

## The Effect of Sodium Ions on the Distribution of Silicate Anions in Tetramethylammonium Silicate Aqueous Solutions

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The distribution of silicate anions in tetramethylammonium silicate aqueous solutions containing various amounts of sodium ions was measured quantitatively by the trimethylsilylation technique combined with gas-liquid chromatography. It was found that recoveries of the low-molecular weight silicate species increased and that of the cubic octameric silicate anion, which was the main species in tetramethylammonium silicate solutions, decreased with increasing amount of addition of sodium ions, and the octamer completely disappeared when the sodium ion-to-tetramethylammonium ion molar ratio was larger than 2.0.

**KEY WORDS:** Tetramethylammonium ions/ Sodium ions/ Silicate-anion  
distribution/ Trimethylsilylation

### INTRODUCTION

Silica-based inorganic polymers, such as zeolites and glasses, are important synthetic materials. For synthesis of such materials, the aqueous solutions containing silicate anions are utilized as silica sources. It is necessary for development of the syntheses of such functionality polymers to investigate the distribution of silicate anions in aqueous solutions. The distribution of silicate anions was obscure, however, until recently.

Polymerization of silicate anions in aqueous solutions is affected by many factors, such as coexisting cations, the cation-to-silica molar ratio,  $\text{SiO}_2$  concentration, pH and temperature. In the silicate solutions containing alkali metal cations, silicate anions polymerize at random, resulting in the complicated widespread distribution of silicate anions. In the silicate solutions containing organic quaternary ammonium ions, however, the selective structure formation of silicate anions occurs and the anions with specific cage-like structures, such as  $\text{Si}_6\text{O}_{15}^{6-}$ ,  $\text{Si}_8\text{O}_{20}^{8-}$  and  $\text{Si}_{10}\text{O}_{25}^{10-}$ , are singularly formed.<sup>1-8)</sup> As one of such effective cations, the tetramethylammonium ion ( $\text{N}^+(\text{CH}_3)_4$ ) is known to contribute to the singular formation of octameric silicate anion with a double four-membered cage (cubic octamer,  $\text{Si}_8\text{O}_{20}^{8-}$ ).<sup>3,6-8)</sup>

For the investigation on the constitution of silicate anions in the solutions,  $^{29}\text{Si}$  NMR and trimethylsilylation technique combined with gas-liquid chromatography have been widely used.  $^{29}\text{Si}$  NMR is an extremely powerful method to determine the structures of silicate species. The information on the structures by  $^{29}\text{Si}$  NMR is obtained for each silicate unit of the species.

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Silicate structures are classified into five building units on the basis of the numbers of silicon atoms which are bonded to a certain silicon atom through oxygen atoms. These units are distinguished as monosilicate, end, middle, branching and crosslinking groups. For instance, the silicate species of linear trimer consists of two end groups and one middle group. Therefore, it is difficult to analyze the distribution of silicate species (not silicate units) quantitatively by  $^{29}\text{Si}$  NMR, although a quantitative study on the distribution of silicate species in sodium silicate solutions is attempted.<sup>9</sup> However, trimethylsilylation has the advantage of making quantitative analysis on each silicate species possible, although some side reactions occurring during the silylation have to be taken into account.

There are a few studies on the distribution of silicate anions in the solutions containing both organic quaternary ammonium ions and alkali metal cations.<sup>7,8,10</sup> Such solutions are of interest for the synthesis of zeolites, since different types of zeolites are synthesized by the combinations of tetramethylammonium ions and alkali metal cations.<sup>11</sup> Since these studies are made with  $^{29}\text{Si}$  NMR, however, the quantitative variation in the distribution of low-molecular weight species by the addition of alkali metal cations is not so clear.

In this study, the distribution of silicate anions in tetramethylammonium silicate aqueous solutions containing various amounts of sodium ions was studied quantitatively by the trimethylsilylation technique combined with gas-liquid chromatography and was compared with the distribution in the silicate solutions containing only sodium ions at the same  $\text{SiO}_2$  concentration.

## EXPERIMENTAL

**Materials.** A 10% tetramethylammonium hydroxide aqueous solution was used for the source of tetramethylammonium ions. Tetraethoxysilane, sodium hydroxide, concentrated hydrochloric acid and 2-propanol were of reagent grade. Hexamethyldisiloxane was obtained by the hydrolysis of chlorotrimethylsilane and was distilled once (bp 100–101°C).

