Preparation of Narrow Size Distribution Silica Particles Using Microemulsions

J. Esquena,[†] Th. F. Tadros,[‡] K. Kostarelos,[‡] and C. Solans*,[†]

Departament de Tecnologia de Tensioactius, CID/CSIC, Jordi Girona, 18-26, 08034 Barcelona, Spain, and Zeneca Agrochemicals, Jealott's Hill Research Station, Bracknell, Berkshire, RG12 6EY, U.K.

Monodisperse silica particles were prepared in microemulsion media using block copolymers and nonionic surfactants. The silica particles were obtained by hydrolysis and condensation of tetraethoxysilane, using NH_3 as a catalyst, and they were characterized by optical and electron microscopy, nitrogen sorption, Fourier transform infrared spectroscopy and thin-layer chromatography. Particles, with average sizes from 0.1 to 1.5 μm and with specific surfaces lower than 100 m²/g could be obtained. The results showed that the size could be controlled by both the cosurfactant chain length and concentration. The higher the cosurfactant concentration and the shorter the chain length, the larger the particles. This has been attributed to the increase of interfacial flexibility with reduction of chain length. This causes an increase in the velocity of particle growth, then producing larger particles.

1. Introduction

The preparation of monodisperse particles has attracted a great deal of attention in the recent years because of its technological applications in the fields of ceramics, magnetic particles, semiconductors, supporters for catalysts, chromatographic adsorbents, etc. Many inorganic colloids, consisting of particles of different chemical composition, shape, and size, have been prepared by precipitation in homogeneous solutions.[1] The synthesis of narrow size distribution silica particles by hydrolysis and condensation of tetraalkylsilanes in a homogeneous alcoholic solution of water and ammonia has been described in detail by Stöber.[2] The overall reaction leading to silica formation from tetraethoxysilane (TEOS) may be represented by,

$$Si(OEt)_4 + 2H_2O \rightarrow SiO_2 + 4EtOH$$
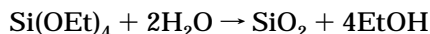
The synthesis of nanoparticles using reactions in microemulsions was first described by Boutonnet et al.,[3] who obtained monodisperse metal particles by reduction of metal salts in water in oil (W/O) microemulsions. Since then, there have been many reports on the use of microemulsions as a reaction media for the synthesis of a variety of nanoparticles such as calcium carbonate,[4] superconductors,[5] magnetic materials,[6] etc. Yanagi[7] described that silica particles could be prepared by the base-catalyzed hydrolysis of TEOS in W/O microemulsions using nonionic surfactants. According to their interpretation, tetraethoxysilane molecules penetrate into the aqueous droplets from the oil phase through the surfactant interface layer, and hydrolysis of tetraethoxysilane takes

place. Friberg et al.[8] studied the distribution of the intermediate species $Si_nO_{2n-r}(OH)_{2r-x}(OR)_x$ during this reaction. ²⁹Si NMR spectra of the microemulsion could detect only two species, namely, $Si(OR)_4$ and SiO_2. They interpreted that in a colloidal system the tetraethoxysilane is located within the lyophilic phase and the reactions proceed rapidly when the molecule reaches the interface toward the water region.

Yamauchi et al.[9] described the characterization of silica particles obtained using an anionic surfactant, AOT. They also showed that the size of the spherical particles (10–80 nm) was larger than those of the corresponding microemulsion droplets (5–10 nm). Osseo-Asare and Arriagada[10] demonstrated that the nanoparticles obtained had an extremely narrow size distribution, which had not been achieved before, using the conventional techniques of TEOS hydrolysis in a homogeneous alcoholic media. They also noticed that the final particle sizes were larger than the aqueous droplet diameters. It was concluded that further particle growth required material exchange between microemulsion droplets, a process that relies on intermicellar collision and transient merging of the colliding droplets.[10]

Arriagada and Osseo-Assare[11] also studied the effect of the presence of benzyl alcohol in the AOT W/O microemulsions. This system produces a relatively rigid surfactant interface, so that the rates of intermicellar exchange are the lowest among typical W/O microemulsion systems.[12–14] They found that the silica particle growth and the particle size were increased by the addition of benzyl alcohol to the AOT microemulsions.[11] The effects of the alcohols on the interfacial properties of the micro-

† CID/CSIC.

‡ Zeneca Agrochemicals.

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emulsions droplets have been widely studied.[15−18] The alcohol produces a lower organization on the interface which becomes more flexible. The longer the alcohol chain length, the more rigid the interface is. Therefore, the alcohol chain length can be an important factor which has not been discussed in detail. This is the objective of the present work. Silica particles were produced by reaction in W/O microemulsions, using nonionic surfactants such as block copolymers and polyethylene glycol alkyl ether. The effects of various alcohols, their chain length and concentration, on the size of the particles obtained have been studied. The alcohol can modify the interfacial properties, changing the dynamics of the system and thus changing the size of the particles.

2. Experimental Section

2.1. Materials. The surfactants used were technical grade. Atlox 4912 (an A−B−A block copolymer whose A is poly(12-hydroxystearic acid) and B is poly(ethylene oxide)) was supplied by ICI. $C_{12-14}E_{4.5}$ (an polyethylene glycol alkyl ether) was supplied by Albright & Wilson Ibérica SA. Isooctane (>99%), ammonia solution 25% (G.R) were from Merck Gmbh. Isopar G, from Esso, is a technical grade aliphatic isoparafine. 1-Butanol, 1-pentanol, 1-hexanol, 1-heptanol, and 1-octanol (>99%) were supplied by BDH. 2-Ethyl-1-hexanol (isooctanol) (>99% pure) was supplied by Fluka. Water was deionized and Millipore filtered by a Milli-Q System. The tetraethoxysilane (tetraethyl orthosilicate or TEOS), 98% pure, was supplied by Merck.

