Sol-emulsion-gel synthesis of ceramic particles

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Abstract. The basic characteristics of the sol-emulsion-gel (SEG) process are described as derived from water-in-oil type emulsions when 'water' is replaced by an aqueous sol and 'oil' indicates water-immiscible organic liquids. The main roles of a surfactant in emulsion formation are discussed. Steps in the generation of ceramic particles from the SEG process through a variety of experimental options are explained. Relevant examples are described where control of surfactant contents (below and above the working range of critical micelle concentration) in a sol-emulsion can lead to oxide particles of different sizes and shapes. Attempts are made to correlate the products of high-surfactant emulsions with micelles and mesophase structures known to form by surfactant molecules in large concentrations.

Keywords. Sol-gel; emulsion; ceramic particles.

1. Introduction

Emulsification of one liquid in another, i.e. generation of a dispersed phase in a continuous phase is a well known industrial process (Johnson 1979). Depending on the relative quantities of the two phases, emulsions can be divided into two types, i.e. water-in-oil (W/O) type and oil-in-water (O/W) type (Berkman and Egloff 1941; Dickinson 1994). Specific surfactants control the interfacial characteristics of the emulsions (Bourrel and Schester 1988).

A feature of the process which is of interest to the ceramist (Wilson and Heathcote 1990; Sherif and Shyu 1991; Ganguli and Chatterjee 1997) is that in an water-in-oil type emulsion, one can use a salt solution, aqueous dispersion of solids or an aqueous sol as the 'water' phase (Akinc and Celikkaya 1987; Liu and Wilcox 1995; Ganguli and Chatterjee 1997). Solidification of the dispersed aqueous phase can be effected by e.g. increasing the basicity of the system or by the removal of the aqueous phase from the solution or sol when precipitation or gelation starts taking place from the surface (Ramamurthi *et al* 1990; Ponthieu *et al* 1992; Liu and Wilcox 1995). The solid product is collected and thermally processed for conversion to ceramic particles. In case of a sol as the dispersed phase in the emulsion, the immediate product is obviously an assemblage of gel particles; hence the process is called sol-emulsion-gel (SEG) synthesis. It is easy to see that the procedure offers a route for obtaining particles of a predetermined size range, controlled by the droplet size distribution, by varying parameters like sol/solvent volume ratio, viscosity of the sol etc when all the physical aspects (e.g. mode of agitation of an emulsion, required to avoid re-coalescence of the droplets) are controlled in a simple engineering system. In addition, the nature and volume

of the surfactant molecules in the emulsion can also control not only the droplet/final particle size, but also the particle shape by their self-aggregation behaviour (Bourrel and Schester 1988; Dickinson 1994). This imparts to the process significant additional versatility, which is being examined currently with great interest.

The present paper describes the basic features of the SEG process and discusses specific situations with respect to surfactant contents in water-in-oil type emulsions of ceramic interest. Examples are presented from the work being carried out at the author's laboratory.

2. The sol-emulsion-gel process

2.1 Experimental options

The major steps in an SEG process are: (i) preparation of a suitable sol, (ii) dispersion of the sol as droplets in an organic solvent, i.e. formation of an emulsion, (iii) stabilization of the sol droplets with a system compatible surfactant, (iv) gelation of the sol droplets by addition of ammonia gas/solution or a variety of amines and (v) calcination of the gel particles to ceramic powder.

An important part of an SEG process is the preparation of a stable, relatively concentrated, aqueous sol. Such sols for use in emulsions can be prepared in different ways. Some examples are: (a) Precipitation-peptization—a widely used method, this comprises dissolution of soluble precursors in water, precipitation of the corresponding hydrated oxide or hydroxide by increasing the pH of the system (very commonly by gradual addition of ammonia solution), and peptization of relatively large precipitated particles into those of colloidal dimensions by addition of acids so as to obtain a translucent, homogeneous and stable dispersion, (b) Ion extraction—in this method, a salt solution of requisite concentration is

treated with an organic amine dissolved in an water-immiscible organic liquid, leading to the extraction of the anions, e.g. Cl^- , $(\text{NO}_3)^-$ from the aqueous part and concomitant supply of OH^- ions into it (Chatterjee *et al* 1995; Deptula *et al* 1995). The two immiscible liquids (with the aqueous part increasing in viscosity) are separated, and the OH^- -rich solution allowed to polymerize into a sol, (c) Solution-sol transformation under heating—this is one of the procedurally simplest methods where a salt solution is heated at 70–80°C with dropwise addition of ammonia solution, leading to cation hydrolysis and formation of polymers in the solution (Ray *et al* 1993) and (d) Partial thermal decomposition of metal salts followed by dissolution in water (applicable for Th, Pu, Zr-nitrate salts; Woodhead 1984).

