^{27}Al NMR Study on the Interaction between Aluminate and Silicate Ions in Alkaline Solution

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Synopsis. An interaction between aluminate and silicate ions in highly alkaline solution was investigated by a high-resolution ^{27}Al NMR study. The interaction greatly varied with alkali concentration, and did not occur at 1.0 mol dm^{-3} NaOH. At 0.10 mol dm^{-3} NaOH, the formation of a monomeric species with an ≡Al–O–Si≡ bond (Si/Al=1) was suggested and the formation constant was estimated to be 22.8 dm^3 mol^{-1}. At 0.015 mol dm^{-3} NaOH, polynuclear species with ≡Al–O–Si≡ bond was expected to be formed.

An important advantage of ^{27}Al is its 100% isotopic abundance, which makes ^{27}Al NMR a very sensitive probe. Much work has been reported on the environment of Al atoms in solid aluminosilicates, while little has been published on the characterization of solutions containing aluminosilicates or aluminate and silicate ions by the ^{27}Al NMR technique. Mueller et al.[1)] observed four resonance lines of ^{27}Al NMR for tetramethylammonium aluminosilicate solutions of different molar ratios of Si and Al and assigned their lines to four kinds of monomeric AlO$_4$ tetrahedrons bonded to zero, one, two, and three silicon atoms, respectively. Glasser and Harvey[2)] reported that for a given alkali–silicate–aluminate composition, the distribution of aluminium between uncomplexed aluminate and aluminosilicate complexes may vary with the cation present.

In this work an interaction between aluminate and silicate ions in strongly alkaline solutions was studied by a high-resolution ^{27}Al NMR.

Experimental

Sample and Reagents. All the reagents used were of analytical reagent grade. The sodium silicate solution (10^{-2} mol dm^{-3} Si) was prepared by dissolving silica gel in sodium hydroxide solution. The silicon concentration in the solution was determined spectrophotometrically. The sodium aluminate solution (10^{-2} mol dm^{-3} Al) was prepared by dissolving $AlCl_3\cdot 6H_2O$ in sodium hydroxide solution. The aluminium concentration was standardized by EDTA titration.

Sample solutions with various molar ratios of Si and Al (Si/Al) up to 5 were prepared by mixing aluminate and silicate solutions. The aluminium concentration was fixed at 10^{-3} mol dm^{-3} and the sodium hydroxide concentration was adjusted to (a) 1.0, (b) 0.10, and (c) 0.015 mol dm^{-3}, respectively.

^{27}Al NMR Measurement. The ^{27}Al NMR spectra were recorded at 52 MHz on a JEOL FX-200 spectrometer. The sample solution was placed in a glass tube of 15 mm diameter. An aqueous $AlCl_3$ solution enclosed in a glass tube of 1 mm diameter was used as an external standard. The $AlCl_3$ solution (10^{-1} mol dm^{-3} Al) was prepared by dissolving $AlCl_3\cdot 6H_2O$ in 1 mol dm^{-3} hydrochloric acid. The D_2O concentration in the standard and sample solutions was ca. 40% to operate the field frequency lock. NMR measurements were carried out at room temperature after allowing the sample solution to stand more than 24 h.

Results and Discussion

System (a) (1.0 mol dm^{-3} NaOH). The ^{27}Al NMR allows a clear distinction between AlO$_6$ octahedral and AlO$_4$ tetrahedral sites in aluminium-oxygen compounds. An ^{27}Al NMR spectrum of the sample solution (Si/Al=0) is shown in Fig. 1. The peak on the right is due to standard $[Al(H_2O)_6]^{3+}$ (Octahedral) and peak on the left (denotes as peak X) is due to the sample solution. The chemical shift (ppm) and the intensity of peak X were determined relative to the peak of standard $[Al(H_2O)_6]^{3+}$. The positive sign of the chemical shift denotes a downfield shift. The chemical shift of the peak X is 80.2 ppm and the signal is typical of monomeric $[Al(OH)_4]^-$ anions.[3)]

In the spectra of the sample solutions of different Si/Al ratios, the peak X always appeared at 80.2 ppm. Moreover, the relative intensity of peak X, defined as follows, was unity independent of the Si/Al ratio:

$$RI = (A_X/A_s)/(A_0/A_s)$$

where A_x is the area of peak X, A_0 is the peak area for $[Al(OH)_4]^-$ (Si/Al=0), and A_s is the peak area for $[Al(H_2O)_6]^{3+}$. These facts indicate that no interaction between aluminate and silicate ions occurs, because of the high alkali concentration.

