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*O. Pasenko, A. Mandryka, Ye. Khrupchyk, V. Vereshchak***STABLE SOLUTIONS OF ORTHOSILICIC ACID****Ukrainian State University of Chemical Technology, Dnipro, Ukraine**

Soluble silicon plays a significant role in living organisms. Orthosilicic acid is the only bioavailable form of silicon. Sodium silicate solutions with various silicate moduli and different types of acids were used in our work to investigate the effect of silicate modulus and types of acids on the stability of the solutions of orthosilicic acid. It was determined that both the silicate modulus and the type of acid have a certain impact on the stability of orthosilicic acid solution. The effect of sulfuric, hydrochloric, orthophosphoric and methanesulfonic acid on the stability of orthosilicic acid solutions was studied depending on the silicate modulus of sodium silicate. It was shown that in the following series of anions  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{CH}_3\text{SO}_3^-$ ,  $\text{PO}_4^{3-}$ , the stability of orthosilicic acid solutions increases. In the following series of alkaline modulus 3.02, 2.72, 2.06, 1.96, the stability increases too. The use of orthophosphoric acid and liquid glass with a silicate modulus of 1.96 allowed obtaining a solution, which is stable for at least 40 days.

**Keywords:** sodium silicate, silicate modulus, orthosilicic acid, bioavailability, stability.

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**Introduction**

Silicon is the second of the most abundant elements on the planet Earth after oxygen. It is a part of most minerals of the Earth's crust (about 28 wt.%). Its average concentration in ocean water varies from 0.03 mg/l in surface water to 2 mg/l in deep layers. Average concentration of silicon in the freshwater sources (rivers, lakes, etc.) is 4 mg/l.

The main sources of the bioavailable silicon are elementary silicon, silica gel or zeolite. Low solubility in the water is the main disadvantage of these materials. For example, water solubility of silicon is 120 mg/l [1], but this is difficult to achieve in practice. To reach the above value, fine ground amorphous elementary silicon should be used at the time exposure of 20, 39, and 62 days. Such method is not suitable for producing concentrated silicone solutions because of its low rate.

Bioavailable silicone in natural waters is largely in the form of orthosilicic acid ( $\text{H}_4\text{SiO}_4$ ). The polymerization of orthosilicic acid occurs when  $\text{pH} \approx 7$  and its concentration is higher than 2 mM [2,3]. It creates a dimer, colloidal particles and solid residue.

Reffitt et al. [4] and Belton et al. [5] showed

that only orthosilicic acid is a bioavailable form of silicone, which provides about 50% of its income in the body that is absorbed.

The last researches have stated a direct dependence between the quantity of the consumed silicone in form of the orthosilicic acid and the bones mineralization, collagen production, the skin, hair, and nails condition. However, the mechanism of action of orthosilicic acid in the body is still unknown.

The existence of the orthosilicic acid as different kinds of its polymers and monomer mostly depends on the solution pH, and then on the anion nature and the presence of stabilizers [6]. The polymerization reactions are shown in Fig. 1. The dimers, trimers and linear or branched polymers are formed in, and then they create spherical structures. After that, the slow gelation occurs.

To predict the behavior of orthosilicic acid in the solution, the charts characterizing the existence of different forms of orthosilicic acid vs. the solution pH have been analyzed (Fig. 2) [7]. When pH is higher than 7, orthosilicic acid starts to lose protons and is transformed into a dimeric form, which undergoes further polymerization and gelation. To

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*O. Pasenko, A. Mandryka, Ye. Khrupchyk, V. Vereshchak*

