The Effect of Tetraalkylammonium Ions on the Distribution of the Silicate Anions in Aqueous Solutions

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The effect of the addition of tetramethylammonium, (2-hydroxyethyl)trimethylammonium and benzyltrimethylammonium ions on the distribution of the silicate anions arising from the hydrolysis of tetraethoxysilane was studied by using the trimethylsilylation method. The selective formation of the octameric silicate anion with a double four-membered cage was confirmed in these solutions. It was found that tetraalkylammonium ions with three methyl groups, whether or not the other group was a methyl group, contributed to the formation of a double four-membered cage octamer.

Tetraalkylammonium ions play an important role in the structure formation involved in zeolite syntheses and constitute one of the principal factors controlling the structure of zeolite.[1] These ions also affect the distribution of soluble silicate anions in aqueous solutions. Generally, silicate anions polymerize at random in aqueous solutions; this makes the distribution of the anions very complicated. By adding tetraalkylammonium ions to the systems under appropriate conditions, however, silicate anions with specific structures are formed. In this manner, the formation of silicate species with a double three-membered cage ($Si_6O_{15}^{6-}$), a double four-membered cage ($Si_8O_{20}^{8-}$) and a double five-membered cage ($Si_{10}O_{25}^{10-}$) have been reported.[2–15]

However, several reports have described the effect of the addition of tetraalkylammonium ions with different alkyl groups or other organic cations such as pyridinium ions.[11–15] In those papers, for example, it has been described that the (2-hydroxyethyl)trimethylammonium ion ($N^+(CH_3)_3C_2H_4OH$) contributes to the formation of the double four-membered cage silicate anion (cubic octamer)[11] as well as the tetramethylammonium ion ($N^+(CH_3)_4$). However, it remains obscure why these two tetraalkylammonium ions contribute to the formation of the cubic octamer similarly.

In order to clarify the interaction between tetramethylammonium ions and silicate anions, it is necessary to study the ratio of controlled silicate species quantitatively. Previous studies by Scheler et al.[11–15] only reported the results of the selective formation of silicate anions at a few SiO_2 concentrations and cation/Si ratios by means of ^{29}Si NMR. Therefore, the purpose of this study is to investigate the effect of tetraalkylammonium ions on the silicate anions over a broader range of variable factors (SiO_2 concentration and tetraalkylammonium ion/Si ratio) by means of trimethylsilylation.

Trimethylsilylation, originally applied to silicate minerals and solutions by Lentz,[16] is an effective chemical method for the structure study of silicates[17] as well as ^{29}Si NMR spectroscopy.[18–24] ^{29}Si NMR is an extremely powerful analytical procedure for the study of silicate structure. However, some doubts remain in its quantitative analysis.[24] Trimethylsilylation has the advantage of making it easy to perform quantitative analysis by means of gas chromatography in spite of the limits imposed by the side reactions upon silylation. Although several methods are available according to the silicate samples, the Lentz method is reported to be most favorable for the trimethylsilylation of aqueous silicate solutions;[25] thus, the Lentz method was used in this study.

Experimental

Materials. Tetraethoxysilane (reagent-grade) was used as a silica source. A 10% tetramethylammonium hydroxide aqueous solution, a 50% (2-hydroxyethyl)trimethylammonium hydroxide aqueous solution, and a 40% benzyltrimethylammonium ($N^+(CH_3)_3CH_2C_6H_5$) hydroxide aqueous solution were used as the tetraalkylammonium ions. The sodium hydroxide, concentrated hydrochloric acid, and 2-propanol were all reagent grade. The hexamethyldisiloxane was obtained by the hydrolysis of chlorotrimethylsilane and was distilled once (bp 100—101 °C).

Preparation of Sample Solutions. A fixed amount of tetraethoxysilane was added to a tetraalkylammonium hydroxide solution whose concentration had been adjusted by adding deionized water. The mixture was stirred for 2 d at room temperature to complete the hydrolysis of tetraethoxysilane. In this manner, two series of sample solutions were prepared --- samples with different SiO_2 concentrations at a constant N/Si ratio (molar ratio of tetraalkylammonium ion against silica), which was 1.0, and samples with different N/Si ratios at a constant SiO_2 concentration (1.0 mol dm^{-3}). In the case of the addition of the tetramethylammonium ion, sample solutions of only the former series were prepared because of the low concentration of the tetramethylammonium hydroxide aqueous solution.

