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Ceramic particles obtained using W/O nano-emulsions as reaction media

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Abstract

Monodisperse ceramic particles can be produced from water-in-oil (W/O) nano-emulsions by hydrolysis and condensation of ceramic alkoxides into aqueous droplets, thereby yielding nanoparticles of controlled size and shape. This study addressed both the formation of W/O nano-emulsions and the resultant ceramic particles obtained in reaction media. Nano-emulsions were prepared by adding water or catalyst aqueous solution to a mixture of decane and surfactants. Droplet size was determined by dynamic light scattering, with mean sizes ranging from 30 to 120 nm. Higher water concentrations resulted in larger droplets. Ceramic nanoparticles were prepared by adding ceramic alkoxides in W/O nano-emulsions. Tetraethyl orthosilicate and tetraisopropyl orthotitanate were used to obtain silica and titania nanoparticles, respectively. Ceramic nanoparticles were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM), and dynamic light scattering (DLS). Particles with average size from 30 to 230 nm were obtained. Particle sizes correlated with droplet sizes of those nano-emulsions were used as reaction media.

Keywords: Span/tween; W/O nano-emulsion; Non-ionic surfactant mixture; SiO_2 nanoparticles; TiO_2 nanoparticles

1. Introduction

Over the last several years, a number of studies on the formation, characterization and application of emulsions have been carried out. Emulsions are thermodynamically unstable liquid/liquid dispersions that are stabilized, in general, by surfactants, polymers or solids particles [1]. As non-equilibrium system's emulsion properties depend not only on physicochemical variables (nature of components, composition, temperature and pressure), but also on preparation methods and the order in which components are added [1–4]. More recently, a new class of emulsions, with droplet sizes ranging in the nanometers and similar to microemulsions has been reported [5–7]. These emulsions, termed nano-emulsions, mini-emulsions or ultra-fine emulsions, are transparent or translucent (with droplet sizes between 50 and 200 nm) or milky (up to 500 nm) [8–12] and exhibit high kinetic stability.

Nano-emulsions are a subject of increasing interest in both theoretical discussions and practical applications due to their singular properties, namely extremely small droplet size, kinetic stability and transparency. In addition, they present several advantages over conventional emulsions, owing principally to their similar characteristics to microemulsion ones [12]. For example, nano-emulsions offer the possibility of using microemulsion-like dispersions without need of high surfactant concentrations. Additionally, nano-emulsions boast a wide variety of diverse applications in the chemical (polymerization), cosmetic, and pharmaceutical industries, etc. [13]. One of the earliest chemicals applications of O/W nano-emulsions was in the preparation of latexes [5,10,14–19] by polymerization. Ugelstad et al. [14] found that the mechanism involved in miniemulsion polymerization was quite different from that of emulsion polymerization, suggesting that the main locus of nucleation for the latter was monomer droplets versus micelles [14]. While so-called miniemulsion polymerization is a broad term used to designate all polymerization processes performed in nano-emulsion (miniemulsion) media, it is also used in a more restrictive sense, referring to instances when

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the polymerization of nano-emulsion droplets is equal to the number of polymer particles and to particle size distribution [10].

The preparation of monodisperse particles has drawn considerable attention in recent years [20]. Several methods have been developed not only to synthesize nano-sized particles, but also to calibrate their size, including Langmuir–Blodgett films [21], vesicles [22], reverse microemulsions [23] and surface-active supports [24]. In fact, silica (SiO_2) and titania (TiO_2) submicron particles have been prepared by the controlled hydrolysis of metal alkoxides in alcohol and water mixtures [25–27]. However, as reported by Bogush et al., one limitation of this method remains a high polydispersity when the size of the particle is less than 100 nm [26]. Reverse microemulsions provide an effective medium for synthesis of monodisperse nanoparticles (typically less than 100 nm) [24]. Indeed, the synthesis of nanoparticles using microemulsion reactions was first described by Boutonnet et al. [28], who obtained monodisperse metal particles by reduction of metal salts in water-in-oil (W/O) microemulsions. Since then, there have been numerous reports on the use of microemulsions as a reaction media for nanoparticle synthesis. One major disadvantage remains in the fact that microemulsion formation requires higher amounts of surfactant than conventional emulsions, typically over 20 wt%. However, nano-emulsion formations require smaller surfactant concentration.