2.2. Methods. Phase Diagrams. The phase boundaries of the microemulsion areas were determined by titration with the aqueous component of the mixtures prepared containing the rest of the other components which were placed in screw-capped vials. After each addition of the aqueous component, the samples were stirred and kept at constant temperature. They were then visually inspected when equilibrium was reached. The process was repeated until the solubilization limit of aqueous component was reached.

Optical Videomicroscopy. The samples were observed with a Reichert Polyvar 2 optical microscope, supplied by Leica, which was equipped with a videocamera, polarizers, and interference contrast prism.

Dynamic Light Scattering Measurements. Photon correlation spectroscopy measurements of silica particles were performed at 25 °C using a Malvern 4700 instrument equipped with an argon laser (λ = 488 nm). The diffusion coefficients were calculated from the autocorrelation function, and the particle size and polydispersity were calculated by the Stokes−Einstein equation.

Sorption Isotherms. The nitrogen sorption isotherms at 77K were volumetrically determined using a Micromeritics ASAP 2010 A. The BET equation was used to analyze the low relative pressure region of the isotherm to obtain the surface areas.[19] The pore size distributions were calculated assuming a cylindrical shape.

Scanning Electron Microscopy. A Leica Instrument, Model STEREOSCAN 360, was used. Silica samples were coated by sputtering with a gold layer 25 nm thick. The best photomicrographs were obtained operating at 2 kV, a working distance of 2 mm, and an intensity of 10 pA.

Fourier Transform Infrared Spectra (FTIR). Infrared spectroscopy analysis of the silica samples, dried at 120 °C, was carried out in KBr pellets with a Nicolet 510 FTIR spectrometer.

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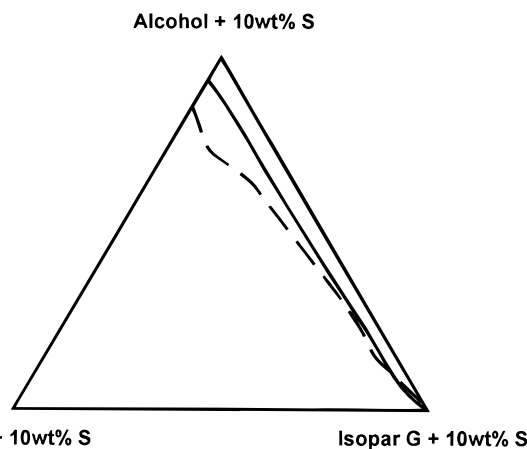(19) Brunauer, S.; Emmet, P. H.; Teller, E. *J. Am. Chem. Soc.* **1938**, *60*, 309.

Figure 1. Solubility regions in the partial pseudoternary phase diagram of the system H_2O/Isopar G/alcohol/Atlox 4912 (S) at 18 °C: (−) 1-octanol; (− − −) 1-butanol.
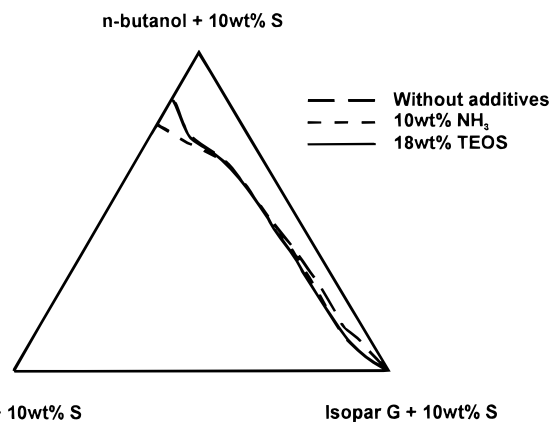

Figure 2. Solubility regions in the partial pseudoternary phase diagram of the system H_2O/Isopar G/alcohol/Atlox 4912 at 18 °C without and with additives, NH_3 in the aqueous component and TEOS in the oil component.

Silica (4.5 wt %) pellets were prepared at 10 MPa using high purity grade KBr. The spectra from 4000 to 500 cm^{-1} were recorded.

Thin Layer Chromatography (TLC). TLC plates 5 × 10 cm were prepared with the silica particles obtained. Carbopol (4 wt %) was used as a binder. The thickness of the layer was 0.25 mm. An aqueous solution of a mixture of dyes (bromophenol blue 0.1 wt %, congo red 0.03 wt %, and phenol red 0.1 wt %) was used to measure the relative retention on the silica plate. A 0.5 μL portion of this mixture was spotted in the plates. The eluent composition was 1-butanol:EtOH:H_2O:25 wt % NH_3 = 21:7:8:1 (mass ratios).

3. Results and Discussion

The hydrolysis and condensation reactions of TEOS were carried out in W/O microemulsions selected from two model systems: one consisted of H_2O/Atlox 4912/Isopar G and the other system consisted of H_2O/$C_{12-14}E_{4.5}$/isooctane. Phase behavior studies of these model systems in the presence of 1-alkanols and a catalyst, NH_3, were carried out in order to determine the solubility regions corresponding to microemulsions. Silica particles were prepared in microemulsions with appropriate concentration of the reactants (TEOS and H_2O). Afterward, they were isolated from the reaction media by centrifugation, washed with 1-butanol and ethanol, and finally dried. They were characterized by electron microscopy, nitrogen sorption, and FTIR.

