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Rapid Solidification of (2-Hydroxyethyl)trimethylammonium Silicate

Isao HASEGAWA[†] and Sumio SAKKA[*]
Institute for Chemical Research, Kyoto University, Uji, Kyoto 611
[†]Division of Molecular Engineering, Graduate School of Engineering,
Kyoto University, Sakyo-ku, Kyoto 606

A large amount of solids of (2-hydroxyethyl)trimethylammonium silicate, whose silicate skeleton has the double four-membered ring structure, was abruptly separated out from the mixed solution of (2-hydroxyethyl)trimethylammonium hydroxide aqueous solution and tetraethoxysilane after a few hours of stirring.

In the aqueous silicate solutions containing organic quaternary ammonium ions, random polymerization of silicate anions is suppressed and the anions with specific cage-like structures are formed selectively.[1-8] These structure-controlled silicate anions are expected to be precursors for the syntheses of inorganic polymers with controlled structures in their silicate skeletons, such as zeolites. In order to utilize such silicates as starting materials, it will be necessary to obtain the silicates not only in the dissolved state but also in the solid state, since the yield of the cubic octamer in the aqueous solution decreases with decreasing SiO_2 concentration,[3,6] that is, by dilution and by the coexistence of alkali metal cations.[8-10] It is possible to obtain such silicates as solids by evaporation to dryness of the organic quaternary ammonium silicate aqueous solutions, but that is a time consuming process and, in addition, a problem of impurity arises.

The (2-hydroxyethyl)trimethylammonium ion ($N^+(CH_3)_3C_2H_4OH$) is known to contribute to the selective structure formation of the octameric silicate anion with a double four-membered ring ($Si_8O_{20}{}^{8-}$, cubic octamer)[4,6] as well as the tetramethylammonium ion ($N^+(CH_3)_4$).[3,6-8] So far, however, studies on the formation of the cubic octamer were limited to the dissolved states of the silicate species in aqueous solutions. The study of the solidification and the solid state would be important for the use of the cubic octamer as a starting material for further syntheses of silica-based materials. However, the solidification of such silicates have not been studied.

This paper presents results of preliminary studies on the rapid solidification of (2-hydroxyethyl)trimethylammonium silicate from the solution. The mixture in which the cation-to-silica molar ratio was 1.0 and the SiO_2 concentration was 2.22 mol kg^{-1} was prepared by adding tetraethoxysilane as a silica source to 50% (2-hydroxyethyl)trimethylammonium hydroxide aqueous solution as a source of the organic cation. At the beginning, the mixture was constituted of two layers, a layer of organic solution consisting of tetraethoxysilane and a layer of aqueous

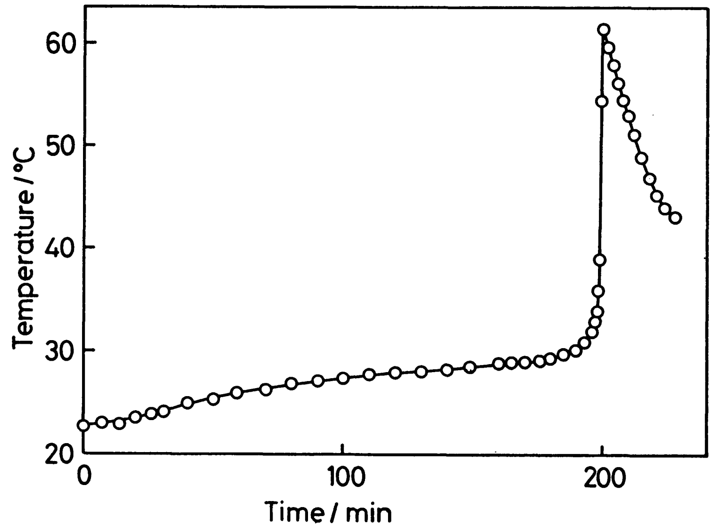

Fig. 1.
Variation of the temperature of the mixture of (2-hydroxyethyl)-trimethylammonium aqueous solution and tetraethoxysilane with time.

solution consisting of (2-hydroxyethyl)trimethylammonium hydroxide. Then the mixture was stirred vigorously for a few hours.

Figure 1 shows the dependence of the temperature of the solution on the stirring time. The exothermal reaction starts at ca. 29 °C. The solution which has been heterogeneous at the beginning becomes homogeneous just when the temperature of the solution reaches a maximum.

During lowering of the temperature, solids begin to separate out in the solution and the whole solution solidifies into wet powder when the temperature drops to 44 °C. X-Ray diffraction pattern of the powder which has been kept standing in a desiccator for dryness is shown in Fig. 2. (The chemical shift is shown relative to tetramethylsilane.) The intensities of the peaks are weak, which might be due to low crystallinity. However, on the solid-state ^{29}Si magic-angle-spinning NMR spectrum, shown in Fig. 3, only one sharp peak appears at -98.74 ppm, that is assigned to the silicate building unit of the branching group. The value of the chemical shift is in good agreement with that of tetramethylammonium silicate, $Si_8O_{20}(N(CH_3)_4)_8$, which has the double four-membered ring structure in the silicate skeleton (-97.7 or -99.3 ppm) reported by Lippmaa et al.[11,12] Moreover, after trimethylsilylation of this solid by the method of Götz and Masson,[13] in which the mixture of chlorotrimethylsilane, hexamethyldisiloxane and 2-propanol was used as the trimethylsilylating reagent, the product was analyzed with gas-liquid chromatography. One large peak appears on the gas chromatogram, which is assigned to $Si_8O_{20}(Si(CH_3)_3)_8$. These indicate that the silicate solid consists of only cubic octameric structures.