In order to compare the effects of tetraalkylammonium ions and those of alkali metal ions, sample solutions with different SiO_2 concentrations at the Na/Si ratio of 1.0, solutions to which the sodium ion had been added, were prepared in the same described above by using a 4 mol dm^{-3} aqueous sodium hydroxide solution.

Trimethylsilylation by the Lentz Method. A 2 cm^3 portion of a sample solution was added to a mixture of concentrated hydrochloric acid (6 cm^3), water (5 cm^3), 2-propanol (12 cm^3), and hexamethyldisiloxane (8 cm^3) which had been stirred for 1 h at room temperature. After the silylation had been completed by stirring the reaction mixture for 1 h at room temperature, the siloxane phase was separated and Amberlyst-15 (cation-exchange resin) was added to complete the trimethylsilylation.

Analytical Procedure. The trimethylsilylated derivatives were analyzed by means of gas-liquid chromatography. Quantitative analysis was performed with respect to SiO_4^{4-}, $Si_2O_7^{6-}$, $Si_3O_{10}^{8-}$, $Si_4O_{12}^{8-}$, and $Si_8O_{20}^{8-}$ by using tetradecane as the internal-standard substance.[26] The results are shown as SiO_2 recovery, which was the proportion of SiO_2 recovered as trimethylsilylated derivatives converted from the SiO_2 component in the starting material. (The ionic charge was omitted for the sake of simplicity in the figures of this report.) The peaks on the chromatograms were identified for the trimethylsilylated derivatives of the monomer, dimer, linear trimer, cyclic tetramer and cubic octamer by means of mass spectrometry. The chromatographic conditions were as follows: Shimadzu GC-8A apparatus, equipped with a hydrogen FID; 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; oven temperature: 80 °C to 270 °C at 8 °C min^{-1}; injection temperature: 300 °C; carrier gas (nitrogen) flow rate: 50 cm^3 min^{-1}.

Results and Discussion

1. Gas Chromatograms and the Effect of Sodium Ions. Figure 1 shows typical gas chromatograms of trimethylsilylated derivatives of soluble silicate anions in (a) a sodium silicate solution and (b) a tetramethylammonium silicate solution. In the case of the sodium ion, it was found that low-molecular species such as the monomer, dimer, linear trimer, and cyclic tetramer, and also unidentified species with relatively higher molecular weights existed. This means that a random polymerization of the silicate anions occurred in the system. After adding the tetramethylammonium ion under proper conditions, however, a considerably large peak appeared, as is shown in Fig. 1(b). This peak was identified as the cubic octamer. In this way, the selective structure formation of silicate anions in the system is shown on a gas chromatogram, for almost always only one peak appeared: peaks of other species hardly ever appeared.

Figure 2 shows the variation in the silicate-anion distribution with the variation in the SiO_2 concentration at the Na/Si ratio of 1.0. With the increase in the SiO_2 concentration, the recovery of low-molecular species from the monomer to the cyclic tetramer was reduced gradually. This means that these low-molecular species polymerized and that higher molecular species were formed in the system. Although the cubic octamer existed in a small amount (the maximum recovery was 1.3% at the SiO_2 concentration of 0.7 mol dm^{-3}), it occurred in the course of the polymerization of the silicate anions because its recovery was relatively low and its lower recovery was observed in the region of higher SiO_2 concentrations, where polymerization proceeded. Therefore, in the sodium-coexisting system, silicate anions polymerize at random and there is no selective structure formation.

