^{29}Si NMR Studies of the Transformation of Silicate Anions in the System Na$_2$O·SiO$_2$·nH$_2$O (n = 9, 5) in Crystals, Melts, and Solution

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A combined solid- and liquid-state ^{29}Si NMR study shows that the monomeric silicate anions of crystalline sodium silicate hydrates Na$_2$H$_2$SiO$_4$·nH$_2$O (n = 8, 4) upon melting undergo rapid condensation to distinct oligomer species, and that recrystallization of the melt involves hydrolysis of the oligomers and reconstitution of the initial monomeric silicate structure.

X-Ray and neutron single crystal diffraction shows[1] that sodium silicate hydrates of the composition Na$_2$O·SiO$_2$·nH$_2$O (n = 9, 8, 6, 5) contain [SiO$_2$(OH)$_2$]$^{2-}$ monomer silicate anions. Upon melting the various hydrates exhibit a single differential scanning calorimetry (DSC) peak, indicating congruent melting.[2] However, the large width of the peak (about 10 K at half height) is unusual for a first order phase transition. Furthermore, no recrystallization could be observed in the DSC experiments after cooling the melts below the melting point. These observations prompted us to study

the structural aspects of the solid–liquid phase transition of the sodium silicate hydrates by solid- and liquid-state variable temperature ^{29}Si NMR.

^{29}Si NMR provides detailed information on the silicate anion species in silicate solutions as well as in solid silicates.[3] Modern NMR instruments permit the measurement of highly resolved ^{29}Si NMR spectra of liquids and solids in tandem, using the same NMR probe and sample. Therefore, *in situ* studies at variable temperature of the melting and recrystallization process of the silicate hydrates can be performed.
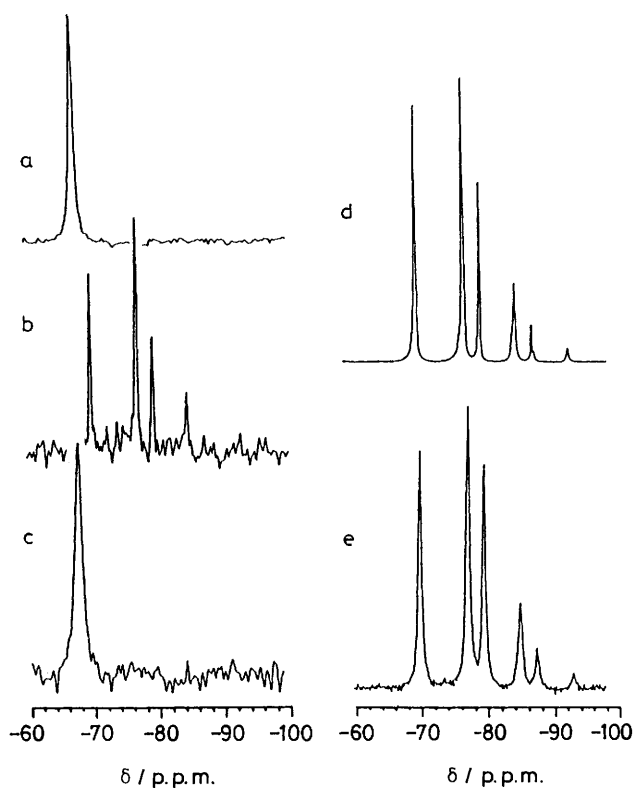
Figure 1. ^{29}Si NMR spectra of the system $Na_2O\cdot SiO_2\cdot 9H_2O$. a, CP MAS spectrum of crystalline $Na_2H_2SiO_4\cdot 8H_2O$ at 296 K; b, MAS spectrum of the melt at 322 K; c, CP MAS spectrum after recrystallization at 296 K; d, conventional liquid-state spectrum of the melt at 322 K; e, conventional liquid-state spectrum of the 5.5 mol l^{-1}, Na/Si = 2 sodium silicate solution at 296 K.