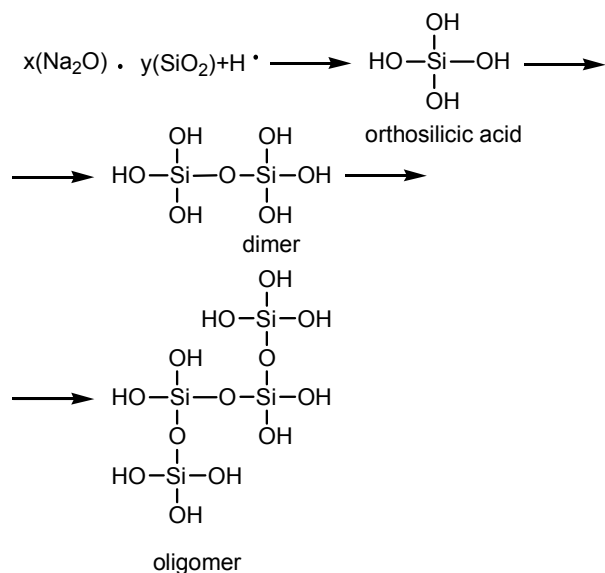


Fig. 1. Polymerization mechanism of orthosilicic acid in solutions

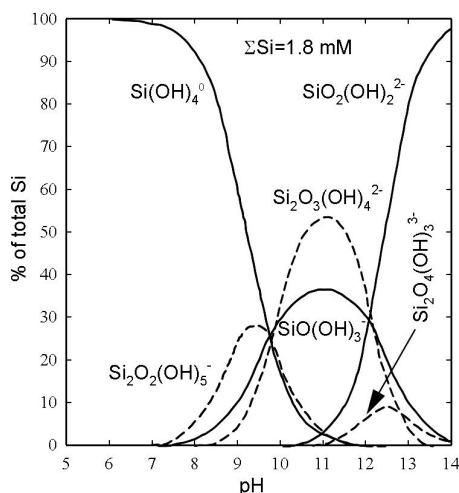


Fig. 2. Dissolved silica speciation vs. pH at 25°C [7] (published by MDPI under the terms of the Creative Commons Attribution 4.0 License)

produce stable solutions of orthosilicic acid, the pH range from 2 to 3.5 has been chosen.

It is generally known that silicic acids are being created during the action of strong acids on liquid glass solutions. The data about the rate of conversion of sodium silicate into orthosilicic acid depending on the type of acid are absent in the literature.

Thus, this study was aimed at establishing the dependence of stability of orthosilicic acid solutions on silicate modulus and the nature of acid anion. In order to fulfill this task, it is necessary to prepare solutions of orthosilicic acid using sodium silicate with different silicate moduli and hydrochloric,

sulfuric, orthophosphoric and methanesulfonic acids and determine the change in the concentration of orthosilicic acid over time.

#### Materials and methods

The measurements of the concentration of the orthosilicic acid were performed using a standard colorimetric method based on the formation of yellow silicomolybdic complex. We used ammonium paramolybdate aqueous solution (50 g/l) and dilute sulfuric acid (5 M).

#### Calibration curve

3.16 g  $\text{Na}_2\text{SiF}_6$  was dissolved in a 1 dm<sup>3</sup> volumetric flask using gradual heating. The solution was intensively mixed for 2–3 hours until all the solids will be dissolved. After that, the solution was poured into the plastic bottle and sealed. To prepare a standard solution with a concentration of 10 mg/l with respect to  $\text{SiO}_2$ , 10 ml of the prepared solution were taken by dosing pipette and dissolved in 1 dm<sup>3</sup> at thorough agitation. The solution could be stored not more than 15 days in a sealed flask.

The doses of 2, 5, 10, 15, and 20 ml of the prepared  $\text{Na}_2\text{SiF}_6$  solution were added to five 50 ml volumetric flasks, which corresponds to 20, 50, 100, 150, and 200 µg of orthosilicic acid in the tube, respectively.

Distilled water was added to achieve the volume of about 40 ml and then 5 ml of the molybdic solution and 1 ml of the diluted sulfuric acid were added. The solution was vigorously stirred and then its volume was adjusted to the mark by distilled water.

After 7 minutes, the absorbance of solutions was measured at the wavelength of 400 nm compared with distilled water. The graph of absorbance vs. concentration of  $\text{SiO}_2$  was used as a calibration curve for further measurements.

#### Analysis procedure

The 20 ml of a solution that should be analyzed was added to the 50 ml volumetric flask, then 5 ml of the molybdic solution and 1 ml diluted sulfuric acid were added to the same flask and filled to the mark by distilled water. The liquid in the flask was vigorously stirred and the absorbance was measured in 5–7 minutes at the wavelength of 400 nm.

The concentration of the  $\text{SiO}_2$  in the flask was determined by the calibration curve and the calculation was performed by the following expression:

$$[\text{SiO}_2] = \frac{M}{V} \cdot 1000, \mu\text{g/l}$$

where M is the mass of orthosilicic acid in the sample determined via calibration curve (µg); and V is the

volume of a sample taken for analysis ( $\text{cm}^3$ ).

#### *Stable solution of orthosilicic acid*

A stable solution of orthosilicic acid should maintain a concentration of 2.0–1.8 g/l for at least 40 days.

#### *Results and discussion*

The orthosilicic acid concentration of 2 g/l was chosen as a working concentration. This concentration responds to the optimum ratio between maximum concentration and polymerization rate.

The time dependences of orthosilicic acid concentration obtained with the use of  $\text{H}_2\text{SO}_4$  are shown in Fig. 3.

