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Silicon-29 NMR evidence of alkoxy substituted aqueous silicate anions

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Received 20th May 1999, Accepted 26th July 1999

Silicon-29 NMR provides the first direct evidence for the presence of stable alkoxy substituted silicate anions in aqueous alkaline silicate solutions to which aliphatic mono- or poly-hydroxy alcohols have been added.

The study of aqueous alkaline silicate solutions is of importance in understanding the formation and growth of zeolites and microporous materials on a molecular level.[1] To date, most of the information available has been derived from ^{29}Si NMR spectroscopic studies.[2,3] Much of the research has focused on the effects of adding various organic solutes to aqueous silicate solutions in order to replicate more accurately the conditions of actual zeolite synthesis.[3] Although changes in the silicate anion equilibria have been noted as a result, there have been very few reports of direct chemical interaction occurring between aqueous silicates and organic additives.[4] The only cases documented are of six-coordinate Si complexes that form when silicon is chelated by catechol, 2-hydroxypyridine *N*-oxide, tropolone or their respective analogues.[5] Indeed, well defined instances of formal Si–O–C bonding in aqueous solution are so rare that the importance of such interactions in nature, even their very existence, has been questioned.[6] Yet simple organisms such as diatoms cannot survive without silicic acid, and actively isolate, transport and deposit silica on a massive scale.[7] Such a feat is difficult to understand without invoking some biochemical function for silicates, and thereby implying the existence of stable organo-silicate complexes under aqueous conditions.

It has long been known, however, that mono- and poly-hydroxy aliphatic hydrocarbons readily react with boric acid to form stable mono- and poly-olato boron complexes in aqueous solution.[8] Indeed, such organic species have also been suspected of complexing aqueous silicate anions, thereby enhancing the solubility of solid silicates,[9] but so far no direct evidence for such complexes has been presented. With this in mind, we undertook the ^{29}Si NMR investigation of a series of aqueous alkaline silicate solutions to which we added a range of aliphatic mono- and poly-hydroxy alcohols. The results are reported here, and provide the first direct evidence for the presence of stable alkoxy-substituted silicate anions in aqueous solution.

We show in Fig. 1 portions of the 99.36 MHz ^{29}Si NMR spectrum of an aqueous tetrabutylammonium silicate solution to which methanol has been added. Together with the well characterized silicate anion signals, a series of additional signals is observed. These are labeled alphabetically in the figure, and the assignments are given in Table 1. By comparing proton coupled and decoupled spectra, it is clear that some of these new signals arise from silicon centres to which protons are bound. Since the aqueous nature of the samples ensures that rapid chemical exchange obscures all evidence of coupling to hydroxy protons, the coupling observed must arise from the aliphatic protons of the hydrocarbon, implying the existence of covalent Si–O–C–H bonding.

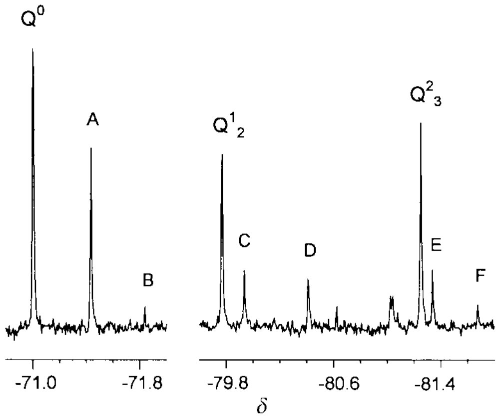

Fig. 1 Portions of the ^{1}H-decoupled (gated nOe-free) ^{29}Si NMR spectrum (99.36 MHz) at 300 K of a tetrabutylammonium (TBA) silicate solution containing 1.1 mol% TBAOH, 1.1 mol% SiO_2, and 36.6 mol% methanol. The labeled resonances correspond to the silicate monomer ($H_{4-q}SiO_4^{q-}$, Q^0), dimer ($H_{6-q}Si_2O_7^{q-}$, Q^1_2), cyclic trimer ($H_{6-q}Si_3O_9^{q-}$ Q^2_3) and, as assigned in Table 1, the corresponding methoxy-substituted anions.[11] The spectrum was recorded using 3200 $\pi/2$ pulses with an interpulse delay of 24 s, and processed using 0.1 Hz linebroadening.

The chemical shift and multiplicity of the various new peaks observed are entirely consistent with those obtained from the hydrolysis of alkoxysilanes,[10] and allow an unambiguous assignment to three alkoxy substituted silicate anions, the monomer, $H_{4-q}SiO_4^{q-}$, the dimer, $H_{6-q}Si_2O_7^{q-}$, and the cyclic trimer, $H_{6-q}Si_3O_9^{q-}$. In these species, one or two of the terminal OH groups on Si are replaced by alcohol derived alkoxy functions. Details of the specific assignments are given in Table 1. We note that the overall extent of complexation, together with the degree of substitution at any individual anion, increases linearly with the solution's pH, or as the temperature is decreased. On the other hand, the nature of the cation present appears to have little effect. Additionally, it is apparent that the larger the polyol, the more hydroxy groups are required for it to react significantly with dissolved silicates. For example, *n*-propane requires a minimum of two hydroxy groups before any complexation occurs, whereas *n*-butane requires a minimum of three. This requirement is complicated by the fact that the position of the hydroxy groups on the hydrocarbon chain appears critical, and we illustrate this in Fig. 2. Here we show the ^{29}Si NMR spectra of three otherwise identical tetrabutylammonium silicate solutions, prepared with 30 mol% 1-propanol (spectrum a), 1,2-propanediol (spectrum b), and 1,3-propanediol (spectrum c). It is apparent that silicate anion complexation is enhanced when the two hydroxy groups are on non-adjacent carbons.