2. Addition of Tetramethylammonium Ions. When tetramethylammonium ions were present in a

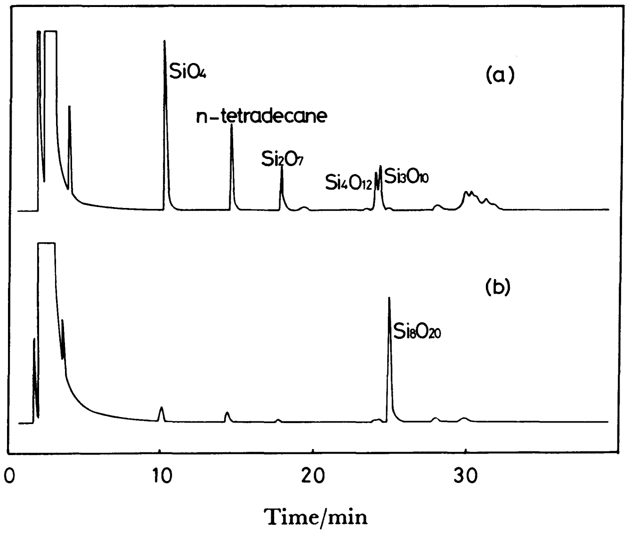

Fig. 1. Gas chromatograms of the trimethylsilylated derivatives of silicate species in (a) sodium silicate solution (Na/Si = 1.0, SiO_2 concentration: 0.4 mol dm^{-3}) and (b) tetramethylammonium silicate solution N/Si = 1.0, SiO_2 concentration: 0.88 mol dm^{-3}).

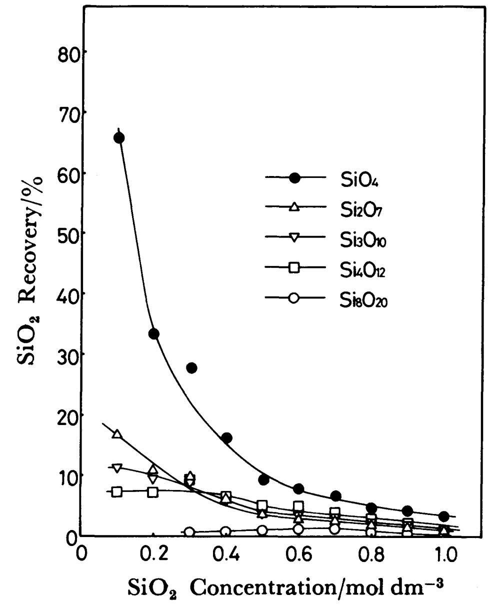

Fig. 2. Variation in the silicate-anion distribution with the SiO_2 concentration (Na/Si = 1.0) in sodium silicate solution.

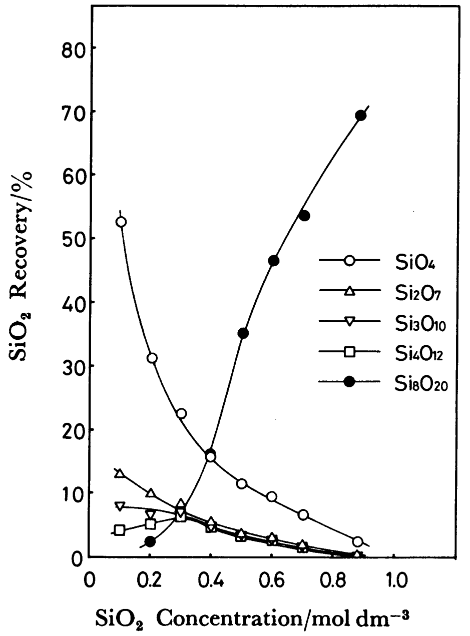

Fig. 3. Variation in the silicate-anion distribution with the SiO$_2$ concentration (N/Si=1.0) in tetramethylammonium silicate solution.

silicate solution, the silicate-anion distribution varied in a different way with the variation in the SiO$_2$ concentration at the N/Si ratio of 1.0, as is shown in Fig. 3. As the SiO$_2$ concentration increased, the recovery of low-molecular species from the monomer to the cyclic tetramer decreased. On the other hand, the recovery of the cubic octamer increased rapidly. In comparison with the results obtained from the Na$_2$O–SiO$_2$ system, shown in Fig. 2, the behavior of low-molecular species showed a similar tendency. As for the formation of the cubic octamer, however, the behavior was obviously different. This was evidently caused by the difference in the added cations. The selective formation of the cubic octamer has also been observed by Hoebbel et al., who used another silica source,[4] and a similar tendency was confirmed in this study. Thus, upon the addition of tetramethylammonium ions to aqueous silicate solutions, random polymerization did not occur, but a specified silicate skeleton was selectively formed.

