Journal of Colloid and Interface Science 453 (2015) 186–193

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

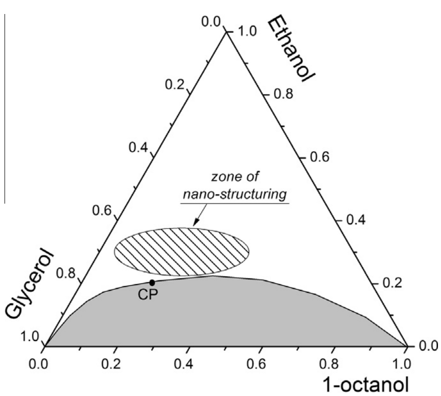
www.elsevier.com/locate/jcis

Toward surfactant-free and water-free microemulsions

Veronika Fischer [a], Julien Marcus [a], Didier Touraud [a], Olivier Diat [b], Werner Kunz [a,*]

[a] Institute of Physical and Theoretical Chemistry, University of Regensburg, 93040 Regensburg, Germany
[b] Institut de Chimie Séparative de Marcoule, UMR 5257 (CEA/CNRS/UM/ENSCM), 30207 Bagnols sur Cèze, France

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 18 March 2015
Accepted 30 April 2015
Available online 9 May 2015

Keywords:
Surfactant-free microemulsions
Water-free microemulsions
Dynamic light scattering
Small-angle X-ray scattering
Fluctuations of nano-structures

ABSTRACT

It was recently demonstrated that a nano-clustering was present in the monophasic “pre-Ouzo” region of ternary liquid mixtures without surfactants. The goal of this work is to check if this nano-clustering is also present in the surfactant-free and water-free “green” microemulsions glycerol/ethanol/1-octanol and deep eutectic solvent/tetrahydrofurfuryl alcohol/diethyl adipate. The deep eutectic solvents used instead of water were ethylene glycol–choline chloride (molar ratio 4–1) and urea–choline chloride (molar ratio 2–1). To our knowledge this is the first time that deep eutectic solvents were used to formulate microemulsions. The surfactant-free and water-free microemulsions were studied using phase diagrams, dynamic light scattering, and small-angle X-ray scattering. The presence of aggregate fluctuations was demonstrated and they were found to be independent of molecular critical fluctuations, except when approaching the critical point where the critical phenomenon is superimposed to the signal. These structures have similarities to classical microemulsions but, in contrast to them, without having a sharp interface between the non-miscible phases, much as it was the case for systems previously investigated like water/ethanol/oil, where the oil was 1-octanol, fragrance molecules, or mosquito repellents.

1. Introduction

Microemulsions are macroscopically homogeneous liquids composed of polar and non-polar constituents. A surfactant and, usually, a cosurfactant are necessary to obtain these translucid and thermodynamically stable solutions [1–3]. According to Winsor, microemulsions can be either a one-phase system

* Corresponding author. Fax: +49 941 943 4532.
E-mail addresses: veronika.fischer@ur.de (V. Fischer), julien1.marcus@ur.de (J. Marcus), didier.touraud@ur.de (D. Touraud), olivier.diat@cea.fr (O. Diat), werner.kunz@ur.de (W. Kunz).

http://dx.doi.org/10.1016/j.jcis.2015.04.069
0021-9797/

(Winsor IV) or part of a multi-phase system as Winsor I, II, or III when it is in equilibrium with the oil phase, the aqueous phase or both phases, respectively [4]. Depending on the composition, a microemulsion can be of three different types: water-in-oil, bicontinuous or oil-in-water. In every case, the surfactant and cosurfactant form always an interfacial film between the aqueous and oil phases. Microemulsions have been proven useful, particularly in the area of enhanced oil recovery [5] but also in the cosmetic [6–8], food [9,10], and pharmaceutical industries [11–13] or as cleaning agents [14,15].

Most examples concerning microemulsions are given by considering the polar constituent as aqueous phase. An aqueous phase is of course the most common one, but it is not essential for the formulation of a microemulsion. In literature many papers deal with water-free microemulsions and their interesting properties. The pioneers in this field were Lattes et al. They replaced water by formamide in a system containing cyclohexane as oil and butanol as cosurfactant and studied the influence of two different surfactants [16]. They published several papers using formamide as a highly structured solvent and used the resulting non-aqueous microemulsion for example as reaction medium to perform Diels–Alder reactions [17–19]. Harrar et al. have studied a non-aqueous microemulsion containing the ionic liquid [emim][$etSO_4$], the oil limonene and the surfactant Triton X-114 [20]. They observed that large temperature stability down to −35 °C can be achieved using high amounts of ionic liquid, which traces the way for applications in extraction processes or as reaction media for water-sensible reactions. Concerning perfumes, the effect of humidity on evaporation from aqueous and non-aqueous microemulsions containing perfume was investigated by Hamdan et al. They observed that the weight loss is greater at lower humidity for both systems, but is higher for the aqueous system [21]. Further, other water-free microemulsions were studied like the system ethylene glycol/sodium dodecyl sulfate (SDS)/decanol/toluene by Friberg et al., who found a critical point in the system [22] or the system N,N-dimethylacetamide (DMA)/sodium di-(2-ethylhexyl) sulfosuccinate (AOT)/octane by Cai et al., who examined the critical behavior of the non-aqueous microemulsion [23]. A quantitative determination of the percolation threshold in water-free microemulsions was also described by Peyrelasse et al. [24]. They showed that a model for microemulsion could be successfully applied for non-aqueous microemulsions. The self-assembly of amphiphiles in the absence of water, the capability of reverse micelles to encapsulate non-aqueous polar organic solvents, the use of ionic liquids, or the possibility to employ non-aqueous reverse micelles as nano-reactors are examples of current research topics on water-free microemulsions [25].

