Available online at www.sciencedirect.com

ScienceDirect

Current Opinion in
Colloid & Interface Science

Applications of surfactant-free microemulsions

Lena Schmauser, Eva Müller, Didier Touraud and Werner Kunz

The applications of surfactant-free microemulsions (SFMEs) as solvents are reviewed, with a strong emphasis on recent research advancements. The discussion covers diverse research fields, including solubilization, extraction processes, use as reaction media, and fuel formulation. Particular attention is paid to mechanistic explanations proposed in the literature with respect to how SFMEs improve specific applications. Key parameters such as the structuring, solubility, and specific interactions are critically evaluated. Additionally, the review highlights the advantages and limitations of SFMEs compared to conventional solvents.

Addresses
University of Regensburg, Universitätsstraße 31, Regensburg, 93053, Bavaria, Germany

Corresponding author: Kunz, Werner (Werner.Kunz@ur.de)

Current Opinion in Colloid & Interface Science 2026, **83**:102001

This review comes from a themed issue on **Nanoprecipitation and nanoemulsification (2025)**

Edited by **François Ganachaud**, **Chun-Xia Zhao**, and **Mingbo Li**

For a complete overview see the Issue and the Editorial

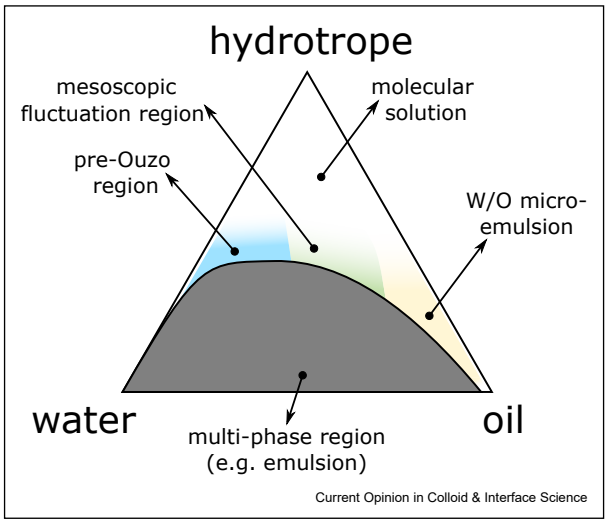
https://doi.org/10.1016/j.cocis.2026.102001

Introduction

Classical microemulsions are commonly known to be thermodynamically stable, transparent, and isotropic solutions formed by the stabilization of two immiscible components. In the most frequent cases, the two immiscible fluids are water and a hydrophobic compound, while there are also some water-free examples. The stability is achieved by the addition of an amphiphilic component. Traditionally, these amphiphilic molecules have both a long hydrophobic tail and a hydrophilic head group. Due to this structure, they adsorb at the interface between the immiscible phases, from which they derive their name surface-active agents or surfactants for short. By adsorbing to the interface, they lower the interfacial tension, resulting in stable microemulsions if the concentration of the surfactant is high enough. It is important to note that the structure of the surfactant is crucial for the formation of SBMEs. In the case of ionic surfactants, co-surfactants, like short-chain alcohols or salts, are often necessary to form microemulsions. Co-surfactants are incorporated into the interfacial film, which leads to an increased flexibility, and thus to a minimization of the interfacial tension. The surfactant-based microemulsions (SBMEs) can exist in three different phases, the oil-in-water (O/W), the bicontinuous (BC), and the water-in-oil (W/O) phase, respectively [1].

Microemulsions can not only form in surfactant-containing solutions. In 1977, Smith et al. found the first surfactant-free microemulsion (SFME). In this case, the system of water and hexane was stabilized by 2-propanol (IPA) rather than by classical surfactants [2]. The IPA is a weak amphiphilic molecule called a hydrotrope. Compared to surfactants, hydrotropes have a shorter hydrophobic part, which leads to a lower amphiphilicity of the molecule. In contrast to surfactants, which can already form micelles in pure water, the structuring of the hydrotrope-containing system is usually enforced by the addition of the third component [3]. To achieve a sub-compartmentalized solubilization, the third component must be completely or partially miscible with the hydrotrope and have a poor solubility in the first component. In addition, hydrotropes cannot form ordered films at the water–oil interface, or lyotropic liquid crystals [3,4]. Typical examples of hydrotropes are short-chain alcohols such as ethanol (EtOH), *n*-propanol (NPA), and *tert*-butanol (TBA), as well as short alkylbenzene sulfonates like sodium xylene sulfonate (SXS), and short-chain monoethers of ethylene [3]. Ternary mixtures of water, a hydrotrope, and a hydrophobic component can be illustrated in a ternary phase diagram (shown in Figure 1). As in the case of SBMEs, there is a multiphase (gray area) and a single-phase region. Above the phase boundary, transparent, thermodynamically stable solutions are formed. Depending on the compositions, O/W-like (shown in blue), mesoscopic fluctuations (MF, shown in green), or W/O-like (shown in yellow) microemulsions can occur as in surfactant-based systems. Near the critical point of the SFME, there is a composition zone, for which high electric conductivity is observed. In this zone, that is sometimes labeled as 'bicontinuous', the microstructure is the coexistence of large fluctuating domains that contain oil-in-water aggregates with other large regions

Figure 1



Schematic ternary phase diagram of a water, hydrotrope, and hydrophobic component (oil) mixture. The gray area represents the two-phase region. The single-phase region can be divided into O/W, also called pre-ouzo region (blue), mesoscopic fluctuation region (MF) (green), and W/O (yellow) microemulsion, and a molecular solution (white). O/W, oil-in-water; W/O, water-in-oil.

containing water-in-oil aggregates without any hardcore interation. [5]. In Figure 1, we call this region the 'mesoscale fluctuation region'. The word 'bicontinuous' would be correct, but the bicontinuity is between highly conducting (water-rich) regions that are dispersed and intertwined with regions of water-in-oil and as such in different from the bicontinuous structure observed in classical microemulsions (SBMEs) [6]. Note that the interface between the aggregates is ultra-flexible and in fact a region in which a slight excess of the hydrotrope [7] is observed rather than a complete interfacial film made by a compact surfactant monolayer. For applications of SFME in chemistry in this region, it is important to understand that reactants may preferentially solubilized in water-poor (with low-water activity) or solvent-poor (with low solvent activity). As a consequence, this region in the phase diagram of SFME is of particular interest.

The three different mesoscopic structures as snapshots of molecular simulations are shown in Figure 2 [8]. The O/W microemulsion is also called pre-ouzo region, with the term being derived from the ouzo effect. Ouzo is a Greek alcoholic beverage that is mainly composed of water ($\sim$ 55%), EtOH ($\sim$ 45%), and trans-anethole ($\sim$ 0.2%). By adding water to the clear beverage, a milky turbid solution is formed. This transition is called the ouzo effect. The trans-anethole previously dissolved in the water/EtOH mixture spontaneously aggregates to metastable droplets. A detailed explanation of the mechanism can be found in the work of Prévost et al. [9] The pre-ouzo region refers to the single-phase, transparent, and thermodynamically stable region near the phase boundary. In this region, aggregates of the hydrophobic component form. The hydrotrope is present in the hydrophilic and hydrophobic phase, with an increased concentration at the interface (O/W microemulsions) [8]. By increasing the hydrotrope concentration, the structured solution is gradually transformed into a molecularly dissolved system.

Since the discovery of SFMEs, many other ternary systems have been investigated to see whether they form SFMEs. Ternary systems, which were and are mostly investigated, are systems consisting of water, a short-chain alcohol, and various hydrophobic components [10–17]. The SFMEs that replace one component with ionic liquids (ILs) [18–26] or deep eutectic solvents (DES) [11–13,27–32] have become increasingly interesting in recent years. Water- and surfactant-free microemulsions have also been studied in this context [18,18,21,26,27,30]. In addition, the number of papers pursuing theoretical approaches to predict structuring in ternary surfactant-free systems is increasing [10,27,33–38]. These approaches can potentially increase the understanding of SFMEs in the future and additionally help to find the optimal SFME for different applications [33]. (Table 1)

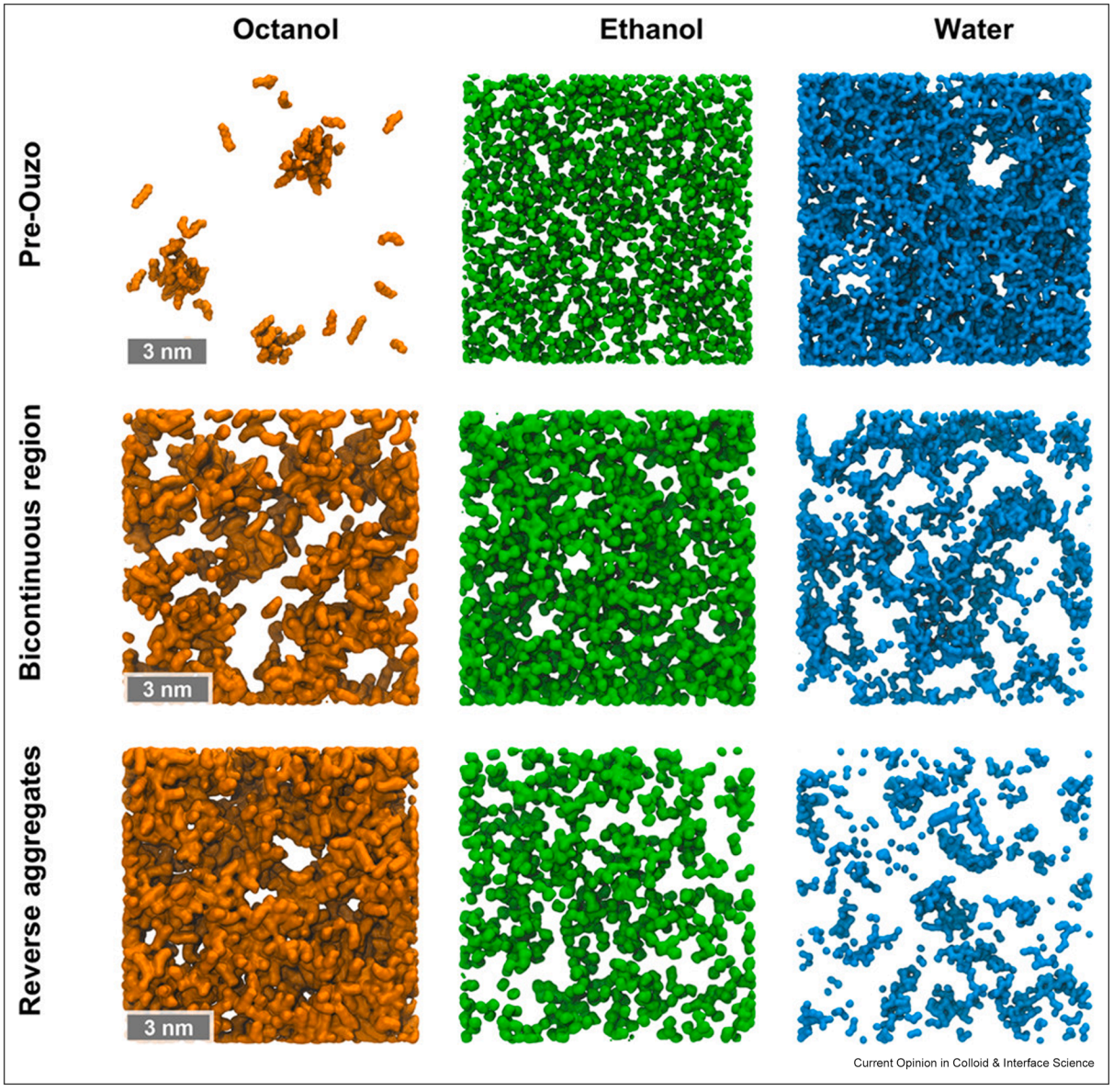
Particularly, the highly dynamical processes, while still keeping a compartmentalization of the system with regions of varying polarity, make SFMEs a broadly interesting media for applications. The formed compartmentalization, with the hydrotrope enriched at the internal interface, can form a weak barrier, but not as distinct as in an SBME. In comparison to SBMEs, in many cases the use of hydrotropes facilitates work-ups as no surfactant residues must be taken into consideration, because volatile hydrotropes can easily be separated by distillation. This is particularly important in order to keep surfactants away, for example, from polymers.