In the classical SEG process, used originally for the preparation of spherical oxide particles for nuclear ceramics (Wymer and Coobs 1967; Zimmer *et al* 1988) but also used later for plasma spray and other ceramic applications (Woodhead 1984; Wilson and Heathcote 1990; Sherif and Shyu 1991; Joshi *et al* 1993), an emulsion is obtained by dispersing aqueous sol droplets in an immiscible organic liquid of significantly lower dielectric constant than water under stirring. For efficient dispersion of the aqueous phase in the form of spherical droplets, it is required to decrease the tension at the interface between the two immiscible liquids, which is evident from the relationship

$$\Delta G = \gamma_i \Delta A,$$

where ΔG is the increase in energy required to increase the surface area of the droplets by ΔA , i.e. increasing the number of droplets and γ_i is the interfacial tension. Lowering of the interfacial tension is achieved by the addition of a surfactant; it also hinders immediate re-coalescence of the newly generated droplets (Dickinson 1994). The surfactant molecules commonly used in SEG process are the so-called amphiphiles consisting of a polar (hydrophilic) head and a non-polar (hydrophobic) tail, e.g. sorbitan monooleate. As any SEG process essentially involves a W/O type emulsion, the amphiphilic molecules at an interface have their heads oriented towards the centre of the sol droplet and the tails, dissolved in the organic continuous phase, in a sunray-like orientation. The relative hydrophilicity of a surfactant molecule is given by the value of its HLB (hydrophilic/lipophilic balance), and a large number of options are available in this regard (Black 1969; Cahn and Lynn 1983). It is obvious that the maximum requirement of surfactant molecules in the preparation of an ordinary sol-emulsion is that corresponding to a monolayer coverage of all the droplet surfaces. In practical systems, much less quantities generally serve the purpose.

It is to be noted on the other hand that when the surfactant concentration just exceeds a critical value

called 'critical micelle concentration' (CMC), the molecules self-aggregate into spherical shapes called micelles. In a W/O emulsion, the inside space of such a sphere is filled with a water droplet, commonly called 'water pool' (in SEG process, it can be called a 'sol pool'). The emulsion thus produced is called a micro-emulsion, and the sol pools are generally smaller in size (Burgard *et al* 1994; Masui *et al* 1997) than droplets produced by emulsions with surfactant concentration below CMC. Unlike such ordinary emulsions, micro-emulsions are thermodynamically stable (Bourrel and Schester 1988), though each micelle has a definite lifetime. With further increase in concentration various self-aggregated mesophases are formed by the surfactants (Ahmad and Friberg 1972; Borisch *et al* 1998), thus offering possibilities of tailoring of the final particle shape.

Gelation of the sol droplets can be effected in two main ways:

(I) Dehydration of the sol: One of the ways of sol-gel conversion is to remove the liquid phase in a sol by evaporation (not applicable here) or other means so that the distance between the dispersed particles (polymeric or colloidal) is minimized and finally a particle network is formed. In the SEG process, the water in the aqueous droplets is generally removed by the addition of partially water-soluble organic liquids in the emulsion. 2-Ethyl hexanol and 1-octanol are typical examples (Montanaro and Guilhot 1989; Deptula *et al* 1995). These liquids extract the water from the sol droplets, so that gelation starts from the surface and proceeds inwards according to the diffusion rates.

(II) Internal gelation process: In this process, requisite quantity of a gelling agent is dissolved in the continuous phase. On heating the emulsion, the gelling agent decomposes, liberating ammonia. The ammonium hydroxide produced from ammonia in contact with the water of the sol exchanges anions present in the sol and causes gelation. Urea is a preferred gelling agent which breaks down at 70°C in the following way:

In an acidic solution,

As the dissociation constant of urea is very low ($K_b = 1.5 \times 10^{-14}$), controlled gelation is possible by this route.

(III) External gelation process: This process involves slow addition of a gelling agent into the emulsion. The agent can be ammonia gas, ammonia solution or various amines. Examples of the latter are given below.

One of the amines used by Woodhead (1984) is Primene JMT, in which a primary amine is attached to a tertiary carbon, i.e. $(\text{R}_3)\text{CNH}_2$. It is soluble in a variety

of organic solvents, but totally insoluble in water, which makes it suitable for W/O emulsions prepared for the SEG process. Another example is triethylamine, $(C_2H_5)_3N$. The amines act in the following way, as shown below for triethylamine (Chatterjee *et al* 1998a):

where A^- = nitrate, acetate etc present in the sol.

