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Aggregation in detergent-free ternary mixtures with microemulsion-like properties

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ABSTRACT

Aggregation in liquid mixtures is a ubiquitous phenomenon when water and at the same time rather unpolar compounds are present. Of special interest in recent years have been systems, in which the tendency of phase separation of a binary mixture is overcome by the solubilization ability of a short-chain alcohol as a third component. In such systems, polar and nonpolar domains coexist in absence of traditional long-chain surfactants. Their microemulsion-like properties, which lead to the names "detergent-less microemulsions" and "surfactant-free microemulsions" (SFMEs), have been studied by a variety of experimental methods and by simulations. In this review we summarize work that has been pursued to characterize these systems and give a short account of their various applications.

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1. Introduction

Mixtures of liquids are known to either form a (meta)stable single phase, or to undergo a phase separation, after which two distinct phases of different compositions are separated by an interface. Added surfactants, typically amphiphilic molecules with a polar head group and a long nonpolar tail [1], locate at these interfaces and lower the surface tension. When the surface tension is close to zero, often with the aid of a co-surfactant, microemulsions can form [2]: the system is macroscopically forming a single phase, but the microscopic (or mesoscopic) structure shows that there are distinct domains of two pseudo phases present [3]. Since the surface tension is close to zero, the decisive term in the free energy of a microemulsion is its bending energy [4], and bending elastic moduli of microemulsions can reach values lower than k_BT [5]. Depending on the microscopic structure, microemulsions are classified as water-in-oil, oil-in-water, or bicontinuous microemulsions [6], and in all cases the surfactant components again form an interfacial film between them [7]. Beside these traditional microemulsions, there is increasing work dealing with ternary systems, in which not a traditional surfactant mediates mutual solubility of water and hydrophobic component, but a simple cosolute in a hydrotrope-like [8] fashion. In this review we will shortly discuss aggregation in liquid mixtures and then present recent progress on the fundamentals and applications of these "surfactant-free microemulsions" (SFMEs). We will present a detailed look at the system octanol/ethanol/water, a typical SFME.

2. Structure formation in water/alcohol mixtures

Structure formation on a molecular level in liquids that contain hydrogen-bonding acceptors and donors is largely driven by the ability or inability of the different present groups to participate in energetically favorable hydrogen bonding. In pure water, hydrogen bonding sites are abundant and an extended three-dimensional hydrogen bonding network is formed [9]. In simple, monovalent alcohols, the nonpolar alkyl groups cannot form hydrogen bonds, and the polar OH head groups predominantly form chains by hydrogen bonding [10,11]. In dry octanol, hydrogen bond aggregates with a variety of structures are present. Also here, linear aggregates are predominant rather than spherical objects [12]. In binary solutions of short-chain alcohols, molecular scale segregation occurs [13], and they have been called molecular emulsions [14]. When water is added to n-octanol up to the solubility limit [15], again a highly organized microscopic structure is observed, but the shape of the aggregates changes to cylindrical reverse-micelle like aggregates [16]. In general, binary mixtures of water and alcohols form complex intriguing structures. An interesting example of fully water-soluble alcohol is t-butanol [17] with its bulky, hydrophobic t-butyl group. T-butanol/water mixtures show several striking thermodynamic anomalies [18]. Molecular dynamics simulations of systems with compositions for which the anomalies occur revealed the presence of spherical molecular aggregates with the shape properties of micelles: a hydrophobic core of t-butyl groups and an interface formed by the hydroxyl groups that are oriented towards the water [19]. Because of this similarity to micelles, these aggregates have been labeled as micelle-like structural fluctuations [20]. Apparently different to the molecular aggregates are mesoscale heterogeneities, Brownian diffusive droplets with sizes of up to several hundred nanometers that have

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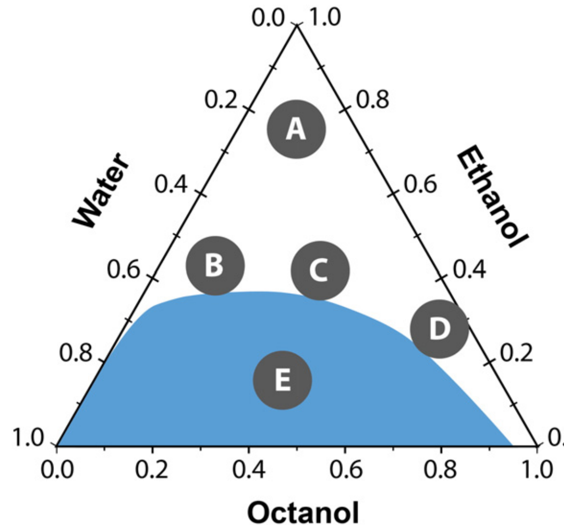

Fig. 1. Ternary phase diagram of the system octanol/ethanol/water. The different regions belong to a molecular solution (A), a direct, water-continuous SFME (B), a bicontinuous SFME (C), a reverse SFME (D), and to a phase-separated state (E).

been observed in many liquid mixtures [21]. For t-butanol in water, many experimental results and theoretical studies are available with conflicting results, showing that these heterogeneities have neither well-defined size nor shape [22]. Due to their size and shape, they are distinct from micelle-like aggregates. An explanation for the aggregates has been related to the presence of a third component like propylene oxide [23,24], where more long-lived aggregation than in the binary system is observed.

