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Effect of surfactants on the size and morphology of the silica particles prepared by an emulsion technique

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Studies were performed on precipitation of silica in an emulsion system from aqueous solution of sodium metasilicate and hydrochloric acid. Cyclohexane formed the organic phase. Anionic, cationic and non-ionic surfactants were used as emulsifiers. Optimum composition of the emulsion and optimum parameters for the precipitation reaction were established. Effects of a dispersing medium on quality of the produced silicas were examined. The silicas were subjected to physicochemical characterization. Bulk density, water, dibutyl phthalate and paraffin oil absorbing capacities were measured. Surface charge of the obtained dispersion, particle size and shape of the formed silicas were estimated. Specific surface area (BET) was defined and the complete pore characteristics was also presented for the selected silicas. Application of Rokanol K-7 ($C_{16-22}O(CH_2CH_2O)_7H$) as an emulsifier resulted in production of almost ideally spherical silica particles of nanometric size and of a monodisperse character.

1. Introduction

In recent years have shown a marked development of studies of production of strictly defined materials (of specific shape, surface character, etc.) [1–5]. Production of such silica substances markedly broadens application potential, the latter including catalysis, chromatography, supplements of polymers, carriers and fillers of paints as well as varnishes and many other. The principal way in which silicas of monodisperse type are obtained involves hydrolysis of alkoxysilane esters [6–10]. Modification of the approach achiws formation of silicas in emulsion or microemulsion systems [11–14].

As indicated by the literature [15–17], several studies have been performed on formation of silica dispersions by precipitation in emulsion systems. In such an approach, the principal raw material involves aqueous solution of sodium metasilicate (water glass) or sodium orthosilicate. In this study we have used aqueous solutions of sodium metasilicate and hydrochloric acid in emulsion system in order to obtain spherical, monodisperse silica particles.

2. Experimental

2.1. Materials

Silicas were obtained by precipitation from aqueous solution of sodium metasilicate, the silicate modulus of which molar ratio equal 3.3 ($Na_2O = 8.50$ wt%; $SiO_2 = 27.18$ wt%, density = 1.39 g/dm^3). The precipitating agent was 5 wt% HCI. Cyclohexane represented the organic phase. Surfactants of various type surface interactions were used as emulsifiers. General characteristics of the applied surfactants is given in Table I.

2.2. Procedures and methods

2.2.1. Emulsion preparation

Two emulsions were prepared. The ‘alkaline’ one (E_1) contained 100 cm^3 5 wt% Na_2SiO_3 solution and 110 cm^3 cyclohexane, supplemented with an emulsifier. The ‘acidic’ emulsion (E_2) consisted on 33 cm^3 5 wt% of HCI and 35 cm^3 of cyclohexane, supplemented with an emulsifier of the same composition as in E_1 but in appropriately lower amount. The predissolved emulsifiers were diluted in cyclohexane. The aqueous phase (for E_l 5 wt% solution of Na_2SiO_3, for E_2 5 wt% solution of HCI) was dosed in few portions and the mixture was homogenized at 19000 rpm for 5 min. The so prepared emulsions were used in precipitation reactions.

2.2.2. Process of formation of colloidal silica

2.2.2.1. Dispersing (precipitation) using a top stirrer. Precipitation was conducted in 0.5 dm^3 capacity reaction vessel. A propeller top stirrer EUROSTAR digital type (IKA LABORTECHNIK, Germany) was fixed in a stand. Using the appliance, the system was subjected to intense mixing (2000 rpm). The E_2 emulsion was placed in the reactive vessel and subjected

TABLE I Basic characteristics of the applied emulsifiers

Compound	Chemical designation	Formula	Character
CTAB	Cetyltrimethyl-ammonium bromide	$C_{19}H_{42}BrN$	Cationic
SDS	Sodium dodecyl sulphate	$C_{12}H_{25}NaO_4S$	Anionic
Rokanol B-2	Oxyethylated saturated alcohols	$RO(CH_2CH_2O)_nH$ $R = C_{12-15,}$ mean $n = 2$	Non-ionic
Rokanol B-3	Oxyethylated saturated alcohols	$RO(CH_2CH_2O)_nH$ $R = C_{12-15,}$ mean $n = 3$	Non-ionic
Rokanol K-7	Oxyethylated unsaturated alcohols	$RO(CH_2CH_2O)_nH$ $R = C_{16-22,}$ mean $n = 7$	Non-ionic

to intense mixing. Emulsion E_1 was dosed to emulsion E_2 at a constant rate using peristaltic pump. As a result of the reaction taking place in the reactive vessel a silica-containing emulsion was obtained. The emulsion was heated to 80°C in order to destabilize it. Subsequently, cyclohexane was separated from it by distillation. The subsequent stage involved filtration of the remaining mixture under a lowered pressure. In this way, the obtained sample was washed with hot water and, then, with acetone in order to wash out the remaining surfactants. Acetone was separated by distillation. Subsequently, the sample was subjected to drying for 48 hours in a stationary drier at 105°C.

