nonionic surfactant C_8E_5 at constant temperature has the same effect on the phase behavior as an increase of the temperature [19]. This finding has turned out to be crucial for the formulation of microemulsions with surfactants that are not temperature-sensitive at all, *e.g.* *n*-alkylpolyglucosides [20–23]. The addition of a long-chain alcohol to the microemulsion has two effects. Firstly, alcohol molecules monomerically dissolve in the oil phase, thus rendering the oil phase less hydrophobic. Secondly, alcohol molecules adsorb at the amphiphilic film, causing a change of the curvature. Since the OH-group of the alcohol is much smaller than the head group of the surfactant, the average head group size decreases with increasing alcohol content in the amphiphilic film. Consequently, increasing the alcohol concentration finally forces a microemulsion to undergo a phase inversion from an oil-in-water microemulsion to a water-in-oil microemulsion [19,21]. The progression of the values for interfacial tensions [19,21,24] and of the self-diffusion coefficients [23,25] which one observes as a function of the interfacial cosurfactant content in quaternary systems corresponds to the changes known from a variation of the temperature in ternary systems [4]. In other words, the role of the temperature to tune the properties of microemulsion systems can be taken over by a cosurfactant (in the case of hydrophilic surfactants this is typically a medium or a long chain alcohol) [24].

The paper at hand deals with the question of whether or not an alcohol can be used as tuning parameter in IL-containing microemulsion systems. Although an alcohol (1-decanol) has already been added to EAN-containing microemulsions stabilized by an ionic surfactant, phase behavior and microstructure were investigated only for constant cosurfactant mass fractions [13,26,27]. Thus it is not yet clear if the amount of added alcohol is a suitable tuning parameter for the adjustment of microemulsions' properties. Since we recently investigated the temperature dependent behavior of the ternary system [14] EAN–*n*-octane–$C_{12}E_3$, we chose the corresponding quaternary system EAN–*n*-octane–$C_{12}E_3$–1-octanol as a model system to investigate the effect of the addition of 1-octanol on the phase behavior, on the EAN/oil-interfacial tension σ_{ab} and on the microstructure. For this purpose we determined the δ,γ-phase diagram and we measured the interfacial tension σ_{ab} via spinning drop tensiometry. Additionally, we determined the self-diffusion coefficients of the two solvents and of the surfactant with pulsed field gradient (PFG) NMR spectroscopy to distinguish between continuous and discrete domains.

2. Material and methods

2.1. Materials

The ionic liquid ethylammonium nitrate (EAN) (purity > 97%) was purchased from Iolitec (Heilbronn, Germany). A detailed discussion about how impurities and water in the IL influence the phase behavior can be found in our previous study [14]. The surfactant triethylene glycolmonododecylether ($C_{12}E_3$) (purity > 95%) was purchased from TCI (Zwijndrecht, Belgium). 1-Octanol (purity ≥ 99%) and *n*-octane (purity ≥ 99%) were purchased from Sigma–Aldrich (Steinheim, Germany). All compounds were used without further purification.

2.2. Sample preparation

In analogy with previous publications on the properties of the microemulsion system EAN–*n*-alkane–C_iE_j [12,14] all experiments were performed with equal masses of EAN and *n*-octane ($\alpha = 0.50$). The *n*-octane mass fraction in the mixture of *n*-octane and EAN is defined as

$$\alpha = \frac{m_B}{m_A + m_B} \tag{1}$$

with m_B being the mass of the *n*-octane and m_A being the mass of EAN. The established procedure to investigate the effect of a cosurfactant (*e.g.* an alcohol) on the phase behavior is to determine the δ,γ-diagram [19,21,23]. This phase diagram resembles the T,γ-diagram which is generally monitored if one wants to characterize the temperature dependent phase behavior of symmetric microemulsions [3,4]. Such T,γ-diagrams were also used to investigate the temperature dependence of the ternary system EAN–*n*-alkane–C_iE_j [12,14]. The amount of cosurfactant is given by the mass fraction of alcohol in the alcohol/surfactant mixture, *i.e.*

$$\delta = \frac{m_D}{m_C + m_D} \tag{2}$$

where m_C and m_D are the mass of surfactant and cosurfactant, respectively. In contrast to ternary T,γ-diagrams, where γ denotes