3.1. Selection of the Reaction Media. The microemulsion regions in the pseudoternary phase diagram for the system H_2O/alcohol/Isopar G at 18 °C containing 10
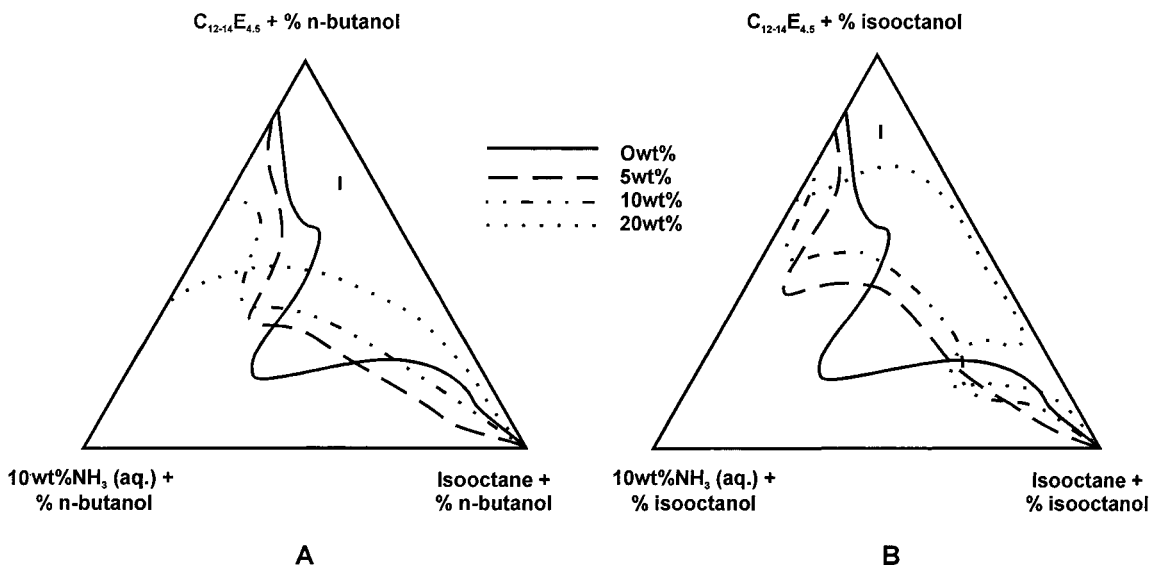
Figure 3. Solubility regions in the partial pseudoternary phase diagrams of the systems 10 wt % $NH_3/C_{12-14}E_{4.5}$/alcohol/isooctane showing the microemulsion areas at different alcohol contents, at 25 °C: (A) 1-butanol; (B) 2-ethyl-1-hexanol (isooctanol).
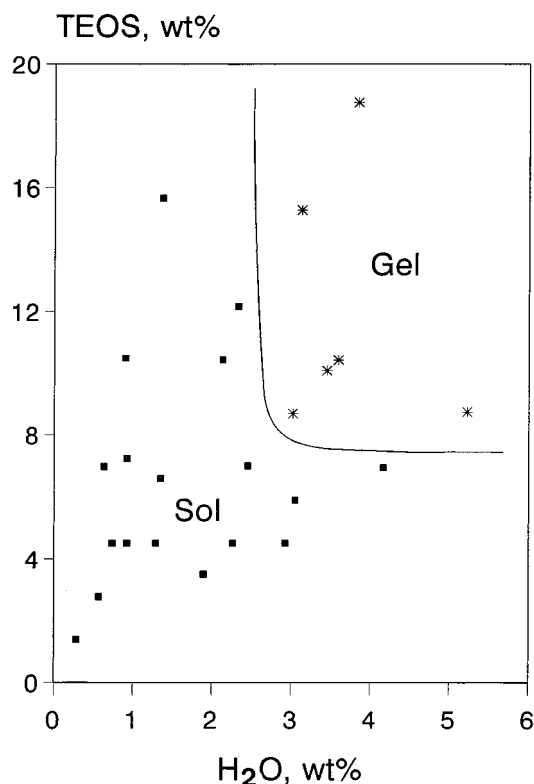

Figure 4. Silica sols and gels obtained in the system 10 wt % NH_3/Atlox 4912/Isopar G/TEOS after 24 h at 18 °C.

Figure 5. Scheme representing the method of preparation of silica particles in microemulsion media.

wt % Atlox 4912 with either 1-butanol or 2-octanol are shown in Figure 1. The solubility regions corresponding to microemulsions can be observed parallel to the alcohol−Isopar axis. It can be seen that water can be solubilized in the solution of surfactant in alcohol, without Isopar G (water−alcohol axis) but it cannot be solubilized in the solution of surfactant in oil, without alcohol (water−Isopar axis). Therefore the presence of a cosurfactant is required to obtain microemulsions in this system. The maximum amount of water solubilized (16 wt %) is obtained in the system with 1-butanol at a oil/1-butanol ratio of 7:1. In the system with 1-octanol water solubilization is considerably lower at high alcohol content. The effect of the additives required for the reaction (the reactant TEOS and the catalyst NH_3) on the phase behavior of the system
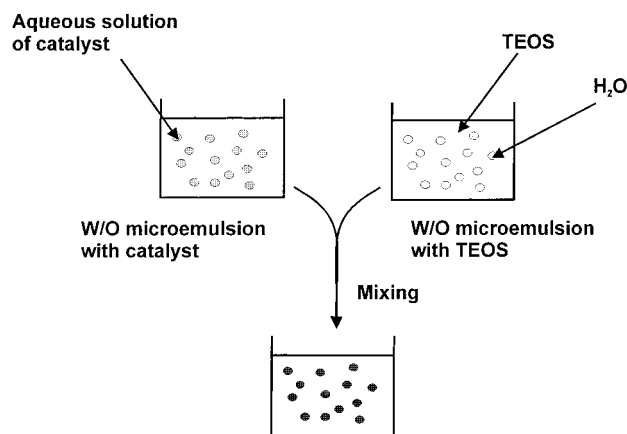
with 1-butanol is shown in Figure 2. These phase diagrams show that the microemulsion region is not modified significantly when 10% NH_3 or 18 wt % TEOS is incorporated in the aqueous and oily components, respectively.