2.2.2.2. Precipitation in an ultrasonic bath. A reactor of 0.5 dm^3 capacity was placed in an ultrasonic bath of INTERSONIG - 102 (30 kHz), 100 W type, in which formation of the silica was conducted using ultrasound. The remaining functions were analogous to those applied in the top stirrer.

2.2.2.3. Formation (precipitation) using a homogenizer. The precipitation was conducted in the reactive vessel of 0.5 dm^3 capacity. Mixing took place in a homogenizer of ULTRA TURRAX T25 basic type (IKA LABORTECHNIK, Germany) at 19000 rpm. The remaining functions were analogous to those used upon application of ultrasound and batch mixing using a top stirrer.

2.2.3. Physicochemical evaluation of the formed silicas

Following the precipitation, the silicas were subjected to physicochemical tests, bulk densities as well as water, dibutyl phthalate and paraffin oil absorbing capacities were estimated. Studies on morphology and microstructure were performed in order to obtain data on dispersion, particle shape and morphology, structure of individual particles and on the silica aggregation and agglomeration type following precipitation. The studies were conducted using scanning electron microscopy (SEM). The observations were performed in the Phillips SEM 515 microscope.

Laser Doppler electrophoretic light scattering determinations were performed with a ZetaPlus instrument (Brookhaven Instruments Inc., USA), in the reference beam mode at the wavelength of laser light source of 635 nm, sampling time 256 its, modular frequency 250 Hz and the scattering angle 15°. The standard error of the zeta potentials, converted from the experimentally determined electrophoretic mobilities according to the Smoluchowski limit of the Henry equation, was typically $<1.0\%$. The zeta potentials were obtained by averaging 10 runs.

The technique of dynamic light scattering (DLS), applied also in the ZetaPlus apparatus, permitted to obtain multimodal particle size distribution pattern on the basis of autocorrelative functions of laser light beam (670 nm) scatter. The most important parameters obtained using the technique included polydispersity and a mean particle diameter. Polydispersity is a measure of nonuniformity in the particle size distribution in the studied system. It gives information about width of the size distribution [18].

Specific surface areas of silica powders were determined by N_2 adsorption (BET method) using ASAP 2010 instrument (Micrometrics Instrument Corporation). Moreover, the volume and size of pores of precipitated materials were examined. Samples were heated at 120°C for 2 hours prior to measurements.

3. Results and discussion

Principal physicochemical parameters of silicas prepared by precipitation from sodium metasilicate/cyclohexane and hydrochloric acid/cyclohexane emulsion are shown in Table II.

The obtained products had bulk densities, ranging between 41 and 161 g/dm^3, and low paraffin oil absorbing capacity, ranging between 150 and 550 $cm^3/100$ g. The water absorbing capacity ranged between 100 and 400 $cm^3/100$ g. The lowest values of bulk density were exhibited by silicas formed during application of CTAB as an emulsifier (samples 3A, 3B and 3C). The silicas had also relatively high paraffin oil absorbing capacities (300 to 500 $cm^3/100$ g). When SDS was used as an emulsifier, no silica precipitate was obtained. For most samples a positive effect was observed of applying ultrasound and a homogenizer. In such cases lower bulk densities and increased of the dibutyl phthalate and paraffin oil absorbing capacities of were obtained.

Values of zeta potential, polydispersity and mean diameter of silica particles, depending upon the applied dispersing technique, are presented in Table III. In cases of tested silica powders, significant changes in surface charge (zeta potential) were observed. Silicas obtained using CTAB/SDS mixture or CTAB alone exhibited positive values of zeta potential, ranging from (+36.92) to (+13.90) mV. Probably, this reflected strong interaction of cetyltrimethylammonium cation with SiO_2 surface, as specified below:

