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PREPARATION OF POLYSILIC ACID SOLS BY ION EXCHANGE METHOD

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In the study application of the macroporous ionite, Amberlyst® 15 (Merck), was tested in the process of production of dilute solutions of silicic acid sols. The process of ion exchange was conducted in a periodic reactor employing batch technique at the temperature of 45°C or 85°C. The products involved clear and stable solutions of sols of mean SiO_2 concentrations of 4.31, 4.72, 6.34 and 6.46 wt.%. A two-stage technique for ionite recovery was also worked out.

Key words: *silica sol, sodium silicate solution, cation exchange, Gaussian distribution*

INTRODUCTION

Silica sols represent stable dispersions of amorphous silica particles of 4 - 5 nm to 100 nm in diameter. In most of sols silica particles manifest a non-porous structure. The idea of silica sol stability is related both to maintenance of stable particle diameter and to prevention against their aggregation. The counteraction against particle aggregation involves introduction to the system of ionic electric charge or steric stabilization of the particles. Such interactions take place in the course of adsorption on silica surface of non-ionic particles (Iler 1979).

The techniques of obtaining silica sols can be categorized into a few groups, employing, respectively,

- neutralization of alkaline solutions with acids,
- electrodialysis,
- ion exchange,
- peptization of silica gel.

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The neutralizing techniques most frequently involve a reaction of sodium silicate solution performed in this way that pH around 2 results, which warrants momentary stability of silica sol solution. This permitted to precipitate and to separate the sodium salt and, following its separation, to alkalize the sol in order to stabilize it and to cause further increase in the particle size. Teicher (1960) neutralized sodium silicate solution using an acid, in presence of water-soluble organic liquids, e.g., alcohols, the presence of which induced precipitation of sodium salts. White (1942) neutralized sodium silicate solution using sulphuric acid solution, and precipitated sodium sulphate by supplementation of the obtained sol with acetone. Marcheguet and Ganddon (1962) in similar experiments employed compounds forming marginally insoluble sodium salts, e.g., involving reaction of sulphate ion and glioxal. Sanchez (1959) patented an electrodialysis process, in which alkaline metal was continuously removed until the moment when the sol developed. Such a process permitted to obtain alkalies, oxygen and hydrogen.

The pioneering studies on removal of sodium from sodium silicate solution by ion exchange were conducted by Bird (1941). Subsequent studies of Bechtold and Snyder (1951) permitted to obtain sols of controlled particle size. The technique was termed the process of particle overlapping. It involves separation into two parts of the diluted silica sol, pH >7, warming one of the parts to a temperature >60°C, so that diameters of dispersed phase reach 4 - 6 nm, which is followed by addition of the second part of the sol at a sufficiently slow rate to deposit the introduced silica on particles suspended in the solution.

Dirnberger (1955) passed sodium silicate solution through a fluidal ionite deposit at such a rate that individual ionite grains were suspended in the solution flowing up the column. Alexander (1956) obtained sol clear as water, free of soluble salts, manifesting mean particle diameters of 5 to 8 nm and specific surface area of the silica of 350 to 600 m^2/g. A possibility to control the growth of the silica colloidal particles during the preparation of the stabilized silica sols by means of regulating medium pH values has been studied (Hayrapetyan 2005). Brykov evaluated regularities of dissolutions of colloidal SiO_2 particles in the formation of concentrated polysilicate solutions from stabilized silica sols (Brykov 2004). Dirnberger and Nelson (1961) obtained sol of minimum turbidity charging the periodic reactor in parallel with sodium silicate solution and ionite in the hydrogen form (temp. 88 – 90 °C, pH = 8.3 – 8.7).

The techniques taking advantage of peptization have been known for a long time and involved addition to the gel of certain amount of alkalies and warming it in water, so that no evaporation could take place (Ahlberg 1959, Mertz 1971).

