
6 Highly Concentrated Emulsions as Templates for Solid Foams

Jordi Esquena and Conxita Solans

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6.1 INTRODUCTION

Highly concentrated emulsions are an interesting class of emulsions characterized by an internal phase volume fraction exceeding 0.74, the critical value of the most compact arrangement of uniform, undistorted spherical droplets [1,2]. Consequently, their structure consists of deformed (polyhedral) and/or polydisperse droplets separated by a thin film of continuous phase, a structure resembling gas–liquid foams, as shown in [Figure 6.1](#). They are high-internal-phase (HIPE) emulsions which are also referred to in the literature as gel emulsions [3–6], hydrocarbon gels [7], biliquid foams [8], etc. In this text they will be referred to as highly concentrated emulsions.

The internal or dispersed phase of highly concentrated emulsions can be either polar or nonpolar and, as ordinary emulsions, they are classified in two categories: water-in-oil (W/O) and oil-in-water (O/W). However, they can be classified according to other criteria such as the microstructure of the continuous phase or the interaction forces between droplets. Phase behavior studies have shown [3,9–11] that highly concentrated emulsions separate into two phases: one phase is a submicellar surfactant solution in water (or a surfactant solution in oil) and the other phase can be either a microemulsion [3,9] or a cubic liquid crystalline phase [10,11]. Studies using

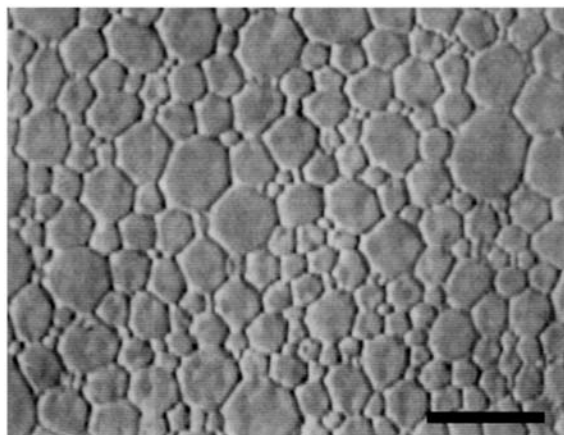


FIGURE 6.1 Example of a highly concentrated emulsion observed by optical microscopy. The scale bar indicates 20 μm .

different techniques, nuclear magnetic resonance (NMR) [9], electron spin resonance (ESR) [12], small angle X-ray scattering (SAXS) [11,13], etc., have confirmed that the continuous phase of these emulsions possess indeed such microstructures. Accordingly, they can be classified as microemulsion-based and cubic-phase-based [14]. Considering the interaction forces between droplets, they can also be classified as adhesive and nonadhesive [15]. Adhesive emulsions, in the presence of attractive forces between droplets, do not relax and maintain a high degree of packing. Nonadhesive emulsions, brought into contact with its continuous phase, relax in a way that the emulsion dilates to the state of spherical (nondeformed droplets). In this chapter, attention is focused to microemulsion-based W/O and O/W highly concentrated emulsions.

The conventional method of preparation for highly concentrated emulsions consists of dissolving a suitable emulsifier in the component that will constitute the continuous phase followed by stepwise addition of the component which will constitute the dispersed phase, with continuous moderate stirring. However, they can be also prepared by weighing all the components at the final composition, followed by shaking or stirring the sample [3–5]. This method of preparation has been termed the multiple emulsification method because at a certain step of the emulsification process, the mixture consists of a multiple W/O/W emulsion [5]. It should be noted that emulsification by the conventional and multiple emulsification methods results in rather large (over a micrometer in diameter) and polydisperse emulsions, as that depicted in Figure 6.1. An interesting method of preparation, which takes advantage of the phase transitions produced during the emulsification process, the so-called spontaneous formation method [16–18], produces emulsions with smaller droplet size and narrower size distributions than those obtained by the other methods.

The spontaneous formation method is based on the phase inversion temperature (PIT) emulsification method [19]. The PIT is the temperature at which polyoxyethylene nonionic surfactants change their preferential solubility from water (oil) to oil (water) and inversion from O/W to W/O emulsions or vice versa is produced [19]. Highly concentrated W/O emulsions form at temperatures above the PIT of the corresponding system while highly concentrated O/W emulsions form below this temperature [3]. The PIT is also designed for hydrophilic–lipophilic balance (HLB) temperature because the hydrophilic–lipophilic properties of the surfactant are balanced. At this temperature, maximum solubilization of oil and water is produced with the minimum amount of surfactant and the interfacial tensions in the system attain ultra-low values

(e.g., 10^{-3} mN m⁻¹) [20]. Therefore, emulsification is favored: emulsions with small droplet size can be obtained with low energy input. However, emulsion stability is very low at this balanced temperature. The PIT emulsification method consists in preparing the emulsions at the HLB temperature (taking advantage of the low interfacial tension values achieved) followed by a rapid cooling or heating of the samples to produce O/W or W/O emulsions, respectively.

Formation of highly concentrated emulsions without the need for mechanical stirring can be achieved, by quickly cooling (or heating) a water-in-oil (or oil-in-water) microemulsion from a temperature higher (or lower) than the HLB temperature of the system to a temperature below (or above) it [5,16,18]. In practice, it may be difficult to obtain a single (microemulsion) phase in a given system at the starting emulsification temperature. Emulsification can be also carried out by the same method starting from a two- or multiple-phase system (i.e., emulsion). However, the temperature change process has to be accompanied by mechanical stirring in order to obtain uniform and small emulsion droplets [21].

