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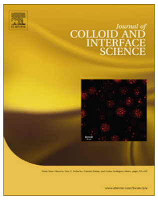

Surfactant-enhanced cellulose nanocrystal Pickering emulsions

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The effect of surfactants on the properties of Pickering emulsions stabilized by cellulose nanocrystals (CNCs) was investigated. Electrophoretic mobility, interfacial tension, confocal microscopy and three-phase contact angle measurements were used to elucidate the interactions between anionic CNCs and cationic alkyl ammonium surfactants didecyldimethylammonium bromide (DMAB) and cetyltrimethylammonium bromide (CTAB). Both surfactants were found to adsorb onto CNCs with concentration-dependent morphology. At low concentrations, individual surfactant molecules adsorbed with alkyl tails pointing outward leading to hydrophobic CNCs. At higher concentrations, above the surfactant's apparent critical micelle concentration, surfactant aggregate morphologies on CNCs were inferred and the hydrophobicity of CNCs decreased. DMAB, which has two alkyl tails, rendered the CNCs more hydrophobic than CTAB which has only a single alkyl tail, at all surfactant concentrations. The change in CNC wettability from surfactant adsorption was directly linked to emulsion properties; adding surfactant increased the emulsion stability, decreased the droplet size, and controlled the internal phase of CNC Pickering emulsions. More specifically, a double transitional phase inversion, from oil-in-water to water-in-oil and back to oil-in-water, was observed for emulsions with CNCs and increasing amounts of DMAB (the more hydrophobic surfactant). With CNCs and CTAB, no phase inversion was induced. This work represents the first report of CNC Pickering emulsions with surfactants as well as the first CNC Pickering emulsions that can be phase inverted. The ability to surface modify CNCs *in situ* and tailor emulsions by adding surfactants may extend the potential of CNCs to new liquid formulations and extruded/spray-dried materials.

1. Introduction

Cellulose nanocrystals (CNCs)[1] are new commercially available nanoparticles which are derived from natural cellulose sources and have recently been demonstrated to stabilize emulsions [1–5]. Due to their "green" nature and non-toxicity [6], CNCs show great promise as emulsifiers, stabilizers and gelation agents in formulated chemical products such as foods, pharmaceuticals, household cleaning agents and personal care products. The intermediate wettability and nanometric size of CNCs allows them to adsorb at oil–water interfaces, similar to the first particle-stabilized emulsions described by Ramsden [7] and Pickering [8]. So-called Pickering emulsions are ubiquitous in nature and have become more common in commercial products because they are generally more stable to coalescence than emulsions stabilized by surfactants alone. The ability to control emulsion stability, the nature of an emulsion's continuous phase, and the internal phase droplet size, has important implications in both chemical processing and new product development.

Pickering emulsion stability is attributed to the formation of a densely packed particle layer at the oil–water interface, which prevents droplet coalescence through a mechanical barrier mechanism and slows creaming or sedimentation [9]. The magnitude of the mechanical barrier is determined by the energy required to remove a particle from the interface, which is a function of the three-phase contact angle of the particle (θ_{ow}) [10]. For contact angles around 90°, this energy is considerably large (on the order of 10^5 k_BT for a 100 nm spherical particle) [11,12]. Therefore, once a partially wettable particle is at the oil–water interface, it will not leave spontaneously. Interestingly, small changes in the chemical composition of the particles or the oil and water phases, salt concentration [13], pH [14], temperature [15] and particle shape [16,17], lead to major changes in emulsion stability, and rich physicochemical phenomena overall.

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[1] CMC = critical micelle concentration; CNCs = cellulose nanocrystals; CTAB = cetyltrimethylammonium bromide; DMAB = didecyldimethylammonium bromide; DTAF = 5-(4,6-dichlorotriazinyl) aminofluorescein; o/w = oil-in-water; w/o = water-in-oil.

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Inorganic or petrochemical-based particles of silica, clay, calcium carbonate, hematite, polystyrene, and microgels, ranging in size from nanometers to micrometers, can all stabilize Pickering emulsions [9,18]. In many applications, however, organic and biocompatible colloidal particles are preferred, making materials like starch [19–22] and cellulose more suitable. Previous work has examined Pickering emulsions with various types of small cellulose particles including cellulose nanocrystals [1–5,23,24], cellulose fibrils [25–30], microcrystalline cellulose [25,26,31], bacterial cellulose [32,33], and cellulose derivatives [34].

Cellulose nanocrystals are rod-shaped, highly crystalline nanoparticles which can be extracted from wood, cotton, bacteria, algae, tunicin and other plant sources. CNCs are most commonly prepared by sulfuric acid hydrolysis [35] which gives nanocrystals with anionic sulfate half-ester groups on their surface (approximately 1 sulfate half-ester per 3 nm^2 or 1 sulfate half-ester in every 6 surface hydroxyl groups). Typical dimensions of CNCs range from 5 to 20 nm in cross-section by hundreds of nanometers long, depending on the cellulose source and hydrolysis conditions (Fig. 1) [36]. CNCs form stable colloidal suspensions in water, above pH 2.5 and below ionic strengths of 100 mM [37,38], and exhibit lyotropic liquid crystalline behavior [39]. The main advantage of using CNCs in new formulations and composites stems from their favorable material properties including a large elastic modulus, high aspect-ratio, high surface-area-to-volume ratio, low density, and general chemical and thermal stability. CNCs and the "Nanocellulose family" are further discussed in a number of comprehensive review articles and books [40–43].