This review gives a brief introduction to the research on current and possible applications of SFMEs and will highlight their advantages and potential drawbacks in comparison to SBMEs.

Applications of surfactant-free microemulsions

Between 2020 and 2025, there has been a noticeable increase in research activity focused on SFMEs, with an estimated 40 to 60 peer-reviewed publications explicitly addressing their formation, structure, and application. However, due to the interdisciplinary nature of the topic, spanning physical chemistry, colloid science, pharmaceuticals, materials science, and formulation technology, it is difficult to determine an exact number

Figure 2



Snapshots of the molecular distribution in the three different mesoscopic structured regions of water, ethanol (EtOH), and 1-octanol. The figure is taken from Lopian et al. and reprinted with permission of American Chemical Society (ACS) [8].

of relevant publications. Many studies appear across diverse journals and research domains, often embedded within broader investigations of soft matter systems or non-classical formulations. Key contributions in recent years include Schöttl et al. (2020), who demonstrated the solubilization capacity of water/EtOH/n-octanol systems without surfactants [34], and Han et al. (2022), who provided mechanistic insights into the criteria governing SFME formation in ternary systems [35]. Moreover, Sedlák and et al. (2023) discussed mesoscale organization in SFMEs, highlighting their potential in drug delivery, cosmetics, and green formulation technologies [39]. Recent studies also show increasing interest in the application of SFMEs as reaction media, particularly in polymer synthesis and nanoparticle (NP) production. The absence of surfactants simplifies downstream processing and reduces environmental impact, making SFMEs attractive for sustainable chemistry approaches. Moreover, the production of SFMEs is straightforward. The thermodynamically stable solvents are obtained by briefly shaking without the need for significant external energy input.

Table 1

Overview over publications discussing SFMEs containing DES or IL.

IL-/DES-SFME	Application	Reference
[Bmim][BF_4]/EtOH/toluene	Proof of concept	[18]
Water/ethylamine Nitrate/[C_{12}bbim[Cl]]	Production of Mg−Al-LDH	[19]
Water/dimethylformamide/BmimPF_6	Production of Mg2Al-layered double hydroxide nanosheets	[20]
[Bmim][BF_4]/NBA/MMA	Production of poly(methyl methacrylate)/TiO_2 nanocomposite	[21]
Water/IPA/AMIMPF_6	Production of poly(ionic liquid), Cu-NP/poly(ionic liquid), carbon black/poly(ionic liquid)	[22–24]
Water/1,2-propanediol/[HMIM][BF_4]	Extraction from *Camptotheca acuminata*	[25]
Ethyl acetate/DMSO/[C_nDMEA[Im]]	Production of ZIF-90	[26]
Urea-ChCl/tetrahydrofurfuryl alcohol/diethyl adipate	Proof of concept	[27]
Water/EtOH/indole-menthol	Proof of concept	[12]
Water/IPA/*n*-octanoic acid-menthol	Proof of concept	[13]
Water/ethanolamine/*n*-decanoic acid-terpenoids	Solubility of [K_3Fe(CN)6]	[11,28]
Water/EtOH/*n*-octanoic acid-menthol	Solubilization of curcumin	[29]
ChCl-Lac/EtOH/TriA	Solubilization and extraction of curcuminoids	[30]
Water/EtOH/octanol-thymol	Extraction from *Eucommia ulmoides*	[31]
1,2-propanediol/matrine-caprylic acid/isopropyl myristate	Solubility of curcumin	[32]

DES, deep eutectic solvents; EtOH, ethanol; IL, ionic liquid; IPA, 2-propanol; MMA, methyl methacrylate; NBA, n-butanol; SFMEs, surfactant-free microemulsions.

Despite their relatively limited representation in the literature compared to conventional microemulsions, the growing interest in SFMEs signals their potential as a versatile and eco-friendly platform for future applications in material science, pharmaceuticals, and agrochemical formulations. In the following work, a short introduction to these applications will be given.

Solubilization

Solubilization of pure natural compounds

Similar to surfactant-based microemulsions, SFMEs have defined nanodomains that may influence and improve the solubility and stability of solutes, e.g. natural compounds. Natural compounds are isolated from plants, minerals, or animal resources, and play an important role in the pharmaceutical, chemical, aroma, and food industry [48, 49].

One example is the poorly water-soluble curcumin I [(E, E)-1,7-bis (4-hydroxy-3-methoxyphenyl)-1,6-heptadiene-3,5-dione], which was studied by different groups [30,32,40–43]. Curcumin I is a natural molecule, extracted from the rhizomes of *Zingiberaceae* (see next subsection), and is widely used in the food and chemical industry as a flavoring and coloring agent, spice, preservative, and therapeutical agent [40,41]. Due to its polyphenolic structure, it has poor water solubility, with reported values between 11 ng mL^{-1} [50] and 10 micoL mL^{-1} [51]. Additionally, the molecule is photosensitive and thermolabile, which further restricts its applications [42]. In an effort to address this problem, Liu et al. investigated the solubility, stability, and the antioxidant activity of curcumin I in an SFME consisting of water, EtOH, and ethyl benzoate [40]. In their work, they proved that they could be able to solubilize 17.5 mg mL^{-1} of curcumin I in an O/W SFME, which is significantly higher than the solubility in pure EtOH (12.4 mg mL^{-1}) and ethyl benzoate (13.4 mg mL^{-1}), respectively [40]. Similar amounts of curcumin I (17.65 mg mL^{-1}) were solubilized in an SFME consisting of water, EtOH, and 1-octen-3-ol [43]. However, in both approaches, the solubility in the binary mixtures of EtOH/ethyl benzoate or EtOH/1-octen-3-ol was not studied. Degot et al. showed that the solubility of curcumin I increased threefold in the binary EtOH/TriA mixture (40/60) compared to the solubility in pure TriA. This synergistic effect could not be observed in the binary DiA/TriA mixture. The solubility of curcumin I was described as being decreased upon the addition of water to the binary mixture of EtOH/TriA, while the addition of 5-10% water to the DiA/TriA mixture increased the solubility [41]. This indicates that different solubilization mechanisms can be present, which should be considered in all studies. Possible mechanisms are outlined at the end of the chapter. In addition, the group of Liu et al. addressed the light and thermal stability of the polyphenol and its potential as an H-atom or electron donor. It was found that the degradation rate of curcumin I in the SFME (water, EtOH, ethyl benzoate) was slowed down compared to the reference system in pure EtOH [40]. This observation was confirmed by the work of Zhang et al. [43] Furthermore, the antioxidant

capacity of curcumin I increased in the SFME system. All properties were reported to be due to the encapsulation and thus altered environment of curcumin I in the oil droplets [40]. No further explanation for the results was provided in these works. Huber et al. [30] and Li et al. [32] also used water-free SFMEs with DES for the solubilization of curcumin I. In the work of Huber et al. water was replaced by a hydrophilic DES consisting of choline chloride (ChCl) and lactic acid (Lac) (1:1). The solubility of the polyphenol increased twofold compared to the EtOH/TriA mixture. The increased solubility was explained by the interaction between the positively charged nitrogen of ChCl and the conjugated π-system of the curcumin I. A ternary mixture of ChCl, EtOH, and TriA was formed, in which the same solubility of curcumin I was achieved with a lower concentration of ChCl. However, the solubility of ChCl in the binary mixture was restricted, which can be improved by the addition of Lac [30]. Li et al. also replaced water with a DES, consisting of the two pharmaceutically active ingredients matrine and caprylic acid. The SFME was formed with propane-1,2-diol as the hydrotrope and isopropyl myristate as the hydrophobic compound. However, the solubility of curcumin I was higher in the DES alone (20 mg mL^{-1}) than in the SFME (8 mg mL^{-1}). The increased solubility in the SFME was mainly attributed to the DES. Further analysis of the mechanism of the solubilization was not pursued.

Other natural compounds, like quercetin [44], all-trans retinoic acid (ATRA) [45], riboflavin [43,46], and α-arbutin (ABN) [47] were solubilized in different SFMEs. Similar to the work of Liu et al. [40], the solubility (SFME: 8.94 mg mL^{-1}, EtOH: 7.92 mg mL^{-1}), antioxidant properties, and the thermal, photo-, and storage stability of quercetin increased in the SFME consisting of water, EtOH, and tributyl citrate. In addition, they studied the dialytic performance of the SFME system, which had a slower release rate compared to the pure EtOH system. The solubilization mechanism and the structure of quercetin-loaded SFMEs were further investigated. With infrared spectral absorption, they showed that, with a low quercetin concentration, no quercetin peaks were detected. This indicates, that quercetin was predominantly solubilized in the inner core of the SFME, which means that the peaks were masked by the outer phase. By increasing the concentration, some peaks were observed, indicating that part of the molecule partitioned into EtOH and therefore into the outer phase [44]. For the solubility of ATRA an O/W SFME consisting of water, NPA, and, eucalyptus oil was used and the same properties were investigated. The highest solubility was observed in the SFME with the highest eucalyptus oil concentration (SFME (water: 17.6%, NPA: 70.4%, eucalyptus oil: 12% (w/w)): 10.08 mg mL^{-1}, water: 0.19 µg mL^{-1}). It was shown that the values increased compared to a pure silicone oil reference system (20 µg mL^{-1}). As the system was intended to be used as a drug delivery system, the *in vitro* transdermal rate was also determined. They reported an increased skin penetration promoted by the SFME. As reference systems, azone and oleic acid systems loaded with ATRA were used (cumulative percentage of the drug release: SFME: 42.8%, azone: 22.61%, oleic acid: 12% after 24 h). One important parameter influencing skin absorption was the size of the droplets. For most freeze-dried SFME samples, the diameter was below 100 nm, which was smaller than that observed for the SBME sample [45]. The application of an SFME (water/short-chain alcohols/triethyl citrate) in cosmetics was presented by Zhang et al. [47] For that purpose, the hydrophilic ABN was solubilized in an O/W (water: 62 %, 1,2-pentanediol: 24 %, TEC: 14 %) and W/O (water: 15 %, 1,2-pentanediol: 21%, TEC: 64%) SFME. The solubility increased twofold compared to the water system. Due to the possible application, the percutaneous penetration on a pig ear skin and the irritation with a hen egg test-on-the-chorioallantoic membrane assay were tested. The experiments showed that the penetration level was higher in the O/W SFME compared to water. In the diluted SFME with a water content of more than 95%, no irritation was detected. The dissolved natural compounds and the respective SFME system are summarized in Table 2.

