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DISPERSION CHARACTERISATION OF COLLOIDAL SILICA AT SUBSEQUENT STAGES OF SILICA SOL PREPARATION

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Dispersion properties of colloidal silica were studied at subsequent stages of silica sols preparation. Dilute sols were obtained from solutions of sodium silicate by ion exchange method. In them SiO_2 particles were built up and next the sols were concentrated. The concentrations of the sols in which SiO_2 particles were built-up ranged from 5.89 to 6.44 wt. % SiO_2, while the mean concentrations of the sols which were added into the heel sols were 3.28 and 6.20 wt. % SiO_2. The particle size distributions were measured by DLS, while the contribution of the ionic form of silica was determined by the colorimetric method on the basis of the intensity of the yellow colour coming from the heteropolycomplexes of silicomolybdic acid.

key words: silicic acid sol, colloidal silica, sodium silicate, water solutions of silicates

INTRODUCTION

Colloidal silica refers to stable dispersions of discrete particles or sols of amorphous silica. This arbitrary definition excludes solutions of polysilicic acids in which the polymer or silica particles are too small to be stable. In most sols of silicic acids, silica particles range from 4 to 100 nm. The most common methods of obtaining the sols of silicic acid are electrodialysis, sol peptisation, ion-exchange, and neutralization of silica solutions with acids. The first attempts at removal of sodium

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from sodium silicate solution by the method of ion-exchange were made by Bird (1941). Iler and Wolter obtained silica sols in periodical and flow-through reactors in which ion-exchange was conducted in the pH range from 8 to 10 and at a temperature above 60°C (Iler, 1953).

The sols obtained were free from dissolved salts. The silica particles ranged from 5 to 8 nm, and the silica specific surface area ranged from 350 to 600 m^2/g. Dirnberger (1955) passed sodium silicate solutions through a fluidal bed of ionite at a rate adjusted so that the individual ionite grains were suspended in the solution flowing up the column. This solution ensured better contact of the solution with the grains, which permitted the use of sodium silicate solutions of the SiO_2 concentrations up to 6 wt. %. Alexander (1956) obtained a sol of water-like clarity, free from dilute salts, with the silica particles from 5 to 8 nm in diameter and silica specific surface area from 350 to 600 m^2/g. The process proposed by Alexander included the following steps: (a) removal of metal cations from a dilute solution of sodium silicate by ion exchange, (b) alkalization of dilute sol with sodium hydroxide or a solution of sodium silicate until stabilisation of the molar ratio of SiO_2/Na_2O from 30:1 to 150:1, (c) heating of the sol at temperatures from 50 to 120°C to promote silica particle growth to reach the surface area from 350 to 600 m^2/g, (d) purification of the sol with cationite and anionite to remove the salt residues, (e) final stabilization of the molar ratio of SiO_2/Na_2O in the range from 20:1 to 300:1 by using sodium hydroxide, and (f) water evaporation to get a SiO_2 concentration in the sol of at least 15 wt. %.

Dirnberger and Nelson (1961) obtained a silica sol of minimum turbidity by adding to the periodical reactor a solution of sodium silicate and ionite in the hydrogen form simultaneously so that the pH of the sol in the reactor was always between 8.3 and 8.7. The content of the reactor was stirred and heated to 88 to 90°C. The silica sol obtained had surface area from 200 to 250 m^2/g, and the SiO_2 concentration was 10 to 20 wt. %.

Mindick and Reven (1969) patented a method overcoming problems with gelation and blockage of the ionite bed in production of acidic silica sols of pH from 2.5 to 4.0 and the content of SiO_2 from 6 to 12 wt. %. Gelation was reduced to 2 wt. % of SiO_2 of maintaining the total amount of silica introduced onto the column. This was achieved by maintaining low temperatures in the bed and increasing the volume flow rate of sodium silicate solution. The minimum flow rate at a lowered temperature should be 245 dm^3/m^2 of the bed cross-section area. For higher temperature, it should be 695 dm^3/m^2 of the bed cross-section area.