TABLE II Physicochemical parameters of obtained silicas

Sample no.	Emulsifiers (mass ratio)	Bulk density (g/dm^3)	Paraffin oil absorbing capacity (cm^3/100 g)	Dibutyl phthalate absorbing capacity (cm^3/100 g)	Water absorbing capacity (cm^3/100 g)
			Top stirrer		
1A	CTAB/SDS (1.5 : 1.5)	161	250	150	250
2A	CTAB/SDS (1.0 : 1.0)	139	250	150	150
3A	CTAB (0.75)	67	500	300	250
4A	SDS (3.0)	–	–	–	–
5A	B-2 (3.0)	121	300	250	150
6A	B-3 (3.0)	116	550	450	400
7A	K-7 (3.0)	102	500	350	300
			Ultrasonic bath		
1B	CTAB/SDS (1.5 : 1.5)	137	200	150	150
2B	CTAB/SDS (1.0 : 1.0)	41	250	125	250
3B	CTAB (0.75)	71	300	250	150
4B	SDS (3.0)	–	–	–	–
5B	Rokanol B-2 (3.0)	112	250	100	150
6B	Rokanol B-3 (3.0)	125	450	400	250
7B	Rokanol K-7 (3.0)	119	450	250	400
			Homogenizer		
1C	CTAB/SDS (1.5 : 1.5)	123	250	150	100
2C	CTAB/SDS (1.0 : 1.0)	102	150	100	200
3C	CTAB (0.75)	70	400	200	250
4C	SDS (3.0)	–	–	–	–
5C	Rokanol B-2 (3.0)	125	300	150	150
6C	Rokanol B-3 (3.0)	121	550	300	250
7C	Rokanol K-7 (3.0)	107	350	250	350

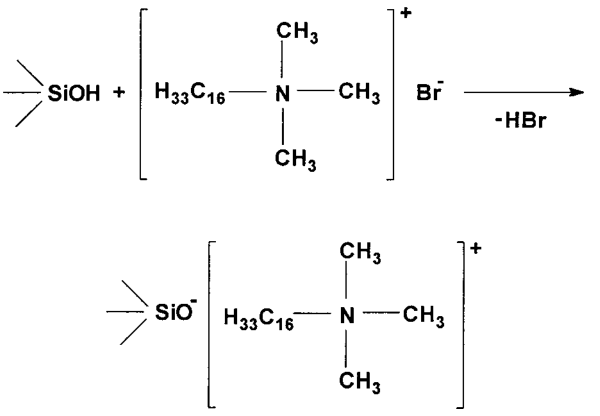


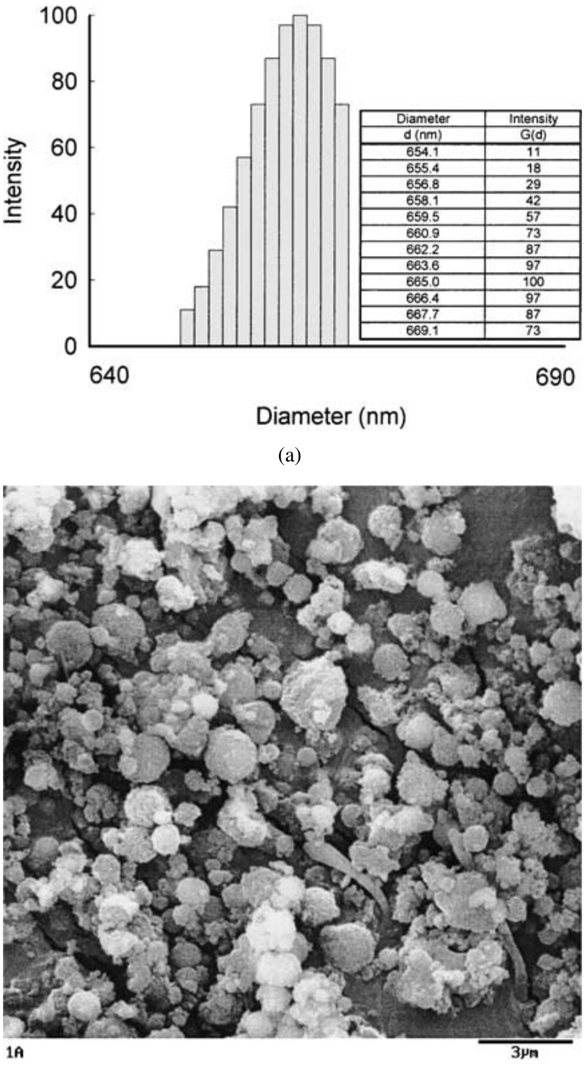
TABLE III Zeta potential, polydispersity and mean diameter of precipitated silicas

