Formation of $CH_3Si_8O_{19}^{7-}$ Cubic Octameric Anion in (2-Hydroxyethyl)trimethylammonium Silicate Aqueous Solutions Containing Hydrolysis Products of Methyltriethoxysilane

Isao HASEGAWA† and Sumio SAKKA*
Institute for Chemical Research, Kyoto University, Uji 611

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$CH_3Si_8O_{19}^{7-}$, in which a $Si(O^-)_4$ unit in the cubic octameric silicate anion ($Si_8O_{20}^{8-}$) is displaced by a $CH_3Si(O^-)_3$ unit, has been formed in aqueous solutions of mixture of hydrolysis and polycondensation products of tetraethoxysilane and methyltriethoxysilane under the presence of (2-hydroxyethyl)trimethylammonium ions. The ammonium ions have not had any significant effects on polymerization of hydrolysis products of methyltriethoxysilane in aqueous solutions and the polymerization has taken place randomly to form a widespread distribution of the species with various structures. The hydrolysis product, however, has taken part in the formation process of the cubic octameric silicate anion with the aid of the organic ammonium cations, resulting in the formation of $CH_3Si_8O_{19}^{7-}$.

Organic quaternary ammonium ions affect polymerization of silicate anions in solutions to form silicate anions with cage-like structures such as $Si_6O_{15}^{6-}$, $Si_8O_{20}^{8-}$, and $Si_{10}O_{25}^{10-}$.[1,2] For preparing silicate solutions in which such silicate anions are dominantly present, various types of silicon sources can be used, for example, silicic acid sol, silicic acid gel, Aerosil, and tetraalkoxysilane.[3–5] In spite of the uses of these different silicon sources to prepare tetramethylammonium silicate solutions, the cubic octameric silicate anion ($Si_8O_{20}^{8-}$) becomes a dominant species in the solutions, although time for reaching the equilibrium among silicate species in the solutions is different with the type of the silicon sources.

Species having cage-like siloxane backbones can be prepared from trifunctional silanes as well as silicate anions with tetrafunctionality.[6] For example, methylsilsesquioxanes with cage-like structures, $(CH_3)_6Si_6O_9$, $(CH_3)_8Si_8O_{12}$, and $(CH_3)_{10}Si_{10}O_{15}$, can be synthesized by hydrolysis and polymerization of methyltriethoxysilane ($CH_3Si(OC_2H_5)_3$, abbreviated to MTEOS) or pyrolysis of the gel thus formed.[7–9] (Methylsilsesquioxanes are a class of compounds composed of a silicon atom connecting to a methyl group and three oxygen atoms as a structural unit.) In these cases, no addition of organic quaternary ammonium ions is necessary. However, there has been no report on the distribution of hydrolysis and polycondensation products of MTEOS in aqueous solutions containing organic quaternary ammonium ions.

In this study, it is aimed to explore the effect of organic quaternary ammonium ions on polymerization of hydrolysis products of MTEOS and that of mixture of hydrolysis products of tetraethoxysilane ($Si(OC_2H_5)_4$, TEOS) and MTEOS in aqueous solutions. At first, the structures and the distribution of hydrolysis and polycondensation products of MTEOS in aqueous solutions containing (2-hydroxyethyl)trimethylammonium ions have been investigated. The organic quaternary ammonium ions were reported to be effective in the selective formation of the cubic octameric silicate anion.[10,11] Then, in order to elucidate whether the species with the cubic octameric structure consisting both of $CH_3Si(O^-)_3$ and $Si(O^-)_4$ units are formed or not, the structures and the distribution of species formed by hydrolysis and polycondensation of TEOS and MTEOS in aqueous solutions containing (2-hydroxyethyl)trimethylammonium ions have been examined. Trimethylsilylation by the method of Lentz[12] has been employed for the investigations.

Experimental

Materials. Methyltriethoxysilane, tetraethoxysilane, 50% (2-hydroxyethyl)trimethylammonium hydroxide aqueous solution, concd hydrochloric acid, and 2-propanol were of reagent grade. Hexamethyldisiloxane was used after a single distillation (bp 100.0—100.5°C).