EXPERIMENTAL

MATERIALS

Dilute silicic acid sols were obtained from sodium silicate solutions (density at 20°C – 1.252 g/cm^3, Na_2O – 6.38 wt.%, SiO_2 – 20.31 wt.%; molar modulus – 3.28). Amberlyst®15 in hydrogen form (particle size 0.3-1.2 mm, ionic exchanging capacity – 1.7 mmol/m^2) as an ionic exchanger was applied.

METHODS OF STUDIES

The process of ion exchange was performed in a periodic reactor using the batch technique at the temperature of 45 or 85°C. The pressure-less reactor, made of acid-proof steel had working capacity of 450 cm^3. Scheme of the equipment for production of silicic acid sols is presented in Fig.1.

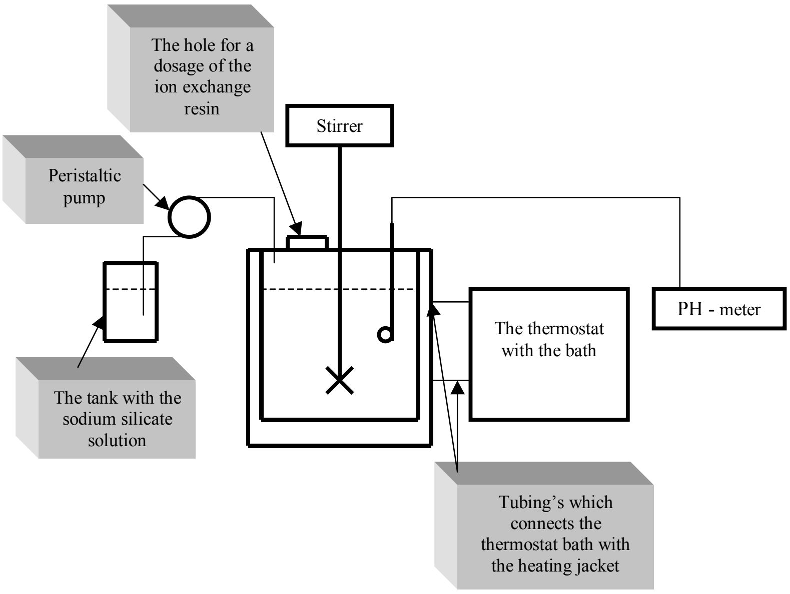


Fig.1. The apparatus for producing of the silica sol by ion exchange method (batch method)

The reactor was charged in parallel with ionite and sodium silicate so that in the sol pH of around 8.5 was maintained.

The ionite was recovered in the column at two stages. At the first stage silica was washed off the deposit using 0.5 wt.% NaOH and, at the subsequent stage, Na^+ ions were exchanged to H^+ ions rinsing the deposit with 5 wt.% HCl solution.

In the obtained solutions of silicic acid sols contents of SiO_2, Na_2O, and pH were estimated. The calculated molar modulus is defined as a ratio of SiO_2 mole number per number of Na_2O moles in any amount of the sol. Exchange capacity of the ionite was established passing 1M NaOH solution through the ionite in its hydrogen form. The number of hydrogen ions exchanged in the deposit was estimated by establishing in the outflow from the deposit the amount of remaining sodium ions, using alkacymetric titration.

For statistical evaluation of the process the normal Gauss'es distribution was applied. The function of probability of density distribution for the normal distribution in the range of (+∞, -∞) has the following form:

$$f(x) = \frac{1}{\sigma\sqrt{2\pi}} e^{-\frac{(x-\mu)^2}{2\sigma^2}} ,$$

where:

μ – expected value of the random variable x

σ – standard deviation.

Definition of the function of probability density $f(x)$ is linked to the following condition:

$$\int_{-\infty}^{+\infty} f(x)d = 1 .$$

Moreover, the value of arithmetical mean is assumed to represent an estimator of the unknown value of the distribution's expected variable.

RESULTS AND DISCUSSION

Histograms for molar modulus and pH of diluted solutions of silicic acid sols are presented in Figs. 2 to 5.