The stability of highly concentrated emulsions is greatly affected, as in conventional emulsions, by the nature of the components, the volume fraction of the dispersed phase, the oil/surfactant weight ratio, presence of additives, and temperature [22]. The time taken for phase separation, which may vary from minutes to years, can be significantly retarded by appropriate selection of the different composition variables and temperature. Accordingly, highly concentrated emulsions with stabilities suitable for their use as reaction media can be obtained. In systems with polyoxyethylene type nonionic surfactants and aliphatic hydrocarbons, a relationship between the stability of highly concentrated emulsions and the HLB temperature of the corresponding system was observed [3]. The stability of O/W (or W/O) highly concentrated emulsions is maximum at about 25 to 30 °C lower (or higher) than the HLB temperature of the corresponding system. This fact was explained by the changes in structure of the continuous microemulsion phase with temperature on the basis of phase behavior, NMR, and conductivity studies [5,9]. At the HLB temperature (minimum stability), the structure of the microemulsion is bicontinuous, while when temperature is increased or decreased, the structure changes to globular W/O or O/W type, respectively. Additives, e.g., electrolytes, may also influence emulsion stability. It was found that salts with large salting-out effect are more effective in stabilizing these emulsions because they decrease more pronouncedly the HLB temperature of the system [12,22]. The hydrophilic part of the surfactant dehydrates in the presence of electrolytes (producing a decrease in the HLB temperature), the surfactant-surfactant interactions increase and, therefore, the interfacial film is more rigid.

One characteristic property of highly concentrated emulsions is their high viscosity as compared to that of the constituent phases. They are non-Newtonian fluids characterized by a yield stress below which they show a solid-like behavior [2,23,24]. Determination of the rheological properties by means of dynamic (oscillatory) measurements showed that they have a viscoelastic response that can be fitted to a Maxwell liquid element: an elastic modulus produced by interfacial area increase and a viscous modulus produced by the loss caused by slippage of droplets against droplets. The values of relaxation time were found to be proportional to the continuous phase viscosity and inversely proportional to the continuous phase volume fraction [25].

The characteristic properties of highly concentrated emulsions are of particular interest for theoretical studies and for applications. Their use for practical applications is well known since long ago. They are widely used as formulations in, for example, cosmetics, foods, and pharmaceuticals. One of the most promising applications is their use as reaction media. In this context, they have received a great deal of attention for the preparation of low-density organic and inorganic materials (solid foams, aerogels) [8,21,26–28] and in chemical and enzyme-catalyzed reactions [29–32] as alternative to conventional solvent media.

6.2 HIGHLY CONCENTRATED EMULSIONS AS TEMPLATES FOR MACROPOROUS FOAMS

Solid macroporous foams, which consist of interconnected sponge-like macropores, can be obtained by polymerization in the continuous phase of highly concentrated emulsions, followed by the removal of the dispersed phase components [33–39]. These materials can possess very high pore volume and very low bulk density. Both organic and inorganic monomers can be used to obtain macroporous solid foams.

6.2.1 PREPARATION OF ORGANIC MACROPOROUS FOAMS IN HIGHLY CONCENTRATED EMULSIONS

The use of highly concentrated emulsions to prepare solid foams with densities smaller than 0.1 g ml^{-1} was first described in a patent from Unilever in 1982 [33]. The foams were obtained in a concentrated W/O emulsion, stabilized by sorbitan fatty esters, with organic monomers such as styrene and the cross-linker divinylbenzene in the continuous phase.

This process, which was later studied by Williams [34,35], has been applied to other highly concentrated emulsions to obtain a wide variety of different macroporous materials using, as monomers, styrene [26,27], styrene/divinylbenzene [26,27,36], divinylbenzene/ethylvinylbenzene [40], acrylamide, alkyl methacrylates, etc. [26,27,37]. These macroporous solid foams have found successful applications as supports for catalysts, immobilization of enzymes, selective membranes, templates for the preparation of other materials, etc. [26,27,36,37,41]. The properties (average cell size and cell size distribution, surface area, macroscopic density, etc.) of the materials obtained using this technology were improved with respect to those obtained by other methods, but their structures were still difficult to control. An example, corresponding to a polystyrene foam, obtained from a highly concentrated W/O emulsion, is shown in Figure 6.2. The polyhedral macropores are interconnected through narrower necks, because the films that separate adjacent droplets in concentrated emulsions are very thin, and polymerization takes place mainly in the emulsion plateau borders.

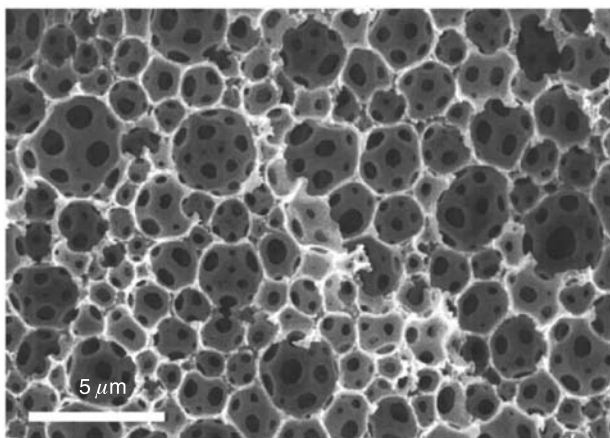


FIGURE 6.2 Micrograph of a polystyrene foam, obtained by polymerizing (60°C , 48 h) in the continuous phase of a water-in-styrene emulsion, which contains 90 wt% aqueous solution, stabilized by 2 wt% $\text{C}_{16}(\text{EO})_6$. The scale bar indicates $5 \mu\text{m}$.

Williams studied the preparation of styrene–divinylbenzene cross-linked solid foams, by polymerization in water-in-monomer highly concentrated emulsions [34]. He demonstrated that the increase in both the volume fraction of the dispersed phase and the surfactant concentration produces a thinning of the films with separate adjacent droplets, increasing the necks which connect the cells that constitute the solid foams [34]. Williams and Sherington studied the formation of the connecting necks between the cells [35,36]. The monomers are adsorbed preferentially on the parts of the surfactant monolayer located in the interstices between adjacent drops [35]. Cameron et al. followed the polymerization process by cryo-SEM [36]. Their results suggested that the formation of necks between the adjacent cells is due to the contraction of the thin monomeric films during the conversion of monomer to polymer. Ruckenstein et al. reported the preparation of composite polymers by simultaneous polymerization of both hydrophilic and lipophilic monomers in highly concentrated emulsions, stabilized either by ionic or nonionic surfactants [37,38]. Some reviews have appeared on this subject [26,27].

The density of the foams can be as low as 0.02 g/ml and the specific surface area can be as high as 350 m²/g, by addition of an inert oil (porogen) [41]. The cell size in the foams is typically in the range of 1 to 20 μm . Foam cell sizes are highly dependent on coalescence during polymerization and addition of electrolyte has been found to greatly decrease the cell size [42].