Bechtold and Snyder (1951) patented a method for obtaining silica sols of particles of controlled size. The method is known as the process of built-up particles. A dilute solution of silica sol with a pH over 7 is divided into two parts. One part is heated to over 60°C so that the diameters of the nuclei of the dispersed phase reach the size of a few nanometers. This part is called the heel sol. The other part of the dilute silica sol solution is introduced into the heel at a rate slow enough to make sure that the introduced silica would deposit on the nuclei of the dispersed phase. At the same tame, water can be evaporated at a rate ensuring maintenance of a constant concentration of SiO_2 in a unit volume of the solution. The mechanism of particle build-up is explained in terms of the Ostwald ripening process. The driving force of the ripening process can be described by the variance of the particle size distribution. Iler (1979) proposed a quantitative description of particle build-up by defining the particles build-up index $\boldsymbol{B_r}$ related to the particle size using equations 1 and 2.

$$B_r = \frac{W_a}{W_n} \quad (1), \qquad \left(\frac{d_f}{d_t}\right)^3 = 1 + B_r \quad (2)$$

where:

W_a represents the amount of silica added to the system; W_n represents the amount of silica in the initial heel sol; d_t represents the initial diameter of the silica particles; d_f represents the final diameter of the silica particles.

The aim of this study was to determine particle size distribution at subsequent stages of production of silica sols. Mutual influence of different sols on the particle size distribution after the build-up process and sol concentration were analyzed.

EXPERIMENTAL

MATERIALS

The sodium silicate solution used in the study had the following properties: density at 20°C of 1.252 g/cm^3; Na_2O content of 6.380 wt. %; SiO_2 content of 20.311 wt. % and silicate modulus of 3.28. This solution was obtained by dilution and filtration of the sodium silicate solution made by Vitrosilicon S.A. For ion exchange, a strong acid ion exchange macroporous resin *Amberlyst® 15* made by ROHM and HASS was used in the hydrogen form with a grain size from 0.3 to 1.2 mm and a guaranteed exchange capacity of 1.7 mmol/cm^3.

METHODS OF STUDIES

The silicic acid sol was obtained at three stages. In the first stage, a dilute sol was prepared. In the second stage, silica particles were built-up. In the third stage, the sol was concentrated. The parameters of the sols in which SiO_2 particles were built-up were similar. The silica concentration in these sols ranged from 5.89 to 6.44 wt. %, and pH ranged from 8.08 to 8.93. The sols introduced into the heel can be divided into two groups. The first group comprises sols with a silica concentration of 3.50, 3.02, 3.49 and 3.10 wt. % and a pH of 10.24, 9.84, 9.00 and 11.33. The second group comprises sols with a silica concentration of 6.02 and 6.21 wt. % and a pH of 9.30 and 8.50. Sols were produced in a periodic reactor using ion exchange. The process of silica particle build-up was carried out in accordance with the method described by Bechtold and Snydera (Bechtold, 1951). Details of the particle build-up processes in particular series of experiments are given in Table 1. Build-up indices were calculated using Equation 2 on the basis of the SiO_2 concentrations and the densities of the sols. During the process of particle build-up, water was evaporated. The sols in which the silica particles were built-up were subjected to concentration in a vacuum evaporator at 94°C.

Table 1. Operational data of the processes of silica particle build-up

Series no. of experiment	Temp. (°C)	Volume of the heel sol in which the build-up process took place (cm^3)	Volume of the sol which was added into the heel (cm^3)	Dosing rate (cm^3/min)	Dosing time (min)	Build-up index
I	92	100	1000	3.31	302	5.54
II		100	1000	3.31	302	4.75
III		100	1000	3.31	302	5.31
IV		340	850	3.31	257	1.30
V		100	1000	3.31	302	9.33
VI		100	1000	3.31	302	10.21

RESULTS AND DISCUSSION

Table 2 presents results collected from six series of experiment. In these series the sols which were added into the heel had the following SiO_2 concentrations: 3.50, 3.02, 3.49, 3.10, 6.02 and 6.21 wt. %. Selected results of particle diameters for the first series are compared in Fig. 1. For sols with a mean SiO_2 concentration of 3.28 and 6.00 wt. %, the correlation curves of the relative content of the ionic form of SiO_2 vs. pH were drawn (Fig. 2). SiO_2 particles of greater size were obtained when the processes were carried out using sols added into the heel at lower SiO_2 concentrations. The SiO_2 particle sizes obtained in series V and VI at subsequent stages of silica sol preparation were practically the same. Results of the first four series point to the positive effect of increasing pH of the sols added into the heel and the sols received as a result of build-up process on the growth of the SiO_2 particles.