Sample no.	Zeta potential (mV)	Polydispersity	Mean diameter (nm)
		Top stirrer	
1A	+27.97	0.005	664
2A	+15.40	0.005	739
3A	+37.45	0.184	664
4A	–	–	–
5A	−15.25	0.135	1225
6A	−31.48	0.116	655
7A	−31.71	0.005	572
		Ultrasonic bath	
1B	+36.92	0.160	3141
2B	+35.38	0.270	1121
3B	+34.99	0.123	891
4B	–	–	–
5B	−29.51	0.250	1143
6B	−23.06	0.248	736
7B	−28.63	0.169	673
		Homogenizer	
1C	+35.04	0.005	630
2C	+32.21	0.101	818
3C	+13.90	0.289	2630
4C	–	–	–
5C	−18.46	0.392	5336
6C	−22.08	0.189	751
7C	−34.21	0.005	427

On the other hand, application of Rokanols B-2, B-3, and K-7 resulted in reversal of the surface potential. The substances formed were characterized by zeta potential values ranging between (−34.21) to (−15.25) mV. Interaction of silica surface with non-ionic emulsifiers caused no changes in electrokinetic potential values.

SEM micrographs and particle size distributions for silicas precipitated using CTAB/SDS surfactant mixture as an emulsifier are presented in Figs 1 to 3. The silica precipitated with the use of a top stirrer (sample 1A) showed a highly uniform particles, ranging between 654 and 669 nm in size. Particles of the highest intensity 100 corresponded to particle diameter of 665 nm (Fig. 1a). SEM micrograph (Fig. 1b) documented silica particles of a relatively variable shape. Spherical particles as well as particles of typically irregular shape were noted. Mean diameter of particles in the sample was 664 nm and its polydispersity amounted to 0.005 (Table III).

A quite distinct microscopical pattern was typical for silicas formed in an ultrasonic bath, in which small size particles as well as very large particles of irregular shape were noted (Fig. 2a). Presence of two bands of particles typical for particle secondary agglomerates and primary agglomerates (aggregates) was confirmed by the data of Fig. 2b. Mean diameter of the silica particles amounted to 3141 nm and the sample polydispersity was 0.160 (Table III). The particle size distribution curve showed one band within the diameter range of 725–1041 nm (maximum intensity of 100

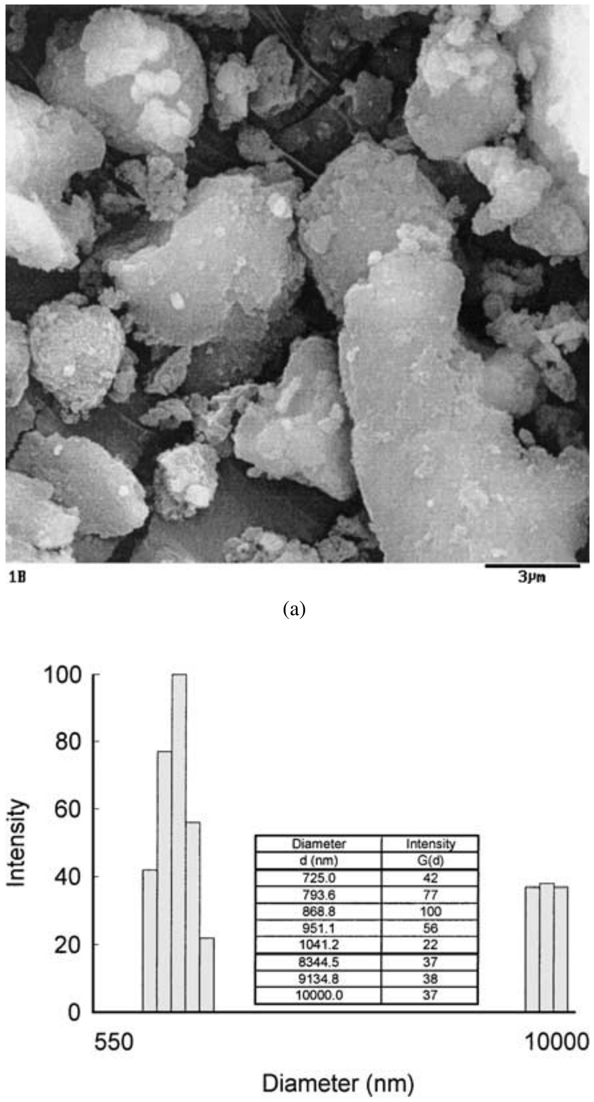


Diameter d (nm)	Intensity G(d)
654.1	11
655.4	18
656.8	29
658.1	42
659.5	57
660.9	73
662.2	87
663.6	97
665.0	100
666.4	97
667.7	87
669.1	73

(a)

(b)

Figure 1 (a) Multimodal particle size distribution and (b) SEM of silica precipitated using a top stirrer with CTAB/SDS surfactants system applied (sample 1A).



