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# Aqueous vanadosilicates

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Silicate anions were shown by $^{51}V$ and $^{17}O$ NMR spectroscopy to combine with aqueous $[HVO_4]^{2-}$ in aqueous alkaline solution, forming the anions $[H_2VSiO_7]^{3-}$, $[H_3VSiO_7]^{2-}$ and various related monovanadooligosilicate species. Approximate equilibrium constants have been derived, and shown to depend only weakly upon ionic strength. The ion $[H_2VSiO_7]^{3-}$ at higher concentrations also dimerises to give an anion with a SiOVOVOSi linkage, as shown by selective inversion-transfer subtraction spectra.

Although vanadium(v) is well known to combine with silicate, both in heteropolyanions with $SiO_4$ centres,[1] and in *e.g.* mesoporous silicas,[2] no reports have been published to date of simple aqueous vanadosilicates, resulting from the interaction of alkaline silicate with $[HVO_4]^{2-}$ or its oligomers. Such dissolved species might be expected to form mainly above pH 10.5, for $SiO_2$ precipitates below this value. One might expect them to be loosely analogous to the alkaline aluminosilicate species that initially form in sol–gel preparations,[3] and indeed they may be important in developing a chemical understanding of such processes. Vanadates are particularly convenient for investigation, because $^{51}V$ NMR is even more sensitive than $^{27}Al$ NMR spectroscopy, by virtue of the much lower quadrupole moment of $^{51}V$.[4]

Our attention was initially drawn to the possible existence of vanadosilicates by the occasional presence of minor peaks in the spectra of alkaline vanadate solutions, contained in glass for some time. These peaks could not be explained in terms of any possible isopolyvanadate anion.[5] They could be greatly amplified by the addition of aqueous sodium silicate at the same pH. We have therefore attempted their analysis by solution-state $^{51}V$ and $^{17}O$ NMR spectroscopy, including the use of one-dimensional inversion-transfer methods.

Two other methods might in principle be considered for the same investigation. Silicon-29 NMR spectroscopy has certainly yielded rich results with silicate oligomers, despite its comparatively low sensitivity. However, the resonances of Si attached through O to V in small anions will almost certainly be seriously broadened by $^{51}V$–$^{29}Si$ coupling, and will therefore be difficult to observe. Potentiometry is also possible,[6] and indeed it has been applied to oligosilicates by Sjöberg and co-workers,[7] using a somewhat simplified chemical scheme, to show that the main monosilicate species in the range pH 10–13 is $[H_3SiO_4]^-$ However, it will not be sufficiently accurate here, because of the high concentrations required, and the likely complexity of the vanadosilicate chemistry. Instead, an attempt is made in the present study to extract approximate equilibrium constants for the most abundant vanadosilicate species using NMR data alone.

## Experimental

Initial solution-state NMR spectra were obtained at 105.5 ($^{51}V$) and 54.2 ($^{17}O$) MHz on a Bruker ACP400 spectrometer and at 295 K in lightly deuteriated 0.60 and 3.00 mol dm$^{-3}$ aqueous Na(Cl). Typical parameters for the $^{51}V$ spectra were: spectral width 28 kHz, acquisition time 0.147 s, no relaxation delay, 8k data points in both domains, 2000 transients, 35° pulse angle. The corresponding values for the $^{17}O$ spectrum were 83 kHz, 0.025 s, no relaxation delay, 4k points, 20 000 transients, no isotopic enrichment, 35°. The $^{51}V$ chemical shifts were referenced to external capillary $VOCl_3$.

Further $^{51}V$ NMR spectra were obtained at 157.6 MHz on a Varian VXR600S spectrometer, at 25 °C, particularly for kinetic studies using selective inversion. Inversion was achieved with the programmable pulse modulator unit on the Varian instrument. The delay between the midpoints of the soft inversion pulse and the hard observation pulse was set as low as possible, because the exchange processes were found to be very rapid. Its effective value was estimated to be *ca.* 1 ms. Thus it was only possible to obtain semiquantitative kinetic information by this means, even though the time allowed for exchange was appreciably shorter than the oxygen relaxation time. Subtraction spectra, which show only those resonances affected by the selective inversion, were obtained by subtracting the normal spectrum from the selectively inverted spectrum.

The areas of the major peaks in the $^{51}V$ NMR spectra could typically be measured to within 10%. However, there was no reliable way of deconvoluting the multiple, overlapping, exchange-broadened monovanadosilicate resonances, and indeed the approximate determination of equilibrium constants was only possible because this cluster of resonances was dominated by the simplest species. Nevertheless, it proved possible to identify the main new species present, by the combination of their shifts, their dependence on pH and concentration and their exchange kinetics.