In all these reports [26,27,33–42], the cells were large, with diameters generally greater than 10 μm , and highly nonhomogeneous due to the high polydispersity of the precursor emulsion. These emulsions were prepared by the classical method of dissolving a suitable emulsifier in the component that will constitute the continuous phase, followed by the slow addition of the dispersed phase components, with stirring over a relatively long period of time. Solans et al. reported that highly concentrated emulsions with smaller and more homogeneous droplet size were obtained by making use of phase behavior [16–18]. Microemulsions were prepared at the PIT, and the temperature was rapidly changed. The PIT or hydrophile–lipophile temperature (THLB) is the temperature at which the hydrophilic and lipophilic properties of the surfactant are balanced in the system [19].

Figure 6.3(a) shows the aspect, as seen by optical microscopy, of a water-in-styrene highly concentrated emulsion that contains 90 wt% of dispersed phase, which has been obtained by a method based on the phase inversion principle, in which emulsification was achieved increasing the temperature, across the PIT, from a diluted O/W emulsion to a concentrated W/O emulsion. The droplets of this emulsion are relatively large, between 3 and 20 μm , similar to highly concentrated emulsions prepared by conventional methods [1–5], because the two-phase system is unstable at the PIT. The droplet size is much smaller, $\approx 1 \mu\text{m}$, if stronger agitation is applied to the sample during the increase in temperature, as shown by Figure 6.3(b). The respective polystyrene macroporous foams are shown in Figures 6.3(c) and (d). It should be pointed out that the foam in Figure 6.3(d) consists of smaller and less polydispersed cells than foams from emulsions prepared by conventional methods, which are generally bigger than 10 μm [33–40]. Therefore, this emulsification method that is based on the PIT principle allows the preparation of homogeneous solid foams, with smaller cell size [21].

Studies by Esquena et al. on mechanical properties of macroporous organic monoliths, by means of compression tests, are described in Figure 6.4. Strength and toughness were determined from the stress/strain curve [21]. Both parameters were normalized by dividing by the monolith bulk densities, to allow better comparisons. The results of mechanical properties (Figure 6.4) clearly show that samples prepared by the PIT method lead to monoliths with higher mechanical properties than those prepared by conventional method, which consists in step-wise addition of

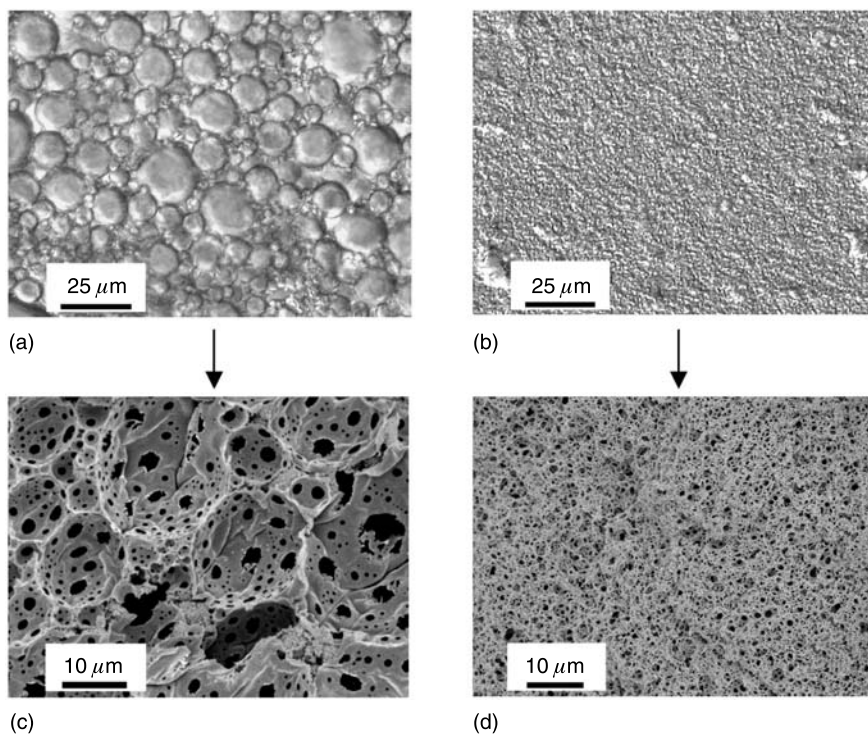


FIGURE 6.3 Preparation of macroporous polystyrene foams in highly concentrated W/O emulsions of the system $\text{H}_2\text{O}/\text{K}_2\text{S}_2\text{O}_8/\text{C}_{16}(\text{EO})_6/\text{C}_{12}(\text{EO})_8/\text{Synperonic L-64}/\text{styrene}/\text{divinylbenzene}/\text{tetradecane}$ containing 90 wt% of dispersed phase. (a) W/O emulsion obtained by PIT method, after heating the sample from 0 °C to 70 °C, while stirring very gently by hand. (b) W/O emulsion obtained by PIT method, from 0 °C to 70 °C, and simultaneously applying strong agitation by hand. (c) Scanning electron micrographs of sample (a) after polymerization and drying. (d) Micrograph of sample (b) after polymerization and drying. (Reproduced from Esquena, J., Sankar, G.S.R.R., and Solans, C. *Langmuir* 19, 2983–2988, 2003. With permission of the American Chemical Society.)

the dispersed phase to the continuous phase, under continuous vibromixer agitation. Strength was approximately three times higher and toughness was approximately 50% higher.

A common issue, which can be solved according to different methods, is the purification process. Generally, organic solvents are removed by evaporation, but small quantities can remain trapped in the final foam. Macroporous organic foams cannot be purified by calcination at high temperature, which is the most general method to purify inorganic foams. Cooper et al. have reported an interesting approach, which produces solvent-free macroporous organic foams, by using supercritical CO_2 -in-water highly concentrated emulsions as templates [43]. This method is described, schematically, in Figure 6.5. High pressure reactions (100 bar, 20 °C) were carried out in a stainless steel reactor. After polymerizations, CO_2 was removed by reducing the pressure. Finally, residual water was removed from the macroporous polymers by drying in air followed by drying under vacuum.