Few research groups have undertaken detailed investigations into the solubilization mechanisms of their respective SFME systems. Among these, Liu et al. [44] and Degot et al. [41] have to be highlighted as they strengthened their observations with computer simulations. Both groups found the highest specific interactions between the hydrotrope (EtOH), the hydrophobic

Table 2

Overview over publications discussing solubilization of different natural components.

Solubilized	System	Reference
Curcumin I	Water/EtOH/ethyl benzoate	[40]
Curcumin I	Water/EtOH/triacetin (TriA), water/diacetin (DiA)/TriA	[41,42]
Curcumin I	Choline chloride + lactic acid/EtOH/TriA	[30]
Curcumin I	Isopropyl myristate/1,2-propanediol/matrine-caprylic acid	[32]
Curcumin I, riboflavin	Water/EtOH/1-octen-3-ol	[43]
Quercetin	Water/EtOH/tributyl citrate	[44]
trans-retinoic acid	Water/NPA/eucalyptus oil	[45]
Riboflavin	Water/EtOH/diethyl malonate	[46]
α-Arbutin	Water/short-chain alcohols/triethyl citrate	[47]

EtOH, ethanol; NPA, *n*-propanol.

component of the SFME, and the natural compound in the systems with the highest solubility. Lui et al. demonstrated through simulations that solubilization is spontaneous, driven by the formation of hydrogen bonds between quercetin and tributyl citrate. In addition, the hydroxy-group of the hydrotrope EtOH was a decisive factor for the solubilization process. On the one hand, three of them interacted simultaneously with the aromatic ring of the quercetin, thereby enhancing its solubilization. On the other hand, interactions between quercetin and tributyl citrate were induced with EtOH as an H-bond donor. Liu et al. validated the simulation results experimentally with nuclear Overhauser enhancement spectroscopy (NOESY) NMR. The spectra exhibited cross-peaks corresponding to intra- and inter-molecular interactions, for example, between quercetin, tributyl citrate, and EtOH [44]. Han et al. employed density functional theory (DFT) calculations to elucidate the potential underlying interactions between ATRA and 1,8-cineole (model substance of the eucalyptus oil). They found that the two molecules primarily interact with each other through electrostatic effects as different parts of the two molecules have different charged electrostatic potentials. The calculations further revealed that the interaction between the two molecules was thermodynamically favorable, due to a positive ΔS [45]. In the work of Zhang et al. the simulations showed that the hydrophilic ABN adsorbed on the interface between the oil and water phase. Therefore, ABN could form a hydrogen-bonded network with water and the hydrophobic compound, whereby the molecule was stably bound in the interface [47].

Different simulation methods show that specific interactions between the solubilized compound and the SFME influence the solubility. Depending on the solubilized molecule and the used SFME, different parts of the SFME interact with the molecule. One key parameter seems to be the hydrophobicity of the solubilized compound. For hydrophobic molecules, the SFME appears to provide a hydrophobic-rich microenvironment, enhancing the solubility as described by Schöttl et al. [34] In addition, the work of Liu et al. [44] and Degot et al. [41] show that interaction with the hydrotrope can also be a decisive parameter in the hydrophobic solubilization mechanism. In the case of the hydrophilic ABN, interactions with water and the hydrophobic compound may be the important factors for an increased solubilization [47]. However, it should be emphasized that further experimental and computational studies are required to deepen our understanding of the underlying formation and solubilization mechanisms of surfactant-free microemulsions. Notably, few of the existing studies to date have provided systematic comparisons with classical microemulsion systems, which would be essential to clearly delineate similarities, differences, and potential advantages of surfactant-free formulations.

Enhanced solubilization of natural compounds during extraction processes

The substitution of conventional, non-sustainable solvents in the extraction of natural compounds represents a rapidly expanding research field. Many approaches have been explored, but the industrial reality is still the use of less sustainable solvents like methanol, acetone, or chlorinated solvents [25]. Pure green solvents (e.g.. EtOH) unfortunately quite frequently show non-satisfactory solubilization and extraction capacities of the desired compounds [41]. To address this problem, the use of SFMEs as extraction solvents is being investigated for different compounds. The most investigated compounds in this context are the three curcuminoids from *Zingiberaceae*. The group of Kunz et al. tested different SFMEs and compared them to Soxhlet extraction in acetone, which is the conventional extraction method with the highest yield at 11.64 mg mL^{-1}. Even if the yield in the SFME consisting of water, EtOH, and TriA, and the water-free SFME with the DES ChCl + Lac as hydrophilic compound was worse than the yield of the Soxhlet extraction, the extractions were performed at room temperature compared to 80 °C (TriA/EtOH/water (36/24/40 (w/w)): 9.21 mg mL^{-1}, DES/EtOH/TriA (35/27.5/37.5 (w/w)): 11.8 mg mL^{-1}) [30,41]. In contrast to the solubility of curcumin I, the addition of water to the binary mixture of EtOH/TriA increased the extraction yield (EtOH/TriA: 8.82 mg mL^{-1}). Additionally to the solubilization of the desired compound, the solvent has to fulfill further requirements in the extraction process, for example, the penetration of the plant matrix and the desorption of the target compounds from binding sites. Thus, the performance increase through the addition of water was explained by the improved swelling of the plant material, which increased the solvent penetration and thus the bursting of the plant cells [41]. In addition, the group showed that the concentration of the curcuminoids increased linearly when carrying out multiple extraction cycles. Due to the low solubility of the curcuminoids in water, saturation was reached already after four extraction cycles with a water content of 30% [42]. These limitations can be overcome by changing the hydrophilic compound of the SFME. The solubility of curcumin I increased twofold in the water-free SFME, further increasing the number of potential extraction cycles. A saturation was reached after 7 cycles, where a total amount of curcuminoids around 170 mg was extracted. In the work of Zhang et al. a system containing water, EtOH, and a DES, consisting of menthol and n-octanoic acid (ME-OA) was analyzed. By using this SFME and the help of an ultrasonic bath, an extraction yield of curcuminoids of 61.4 mg g^{-1} per rhizome was obtained, which is more than the extracted amount in pure acetone (53.8 mg g^{-1} per rhizome). These authors also performed molecular dynamics simulations and determined the interaction energy, hydrogen bond, and the solvent accessible surface area

in the SFME, EtOH, ME-OA, water, and acetone, respectively. The interaction energy and the number of hydrogen bonds between the solvent molecules and the extracted compound were the strongest in the SFME. Similar to the solubilization simulations, this may show that specific interactions are one of the important parameters in the extraction process [29].

In a very sophisticated approach, Luo et al. and Wang et al. used a temperature-responsive SFME to simultaneously extract hydrophilic and hydrophobic compounds and separate them through the temperature-dependent demulsification of the SFME [25,52]. In the work of Wang et al. eight different components (see Table 3) from *Rosa roxburghii* leaves were extracted with an SFME consisting of water, EtOH, and octanol. The yield increased by a factor of 1.03−3.90 compared to traditional solvents, under the optimal reaction condition of 70 °C and an ultrasound time of 42 min. By decreasing the temperature, the SFME demulsified and a pre-separation of the hydrophilic and hydrophobic compounds was possible [52]. Table 3 gives an overview of all the extracted molecules and the SFMEs used.

Further applications of surfactant-free microemulsions in solubilization processes

In addition to the extraction of natural compounds, SFMEs were tested as an extraction solvent for other compounds like crude oil from oil sands. Oil sands are a mixture of bitumen, water, sand, and clays, which are mostly mined in open pits. For the separation, normally large volumes of hot water are used, resulting in the production of substantial quantities of waste known as *oil sands tailings* [53]. To minimize waste generation, SFMEs were evaluated as alternative solvents. To this purpose, the solubility of diesel, dodecan, and crude oil as model compounds was tested [54−56]. Ternary and CO_2-responsive amines were used as components of the SFME. In the works of Li et al. [54] and Song et al. [56], ternary amines were used as the hydrophobic compound with EtOH as the hydrotrope (for example: N,N-dimethylbenzylamine). Li et al. also investigated an SFME consisting of a ternary amine as a hydrotrope and a second one as the hydrophobic compound [55]. In this SFME (water, hydrotrope: N- butyldiethanolamine, hydrophobic phase: N,N-dimethylbutylamine), between 0.02-0.14 mg g^{-1} solvent of diesel oil in different compositions of the SFME was solubilized [55]. After the solubilization, the oil were separated, by purging the samples with CO_2. As the hydrophilicity of the amine increased, it became soluble in the water-phase, causing the SFME to transition to a molecular solution. Thereby, a separate oil phase was formed. After the separation, the SFME could be regenerated by purging the samples with N_2 [54−56]. In the works of Li et al. [54] and Song et al., [56] similar mesostructure sizes were obtained. In the case of the SFME with two ternary amines, the size of the structures increased [55]. To further investigate the application, clean oil sands were mixed with crude oil and then washed with the tested SFMEs. In the first cycle, oil removal rates around 90% were obtained in the MF SFMEs with EtOH as a hydrotrope [54,56]. In the subsequent study by Li et al. removal rates exceeding 95% were achieved in W/O SFMEs [55].

Another application of SFMEs in the context of solubilization in the literature is their ability to dissolve petroleum pollutants, which are produced during gas exploration. Thereby, researchers showed that it is possible to separate the oil components and the deoiled oil-based cuttings (OBCs) in SFMEs consisting of water, TBA, and hexane [57,58]. In the work of Jiang et al. less than 1% of the organic molecules remained on the inorganic OBCs [57]. Li et al. showed that relatively small organic molecules were solubilized, while molecules with

Table 3

Overview over publications discussing extractions of different components.

Extraction media	Extracted molecules	System	Reference
Curcuma longa	Curcuminoids	Water/EtOH/TriA, water/DiA/TriA	[41,42]
Curcuma longa	Curcuminoids	ChCl + Lac/EtOH/TriA	[30]
Curcuma longa	Curcuminoids	Water/EtOH/menthol-n-octanoic acid (ME-OA)	[29]
Camptotheca acuminata	Phenolic acids, alkaloids	Water/1,2-propanediol/1-hexyl-3-methylimidazolium tetrafluoroborate	[25]
Rosa roxburghii	gallic acid, catechin, ellagic acid, rutin, isoquercitrin, quercitrin, kajiichigoside F1, roxburic acid	Water/EtOH/*n*-octanol	[52]
Eucommia ulmoides	geniposidic acid, chlorogenic acid, quercetin-3-O-sambubioside, rutin, geniposide, isoquercitrin, astragalin	Water/EtOH/octanol-thymol	[31]

EtOH, ethanol; TriA, triacetin; DiA, diacetin; ChCl, choline chloride; Lac, lactic acid.

a higher molar mass and a complex aromatic structure were less soluble in the SFME [58]. To get a better understanding of this topic, further research is needed. In addition, it is necessary to investigate if the structuring has any influence on the solubility or if there are other crucial parameters.

Notably, it should be mentioned here that El Maangar et al. investigated the solubilization of lanthanides in the ternary mixture of water, sodium salicylate, and ethyl acetate. Depending on the composition of the mixture, different solubilization mechanisms were reported. The solubility was enhanced in the SFME, but the highest solubility was achieved around the critical point [59].

Reactions

In addition to their established role in solubilization and extraction processes, SFMEs have recently been explored as versatile reaction media in a selection of synthetic applications. Among these, especially the production of nanomaterials, e.g., NPs and polymerizations should be mentioned.

