^{27}Al NMR STUDIES OF ALUMINOSILICATE SOLUTIONS.
INFLUENCES OF THE SECOND COORDINATION SPHERE ON THE SHIELDING OF ALUMINIUM

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Aluminosilicate solutions have been studied by ^{27}Al NMR to investigate effects of the second coordination sphere on Al shielding. The spectra show four distinct peaks. ^{27}Al chemical shifts are compared with ^{29}Si data. An analogous classification of the ^{27}Al chemical shifts in terms of AlO_4 units of different environments and different degrees of condensation is proposed Observed resonances are correlated to aluminiumoxygen tetrahedra with different numbers of $\equiv$Si—O—Al$\leqslant$ bonds.

1. Introduction

Preliminary results of solid-state high-resolution ^{27}Al NMR investigations of polycrystalline aluminates and aluminosilicates have been reported [1,2]. By means of ^{27}Al chemical shifts, one can distinguish between tetrahedrally and octahedrally coordinated aluminium atoms. The wide range of chemical shifts for four-coordinated aluminium from ≈50 ppm up to 80 ppm indicates that in addition to the direct-neighbour oxygen atoms, the nuclei of the second coordination sphere (e.g. Al or Si) contribute to the shielding of the aluminium. In order to study such effects it is useful to continue with liquids since the solid-state spectra of ^{27}Al NMR are dominantly broadened by the quadrupole interaction between the nuclear quadrupole moment of the aluminium and the electric field gradient at the nuclear site and by the dipolar interaction.

In aqueous solutions with four-coordinated aluminium, only the isolated $Al(OH)_4^-$ anion (δ = 80 ppm) and the central AlO_4 tetrahedron of the $[AlO_4 Al_{12}(OH)_{24}(H_2O)_{12}]^{7+}$ cation (δ = 62.5 ppm) could be observed with ^{27}Al NMR [3,4]. The latter AlO_4 tetrahedron is linked by the corners with twelve distorted, and in the ^{27}Al spectra not detectable, AlO_6 octahedra. In Al metal-hydrolyzed $AlCl_3$ solutions, Akitt and Farthing [5] found a line at 72.6 ppm which could not be correlated with a known structure. More

^{27}Al NMR lines for four-coordinated condensed aluminate anions were not observed. Possibly their concentrations are too small, or with the condensation a line broadening could occur due to a distortion of the symmetry of the aluminium environment rendering the detection more difficult.

For these reasons we chose the recently described tetramethylammonium (TMA) aluminosilicate solutions for our ^{27}Al NMR investigations. In these solutions aluminosilicate anions predominate as was shown by ^{29}Si NMR in connection with the trimethylsilylation method [6,7].

2. Experimental

The ^{27}Al NMR spectra were recorded at 15.8 MHz on an FKS 176 NMR spectrometer using a conventional FT NMR technique. $\pi/2$ pulses of 5 μs were applied and from 1000 to 10000 FIDs of 2k data points were accumulated with a repetition time of 0.3 s. A sample tube of 10 mm diameter was rotated at 50 Hz. The magnetic field homogeneity and stability was better than 0.5 ppm. The chemical shifts were determined relative to an external standard of an aqueous $AlCl_3$ solution. The positive sign of the shifts denotes low-field shifts.

TMA aluminosilicate solutions of different molar

Table 1
^{27}Al chemical shifts in TMA aluminosilicate solutions

Molar ratio N : Si : Al [a]	c_{Al} (M)	Chemical shift (ppm from $Al(H_2O)_6^{3+}$)			
1.5 : 0.0 : 1	0.8	79.5			
1.8 : 0.33 : 1	0.13	79.0		70.0	64.8
2.0 : 0.6 : 1	0.093	79.5	74.3	69.5	65.0
2.4 : 1.0 : 1	0.063	78.3		69.5	64.8
3.0 : 1.67 : 1	0.042	77.6		69.5	65.0
3.8 : 2.3 : 1	0.031	77.1		69.5	65.0
4.5 : 3.0 : 1	0.023	77.5		69.2	64.8

[a] $N = N(CH_3)_4OH$, $Si = SiO_2$, and $Al = \frac{1}{2}Al_2O_3$.