Solutions were prepared from sodium metavanadate ($NaVO_3$) and hydrated sodium metasilicate ($Na_2SiO_3{\cdot}5H_2O$, BDH) and sodium chloride AR (Fisons). A Radiometer PHM84 pH meter was used with a type B electrode, with which the sodium ion corrections were small.

## Results and Discussion

### Shifts

No resonances beyond those expected for isopolyvanadates were found above pH 13.5, but on progressive lowering of the pH value vanadosilicate resonances appeared in increasing proportion and complexity, down to pH 10, where precipitation occurred. Fig. 1 shows one of the richer, 157.6 MHz $^{51}V$ NMR spectra, obtained at pH 11.1 with V, Si and Na(Cl) respectively 0.1, 0.04 and 0.6 mol dm$^{-3}$. The three isopolyvanadates expected under these conditions are: $[HVO_4]^{2-}$ ($V_1$), $[V_2O_7]^{4-}$ ($V_2$) and $[V_3O_{10}]^{5-}$ ($V_3$, two resonances). A cluster of vanadosilicate resonances is apparent from δ −564 to −570, together with a broad but reproducible peak at δ −603.3 (see vertical expansion). The area of the main cluster is comparable with that of $V_2$. Similar spectra were seen with different concentrations of reagents, although the more minor peaks were not always present, or resolvable. Fig. 2 shows how the

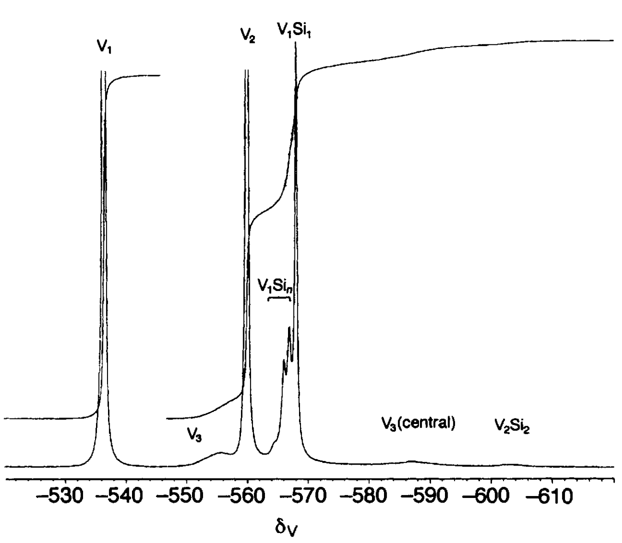


**Fig. 1** The 157 MHz $^{51}V$ NMR spectrum of a solution with 0.1, 0.04, 0.6 mol $dm^{-3}$ V, Si and NaCl respectively, pH 11.1, 295 K

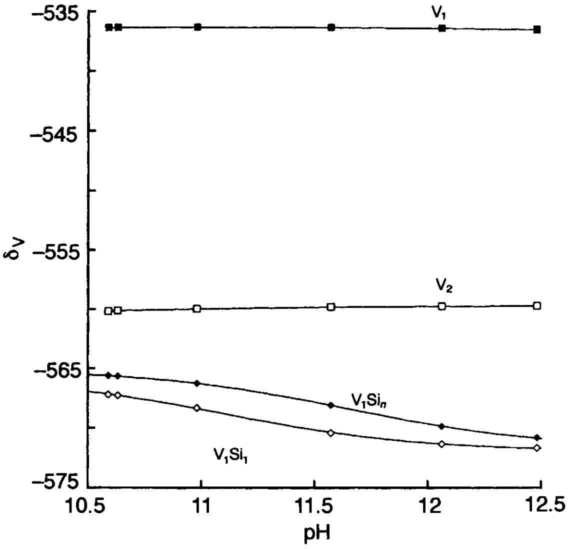


**Fig. 2** Vanadium shifts *vs.* pH for solution of 0.01, 0.04 and 0.6 mol $dm^{-3}$ V, Si and NaCl respectively at 295 K. The $V_1$ = $[HVO_4]^{2-}$ and $V_2$ = $[V_2O_7]^{4-}$ shifts are temperature-invariant, whereas those for $V_1Si_1$ and $V_1Si_n$ are fitted to Henderson–Hasselbalch equations, with $pK_a$ = 11.2 and (averaged) 11.6 respectively