Nanomaterials and microcrystals

Nanomaterials are a class of materials, in which at least one dimension is in the nanometer range. Due to their size, the physical and chemical properties, like surface area, magnetic behavior, optical characteristics, and catalytical activity, differ significantly from their bulk counterparts. The properties of the material can be tuned by controlling its size, shape, surface properties, and uniformity [71]. This can be achieved through the choice of production method as well as post-production treatments [60,72] Different bottom-up and top-down methods are known including hydrothermal synthesis, thermal decomposition, microwave-assisted synthesis, solvothermal synthesis, chemical vapor decomposition, and the sol−gel process [72]. A special case of nanomaterials are NPs, where all dimensions are in the nanometer range [71].

Similar to SBMEs [73,74], the structure of SFMEs can provide nanoreactors, which can constrain the growth of the nanomaterials [38,65,66,68]. In addition, the use of hydrotropes instead of surfactants prevents the adsorption of surfactants on the surface, which for example, can limit the catalytical activity of the NPs [65,67,75]. In the literature, SFMEs are examined as solvents to produce nanomaterials at room temperature by precipitation reactions [60−64,67−69,75], by using an ultrasonic-assisted method [66], and by using them as a solvent in the hydrothermal process [19,38,65].

The production of silica NPs [60−62], BaF_2 NPs [63], PbS NPs [64], TiO_2 NP [65], and Ag NPs [75], using a precipitation method, is reported. Sun et al. [60] and Gudelj et al. [61] produced silica NPs with the same experimental protocol. In a common approach, silica NPs are synthesized with the Stöber or microemulsion method [60]. Instead, an SFME consisting of water, EtOH, and dichloromethane was used in the work of Sun et al. They showed that the use of an O/W SFME decreased the particle size and radius distribution compared to the water/EtOH reference system (water/EtOH: 508 nm SFME: 375 nm). Another difference from the conventional Stöber synthesis was the preparation method. In the Stöber process, TEOS was added to the solution, consisting of EtOH and an ammonium hydroxide solution. In this present case, an ammonium hydroxide solution was added to the SFME without stirring. In addition, they investigated the influence of the tetraethyl orthosilicate (TEOS) and ammonium hydroxide concentration, and the composition of the SFME. They showed that the morphology of the NPs changed from spherical NPs in an O/W SFME, to nanowires-like nanomaterials in a MF SFME, to clusters of the NPs in the W/O SFME. These variations were attributed to the change in the structure of the SFME. The TEOS was expected to dissolve in the oil phase of the SFME. It was proposed that in the O/W SFME, TEOS was solubilized in the core of the SFME, which provided the opportunity to produce uniform spherical NPs. The network-like structure of a MF SFME could be used as a solvent for nanowire-like structure, although this nanomaterial showed a tendency toward aggregation. For further investigations, compositions of the SFME in the O/W regions were selected. By increasing the TEOS or the ammonium hydroxide concentration, the size of the NPs increased. The biggest influence was seen by varying the ammonium hydroxide concentration. With a low concentration (0.113 mol L^{-1}) the average diameter of the NPs was around 35 nm, which increased to 250 nm with an ammonium hydroxide concentration of 0.442 mol L^{-1}. This trend was attributed to the increased hydrolysis rate of the TEOS at higher hydroxide ion concentration, resulting in bigger and fewer NPs [60]. Gudelj et al. used 1-heptanol as the hydrophobic compound. The range of the particle sizes was 400-800 nm [61]. Another approach was to directly use TEOS as the hydrophobic phase in an SFME with EtOH and water. The O/W SFMEs with droplet sizes of 210-240 nm were found. NPs with a diameter of 250-300 nm were produced, which is comparable with the size of the SFME droplets. They also showed that only in O/W SFMEs non-aggregating NPs were formed. They proposed that the hydrolysis and the condensation of TEOS upon addition of ammonium hydroxide took place both at the interface and in the oil droplets of the SFME. According to their explanation, the reaction proceeded first on the interface, followed by progressive thickening of the shell. In addition, silica species solubilized in the outer phase preferably reacted with the already existing nuclei.

Furthermore, the authors showed that by decreasing the reaction temperature to −20 °C after 1 min, ring-like spheres instead of spherical NPs were formed. This observation was explained with an expansion of the oil droplet volume, resulting from an increased chemical potential of TEOS, which led to the formation of larger spheres. Below the temperature of −20 °C, this expansion could not be hindered by the already formed silica shell, resulting in ring-like structures [62]. Wu et al. reported the synthesis of BaF_2 NPs in a DES-based SFME [63]. They showed that the SFME demulsified when the samples were purged with CO_2, whereby the NPs were regenerated. This approach could reduce the amount of energy required to regenerate NPs, for instance, compared to centrifugation. However, the resulting NPs had a lamellar structure, while the NPs separated with centrifugation were almost spherical. A possible explanation was that the structure of the SFME was destroyed by purging the samples with CO_2, promoting the aggregation of the NPs and leading to the formation of lamellar structures [63]. Cui et al. prepared amorphous TiO_2 NPs in an O/W SFME (water, IPA, ethyl acetate). Subsequently, the NPs were dispersed in water and tempered to obtain anatase crystalline TiO_2 NPs. The size and the shape of the NPs depended on the composition of the SFME. By increasing the oil content in the O/W region, the shape changed from spheres (size around 10 nm) to polygons with a slightly increased diameter. This difference was explained by an increased number of oil droplets in the SFME, which likely enhanced droplet collision and therefore increased the droplet diameter. These NPs were compared to NPs formed in W/O SBMEs from literature, which exhibited similar sizes (diameter between 5-35 nm). Furthermore, they showed that the produced NPs were photocatalytically active. The degradation rate of methyl orange (MO) was around 97% with the NPs produced at 190 °C. In contrast, TiO_2 NPs produced in an SBME exhibited almost no catalytic activity, which was attributed to the blocked interface by surfactants during synthesis [65]. Zhang et al. demonstrated the formation of Ag NPs in a W/O SFME consisting of water, DMSO, and n-butanol (NBA). The formed NPs were separated by the demulsification of the SFME by decreasing the temperature to 15 °C. In addition, they showed that the Ag NPs were catalytically active, by reducing 4-nitrophenol. They compared the reactivity with NPs produced in an SBME system with cetyltrimethylammonium bromide, which had almost no catalytical activity [75]. The adsorption of surfactants at the NP interface also limited the catalysts activity in this reaction.

Spherical, bioactive glass NPs, with a size around 200-240 nm were reported by Wu et al. They used an O/W SFME consisting of water, EtOH, and dichloromethane as a solvent in an ultrasonic-assisted method. The produced NPs showed the ability to induce the formation of hydroxyapatite on the surface in an *in vitro* cellular biomineralization assay, which could be used in bone regeneration [66].

Han et al. investigated an SFME as a solvent in the hydrothermal method to produce α−Fe_2O_3 NPs. Different parameters like temperature and time of the reaction were examined. By adjusting the temperature, the aggregation of the NPs was reduced, with 180 °C identified as the optimal temperature. Increasing the reaction time from 3 h to 6 h led to a morphological transition from spherical to rhombic NPs. The spherical NPs showed a relatively narrow size distribution with an average particle size of 60 nm, whereas the rhombic NPs exhibited a broader distribution between 25 and 120 nm. These observations were explained by the formation restriction of the NPs due to the SFME used. Increasing either the temperature or the reaction time overcame this constraining effect, promoting Ostwald ripening. In addition, they showed that the NPs can be used in a Fenton-like reaction to degrade pollutant like Rhodamine B. The NP surfaces contained a high density of free ions, which catalyzed the decomposition of H_2O_2 to OH and O_2 radicals. They also demonstrated that the reaction proceeded spontaneously [38].

Further examples, like microcrystals or other micromaterials are shown in Table 4.

Thus, SFMEs have attracted increasing attention as modern reaction media for diverse NPs, enabling a variety of synthetic routes under mild conditions, overcoming the drawbacks of a surfactant-based approach. However, the real influence of the structuring on the formation of NPs has not been investigated until now, but should play an important role in future works, for example, combining simulations with experimental works.

Polymerization

Polymers are defined by IUPAC as ‘a substance composed of macromolecules’. Macromolecules are molecules with a ‘high relative molecular mass’ and a structure determined of ‘multiple repetition of units derived’ of small molecules (monomers) [76]. Depending on the used method, like microemulsion, microsuspension, or bulk polymerization, polymers with different sizes and morphologies can be produced [77]. When microemulsions are used as a solvent, small polymers are prepared, which are important for additives, like pigments, filler, or propellants [78]. Blahnik et al. showed that SFMEs can be used for microsuspension and microemulsion polymerization, which could decrease the impurities in the polymers, due to the lack of surfactants. They tested different short-chain alcohols as a hydrotrope for the O/W microemulsion with water as the hydrophilic phase and methyl methacrylate (MMA) as the hydrophobic phase

Table 4

Overview over publications discussing nanomaterials and mircocrystals.

Type	Solvent	Particle size	Reference
Silica	Water/EtOH/CH_2Cl_2	35-375 nm	[60]
Silica	Water/EtOH/heptanol	400-800 nm	[61]
Silica	Water/EtOH/TEOS	250-300 nm	[62]
BaF_2	Water/EtOH/DES (4-methoxyphenol + N,N-dimethylcyclohexylamine)	Centrifugation: 38-50 nm; CO2: Lamellar structure, 2μm	[63]
PbS	DMSO/IPA/cyclohexane	10-15 nm	[64]
TiO_2	Water/IPA/ethyl acetate (EA)	10-30 nm	[65]
Ag	Water/DMSO/NBA	30-40 nm	[14]
Bioactive glass	Water/EtOH/CH_2Cl_2	200-240 nm	[66]
Fe_2O_3	Water/EtOH/decanol	~ 60 nm	[38]
ZnO	Water/IPA/hexane	5μm	[67]
Ag_2CO_3	Water/IPA/hexane	1μm	[68]
Imidazolate framework-8	Water/DMEA/octanol	20-40 nm	[69]
Mg–Al-LDH	Water/ethylamine nitrate/IL (C12bbim)Cl	Pore sizes around 11.31 nm	[19]
Mg_2Al–Cl	Water/IPA/*n*-hexane	Thickness: 10 nm	[70]
Mg_2Al-LDH	Water/dimethylformamide/BmimPF6	Lateral dimension: ~ 31 nm; thickness: 0.71 nm	[20]

DES, deep eutectic solvents; EtOH, ethanol; IL, ionic liquid; IPA, 2-propanol; NBA, n-butanol; NPs, nanoparticles; TEOS, tetraethyl orthosilicate.

and polymerizable monomer. Replacing the hydrotrope EtOH with TBA led to the formation of mesostructures in the initial solution, resulting in higher yields and smaller molar masses of the polymers. This effect was attributed to the composition of the MMA-rich oil phase and the increased concentration of the alcohol at the interface, resulting in repulsive forces between the formed mesostructures. Furthermore, similar effects were observed upon increasing the hydrotrope concentration in an SFME system, thereby decreasing the mesoscopic structuring. The structure of the polymers obtained also changed to a more compact polymer [77]. In a second work, they proved that by switching the nature of the SFME from O/W to MF, and W/O SFMEs, the morphology of the poly(methyl methacrylate) (PMMA) and the copolymers poly(methyl methacrylate)-poly(2-hydroxyethyl methacrylate) (PMMA-PHEMA) could be changed. Drop-like shapes were obtained by using O/W microemulsions, while sponge-like shapes were derived from MF and W/O SFMEs. Polymers obtained in the oil-rich region, where no structuring was detected, were transparent, solid, and without nanostructuring. The observed differences in polymer morphology were attributed to the different structures of the SFME, even though the polymer sizes were 100−1000 times larger. They also showed that morphologies similar to those in a surfactant-based system can be produced, with pore sizes between 200 nm to a few micrometers [79].

