Surfactant-free microemulsions

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ABSTRACT

Surfactants (or amphiphiles) are generally believed to be a necessary component of microemulsions. However, research has found that in the absence of traditional surfactants, microemulsions can also form in a ternary system of two immiscible fluids and an "amphi-solvent". Such microemulsions are called "surfactant-free microemulsions" (SFMEs). The so-called amphi-solvent is a solvent that is completely or at least partially miscible with each of the two immiscible fluids. The structures and properties of SFMEs are similar to those of traditional surfactant-based microemulsions (SBMEs) to some extent. This review focuses on recent advances in SFMEs, including their phase behavior, structures, properties and potential applications.

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1. Introduction

Microemulsions have received considerable attention [1–4] because of their extensive applications in various fields, such as separation [1], chemical reactions [2], nanomaterial preparation [3,5], and drug delivery [4]. In 1943, Hoar and Schulman [6] first introduced the microemulsion structure, termed "oleopathic hydro-micelle" at that time, to describe the transparent water-in-oil dispersions containing soap and short-chain alcohols. In 1948, Winsor [7] found four types of phase equilibrium systems from mixtures of water, oil, and an amphiphilic compound, later called Winsor I, II, III, and IV systems. The Winsor I system is a lower dispersion in equilibrium with an excess oil upper phase, while the Winsor II system is an upper dispersion in equilibrium with an excess water lower phase. The Winsor III system has a three-phase structure, with a middle dispersion in equilibrium with both excess oil upper and excess water lower phases. The last one, Winsor IV, is a macroscopically single-phase dispersion [1]. These observed dispersions are actually microemulsions, a term introduced by Schulman et al. in 1959 [8] to describe optically isotropic transparent dispersions consisting of water, oil, and amphiphiles (soap and alcohol) and widely used afterwards.

Nowadays, microemulsions are defined as thermodynamically stable and optically isotropic transparent dispersions of at least two immiscible fluids (generally a polar and an apolar component) and an amphiphilic compound [3,4]. The polar liquids, traditionally called the

water phase, include water, aqueous solutions, and hydrophilic organic solvents. The apolar liquids, traditionally called the oil phase, are commonly hydrophobic organic substances. The amphiphilic compounds refer to substances with affinity for both the water and oil phases [7]. In fact, for a long time, this term was used exclusively for surfactants. A traditional surfactant is a molecule that possesses both polar head(s) and apolar long chain tail(s). The strong amphiphilic character of surfactants drives them to the interface between water and oil phases to stabilize the microemulsions. Indeed, most of the microemulsions reported in the literature were formed in the presence of surfactants and sometimes also cosurfactants. These surfactant-based microemulsions (SBMEs) can exhibit three structures, namely, oil-in-water (O/W), bicontinuous (BC), and water-in-oil (W/O) structures [1]. In an O/W (or W/O) microemulsion, the oil (or water) droplets stabilized by surfactant molecules are dispersed in the water (or oil) continuous phase. In a BC structure, both oil and water exist as a continuous phase [1]. The Winsor I, II, and III dispersions correspond to the O/W, W/O, and BC microemulsions, respectively.

However, microemulsions can also form in the absence of traditional surfactants, from ternary mixtures of oil, water, and an "amphi-solvent", and such microemulsions are called "surfactant-free microemulsions" (SFMEs) [9**–30**]. The so-called amphi-solvent [16,17,22**], an amphiphilic substance but not a surfactant, is a solvent that is completely or at least partially miscible with both the water and oil phases; it cannot form either micelles in bulk solutions or ordered films at the water–oil interface, i.e., it does not have the features of classical surfactants. The first SFME with a W/O structure was found by Smith et al. in 1977 [9**] in the ternary system of hexane, water, and *i*-propanol. The formation

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of SFMEs was subsequently confirmed in many surfactant-free ternary systems, and the O/W and BC structures similar to those in SBMEs have been identified in SFME systems [15[*]–17,20[**]–22[**],28[**]]. Notably, "surfactant-free emulsions" consisting of oil and water have also been reported [31], and have attracted much attention [32–35]. Unlike the SFMEs, the surfactant-free emulsions are turbid and thermodynamically unstable: they can remain well dispersed for months or even longer, but will eventually break down [32]. The presence of amphi-solvents plays a crucial role in SFME formation. Similar to the SBMEs, SFMEs are also expected to have extensive potential applications, and some related research has been carried out [11[**],36–48]. However, SFMEs have received much less attention so far in comparison to SBMEs [26[**]]. Perhaps this is because many people still erroneously believe that the presence of a significant amount of surfactants is necessary for the formation of microemulsions, and that the existence of SFMEs is impossible [26[**]]. Thus, a consensus on the mechanism for SFME formation needs to be established [30[**],49].

This review gives a brief introduction on the recent advances in SFMEs, including the phase behavior of surfactant-free ternary systems, the structures and properties of SFMEs as well as their practical applications.