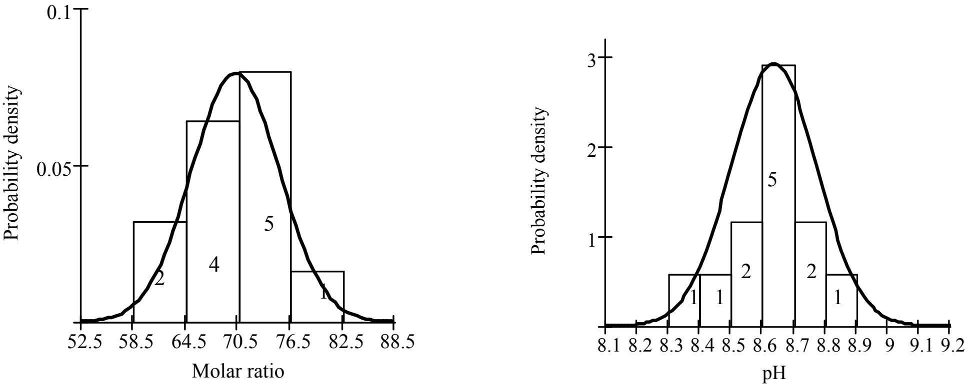


Fig. 2. The probability density functions for molar ratio and pH, concerning silica sols obtained at temperature 45°C, for scheduled SiO_2 concentration of 5 wt.%. The molar ratio probability for the range $\langle 77 ; 60 \rangle$ is equal to 0.89. The pH probability for the range $\langle 8.86 ; 8.39 \rangle$ is equal to 0.91

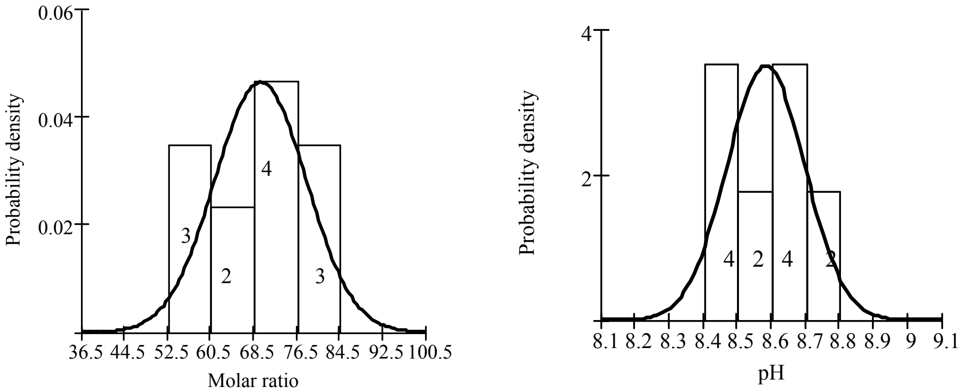


Fig. 3. The probability density functions for molar ratio and pH, concerning silica sols obtained at 45°C for scheduled SiO_2 concentration of 7.5 wt.%. The molar ratio probability for the range ⟨81 ; 55⟩ is equal to 0.86. The pH probability for the range ⟨8.72 ; 8.41⟩ is equal to 0.82

Taking advantage of the function of density distribution probability for pH and molar modulus the probability was estimated of fitting the range defined by threshold values of the variables, obtained in consecutive series of experiments. The numbers in bars denote number of measurements in a given compartment. In the case of histograms of molar modulus, rational values were accepted as limits of consecutive compartments since values of molar modulus were rounded up to integers.