Diameter d (nm)	Intensity G(d)
725.0	42
793.6	77
868.8	100
951.1	56
1041.2	22
8344.5	37
9134.8	38
10000.0	37

(a)

(b)

Figure 2 (a) SEM and (b) multimodal particle size distribution of silica precipitated using an ultrasonic bath with CTAB/SDS surfactants system applied (sample 1B).

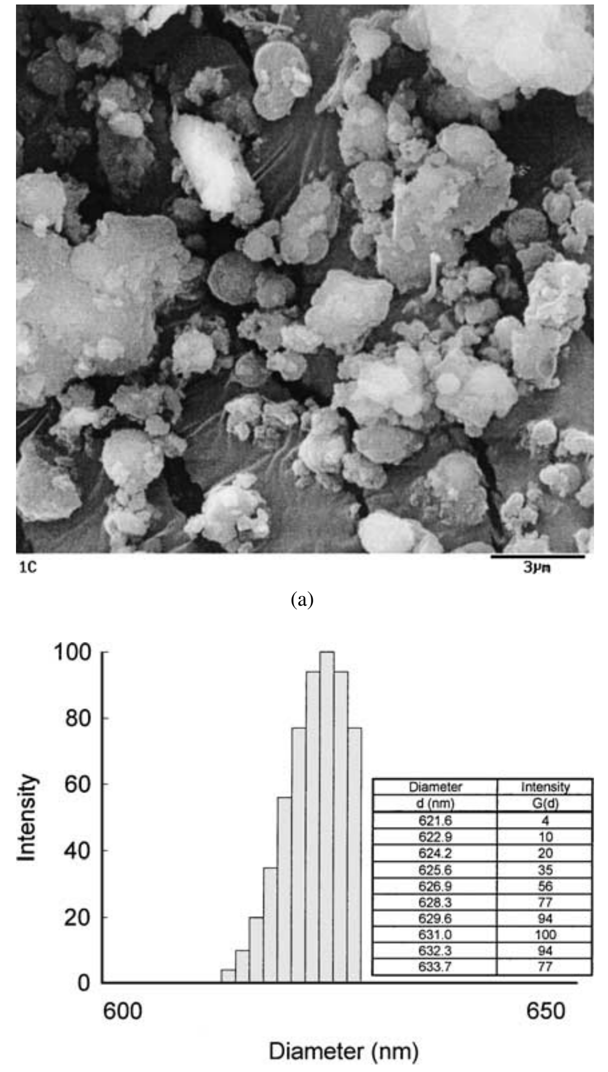
corresponded to particle diameter of 869 nm) and another band of very large particles with diameters ranging between 8345 and 10000 nm.

A microscopical pattern similar to that obtained for sample 1A was obtained also for the silica formed using a homogenizer (sample 1C, Fig.3a). The pronounced monodisperse character of particles (622–634 nm in diameter) was observed also in the particle size distribution. Maximum intensity of 100 corresponded to the particle diameter of 631 nm (Fig. 3b). The most uniform silicas of smallest particles were obtained during precipitation from emulsion, employing either a top stirrer or a homogenizer.

Silica precipitated from emulsions prepared in the presence of CTAB only, in a reactor equipped with a top stirer, exhibited a very uniform particle character and presence of small diameter particles, first of all in the 314–430 nm range. In the particle size distribution curve (Fig. 4), the band was also observed of secondary agglomerates were observed in the range of 1098–1501 nm, of a much lower intensity (maximum intensity of 46 corresponded to the diameter of 1325 nm). Silicas precipitated in an ultrasonic bath or using a homogenizer, in presence of CTAB emulsifier, exhibited a much less uniform character and showed presence of secondary agglomerates (this pertained in particular the silicas precipitated in a homogenizer).

In the particle size distribution curves, two bands of particles could be seen (Fig. 5). Silicas precipitated in an ultrasonic bath showed prevalence of mean size particles, in the 453–634 nm range (maximum intensity of 100 corresponded to the diameter of 518 nm). The secondary agglomerates in the range of 1986–2779 nm showed maximum intensity of 25, which corresponded to particle diameter of 2124 nm (Fig. 5a). The silica precipitated in a homogenizer showed two bands of particles with similar intensities (Fig. 5b). One of the bands corresponded to primary agglomerates in the range 502–710 nm (maximum intensity of 97 corresponded to particles of 651 nm in diameter) while the other corresponded to secondary agglomerates, in the range of 3681–5667 nm (maximum intensity of 100 corresponded to agglomerates of 4378 nm in diameter).