**Preparation of solutions.** Various amounts of  $4.0 \text{ mol dm}^{-3}$  aqueous sodium hydroxide solution and distilled water were added to a given amount of 10% tetramethylammonium hydroxide solution. Then tetraethoxysilane was added to the mixture as a silica source. The mixture was stirred for 2 days at room temperature. In this way, the solutions were prepared whose  $\text{SiO}_2$  concentration was  $0.5 \text{ mol dm}^{-3}$ , N/Si ratio (molar ratio of tetramethylammonium ion to silica) was 1.0 and Na/Si ratio (molar ratio of sodium ion to silica) was from 0 to 3.33. For comparison, the solutions containing sodium ions at the various Na/Si ratios and no tetramethylammonium ions were also prepared.

**Analytical procedure.** Each silicate species was analyzed by gas-liquid chromatography after the trimethylsilylation. The method of Lentz<sup>12</sup> was adopted for the silylation. This method is reported to be most favorable for the silylation of silicate solutions.<sup>13</sup> In this method, a mixture of concentrated hydrochloric acid ( $6 \text{ cm}^3$ ), water ( $5 \text{ cm}^3$ ), 2-propanol ( $12 \text{ cm}^3$ ) and hexamethyldisiloxane ( $8 \text{ cm}^3$ ) which has been stirred for 1 h at room temperature is used as the trimethylsilylating reagent. A  $2 \text{ cm}^3$  portion of a solution was added to the trimethylsilylating reagent and the mixture was stirred for one more hour at room temperature for the silylating reaction. After the reaction, the organic phase was separated and Amberlyst 15 cation-exchange resin was added to it for completion of trimethylsilylation. The trimethyl-

silylated derivatives obtained were analyzed with a Shimadzu GC-8A gas chromatograph, equipped with a hydrogen flame-ionization detector and a stainless-steel column (length: 6 m, internal diameter: 2.6 mm) packed with OV-17 2% Chromosorb W for 3 m and SE-30 5% Shimalite W for 3 m. The injection temperature was 300°C and the oven temperature was programmed to rise at 8°C min<sup>-1</sup> from an initial temperature of 80°C to a final temperature of 270°C. The carrier gas was nitrogen and the flow rate was 50 cm<sup>3</sup> min<sup>-1</sup>. Quantitative analysis was performed for SiO<sub>4</sub><sup>4-</sup>, Si<sub>2</sub>O<sub>7</sub><sup>6-</sup>, Si<sub>3</sub>O<sub>10</sub><sup>8-</sup>, Si<sub>4</sub>O<sub>12</sub><sup>8-</sup> and Si<sub>8</sub>O<sub>20</sub><sup>8-</sup> by using tetradecane as the internal-standard substance.

### RESULTS AND DISCUSSION

The distribution of soluble silicate anions in the silicate solutions at the SiO<sub>2</sub> concentration of 0.5 mol dm<sup>-3</sup> and the N/Si ratio of 1.0 varies with the amount of addition of sodium ions, as is shown in Fig. 1. The recovery of the cubic octamer decreases with increasing Na/Si ratio and becomes almost none when the Na/Si ratio is more than 2.0. In other words, the cubic octamer is not formed when sodium ions are present in more than two times as much as tetramethylammonium ions in the molar ratio. On the other hand, the recoveries of the monomer (SiO<sub>4</sub><sup>4-</sup>), dimer (Si<sub>2</sub>O<sub>7</sub><sup>6-</sup>) and linear trimer (Si<sub>3</sub>O<sub>10</sub><sup>8-</sup>) increase with increasing Na/Si ratio. The recovery of the cyclic tetramer (Si<sub>4</sub>O<sub>12</sub><sup>8-</sup>) decreases slightly at the Na/Si