In the initial moment of the observation, the maximum concentration of the orthosilicic acid was 67% for the liquid glass with a silicate modulus of 1.96. The maximum content of orthosilicic acid is observed in 40 days with a silicate modulus of 2.06

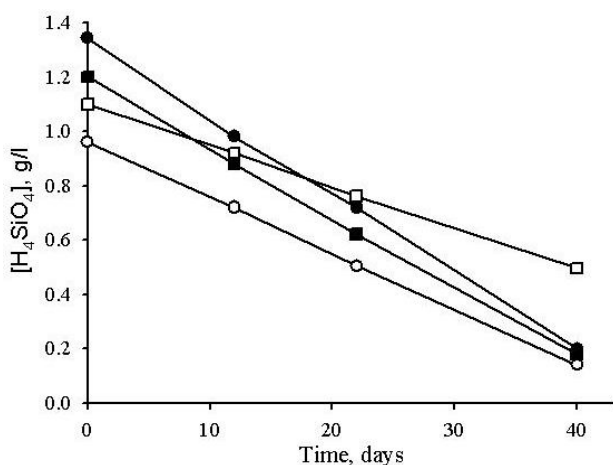


Fig. 3. Concentration change of  $\text{H}_4\text{SiO}_4$  vs. time.  $\text{H}_2\text{SO}_4$  was used. Silicate modulus: ● – 1.96; □ – 2.06; ■ – 2.72; and ○ – 3.02

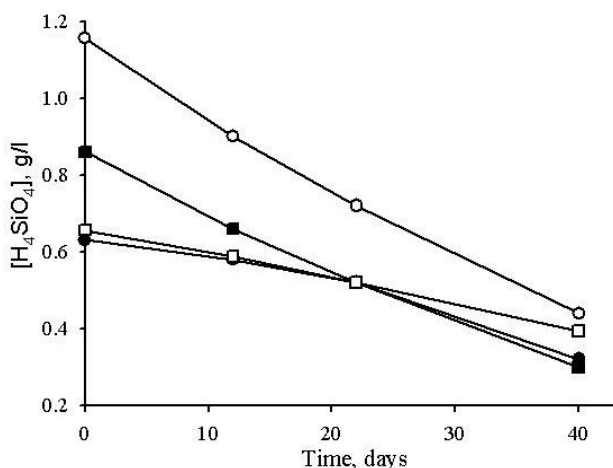


Fig. 4. Concentration change of  $\text{H}_4\text{SiO}_4$  vs. time. HCl was used. Silicate modulus: ● – 1.96; □ – 2.06; ■ – 2.72; and ○ – 3.02

that represents 25% of the maximum expected concentration (2 g/l).

Figure 4 shows time dependences of orthosilicic acid concentration obtained with the use of HCl. The use of hydrochloric acid in the reaction of neutralization of sodium silicate with various silicate moduli yields low stable solutions of orthosilicic acid. The maximum initial concentration of the orthosilicic acid can be achieved in the test with sodium silicate with silicate modulus of 3.02. In 40 days, irrespective of the silicate modulus, the concentration of orthosilicic acid will reduce to 15–20% of the maximum expected concentration (2 g/l).

Figure 5 shows that the use of orthophosphoric acid allows producing a stable solution of orthosilicic acid during a long time (40 days). A decrease in the concentration up to 8% is observed for the sodium silicate with silicate moduli of 1.96 and 2.06. It is

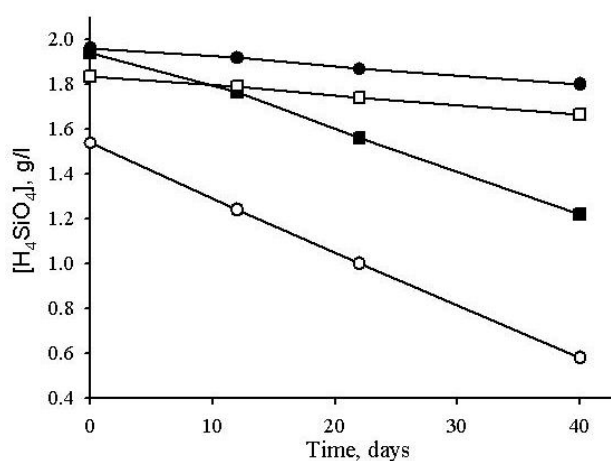


Fig. 5. Concentration change of  $\text{H}_4\text{SiO}_4$  vs. time.  $\text{H}_3\text{PO}_4$  was used. Silicate modulus: ● – 1.96; □ – 2.06; ■ – 2.72; and ○ – 3.02