Application of Rokanol B-2 as an emulsifier resulted in precipitation of silica particles of irregular shape,

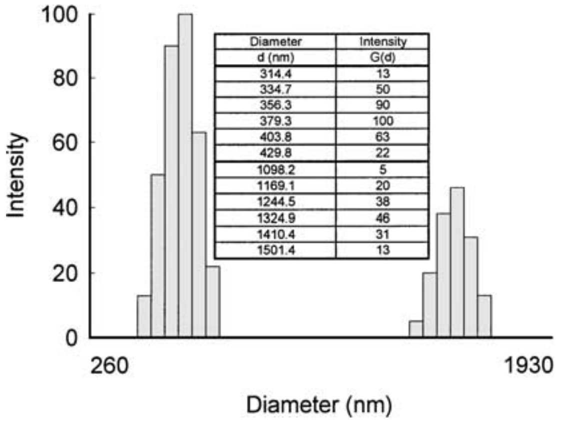


Diameter d (nm)	Intensity G(d)
621.6	4
622.9	10
624.2	20
625.6	35
626.9	56
628.3	77
629.6	94
631.0	100
632.3	94
633.7	77

(a)

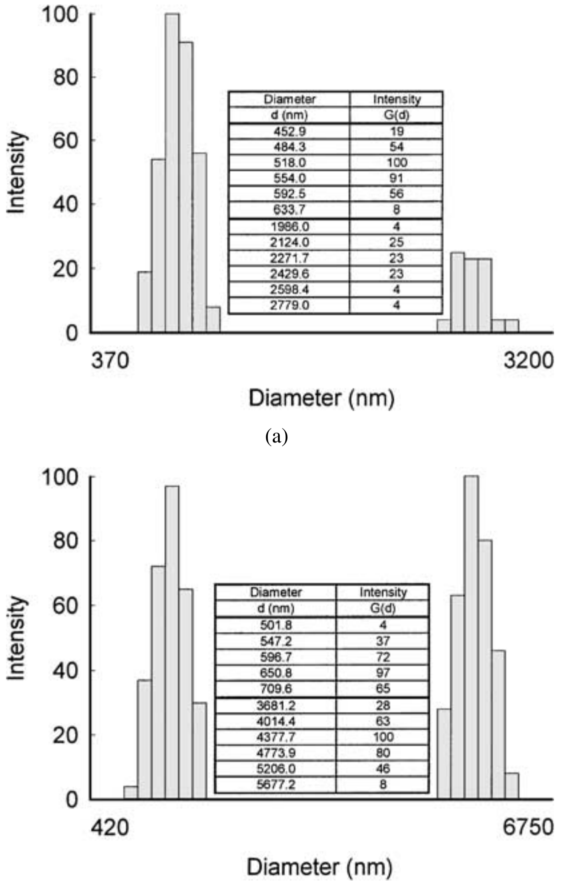
(b)

Figure 3 (a) SEM and (b) multimodal particle size distribution of silica precipitated using a homogenizer with CTAB/SDS surfactants system applied (sample 1C).



Diameter d (nm)	Intensity G(d)
314.4	13
334.7	50
356.3	90
379.3	100
403.8	63
429.8	22
1098.2	5
1169.1	20
1244.5	38
1324.9	46
1410.4	31
1501.4	13

Figure 4 Multimodal particle size distribution of silica precipitated using a top stirrer with CTAB surfactant system applied (sample 3A).



Diameter d (nm)	Intensity G(d)
452.9	19
484.3	54
518.0	100
554.0	91
592.5	56
633.7	8
1986.0	4
2124.0	25
2271.7	23
2429.6	23
2598.4	4
2779.0	4

(a)

Diameter d (nm)	Intensity G(d)
501.8	4
547.2	37
596.7	72
650.8	97
709.6	65
3681.2	28
4014.4	63
4377.7	100
4773.9	80
5206.0	46
5677.2	8

(b)

Figure 5 Multimodal particle size distribution of silica obtained (a) using an ultrasonic bath (sample 3B) and (b) using a homogenizer (sample 3C)—CTAB surfactant system applied.

with agglomerates consisting of smaller and larger particles. Mean particle diameter in the sample was 1143 nm. However, the silica precipitated in a homogenizer in presence of Rokanol B-2 as an emulsifier (sample 5C) was not uniform. Mean particle diameter in the sample was 5336 nm.