These observations demonstrate that alkoxy substituted silicates are readily formed in aqueous solution given appropriate conditions, and that, contrary to prevailing opinion, Si–O–C bonds may not be so rare in aqueous solution. Work on the

Table 1 ^{29}Si NMR assignments of alkoxy substituted four-coordinate silicate complexes formed by addition of mono- and poly-hydroxy alcohols to alkaline silicate solutions

Alcohol added	Species[a]	Peak label[b]	$\Delta\delta^{c,d}$ (ppm)	Peak multiplicity [$^3J(^{29}\mathrm{Si–O–C–^1H})$/Hz]
Methanol	$\mathrm{(HO)_3SiOCH_3}$	A	−0.31, −0.43[e]	Quartet [3.7]
	$\mathrm{(HO)_2Si(OCH_3)_2}$	B	−0.75, −0.84[e]	Apparent septet [3.7]
	$\mathrm{(HO)_3Si^COSi^D(OH)_2OCH_3}$	C	−8.99, −8.93[e]	Singlet
		D	−9.47, −9.41[e]	Quartet [3.7]
	$\overline{\mathrm{OSi^E(OH)_2Si^E(OH)_2OSi}}\mathrm{^F(OH)OCH_3}$	E	−10.45, −10.34[e]	Singlet
		F	−10.59, −10.68[e]	Indeterminate
Ethanol	$\mathrm{(HO)_3SiOCH_2CH_3}$	A	−1.23	
1,2-Ethanediol	$\mathrm{(HO)_3SiOCH_2CH_2OH}$	A	−0.70	
1-Propanol	Negligible substitution	—	—	
1,2-Propanediol	$\mathrm{(HO)_3SiOCH_2CH(OH)CH_3}$	A	−0.81	
1,3-Propanediol	$\mathrm{(HO)_3SiOCH_2CH_2CH_2OH}$	A	−0.87	
	$\mathrm{(HO)_3Si^COSi^D(OH)OCH_2CH_2CH_2OH}$	C	−9.01	
		D	−9.64	
	$\overline{\mathrm{OSi^E(OH)_2Si^E(OH)_2OSi}}\mathrm{^FOCH_2CH_2CH_2OH}$	E	−10.37	
		F	−11.28	
1,2,3-Propanetriol	$\mathrm{(HO)_3SiOCH_2CH(OH)CH_2OH}$	A	−0.47[f]	

[a] Represented are the substituted silicate monomer, dimer and cyclic trimer anions; they are deprotonated to varying degrees depending on solution pH, however, the degree of deprotonation is not considered here. [b] Refer to spectra in Figs. 1 and 2. [c] Chemical shift from the orthosilicate monomer peak, assigned here at −71 ppm from tetramethylsilane; the values vary with solution conditions and are especially dependent on alcohol concentration and pH. [d] Unless noted otherwise, shifts correspond to solutions containing 2.0 mol% in both $\mathrm{SiO_2}$ and tetrabutylammonium hydroxide (TBAOH), and 30.0 mol% alcohol. [e] For a solution containing 1.1 mol% in both $\mathrm{SiO_2}$ and TBAOH, and 36.6 mol% methanol (see Fig. 1). [f] For a solution containing 4.2 mol% in both $\mathrm{SiO_2}$ and NaOH, and 13.4 mol% 1,2,3-propanetriol.

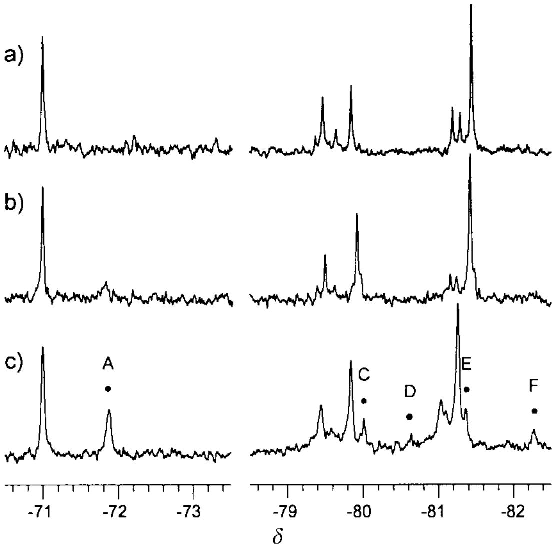

Fig. 2 Portions of the ^{29}Si NMR spectra (99.36 MHz) at 300 K of TBA silicate solutions containing 2.0 mol% TBAOH, 2.0 mol% $\mathrm{SiO_2}$ and 30.0 mol% (a) 1-propanol, (b) 1,2-propanediol and (c) 1,3-propanediol. The labeled resonances correspond to alkoxy-substituted silicate anions and are assigned in Table 1. The spectra were recorded using 1000 π/2 pulses with an interpulse delay of 43 s, and processed using 1 Hz linebroadening.

effects of adding a wider range of polyhydroxy compounds to silicate solutions is in progress.

Acknowledgements

We are grateful to the National Institute of Health (PHS 1 S10 RR 10444-01; GM-42208 and RR 01811), the National Science Foundation (NSF CHE 96-10502) and the Natural Science and Engineering Council of Canada (NSERC) for providing funding. Facilities were provided by the NIH supported Illinois EPR Research Center, and the NSERC supported Prairie Regional NMR Centre (Winnipeg).

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11 By convention, the $\mathrm{Q}^y{}_z$ symbol is used to denote a quadrifunctional Si centre with *y*-coordinated $\mathrm{SiO_4}^{4-}$ tetrahedra and, when applicable, *z* indicates the number of equivalent centres in a totally symmetric anion.

Communication 9/04073K