Preparation of Solutions. A given amount of MTEOS was added to a (2-hydroxyethyl)trimethylammonium hydroxide aqueous solution whose concentration had been adjusted by adding deionized water to 50% (2-hydroxyethyl)trimethylammonium hydroxide aqueous solution. The mixture was stirred for 2 days at room temperature to hydrolyze MTEOS completely and obtain a homogeneous solution. In this manner, aqueous solutions of hydrolysis and polycondensation products of MTEOS containing (2-hydroxyethyl)trimethylammonium ions were prepared, whose Si concentration ranged from 0.1 to 2.34 mol dm^{-3} and N/Si ratio (molar ratio of (2-hydroxyethyl)trimethylammonium ions to silicon) was fixed at 1.0.

Aqueous solutions of mixture of hydrolysis and polycondensation products of TEOS and MTEOS containing (2-hydroxyethyl)trimethylammonium ions were prepared by adding TEOS and MTEOS to (2-hydroxyethyl)trimethylammonium hydroxide aqueous solutions. An N/Si ratio of the solutions was kept constant at 1.0. The total Si concentration, that is, the sum of concentrations of silicon atoms in species formed from TEOS and MTEOS, was fixed

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† Present address: The Institute of Physical and Chemical Research, 2-1, Hirosawa, Wako 351-01.

at 1.5 mol dm^{-3}. The molar ratio of TEOS and MTEOS denoted as the TEOS/(MTEOS+TEOS) ratio ranged from 0.25 to 0.75.

Analytical Procedure. The structures of species present in the solutions were examined by the trimethylsilylation technique combined with a gas-liquid chromatography. The method of Lentz[12] was adopted for the trimethylsilylation. It has been reported that the method of Lentz is most favorable for trimethylsilylation of silicate solutions[13] and is applicable for trimethylsilylation of hydrolysis and polycondensation products of MTEOS in solutions.[14] Peaks which appear on gas chromatograms were identified based on combined gas chromatograph-mass spectrometry. Quantitative analysis was performed for $CH_3SiO_3^{3-}$, SiO_4^{4-}, $Si_2O_7^{6-}$, and $Si_8O_{20}^{8-}$ using tetradecane as an internal standard. Since trimethylsilylated derivatives of the other species could not be obtained in a pure state, the distribution of species in the solutions is expressed in terms of percentages of total peak area on a gas chromatogram. The experimental conditions for the trimethylsilylation, gas-liquid chromatography, and gas chromatograph-mass spectrometry were the same as those described previously.[11,14]

Results and Discussion

1. Constitution of Hydrolysis and Polycondensation Products of MTEOS in the Aqueous Solutions Containing (2-hydroxyethyl)trimethylammonium Ions. Figure 1 shows the gas chromatogram of trimethylsilylated derivatives obtained from an aqueous solution of hydrolysis and polycondensation products of MTEOS containing (2-hydroxyethyl)trimethylammonium ions at an N/Si ratio of 1.0 and a Si concentration of 1.5 mol dm^{-3}. On the basis of the previous study,[15] assignment of the peaks is given in the figure caption. The presence of 11 kinds of hydrolysis and polycondensation products of MTEOS is found in the solution.

The variations with the Si concentration in the peak area ratios of the trimethylsilylated derivatives of hydrolysis and polycondensation products of MTEOS and the recovery of monomer ($CH_3SiO_3^{3-}$) in the aqueous solutions containing (2-hydroxyethyl)trimethylammonium ions at an N/Si ratio of 1.0 are shown in Fig. 2. The values of peak area ratios of the compounds corresponding to peaks c, f, g, i, j, and k are all under 4.0% at the maximum and so plots of these compounds are omitted from the figure.

The recovery of methylsilanetriol decreases and the peak area ratios of trimers and the higher molecular weight species increase with increasing Si concentration. The peak area ratio of the dimer increases with the increment of Si concentration up to 1.0 mol dm^{-3}, then decreases. These facts indicate that the polymerization proceeds with the rise in the Si concentration. The values of peak area ratio of each hydrolysis and polycondensation product of MTEOS and the recovery of monomer in the aqueous solutions containing (2-hydroxyethyl)trimethylammonium ions at an N/Si ratio of 1.0 and a certain Si concentration are almost the same as those in the aqueous solutions containing sodium ions at the same cation-to-silicon molar ratio and the same Si concentration.[16] This means that the variety of coexisting cations does not make any significant difference in the process of polymerization of hydrolysis products of MTEOS in aqueous solutions.