Gruber et al. synthesized 2D covalent organic frameworks (COFs) in an SFME consisting of an acetic acid water solution, 1,4-dioxane, and mesitylene [80]. They investigated the nucleation and the growth at the early stages with an optical technique, an interferometric scattering microscope. They showed that by inducing a structuring in the solvent, a barrier between the reactants and the catalyst was built. This barrier led to an increased long-range order of the COFs compared to the material produced in the binary reference system. In addition, they investigated the influence of the salt concentration on the structuring and the COFs. A high salt concentration induced a phase inversion from an O/W to a W/O microemulsion. As a result, the reactants were located in the continuous phase and were able to build an ordered framework, which is their thermodynamically stable state. With this reaction, the group of Gruber et al. showed that the highly fluctuating structure of an SFME can have a positive influence on reactions, by separating reactants and catalysts [80].

Nanocomposite materials consist of a matrix material, like metal, ceramic or polymers, which is combined with a material in the nanometer range, like NPs [81]. Due to the engineered structure, special chemical and physical properties can be obtained. These properties depend on the size, the size distribution, and the homogeneity of the materials, which are related to the preparation method. SBMEs as a reaction medium for polymer-based nanocomposites could have the advantage of obtaining monodisperse and homogeneous materials [82]. A special case of a polymer nanocomposite material can be produced with poly(ionic liquid)s (poly-ILs) as the matrix material. The polymer combines a polymeric backbone and IL monomers in repeating units [83]. Advantages similar to those of SBMEs may be achieved

with SFMEs. Wang et al. reported the production of poly(ionic liquid)s with a thio-ene "click reaction'. The ionic liquid was used as one phase in the SFME and polymerized by adding a photoinitiator [22–24]. One polymerization step occurred in the inner phase of the SFME, resulting in the formation of microspheres, while crosslinking polymerization took place at the interface, leading to the connection of the microspheres and the formation of a network structure. The morphology of the material was influenced by increasing the amount of the hydrotrope. A higher concentration of the hydrotrope led to decreased bead sizes and an increased crosslinking, due to higher amounts of microstructures of the SFMEs and a change in interfacial tension. The material produced in the SFME showed good adsorption performance for anionic and non-ionic dyes. Minimal adsorption of positive charged dyes was observed, likely due to electrostatic repulsions with the positively charged poly-ILs. Poly-Ils, which were synthesized with higher hydrotrope concentration, showed better adsorption performance as a result of a higher specific surface area with smaller bead sizes [22]. The SFME and the poly-IL were further used to synthesize copper NPs/poly-IL composite materials. This material could also be used as a physical adsorption material as the poly-IL itself, but it worked additionally as a reduction catalyst for the dyes due to the catalytical activity of the Cu, with $NaBH_4$ as the reducing agent [23]. Salabat et al. also prepared a nanocomposite material for the degradation of dyes. To this purpose, a poly(MMA)/TiO_2 nanocomposite was produced in an SFME consisting of 1-butyl-3-methylimidazolium tetrafluoroborate, NBA, and MMA. They showed that the absorbance of the TiO_2 composites was shifted to a higher wavelength, as a result, visible light could be used to degrade dyes, like MO [21].

Other nanocomposites were prepared in SFMEs to obtain materials with different properties. Mirhoseini et al. synthesized a poly(MMA)/Ag composite in an SFME consisting of water, NBA, and MMA. As a reference system, an SBME containing the surfactant tween 80 was used. In both cases, spherical NPs with an average diameter between 10 and 25 nm were observed. These results indicate that aggregation can be effectively prevented in both systems during the polymerization reaction, suggesting that SFMEs can serve as a simplified model for the production of such materials. The produced materials exhibited similar antibacterial activity toward *Escherichia coli* to that of the reference system containing pure Ag NPs. The pure poly(MMA) showed no antibacterial activity. It was shown that surfactants had no positive influence on the antibacterial activity; therefore, the simplified SFME system could be used [84]. In addition, Wang et al. produced a poly-IL nanocomposite material with carbon black. The SFME used consisted of water, IPA, and the IL (1-allyl-3-methylimidazolium hexafluorophosphate). The structure of this material was sheet-like networks with U-link chains, with a higher electrical conductivity compared to other carbon black nanocomposite materials. Furthermore, they showed that the material had a good stability in cyclic stain tests. The effect of the SFME on the production of the material was not investigated [24].

Li et al. also investigated conductive materials. In this case, the goal was to produce conductive fabrics, with the softness of fabrics and the conductivity of metals. To this purpose, polyester (PET) fabrics were pre-coated with polyaniline (PANI) in an SFME (hydrochloric acid, EtOH, dichloromethane). Afterward, the material was electroplated with Cu to obtain conductive fabrics. These fabrics showed good conductivities, with some of the wearing comfort being preserved [85].

The influence of the structuring on polymerization was only investigated in few publications, where the structure of the polymer depends on the composition of the SFME [79,80]. In some cases, the materials were also compared to those prepared in SBMEs, providing a better understanding of the influence of the structuring on these materials [84]. However, it should be mentioned that it is possible that not the structure, but rather more specific interactions like hydrogen bonds play the decisive role in the selectivity and stability of the products [86].

Solubilization and degradation of lignin

Biomass, and lignin as a component, is considered a biological substitute for fossil resources. Lignin could be a good precursor for aromatic molecules, due to its highly aromatic structure. However, the problem is its complex structure and poor solubility [87]. Kong et al. used two different SFMEs to solubilize and degradate lignin [87,88]. In these works, SFMEs consisting of water, NPA/IPA, and *n*-octane were used. The solubility of lignin increased in both ternary systems, compared to the reference systems (pure water, *n*-octane, NPA/IPA, and the binary systems). In the O/W SFME with NPA, 79.1 g L^{-1} [87] and with IPA, 64.9 g L^{-1} [88] of lignin were solubilized. By adding lignin to the SFME, the mesostructure sizes increased, which suggests that lignin was deposited on the interface. The solubility in the SFME was thereby influenced by the polarity of the solvent and the accumulation of lignin at the surface of the mesostructure. In the next step, lignin was degraded in a solvothermal reaction [87,88]. $CuSO_4$ was used as a catalyst. A maximum yield of 90.2 mg g^{-1} biomass of aromatic monomers was obtained in an O/W microemulsion (pure water: 15 mg g^{-1}, water/NPA (50/50): 62 mg g^{-1}) [87]. In the second work, acidic ILs (for example 1-carboxymethyl-3-methylimidazolium chloride) were used as catalysts [88]. A yield of 128.1 mg g^{-1} of phenolic monomers was obtained. Different starting

materials, like corncob lignin were used. In addition, they proved in this work that 4-phenylethanol was produced with a high selectivity (75.7 mg g^{-1}). In the proposed degradation mechanism, the lignin is found in the interface, due to its hydrotropicity. As a result, p-cinnamic acid and ferulic acid are selectively produced by deesterification as an intermediate [88]. Both works suggest that SFMEs can be considered good solvents for lignin. However, the influence of the structuring is not really investigated in the works, and should play an important role in further research.

Surfactant-free microemulsion in fuels

The search for alternative and more eco-friendly fuels is a constant need in the context of an accelerating climate change. Some contributing efforts were also made with SFMEs, in the works of Abrar et al. Generally, surfactants are required in diesel formulations to combine hydrophilic and hydrophobic compounds, thereby producing a stable monophasic system; however, their presence can reduce the overall sustainability effect of the formulation. Additionally, the needed surfactant could increase the price of the fuel. Due to similar vapor penetration and liquid length, these formulations could be used in the same engine as conventional fuels. Abrar et al. replaced pure diesel by SFMEs consisting of water, linear-chain alcohols and alcohol mixtures, and diesel (water: 0.22% (v/v), alcohol: 19.6-39.5% (v/v), diesel: 60-80% (v/v)), which decreased the amount of diesel and therefore increased the sustainability of the formulation [89,90]. Droplet sizes around 10 nm were found in the SFME, consisting, of e.g., water, NBA, and diesel [90]. They showed that the properties of this SFME, like heating values, density, and kinematic viscosity were lower than in pure diesel. However, the values were all within the ASTM D975 standard specifications of diesel-fuel oils. They also performed some tests with a single-cylinder constant-speed compression-ignition engine. The experiments showed that, by using an SFME equal or even lower fuel and energy was consumed, which led to equal or even higher amounts of work. In addition, by using the right compositions of the SFME and the right loading, CO, NO_x, unburned hydrocarbon (HC), and particulate matter (PM) could be reduced. The economic analysis in India revealed that this formulation is more economically friendly compared to normal fossil fuels [89].

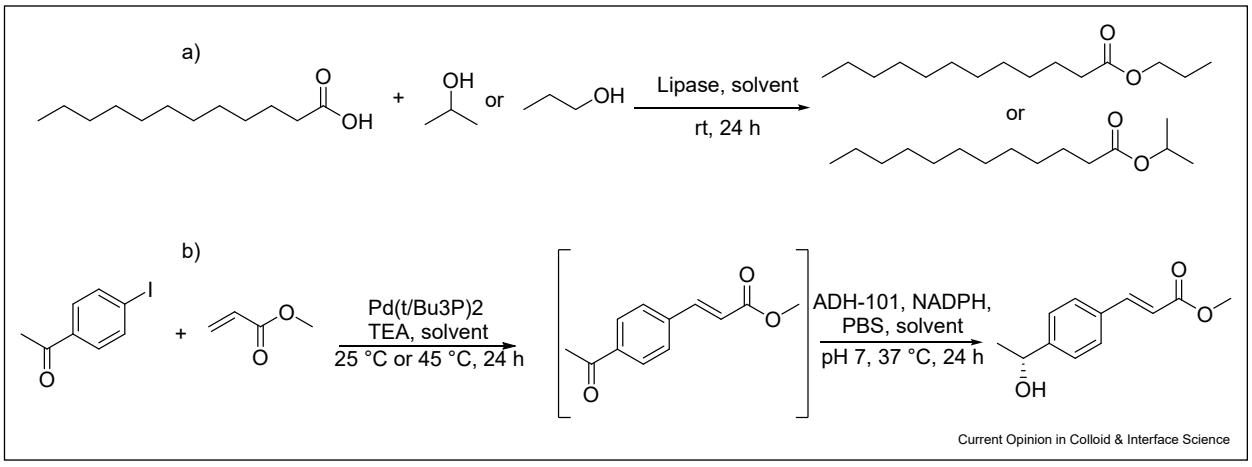
An even better alternative for sustainable fuels would be plant-oil based diesels, due to an environmental aspect. These fuels would be renewable, and free of sulfur, aromatic hydrocarbons, and metals. However, these suffer from many drawbacks, like high viscosity, low volatility, and polyunsaturated chemical structure, making them currently still less interesting for applications. Yet, a work by Kunz et al. showed that, by using EtOH, ethanolotropes (hydrotropes for EtOH and other water-free systems), and bio-oils, the kinematic viscosity was reduced, which could help to overcome these problems of vegetable oils. In addition, the solubility of EtOH in the plant-oils was increased in these formulations [91]. Rapeseed oil [91], safflower oil [92], moringa oil [92], and *salicornia persica* oil [93] were used as plant-based oils in SFMEs. Ethanolotropes like 2-methyltetrahydrofuran [91], 1-heptanol [92,93], or 1-octanol [92,93] were investigated. The low-temperature behavior, the kinematic viscosity, density, and the structuring of the systems were examined. By adjusting the components and the compositions of the SFMEs, the ASTM D6751 standard for biodiesel could be achieved for different properties of the systems [92,93].