The quantitative analysis was performed on the distribution of silicate anions in the solution by the trimethylsilylation combined with gas-liquid chromatography when the solution became homogeneous at the maximum temperature. In this silylation, the method of Lentz[14] was adopted, in which the mixture of conc. hydrochloric acid, water, 2-propanol and hexamethyldisiloxane was used as the trimethylsilylating reagent. It has been confirmed that the Lentz method for the trimethylsilylation of silicate species in solutions gives most reliable way of

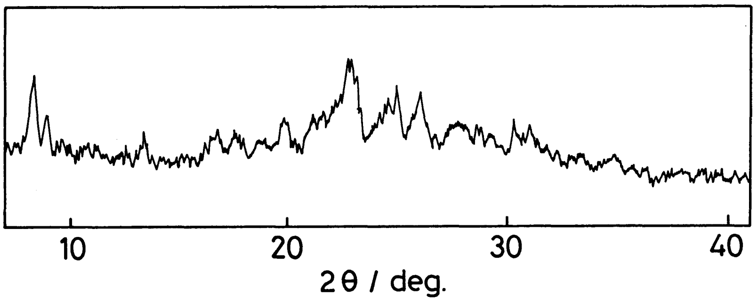

Fig. 2.
X-Ray diffraction pattern of (2-hydroxyethyl)trimethylammonium silicate.

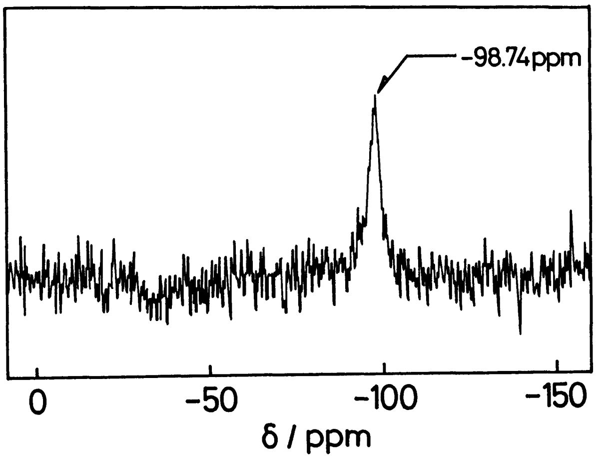

Fig. 3.
Solid-state ^{29}Si magic-angle-spinning NMR spectrum of (2-hydroxyethyl)-trimethylammonium silicate.

trimethylsilylation of low-molecular weight as well as higher molecular weight silicate species.[15-17] The recovery of monomer is 0.2% and that of the cubic octamer is 10.3%. The other low-molecular weight species are not recovered from the solution. These findings mean that the silicate anions in the solution should be present as higher molecular weight species than the cubic octamer at the maximum temperature and that the singular formation of the cubic octamer occurs very abruptly together with the solidification when the temperature of the solution drops from 61 °C to 44 °C since the solids precipitating from the solution consist of only the $Si_8O_{20}{}^{8-}$ silicate structures.

The abrupt formation of the cubic octamer in the present study appears not to be consistent with the result of Knight et al.[18] They indicated that on heating 1.0 mol dm^{-3} tetramethylammonium silicate solution at the Si:N(CH$_3$)$_4$ ratio of 1:2 to boiling, the cubic octamer, which was the dominant species present in the solution before heating, disappeared and then an equilibrium was established after several weeks on keeping the solution at room temperature. The formation of the cubic octamer in this study takes place abruptly during the deposition of the solid. Therefore, it is considered that a small amount of the cubic octamer found in the homogeneous solution at the maximum heating temperature might act as seeds for the solidification of the cubic octamer upon cooling.

In addition, the distribution of silicate anions in (2-hydroxyethyl)trimethylammonium silicate aqueous solution with different SiO$_2$ concentration at the cation-to-silica molar ratio of 1.0 was reported[6] and the recovery of the cubic octamer was ca. 93% in the (2-hydroxyethyl)trimethylammonium silicate solution with the cation-to-silica molar ratio of 1.0 and the SiO_2 concentration of 1.75 mol dm^{-3}. This fact suggests that the recovery of the cubic octamer in the homogeneous solution at the maximum temperature is too low to explain its high SiO_2 concentration. Ray and Plaisted[19)] reported that the recovery of the cubic octamer in 1.0 mol dm^{-3} tetramethylammonium silicate solution at the $SiO_2/[N(CH_3)_4]_2O$ molar ratio of 3.0 decreased with a rise of temperature and practically disappeared above 50 °C. This indicates that the low recovery of the cubic octamer in the homogeneous solution should be attributed to high temperature of the solution when the solution becomes homogeneous.

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