Si/Al ratios and the pure TMA aluminate solution, which was used for the preparation of the aluminosilicate solutions, were studied. The aluminium concentrations were 0.02–0.8 M. Table 1 contains the contents of the solutions. Detailed information about the preparation and characterization of the solutions is given in ref. [6].

3. Results

In these TMA aluminosilicate solutions, for the first time additional separated ^{27}Al NMR lines could be observed in the range between 64 and 80 ppm. The chemical shifts are given in table 1. In fig. 1 a few representative ^{27}Al NMR spectra of the TMA aluminosilicate solutions of different Si/Al ratios are shown together
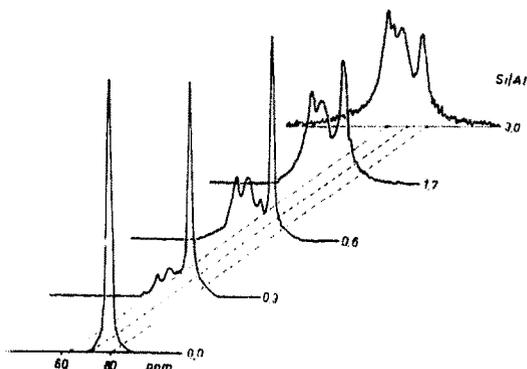

Fig. 1. ^{27}Al NMR spectra of TMA aluminate solution (Si/Al = 0.0) and TMA aluminosilicate solutions of different Si/Al ratios. The unnormalized areas of the spectra do not reflect the Al content.

with that of the TMA aluminate solution. Apart from the line at 79.5 ppm caused by the TMA aluminate anions independent of the Si/Al ratio, all spectra of aluminosilicate solutions show two additional peaks at 64.8 and 69.5 ppm. In the spectrum of the solution with Si/Al = 0.6 even a third weak separate peak at 74.5 ppm occurs. Due to an overlapping of the resonance lines, this peak could not be separated in the spectra of solutions with higher Si/Al ratios. Connected with this overlapping, the maximum of the peak of the TMA aluminate anions is gradually high-field shifted up to 2 ppm with increasing Si/Al ratios. In TMA aluminosilicate solutions of higher concentration the resolution of the ^{27}Al spectra was reduced because of broadening of the lines.

4. Discussion

Comparing the intensities of the resonance lines in fig. 1, it can be seen that with increasing Si/Al ratio the number of the more shielded Al atoms increases. The increase of the shielding has to be attributed to a condensation of the AlO_4 tetrahedra or to the formation of $\geqslant Al{-}O{-}Si\leqslant$ bonds. Such conclusions have been confirmed with numerous studies using ^{29}Si NMR both in silicates and in aluminosilicates and in appropriate solutions [6–9].

To illustrate the chemical and electronic relationship between the aluminium and silicon nuclei, in fig. 2 the range of the isotropic shifts of the ^{29}Si NMR in silicates and aluminosilicates [9] is shown in comparison to that of the ^{27}Al NMR in aluminates [1] and aluminosilicates [2,10,11]. This relationship is of in-
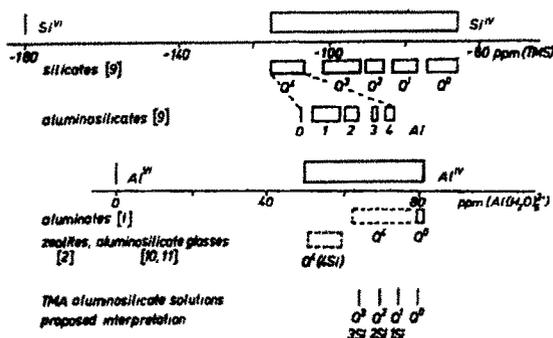
Fig. 2. Comparison of ^{29}Si and ^{27}Al isotropic chemical shifts in silicates, aluminates and aluminosilicates.

terest for the interpretation of the ^{27}Al spectra. In fig. 2 the ^{27}Al NMR scale is shifted in such a manner that the Me_4Si standard of the ^{29}Si NMR (δ = 0 ppm) is aligned with the analogous aluminium compound Al_2Me_6 (δ = 156 ppm [12]).