Light scattering measurements were attempted in samples within the solubilization region. However, the scattering was very weak, which may be due to the small difference of refractive index between the different nano-structures in the system. Nevertheless, Tadros et al.[20] could measure light scattering in the system H_2O/ Hypermer B246/1-butanol/tetradecane and obtain micro-emulsion droplets with diameters between 2 and 5 nm, at 10 wt % of surfactant. Hypermer B246 is an A−B−A block copolymer chemically identical to Atlox 4912. The assumption could be made that the droplets obtained in the present system of H_2O/Atlox 4912/1-butanol/Isopar G are of similar radii to that obtained using Hypermer B246 and tetradecane.

Figure 3 shows the microemulsion boundaries of the pseudodoternary systems 10 wt % $NH_3/C_{12-14}E_{4.5}$/isooctane at 25 °C, without alcohol and with 1-butanol and isooctanol as cosurfactants. The percentage of the aqueous phase solubilized into the W/O microemulsion was dependent on both the surfactant/oil ratio and the alcohol concentration. Without alcohol, the maximum water solubilization

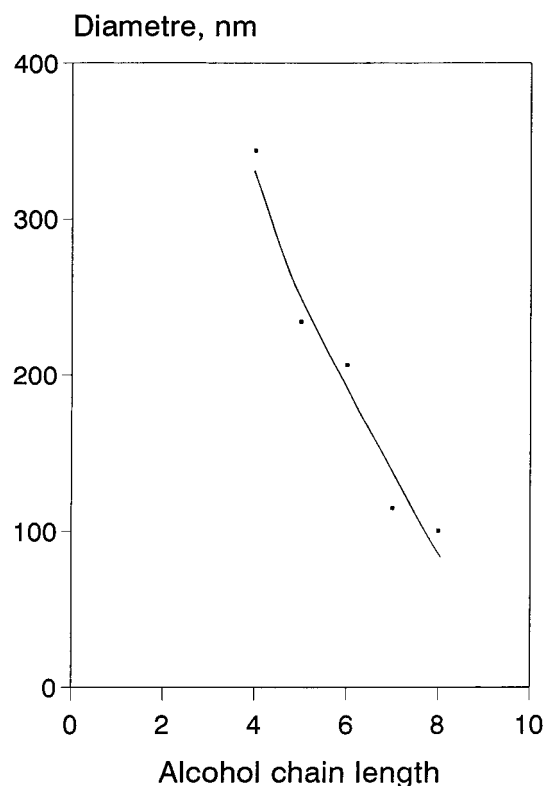(20) Tadros, Th. F.; Luckham, P. F.; Yanaranop, C. *ACS Symp. Ser.* **1989**, *No. 384*, 22−33.

Figure 6. Silica particle size as a function of alcohol chain length. Silica particles were obtained in the system 10 wt % NH_3/Atlox 4912/alcohol/Isopar G/TEOS (10 wt % Atlox, alcohol: Isopar = 1:4, 4.5 wt % TEOS, 2.3% H_2O).
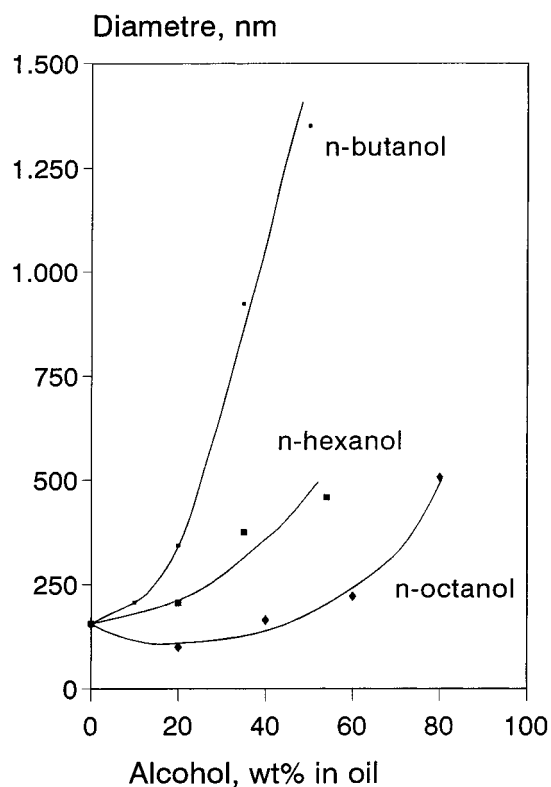

Figure 8. Photomicrograph of silica particles obtained in the system 10 wt % NH_3/Atlox 4912/1-butanol/Isopar G/TEOS (10 wt % Atlox, alcohol:Isopar = 2:3, 4.5 wt % TEOS, 4 wt % H_2O).

Figure 7. Silica particle size as a function of alcohol concentration in the oil. Silica particles were obtained in the system 10 wt % NH_3/Atlox 4912/alcohol/Isopar G/TEOS (10 wt % Atlox, alcohol:Isopar = 1:4, 4.5 wt % TEOS, 2.3% H_2O).