It was reported that $(CH_3)_8Si_8O_{12}$, which has the

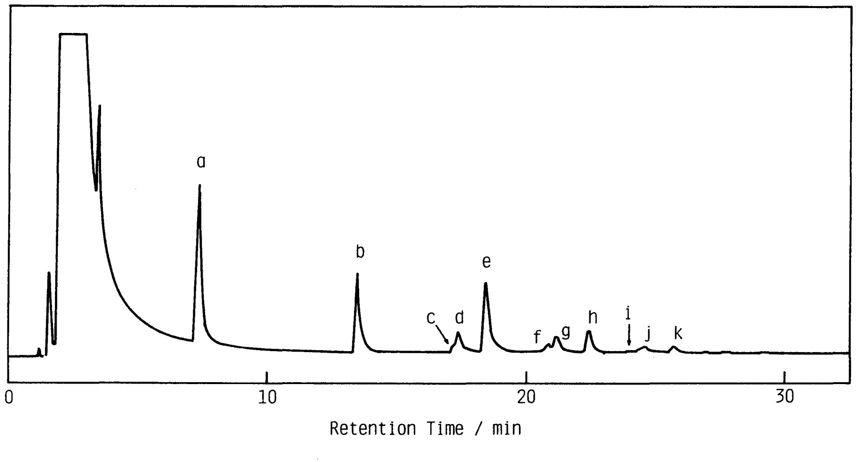

Fig. 1. Gas chromatogram of the trimethylsilylated derivatives obtained from an aqueous solution of hydrolysis and polycondensation products of methyltriethoxysilane under the presence of (2-hydroxyethyl)trimethylammonium ions at an N/Si ratio of 1.0 and a Si concentration of 1.5 mol dm^{-3}. Peaks correspond to (a) $CH_3SiO_3[Si(CH_3)_3]_3$, (b) $(CH_3)_2Si_2O_5[Si(CH_3)_3]_4$, (c) $(CH_3)_4Si_4O_8[Si(CH_3)_3]_4$ (isomer 1), (d) $(CH_3)_4Si_4O_8[Si(CH_3)_3]_4$ (isomer 2), (e) $(CH_3)_3Si_3O_7[Si(CH_3)_3]_5$, (f) $(CH_3)_5Si_5O_{10}[Si(CH_3)_3]_5$ (isomer 1), (g) $(CH_3)_5Si_5O_{10}[Si(CH_3)_3]_5$ (isomer 2), (h) $(CH_3)_4Si_4O_9[Si(CH_3)_3]_6$, (i) $(CH_3)_6Si_6O_{12}[Si(CH_3)_3]_6$ (isomer 1), (j) $(CH_3)_6Si_6O_{12}[Si(CH_3)_3]_6$ (isomer 2), and (k) $(CH_3)_5Si_5O_{11}[Si(CH_3)_3]_7$.

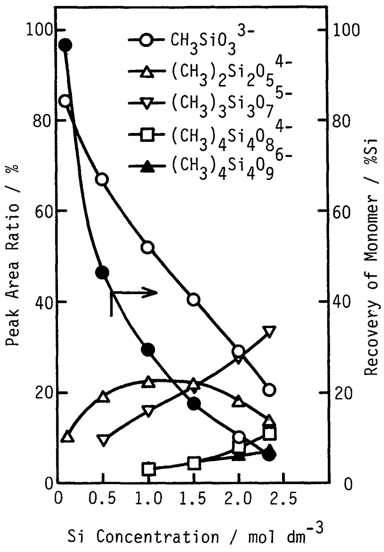

Fig. 2. Variations with the Si concentration in the peak area ratios of the trimethylsilylated derivatives of hydrolysis and polycondensation products of methyltriethoxysilane and the recovery of monomer in the aqueous solutions containing (2-hydroxyethyl)trimethylammonium ions at an N/Si ratio of 1.0.

cubic octameric siloxane structure, was formed as a result of hydrolysis and polymerization of MTEOS,[7–9] indicating that the cubic octameric structure can be constructed only with $CH_3Si(O^-)_3$ units. It was also reported that the silicate anion of $Si_8O_{20}^{8-}$ became a dominant species at increased Si concentrations in (2-hydroxyethyl)trimethylammonium silicate aqueous solutions at an N/Si ratio of 1.0.[5] From the present study, however, it can be stated that $(CH_3)_8Si_8O_{12}$ is not formed and also a species with a specific structure is not formed selectively in aqueous solutions of hydrolysis and polycondensation products of MTEOS under the presence of (2-hydroxyethyl)trimethylammonium ions. One of the reasons for the absence of $(CH_3)_8Si_8O_{12}$ in the present system is the difference in the reaction conditions. In the present aqueous system, there is enough water to hydrolyze MTEOS completely, resulting in the random polymerization with a widespread distribution of the hydrolysis and polycondensation products of different structures. In the systems, in which $(CH_3)_8Si_8O_{12}$ is obtained, an organic solvent like benzene or methanol is used and the amount of water added for the hydrolysis is relatively small. It appears that the amount of water would control the degree of hydrolysis of MTEOS, and polymerization behavior of the hydrolysis products as well.