3. Addition of (2-Hydroxyethyl)trimethylammonium Ions. In order to clarify the effect of another tetraalkylammonium ion, the (2-hydroxyethyl)trimethylammonium ion was employed initially. When the N/Si ratio was varied in a 1.0 mol dm^{-3} SiO$_2$ sample solution, the variation in the silicate-anion distribution indicated a highly selective formation of a silicate framework. As Fig. 4 shows, the low-molecular species decreased, and only the cubic octamer was formed singularly, with an increase in the N/Si ratio.

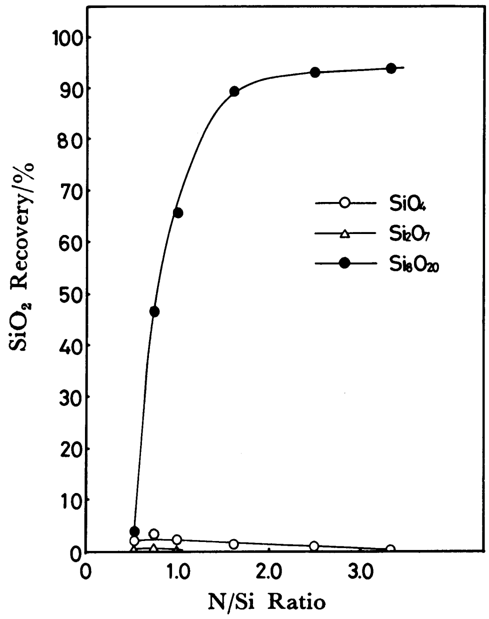

Fig. 4. Variation in the silicate-anion distribution with the N/Si ratio in 1.0 mol dm^{-3} (2-hydroxyethyl)-trimethylammonium silicate solution.

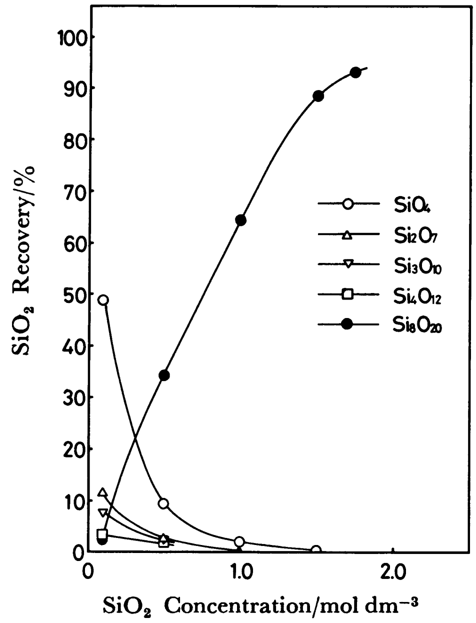

Fig. 5. Variation in the silicate-anion distribution with the SiO$_2$ concentration (N/Si=1.0) in (2-hydroxyethyl)trimethylammonium silicate solution.

The variation in the silicate-anion distribution with the SiO$_2$ concentration at the N/Si ratio of 1.0 is shown in Fig. 5. The cubic octamer was formed singularly at higher SiO$_2$ concentrations, as was previously shown in the case of the addition of the tetramethylammonium ion. In (2-hydroxyethyl)trimethylammonium silicate solutions whose N/Si ratios were 1.0 and 2.0, the singular formation of the cubic octamer in both solutions was confirmed by Scheler et al.[11] using ^{29}Si NMR. Although the SiO$_2$ concentration in this work was different from that in the earlier report, there was yet a pronounced difference in the recovery of the cubic octamer between the N/Si ratios of 1.0 and 2.0. When trimethylsilylation is used as an analytical tool, it is impossible to obtain trimethylsilylated derivatives which reflect the original distribution of the silicate anions completely, as side reactions necessarily occur. Nevertheless, the fact that the cubic octamer was recovered in a yield of ca. 90% means that virtually only the cubic octamer existed.