Figure 9. Silica particle size as a function of alcohol content in the oil: (A) 1-butanol, (B) 2-ethyl-1-hexanol (isooctanol). Silica particles were obtained in the system 10 wt % NH_3/$C_{12-14}E_{4.5}$/isooctane/1-butanol/TEOS. ($C_{12-14}E_{4.5}$:isooctane = 1.4, 2.5 wt % H_2O, 10 wt % TEOS).

occurs at a $C_{12-14}E_{4.5}$:isooctane ratio of about 4:6. When the alcohol is added, the maximum water solubilization occurs at higher surfactant:oil ratios. If the percenta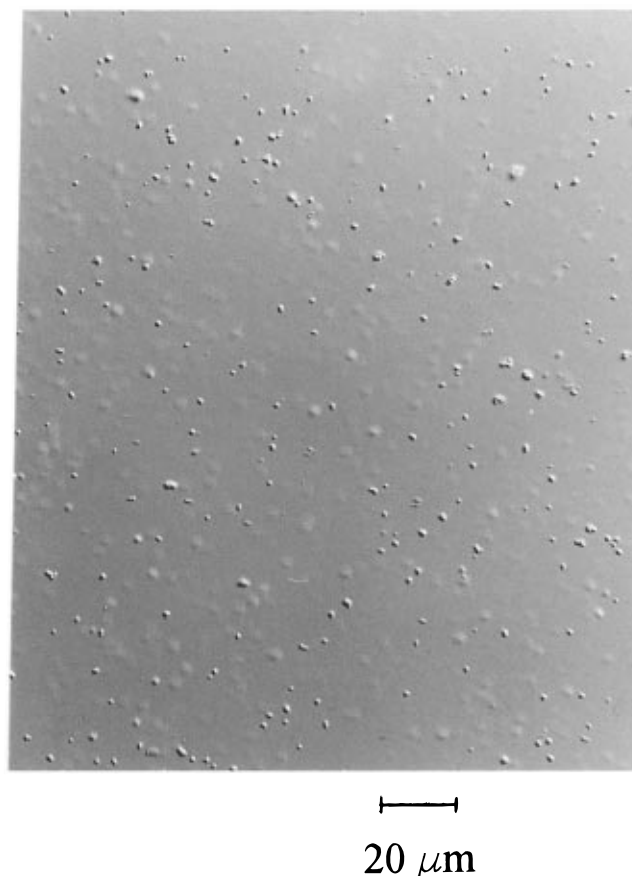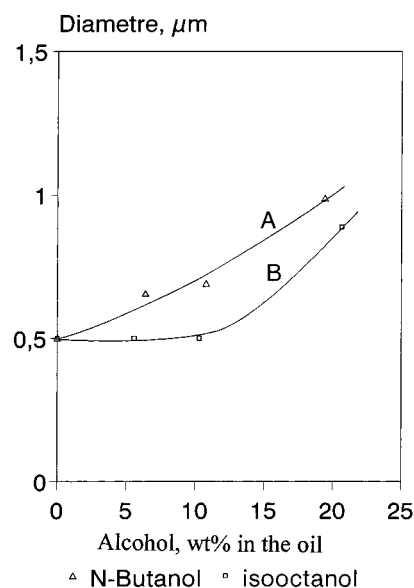ge of alcohol is higher than 10 wt %, a decrease in the concentration of solubilized aqueous component was observed. Although both alcohols produce this reduction in solubility, it is more pronounced in the system with 2-ethyl-1-hexanol.
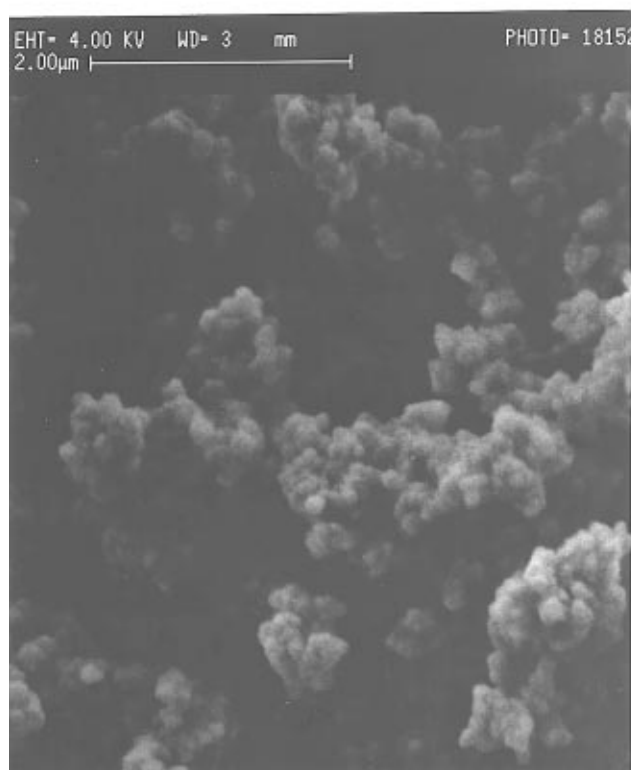
Figure 4 displays the sol−gel transition obtained in the system 10 wt % NH_3 aqueous solution/Atlox 4912/Isopar G/TEOS, as a function of water and TEOS concentrations. Each composition was stirred for 24 h at 18 °C, and the
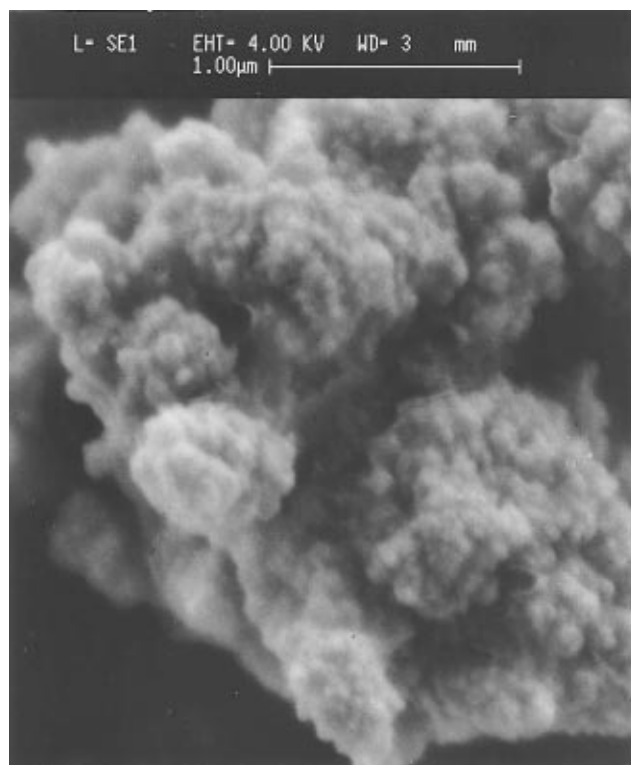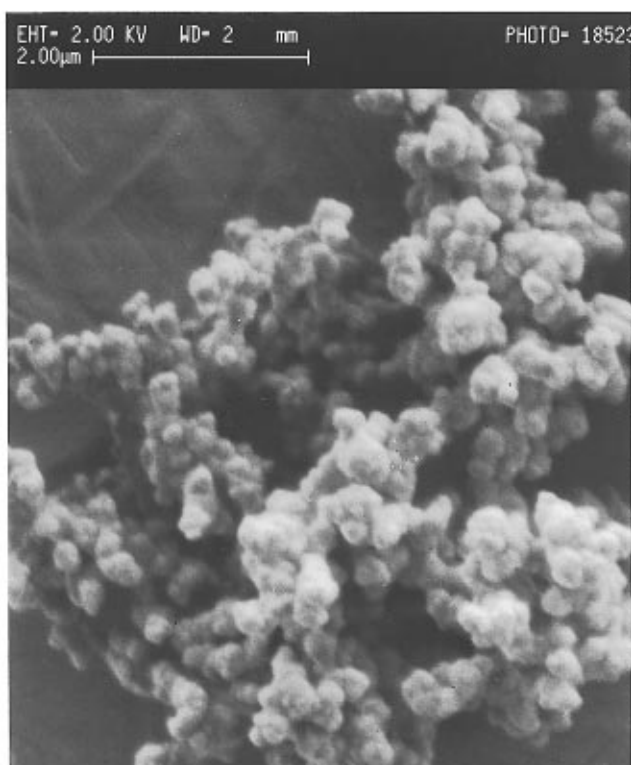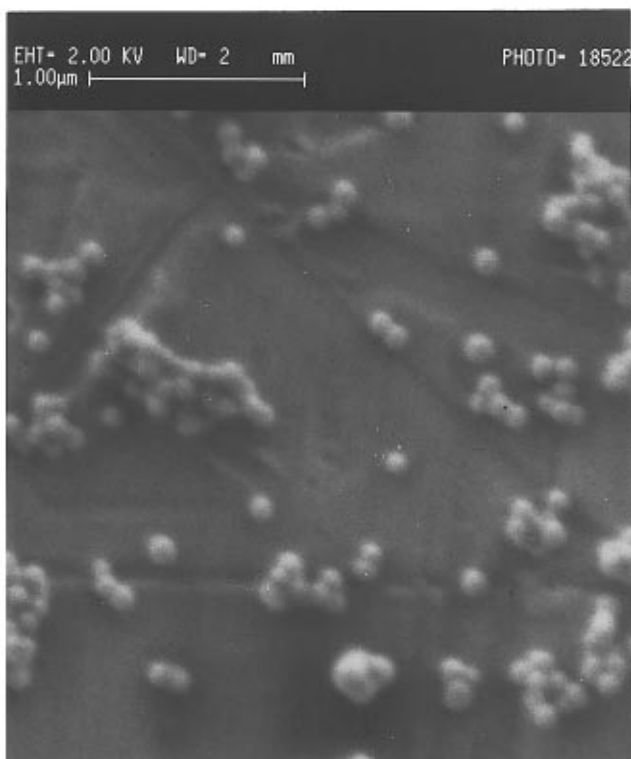
Figure 10. Scanning electron micrographs of the silica samples obtained in microemulsions A, B, C, and D, indicated in Table 1.