It is obscure at present how the interaction between organic quaternary ammonium ions and silicate anions occurs during the selective formation of the $Si_8O_{20}^{8-}$ silicate anion. From the facts described above, however, the tetrafunctionality of silane would be required for the selective structure formation with the aid of organic quaternary ammonium ions.

2. Constitution of Species Present in Aqueous Solutions of Mixture of Hydrolysis and Polycondensation Products of TEOS and MTEOS under the Presence of (2-Hydroxyethyl)trimethylammonium Ions.

Figure 3 shows the gas chromatogram of trimethylsilylated derivatives obtained from an aqueous solution of mixture of hydrolysis and polycondensation products of TEOS and MTEOS under the presence of (2-hydroxyethyl)trimethylammonium ions at an N/Si ratio of 1.0 and a total Si concentration of 1.5 mol dm^{-3}. The M-15 peak, which is due to the loss of a methyl radical from the molecular ion, is characteristic on every mass spectrum of compounds due to the

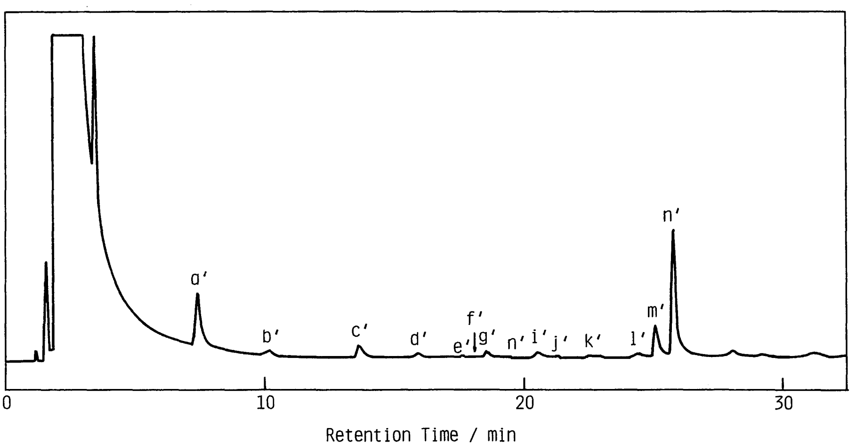

Fig. 3. Gas chromatogram of the trimethylsilylated derivatives obtained from an aqueous solution of mixture of hydrolysis and polycondensation products of tetraethoxysilane and methyltriethoxysilane under the presence of (2-hydroxyethyl)trimethylammonium ions at an N/Si ratio of 1.0, a total Si concentration of 1.5 mol dm^{-3}, and a TEOS/(MTEOS+TEOS) ratio of 0.75.

Table 1. Assignment of the Peaks on the Gas Chromatogram Shown in Fig. 3

Peak	Formula	Molecular weight
a′	$CH_3SiO_3[Si(CH_3)_3]_3$	310
b′	$SiO_4[Si(CH_3)_3]_4$	384
c′	$(CH_3)_2Si_2O_5[Si(CH_3)_3]_4$	458
d′	$CH_3Si_2O_6[Si(CH_3)_3]_5$	532
e′	$(CH_3)_4Si_4O_8[Si(CH_3)_3]_4$	592
f′	$Si_2O_7[Si(CH_3)_3]_6$	606
g′	$(CH_3)_3Si_3O_7[Si(CH_3)_3]_5$	606
h′	$Si_3O_9[Si(CH_3)_3]_6$	666
i′	$(CH_3)_2Si_3O_8[Si(CH_3)_3]_6$	680
j′	$(CH_3)_5Si_5O_{10}[Si(CH_3)_3]_5$	740
k′	$CH_3Si_4O_{11}[Si(CH_3)_3]_7$	814
l′	Unknown	
m′	$CH_3Si_8O_{19}[Si(CH_3)_3]_7$	1054
n′	$Si_8O_{20}[Si(CH_3)_3]_8$	1128

peaks on the gas chromatogram, which is significant for the identification of trimethylsilylated derivatives of silicates and hydrolysis and polycondensation products of MTEOS.[14–16] Species which have the same molecular weight have been identified on the basis of their retention times on the gas chromatograms. The assignments are shown in Table 1. Copolymerization products formed from TEOS and MTEOS, which correspond to peaks d′, i′, k′, and m′, are seen to be present together with species consisting of $CH_3Si(O^-)_3$ or $Si(O^-)_4$ units solely.