Macropore templating by supercritical CO_2 droplets has the advantage that it does not require volatile organic solvent, either in the synthesis or in the purification steps [43]. Unlike other

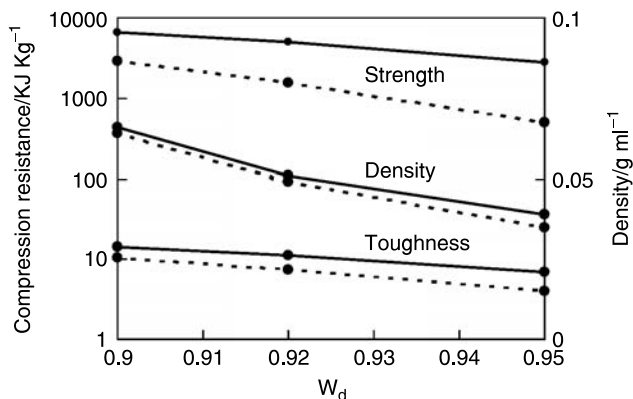


FIGURE 6.4 Density and normalized mechanical properties as a function of the weight fraction of the dispersed phase, for the two preparation methods. Solid line: PIT method, Dashed line: conventional method. (Reproduced from Esquena, J., Sankar, G.S.S.R., and Solans, C. *Langmuir* 19, 2983–2988, 2003. With permission of the American Chemical Society.)

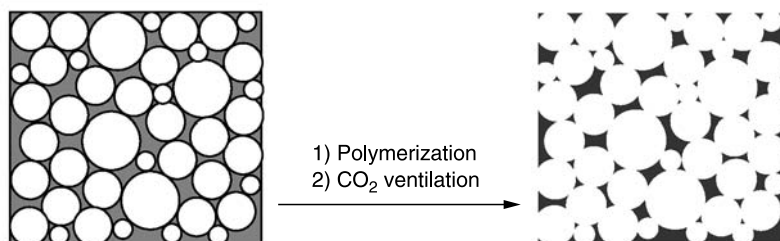


FIGURE 6.5 Preparation of macroporous materials by supercritical CO_2 -in-water emulsion templating. (Redrawn from Butler, R., Davies, C.M., and Cooper, A.I. *Adv. Materials* 13, 1459–1463, 2001. With permission of Wiley-VCH Verlag GmbH.)

solvents, which may be difficult to remove completely, supercritical CO_2 is nontoxic, non-flammable, and reverts to the gaseous state upon de-pressurization. However, this method has the inconvenience that expensive equipment is required, and fluoro-containing surfactants are needed because conventional surfactants do not adsorb on supercritical CO_2 droplets.

6.2.2 PREPARATION OF INORGANIC MACROPOROUS FOAMS IN HIGHLY CONCENTRATED EMULSIONS

The previous section has described different methods, which involve the use of highly concentrated emulsions as templates, to obtain macroporous organic foams. Macroporous inorganic materials can also be templated in highly concentrated emulsions. Imhof and Pine described a method that makes use of monodisperse emulsions [44], which were obtained according to the Bibette repeated fractionation procedure [45]. Droplet volume fractions can exceed the close-packing limit of 74%. Starting with highly concentrated O/W emulsions of monodisperse droplets,

macroporous materials (silica, titania, and zirconia) were formed by using the emulsion droplets as templates [44]. The inorganic oxides were produced through sol–gel processes, at the aqueous external phase of the emulsions. Subsequent drying and heat treatment yields solid materials with spherical pores left behind by the emulsion droplets. These pores are highly ordered, reflecting the self-assembly of the original monodisperse emulsion droplets into a nearly crystalline array [45]. Macroporous foams, made of titania, zirconia, and silica, obtained in isooctane-in-formamide emulsions, are shown in Figure 6.6.

Highly ordered honeycomb-like macropores can be obtained by this method, depending on the emulsion polydispersity. However, it should be pointed out that a high degree of monodispersity is difficult to achieve, and that the whole process required long and tedious repeated fractionation steps.

Macroporous materials, templated in emulsions prepared by the repeated fractionation technique, were also obtained by Yi and Yang in silicone oil-in-water emulsions [46]. The emulsion droplets were flocculated and tended to migrate to certain regions, which eventually led to the formation of highly concentrated emulsions. The aspect of macroporous silica, obtained in one such concentrated region, is shown in Figure 6.7.

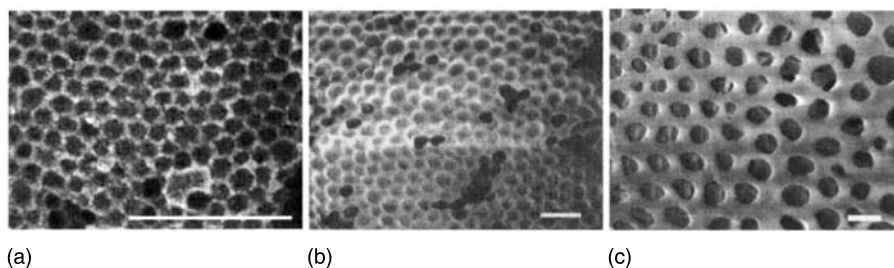


FIGURE 6.6 Scanning electron micrographs of macroporous inorganic oxides, obtained after calcinations. Scale bars, 1 μm . (a) Titania, (b) Zirconia, (c) Silica (89% porosity). (Reproduced from Imhof, A. and Pine, D.J. *Nature* 389, 948–951, 1997. With permission of the Nature Publishing Group.)

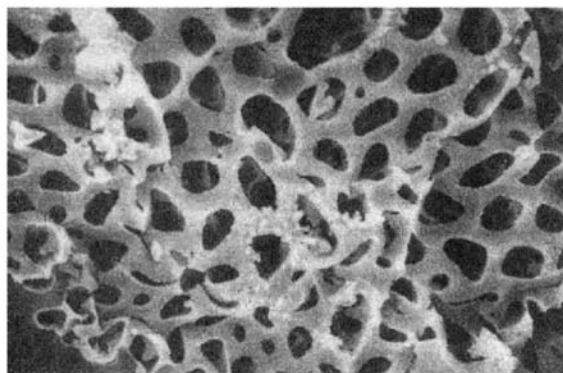


FIGURE 6.7 Image of macroporous silica, obtained by scanning electron microscopy, of a region that consisted of highly concentrated emulsion droplets. (Reproduced from Yi, G.R. and Yang, S.M. *Chem. Mater.* 11, 2322–2325, 1999. With permission of the American Chemical Society.)