Nevertheless, there remain many techniques for obtaining size information. Indeed, emulsion droplet or nanoparticles size data may be compiled in various ways: (1) in terms of the number N of droplets; (2) by specific particle length, namely the diameter D, using optical or electron microscopy; (3) as diameter versus droplet or particle projected area S by employing turbidity techniques; (4) as diameter versus surface area A utilizing light scattering measurements; (5) as number versus volume V by electrical resistance counting; and (6) in terms of diameter versus mass M by X-ray transmission coupled with sedimentation, or perhaps, by hydrodynamic chromatography [41]. Thus, evaluation of size can involve measures of number, length (diameter), area, volume, or mass [41–43]. As different ways of expressing the average diameter of particle distribution are frequently encountered in the literature [45,46] it is important to specify which definition is being used to avoid confusion [43]

While O/W nano-emulsion studies have been undertaken [12,13,29–35] in recent years, relatively few publications on W/O nano-emulsions currently exist. Indeed, until now, few scientists have investigated either W/O nano-emulsions [36,37] or W/O miniemulsions [38]. In the present study, W/O nano-emulsion formations were analyzed using nonionic surfactant mixtures. To both characterize and evaluate their potential application as nanoreactors for nanoparticles, nano-emulsion size and stability were closely scrutinized. In the second part of this study, the formation of SiO_2 and TiO_2 ceramic particles using W/O nano-emulsions as reaction media was explored.

2. Experimental

2.1. Materials

Sorbitan ester surfactants (Span and Tween series), Sorbitan monolaurate or Span 20 (S20), Sorbitan monooleate or Span 80 (S80), PEO 20 Sorbitan monolaurate or Tween 20 (T20) and PEO 20 Sorbitan monooleate or Tween 80 (T80) technical grade were purchased from Sigma–Aldrich Chemical. *N*-decane (purity > 99%) was obtained from Panreac. Water was de-ionized and Millipore filtered by a Milli-Q system. 25% Ammonia in aqueous solution (G.R.), hydrochloric acid in aqueous solution (G.R.) were obtained from Panreas. The tetraethyl orthosilicate (TEOS) and tetraisopropyl orthotitanate (TTIP), 98% pure, were supplied by Merck. The systems studied were S80:T80 (51:49)/decane/water, S20:80 (62:38)/decane/water, and S20:20 (60:40)/decane/water. Optimum surfactant ratio was determined in previous experiments (data not shown), and it is the ratio that permits to solubilize highest water [39,40].

2.2. Methods

2.2.1. Regions of microemulsion and nano-emulsion

Emulsions were formed by adding water to a mixture of the other components at 25 °C and using a magnetic stirrer at 700 rpm. The limit demarcating microemulsion and nano-emulsion regions was determined by observing the evolution of back-scattered light as a function of time. This study was carried out using multiple light scattering at a wavelength of 850 nm.

2.2.2. Nano-emulsion formation

These were prepared by adding water or ammonia solution to a mixture of decane and surfactants (Span 20:Tween 80 and Span 80:Tween 80). The rate of addition was kept constant at 0.03 ml/min and temperature was maintained at 25 °C, while the solution was mixed using a magnetic stirrer at 700 rpm.

2.2.3. Nano-emulsions characterization: nano-emulsions droplet size

For this study, the average droplet and nano-emulsion distribution sizes were determined by dynamic light scattering (DLS), using a Malvern 4700 photon correlation spectrometer (Malvern Instruments, Malvern, U.K.). An argon laser ($\lambda = 488$ nm) with variable intensity was used to cover the wide size range involved. The hydrodynamic radius measurements were consistently carried out at a scattering angle of 90° and a temperature of 25 °C. When measurements had been completed, DLS data were processed via the CONTIN method [4,5,13] with a software package which permits the expression of diameter distribution in terms of intensity, number, or volume and permits to obtain the polydispersity data of the sample [52]. Intensity distribution shows