formation of gels was noticed by direct visual observation. The samples whose composition is in the gel area became semisolid within 24 h because particle aggregation occurs and, hence, no individual particles can be produced. The most appropriate compositions for sols (when individual particles could be obtained), are those with a composition

below 2.5 wt % of water or below 7 wt % of TEOS. The silica particles described in this work have been obtained mainly using 4.5 wt % TEOS and 2.3 wt % H_2O. This concentration of water, below 3 wt %, is small enough to be solubilized at different alcohol contents, as is shown in Figures 1, 2, and 3. In addition, this H_2O:TEOS molar
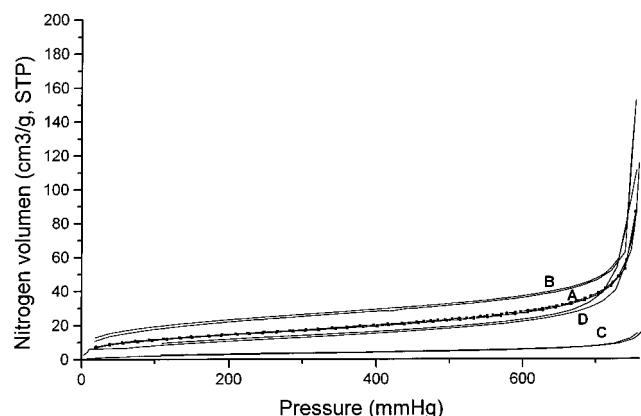
Figure 11. Nitrogen sorption isotherms of the silica samples obtained in microemulsions A, B, C, and D indicated in Table 1.