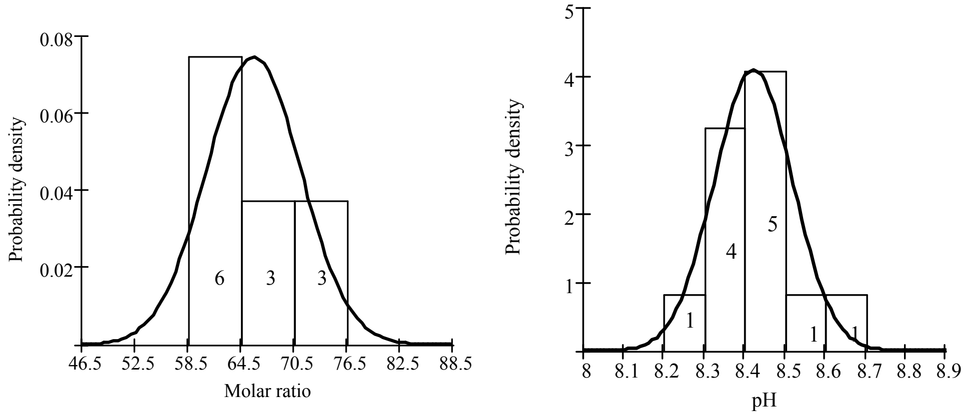


Fig.4. The probability density functions for molar ratio and pH, concerning silica sols obtained at temperature 85°C for scheduled SiO_2 concentration of 5 wt.%. The molar ratio probability for the range ⟨75 ; 59⟩ is equal to 0.86. The pH probability for the range ⟨8.62 ; 8.29⟩ is equal to 0.89

Due to the low number of measurements not all the histograms reflect symmetric nature of the normal distribution in respect to mean value and its unimodal character. Parameters of silicic acid sols obtained at the same temperatures for various planned

SiO_2 concentrations and of sols obtained at various temperatures for the same planned concentrations of SiO_2 are presented in Figs. 6 to 7.

The data of Fig. 6 indicate that at the temperature of 45°C the highest scatter of molar modulus values characterized higher concentrations of SiO_2, while mean values of the modulus were very similar for both concentrations of SiO_2. The small difference between mean values of the two modulus reflected higher content of Na_2O in the sol of higher SiO_2 content and lower content of Na_2O in the sol of lower silica content. Values of pH in two cases demonstrated similar mean values and scatters.

At the temperature of 85°C similar scatters of molar modulus and of Na_2O were obtained for both concentrations of SiO_2. In the case of molar modulus peak of density probability was clearly shifted toward higher values for higher SiO_2 concentration since positions of peak Na_2O content were almost the same. Both peaks of probability density for pH manifested similar scatters and mean values.

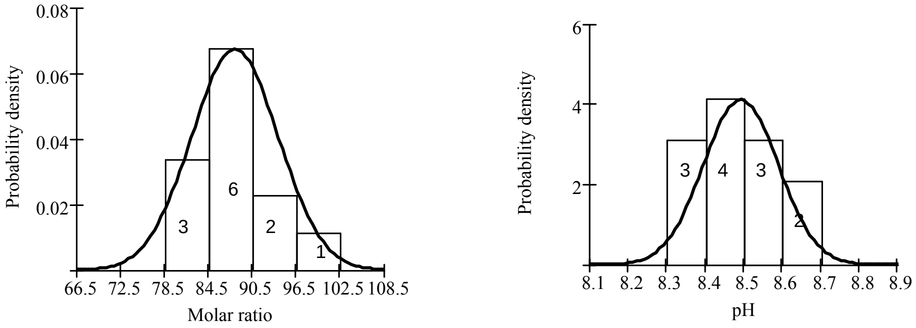


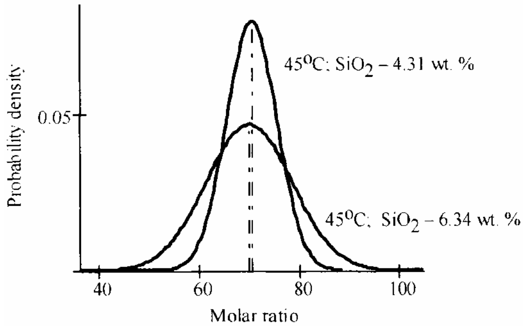
Fig.5. The probability density functions for molar ratio and pH, concerning silica sols obtained at 85°C for scheduled SiO_2 concentration of 7.5 wt%. The molar ratio probability for the range ⟨102 ; 81⟩ is equal to 0.87. The pH probability for the range ⟨8.67 ; 8.38⟩ is equal to 0.84

