



Highly water dilutable green microemulsions

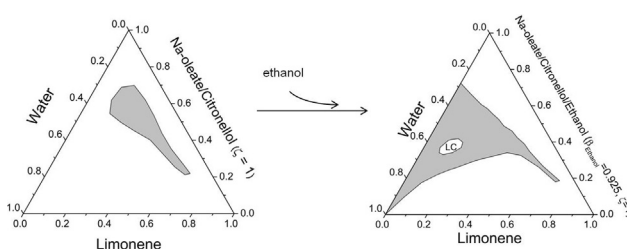
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HIGHLIGHTS

- ▶ Formulation of green microemulsions.
- ▶ Formulation of highly water dilutable microemulsions.
- ▶ Investigation of the influence of mixed cosurfactants on the microemulsion area.

GRAPHICAL ABSTRACT



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ABSTRACT

The realms of existence of “green” microemulsions are reported and their pseudo-ternary phase diagrams as well as electrical conductivities. For the investigations, the model system water/sodium oleate/citronellol/limonene is used. Herein, sodium oleate is the surfactant and citronellol the cosurfactant. The optimal surfactant-to-cosurfactant mass ratio is found to be 1:1. By replacing successively citronellol with ethanol the homogeneous single phase can be extended. At first, an anti-percolative behaviour of the system is obtained that can be converted into a percolative one. For low ethanol content microemulsions remain of water-in-oil (w/o) type. With increasing ethanol, between 30 and 90 wt% of ethanol in the blend, the monophasic region is diminished whereas liquid crystalline phases (lamellar and mixed lamellar and cubic ones) extend in the water-rich area. Above 90% the realms of existence of microemulsions are increased again and bicontinuous structures and oil-in-water (o/w) microemulsions were found. For a certain percentage of ethanol (92.5%) in the blend with citronellol and a surfactant + cosurfactant-to-oil ratio equal to or higher than 4:1 a highly water dilutable concentrated microemulsion is formed which can incorporate 99 wt% of water. By adding water rapidly to the water-rich areas of this system, thermodynamically unstable translucent nanoemulsions can occur, which turn into transparent microemulsions with time.

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1. Introduction

Microemulsions (mEs) are optically transparent, thermodynamically stable, isotropic solutions [1–3] with ultralow interfacial tensions [4,5] consisting of at least a hydrophilic and hydrophobic liquid separated by a surfactant molecular film [6,7]. Often also a cosurfactant is necessary, usually a short or medium chain alcohol (aliphatic alcohols) [6]. On the microscopic scale these solutions

consist of droplets of well defined size [8,9]. These droplets can merge and form bicontinuous structures [10,11].

A key method of investigating the microstructure of mEs is the measurement of the electrical conductivity, especially in the case of w/o mEs with ionic surfactants [12,13]. Two phenomena are possible. The first one is a percolative behaviour where the electrical conductivity undergoes a significant change over many orders of magnitude when the volume fraction of dispersed matter, here water, is increased above a certain threshold. The second one is an anti-percolative behaviour where no specific change of the electrical conductivity can be observed. This phenomenon can be associated to the formation of droplets with a rigid interfacial film thus preventing the reversed micelles to merge [14]. Applications of

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mEs can be found in several industrial fields, e.g. in cosmetic [15,16], pharmaceutical [17–19], food [20–22], etc., due to the high solubilization capacity of hydrophilic and lipophilic compounds [23]. Especially flavours and perfumes are important active-ingredients in cosmetics, pharmaceuticals and foods and beverages, where the behaviour of fragrance molecules and the potential interaction with surfactants in mE systems is important. Only a few articles deal with the distribution of the perfume molecules between the aqueous and micellar phase [24] or with the distribution within micelles [25]. Recently, Tchakalova et al. investigated the formation of mixed surfactant–cosurfactant films of fragrances using the hydrophilic–lipophilic deviation (HLD) quantified with the Equivalent Alkane Carbon Number (ECAN) [26]. They found a classification of the chemicals using their property of forming mixed surfactant–cosurfactant films according to their chemical functionalities following the order alcohols \geq aldehydes \geq terpenes \geq aromatics \geq alkanes. Further, it could be confirmed that primary alcohols have a high interfacial solubility and play the role of cosurfactants.

Flavours and perfumes have already been extensively used in the formation of biocompatible mEs [27–36]. Especially mEs with the citrus oil limonene can be found in literature [31,35,37,38].