On the other hand, application of Rokanol B-3 as an emulsifier during precipitation of silicas in the emulsion medium improved very little the uniform character of the sample or size of precipitated particles. A much more favourable effect on the final silica parameters resulted from application of an ultrasonic bath in the emulsion mixing.

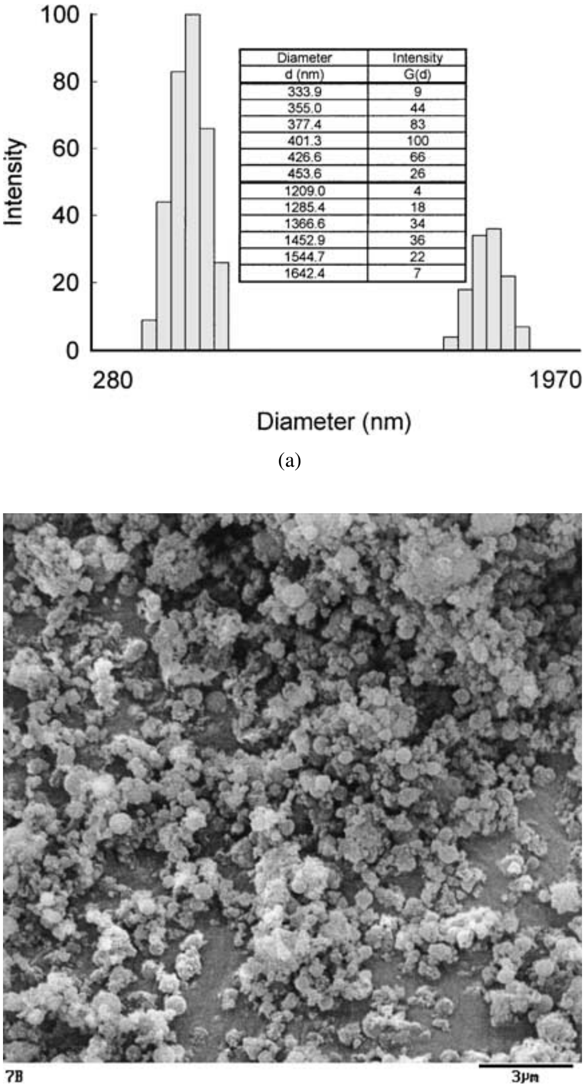
Silica of an almost ideal spherical particle shape and of a monodisperse character was obtained by precipitation in the emulsion system containing Rokanol K-7 as an emulsifier. The sample 7B (Fig. 6), obtained by precipitation in an ultrasonic bath, contained particles of a similar diameter. The particle size distribution (Fig. 6a) showed two bands. In the band of a high intensity (334–454 nm) particles were present of the maximum intensity of 100, corresponding to the diameter of 401 nm. A particle band was also present of a much lower intensity (1209–1642 nm). Particles of 1453 nm in diameter exhibited intensity of 36. Manifestation of the other band, reflecting presence of particles with greater diameters, resulted from appearance of few particle chains forming the secondary agglomerates typical for precipitated silicas.

The silica obtained using a homogenizer (sample 7C) exhibited an extensively monodisperse character and presence of almost ideally spherical particles (Fig. 7a). The highly uniform particle character could also be concluded from particle size distribution curve (Fig. 7b), presenting a band of a high intensity which corresponded to particles of 255–377 nm in diameter.

TABLE IV Specific surface area, volume and average size of pores of obtained silicas

Sample no.	Specific surface area BET (m^2/g)	Total pores volume (cm^3/g)	Pores volume 8.5 do 1500 Å (cm^3/g) From adsorption curve	Pores volume 8.5 do 1500 Å (cm^3/g) From desorption curve	Average size of pores[a] (Å)
1A	61	0.1899	0.2275	0.2276	124.2
1B	48	0.1301	0.1445	0.1448	108.2
1C	35	0.0972	0.1161	0.1163	111.6
3B	54	0.1292	0.1685	0.1682	95.9
3C	211	0.3182	0.3683	0.3681	60.4
7B	149	0.4529	0.5527	0.5532	121.6
7C	64	0.1329	0.1755	0.1753	83.8

[a] Calculated from BET equation (4 V/A).