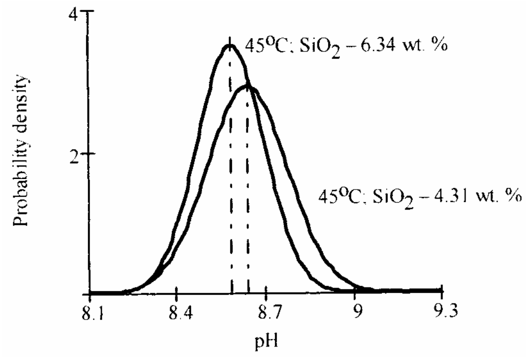
As indicated by data of Fig. 7, the peak of probability density for molar modulus at the temperature of 85°C was shifted toward higher modulus, since the peak of probability density of Na_2O content at the temperature of 85°C was present among lower values as compared to the analogous peak at the temperature of 45°C. At the temperature of 85°C lower scatters of molar modulus and of sodium oxide content were obtained. The function courses for probability density distribution for pH were similar at the two tested temperatures.

The evaluation included also the ionite which was sixfold recovered and recycled in the process of sol production. In order to evaluate ionite suitability the exchanging capacity was estimated for each of the samples and compared to exchanging capacity of ionite not used in the process. The ion exchanging capacities of the samples are compared to each other in Table 1. The ion exchanging capacities of samples used in the process were slightly lower that capacity of the not yet used sample. Nevertheless, data of Table 1 documented no significant effect of sol production parameters on ionite exchanging capacity.

Table 1. Exchanging capacity of ionite samples

Estimated parameter	Exchanging capacity of ionite not used in the process	Parameters of sol production process			
		45°C		85°C	
		SiO_2 (5 wt.%)	SiO_2 (7.5 wt.%)	SiO_2 (5 wt.%)	SiO_2 (7.5 wt.%)
Ion exchanging capacity (mmol/cm^3)	1.677	1.663	1.657	1.653	1.649
		1.658	1.654	1.650	1.651





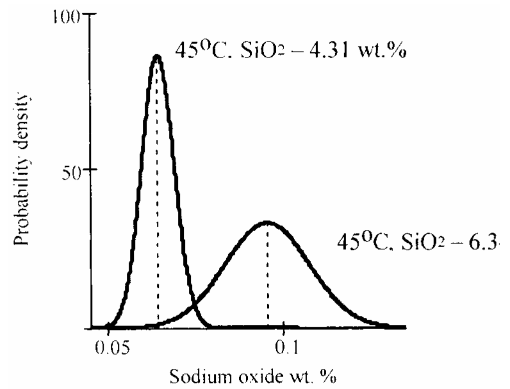


Fig. 6. The confrontation of Gaussian distributions for molar ratio, pH, and Na_2O wt.% for 45°C and scheduled SiO_2 concentrations of 5 wt.% and 7.5 wt.%