System (b) (0.10 mol dm^{-3} NaOH). The ^{27}Al NMR spectra did not change for several days after preparation of the sample solutions, indicating that an equilibrium was rapidly achieved in the system (b). Peak X of the sample solution (Si/Al>0) shifted

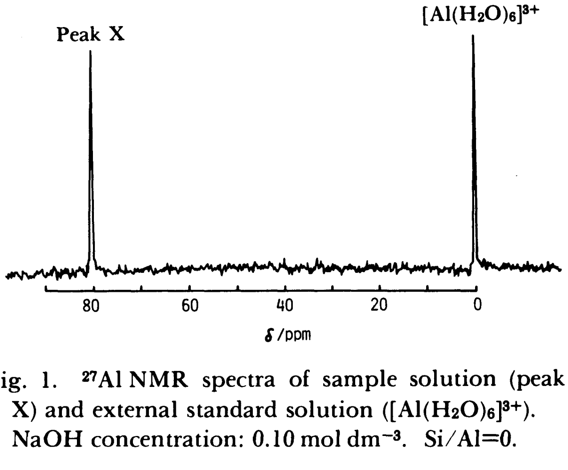

Fig. 1. ^{27}Al NMR spectra of sample solution (peak X) and external standard solution ($[Al(H_2O)_6]^{3+}$). NaOH concentration: 0.10 mol dm^{-3}. Si/Al=0.

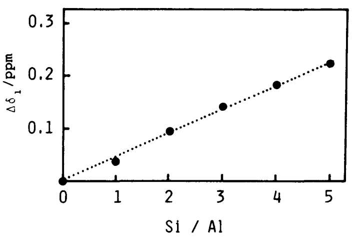

Fig. 2. Variation of chemical shift ($\Delta\delta_1$) with Si/Al ratio.
NaOH concentration: 0.10 mol dm^{-3}.

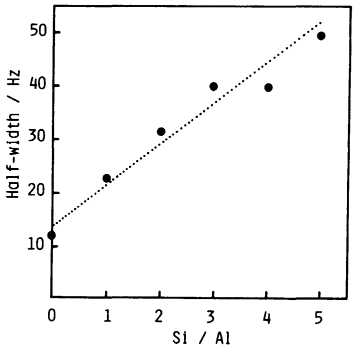

Fig. 3. Variation of half-width of peak X with Si/Al ratio.
NaOH concentration: 0.1 mol dm^{-3}.

slightly toward higher field from the peak of $[Al(OH)_4]^-$. The chemical shift difference between the peak X and the peak of $[Al(OH)_4]^-$, $\Delta\delta_1$, increased with increasing Si/Al ratio. Figure 2 shows the variation of $\Delta\delta_1$ with the Si/Al ratio. The half-width for peak X also increased with increasing Si/Al ratio, as shown in Fig. 3.

The electron donating property of the substituent to aluminium is a major factor in determining the chemical shift. The ^{27}Al upfield shift is due to the increased overall electron density of aluminium. The increase in the half-width of the peak X with increasing Si/Al ratio resulted from an increment of tetrahedrally coordinated aluminium atoms with low symmetry compared with the $[Al(OH)_4]^-$ tetrahedron. Consequently, the formation of species with an ≡Al-O-Si≡ bond was suggested. The relative intensity of peak X was unity regardless of the difference in the Si/Al ratio, indicating that all the aluminium was detected.

It seems reasonable that the species formed is assumed to be a 1:1 complex of aluminium and silicate (Si/Al=1) since the alkali concentration is high, the Al and Si concentrations are relatively low, and the $\Delta\delta_1$ values are small. Considering only a 1:1 complex formation, the reaction can be written as follows:

$$A + L \rightleftarrows AL \tag{1}$$

where A is aluminate ion, L is silicate ion, and AL is a 1:1 complex. The formation constant of AL, K, is

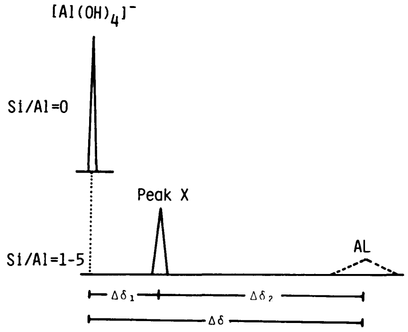

Fig. 4. Chemical shift profile in the system (b).
Peak A and Peak X can be observed, while peak AL is hypothetical one.