Moreover, for partially melted samples a clear distinction between the spectra of the solid and liquid phases is possible by means of ^{1}H-^{29}Si cross-polarization (CP). Application of CP yields the spectrum of the solid part of the sample, while a single pulse sequence with short pulse intervals (5 s) yields the spectrum of the liquid phase. The spectrum of the whole sample, i.e., of the liquid and solid phases, is obtained without CP at long pulse intervals (200 s).

Experiments were carried out with the two sodium silicate hydrates of composition $Na_2H_2SiO_4\cdot 8H_2O$ and Na_2H_2-$SiO_4\cdot 4H_2O$. The samples were crystallized from aqueous sodium silicate solutions (prepared from a commercial water glass solution and NaOH) and characterized by X-ray powder diffraction.[4] In situ ^{29}Si NMR studies of the melting and recrystallization process were performed at 79.5 MHz using a Bruker MSL-400 spectrometer and magic-angle spinning (MAS) and cross-polarization (CP) or single pulse sequences (Figure 1a—c). In addition, conventional liquid-state ^{29}Si NMR spectra of the melts and of a sodium silicate solution with the composition of the octahydrate were measured at 79.5 MHz with a JEOL GX-400 spectrometer (Figure 1d,e).

The ^{29}Si CP MAS NMR spectrum of crystalline Na_2H_2-$SiO_4\cdot 8H_2O$ at 296 K (Figure 1a) shows a single line at δ -67.7 p.p.m. (referenced to tetramethylsilane) for the monomer silicate anion. In agreement with the X-ray structure, no other

silicate anion species can be detected in the spectrum of the crystalline sample. At 322 K the crystals start to melt and besides the single-line solid-state spectrum (measured with CP) a liquid-state spectrum (measured without CP) is observed showing several lines attributable to distinct silicate anions. After the melting is completed, no CP spectrum could be obtained and the spectrum of the liquid melt (Figure 1b) displays sharp lines for the monomer (δ -69.8 p.p.m.), dimer (δ -76.9 p.p.m.), cyclotrimer (δ -79.4 p.p.m.), and cyclo-tetramer (δ -84.7 p.p.m.) silicate anions. After cooling the sample at 264 K for about one hour, the intensities of the lines in the liquid-state spectrum decrease and the single line at δ -67.7 p.p.m. of the initial solid silicate octahydrate appears again in the CP spectrum (Figure 1c). The recrystallization of the octahydrate has also been confirmed by X-ray powder diffraction. The conventional liquid-state spectrum of the melt at 322 K shown in Figure 1d resembles that of Figure 1b but shows more clearly the lines of the prismatic hexamer silicate anion at δ -87.6 p.p.m. and of small proportions of $Si(OSi)_3O^-$ branching groups at δ -93.0 p.p.m.[5] Figure 1e shows the spectrum of a sodium silicate solution with the composition of the octahydrate (5.5 mol l^{-1}, Na/Si = 2) before crystallization. It is strikingly similar to the spectrum of the melt.

The ^{29}Si NMR spectra of the crystalline, molten, and recrystallized tetrahydrate $Na_2H_2SiO_4\cdot 4H_2O$ are very similar to those of the octahydrate. The chemical shift of the crystalline tetrahydrate (δ -67.7 p.p.m.) is identical with that of the octahydrate and the same anion species could be detected in the liquid melt but with some preference of the cyclotrimer and cyclotetramer species to the higher oligomers.

Our results clearly show that the condensation of the monomer silicate anion to distinct oligomeric species occurs immediately upon melting the crystalline silicate hydrates. The distribution of the oligomeric silicate anions in the melt is very similar to that in a sodium silicate solution of the same compostion. Recrystallization of the melt at temperatures below the melting point involves hydrolysis of the oligomeric species and reconstitution of the monomer silicate anions in the crystalline solid.

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