It should be noted that $CH_3Si_8O_{19}{}^{7-}$ corresponding to peak m′ is formed in the solution. When a trimethylsiloxyl group on a silicon compound is substituted for a methyl group, a retention time of the methyl-substituted compound on a gas chromatogram becomes shorter than that of the original one, as can be seen, for example, in the case of $CH_3Si[OSi(CH_3)_3]_3$ (peak a′) and $Si[OSi(CH_3)_3]_4$ (peak b′) on Fig. 3. From this fact and its molecular weight, it is considered that this compound has a structure in which a $Si(O^-)_4$ unit in the cubic octameric silicate anion is substituted for a $CH_3Si(O^-)_3$ unit. As described above, hydrolysis and polycondensation products of MTEOS can not be converted into the cubic octameric structure in aqueous solutions even if (2-hydroxyethyl)trimethylammonium ions are present. It appears, however, that $CH_3Si(O^-)_3$ units can be incorporated into the structure consisting mainly of $Si(O^-)_4$ units.

Figure 4 shows the variation with the TEOS/(MTEOS+TEOS) ratio in the peak area ratios of species in aqueous solutions of mixture of hydrolysis and polycondensation products of TEOS and MTEOS under the presence of (2-hydroxyethyl)trimethylammonium ions at an N/Si ratio of 1.0 and a total Si concentration of 1.5 mol dm^{-3}. Species whose values of peak area ratios are less than 6% at the maximum are not shown in the figure.

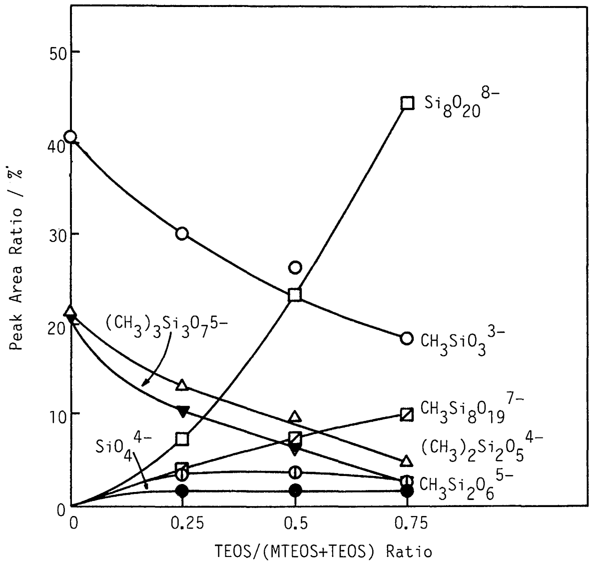

Fig. 4. Variation with the TEOS/(MTEOS+TEOS) ratio in the peak area ratios of hydrolysis and polycondensation products of tetraethoxysilane and methyltriethoxysilane in the aqueous solutions containing (2-hydroxyethyl)trimethylammonium ions at an N/Si ratio of 1.0 and a total Si concentration of 1.5 mol dm^{-3}.

Among species consisting only of $CH_3Si(O^-)_3$ units, low-molecular weight species, such as the monomer and dimer, are dominant. Peak area ratios of the low-molecular weight species decrease with increasing TEOS/(MTEOS+TEOS) ratio. This is not ascribed to the fact that polymerization of hydrolysis products of MTEOS proceeds with the rise in the ratio. Because peak area ratios of the higher molecular weight species, which are not shown in the figure, also decrease with increasing ratio. It is considered that the decrease is caused by low concentrations of hydrolysis and polycondensation products of MTEOS in the solutions at increased ratios, since smaller amounts of MTEOS have been added for preparing the solutions at higher TEOS/(MTEOS+TEOS) ratios. The degree of polymerization of hydrolysis products of MTEOS does not increase in aqueous solutions even at high Si concentrations, as described in the former part of this paper.