As the build-up process is an effect of polymerization of silicic acid monomers, the results in Table 2 can be explained using the correlation curves given in Figure 1. Particle build-up took place when the pH was between 9.5 and 11.0. Sols with a mean SiO_2 concentration of 3.38 wt. % had much more ionic silica than similar sols with a mean SiO_2 concentration of 6.00 wt. %. The predicted diameters of the built-up particles were calculated from Equations 1 and 2 of and compared with the experimental data (Table 3).

Table 2. The particle diameters, pH, sol densities and total content of SiO_2 in the sols at subsequent stages of their preparation

Series no.	Parameter measured	Heel sol	Sol added into the heel	Sol after the build-up process	Sol after evaporation
I	Density at 20°C (g/dm^3)	1.041	1.023	1.039	1.112
	SiO_2 (wt. %)	6.21	3.50	5.63	19.31
	pH	8.33	10.24	10.90	10.74
	Diameter of dominant particles (nm)	1.46	2.06	6.27	9.02
	Volume of dominant particles (%)	99.8	99.3	100	100
II	Density at 20°C (g/dm^3)	1.041	1.017	1.033	1.160
	SiO_2 (wt. %)	6.21	3.02	5.68	23.81
	pH	8.33	9.84	10.69	10.62
	Diameter of dominant particles (nm)	1.46	1.20	6.67	3.51
	Volume of dominant particles (%)	99.8	99.7	100	99.3
III	Density at 20°C (g/dm^3)	1.038	1.018	1.040	1.110
	SiO_2 (wt. %)	6.44	3.49	5.81	17.12
	pH	8.08	9.00	9.46	9.34
	Diameter of dominant particles (nm)	1.66	1.43	2.15	1.61
	Volume of dominant particles (%)	99.8	99.6	99.0	99.9
IV	Density at 20°C (g/dm^3)	1.029	1.019	1.033	1.061
	SiO_2 (wt. %)	5.89	3.10	6.10	12.04
	pH	8.93	11.33	11.15	11.11
	Diameter of dominant particles (nm)	1.36	3.43	7.29	7.19
	Volume of dominant particles (%)	99.8	99.9	100	100
V	Density at 20°C (g/dm^3)	1.038	1.036	1.059	1.156
	SiO_2 (wt. %)	6.44	6.02	8.80	22.36
	pH	8.08	9.30	9.50	9.42
	Diameter of dominant particles (nm)	1.66	1.25	1.41	1.43
	Volume of dominant particles (%)	99.8	99.8	99.7	100
VI	Density at 20°C (g/dm^3)	1.041	1.036	1.047	1.110
	SiO_2 (wt. %)	6.05	6.21	7.96	17.69
	pH	8.74	8.50	9.31	9.12
	Diameter of dominant particles (nm)	1.21	1.63	1.49	1.16
	Volume of dominant particles (%)	99.9	100	99.8	100

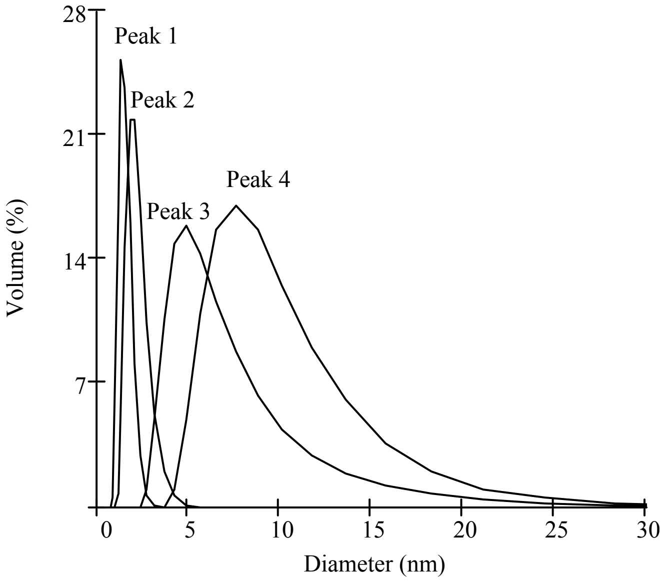

Fig. 1. Comparison of particle size distributions at subsequent stages of silica sol preparation: Peak 1. size distribution of particles in the heel sol, by volume – 1,46 nm (Series I); Peak 2. size distribution of particles in the sol which was added to the heel sol, by volume – 2,06 nm (Series I); Peak 3. size distribution of particles in the result sol after build-up process, by volume – 6,27 nm (Series I); Peak 4. size distribution of particles in the result sol after evaporation process, by volume – 9,02 nm (Series I)

