

Multicomponent Polyanions. 36. Hydrolysis and Redox Equilibria of the $\text{H}^+ - \text{HVO}_4^{2-}$ System in 0.6 M Na(Cl). A Complementary Potentiometric and ^{51}V NMR Study at Low Vanadium Concentrations in Acid Solution

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Combined potentiometric (glass electrode) and ^{51}V NMR measurements in 0.6 M Na(Cl) medium at 25 °C, covering the acidity range $2.5 \leq -\lg[\text{H}^+] \leq 4.5$ at the two vanadium concentrations 0.3125 and 1.25 mM, have been performed. The data can be completely explained with the previously established decavanadate complexes and the monomers VO_2^+ and H_2VO_4^- . Thus no evidence of any uncharged monomer is found even at such a low total concentration of vanadium as 0.3 mM. The chemical shift values of the monomeric peak show a gradual change from H_2VO_4^- to VO_2^+ in a two-proton step. From coulometric measurements the V(V)/V(IV) redox reaction $\text{VO}_2^+ + 2\text{H}^+ + e^- \rightleftharpoons \text{VO}^{2+} + \text{H}_2\text{O}$ has been established in acid solution with $\lg(K_{\text{red}} \pm 3\sigma) = 17.37 \pm 0.01$ ($E^\circ = 1027.6 \pm 0.6$ mV). In the calculations the least-squares computer program LETAGROPVRID was used.

In a recent paper¹ a combined potentiometric and ^{51}V NMR study of vanadates in the range $1 \leq pH \leq 10$ and in 0.6 M Na(Cl) was reported. In the acid region the lowest vanadium concentrations studied were 1.25 mM (emf) and 5 mM (NMR). We found no indication of the uncharged monomer, H_3VO_4 , and it was considered to exist in significant amounts only at vanadium concentrations less than 1.25 mM. To check this assumption, and to determine the NMR-characteristics of H_3VO_4 , the present complementary study was carried out. Moreover, some results concerning the redox chemistry of vanadium in the acid range are included in the paper.

A brief survey of the V(V) literature was given in the previous paper.¹ However, a survey of ^{51}V NMR spectroscopy² was not known by us at that time, and since then a book on heteropoly and isopoly oxometallates, containing a short review of vanadates, has been published.³ No recent studies of the uncharged monomer have been reported. The most reliable results are found in the distribution study of Dyrssen and Sekine from 1964.⁴ In very acid media the existence of $\text{V}_2\text{O}_3^{4+}$, a dimeric V(V) cation⁵ and $\text{V}_2\text{O}_3^{3+}$, a mixed-valence V(IV)/V(V) cation,⁶ has been demonstrated.

Reduced vanadates have been extensively studied and the results are critically summarized in Ref. 7. It is well known that V(IV) is present as VO^{2+} for $pH \leq 3$. The equilibrium constant of the $\text{VO}_2^+/\text{VO}^{2+}$ redox couple is derived from studies in the early