Values of recoveries of silicate anions in the solutions, calculated on the basis of the amount of TEOS used for the preparation, are shown in Table 2. Among low-molecular weight silicate species, the amount of monomer is very small. The dimer is formed just in a trace scale at every TEOS/(MTEOS+TEOS) ratio. Linear trimeric and cyclic tetrameric silicate anions are not seen in the solutions. These facts indicate that low-molecular weight silicate species are scarcely present in the solutions. On the other hand, the amount of $Si_8O_{20}{}^{8-}$ formed is very large compared with those of other silicate species. With the increase of the TEOS/(MTEOS+TEOS)

Table 2. Recoveries of Silicate Anions at Various TEOS/(MTEOS+TEOS) Ratios in Aqueous Solutions of Hydrolysis and Polycondensation Products of TEOS and MTEOS Containing (2-hydroxyethyl)trimethylammonium Ions at an N/Si Ratio of 1.0 and a Total Si Concentration of 1.5 mol dm^{-3} (The values of the recoveries have been calculated from the amount of TEOS used for preparing the solutions)

TEOS/(MTEOS+TEOS) Ratio	Recovery/%		
	SiO_4^{4-}	$Si_2O_7^{6-}$	$Si_8O_{20}^{8-}$
0.25	2.3	Trace	46.6
0.5	1.1	Trace	63.7
0.75	0.6	Trace	69.3

ratio, the amount of $Si_8O_{20}^{8-}$ formed increases, which would be due to the increase of amount of TEOS and, correspondingly, the decrease of amount of MTEOS added as silicon sources for preparing the solutions at higher ratios. It is noteworthy that 46.6% of TEOS added as a Si source are present in the form of $Si_8O_{20}^{8-}$ even in a solution at a TEOS/(MTEOS+TEOS) ratio of 0.25. This fact indicates that formation of $Si_8O_{20}^{8-}$ with the aid of (2-hydroxyethyl)trimethylammonium ions occurs selectively even when relatively large amount of hydrolysis and polycondensation products of MTEOS, whose reaction behavior is not influenced by the presence of the organic quaternary ammonium ion, is present together with silicate anions. In addition, the formation of $CH_3Si_8O_{19}^{7-}$ in the present system would suggest that silicate species, which are constructed into the cubic octameric structure without any interactions with the ammonium ions, may be present when the singular formation of $Si_8O_{20}^{8-}$ takes place in (2-hydroxyethyl)trimethylammonium silicate solutions.

The amount of $CH_3Si_8O_{19}^{7-}$ formed also increases with increasing TEOS/(MTEOS+TEOS) ratio. In other words, the amount of $CH_3Si_8O_{19}^{7-}$ increases with the increase of amount of $Si_8O_{20}^{8-}$. This fact suggests that there is no selectivity on the formation of $CH_3Si_8O_{19}^{7-}$ and the species would be formed in the course of the formation of $Si_8O_{20}^{8-}$ by the incorporation of hydrolysis products of MTEOS into polymerization of silicate species affected by (2-hydroxyethyl)-trimethylammonium ions.

Co-hydrolysis of TEOS and MTEOS in aqueous solutions containing the organic quaternary ammonium ions appears to be an easy way to obtain the $CH_3Si_8O_{19}^{7-}$ cubic octameric anion. As the formation of aluminum or germanium substituted silicate cages in tetramethylammonium alumino- or germanosilicate solutions has also been reported,[1,17] it can be expected that various types of partially substituted silicate species having cage-like structures are synthesized by adding substituents to organic quaternary ammonium silicate solutions while the reaction of silicate structure formation proceeds.

Conclusions

Random polymerization of hydrolysis products of MTEOS has taken place in aqueous solutions containing (2-hydroxyethyl)trimethylammonium ions. The reaction behavior has been almost the same as that seen in the solutions containing sodium ions, suggesting that the variety of coexisting cations hardly influences polymerization of the hydrolysis products. By co-hydrolyzing TEOS and MTEOS in aqueous solutions under the presence of (2-hydroxyethyl)trimethylammonium ions, however, $CH_3Si_8O_{19}^{7-}$ in which a $Si(O^-)_4$ unit of the $Si_8O_{20}^{8-}$ silicate anion is displaced by a $CH_3Si(O^-)_3$ unit has been formed, which would have been formed by the incorporation of hydrolysis products of MTEOS in the process of polymerization of silicate anions for the formation of $Si_8O_{20}^{8-}$.

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