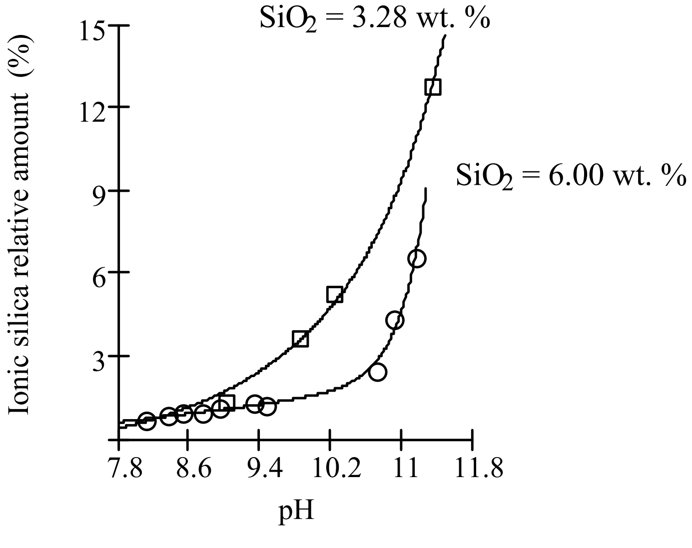

Fig. 2. The influence of pH on ionic silica contents in sols with a mean silica concentrations of 6.00 and 3.28 wt. %

Table 3. Comparison of SiO_2 particle diameters calculated theoretically with results of experiments

Series no.	Diameter of dominant particles in the heel sol (nm)	Calculated diameter of particles in sol after the build–up process (nm)	Determined diameter of dominant particles in sol after the build–up process (nm)	Build-up index
I	1.46	2.73	6.27	5.54
II	1.46	2.61	6.67	4.75
III	1.66	3.07	2.15	5.31
IV	1.36	1.79	7.29	1.30
V	1.66	3.61	1.41	9.33
VI	1.21	2.71	1.49	10.21

According to the results collected in Table 3, all SiO_2 particles in the solution took part in the process of the particle build-up, not only those introduced with the sols added into the heel. The sols added into the heel in series I and IV were obtained at 25°C, while those used in series II and III were obtained at 40°C. The size of the SiO_2 built-up particles obtained after concentration was the same or greater for series I, IV but smaller for series II, III. A probable explanation is that, in sols from series II and III, the process of particle agglomeration was more effective during the build up stage and in the process of concentration the agglomerates underwent redispersion.

CONCLUSIONS

It was expected that an increase in the silica concentration of the sols which were added into the heel to 6.02 and 6.21 wt. % would increase build-up indices and make the process of sol preparation more economic, especially at the evaporation stage. Unfortunately, the expected improvement was not achieved in the pH range of 9.5 to 11. The sol with a SiO_2 concentration of 6 wt. % contained much less silica in the ionic form than the sol with a mean SiO_2 concentration of 3.28 wt. %. The increase in silica particle size was a result of the build-up of monomeric silica ions on the surface of particles. Sols added into the heel at room temperature were more able to elicit stable build-up of colloidal silica particles.

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W pracy badano charakterystykę dyspersyjną krzemionki koloidalnej w kolejnych etapach otrzymywania zolu kwasu krzemowego. Rozcieńczone zole otrzymywano z roztworów krzemianu sodu metodą wymiany jonowej, nabudowywano w nich cząstki SiO_2 i następnie zatężano. Stężenia zoli, w których nabudowywano cząstki zawierały się w przedziale 5,89÷6,44 % wag. SiO_2, a zole stosowane do nabudowania miały średnie stężenia 3,28 i 6,20 % wag. SiO_2. Rozkłady wielkości cząstek mierzono techniką DLS, a udział formy jonowej krzemionki oznaczano kolorymetrycznie mierząc intensywność żółtego zabarwienia heteropolikompleksu kwasu molibdenowo–krzemowego.

słowa kluczowe: zol kwasu krzemowego, krzemionka koloidalna, krzemian sodu