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Aqueous food-grade and cosmetic-grade surfactant systems for the continuous countercurrent cloud point extraction

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ABSTRACT

Nonionic surfactant aqueous two-phase systems represent an alternative extracting media to conventional organic solvents by ensuring a mild process temperature in an aqueous environment. However, their large-scale implementation is limited due to the challenging stripping of the target substances from the surfactant. In this study, we demonstrate the application of aqueous food-grade and cosmetic-grade surfactant systems as extraction media for solutes of natural origin. We suggest that no separation of surfactant and target product (or only rough separation is sufficient) is needed in this case due to the application of both substances in the final food or cosmetic formulation. To this purpose, sixteen potential commercial surfactants applied in food or in the personal care industry were investigated for their cloud point temperature and their phase separation kinetics. Among those, the aqueous surfactant systems containing Silwet L-7230 (poly[dimethylsiloxane-co-methyl(3-hydroxypropyl)siloxane]-*graft*-poly(ethylene/propylene glycol) and ROKAnol NL5 (C_{9-11}, branched and linear, ethoxylated alcohol) separated in two phases rapidly at temperatures below 50 °C. Therefore, the liquid-liquid equilibria of the mixtures Silwet L-7230/water and ROKAnol NL5/water were determined, exhibiting lower critical solution temperatures (LCSTs) of 37.3 °C and 33.5 °C, respectively. Additionally, the mixtures were investigated for their capacity to extract the model solute cinnamic acid ((2E)-3-phenylprop-2-enoic acid, CA). Batch separations with $10logP_{CA} = 0.9$ for ROKAnol NL5 and $10logP_{CA} = 1.6$ for Silwet L-7230 were achieved, proving the potential of these surfactants for the extraction of hydrophobic compounds. To further design a stable liquid-liquid extraction process, the density and viscosity of the surfactant-water mixtures were measured. The density differences between the micellar and aqueous phases was found to be sufficient for continuous extraction, whereby the system with ROKAnol NL5 consisted of an upper surfactant-rich phase and a lower surfactant-lean phase, and vice versa for the Silwet L-7230 system. The formation of a liquid crystalline structure with high viscosity was observed in the Silwet L-7230 micellar phase. Based on these investigations, the corresponding processes were designed and finally, for the first time, the food-grade Silwet L-7230 and the cosmetic-grade ROKAnol NL5 surfactant systems could be successfully implemented in the batch (yield = 77% and 80%) and in the continuous (yield = 96% and 100%) cloud point extraction of cinnamic acid.

1. Introduction

Molecules of nonionic surfactants arrange into micelles when added to an aqueous solution above their critical micelle concentration (cmc). Micelles are dynamic aggregates composed of a hydrophobic core, formed by the lipophilic tails of the monomers, and a hydrophilic outer layer of the water-soluble monomer moieties. Such aqueous surfactant solutions can undergo a temperature-induced clouding followed by a phase separation. Subsequently, the mixture splits into a coexisting surfactant-rich (micellar) phase and a surfactant-lean aqueous phase. The temperature at which the phases separate is referred to as cloud point temperature (CPT) and depends on the surfactant's chemical structure and the composition of the aqueous solution [1,2]. The micelles can solubilize hydrophobic species (solutes). Hence, the accumulation of micelles in the surfactant-rich phase at temperatures above the CPT leads to higher concentration of the solute as well. This separation technique is applied to isolate solutes from aqueous bulks and is referred to as cloud point extraction [3].

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Cloud point extraction is usually performed at a mild temperature and often does not involve toxic solvents. Therefore, the technique has been widely studied for the isolation of biological solutes, e.g. polyphenols and tocopherol from olive mill wastewater [4]. Further studies demonstrated the suitability of aqueous surfactant solutions for the separation of valuable plant compounds such as bio-pesticide phorbol esters [5], soy isoflavones [6], mangostin [7], or flavonoids and alkaloids [8] from different plant solid materials. Furthermore, the high water content in the micellar two-phase systems makes them attractive for the *in situ* isolation of solutes out of living cell cultures. For instance, our group demonstrated a successful application of the cloud point extraction with living green microalgae cultures [9,10]. Pan et al. also carried out an extractive biodecolorization of triphenylmethane dyes with a bacterial aqueous culture in a surfactant-based two-phase system [11].

To the best of our knowledge, most studies on cloud point extraction have been carried out in batch mode, with only a few exceptions. Benkheda et al. conducted a successful transfer of the batch cloud point extraction to a continuous mixer-settler set-up [12]. The group of Scamehorn demonstrated a successful continuous application in a rotating disc contactor. The authors managed to implement the surfactant Triton X-114 in a countercurrent liquid-liquid extraction for the separation of phenol from wastewater [13–15]. Our group also studied the continuous surfactant-based extraction with Triton X-114 for the separation of other phenolic compounds such as vanillin, syringic acid, and salicylic acid [16]. Furthermore, the continuous application of mixed surfactant system for the separation of ionized solutes from aqueous bulk solutions was demonstrated [17].