In the present work we study the realms of existence of the mE in the system water/sodium oleate/citronellol/limonene by making pseudo ternary phase diagrams (PTPD) and through conductivity measurements. The long time stability of the system is checked with dynamic light scattering experiments. All used components are either from natural origin or are derived from natural sources. Citronellol, found in the oils of roses or geraniums is an acyclic oxidized terpene, and as a primary long alcohol it can be considered as cosurfactant. Limonene is a cyclic monoterpene produced from renewable feedstock and the major constituents of citrus oils [39]. Limonene itself is one of the most commonly used perfume molecules or active substances in technical and fine products [40,41] with a typical concentration between 50 ppm and 2.300 ppm [40]. It is not allergenic [42] and has anti-carcinogenic properties [43]. At high concentrations it is a skin irritant and a sensitizer [44]. Sodium oleate, a colour- and odourless classical soap from animal and vegetable fats and oils, classified by the Food and Drugs Administration (FDA) as food additive (E470) [45], is used as surfactant. Further, the effect of adding a short chain alcohol (ethanol) to the system is investigated. The addition of alcohols or glycols to surfactant systems is frequently used to influence the extent and the internal structures of mEs [46–50]. The aim is to formulate a fully or at least highly water dilutable mE where water can be added in any amounts without phase transition [51–54]. The great advantage of fully or highly water dilutable mEs is the fact that they allow a very good dispersion of active in a huge volume of water. Though several papers can be found dealing with solubilizing essential oils in mEs or micellar systems [20,55–57] fully dilutable systems with fragrances are rarely reported. This is the purpose of the present paper. For the first time, we present low toxic and highly water dilutable mEs using a long chain natural alcohol like citronellol as cosurfactant and a short chain natural one like ethanol.

2. Experimental

2.1. Materials

R-(+)-limonene (purity \geq 94%) and citronellol (purity \geq 97%) were purchased from Merck (Hohenbrunn, Germany). Sodium oleate (purity \geq 82%) was purchased from Sigma–Aldrich Chemie GmbH (Steinheim, Germany) and ethanol (purity \geq 99.9%) from Baker (Deventer, Netherlands). All chemicals were used without

further purification. All solutions and microemulsions were prepared using water with a resistivity of 18 M Ω cm.

2.2. Methods and techniques

2.2.1. Phase diagrams

Pseudo-ternary phase diagrams were established by using a dynamic process according to Clausee et al. [58]. In a screwable tube a blend of the emulsifying agents (sodium oleate, citronellol, ethanol) was filled in appropriate proportions and melt with limonene or water at various weight ratios to obtain a starting weight of 3 g. Water (limonene) was added with Eppendorf pipettes until a change in the phase occurs. Further to mEs, liquid crystalline (LC) phases, “classical” emulsions and homogeneous solutions in equilibrium with undissolved sodium oleate were observed. The phase transitions were determined with the naked eye and through cross polarized filters in order to differentiate between LC and mE phases. Between polarizing filters most of the liquid crystalline phases appeared birefringent. The weight fractions of water and limonene at which transparency-to-turbidity occurred were derived from precise weight measurements. The composition of the solution was then calculated from the masses of all components. It was estimated that the accuracy of the measurements for the transparency-to-turbidity transition was better than 2%. The temperature was kept constant at 25 °C with a temperature controlled test tube rack. For a faster screening of the countless possibilities of mixing five components only one line of the PTPD was chosen, along which most of the experiments were recorded. Fig. 1 shows the experimental paths. b^* is the dilution line with a surfactant + cosurfactant-to-oil ratio of 3:2 and a^* is the path within the mE area.

2.2.2. Conductivity

Conductivity measurements were carried out at 25 °C with an *inoLab® Vario Cond 730* Conductometer. The temperature was controlled by a thermostated cell. All measurements were conducted twice. The experimental error is approximately 2.5%. Limonene based w/o mEs were prepared as described above whereas the content of water was as low as possible. Water was then

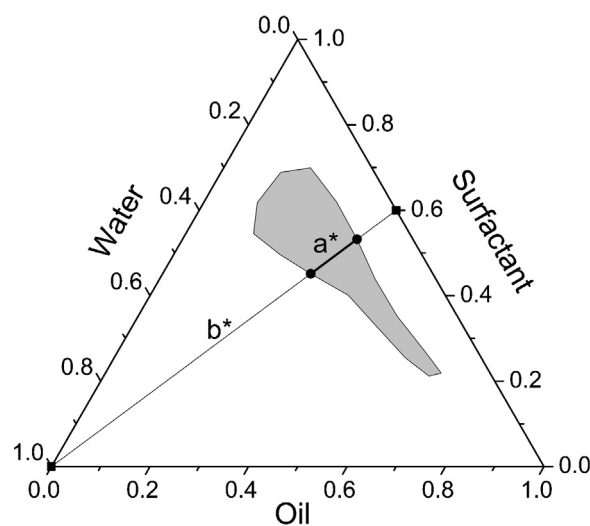


Fig. 1. Illustration of a representative pseudo-ternary phase diagram with water/surfactant/oil. The grey area represents the mE region. Additionally, two experimental paths are shown. b^* is the path of choice for investigating different surfactant-to-cosurfactant and cosurfactant-to-cosolvent blends. The ratio surfactant + cosurfactant-to-oil was always kept constant 3:2. Path a^* is the part of b^* within the mE area. The aim was to find the best mixture of four respectively five components to obtain the largest a^* .

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