2.2 Critical micelle concentration (CMC)

When surfactant molecules are dissolved in water in low concentrations, they either remain as individual entities or form small aggregates, e.g. dimers and trimers. With increase in surfactant concentration, the relevant properties of the solution, e.g. viscosity, surface tension, optical absorption show incremental changes until a state of self-aggregation (micelle formation) is reached when there is a distinct and abrupt break in the property curves. This break point is the CMC referred to in § 2.1. In the case of SEG process (W/O emulsion), where the surfactants are dissolved in an organic liquid, the aggregation number at CMC is generally low, so the break in properties is also not very sharp. As a result, determination of CMC in such cases is difficult, if not impossible (Ruckenstein and Nagarajan 1980). However, as self-aggregation of surfactants in an emulsion leads to reduction in droplet size of the dispersed phase into much smaller ones, an approximate knowledge of the CMC in a given system is important for tailoring the sol droplet size and hence, the ceramic particle size in an SEG process.

As most of the work carried out in the author's laboratory was based on 1,1,1-trichloroethane (TCE) as the organic phase and Span 80 (sorbitan monooleate), a non-ionic surfactant, attempts were made recently to determine the CMC of the surfactant in TCE (Siladitya *et al* 1998). Examples of break in property of TCE-Span 80 are shown in figure 1. The overall results indicate that a working value of CMC should lie somewhere between 2 and 3 vol % of Span 80 in TCE.

3. Sol-emulsion-gel synthesis of ceramic particles under different conditions

3.1 Particles from low-surfactant emulsions under mechanical agitation

Preparation of an unstable emulsion in an organic solvent with low (below CMC) surfactant contents by dispersing the sol via mechanical agitation is a well-practised method for obtaining micron-sized spherical particles. It has been demonstrated (Chatterjee *et al* 1993, 1995; Ray *et al*

1993) that the process is suitable for obtaining specific size ranges by adjusting chemical (e.g. sol viscosity, sol/solvent ratio) and physical (e.g. volume of emulsion, volume and dimensions of reactor, speed and mode of agitation) parameters. Some commonly used experimental conditions and the corresponding product characteristics are shown in table 1.

Following the droplet geometry, particles obtained from emulsions of the above type are generally spherical or spheroidal in external morphology (figure 2a). However, such spherical/spheroidal particles can be solid or hollow (figure 2b). It was shown by Liu and Wilcox (1995) and Chatterjee *et al* (1998a) that above a critical size of the sol droplet which is gelled by water extraction or ion extraction, the solidification starting from the surface may not reach the centre; this generates hollow particles of different aspect ratios (a measure of the wall thickness of the shell) even in the same batch of particles. When the shell density is high, incomplete diffusion of the gelling agent through the shell leads to separate

Figure 1. a. Change in surface tension with increase in Span 80 in TCE and b. change in absorbance (650 nm) in presence of methylene blue with increase in Span 80 in TCE.

solidification of the internal fluid during calcination (Chatterjee *et al* 1998a).

3.2 Particles from low- to high-surfactant emulsions under mechanical agitation and sonication

In view of the fact that surfactants in a liquid show significant and specific change in their nature of aggregation below and above the corresponding CMC, it is interesting to examine the SEG products in emulsions with increasing surfactant contents through the CMC value. Siladitya *et al* (1998) carried out a study on an alumina sol emulsion in TCE containing 0.5–15 vol % Span 80 under mechanical stirring and sonication at 26 kHz. One of the striking features of this work was the drastic drop in the particle size range from 20–40 μ to 20–50 nm (figure 3) when the surfactant content was increased from 0.5 to 2 vol % while the other conditions remained constant. This clearly matched the concept that when surfactant content came close to CMC, the μ -sized dispersed phase droplets became significantly smaller and apparently occupied only the inside space of the nanosized spherical micelles.

It has been already mentioned that the CMC of Span 80 in TCE was determined to be 2–3 vol %; indication of micelle formation already at 2 vol % surfactant only supports the earlier observation that the CMC of a surfactant in an oil phase can have only an approximate value. The results described briefly in this section also show that the sol-emulsion-gel process involving a series of emulsions with increasing surfactant content can be utilized as a total process for obtaining ceramic particles of average size ranging from tens of micrometers to tens of nanometers. The question of shape is discussed in the next section.

3.3 Particles from low- to high-surfactant emulsions under mechanical agitation

What happens when the surfactant content in the continuous phase is progressively increased to an order of magnitude higher than that corresponding to the CMC? The answer is not straightforward because various factors get involved, e.g. the nature of the continuous (and dispersed, when an emulsion is considered) phase, the nature of the surfactant (e.g. cationic, anionic, non-ionic)

Table 1. Selected experimental results on oxide particle preparation from sol-emulsions containing small quantities of Span 80 in 1,1,1-trichloroethane.