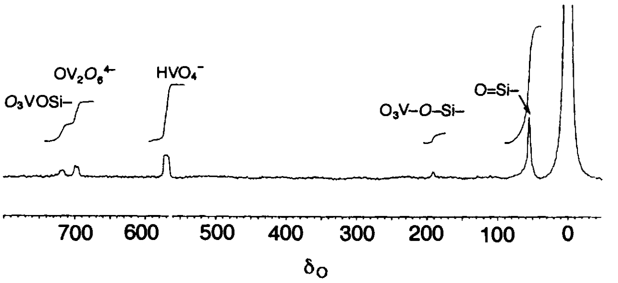


**Fig. 3** Oxygen-17 NMR spectrum of a solution of 0.3, 0.6 and 0.6 mol $dm^{-3}$ V, Si and Na respectively, pH 13.3, showing the 3 : 1 area ratio for the two types of O bound to V in $V_1Si_1$, and the fast exchange between the silicate oxygens

shifts of the resonances vary with pH, and also the actual pH values studied at this concentration. The $V_1$ and $V_2$ peaks are independent of pH in this range, but all the vanadosilicate peaks move somewhat to higher frequency with increasing acid. This increment is less than, and opposite in sign to those of $V_1$ and $V_2$, at lower pH,[5] perhaps indicating protonation at silicate rather than vanadate oxygen.

An integrated $^{17}O$ NMR spectrum, Fig. 3, was obtained for a pH 13.3 solution of 0.3, 0.6 and 0.6 mol $dm^{-3}$ V, Si and Na respectively. At this pH the only vanadosilicate resonance in the $^{51}V$ NMR spectrum is the major one, at δ −572. The $^{17}O$ peaks are mostly broadened by $^{51}V$–$^{17}O$ couplings, and indeed these are sufficient to render invisible the bridging oxygen resonance in species $V_2$. All the oxygens bound solely to Si are in sufficiently fast exchange to merge into the peak near δ 55. The other peaks are readily identified from previous data for $V_1$ (δ 570) and from their areas, relative to those of the corresponding $^{51}V$ NMR spectrum. The two resolved vanadosilicate oxygen resonances appear at δ 720 and 190, in area ratio 3 : 1. They thus prove the presence of an $O_3VOSi$ unit. The actual anion is almost certainly $[O_3VOSiO(OH)_2]^{3-}$ at this pH, given the equilibrium constants and the general trends in vanadate[5] and silicate[7] anionic charge. Its shifts are entirely consistent with this formulation. Those of the terminal oxygens are similar to those of $V_2$, and the bridging O is intermediate between the bridging O in $V_2$ (δ 440) and averaged O in silicates (δ 55). These shifts, and the 3 : 1 area ratio, rule out the possibility of V and Si linked by more than one O. Also, the $^{51}V$ shifts rule out octahedrally co-ordinated V.[4]

This identification as $V_1Si_1$ is supported below by equilibrium calculations. If it is accepted, then the more minor peaks with similar shift can only be reasonably assigned to $V_1Si_n$ oligomers. Thus silicate esterification of vanadate decreases the $^{51}V$ shift by about 35 ppm. The other, much weaker vanadosilicate resonance, at δ −603, is about 33 ppm to low frequency of $V_2$. It would therefore seem on shift grounds to be a $V_2Si_n$ species, with a VOV bond. The symmetrical $V_2Si_2$ anion is the most probable, because it has only one $^{51}V$ resonance. The evidence below implies that it forms from two $V_1Si_1$ units, rather than from *e.g.* direct esterification of $V_2$.

## Exchange

The monovanadosilicate peaks broaden and merge if the temperature is raised, even though exchange between $V_1$ and $V_2$ remains negligible. Thus SiOSi bonds are more labile than VOV bonds, or indeed VOSi bonds, as adjudged from the $^{17}O$ NMR data. The exchange of vanadate units was investigated by selective inversion of vanadate resonances. Even though short selective pulses were necessary to cope with rapid exchange, nevertheless a shift selectivity of *ca.*. 3 ppm was achievable. Figs. 4 and 5 show two examples of subtraction spectra (*b*), obtained by subtracting the unperturbed spectrum (*a*) from the spectrum taken immediately following selective inversion of the chosen $^{51}V$ resonance. Any transfer of inversion indicates exchange not much slower than $1/T_1$, which is typically 400 $s^{-1}$ here.