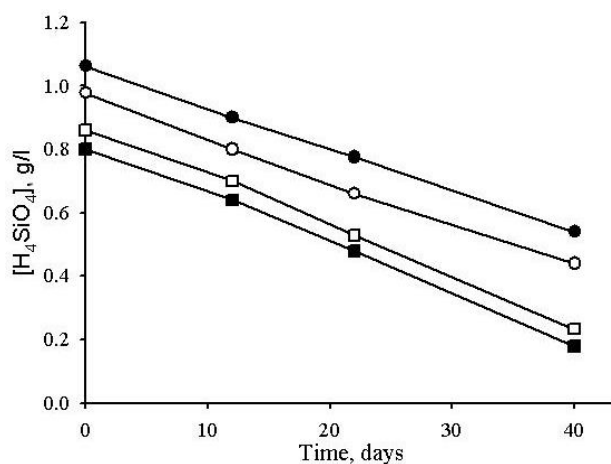


Fig. 6. Concentration change of  $\text{H}_4\text{SiO}_4$  vs. time.  $\text{CH}_3\text{SO}_3\text{H}$  was used. Silicate modulus: ● – 1.96; □ – 2.06; ■ – 2.72; and ○ – 3.02

90% of the expected concentration when using  $H_3PO_4$ .

It is known that methanesulfonic acid is highly biodegradable and biocompatible, so we used it to produce orthosilicic acid. However, as shown in Fig. 6, the use of methanesulfonic acid for the production of orthosilicic acid is not suitable. The character of the dependences of graphs for all modules is symbatic. The initial concentration of the orthosilicic acid was 40–50% of the expected concentration. It was only 9–27% in 40 days, depending on the silicate modulus of sodium silicate. That shows that the use of methanesulfonic acid results in the formation of unstable solutions of orthosilicic acid.

### Conclusions

Preparation of the stable solution of orthosilicic acid with a given concentration depends both on the nature of acid anion and on the silicate modulus. The stability of the solution of orthosilicic acid increases in the series of anions:



and in the series of silicate modulus: 3.02, 2.72, 2.06, 1.96.

The effect of the acid anion on the stability of orthosilicic acid solutions can be explained by the strength of the hydrogen bonds between  $H_4SiO_4$  and the anion of the corresponding acid.

Icopini et al. [8] point to a close relationship between the stability of orthosilicic acid solutions and pH and the ionic strength of the solution. In a series of increasing silicate modulus, there is a decrease in the amount of sodium oxide in liquid glass, which leads to a decrease in the ionic strength of the orthosilicic acid solution. It can be assumed that the combination of the strength of hydrogen bonds between molecules of orthosilicic acid and anion and ionic strength is responsible for the stability of the orthosilicic acid solution. There is no doubt that the establishment of a more precise mechanism for the formation of stable solutions of orthosilicic acid requires further researches.

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### СТАБІЛЬНІ РОЗЧИНИ ОРТОКРЕМНІЄВОЇ КИСЛОТИ

*О.О. Пасенко, А.Г. Мандрика, Є.С. Хрунич, В.Г. Верещак*

Розчинний кремній має важливе значення в життєдіяльності живих організмів. Ортокремнієва кислота – це єдина біодоступна форма кремнію. Розчини натрій силікату з різноманітним силікатним модулем та різні види кислот були використані для дослідження їх впливу на стабільність розчинів ортокремнієвої кислоти. Встановлено, що і силікатний модуль, і тип кислоти значно впливають на стабільність розчинів ортокремнієвої кислоти. Було вивчено вплив сірчаної, соляної, ортофосфорної та метансульфонової кислот в залежності від силікатного модуля. Встановлено, що в ряду аніонів кислот  $SO_4^{2-}$ ,  $Cl^-$ ,  $CH_3SO_3^-$ ,  $PO_4^{3-}$  стабільність розчинів ортокремнієвої кислоти збільшується. В ряду силікатних модулів 3,02; 2,72; 2,06; 1,96 також відбувається збільшення стабільності. Використання ортофосфорної кислоти та рідкого скла із силікатним модулем 1,96 дозволяє отримати стабільні розчини ортокремнієвої кислоти, стійкі протягом мінімум 40 днів.

**Ключові слова:** натрій силікат, силікатний модуль, ортокремнієва кислота, біодоступність, стабільність.

**STABLE SOLUTIONS OF ORTHOSILICIC ACID**

*O. Pasenko* \*, *A. Mandryka*, *Ye. Khrupchyk*, *V. Vereshchak*  
Ukrainian State University of Chemical Technology, Dnipro,  
Ukraine

\* e-mail: [zirconia@ukr.net](mailto:zirconia@ukr.net)

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