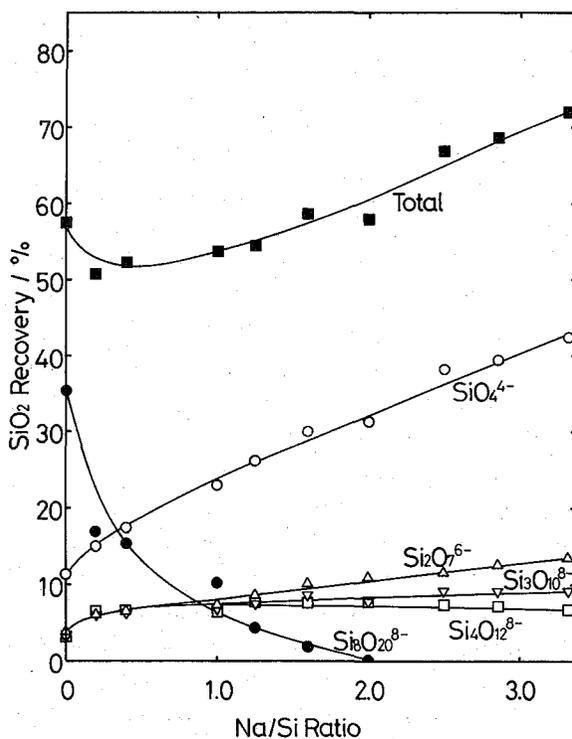


Figure 1. Variation in the distribution of silicate anions with the Na/Si ratio in 0.5 mol dm<sup>-3</sup> sodium tetramethylammonium silicate solutions at the N/Si ratio of 1.0.

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ratios over 2.0, while the recovery increases at the Na/Si ratios between 0 and 2.0. These facts suggest that the depolymerization from higher molecular weight species to lower molecular weight species occurs with the increase of the Na/Si ratio.

The variation in the distribution with the Na/Si ratio in  $0.5 \text{ mol dm}^{-3}$  aqueous sodium silicate solutions is shown in Fig. 2. The recoveries of low-molecular weight species from the monomer to the cyclic tetramer increase with increasing Na/Si ratio. The tendencies of the variation in the distribution of these species are similar to the data shown in Fig. 1. Particularly, when the Na/Si ratio is over 2.0, the recovery of each silicate species shows almost the same value. This indicates that the effect of tetramethylammonium ions is inhibited completely by the presence of sodium ions, as was reported by other workers,<sup>8,10)</sup> and the effect of sodium ions becomes dominant when the sodium ion-to-tetramethylammonium ion ratio is more than 2.0.

In the previous paper, it was stated that the cooperation of tetramethylammonium ions and water might lead to the selective structure formation of the cubic octamer.<sup>14)</sup> This suggests that water plays an important role in the selective structure formation. Then, the inhibition of formation of the cubic octamer by sodium ions in the present  $\text{Na}_2\text{O}-(\text{N}(\text{CH}_3)_4)_2\text{O}-\text{SiO}_2$  system may be attributed to the lack of effective water. It is assumed that in this system water is consumed to form hydrated sodium ions and so no interaction between tetramethylammonium ions and water is expected.

In short, the sodium ion has the inhibiting effect on the formation of the cubic octamer and the cubic octamer disappears when the sodium ion is present in more than twice as much as the

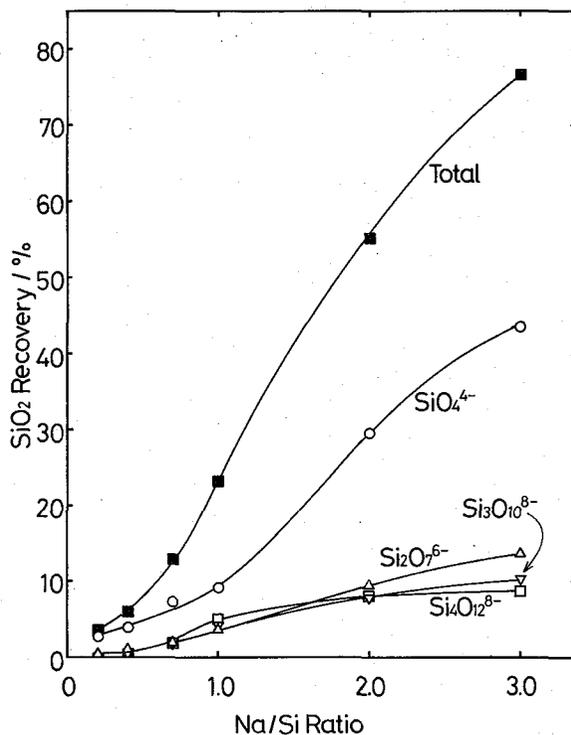


Figure 2. Variation in the distribution of silicate anions with the Na/Si ratio in  $0.5 \text{ mol dm}^{-3}$  sodium silicate solutions.

tetramethylammonium ion in the molar ratio. This effect would be attributed to the destruction of the interaction between tetramethylammonium ions and water by the hydration of sodium ions.

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