Oxide	Sol/solvent volume ratio	Surfactant (vol %)	Sol viscosity (mPa · s)	Calcined product
Al_2O_3	1 : 3	2	32–35	Spheres (8–15 μm)
	1 : 4	1.5	32–35	V few spheres (2–10 μm) + mostly irregular-shaped particles
	1 : 4	2	32–35	Spheres (5–30 μm)
	1 : 4	2	28–30	Mostly spheres (10–25 μm) + some irregular-shaped particles
Cr_2O_3	1 : 4	1	28–30	Distorted spheres (20–40 μm)
	1 : 4	2	28–30	Spheres (3–30 μm)
	1 : 4	2	22–25	Mostly irregular-shaped particles + V few spheres (4–15 μm)
	1 : 5	2	28–30	Spheres (2–45 μm)
TiO_2	1 : 4	2	30–32	Spheres (5–40 μm)
	1 : 4	2	25–30	Mostly spheres (4–35 μm) + some irregular-shaped particles
	1 : 4	2	10–12	No sphere; all irregular-shaped particles
	1 : 4	3	30–32	Spheres (3–20 μm)
ZrO_2 – 5 wt% Y_2O_3	1 : 4	1	88–90	Irregular-shaped particles
	1 : 4	2	130–135	Dumb-bell shaped particles + V few spheres (50–60 μm)
	1 : 4	2	115–120	Spheres (5–55 μm)
	1 : 6	2	98–100	Spheres (7–30 μm)

and its interaction with the continuous phase, and presence or absence of co-surfactants and/or electrolytes. However, in general it is taken for granted that at CMC, spherical or near-spherical micelles are formed. With increase in surfactant content, the molecules self-aggregate to rod-like shapes (M1 or M2 mesophase) which can have end cappings. Further increase in the number of surfactant molecules gives rise to more complicated aggregations like the so-called lamellar (G phase) and cubic mesophases which are generally architectural patterns formed out of periodic arrangements of simpler aggregations mentioned above (Bourrel and Schester 1988).

It has been already indicated that a spherical micelle in a sol-organic, i.e. W/O emulsion will have its inner space filled by the aqueous phase (sol pool) with the hydrophilic heads of the surfactant molecules pointing inside. The low aggregation number and sphericity of

such micelles dictate the nanometric size and spherical shape of the ceramic particles, respectively. When the aggregation is rod-shaped, the internal space will still contain a rod-shaped sol pool, transformable to a rod-like particle after gelation and thermal treatment. Other shapes (on increasing the surfactant content) of the aggregates or their combined architectures do not always offer straightforward possibilities of harbouring sol pools inside them.

Unfortunately there is apparently no systematic published account of if and how particles of non-spherical shapes with regular geometry can be obtained through mesophase formation in the SEG process with high surfactant contents. In the author's laboratory, a preliminary investigation (Chatterjee *et al* 1998b) has been carried out recently on the formation of tetragonal barium titanate particles of different shapes through SEG process.

The sequence obtained for surfactant content (0–25 vol %) is as follows:

III-formed sphere $\rightarrow$ sphere $\rightarrow$ distorted sphere $\rightarrow$ rod + distorted sphere $\rightarrow$ cube-like/lamellar + rod $\rightarrow$ cube-like/lamellar $\rightarrow$ irregular.

Some typical shapes of the barium titanate particles obtained from the process are shown in figure 4. However, exact templates for such shapes are yet to be assigned (e.g. Auvray *et al* 1994). This requires critical experiments on the mesophase architectures in specific sol-organic systems to find out possible interstitial spaces with hydrophilic surfactant heads at their boundaries, so that sol pools of specific shapes can be accommodated in such interstices.

4. Conclusion

Sol-organic emulsions with progressively increasing surfactant content can be used as effective sources for

Figure 2. Scanning electron micrographs of **a.** spherical particles of yttria-doped zirconia obtained through the SEG process with 2 vol % surfactant and **b.** spherical and hollow particles of alumina obtained through the SEG process with 2 vol % surfactant.

Figure 3. Transmission electron micrograph of nanospheroids of alumina in chain-like agglomerate obtained through the SEG process with 2 vol % surfactant, but under sonication (26 kHz).

Figure 4. Transmission electron micrograph of barium titanate particles obtained through the SEG process: (a) 15 vol % Span 80 in TCE and (b) 20 vol % Span 80 in TCE.

obtaining spherical gel particles and on their calcination, ceramic particles varying in size from tens of micrometers to tens of nanometers, and under specific circumstances (one of which is high surfactant content), of specific shapes. The shape control is dependent on the micelle architecture and the orientation of the hydrophilic heads of the surfactants in such mesophases. Various oxide powders of tailored size and shape can be obtained via this sol-emulsion-gel process.

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