Further to water-free microemulsions, surfactant-free microemulsions are currently investigated at our institute. As it is well known now, the necessary condition for the so-called Ouzo effect (fine and very stable emulsions without surfactants) is the rapid addition of water, or any other solvent, to a highly or entirely miscible second solvent (e.g. ethanol) and a third component that is highly soluble in the second solvent, but not in the first one (e.g. anethole or octanol). While studying the Ouzo effect, it was discovered that nano-structures were present in the single-phase region, near the demixing boundary. We called this phenomenon the "pre-Ouzo effect" [26]. The presence of these nano-structures was studied using dynamic and static light scattering in surfactant-free microemulsions containing various types of hydrophobic liquids, i.e. in the ternary mixtures water/benzyl alcohol/ethanol, or with ethyl lactate or γ-valerolactone [27]. To gain more knowledge about the molecular-level shape and the structure of these aggregates, molecular dynamics simulations were carried out with the system water/ethanol/octanol [28]. And indeed, swollen micelle-like aggregates were observed in the pre-Ouzo region. Combining small-angle neutron scattering with small- and wide-angle X-ray scattering Diat et al. found that the single-phase in the pre-Ouzo region consists of two distinct nanoscopic pseudo-phases, one octanol-rich and one water-rich [29]. The ethanol molecules were distributed between octanol-rich nano-domains and a water pseudo-phase with a slight accumulation at the interface and an exponential decay concentration on the water side. They could calculate the distribution coefficient of ethanol between the two pseudo-phases and proved the existence of fatty alcohol-rich domains of well-defined size of the order of 2 nm.

Numerous surfactant-free microemulsion formulations on the market present this nano-clustering. Such a nano-structuring may have an impact on the behavior of mosquito repellents on the skin, or their diffusion into the upper skin layers [30]. In perfume or tinctures, Marcus et al. observed a nano-structuring in the pre-Ouzo region with four different perfumery molecules. From model formulations nano-droplets can be predicted in Eau de Toilette, Eau de Parfum and they can possibly appear in perfumes in presence of very hydrophobic fragrance molecules [31]. Tchakalova et al. showed that the evaporation rate can be triggered by the structures in such ternary solutions. They observed a strong evaporation of ethanol in the pre-Ouzo region, used in fresheners, while there is a noticeable auto-encapsulation of the fragrance when spontaneous emulsification is produced (Ouzo-region) and the bulk water evaporates. In the case of pre-Ouzo long living aggregates that have to be distinguished from critical concentration fluctuations, evaporation follows a non-linear path with a cross-over as an embedded eutectic occurs [32]. Surfactant-free microemulsions showed the possibility to dissolve hydrophobic compounds, such as ibuprofen, in the presence of large amounts of water in the pressurized system water/acetone/CO_2 [33]. Many other examples of practical applications could be added.

Concerning the possible existence of surfactant-free and water-free microemulsions, we can also mention organic blends of biodiesel and diesel with ethanol and various additives, used as fuel. Biodiesel, a blend of fatty acid alkyl esters, is industrially produced by transesterification. The latter is a reaction of vegetable oils or a fat with an alcohol and yields fatty acid esters and glycerol. The exact knowledge of the phase equilibrium is essential for the optimization of the biodiesel production and purification. Liquid–liquid equilibriums for the glycerol/ethanol/biodiesels systems were therefore studied, where biodiesels came from canola oil, cottonseed oil, soybean oil, coconut oil, and sunflower oil [34–38]. The term "microemulsion" is never used in the related papers, as no connection between these solutions and surfactant-free water-free microemulsions was made. Recently, Arpornpong et al. reported the possible existence of nano-droplets in such blends by investigating the effects of co-solvent saturation and unsaturation on the phase behavior and on the viscosity of a biofuel [39]. The question of the existence of nano-droplets in water-free and surfactant-free microemulsion is set. It can be noted that Silva et al. also observed nano-structures in mixtures of ethanol and diesel oil (or synthetic diesel) in presence of additives, also inferred from dynamic light scattering data [40]. However, the technique used in these two last studies is not enough to postulate the presence of a microemulsion, as critical molecular fluctuations may occur and give a signal in dynamic light scattering similar to those arising from fluctuating nano-droplets.

The goal of this paper is to formulate and characterize unambiguously green surfactant-free and water-free microemulsions. First, water was replaced with glycerol and the system glycerol/ethanol/octanol was studied. Second, water was replaced with two different deep eutectic solvents (DESs), i.e. the deep eutectic ethylene glycol–choline chloride (4–1) and the deep eutectic