The difference of the chemical shifts between octahedrally coordinated silicon atoms (thaumasite δ = −180 ppm [13]) and tetrahedrally coordinated silicon atoms can amount to 115 ppm while the difference between six- and four-coordinated aluminium atoms comes only to $\approx$80 ppm. The ranges of the chemical shifts for tetrahedrally coordinated silicon and aluminium show a similar behaviour with 50 ppm and 30 ppm respectively.

According to Engelhardt et al. [8] the total range of ^{29}Si chemical shifts in solid silicates as well as in solutions of silicic acids can be subdivided into five well separated ranges. These are attributed to non-equivalent SiO_4 tetrahedra Q^0−Q^4 which are attached to a different number of other silicon−oxygen tetrahedra, the superscript denoting the number of bridging oxygen atoms of the SiO_4 tetrahedron, e.g. Q^0 for isolated tetrahedra, Q^1 for chain end groups, Q^2 for middle groups in chains or rings, etc. The shielding of the Si atom increases with its number of bridging oxygen atoms from Q^0 to Q^4 as illustrated in fig. 2.

In solid aluminosilicates additional paramagnetic ^{29}Si shifts appear which allow us to distinguish in Q^3 or Q^4 units whether Al or Si atoms are arranged in the second coordination sphere of the SiO_4 tetrahedron under study. The substitution of one neighbouring silicon atom by aluminium effects a low-field shift of the ^{29}Si resonance of $\approx$5 ppm [9]. Dependent on the

number of neighbouring Al atoms, the ranges of different Q units can overlap which renders a defined correlation of the peaks to structural groups more difficult.

The results of the ^{27}Al NMR can be discussed in the same way if the concept of Q^0−Q^4 is applied to the AlO_4 tetrahedra. With increasing number of bridging oxygen atoms at the aluminium, an increase of the shielding is expected. This is supported by ^{27}Al NMR studies of aluminate solutions with monomeric $Al(OH)_4^-$ anions (Q^0) which provide lines in the region of weakest shielding for AlO_4 tetrahedra at 80 ppm while the range of ^{27}Al shifts for Al atoms of the Q^4 type in pure aluminium−oxygen compounds extends up to 62.5 ppm in the case of the central AlO_4 tetrahedron of the $Al_{13}O_{40}$ cation [3] (see fig. 2).

Besides the shift of the ^{27}Al resonance due to a different degree of condensation of the AlO_4 tetrahedra, likewise in aluminosilicates an influence of the substitution of neighbouring Al atoms by Si atoms must be expected. In that manner, as the formation of $\equiv$Si−O−Al$\equiv$ bridges by substitution of neighbouring Si atoms by Al atoms causes a decrease of the shielding of the silicon under study, so with $\equiv$Al−O−Al$\equiv$ bridges an incorporation of Si atoms has to correspond to an increase of the shielding of the Al nucleus. This can be understood in terms of the different electronegativities of the substituted Al and Si atoms which affect the character of the Si−O and Al−O bonds of the $\equiv$Si−O−Al$\equiv$ bridges in contrary ways. These considerations are confirmed experimentally by the ^{27}Al chemical shifts of aluminosilicate-glasses (δ = 51−57 ppm [10,11]) and zeolites (δ = 53−59 ppm [2]) which contain AlO_4 tetrahedra of the Q^4 type surrounded by four silicon−oxygen tetrahedra. As shown in fig. 2, the range of chemical shifts of these groups is markedly shifted upwards compared with that of aluminates.

The degree of condensation of the silicon−oxygen and aluminium−oxygen tetrahedra and the number of $\equiv$Si−O−Al$\equiv$ bridges affect the ^{27}Al and ^{29}Si shifts in a different way. In ^{29}Si NMR they act in contrary directions, while in ^{27}Al NMR both effects add and lead to high-field shifts.