Table 1. Sample Identification and Microemulsion Compositions

sample	surfactant (S)	oil (O)	water or aq. Sol., wt %	butanol, wt %	(S:O) mass ratio	TEOS, wt %
A	$C_{12-14}E_{4.5}$	isooctane	1.3	20	1:4	4.5
B	Atlox 4912	Isopar G	1.3	40	1:4	4.5
C	$C_{12-14}E_{4.5}$	isooctane	15	20	8:3	10
D	$C_{12-14}E_{4.5}$	isooctane	15	10	8:3	10

Table 2. Specific Surface (S), Porous Volume (V_p), Apparent Diameter (d), and Calculated Specific Surface (S_E) of Silica Particles Obtained in the Microemulsions Indicated in Table 1

sample	S (m²/g)	V_p (cm³/g)	d (µm)	S_E (m²/g)	S_E/S
A	49	0.134	0.09	32	0.6
B	76	0.236	0.17	17	0.2
C	11	0.018	0.15	11	1
D	39	0.099	0.26	19	0.5

ratio of 6 may provide a faster reaction, as it is shown by reaction in ethanol solution.[21]

3.4. Preparation of Silica Particles. The reactions were carried out in microemulsions according to the method represented schematically in Figure 5. Two different W/O microemulsions are prepared, one contains the catalyst (NH_3) in the aqueous droplets and the other contains the reactant TEOS, oil soluble, in the continuous phase. The reaction starts when both microemulsions are mixed. This method of preparation allows a homogeneous start. Microemulsions are very dynamic systems, and the interdroplet exchange of material is very fast. Figure 6 shows the influence of the alcohol chain length on the size of the silica particles in the system 10 wt % NH_3/Atlox 4912/alcohol/Isopar G (10 wt % Atlox, alcohol:Isopar = 1:4, 4.5 wt % TEOS, 2.3 wt % H_2O). The longer the alcohol chain length, the smaller the silica particle size. This effect can be attributed to the fact that interfaces with a long chain alcohol are more rigid than those with shorter alcohols. A more flexible interface can allow a faster diffusion of material, producing a higher growth of the particles. In addition, a faster diffusion could inhibit the nucleation processes and thus reduce the number of existing particles. Very big particles are obtained using 1-butanol. These particles are much larger than those obtained in microemulsion media described before.[22]

If the microemulsion droplets have diameters about several nanometers, then they are considerably smaller than the silica particles. During the reaction the particles can reach a size 2 decades larger than the initial microemulsion droplets. It means that the rate of growth is very important. This process could depend on the alcohol as is inferred from Figure 6. The influence of the alcohol concentration on the size of the silica particles is shown in Figure 7. The particles obtained using a short length alcohol, as 1-butanol, are always larger than the particles obtained using longer chain lengths, as 1-hexanol and 1-octanol. The interfaces could became more flexible with 1-butanol than with other alcohols with higher chain length.

The size of the particles was confirmed by optical microscopy. The photomicrograph shown in Figure 8 corresponds to the particles obtained in the system 10 wt % NH_3/Atlox 4912/1-butanol/Isopar G/TEOS (4:10:32:50: 4.5 mass ratios). The average size is about 1500 nm, which is close to that obtained by light scattering (1255 nm).

Similar results were obtained in the system 10 wt % NH_3/ $C_{12-14}E_{4.5}$/isooctane/1-butanol ($C_{12-14}E_{4.5}$:isooctane = 1.4, 2.5 wt % ammonia aqueous solution, 10 wt % TEOS), at different alcohol concentrations (Figure 9). Although the results in Figure 9 should be considered qualitatively, since the resolution of the optical microscopy is 0.5 µm, the same trends as those obtained by light scattering (Figure 7) are observed. The higher the alcohol concentration, the larger the size. In addition, particles obtained in systems with 1-butanol are larger than those obtained with 2-ethyl-1-hexanol.

3.5. Particle Characterization. Characterization was carried out with silica particles obtained in the microemulsions with butanol, listed in Table 1. Figure 10 shows photomicrographs by electron microscopy of silica particles obtained in the microemulsions indicated in Table 1. Judging from the pictures, most of the particles are spherical. It should be noted that some of the particles seem to be highly aggregated. The estimated aparent diameters (d) of the individual particles are 90, 170, 260, and 150 nm for samples A, B, C, and D, respectively. The composition of the reaction media in samples C and D was the same except for the alcohol content (20 and 10 wt %, respectively). This result agrees with those obtained by light scattering and optical microscopy. The specific surface area of the particles $S_E = 3/\rho r$, where r is the particle radii and ρ is the density of the particles, can be calculated from the aparent diameters assuming that the particles are spherical, nonaggregated, and nonporous. The calculated specific surface areas (S_E) are shown in Table 2.

Figure 11 shows the nitrogen sorption isotherms obtained with the four silica samples. The isotherms do not show much hysteresis loop. This indicates an absence of mesopores (2 nm ≤ pores ≤ 50 nm). To test if micropores (pores < 2 nm) were present, t-plots were drawn[23] and they showed absence of micropores in these samples. Therefore, the only significant porous structure in these systems is the macropore structure (pores > 50nm). The results of nitrogen sorption within low pressure were used to calculate the specific surface areas (S) using the BET equation.[19] The values of S obtained are shown in Table 2 together with the porous volume (V_p), the aparent diameter sized by scanning electron microscopy (d), and the specific surface calculated assuming discrete, spherical, and nonporous particles (S_E).