The overall kinetic pathways thus revealed are illustrated in Scheme 1. No exchange was detected between $V_2$ and the species identified above as $V_2Si_2$, indicating that the latter forms instead from two $V_1Si_1$ units. There was no clear evidence for the presence of any $V_2Si_1$.

## Equilibria

Since it was not possible to separate the integral for the $V_1Si_1$ peak from those for $V_1Si_n$, it was necessary to make the approximation that the total integral was dominated by $V_1Si_1$. This overestimates the true $V_1Si_1$ concentration by 10–20% in the calculations described below, judged by crude attempts at deconvolution. Equilibrium constants were then calculated for '$V_1Si_1$' as follows. The concentrations of $V_1$ and of '$V_1Si_1$' in each of 18 solutions were calculated directly from the total vanadium concentration and the relevant integrals. The concentration of $Si_1$, as both $[H_3SiO_4]^-$ and $[H_2SiO_4]^{2-}$, was calculated from the total [Si] and the data in ref. 7 where the relevant equilibrium constants are presented as functions of

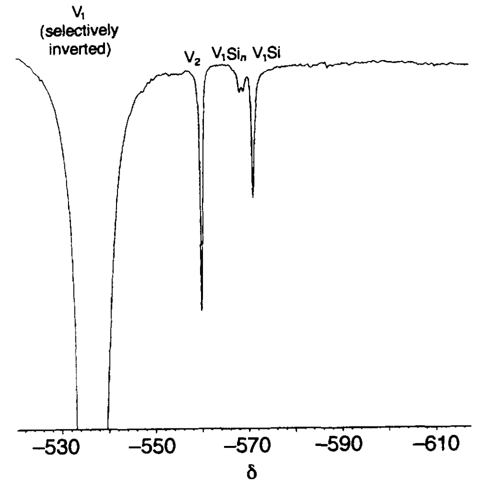


Fig. 4 The 157 MHz $^{51}$V NMR subtraction spectrum of a solution with 0.1, 0.04, 0.6 mol dm$^{-3}$ V, Si and NaCl respectively, pH 11.94, 295 K. The $V_1$ peak was selectively inverted *ca.* 1 ms before data capture, and the normal spectrum was subsequently subtracted

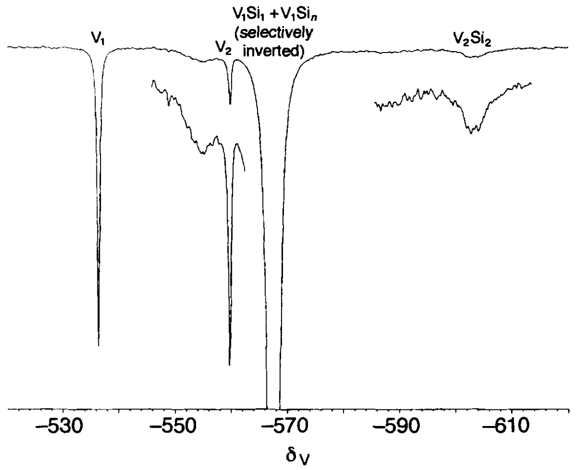
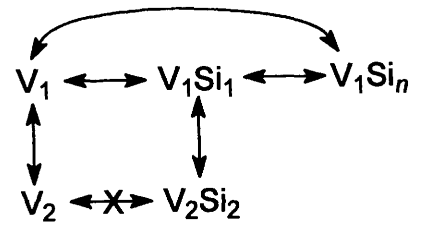


Fig. 5 As in Fig. 4, but with pH 11.1 and inversion at the $V_1Si_1$ peak. Intensity transfer to $V_2Si_2$ occurs in this case, but not when the $V_2$ peak from the same sample is inverted



Scheme 1 The $V_1S_1 \longleftrightarrow V_1Si_n$ interconversion was deduced from temperature dependence

[Na$^+$]. A small allowance was necessary for the presence at high pH of deprotonated $V_1$, *i.e.* $[VO_4]^{3-}$, using [NaCl]-dependent p$K_a$ values extrapolated from Pettersson's data.[8]

Separate equilibrium constants, $[`V_1Si_1']/[V_1][Si_1][H^+]_m$, were then calculated for both the diprotonated anion $[H_2VSiO_7]^{3-}$ and the triprotonated anion $[H_3VSiO_7]^{2-}$, at each of the ionic strengths used. Thus the reaction (1) gives expression (2). A least-squares fit (Microsoft Solver) was used to minimise the difference between the observed and calculated concentrations. The results are shown in Fig. 6 as plots of observed *vs.* calculated concentrations for total '$V_1Si_1$', and the log constants are given in Table 1. The calculated concentrations are indicated by the segmented lines. The fits of the points by these are far better than could be obtained with any other formulations for the vanadosilicate anions.