These results show that macroporous foams of inorganic oxides can be obtained by using highly concentrated emulsions as templates, by carrying out the reactions in the external phase. It is worthwhile noting that many other materials, different from inorganic oxides, could be obtained by templating in highly concentrated emulsions, despite the fact that most of the studies deal with inorganic oxides, specially with silica.

6.3 HIGHLY CONCENTRATED EMULSIONS AS TEMPLATES FOR HIERARCHICALLY TEXTURED FOAMS

Materials with extremely high specific surface areas, such as zeolites or micro/mesoporous materials, are important in applications such as in catalysis and molecular separations [47]. However, these materials usually have rather poor pore volumes ($<2 \text{ cm}^3 \text{ g}^{-1}$), which restrict their performance in certain applications in which large molecules (enzymes, polymers, etc.) are involved.

The inclusion of macropores can provide enhanced mass transport into and out of the porous structure. This becomes very important for processes that have low diffusion rates. Recently, materials with dual meso- and macroporous properties have attracted much attention because they combine the advantages of high specific surface with the accessible diffusion pathways associated with macroporous structures. The large active surface of mesopore walls can be reached easily, with good diffusion coefficients, from the macropores. Because of these dual properties, these meso/macroporous materials are very important in many industrial applications, which include catalytic surfaces and supports [48], adsorbents, chromatographic materials, filters [49,50], light-weight structural materials [51], and thermal, acoustic [52], and electrical insulators [53]. Some novel applications include catalytic supports in fuel cells or energy storage in double-layer capacitors [54].

The capability to control the pore size and morphology at different length scales is of utmost importance. In addition, it is also very important to obtain such materials by simple and cost-effective methods. Several methods to prepare hierarchically textured materials have been described. Many of these use different kinds of emulsions as templates, because they allow the control of large macropores. Highly concentrated emulsions have the advantage that materials with a very high pore volume and with well-connected macropores can be obtained. The methods to obtain hierarchically textured foams, from highly concentrated emulsions, are reviewed in the next section.

6.3.1 PREPARATION OF HIERARCHICALLY TEXTURED FOAMS IN HIGHLY CONCENTRATED EMULSIONS STABILIZED BY SURFACTANT MOLECULES

6.3.1.1 Two-Step Methods

Esquena et al. have used highly concentrated emulsions as templates for the preparation of materials, with dual meso/macroporous structures, by a two-step templating process [28]. The first step consists in the preparation of organic macroporous foams by polymerizing in the continuous phase of highly concentrated O/W emulsions [21], as described in a previous section. These solid foams can be used as scaffolds for the preparation of the meso/macroporous inorganic oxides. The second step consists in imbibing with ethanol sol-gel solutions that contain inorganic precursors and block copolymer surfactants [28]. The cooperative self-assembly of the surfactant molecules, together with the inorganic oxide precursor species, leads to the formation of ordered mesostructures. The resulting organic-inorganic composite materials were dried and then calcined in air at high temperature in order to remove all organic components and to obtain the meso/macroporous

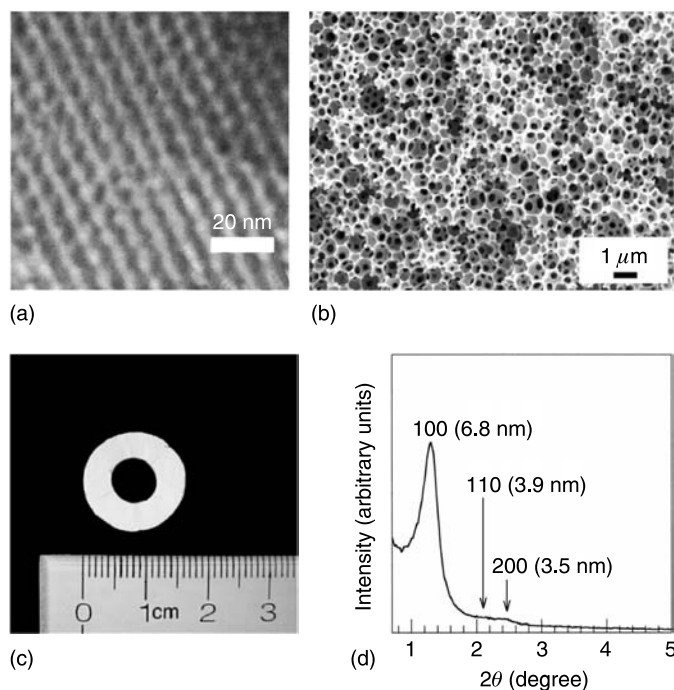


FIGURE 6.8 (a) Image, obtained by transmission electron microscopy, of a calcined meso/macroporous silica monolith. (b) Image, obtained by scanning electron microscopy, of a calcined meso/macroporous silica monolith. (c) An annulus-shaped silica monolith, after calcination. (d) X-ray diffraction spectra, at small angle, of the same sample shown in (a). (Reproduced from Maekawa, H., Esquena, J., Bishop, S., Solans, C., Chmelka, B.F. *Adv. Materials* 15, 591–596, 2003. With permission of Wiley-VCH Verlag GmbH.)

inorganic materials. Therefore, these materials are obtained by a double templating process: Highly concentrated emulsions for the macropores and supramolecular self-assembly for the mesopores [28]. The bimodal distribution of pores was characterized by highly ordered mesopores, in the size regime 5 to 10 nm (Figure 6.8(a)), and by interconnected macropores between 0.1 and 5 μm (Figure 6.8(b)).

The meso/macroporous materials obtained by this method are moldable, since the macroscopic external shape depends on the size and morphology of the mold used to carry out the first polymerization process. For instance, an annulus-shaped meso/macroporous monolith is displayed in Figure 6.8(c). The inorganic oxide materials were also characterized by nitrogen sorption and by X-ray diffraction using small-angle techniques (Figure 6.8(d)). The results were consistent with those obtained by electron microscopy techniques.