As concerns our system of TMA aluminosilicate solutions, without additional information it is not possible to distinguish between the influences of the two effects on the observed ^{27}Al shifts. Theoretically fifteen different aluminium structural units $Q^n(m$Si) with

Table 2
Interpretation of the observed four resonance lines of the TMA aluminosilicate solutions

^{27}Al chemical shift (ppm)	Structural unit	
79.5	Q^0 isolated AlO_4 tetrahedron	$-\overset{\textstyle\mid}{\underset{\textstyle\mid}{Al}}-$
74.3	Q^1(1Si) chain end groups	$\geqslant Si-O-Al\leqslant$
69.5	Q^2(2Si) middle groups of chains or rings	$\geqslant Si-\overset{\textstyle\mid}{\underset{\textstyle\mid}{Al}}-O-Si\leqslant$
64.2	Q^3(3Si) chain branching sites	$\geqslant Si-O-\overset{\textstyle\mid}{\underset{\displaystyle O}{Al}}-O-Si\leqslant$ $-Si-$

eventually different ^{27}Al shifts are imaginable. The index n denotes the number of bridging oxygen atoms of the AlO_4 tetrahedron as mentioned above while m ($m = 0-n$) characterizes the number of directly neighboured SiO_4 tetrahedra.

The existence of anions with $\geqslant Si-O-Al\leqslant$ bridges was previously proved in such solutions [6,7]. In alkali aluminate solutions monomeric $Al(OH)_4^-$ anions predominate. Only in very concentrated solutions IR spectroscopic hints at minor quantities of dimeric aluminate anions are found [14]. Comparing the ^{27}Al spectra of alkali aluminate and TMA aluminate solutions, a similar situation is supposed. It seems unlikely that under the conditions of the preparation of the aluminosilicate solutions by adding TMA silicate solutions to diluted TMA aluminate solutions, additional $\geqslant Al-O-Al\leqslant$ bonds should originate particularly as dilute solutions were used.

These facts suggest applying the Loewenstein rule [15] to our TMA aluminosilicate solutions. According to this rule in solid aluminosilicates the existence of $\geqslant Al-O-Al\leqslant$ bonds is excluded. In crystalline TMA aluminosilicates the validity of the rule could be confirmed [7].

The exclusion of $\geqslant Al-O-Al\leqslant$ bonds diminishes the number of possible structural units of the aluminium to five combinations Q^n(nSi) with $n = 0-4$ which rep-

resent AlO_4 tetrahedra with only $\geqslant Al-O-Si\leqslant$ bridges. Q^4(4Si) units have to be excluded because of experimental evidence. As discussed above these groups cause ^{27}Al shifts in the range of ≈ 55 ppm and the TMA aluminosilicate solutions show no signal in that region.

Including the resonance line of the TMA aluminate solution at 79.5 ppm which can be attributed unambiguously to isolated AlO_4 tetrahedra, the interpretation of the observed four resonance lines of the TMA aluminosilicate solutions is given in table 2.

In concentrated TMA aluminosilicate solutions mainly double four-ring anions are assumed which are built up by Q^3 units [6]. With increasing dilution however this anion decomposes into low-molecular weight fragments. To what extent the observed Q^3 groups in our dilute TMA aluminosilicate solutions come from the remaining double four-ring anions or from fragments of the decomposed species cannot be decided at present.

This study provides further evidence for the existence of $\geqslant Al-O-Si\leqslant$ bonds in the system of TMA aluminosilicate solutions. Moreover it represents a first step to systematize the ^{27}Al NMR shifts in aluminosilicates as has succesfully been done for the ^{29}Si NMR shifts. Further investigations by solid-state high-resolution ^{27}Al NMR in defined crystalline aluminosilicates

should confirm the correlations and complete the system of ^{27}Al shifts of AlO_4 tetrahedra.

Acknowledgement

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