Despite the diverse applications of the cloud point extraction as an alternative to the extraction with organic solvents, the technique faces a major drawback in form of the difficult and often cost-intensive surfactant recycling and solute purification. As a solution to this problem, Dhamole et al. conducted a cloud point extraction of butanol with a block-copolymer with a high boiling point. Hence, it was possible to separate the surfactant from the solute by the means of distillation [18]. Our group utilized pervaporation as a suitable unit operation for the removal of toluene from the micellar phase of the Triton X-114 cloud point systems [19]. Furthermore, there are reported techniques for the separation of solutes with a high boiling point or thermal sensitivity as well. An extraction with Winsor I emulsion was used in order to separate tannic acid from the Triton X-114 micellar phase. The authors selected diethyl ether as excess oil phase and thus separated tannic acid and the surfactant from each other. Subsequently, the solute-free coacervate was successfully applied for a second extraction [20]. Liang et al. introduced a novel system based on polyethylene glycol and a hydrophilic surfactant in order to allow stripping of organic compounds from the surfactant aqueous solution with Winsor I microemulsion extraction. The authors successfully regenerated compounds such as phenol, p-nitrophenol and, 1-naphthol phenol [21]. Shen et al. introduced a hydrophobic ionic liquid to the surfactant-rich extract, containing hydrophobic pigments. Due to the polarity of the solute, a back-extraction of the target species using the hydrophobic ionic liquid–nonionic surfactant–water Winsor I microemulsion was observed [22]. Zhao et al investigated the same approach for solute regeneration from the Triton X-114 micellar phase. The authors demonstrated a successful back-extraction of ionic dyes in the ionic liquid-rich phase [23]. Our group also reported a method for stripping the surfactant and the solute by shifting the pH of the micellar phase. A target substance which dissociated in aqueous solutions could be back-extracted in the aqueous phase since the partition coefficient changed drastically [24]. However, most of those reported applications involved additional solvent or energy input.

On the other hand, cloud point extraction can be utilized for isolation of phenolic compounds, antioxidants or pigments, which are mainly applied as ingredients in foods and cosmetics [25]. A common technique for the even distribution of such substances in beverages or personal care products is the addition of commercial surfactants [26]. Therefore, it can be beneficial to design a cloud point extraction of the natural substance with a surfactant, which is applied in the final market formulation (leave-in surfactant). Hence, there will be no need for a cost-intensive separation (or just a rough separation) of the target molecule from the surfactant.

For instance, polysorbate derivatives are applied as emulsifiers in different food products [26]. These surfactants are known to exhibit a phase separation above their CPT. Tween 20 (polysorbate 20) or Tween 80 (polysorbate 80) can form a micellar two-phase system at 25 °C in presence of sodium and potassium salts [27,28]. Therefore, those systems were applied for the mild separation of phenols and carotenoids from olive mill wastewater and red-flesh orange juice [25]. Further, silicone polyethers are applied as wetting or antifoaming agents, but also as additives in food. Grafted silicone copolymers form cloudy aqueous solutions at temperatures above 25 °C [29]. Soni at al. reported a pronounced influence of additives such as sugars or hydrotrope compounds (polyethylene glycols, polyethylene glycol triblock polymers) on the phase behavior of silicone-based surfactants. The authors observed a stable formation of two-phases at elevated temperatures [30,31]. However, the recycling of such additives requires an additional downstream step and could lead to higher costs. Diverse cosmetic products also contain ethoxylated alcohols as secondary surfactants [3,32]. Aqueous solutions of these amphiphiles were also reported to form two phases in water, whereby a closed-loop was observed at temperatures higher than 60 °C [3]. Consequently, the classes of the polysorbate derivatives, silicone polyethers, and polyethoxylated alcohols are attractive as leave-in surfactants for the cloud point extraction of solutes for food or cosmetics.

The aim of this study was to develop a suitable food-grade and cosmetic-grade aqueous surfactant system for the cloud point extraction of hydrophobic biological compounds. We conducted a screening of sixteen commercial food-grade and cosmetic-grade surfactants based on their cloud point temperature and phase separation kinetics. The amphiphiles with fast separation kinetics and a mild clouding temperature were further investigated concerning their phase behavior in water and their ability to extract a model solute. Hence, we measured the liquid-liquid equilibria of the aqueous surfactant systems, as well as the partitioning of the model substance cinnamic acid between the coexisting phases. A further assessment of the suitability of these systems for extraction processes was conducted based on density and viscosity measurements. Finally, extraction experiments in batch and in continuous mode were conducted in order to demonstrate the applicability of the chosen surfactants in the cloud point extraction of products with a natural origin. Based on the findings in this study, surfactants for food and cosmetic applications are given attention as new permitted solvents in a technically relevant extraction process

2. Materials and methods

The materials and methods described in this chapter were applied to prove the concept for a feasible cloud point extraction based on food-grade and cosmetic-grade surfactants. The first step was to indicate suitable surfactants according to the manufacturer data and the measured clouding temperature and phase separation in an aqueous solution (Table 1). That after, the liquid-liquid equilibria of the binary mixtures surfactant/water was measured for the selected amphiphiles using the cloud point method. Subsequently, the corresponding temperature and concentration values, at which the phase separation was stable, were applied for the extraction of the tracer cinnamic acid in a laboratory scale. The distribution of that solute was measured using a HPLC analysis. Additionally, the physical properties of the coexisting phases were determined by density and viscosity measurements. Thus, it was possible to characterize the suitability of the surfactant-based aqueous two-phase systems for an extraction process. Finally, a continuous extraction in a stirred heated column was utilized with the