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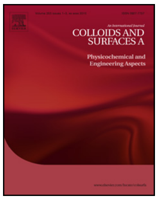

Kinetics of formation of polysaccharide-covered micrometric oil droplets under mechanical agitation

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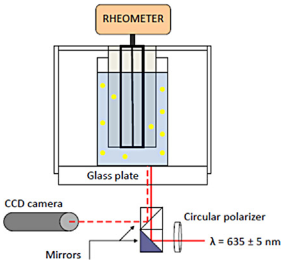
HIGHLIGHTS

- Amphiphilic dextrans were used for preparing emulsions under mechanical agitation.
- Kinetics of droplet formation was investigated by in situ rheo-optical measurements.
- Droplet rupture was controlled by the ratio of shear forces to Laplace pressure.
- Oil volume fraction had no effect on the kinetics of droplet formation.

GRAPHICAL ABSTRACT



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ABSTRACT

Hexadecane-in-water emulsions were prepared by mechanical agitation in vane geometry using amphiphilic derivatives of dextran (nonionic bacterial polysaccharide) as stabilizers. Thanks to a laboratory-made experimental device coupling rheometry and back-scattered light analysis, we investigated the kinetics of droplet formation and the simultaneous variation of global shear stress. Oil volume fraction was varied between 10 and 50% and rotation speed between 40 and 100 rad s^{-1}. The viscosity of aqueous phase was controlled by addition of sodium alginate and thus exhibited non-Newtonian rheological behavior. After forming a coarse emulsion, droplet rupture led to emulsions with volume-average droplet radius between 5 and 10 μm provided that rotation speed and aqueous phase viscosity were high enough. Monitoring was consistent with droplet rupture occurring under shear forces such that capillary number remained approximately constant and close to its critical value. Although rotational speed and sodium alginate concentration had strong effect on emulsification kinetics, oil volume fraction had no significant effect.

1. Introduction

Nano- and microparticles based on biodegradable and biocompatible polymers like aliphatic polyesters and polysaccharides have been widely studied over the last 20 years [1–3]. One of their main applications was encapsulation and controlled release of poorly water-soluble molecules [3–7]. Manufacturing such particles with targeted properties requires both physicochemical and engineering studies [8–13]. Indeed, the main characteristics of individual particles (size distribution, surface coverage, drug loading) have to be

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controlled at length scales typically between 0.1 and 100 μm on the basis of physicochemical properties of reactants while the design of industrial processes involve should provide enough production capacity with convenient product properties. Several processes reported for preparing polymer-based particles or capsules with diameters falling between 1 and 100 μm may be schematically represented as two-stage procedures: in a first step, liquid–liquid dispersion is prepared using mechanical agitation and in a second step liquid droplets are converted into spherical solid particles or capsules (with a solid shell surrounding a liquid core) either by physical phenomena (like evaporation or diffusion of solvent) or by chemical reaction (like polymerization). It has been largely documented that the first step had an important influence on the characteristics of final particles [14–22]. Thus it is of primary importance to investigate how processing parameters as well as initial feed formulation influence previous properties. One challenge is to obtain scalable results about kinetics of phenomena in order to design industrial processes that may provide particle suspensions with similar properties as those prepared in the laboratory. To that goal, in situ measurement of particle size distribution has been investigated since it allowed obtaining experimental data in same physico-chemical conditions as those of the process [23–26]. In order to carry out experimental investigation, we previously designed and reported a device combining rheological and average-droplet radius (using back-scattered light) in situ measurements [27]. This experimental system appeared particularly convenient for investigating kinetics of emulsion formation under mechanical agitation. It allowed working with concentrated systems and it provided in situ information both at the scale of oil droplets (between 1 and 100 μm) and at the macroscopic scale through overall shear stress and shear rate. Apart from the challenge of designing experimental conditions that may be representative of large scale process, there was another difficulty related to the choice of components. Indeed, many fundamental studies were carried out with model systems involving molecular surfactants and Newtonian fluids. Nevertheless, when real systems are considered, their structural specificities are at the origin of more complex behaviors either in solution (non-Newtonian fluids) or at interfaces (viscoelasticity, adsorption kinetics). For instance, amphiphilic polysaccharides or proteins are often used as stabilizers for covering the surface of final particles so as to confer important properties like efficient colloidal stability, stability to dilution, specific recognition and so on [4,28,29]. In our previous work, we particularly investigated the chemical and enzymatic modification of dextran (non ionic bacterial polysaccharide containing a majority of α-(1→6) linked D-glucose units with some short branches) [30,31]. These polymers were shown to adsorb at oil/water and solid/water interfaces thus producing emulsions or particles with controlled surface properties [32–34]. Similarly, native polysaccharides like alginate have been applied as thickeners or hydrogel-makers in fields like tissue engineering, localized drug delivery, etc. [35,36].