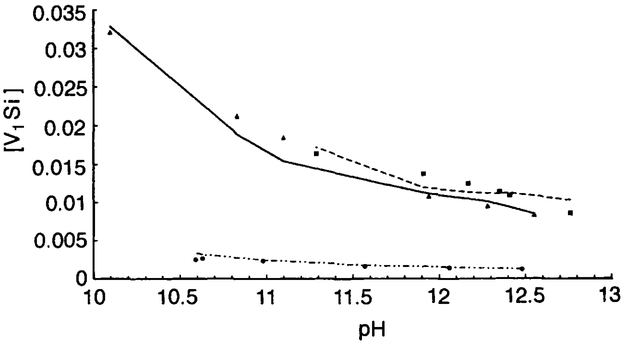


Fig. 6 Observed (points) and calculated (line segment joins) concentrations in mol dm$^{-3}$ of $V_1Si_1$ and $V_1Si_n$ combined *vs.* pH. Conditions: 3 mol dm$^{-3}$ NaCl, 0.05 mol dm$^{-3}$ V (■, - - -); 0.6 mol dm$^{-3}$, NaCl, 0.1 mol dm$^{-3}$ V (▲, ——); 0.6 mol dm$^{-3}$ NaCl, 0.01 mol dm$^{-3}$ V (●, – • •)

Table 1 Logarithmic equilibrium constants

| | Medium | |
|---|---|---|
| | 0.60 mol dm$^{-3}$ NaCl | 3.00 mol dm$^{-3}$ NaCl |
| Approximate log β for $[H_2VSiO_7]^{3-}$ * | 1.12 | 1.20 |
| Approximate log β for $[H_3VSiO_7]^{2-}$ * | 12.66 | 12.83 |
| p$K_a$ for $[H_3VSiO_7]^{2-}$ * | 11.54 | 11.63 |
| Estimated p$K_a$ for $[HVO_4]^{2-}$ | 13.0 | 12.6 |

* Notional formula; integral data include all $V_1Si_1$ and $V_1Si_n$ peaks.

$$H^+ + [H_3SiO_4]^- + [HVO_4]^{2-} \rightleftharpoons [H_3VSiO_7]^{2-} + H_2O \quad (\text{here } m = 1) \quad (1)$$

$$\beta(H_3V_1Si_1) = \log[H_3VSiO_7{}^{2-}] - \log[H_3SiO_4{}^-] - \log[HVO_4{}^{2-}] + pH \quad (2)$$

Although the constants in Table 1 are unavoidably approximate, they clearly show that neither the p$K_a$ values nor the formation constants for the monovanadosilicates depend strongly upon ionic strength. This is consistent with reaction (1), where the product has the same anionic charge as $V_1$, and also consistent in general with the prevalence of rather low anionic charges.

Although the calculations could not include $V_1Si_n$ species, it was qualitatively apparent that the proportion and complexity of these relative to $V_1Si_1$ rose slowly with decreasing pH. Their rise fits well with the corresponding rises in the various $[Si_n]/[Si_1]$, deduced as above.[7] It therefore appears that $V_1$ is not very selective in its combination with oligosilicates, in this pH region. This must be in part because most of the $Si_n$ anions have the same charge here, and offer few steric constraints. The corresponding conclusion does not hold for aluminosilicates, where the aluminate units are frequently bound through several oxygens.[9]

## Conclusion

It is perhaps not surprising that the main anions to form are $[H_2VSiO_7]^{3-}$ and $[H_3VSiO_7]^{2-}$, with single VOSi bridges, for these are closely analogous to the main $V_2$ and $Si_2$ anions also present, namely $[V_2O_7]^{4-}$ and $[Si_2O_2(OH)_5]^-$. The equilibrium constants also indicate a similar strength for the VO and SiO bonds. More surprising is the SiOVOVOSi linkage in $V_2Si_2$, for this is counter to Löwenstein's rule for zeolites.[10] Indeed, Catlow *et al.*[11] have recently argued on theoretical grounds that Löwenstein's rule also holds for aluminosilicate oligomers. However, V is known to prefer to be *cis* to another V, in a variety of mixed-metal vanadates,[4] and this tendency may override Löwenstein's constraint.

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