Limitations of surfactant-free microemulsions

While the highly fluctuating and less rigid interface of SFMEs can have its advantages due to enhanced exchange rates and dynamics compared to SBMEs, it can likewise have its limitations. For example, Mitsou et al. reported that the yield of the esterification of lauric acid (LA) with NPA or IPA with a lipase in general was much higher in a bis-(2-ethylhexyl)sulfosuccinate sodium salt (AOT) SBME system than in an SFME (reaction equation is shown in Figure 3 (a)). By using the *Thermomyces lanuginosa* as a lipase, similar yields for the esterification with NPA in SFMEs were achieved, while even here the yield for the esterification with IPA was lower. It is therefore evident that the SBME system with AOT exhibited broader applicability, whereas SFME systems appear to achieve high yields only under specific reaction conditions [94].

In addition, it is critical to evaluate whether the observed reaction outcomes are governed by the SFME structuring itself or merely by the overall solubility of reactants. In the study by Hofmann et al. a system was investigated where the yield of a tandem-reaction (reaction equation is shown in Figure 3 (b)) was not increased by the structuring of the SBME or SFME systems, but rather by the solubility of the products and the enzyme used. Specifically, the addition of IPA to water induced the enzyme to be salted-out, preserving its folding structure and catalytic activity. By adding the benzylic alcohol as the oil phase into this binary mixture, the solubility of the other reaction components increased, boosting the yield compared to the binary system. All the binary and ternary solvent systems outperformed the surfactant-based system in terms of yield. The highest yield was obtained in a ternary mixture with minimal structuring, suggesting that the reaction performance was primarily driven by the solubilization effects of the ternary mixtures rather than by any structuring features [95].

Figure 3



Reaction equation (1) of the esterification from the work of Mitsou et al. [94] and (2) the tandem-reaction from the work of Hofmann et al. [95].

Conclusion and visions of surfactant-free microemulsions

Ternary systems with hydrotropes can form microemulsions without surfactants. Recent publications have increasingly focused on elucidating the complete mechanism of SFME formation using computational approaches. Furthermore, a significant amount of published research has dealt with SFMEs as solvents for diverse applications including solubilization and extraction of natural compounds, the synthesis of NPs, polymerization processes, and fuel formulation. In many of these cases, the structuring of the SFMEs seem to influence the solvent properties and, consequently, their application. In this context, it should be noted that SFME is currently used as a fashionable term. It is therefore important to carefully examine individual publications to determine whether they refer to an SFME or merely a ternary solution without structuring. The use of SFMEs as solvents inherently increases the complexity of the system. While computational simulations have been employed to investigate the solubility of natural molecules, the impact of SFME structuring on other applications remains predominantly uninvestigated. In certain systems, properties like solubility or polarity can take precedence over structuring in determining performance. Future research must prioritize determining the critical parameters governing SFME applications including whether solvent structuring plays a decisive role.

Looking ahead, SFMEs offer promising opportunities for the development of greener, more sustainable, and/or efficient chemical processes. This is especially important when surfactants hinder further processing. While recent studies have demonstrated their potential in solubilization, extraction, and even as media for various synthetic reactions, many of these examples still rely on conventional or environmentally questionable solvents, particularly chlorinated hydrocarbons such as dichloromethane or chloroform. This reliance not only contradicts the sustainability goals often associated with SFMEs, but also limits their broader applicability, especially in industrial or pharmaceutical contexts, where regulatory pressure on hazardous solvents is increasing. To fully realize the environmental advantages of SFMEs, future research must focus on integrating truly green solvent systems into microemulsion formulations. Bio-based solvents (e.g., ethyl lactate, γ-valerolactone), low-toxicity esters, short-chain alcohols, or even supercritical fluids could serve as viable alternatives, provided that the physicochemical parameters needed for stable SFME formation, such as polarity balance, hydrogen bonding capacity, and miscibility, are maintained. Furthermore, the development of predictive models or design rules for selecting compatible green solvent mixtures would significantly accelerate innovation in this field.

Credit Author statement

Lena Schmauser: Writing -Original Draft, Visualization, Investigation.

Eva Müller: Writing -Review & Editing, Investigation.

Didier Touraud: Investigation.

Werner Kunz: Supervision, Project administration, Review & Editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

No data was used for the research described in the article.

References

Papers of particular interest, published within the period of review, have been highlighted as:

* of special interest
** of outstanding interest

1. Kumar P, Mittal KL: *Handbook of microemulsion science and technology*. New York: Macel Dekker; 1999, https://doi.org/10.1201/9780203752739.

2. Smith GD, Donelan CE, Barden RE: **Oil-continuous microemulsions composed of hexane, water, and 2-propanol**. *J Colloid Interface Sci* 1977, **60**:488–496. Available from: https://linkinghub.elsevier.com/retrieve/pii/0021979777903137.

3. Kunz W, Holmberg K, Zemb T: **Hydrotropes**. *Curr Opin Colloid Interface Sci* 2016, **22**:99–107. Available from: https://linkinghub.elsevier.com/retrieve/pii/S1359029416300334.

4. Hou W, Xu J: **Surfactant-free microemulsions**. *Curr Opin Colloid Interface Sci* 2016, **25**:67–74. Available from: https://linkinghub.elsevier.com/retrieve/pii/S1359029416300711.

5. Prévost S, Lopian T, Pleines M, Diat O, Zemb T: **Small-angle scattering and morphologies of ultra-flexible microemulsions**. *J Appl Crystallogr* 2016, **49**:2063–2072.

6. Schmidt RF, Prévost S, Gradzielski M, Zemb T: **Structure of microemulsions in the continuous phase channel**. *Eur Phys J E* 2023, **46**:76.

7. Schöttl S, Marcus J, Diat O, Touraud D, Kunz W, Zemb T, *et al.*: **Emergence of surfactant-free micelles from ternary solutions**. *Chem Sci* 2014, **5**:2949–2954.

8. Lopian T, Schöttl S, Prévost S, Pellet-Rostaing S, Horinek D, Kunz W, *et al.*: **Morphologies observed in ultraflexible microemulsions with and without the presence of a strong acid**. *ACS Cent Sci* 2016, **2**:467–475. Available from: https://pubs.acs.org/doi/10.1021/acscentsci.6b00116.

9. Prévost S, Krickl S, Marčelja S, Kunz W, Zemb T, Grillo I: **Spontaneous ouzo emulsions coexist with pre-ouzo ultraflexible microemulsions**. *Langmuir* 2021, **37**:3817–3827.

10. Chen C, Gao Y, Li M, Sun C: **Unraveling the phase behavior and stability of surfactant-free microemulsions: from molecular interactions to macroscopic properties**. *Langmuir* 2024, **40**:26227–26238. Available from: https://pubs.acs.org/doi/10.1021/acs.langmuir.4c03761.

11. Pandey A, Pandey S: **Formation of ethanolamine-mediated surfactant-free microemulsions using hydrophobic deep eutectic solvents**. *Langmuir* 2024, **40**:2254–2267. Available from: https://pubs.acs.org/doi/10.1021/acs.langmuir.3c03324.

12. Jing J, Qi J, Yang Y, Yue W, Wang N, Li X, *et al.*: **Multiple-stimuli-responsive surfactant-free microemulsions based on hydrophobic deep eutectic solvents**. *Langmuir* 2023, **39**:6730–6739. Available from: https://pubs.acs.org/doi/10.1021/acs.langmuir.3c00205.

13. Jing J, Li X, Zhang Y, Liu Y, Lu H, Wang J, *et al.*: **pH-Responsive regulation of a surfactant-free microemulsion based on hydrophobic deep eutectic solvents**. *Langmuir* 2022, **38**:7898–7905. Available from: https://pubs.acs.org/doi/10.1021/acs.langmuir.2c00181.

14. Zhang Y, Chen X, Liu X: **Temperature-induced reversible-phase transition in a surfactant-free microemulsion**. *Langmuir* 2019, **35**:14358–14363. Available from: https://pubs.acs.org/doi/10.1021/acs.langmuir.9b02842.

15. Qi W, Deng Q, Du N, Hou W: **Surfactant-free microemulsions of n-butanol, ethanol, and water**. *J Mol Liq* 2023, **390**, 122980. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0167732223017865.

16. Li M, Wakata Y, Zeng H, Sun C: **On the thermal response of multiscale nanodomains formed in trans-anethol/ethanol/water surfactant-free microemulsion**. *J Colloid Interface Sci* 2023, **652**:1944–1953. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0021979723016545.

17. Ashfaq B, Sen A, Zarzar LD: **Uncovering chemical principles governing nanophase formation in ternary solvents**. *Angew Chem* 2025, e202421167. Available from: https://onlinelibrary.wiley.com/doi/10.1002/ange.202421167; 2025.

18. Li Z, Fan Z, Chen Z: **Depiction of a non-aqueous ionic liquid surfactant-free microemulsion by dielectric relaxation spectroscopy**. *Colloids Surf A Physicochem Eng Asp* 2022, **649**, 129482. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0927775722012377.

19. Huang Y, Fan X, Wang H, Li Z, Xiong D, Pei Y: **Tuning Mg-Al layered double hydroxides synthesized from the novel ionic liquid-based surfactant-free microemulsion for efficiently phosphate removal in aqueous solutions**. *J Mol Liq* 2023, **382**, 121826. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0167732223006293.

20. Zhan T, Zhang Y, Yang Q, Deng H, Xu J, Hou W: **Ultrathin layered double hydroxide nanosheets prepared from a water-in-ionic liquid surfactant-free microemulsion for phosphate removal from aquatic systems**. *Chem Eng J* 2016, **302**:459–465. Available from: https://linkinghub.elsevier.com/retrieve/pii/S1385894716307094.

21. Salabat A, Mirhoseini BS, Mirhoseini F: **Ionic liquid based surfactant-free microemulsion as a new protocol for preparation of visible light active poly(methyl methacrylate)/TiO2 nanocomposite**. *Sci Rep* 2024, **14**, 15676. Available from: https://www.nature.com/articles/s41598-024-66872-7.

22. Wang A, Liu Z, Xu L, Lou N, Li M, Liu L: **Controllable click synthesis of poly(ionic liquid)s by surfactant-free ionic liquid microemulsions for selective dyes reduction**. *React Funct Polym* 2020, **147**, 104464. Available from: https://linkinghub.elsevier.com/retrieve/pii/S1381514819310764.

23. Wang A, Liu Z, Li S, Liu Y, Zhao H, Liu Y, *et al.*: **In-situ preparation and properties of copper nanoparticles/poly(ionic liquid) composites by click chemistry within surfactant-free ionic liquid microemulsions**. *J Mol Liq* 2021, **342**, 117572. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0167732221022972.

24. Wang A, Ye T, Liu Y, Song M, Lou N, Wu G, *et al.*: **Facile in-situ synthesis of carbon black@poly(ionic liquid) composites with a smooth U-link chain macrostructure within surfactant-free ionic liquid microemulsions**. *Compos Appl Sci Manuf* 2024, **176**, 107859. Available from: https://linkinghub.elsevier.com/retrieve/pii/S1359835X23004359.