The two meso/macro length scales can be adjusted independently because the surfactant molecules, which form the mesostructure, are introduced after the first step of polymerization of a highly concentrated emulsion. Therefore, the two templating systems do not interfere with each other, and consequently the meso- and macro-structures can be optimized separately [28]. Inorganic oxides, such as silica, titania, and zirconia, were obtained by this two-step process. High pore volumes ($17 \text{ cm}^3 \text{ g}^{-1}$) could be obtained. The specific surface areas, determined by the Brumauer-Emmett-Teller (BET) method applied to the nitrogen adsorption isotherm, were

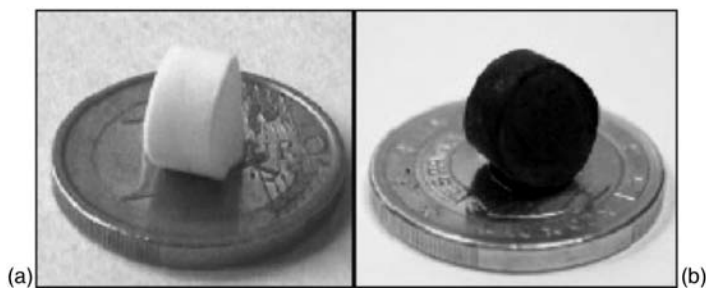


FIGURE 6.9 Photographs of a meso/macroporous silica monolith (a) and the templated meso/macroporous carbon monolith (b). The diameter of the coin is 2.3 cm. (Reproduced from Alvarez, S., Esquena, J., Solans, C., and Fuertes, A.B. *Engineering Materials* 6, 897–899, 2004. With permission of Wiley-VCH Verlag GmbH.)

between 250 and 750 m² g⁻¹. The higher surface areas were obtained at higher inorganic precursor concentrations and correlate with reduced macropore volumes.

The meso/macroporous inorganic oxide monoliths can be used as templates for obtaining porous carbon monoliths, as shown by Alvarez et al. [54]. Silica monoliths were impregnated with furfuryl alcohol, which was polymerized. Then, the materials were carbonized by heating at 800 °C in the absence of oxygen, obtaining an exact meso/macroporous carbon replica of the initial monolith. Finally, the silica was dissolved in HF. Examples of the initial silica monoliths and the final carbon meso/macroporous replicas are shown respectively in Figure 6.9(a) and (b).

Nitrogen sorption and electron microscopy results indicated that the meso/macroporous carbon is a perfect replica of the meso/macroporous silica monoliths [54]. The carbon monoliths have a macroporosity approximately equal to 80%, consisting of a fully interconnected macroporous network composed of hierarchically organized cells. The mesopores possess a narrow range of sizes, centered around 5 nm, which allow a high BET surface area (1500 m² g⁻¹).

Another type of hierarchically textured foam, which has been obtained in highly concentrated emulsions in a two-step process, was described by Zang et al. [47]. An oil-in-water highly

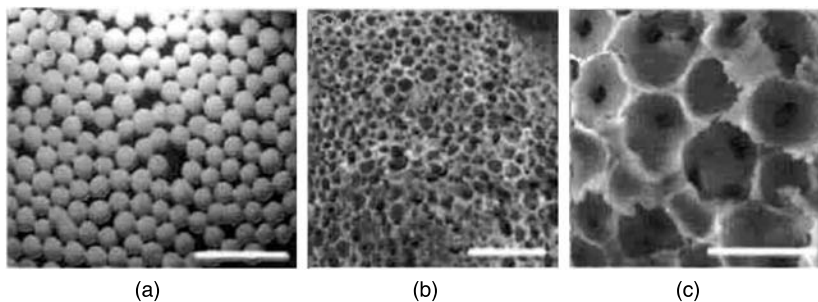


FIGURE 6.10 Images of silica beads at three different magnifications. (a) Optical microscopy, scale bar = 5 mm. (b) Scanning electron microscopy, scale bar = 200 μm. (c) Scanning electron microscopy, scale bar = 50 μm. (Reproduced from Zhang, H., Hardy, G.C., Rosseinsky, M.J., and Cooper, A.I. *Adv. Materials* 15, 78–81, 2003. With permission of Wiley-VCH Verlag GmbH.)

concentrated emulsion was formed by slowly adding mineral oil, while vigorously stirring, to a mixed solution containing acrylamide, a cross-linker, and a silica precursor. Next, the O/W emulsion was then injected as individual droplets into a hot oil sedimentation medium. Organic polymer/silica composite beads were obtained by polymerization of the mixture. This method allows the semi-continuous preparation of organic/inorganic composite beads, with uniform macroscopic particle sizes, high pore volumes, and interconnected emulsion-templated macropore structures [47]. Finally, the polymer was removed by calcination. Images of the calcined silica beads are shown in Figure 6.10. Silica porous beads, with an average bead diameter of 1.3 mm and high pore volume ($\approx 6 \text{ cm}^3 \text{ g}^{-1}$), have been obtained [47]. The structure of the highly concentrated emulsions was retained in the beads and the materials had a large specific surface area ($420 \text{ m}^2 \text{ g}^{-1}$).

6.3.1.2 Single-Step Methods

Materials with meso/macroporous hierarchical porosity can be obtained in a simple single-step method, by directly carrying out polymerization reactions in the external phase of highly concentrated emulsions, as described by different authors [55,56]. This method makes use of the common structure of highly concentrated emulsions, which consist of emulsion droplets that template the formation of macropores and micellar aggregates, located in the external phase of the emulsions, that template the formation of mesopores [55,56]. This method can allow a high degree of control over both sizes and morphologies. All organic components can be removed, by calcinations in the presence of air, to prepare inorganic porous materials. Silicas with high specific surface areas, such as $800 \text{ m}^2 \text{ g}^{-1}$, associated with bulk density as low as 0.08 g cm^{-3} , have been obtained by Carn et al. [55]. These values are comparable to those obtained for silica aerogels obtained by reactions in the vapor phase.

It is worthwhile noting that powder materials are obtained rather than monoliths, at volume fractions of the dispersed phase above 0.8 [55,56]. No large monoliths have yet been obtained by this method, using highly concentrated emulsions. This feature has been attributed to the fact that the wall thickness decreases and does not have the expected mechanical strength, inducing the collapse of the inorganic scaffolds.