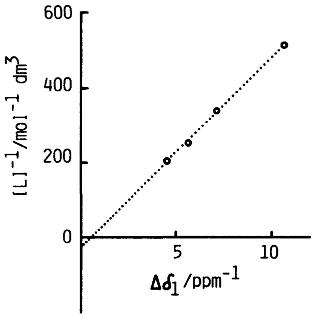

Fig. 5. Plot of $1/[L]$ against $1/\Delta\delta_1$.

represented by Eq. 2.

$$K = [AL]/[A]\cdot[L] \tag{2}$$

When an exchange rate between A and AL is rapid on the NMR time scale, the following relations can be valid.

$$\Delta\delta_1 : \Delta\delta_2 = [AL] : [A] \tag{3}$$

$$\Delta\delta = \Delta\delta_1 + \Delta\delta_2 \tag{4}$$

$\Delta\delta_2$ and $\Delta\delta$ are the chemical shift difference between peak X and peak AL and between peak A and peak AL, respectively (Fig. 4). From these equations, a following equation can be derived.

$$1/[L] = K\cdot\Delta\delta/\Delta\delta_1 - K \tag{5}$$

Since $\Delta\delta_1$ values were small, it can be considered that K is small and $[L]\simeq[L^*]$, ($[L]$: the concentration of free Si at equilibrium, $[L^*]$: total concentration of Si). K and $\Delta\delta$ values were determined by a succesive approximation method. A plot of $1/[L]$ against $1/\Delta\delta_1$ is shown in Fig. 5. The plot gave a straight line and the correlation coefficient was 0.999. From the intersection and the slope of this line, K and $\Delta\delta$ values were calculated to be 22.8 (dm^3 mol^{-1}) and 2.2 (ppm), respectively.

On the other hand, the half-width for peak X, W_X, can be represented by Eq. 6, where W_A and W_{AL} denote the half-width for peak A and peak AL, respectively.

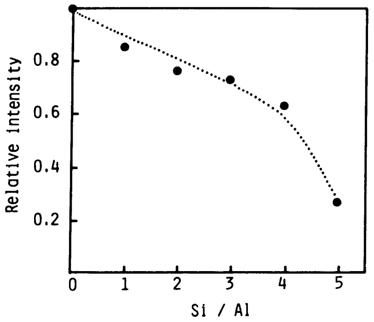

Fig. 6. Variation of the relative intensity for peak X with Si/Al ratio.
NaOH concentration: 0.015 mol dm^{-3}.

$$W_X = W_A \cdot [A]/([A] + [AL]) + W_{AL} \cdot [AL]/([A] + [AL]) \qquad (6)$$

From Eqs. 2 and 6

$$W_{AL} = (W_X - W_A)/(K[L]) + W_X \qquad (7)$$

The half-width of peak AL was calculated to be about 400 Hz, putting W_A, K, W_X, and [L] values in Eq. 7.

When the sample solution of Si/Al=4 was heated at 42 °C and 55 °C, the $\Delta\delta_1$ value and the half-width were found to approach those of the Si/Al=0 solution with increasing temperature, though the relative intensities were almost constant. The interaction between aluminate and silicate ions may not be allowed at higher temperature.

System (c) (0.015 mol dm^{-3} NaOH). Peak X appeared at 80.2 ppm independent of Si/Al ratio, while the relative intensity of peak X decreased with increasing Si/Al ratio (Fig. 6), indicating that the $[Al(OH)_4]^-$ species left in the solution decreases with increasing Si/Al ratio. Part of the aluminate ions in the solution is supposed to be irreversibly changed to a polynuclear species with an ≡Al–O–Si≡ bond. The relative intensity of the peak X decreased gradually over several days. The ^{27}Al NMR signal of the polynuclear species is considered to be too broad to be observed because of its lower symmetry.

The interaction between aluminate and silicate ions is greatly influenced by the alkali concentration.

References

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