25. * Luo Z, Tian M, Ahmad N, Qiu W, Zhang Y, Li C, *et al.*: **A switchable temperature-responsive ionic liquid-based surfactant-free microemulsion for extraction and separation of hydrophilic and lipophilic compounds from Camptotheca acuminata and extraction mechanism**. *Colloids Surf B Biointerfaces* 2023, **222**, 113067. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0927776522007512.
This publication highlights the usability of SFMEs as an extraction medium, adding that the demulsification of the SFME for the pre-separation of components can easily be achieved by decreasing the temperature.

26. Pei X, Li Z, Wang H, Zhou Q, Liu Z, Wang J: **CO_2-Switchable phase separation of nonaqueous surfactant-free ionic liquid-based microemulsions**. *ACS Sustainable Chem Eng* 2022, **10**:1777–1785. Available from: https://pubs.acs.org/doi/10.1021/acssuschemeng.1c05737.

27. Fan T, Chen L, Xia X, Wu Y, Zhang J, Yin K, *et al*.: **Dissipative particle dynamics quantitative simulation of the formation mechanism and emulsification driving force of deep eutectic solvent-based surfactant-free and water-free microemulsion**. *Ind Eng Chem Res* 2021, **60**:3249–3258. Available from: https://pubs.acs.org/doi/10.1021/acs.iecr.0c06193.

28. Pandey A, Pandey S: **Density and dynamic viscosity of hydrotrope-assisted surfactant free microemulsions formed with hydrophobic deep eutectic solvents**. *J Chem Eng Data* 2024, **69**:3718–3729. Available from: https://pubs.acs.org/doi/10.1021/acs.jced.4c00182.

29. Zhang L, Dai S, Zhou L, Liu X, Zhu Y, Zhao X: **Extraction of curcumin from turmeric rhizome utilized by a surfactant-free microemulsion based on deep eutectic solvent**. *Colloids Surf A Physicochem Eng Asp* 2024, **701**, 134984. Available from: https://linkinghub.elsevier.com/retrieve/pii/S092777572401848X.

30. Huber V, Muller L, Degot P, Touraud D, Kunz W: **NADES-based surfactant-free microemulsions for solubilization and extraction of curcumin from Curcuma Longa**. *Food Chem* 2021, **355**, 129624. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0308814621006300.

31. Wang JD, Liu YH, Fu YJ: **Extraction of natural active ingredients from Eucommia ulmoides leaves by natural deep eutectic solvent-based surfactant-free microemulsion: experimental and mechanism study**. *Microchem J* 2025, **212**, 113199. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0026265X25005533.

32. Li M, Yuan J, Yang Q, Liu Z, Meng S, Wang X, *et al*.: **Therapeutic deep eutectic solvents based on natural product matrine and caprylic acid: physical properties, cytotoxicity and formation of surfactant free microemulsion**. *J Drug Deliv Sci Technol* 2023, **90**, 105177. Available from: https://linkinghub.elsevier.com/retrieve/pii/S1773224723010298.

33. Seo S, Lee Hs, Yoon TJ: **Kirkwood-Buff analysis of binary and ternary systems consisting of alcohols (methanol, ethanol, 1-Propanol, and 2-Propanol), water, and *n* -Hexane to understand the formation of surfactant-free microemulsions**. *J Phys Chem B* 2024, **128**:5092–5108. Available from: https://pubs.acs.org/doi/10.1021/acs.jpcb.4c01563.

34. Schöttl S, Matubayasi N, Horinek D: **Solubilization power of surfactant-free microemulsions**. *Phys Chem Chem Phys* 2020, **22**:22185–22189. Available from: https://xlink.rsc.org/?DOI=D0CP02933E.

35. Han Y, Pan N, Li D, Liu S, Sun B, Chai J, *et al*.: **Formation mechanism of surfactant-free microemulsion and a judgment on whether it can be formed in one ternary system**. *Chem Eng J* 2022, **437**, 135385. Available from: https://linkinghub.elsevier.com/retrieve/pii/S1385894722008889.

36. Ma W, Du N, Hou W: **Thermodynamic explanation of surfactant-free microemulsions**. *J Phys Chem B* 2025, **129**:2115–2127. Available from: https://pubs.acs.org/doi/10.1021/acs.jpcb.4c08376.

37. Stemplinger S, Zemb T, Horinek D, Dufrêche JF: **Aggregating fluids under centrifugal fields**. *J Mol Liq* 2023, **386**, 122358. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0167732223011625.

38. Han Y, Pan N, Liu S, Chai J, Li D: **Growth of nano metal oxide in surfactant-free microemulsion template and its catalytic mechanism simulation**. *J Environ Chem Eng* 2022, **10**, 108006. Available from: https://linkinghub.elsevier.com/retrieve/pii/S221334372200879X.

39. Sedlák M: **Surfactant-free self-assembled mesoscale structures in multicomponent mixtures comprising solids, liquids, and gases: nanoparticles, nanodroplets, and nanobubbles**. *Front Soft Matter* 2023, **3**. Publisher: Frontiers Media SA. Available from: https://www.frontiersin.org/articles/10.3389/frsfm.2023.1225709/full.

40. Liu W, Pan N, Han Y, Li D, Chai J: **Solubilization, stability and antioxidant activity of curcumin in a novel surfactant-free microemulsion system**. *LWT* 2021, **147**, 111583. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0023643821007362.

41. Degot P, Huber V, Hofmann E, Hahn M, Touraud D, Kunz W: **Solubilization and extraction of curcumin from Curcuma Longa using green, sustainable, and food-approved surfactant-free microemulsions**. *Food Chem* 2021, **336**, 127660. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0308814620315223.

42. Degot P, Huber V, Touraud D, Kunz W: **Curcumin extracts from Curcuma Longa – improvement of concentration, purity, and stability in food-approved and water-soluble surfactant-free microemulsions**. *Food Chem* 2021, **339**, 128140. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0308814620320021.

43. Zhang X, Song M, Chai J, Cui X, Wang J: **Preparation, characterization and application of a surfactant-free microemulsion containing 1-octen-3-ol, ethanol, and water**. *J Mol Liq* 2020, **300**, 112278. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0167732219348482.

44. Liu S, Han Y, Liu X, Wang R, Sun B, Nakabayashi A, *et al*.: **Improving the solubilization, stability, dialysis performance and antioxidant properties of quercetin in surfactant-free microemulsion**. *J Mol Liq* 2024, **409**, 125531. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0167732224015903.

45. Han Y, Liu S, Du Y, Li D, Pan N, Chai J, *et al*.: **A new application of surfactant-free microemulsion: solubilization and transport of drugs and its transdermal release properties**. *J Taiwan Inst Chem Eng* 2022, **138**, 104473. Available from: https://linkinghub.elsevier.com/retrieve/pii/S187610702200270X.

46. Song M, Liu W, Wang Q, Wang J, Chai J: **A surfactant-free microemulsion containing diethyl malonate, ethanol, and water: microstructure, micropolarity and solubilizations**. *J Ind Eng Chem* 2020, **83**:81–89. Available from: https://linkinghub.elsevier.com/retrieve/pii/S1226086X19306070.

47. * Zhang Z, Song Q, Zhao Z, Chang K, Shu P, Wang J, *et al*.: **Cosmetically approved short-chain alcohol/triethyl citrate/water surfactant-free microemulsions and potential application to transdermal penetration of α-Arbutin**. *Langmuir* 2024, **40**:11011–11022. Available from: https://pubs.acs.org/doi/10.1021/acs.langmuir.4c00382.
This publication investigates the solubility of α-arbutin as a bioactive molecule and outlines the usability, versatility, and improvement by using a cosmetically improved SFME.

48. Alshamrani M, Khan MK, Khan BA, Salawi A, Almoshari Y: **Technologies for solubility, dissolution and permeation enhancement of natural compounds**. *Pharmaceuticals* 2022, **15**:653. Available from: https://www.mdpi.com/1424-8247/15/6/653.

49. Azmir J, Zaidul ISM, Rahman MM, Sharif KM, Mohamed A, Sahena F, *et al*.: **Techniques for extraction of bioactive compounds from plant materials: a review**. *J Food Eng* 2013, **117**:426–436. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0260877413000277.

50. Kharat M, Du Z, Zhang G, McClements DJ: **Physical and chemical stability of curcumin in aqueous solutions and emulsions: impact of pH, temperature, and molecular environment**. *J Agric Food Chem* 2017, **65**:1525–1532. Available from: https://pubs.acs.org/doi/10.1021/acs.jafc.6b04815.

51. Nelson KM, Dahlin JL, Bisson J, Graham J, Pauli GF, Walters MA: **The essential medicinal chemistry of curcumin: miniperspective**. *J Med Chem* 2017, **60**:1620–1637. Available from: https://pubs.acs.org/doi/10.1021/acs.jmedchem.6b00975.

52. Wang JD, Cai ZH, Chang YH, Wang YQ, Fu LN, Yan XY, *et al*.: **Temperature-responsive surfactant-free microemulsion solvent: preparation, characterization and application of extraction hydrophobic and hydrophilic components in plant matrix**. *Ind Crop Prod* 2022, **186**, 115216. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0926669022006999.

53. Vedoy DRL, Soares JBP: **Water-soluble polymers for oil sands tailing treatment: a review**. *Can J Chem Eng* 2015, **93**:888–904. Available from: https://onlinelibrary.wiley.com/doi/10.1002/cjce.22129.

54. Li X, Lu H, Wang L, Dai S, Wang B, Wu Y: **Oil removal from solid surface by using surfactant-free microemulsion**

regulated by CO2: a sustainable approach for treating oily waste. *J Clean Prod* 2022, **345**, 130990. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0959652622006254.

55. Li X, Liu X, Qi J, Yang Y, Wang J, Dai S, *et al*.: **Treating oily solids using a CO2-responsive surfactant-free microemulsion: an enhanced approach for oil removal from solid surfaces**. *Chem Phys Mater* 2023, **2**:217–224. Available from: https://linkinghub.elsevier.com/retrieve/pii/S2772571522000584.

56. * Song L, Jia H, Zhang F, Jia H, Wang Y, Xie Q, *et al*.: **Sustainable utilization of surfactant-free microemulsion regulated by CO_2 for treating oily wastes: a interpretation of the response mechanism**. *Langmuir* 2024, **40**:960–967. Available from: https://pubs.acs.org/doi/10.1021/acs.langmuir.3c03162.
This publication outlines the positive influence of the phases of the SFME on the clearance of oil sands, and the recovery by the demulsification of the SFME with CO_2.

57. Jiang G, Li J, Zhao L, Meng T, Yu J, Wang H, *et al*.: **Insights into the deoiling efficiency of oil-based cuttings by surfactant-free microemulsions**. *J Environ Chem Eng* 2022, **10**, 107306. Available from: https://linkinghub.elsevier.com/retrieve/pii/S2213343722001798.

58. ** Li J, Yue H, Wen M, Zhao L, Jiang G, Yu J, *et al*.: **Conversion mechanism of organic matter while cleaning oil-based drilling cuttings using surfactant-free microemulsions**. *ChemistrySelect* 2023, **8**, e202301921. Available from: https://chemistry-europe.onlinelibrary.wiley.com/doi/10.1002/slct.202301921.
This publication shows the versatility of SFMEs by using them to clean oil-based drillings. In addition, they investigated the solubility of the different compounds on a molecular level with positive ion atmospheric pressure photoionization Fourier transform ion cyclotron resonance mass spectroscopy.