Overall, meso/macroporous inorganic materials consisting of well interconnected macropores and monodispersed mesopores can be obtained. Commercially available alkoxysilanes, such as tetraethoxysilane (commonly denoted tetraethyl orthosilicate, TEOS), can be used as inorganic precursors. Selection of the most appropriate surfactant system is crucial, since TEOS hydrolysis produces ethanol, which may decrease emulsion stability. The surfactants can be either ionic [55] or nonionic [56]. Tetradecyltrimethyl ammonium bromide (TTAB) and poly(ethylene oxide)-block-poly(propylene oxide)-block-poly(ethylene oxide) triblock copolymer surfactants (EO) n -(PO) m -(EO) n have been described [55,56].

TEOS reactions in the continuous phase of the highly concentrated emulsions may require long times, as much as 1-week periods [55]. A strategy to obtain meso/macroporous materials, by a faster single-step method, is to accelerate the condensation reactions by evaporating the ethanol produced by TEOS hydrolysis, as described by Esquena et al. [56]. The highly concentrated emulsions, containing TEOS, are placed in open dishes at constant temperature. The ethanol produced by the reactions is removed and solid foams can be obtained in less than 24 h. The highly concentrated emulsions remain stable, which allows the control of the macropore size.

Examples of the highly concentrated O/W emulsions and the meso/macroporous silica materials are shown in Figure 6.11(a) and (b), respectively. The emulsion droplets template the formation of the macropores, and the size and polyhedral morphology of the droplets remains preserved.

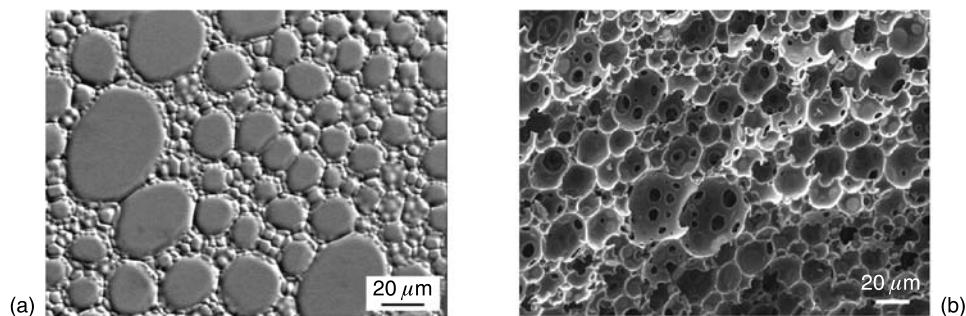


FIGURE 6.11 (a) Optical microscopy image of highly concentrated emulsion, consisting of HCl 0.2 M/(EO)₂₀-(PO)₇₀-(EO)₂₀/decane (8/2/90 mass ratios). (b) Scanning electron microscopy image of meso/macroporous silica obtained in the system HCl 0.2 M/(EO)₂₀-(PO)₇₀-(EO)₂₀/decane/TEOS (6/2/85/7 mass ratios). Condensation was favored by placing the sample in an open dish at 45 °C.

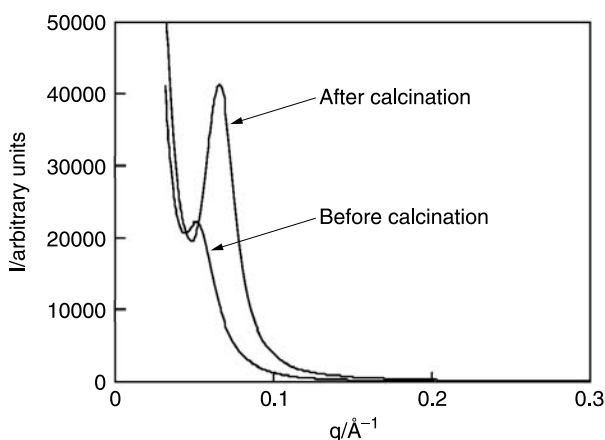


FIGURE 6.12 Small angle X-ray scattering (SAXS) spectra of a silica sample obtained in the system HCl 0.2 M/P123/decane/TEOS (6/2/85/7 mass ratios), before and after calcinations at 500 °C in the presence of air. The calcined sample shows a relatively intense peak, which is not observed in the noncalcined sample.

The spectra obtained by small-angle X-ray scattering is shown in Figure 6.12. The as-synthesized noncalcined sample produces a low-intensity peak, and no high order peaks are observed in the spectra. Therefore, the mesostructure probably consists of disordered pores, which does not lead to X-ray diffraction patterns. The peak is probably due to the pore–pore average correlation distance (d -spacing = 121.7 Å). The peak intensity significantly increased after calcination and its position was shifted to a higher q value (d -spacing = 95.8 Å). Again, no high order peaks are observed.

The reduction in d -spacing produced by calcination indicates a certain degree of shrinkage induced by the removal of the organic core or the mesopores. The increase in peak intensity may indicate a less polydispersed pore–pore correlation distance. The specific surface area of the calcined sample, determined by applying the BET method to the nitrogen adsorption isotherm,

is approximately $300 \text{ m}^2 \text{ g}^{-1}$. This specific surface area is relatively high, considering that it has been achieved with only 2 wt% surfactant [56]. Larger specific surface areas, around $800 \text{ m}^2 \text{ g}^{-1}$, can be obtained, but higher surfactant concentrations ($\approx 9 \text{ wt\%}$) are required [55].

6.3.2 PREPARATION OF HIERARCHICALLY TEXTURED FOAMS IN HIGHLY CONCENTRATED EMULSIONS STABILIZED BY SOLID PARTICLES

A simple and effective way of preparing porous silica materials arises from emulsions stabilized by solid particles alone, in the absence of surfactant [57]. Emulsions stabilized by solid particles, generally called Pickering emulsions [58,59], were first described long ago. Solid particles can function in similar ways to surfactant molecules, with the relevant parameter in the case of spherical particles being the contact angle of the particle with the liquid–liquid interface. Solid particles may possess high energy of attachment to interfaces, which produces irreversible adsorption. As a result, emulsion droplets coated with solid particles can be remarkably stable to coalescence.