Recent results of Capron and co-workers have highlighted the use of CNCs as emulsion stabilizers [1–5]. They have established that despite the fact that cellulose and CNCs are normally considered hydrophilic (due to the high density of hydroxyl groups and an air–water contact angle around 20°) [44], the crystalline organization of polymer chains allows for a "hydrophobic edge" to the nanocrystals and thus amphiphilic properties overall [1]. The insolubility of cellulose in common solvents is also attributed to these hydrophobic interactions which contribute to the crystalline organization of cellulose chains, along with extensive hydrogen bonding [45]. Unmodified CNCs are effective at stabilizing emulsions when they have a low surface charge density, or when the surface charge is screened in the presence of salt [1–3]. Furthermore, lower concentrations of CNCs are needed for stable emulsions when nanocrystals with larger aspect ratios are used. For example, long bacterial cellulose-derived CNCs only need to cover 40% of the emulsion droplet surface area to impede droplet coalescence as the CNCs form an interconnected mesh-like structure, compared to 84% surface coverage required for shorter cotton-derived CNCs [3]. High-internal-phase emulsion "gels" have also been prepared by making CNC-stabilized emulsions with equal parts oil and water and then slowly increasing the oil content; this is possible because the high aspect ratio CNCs are close-packed in the original emulsion but are then separated into a diluted mesh network, without leaving the oil–water interface, as oil is added [4]. In another literature example, grafting thermo-responsive polymers to CNCs to control the hydrophobicity with temperature also led to successful stabilization of emulsions [24]. To the best of our knowledge all CNC Pickering emulsions described to-date have been oil-in-water type (o/w) emulsions [46].

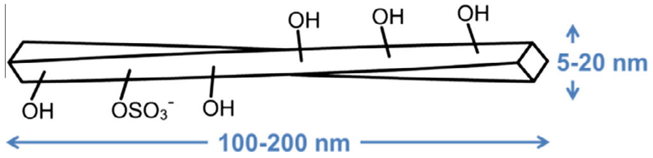

Fig. 1. Schematic representation of a cellulose nanocrystal which is composed of high molecular weight homopolymer chains of β-1,4 linked anhydro-D-glucose units. The cellulose chains are arranged parallel into the native cellulose I crystal structure where the hydroxyl groups are positioned in the equatorial plane and the hydrogen atoms are in the axial position. The sulfuric acid hydrolysis production method replaces some surface hydroxyl groups with anionic sulfate half-ester groups (not drawn to scale).

The internal emulsion phase (oil or water) and the stability of Pickering emulsions can be controlled by combining surfactants with colloidal particles [47]. As a result of particle–surfactant synergy, relatively small amounts of both emulsifiers are needed and properties can be finely tuned by varying the ratio of the two components. Binks et al. [48–55]. demonstrated that surfactant-containing Pickering emulsions may undergo single phase inversions (o/w to w/o) or double phase inversions (o/w to w/o [phase inversion 1], followed by w/o to o/w [phase inversion 2]) by increasing the surfactant concentration. Such transitional phase inversions have been observed for silica and calcium carbonate nanoparticles with oppositely charged surfactants, i.e., cationic alkyl-ammonium surfactants for silica, and anionic C_6–C_{12} sodium carboxylate fatty acids, sodium dodecylsulfate and sodium 2-ethylhexylsulfosuccinate for $CaCO_3$. The phase inversions are attributed to the adsorption of oppositely charged surfactant at the particle surface which changes the particle's wettability. Surfactants that can pack densely on the particle surface or that have long (or multiple) alkyl tails easily lead to more hydrophobic particles at low surfactant concentration which then become hydrophilic again at high surfactant concentration due to surfactant bilayer adsorption (or perhaps more precisely, admicelle aggregates adsorbed on the nanoparticle surfaces).

This work aims to understand how surfactants influence the stability of CNC Pickering emulsions. Specifically, single C_{16} alkyl tail cetyltrimethylammonium bromide (CTAB) and double C_{10} alkyl tail didecyldimethylammonium bromide (DMAB) surfactants with lab-made sulfuric acid hydrolyzed CNCs (from cotton) are investigated. Particle–surfactant interactions are measured by electrophoretic mobility, interfacial tension and contact angle and correlated with CNC-stabilized water–dodecane emulsion properties. By adding surfactant, we demonstrate for the first time a double phase inversion in CNC Pickering emulsions, and as a result, obtain the first water-in-oil type emulsion with CNCs. Emulsions are characterized by confocal microscopy, conductivity and droplet sizing and the stability mechanism is elucidated using fluorescently labeled CNCs. To the best of our knowledge, this is the first report of tailored CNC Pickering emulsions enhanced with surfactants and represents progress towards developing related CNC-based products, such as CNC-containing emulsions, biphasic gels, foams and extruded/spray-dried materials.

2. Experimental

2.1. Materials

Cetyltrimethylammonium bromide (CTAB), didecyldimethylammonium bromide (DMAB), dodecane, Nile red and sulfuric acid were obtained from Sigma–Aldrich. All measurements were performed at room temperature unless otherwise specified.

2.2. Preparation of cellulose nanocrystals

A suspension of cellulose nanocrystals (CNCs) was prepared by sulfuric acid hydrolysis, as previously described [56]. 40 g of cotton (Whatman ashless filter aid) was treated with 700 mL of 64 wt.% sulfuric acid at 45 °C for 45 min with continuous stirring. Immediately after, the reaction was quenched with 4 °C purified water (Barnstead NANOpure DIamond system, ThermoScientific,