In that work, we investigated the kinetics of formation of polysaccharide-covered micrometric oil droplets under mechanical stirring using the above mentioned experimental device with vane geometry. The continuous aqueous phase was a solution of sodium alginate and exhibited a non-Newtonian rheological behavior. The dispersed phase was a linear aliphatic hydrocarbon oil, *n*-hexadecane. Amphiphilic polysaccharides obtained by hydrophobic modification of dextran (covalent attachment of aliphatic hydrocarbon chains via the formation of ether links) were used as stabilizers. Amphiphilic dextran derivatives have been already reported for preparing miniemulsions or biodegradable nanoparticles using sonication [37]. Nevertheless, there was no detailed study about the kinetic aspects of emulsion formation when using mechanical agitation together with such stabilizers. We chose to use a non-reactive system since it allowed focusing on physical phenomena involved in the formation of micrometric droplets covered by polysaccharide-based stabilizer. We focused our experiments on the influence of rotational speed and oil volume fraction on the kinetics of droplet fragmentation till steady state was reached. Experimental results were discussed qualitatively and quantitatively on the basis of physical phenomena.

2. Experimental

2.1. Materials

All chemicals were from Aldrich® and were used without further purification. MilliQ water was used in all experiments. Native dextran was a commercial product, T40®, from Amersham Pharmacia®. This sample was characterized by size exclusion chromatography with aqueous eluent. Its weight-average and number-average molar masses were found equal to 40,000 g mol^{-1} and 33,000 g mol^{-1}, respectively. A commercial sample of sodium alginate from Sigma Aldrich® was used (weight-average molar mass equal to 2.4×10^6 g mol^{-1} and polydispersity index $I_p = 1.3$ according to the company).

2.2. Synthesis of amphiphilic dextran derivatives

Amphiphilic derivatives of dextran were prepared following a procedure that was described previously [38]. Briefly, commercial dextran T40® (5 g) was dissolved in 100 mL of milliQ water. The required amount of tetrabutylammonium hydroxide (40 wt% solution in water) was added (1.5 mol per repeat unit). After 1 h stirring, the mixture was freeze-dried. The resulting solid was dissolved in 100 mL dimethylsulfoxide (DMSO) and, if necessary, heated to 50 °C. Then, the required amount of 1,2-epoxyoctane was added. The reaction was left to proceed during 96 h under magnetic stirring. The crude reaction medium was transferred to a dialysis bag (molar mass cut off equal to 6–8000 g mol^{-1}) and dialyzed against water/ethanol mixture (50/50 v/v) and finally water. The final aqueous solution was freeze-dried. The purity and degree of substitution (τ) was checked by ^{1}H NMR in deuterated DMSO. The polymers were named DexC6$_\tau$.

2.3. Preparation and characteristics of biphasic mixtures

Aqueous phase was prepared as follows. Dextran derivative was weighted and dissolved in water at a concentration of 20 g L^{-1} during 48 h under magnetic stirring. Sodium azide was added at a concentration of 0.02 g L^{-1}. Afterward, 0.750 g of sodium alginate were added and the mixture was stirred during 48 h at room temperature. Refractive indices were experimentally determined at 25 °C and were found equal to 1.35 for aqueous phase and 1.46 for hexadecane. The viscosity of hexadecane was measured using cone-plate geometry and found equal to 3.45 ± 0.1 mPa s at 20 °C. Interfacial tension between aqueous phase containing sodium alginate and hexadecane was measured at 25 °C using Krüss tensiometer with De Noüy platinum ring which was immersed at interface during 25 min. Three successive determinations were carried out every 20 min.

2.4. Rheo-optical device and experimental procedure

The rheo-optical device combined a rheometer (AR 2000® TA Instrument) and an optical part. The detailed description of the apparatus, vane geometry calibration procedure and determination of average droplet radius had been given in previous publications [27,39–41]. Biphasic mixtures containing aqueous phase and hexadecane were initially loaded into the vane geometry.