Pickering emulsions can be oil-in-water or water-in-oil. Hydrophilic solid particles produce contact angles smaller than 90° , and the preferred emulsions are O/W. For lipophilic particles the contact angle is bigger than 90° , and W/O emulsions are obtained.

The balance between the hydrophilic and the lipophilic properties of solid particles can be easily controlled. For instance, fumed silica particles (diameter $\approx 10 \text{ nm}$), which are hydrophilic because of silanol groups (Si-OH) in its surfaces, can become lipophilic by functionalization with alkyl silanes [60]. Therefore, the contact angle between a spherical particle and a given liquid–liquid interface can be tuned by the degree of functionality, in order to achieve the maximum emulsion stability.

Recently, Pickering emulsions were used to obtain porous silica with controlled pore size by Binks [57]. This method has the advantage that no surfactant is required and therefore no calcination at high temperature is needed for silica purification. Evaporation in air of Pickering emulsions stabilized by fumed silica particles leads to the formation of porous silica, as shown in Figure 6.13. Monolith (tablet-like) materials that retain the shape of the container can be obtained. The surface area of silica particles was 200 to $250 \text{ m}^2 \text{ g}^{-1}$. The SEM images of Figure 6.13 show the macropores of silica materials. They resemble other kinds of materials obtained by other

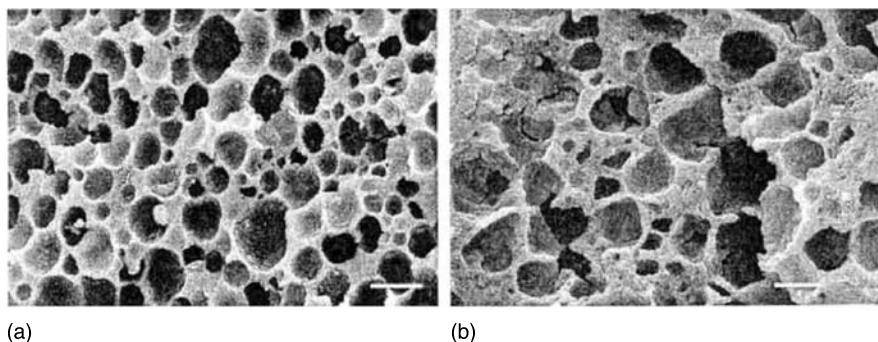


FIGURE 6.13 SEM images of porous silica following evaporation of both oil and water from silica particle-stabilized emulsions. Scale bar = $10 \mu\text{m}$. (a) 10 vol% decane-in-water with 4 wt% silica (silanol content = 76%). (b) 10 vol% water-in-hexane with 4 wt% silica (silanol content = 50%). (Reproduced from Binks, B.P. *Adv. Materials* 14, 1824–1827, 2002. With permission of Wiley-VCH Verlag GmbH.)

means in highly concentrated emulsions. The fact that the most volatile emulsion component is the continuous phase induces the formation of highly concentrated emulsions during the solvent evaporation. Oil evaporation must be slow enough to allow the rearrangement and bonding of the silica particles before water is lost completely [57].

6.4 SUMMARY

Highly concentrated emulsions, which possess a volume fraction of the dispersed phase higher than 0.74 [1,2], are very appropriate systems for the preparation of low-density macroporous materials, also designated aerogels, which have very large pore volume and very low bulk density. These materials can be obtained by polymerization in the continuous phase of highly concentrated emulsions followed by the removal of the dispersed phase components [21,33–44]. The macroporous solid foams produced by this method consist of interconnected sponge-like macropores and possess low bulk densities. The droplet size distribution of the highly concentrated emulsion is a crucial factor in determining the mechanical properties of macroporous monoliths. Strength and toughness of organic foams can be improved by selecting the most appropriate system components and emulsification methods [21]. Highly ordered honeycomb-like macroporous materials can be obtained by making use of monodisperse emulsions prepared by fractionation techniques [44]. Both organic and inorganic monomers can be used to obtain macroporous solid foams, and the results show that a very wide variety of low-density macroporous materials can be obtained.

These macroporous materials have received widespread attention because of their successful applications as supports for catalysts, immobilization of enzymes, selective membranes, templates for the preparation of other materials, etc. Mesoporous materials that possess a high surface area and a uniform porosity are also very important because of their potential applications as catalytic surfaces and supports, adsorbents, energy storage devices, chromatographic materials, filters, etc. [48–54]. In order to obtain technological useful materials, the porous structure must have a dual meso/macroporous network. The presence of mesopores ensures large surface areas for reaction and/or adsorption, whereas the macropores guarantee surface accessibility, permitting the rapid transport of chemical species.

Highly concentrated emulsions are also very appropriate systems for the preparation of hierarchically textured foams [28]. These are materials that possess structural organization at different size ranges. Several methods for the preparation of materials with dual meso/macroporous properties have been described [28,47,54–57]. Mesopores are templated by supramolecular aggregates and macropores by the emulsion droplets. Materials that possess high specific surface area and high macropore volume have been obtained. The preparation methods can be classified as two-step and single-step methods.

Two-step methods permit an independent control of the mesopore and the macropore sizes. The first step consists of the preparation of organic macroporous foams by polymerizing in the continuous phase of highly concentrated O/W emulsions [21]. These solid foams are used as scaffolds for the preparation of the meso/macroporous inorganic materials. The second step consists of imbibing with ethanol sol–gel solutions that contain inorganic precursors and surfactants [28].

Hierarchically porous beads can be obtained by a two-step method. Emulsion-templated polymer/silica composite beads have been obtained by polymerization of the continuous phase of highly concentrated emulsions [47]. The emulsions are then injected as individual droplets into a hot oil sedimentation medium, allowing the semi-continuous preparation of organic/inorganic composite beads, with uniform macroscopic particle sizes, high pore volumes, and interconnected emulsion-templated macropore structures.

In the single-step methods polymerization reactions are carried out directly in the continuous phase of highly concentrated emulsions [55,56]. Some of these methods make use of the common structure of highly concentrated emulsions, which consist of emulsion droplets that template the formation of macropores and micellar aggregates, located in the external phase of the emulsions, that template the formation of mesopores. Another single-step method consists of the use of highly concentrated emulsions stabilized by solid particles (Pickering emulsions) [57]. No surfactant is required and therefore no calcination at high temperature is needed for silica purification.

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