59. * El Maangar A, Gramüeller J, Huber V, Degot P, Touraud D, Gschwind R, *et al*.: **Solubilisation–microstructure relationship of trivalent salts in hydrotropic ternary systems**. *C R Chim* 2025, **27**:185–202. Available from: https://comptes-rendus.academie-sciences.fr/chimie/articles/10.5802/crchim.310/.
This publication investigates a completely new research field by the solubilization of lanthanides. In addition, they used an anionic hydrotrope and showed that different solubilization mechanisms can be present in a ternary mixture.

60. Sun B, Chai J, Chai Z, Zhang X, Cui X, Lu J: **A surfactant-free microemulsion consisting of water, ethanol, and dichloromethane and its template effect for silica synthesis**. *J Colloid Interface Sci* 2018, **526**:9–17. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0021979718304570.

61. Gudelj M, Kranjac M, Jurko L, Tomšič M, Cerar J, Prkić A, *et al*.: **Structure and potential application of surfactant-free microemulsion consisting of heptanol, ethanol and water**. *Colloid Interf* 2024, **8**:53. Available from: https://www.mdpi.com/2504-5377/8/5/53.

62. * Lu J, Peng L, Zhang A, Xu J, Wu M, Ma S: **Fabrication of tetraethyl orthosilicate/ethanol–water surfactant-free microemulsions and their applications in self-templating synthesis of monodispersed silica colloidal spheres**. *RSC Adv* 2024, **14**:39040–39049. Available from: https://xlink.rsc.org/?DOI=D4RA07679F.
This review outlines that it is possible to produce nanoparticles in SFMEs with tetraethyl orthosilicate as the hydrophobic phase and the starting material for the nanoparticles. They also proved that the form and size of the NPs depends on the phase of the SFME.

63. Wu Y, Jing J, Li X, Yue W, Qi J, Wang N, *et al*.: **CO_2-Responsive hydrophobic deep eutectic solvent based on surfactant-free microemulsion-mediated synthesis of BaF_2 nanoparticles**. *Langmuir* 2023, **39**:1181–1189. Available from: https://pubs.acs.org/doi/10.1021/acs.langmuir.2c02991.

64. Tarkas H, Rokade A, Upasani D, Pardhi N, Rokade A, Sali J, *et al*.: **Pioneering method for the synthesis of lead sulfide (PbS) nanoparticles using a surfactant-free microemulsion scheme**. *RSC Adv* 2024, **14**:4352–4361. Available from: https://xlink.rsc.org/?DOI=D3RA07679B.

65. Cui X, Wang J, Zhang X, Wang Q, Song M, Chai J: **Preparation of Nano-TiO_2 by a surfactant-free microemulsion–hydrothermal method and its photocatalytic activity**. *Langmuir* 2019, **35**:9255–9263. Available from: https://pubs.acs.org/doi/10.1021/acs.langmuir.9b01392.

66. Wu Y, Tang L, Zhang Q, Kong F, Bi Y: **A novel synthesis of monodispersed bioactive glass nanoparticles via ultrasonic-assisted surfactant-free microemulsion approach**. *Mater Lett* 2021, **285**, 129053. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0167577X20317602.

67. Zhang X, Han Y, Liu W, Pan N, Li D, Chai J: **A novel synthesis of hexagonal cylinder-like ZnO with an excellent performance by a surfactant-free microemulsion-hydrothermal method**. *J Ind Eng Chem* 2021, **97**:326–336. Available from: https://linkinghub.elsevier.com/retrieve/pii/S1226086X21000964.

68. Pan N, Liu S, Han Y, Li D, Chai J: **A comparison study of the performance of Ag2CO3 photocatalysts synthesized respectively in a surfactant-free microemulsion, water, and a water/propan-2-ol mixture**. *J Materiomics* 2022, **8**:781–789. Available from: https://linkinghub.elsevier.com/retrieve/pii/S2352847822000259.

69. Zhou Y, Zhao S, He S, Zhang Y: **Adsorption of sodium dodecyl benzene sulfonate on zeolitic imidazolate framework-8 synthesized using surfactant-free microemulsion as template**. *Colloids Surf A Physicochem Eng Asp* 2022, **650**, 129620. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0927775722013759.

70. Xu J, Deng H, Song J, Zhao J, Zhang L, Hou W: **Synthesis of hierarchical flower-like Mg2Al-Cl layered double hydroxide in a surfactant-free reverse microemulsion**. *J Colloid Interface Sci* 2017, **505**:816–823. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0021979717307464.

71. Baig N, Kammakakam I, Falath W: **Nanomaterials: a review of synthesis methods, properties, recent progress, and challenges**. *Mater Adv* 2021, **2**:1821–1871.

72. Iravani S: **Surfactant-free synthesis of metal and metal oxide nanomaterials: a perspective**. *RSC Sustain* 2023, **1**:72–82. Available from: https://xlink.rsc.org/?DOI=D2SU00088A.

73. Wolf S, Feldmann C: **Microemulsions: options to expand the synthesis of inorganic nanoparticles**. *Angew Chem Int Ed* 2016, **55**:15728–15752.

74. Denk P, Reigl S, Rödig B, Sztucki M, Prévost S, Zemb T, *et al*.: **Biliquid oil-in-water nanofoams and spontaneous emulsification obtained with a surfactant resistant to curvature changes**. *J Colloid Interface Sci* 2025, **684**:105–121.

75. Zhang Y, Chen X, Zhu B, Zhou Y, Liu X, Yang C: **Temperature-switchable surfactant-free microemulsion**. *Langmuir* 2020, **36**:7356–7364. Available from: https://pubs.acs.org/doi/10.1021/acs.langmuir.0c00828.

76. Gold V. *The IUPAC compendium of chemical terminology: the Gold book*. 4th ed. Research Triangle Park, NC: International Union of Pure and Applied Chemistry (IUPAC); 2019 Available from: https://goldbook.iupac.org/.

77. Blahnik J, Krickl S, Schmid K, Müller E, Lupton J, Kunz W: **Microemulsion and microsuspension polymerization of methyl methacrylate in surfactant-free microemulsions (SFME)**. *J Colloid Interface Sci* 2023, **648**:755–767. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0021979723010366.

78. Wilkes CE, Summers JW, Daniels CA, Berard MT. *PVC handbook*. Munich ; Cincinnati: Hanser; 2005.

79. ** Blahnik J, Schuster J, Müller R, Müller E, Kunz W: **Surfactant-free microemulsions (SFMEs) as a template for porous polymer synthesis**. *J Colloid Interface Sci* 2024, **655**:371–382. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0021979723020957.
This publication outlines the influence of the different phases (O/W, BC, W/O) of the SFME on the morphology of the polymers.

80. ** Gruber CG, Frey L, Guntermann R, Medina DD, Cortés E: **Early stages of covalent organic framework formation imaged in operando**. *Nature* 2024, **630**:872–877. Available from: https://www.nature.com/articles/s41586-024-07483-0.
This publication demonstrates, using an optical technique interferometric scattering microscope, that the decisive parameter can be the highly fluctuating structure of the SFME.

81. Omanović-Mikličanin E, Badnjević A, Kazlagić A, Hajlovac M: **Nanocomposites: a brief review**. *Health Technol* 2020, **10**: 51–59. Available from: http://link.springer.com/10.1007/s12553-019-00380-x.

82. Salabat A, Mirhoseini F: **Polymer-based nanocomposites fabricated by microemulsion method**. *Polym Compos* 2022, **43**:1282–1294. Available from: https://4spepublications.onlinelibrary.wiley.com/doi/10.1002/pc.26504.

83. Qian W, Texter J, Yan F: **Frontiers in poly(ionic liquid)s: syntheses and applications**. *Chem Soc Rev* 2017, **46**: 1124–1159. Available from: https://xlink.rsc.org/?DOI=C6CS00620E.

84. Sadat Mirhoseini B, Salabat A: **A novel surfactant-free microemulsion system for the synthesis of poly(methyl methacrylate)/Ag nanocomposite**. *J Mol Liq* 2021, **342**, 117555. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0167732221022807.

85. Li Y, Li Y, Li F: **The electroplating of Cu on PANI coated polyester conductive fabric with surfactant-free microemulsion polymerization**. *Mater Lett* 2025, **384**, 138046. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0167577X25000758.

86. Schweiger M, Lang T, Müller E, Jeřábek V, Heyda J, Klajmon M, *et al*.: **Complete biodiverse lignocellulosic biomass fractionation process using the green solvent γ-Valerolactone**. *RSC Sustain* 2025, **3**:4533–4555.

87. Kong J, Li L, Zeng Q, Cai Z, Wang Y, He H, *et al*.: **Oxidation of organosolv lignin in a novel surfactant-free microemulsion reactor**. *Bioresour Technol* 2021, **321**, 124466. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0960852420317405.

88. Kong J, Li L, Zeng Q, Long J, He H, Wang Y, *et al*.: **Production of 4-Ethylphenol from lignin depolymerization in a novel surfactant-free microemulsion reactor**. *Ind Eng Chem Res* 2021, **60**:17897–17906. Available from: https://pubs.acs.org/doi/10.1021/acs.iecr.1c03636.

89. Abrar I, Bhaskarwar AN: **Performance and emission characteristics of constant speed diesel engine fueled by surfactant-free microemulsions**. *Sustain Energy Technol Assessments* 2021, **47**, 101414. Available from: https://linkinghub.elsevier.com/retrieve/pii/S2213138821004240.

90. Abrar I, Bhaskarwar AN: **Effect of alcohols on water solubilization in surfactant-free diesel microemulsions**. *Energy Rep* 2022, **8**:504–512. Available from: https://linkinghub.elsevier.com/retrieve/pii/S2352484722020935.

91. Khoshsima A, Brock D, Touraud D, Kunz W: **Pre-formulation of biofuels: kinematic viscosities, low-temperature phase behaviour and nanostructuring of ethanol/"ethanolotrope"/rapeseed oil mixtures**. *Fuel* 2017, **191**:212–220. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0016236116311760.

92. Shenavaei Zare T, Khoshsima A, ZareNezhad B: **Production of new surfactant-free microemulsion biofuels: phase behavior and nanostructure identification**. *Energy Fuels* 2020, **34**: 4643–4659. Available from: https://pubs.acs.org/doi/10.1021/acs.energyfuels.9b04430.

93. Shenavaei Zare T, Khoshsima A, ZareNezhad B: **Development of surfactant-free microemulsion hybrid biofuels employing halophytic salicornia oil/ethanol and oxygenated additives**. *Fuel* 2021, **292**, 120249. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0016236121001253.

94. Mitsou E, Theochari I, Gad E, Vassiliadi E, Karpenisioti E, Koulis G, *et al*.: **Enzymatic modification of triglycerides in conventional and surfactant-free microemulsions and in olive oil**. *Colloids Surf A Physicochem Eng Asp* 2022, **647**, 129170. Available from: https://linkinghub.elsevier.com/retrieve/pii/S0927775722009256.

95. * Hofmann E, Schmauser L, Neugebauer J, Touraud D, Gallou F, Kunz W: **Sustainable cascade reaction combining transition metal-biocatalysis and hydrophobic substrates in surfactant-free aqueous solutions**. *Chem Eng J* 2023, **472**, 144599. Available from: https://linkinghub.elsevier.com/retrieve/pii/S1385894723033302.
This publication cements the issues regarding the importance of structuring in an SFME on chemical reactions. In this case the enhanced solubility and not the structuring of the SFME or SBME is the decisive parameter.