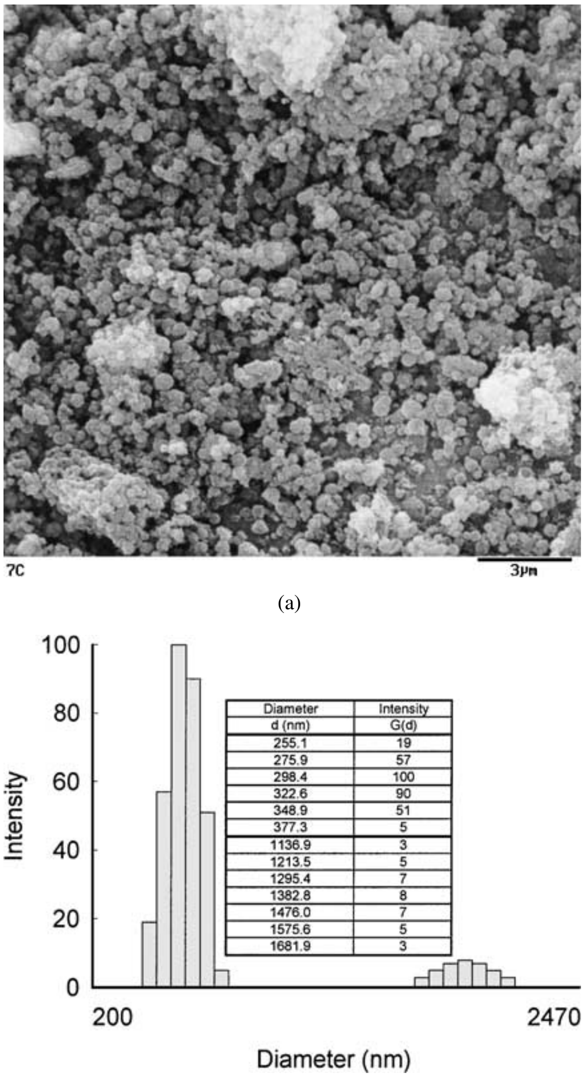


Diameter d (nm)	Intensity G(d)
333.9	9
355.0	44
377.4	83
401.3	100
426.6	66
453.6	26
1209.0	4
1285.4	18
1366.6	34
1452.9	36
1544.7	22
1642.4	7

(a)

(b)

Figure 6 (a) Multimodal particle size distribution and (b) SEM of silica precipitated using an ultrasonic bath with Rokanol K-7 surfactant system applied (sample 7B).



Diameter d (nm)	Intensity G(d)
255.1	19
275.9	57
298.4	100
322.6	90
348.9	51
377.3	5
1136.9	3
1213.5	5
1295.4	7
1382.8	8
1476.0	7
1575.6	5
1681.9	3

(a)

(b)

Figure 7 (a) SEM and (b) multimodal particle size distribution of silica precipitated using a homogenizer with Rokanol K-7 surfactant system applied (sample 7C).

Maximum intensity of 100 corresponded to particles of 298 nm in diameter. Another band showed a very low intensity and reflected presence of particles of 1137–1682 nm in diameter (maximum intensity of 8 corresponded to agglomerates of 1383 nm in diameter). The sample 7C exhibited a very low polydispersity (0.005), pointing to its highly uniform character, and the mean particle diameter of 427 nm.

Specific surface area and pore volume of silicas precipitated in emulsions, depending upon the type of the applied emulsifier (a surfactant), are listed in Table IV. Specific surface area strictly depended upon the type of emulsifier used in the process of silica precipitation. The lowest specific surface area values were obtained for silica precipitated in presence of such emulsifiers as CTAB/SDS system or CTAB alone (specific surface areas of around 35–61 m^2/g). Also the silica obtained in presence of Rokanol K-7 during precipitation in a homogenizer showed low values of specific surface area (64 m^2/g) The highest specific surface area of 211 m^2/g was demonstrated by the silica precipitated in presence of CTAB using a homogenizer for mixing the emulsion.

4. Conclusions

- The obtained silicas showed low bulk densities (41 to 161 g/dm^3) and low values of the paraffin oil absorbing capacity (150–500 $cm^3/100$ g). Their water absorbing capacity ranged between 100 and 400 $cm^3/100$ g.
- Silicas precipitated using CTAB mixture alone exhibited positive values of zeta potential, ranging between (+36.92) and (+13.90) mV, while silicas obtained in the presence of non-ionic emulsifiers carrie a nagative surface charge.
- Silica of an almost ideal spherical shape of particles, highly uniform and low particle diameter (around 300 nm), was obtained using Rokanol K-7 as an emulsifier during precipitation.
- Application of cationic surfactants as emulsifiers yielded silicas of irregular particle hape, less uniform and of higher particle diameters.

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