Considering the data in Table 2, it could be inferred that most of the specific surface is due to the external surface of the particles. The discrepancy between the

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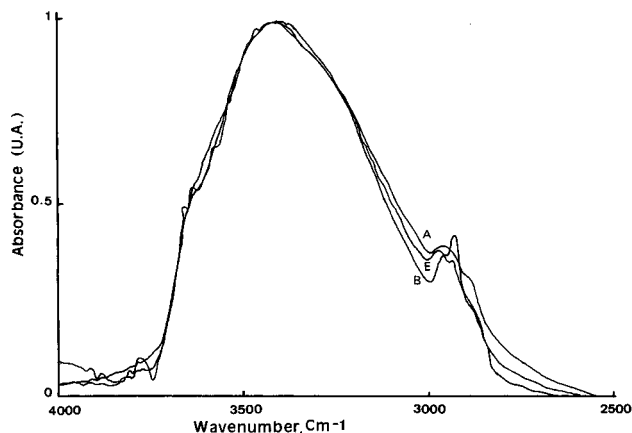(23) Lippens, B. C.; De Boer, J. H. *J. Catal.* **1965**, *4*, 319.

Figure 12. FTIR spectra of silica particles obtained in: microemulsion media (A and B, compositions in Table 1) and in an emulsion with $C_{12-15}E_3$ (E).
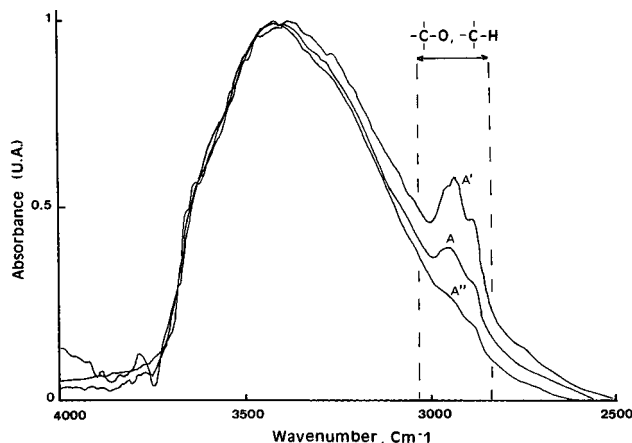

Figure 13. FTIR spectra of silica particles obtained in microemulsion A (Table 1): (A') not washed silica; (A) silica washed three times with ketone; (A'') silica washed once with HCl and twice with ketone.

experimental specific surface (S) and the external specific surface (S_E), expressed as the ratio S_E/S, could be due to the fact that the size of silica particles is smaller than that estimated by scanning electron microscopy. It should be noted that it is required to cover the particles by a gold layer in this technique. Only in sample B, silica obtained using the block copolymer surfactant, is the measured specific surface much higher than that calculated assuming discrete spherical nonporous particles ($S_E/S = 0.2$). On comparison of samples A and B, whose main difference is the surfactant used, the different specific surfaces and pore volumes can be noticed. Nevertheless, the influence of the surfactant on the porosity should be confirmed in further experiments.

Figure 12 shows the FTIR spectra for silica samples prepared in microemulsions based on $C_{12-14}E_{4.5}$ (sample A) and based on Atlox 4912 (sample B). For comparison, the spectrum for a silica sample prepared in an emulsion medium (sample E) is shown in the same graph. These samples show very similar spectra. The peak at 2900 cm^{-1} is believed to be due to organic impurities in the sample (the peak could correspond to the stretching of C−H and CH$_2$−O bonds, which appear close to each other). All the samples show a wide peak at 3400 cm^{-1}, which is

due to physically adsorbed water. They also show a shoulder at 3660 cm^{-1}, characteristic of the vicinal silanols (SiO−H) that are interacting with each other by hydrogen bonding. There is no indication in these samples of the presence of isolated silanols, which should give a peak at 3747 cm^{-1}.[24] The FTIR spectra did not show any peak at 1750 cm^{-1}, characteristic of an ester. It clearly shows that silica particles in sample B did not contain residual block copolymer surfactant, which ought to be removed by washing. The effect of washing of a silica sample (sample A in Table 1) on the FTIR spectra is shown in Figure 13. The peak at 2900 cm^{-1} in the spectrum A' (sample A without washing) disappears when the sample is washed with HCl and with ketone (spectrum A''). The peak is not completely removed when washing only with ketone (spectrum A). This is an indication that part of the impurities detected could be due to unhydrolyzed ethoxy groups SiOCH$_2$CH$_3$, which can be removed only by washing with a catalyst such as HCl.

The chromatographic behavior of some silica samples was examined by preparing thin layer chromatography plates with the sample and measuring the relative retention of a mixture of dyes, as described in the Experimental Section. The retention of silica samples was very low, which was attributed to its low specific surface.

4. Conclusions

Monodisperse spherical silica particles were obtained using W/O microemulsions as reaction media. The particles (aproximately 0.1−1.5 μm) are larger than particles normaly obtained in microemulsion media. The results show that the longer the alcohol chain length, the smaller the silica particle size. This effect can be attributed to the fact that interfaces with a long chain alcohol are more rigid that with shorter alcohols. A more flexible interface can allow a faster diffusion of material, producing a higher growth of the particles. In addition, a faster diffusion could inhibit the nucleation processes and thus reduce the number of existing particles.

BET nitrogen adsorption results show that the particles have low specific surface, which can be mostly attributed to the external surface of the particles. There was no indication of presence of any significant microporosity or mesoporosity. This fact could suggest that the particles are not formed by aggregation of smaller primary particles. The low specific surface accounts for the low chromatographic performance observed by thin layer chromatography. FTIR spectra of silica particles obtained in microemulsion and in emulsion media did not show significant differences. FTIR determinations also showed that most of the silanol groups were of the vicinal type that are hydrogen bonded together.

(24) Unger, K. K. In *Porous Silica*; Elsevier Scientific Publishing: Amsterdam, 1979.