3. Surfactant-free microemulsions

In ternary systems, aggregation can be more complex, and of special interest are ternary systems, where a rather hydrophobic organic solute that is not soluble in pure water is solubilized by the addition of a cosolute like ethanol. A famous effect occurs when water is rapidly added to such solutions and the ethanol content gets too small to keep the solution stable: the system becomes turbid and micrometer-sized droplets form, which exhibit an amazing temporal stability. This effect is prominently known as “Ouzo effect” [25] and occurs when beverages containing anethole, a rather nonpolar organic ether, are diluted. The addition of water drives the system into a region of the phase diagram, in which the mixture is not thermodynamically stable anymore. Aggregates are also present in such solutions with compositions that belong to the one-phase region, where the systems are macroscopically homogeneous and transparent. Already in the 1970s, the microemulsion-like properties of such systems, a mixture of hexane, water, and 2-propanol [26–28] and a mixture of toluene, 2-propanol and water [29] in some parts of the one-phase region have been described. Different zones in

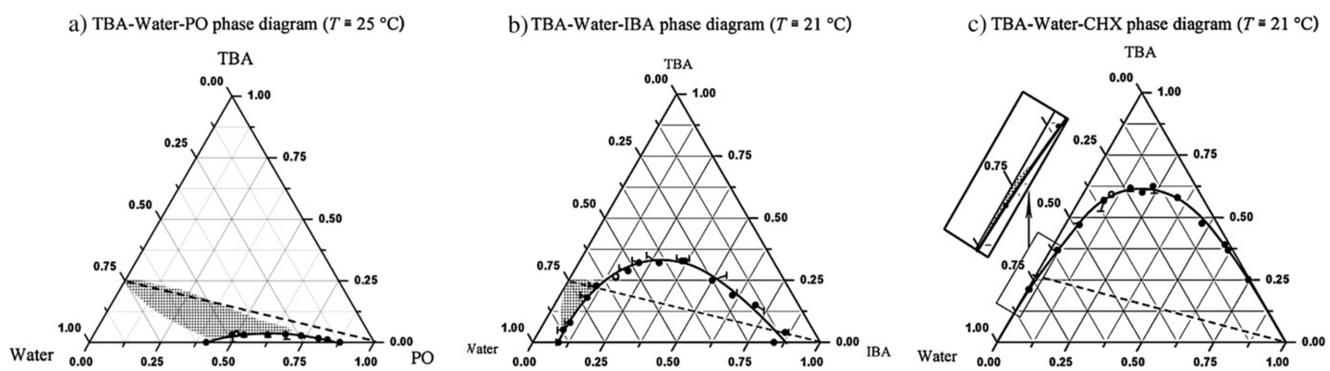

Fig. 2. Ternary phase diagrams of a) t-butanol/water/propylene oxide, b) t-butanol–water–isobutyl alcohol, and c) t-butanol–water–cyclohexane. The region in which mesoscopic droplets were observed is dotted.
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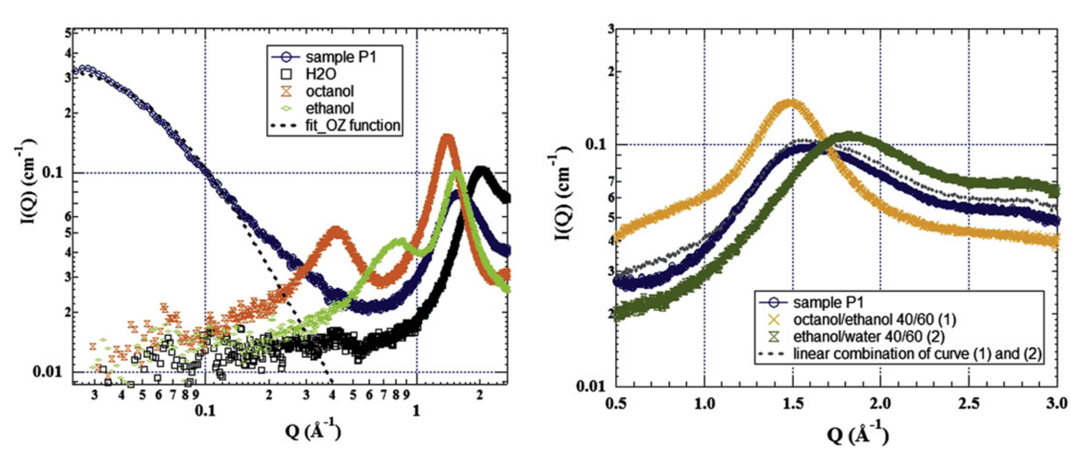

Fig. 3. A: SWAXS curves of an octanol/ethanol/water direct SFME (“P1”) and of the three pure liquids. The Ornstein–Zernike peak for small scattering angles is an indication for SFME aggregates. B: The high-q region is well described by a weighted sum of the scattering intensities of an ethanol/water and an octanol/ethanol mixture with compositions close to the two pseudo phases.
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