4. Addition of Benzyltrimethylammonium Ions. The effect of tetraalkylammonium ions with a different alkyl group was investigated by the use of benzyltrimethylammonium ion as well as (2-hydroxyethyl)trimethylammonium ions. Figure 6 shows the variation in the silicate-anion distribution with the N/Si ratio in a 1.0 mol dm^{-3} sample solution, while Fig. 7 shows the variation in the SiO_2 concentration at the N/Si ratio of 1.0. In the two cases, similar tendencies were recognized, and in both, singularly the cubic octamer was also formed. Thus, it was found that benzyltrimethylammonium ions also contributed to the formation of the cubic octamer.

From these results, it was obvious that a tetraalkylammonium ion with three methyl groups could contribute to the selective formation of the cubic octamer, even if one of the four alkyl groups was not a methyl group but was either hydrophilic or hydrophobic.

As for the structure of crystalline tetramethylammonium silicate ($Si_8O_{20}(N(CH_3)_4)_8$), a detailed structure study by means of X-ray diffraction analysis was performed by Smolin et al.[27] It remains obscure, however, how the tetramethylammonium ion contributes to the selective formation of the cubic octamer in an aqueous silicate solution. Also, several investigators have reported that the formation of silicate species with cage-like structures was affected by the structure of the tetraalkylammonium ions.[2-9] As compared with those reports, we ourselves have found that the interaction of silicate anions and tetraalkylammonium ions is not influenced by a bulky group such as the benzyl group during the selective formation and that only three methyl groups are essential for the formation of the cubic octamer, even if the other alkyl group was hydrophilic or hydrophobic. From the results in this study, it was concluded that not all four methyl groups in a tetramethylammonium ion always contribute to the selective structure formation.

The application of the trimethylsilylation technique to the early stages of the hydrolysis of tetraethoxysilane would be useful for a better understanding of this system, which requires further study.

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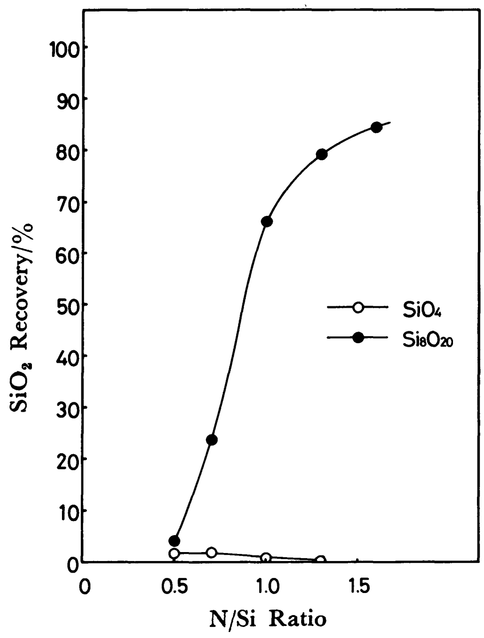

Fig. 6. Variation in the silicate-anion distribution with the N/Si ratio in 1.0 mol dm^{-3} benzyltrimethylammonium silicate solution.

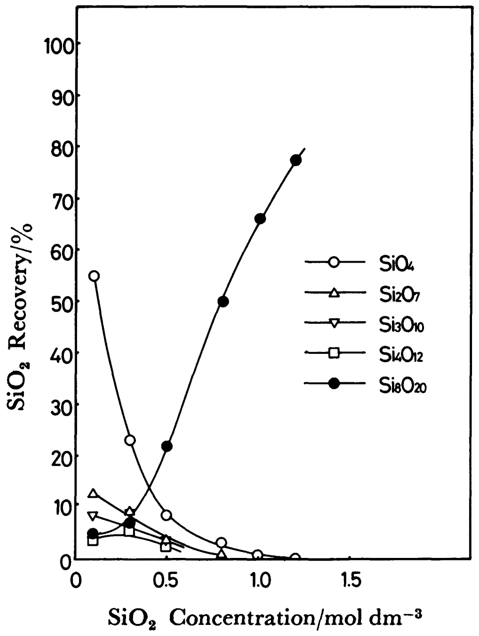

Fig. 7. Variation in the silicate-anion distribution with the SiO_2 concentration (N/Si = 1.0) in benzyltrimethylammonium silicate solution.

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