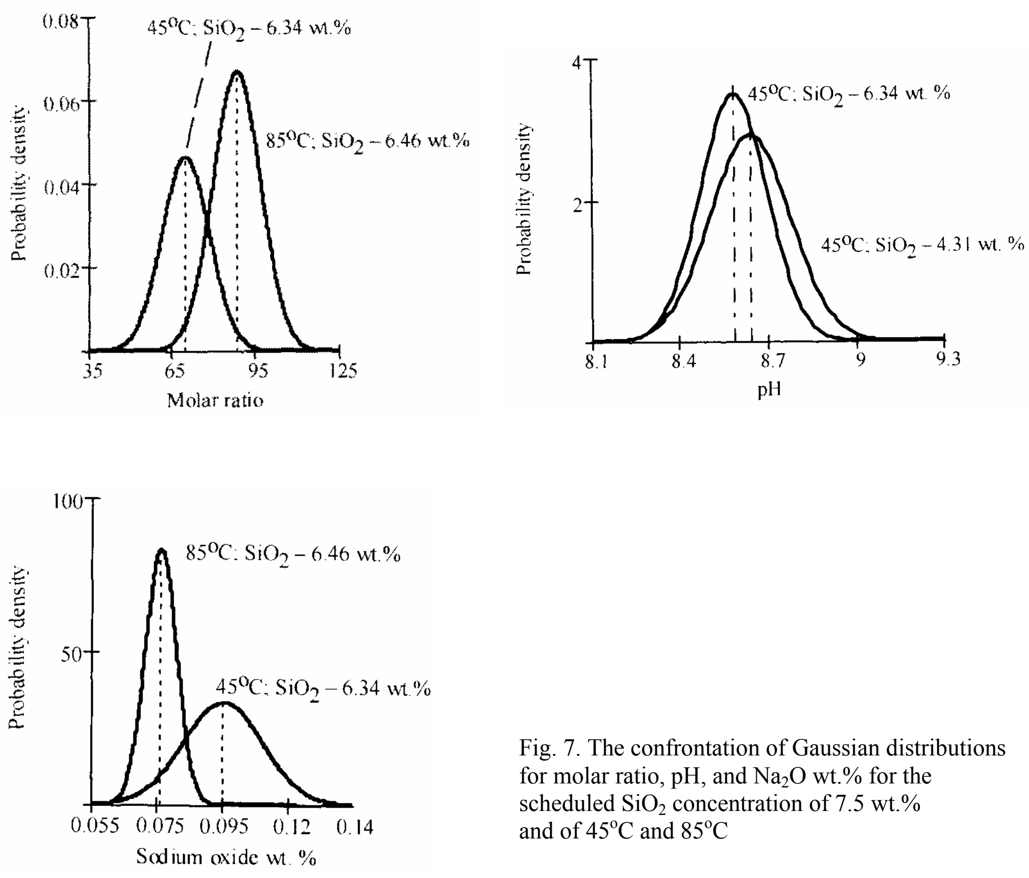


Fig. 7. The confrontation of Gaussian distributions for molar ratio, pH, and Na_2O wt.% for the scheduled SiO_2 concentration of 7.5 wt.% and of 45°C and 85°C

CONCLUSIONS

Silica gels having relatively high modulus (70–90) were obtained. Analysis of statistical data showed that increase in SiO_2 concentration in processes conducted at the temperature of 45°C induced no significant changes in molar modulus while analogous increase in processes conducted at the temperature of 85°C induced an increase in molar modulus. In all solutions of silicic acid sols pH fitted the range of (8.29 – 8.86). All the obtained sol solutions were clear.

From the point of view of ionite suitability evaluation, the batch yielded better results than the column technique. The former technique secured full access of the solution to ionite grains and precisely maintained pH in the entire reactor. Statistical evaluation confirmed high reproducibility of parameters of the obtained sols: probability of hitting the range between threshold values of pH and molar modulus always exceeded 0.8.

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Malewski W., Krysztafkiewicz A., Jesionowski T., *Otrzymywanie zoli kwasu krzemowego metodą wymiany jonowej,* Physicochemical Problems of Mineral Processing, 40 265-273, (2006) (w jęz. ang.).

W pracy przetestowano makroporowaty jonit Amberlyst® 15 (prod. Merck) w procesie otrzymywania rozcieńczonych roztworów zolu kwasu krzemowego. Proces wymiany jonowej prowadzono w reaktorze okresowym metodą batch w temp. 45 i 85°C. Produktami były klarowne roztwory zoli o średnich stężeniach SiO_2 4,31; 4,72; 6,34; 6,46 %wag. Opracowano również dwuetapową metodę regeneracji jonitu.