2. Phase behavior of surfactant-free ternary systems

The phase behavior of surfactant-free ternary mixtures of oil, water, and amphi-solvent can be represented using the triangular phase diagram. Table 1 summarizes the surfactant-free ternary systems studied by researchers. In these systems, the amphi-solvents include short chain alcohols (ethanol, propanol, and butanol), N,N-dimethyl formamide (DMF), acetone, and tetrahydrofurfuryl alcohol (THFA). The oil phases involve the hydrophobic room temperature ionic liquid (IL) 1-butyl-3-methylimidazolium hexafluorophosphate (bmimBF$_6$) and the pressurized CO_2. The water phases involve the hydrophilic IL 1-butyl-3-methylimidazolium tetrafluoroborate (bmimBF$_4$) and the deep eutectic solvents (DESs) ethylene glycol–choline chloride (molar ratio 4–1, EG-ChCl) and urea–choline chloride (molar ratio 2–1, Urea-ChCl). Similar ternary phase diagrams were observed for all these surfactant-free systems. As schematically illustrated in Fig. 1, there is a single-
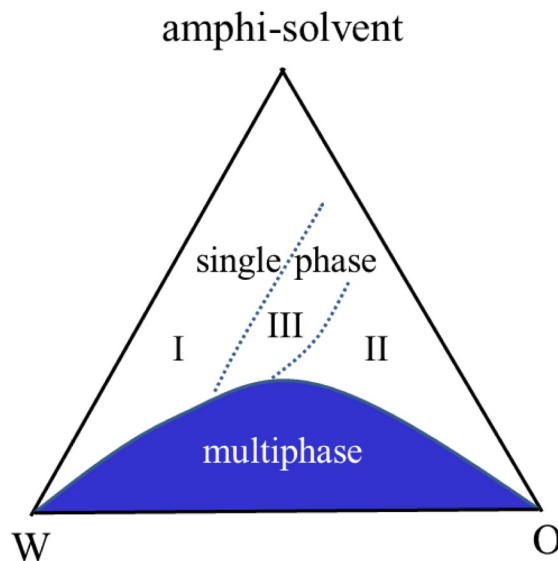

Fig. 1. Schematic ternary phase diagram of the surfactant-free system of oil, water, and amphi-solvent. I, II and III represent three subregions, which may correspond to the O/W, W/O, and BC microemulsions respectively.

phase region and a multiphase region. In the single-phase region, the compositions are optically isotropic and transparent, while in the multiphase region they are turbid under stirring and break quickly into two phases when left standing. The area of the single-phase region differs greatly for different systems. For example, it occupies over 75% area in the total phase diagram for the toluene–bmimBF$_4$–ethanol system [21[**]], while it occupies less than 5% for the limonene–water–ethanol system [23]. The matching principle among various components to achieve a large single-phase region is still unclear. Moreover, environmental factors, such as the temperature, pH, and ionic strength, have little influence on the location of the boundary between the two regions [10[*],21[**],22[**]].

Different microstructures have been identified using various techniques (Table 1) for compositions in the single-phase region. Generally, this region is further divided into three subregions (marked I, II, and III in the schematic illustration in Fig. 1) that correspond to three types of microstructures. Note that the locations of subregion boundaries may be significantly different for different systems [10[*],12,15[*],22[**],28[**]]. In addition, obvious effects of ionic strength and pH on the location of the subregion boundaries were detected by Barden's group [10[*],11[**]]. Nevertheless, the types of microstructures in the single-phase region seem to be dependent of environmental factors.

Regarding the specific microstructure in each subregion, different characterization results have been reported in the literature [9[**],12,15[*],22[**],28[**]]. Barden, Holt and their coworkers [9[**]–12] investigated the phase behavior of surfactant-free ternary systems of hexane–water–i-propanol and toluene–water–i-propanol. They found that a W/O microemulsion structure exists in subregion II, because the sedimentation of water-rich droplets was clearly observed after ultracentrifugation [9[**],10[*],12]. This confirms the formation of a microemulsion, namely SFME, from a ternary mixture of oil, water, and a short chain alcohol (amphi-solvent), in the absence of any traditional surfactants. However, the compositions from subregions I and III were considered as normal ternary solutions and small H-bonded aggregates of water–alcohol dispersed in an oil-rich medium, respectively, because no signs of phase separation were observed for these compositions after ultracentrifugation [9[**],10[*],12].

Subsequently, Lara et al. [13[*]] determined the heat capacity and molar volume of the benzene–water–i-propanol mixture in the single-phase region. Their results suggest that the O/W and W/O microemulsions may have formed in the water-rich and oil-rich regions,

Table 1
Surfactant-free ternary systems previously studied, and the methods used for investigating the SFME structures.

System	Method	Reference
Hexane–water–propanol	Conductivity, ultracentrifugation, NMR, fluorescence, EPR	[9[**]–11[**],14[**],43]
Toluene–water–propanol	Conductivity, NMR, DLS	[12]
Benzene–water–propanol	Heat capacity, density	[13[*]]
Butanol–water–propanol	Cyclic voltammetry, DLS	[15[*]]
Furaldehyde–water–DMF	Conductivity, FF-TEM	[16]
Furaldehyde–water–ethanol	Conductivity, FF-TEM, DLS	[17]
Benzene–water–ethanol	Conductivity, FF-TEM	[18]
Oleic acid–water–propanol	Conductivity, FF- and Cryo-TEM, DLS, SAXS, UV–vis	[20[**]]
Toluene–bmimBF$_4$–ethanol	Conductivity, cyclic voltammetry, NMR, FF-TEM, UV–vis	[21[**]]
BmimBF$_6$–water–DMF	Conductivity, cyclic voltammetry, fluorescence, FF-TEM, DLS, UV–vis	[22[**]]
Octanol–water–ethanol	Conductivity, DLS, SANS, SWAXS, molecular dynamics simulation	[19[*],24,26[**],28[**],30[**]]
Perfume–water–ethanol	DLS	[23]
Pressurized CO$_2$–water–acetone	Raman spectroscopy	[27[**]]
Octanol–glycerol–ethanol	DLS, SAXS	[29[**]]
Diethyl adipate–DES–THFA	DLS, SAXS	[29[**]]