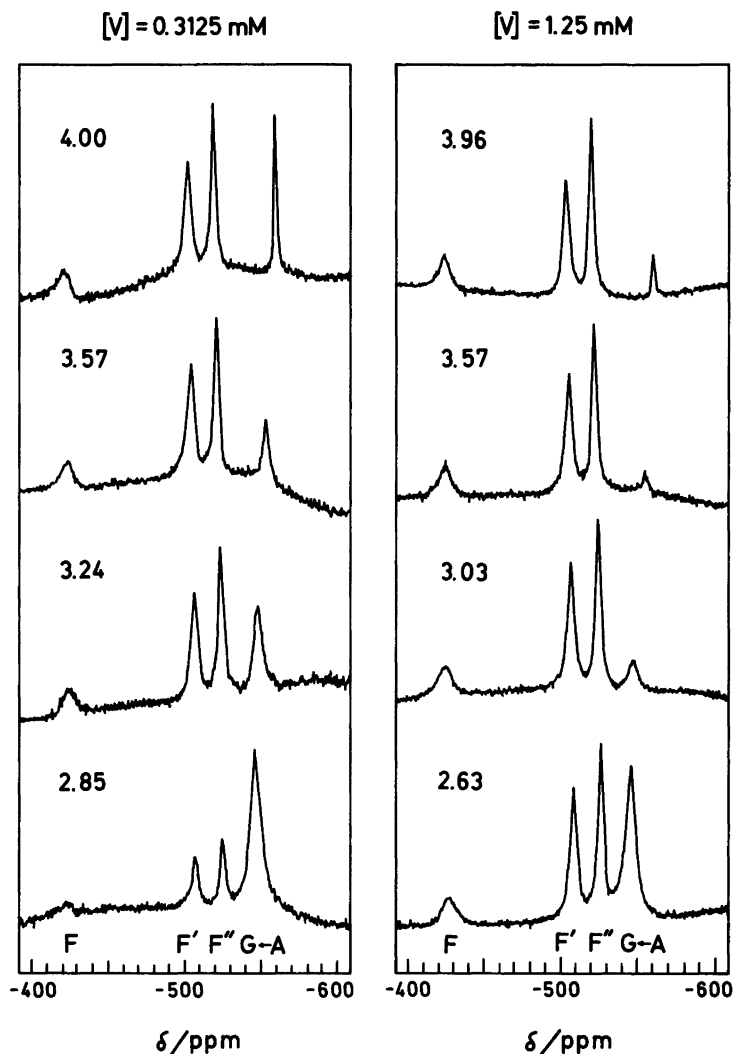


Fig. 1. ^{51}V NMR spectra from solutions with $[\text{V}] = 0.3125$ and 1.25 mM. For each solution $-\lg[\text{H}^+]$ is given. F, F' and F'' denote the three structurally different vanadium atoms in the decavanadate anions $\text{H}_n\text{V}_{10}\text{O}_{28}^{-6+n}$ ($n=0-3$), G the VO_2^+ cation and A the monomeric anions $\text{H}_n\text{VO}_4^{-3+n}$ ($n=0-2$). The spectra have been normalized to give the highest peak the same intensity value. Capillary liquid VOCl_3 was used as external ^{51}V standard with a positive chemical shift (δ) corresponding to a higher frequency.

thirties.^{8,9} The value of $\lg K_{\text{red}}$ is in reference publications evaluated to 16.9 (1.00 V) at 25 °C and at zero ionic strength.¹⁰

The redox conditions in less acidic solutions are, however, much more complicated. Ostrowetsky¹¹ found evidence for decaspecies where two to seven V(V) were reduced to V(IV), but with $\text{V(V)}/\text{V(IV)} = \frac{7}{3}$ and $\frac{3}{2}$ as the only stable species.

Table 1. Experimental and calculated percentage of vanadium bound in the monomers at $[V]=0.3125$ mM. In the calculations on emf models the equilibrium constants from Ref. 1 have been used.

$-\lg[H^+]$	% V in monomers			
	From experimental NMR data	Calculated from emf models with		
		no (2,1)	$\lg \beta_{2,1}=11.72$	$\lg \beta_{2,1}=11.00$
4.00	17	18	28	20
3.92	14	17	28	19
3.79	13	16	29	18
3.72	13	15	29	18
3.57	14	16	31	19
3.40	17	19	37	22
3.24	25	25	46	29
3.06	37	38	61	42

EXPERIMENTAL

The same chemicals, analyses, notations, methods, apparatus and computer programs as in the previous study¹ were used. However, at the low total concentration of vanadium, $[V]$, studied by NMR in the present investigation, it was found convenient not to perform titrations but to prepare a number of solutions of desired composition, calculated by a computer simulation using the program SOLGASWATER.¹² For each of these solutions the NMR spectrum was first recorded, after which the emf measurements were carried out on the *same* sample. Owing to the low vanadium concentration, 1.25 and 0.3125 mM, $\approx 80\ 000$ – $400\ 000$ transients had to be accumulated to obtain spectra with a high signal/noise ratio.

The redox experiments were performed coulometrically at 250 mV vs NHE using an integrating potentiostat built at our department. The platinum electrodes used were cleaned in boiling *aqua regia*, rinsed in distilled water and heated in an ethanol flame.

DATA, EVALUATION AND DISCUSSION

NMR-pH data. The measurements were performed at two vanadium concentrations 1.25 and 0.3125 mM. Some representative spectra are given in Fig. 1. The notation of the peaks is the same as in the previous paper.¹ As seen both from this figure, and particularly from Fig. 2, where the chemical shift (δ) is plotted as a function of $-\lg[H^+]$, the δ of the A peak is pH-dependent in the range 4–2.6. This continuous change from the A-value at -560 ppm to the G-value at -545 ppm, was not detected in the previous study, the reason being that the decavanadates are the only species significantly present in this pH-range at $[V] \geq 5$ mM. Even at four times lower concentration, $[V]=1.25$ mM, they are still quite predominating (Fig. 1). The continuous δ -change from the $H_2VO_4^-$ -value at -560 ppm to the VO_2^+ -value at -545 ppm made us initially believe in the existence of the uncharged monomer, H_3VO_4 . However, no sign of any plateau formation at the half height ($pH \approx 3.5$) was indicated. Moreover, a comparison at $[V]=0.3125$ mM between the concentrations of the monomer as obtained from the peak areas, and the sum of the VO_2^+ and $H_2VO_4^-$ concentrations as calculated from the earlier determined formation constants,¹ showed good accordance. These experimental and calculated values are found in Table 1. The uncertainty in the percentage of vanadium bound in the monomers, as calculated from the experimental peaks,

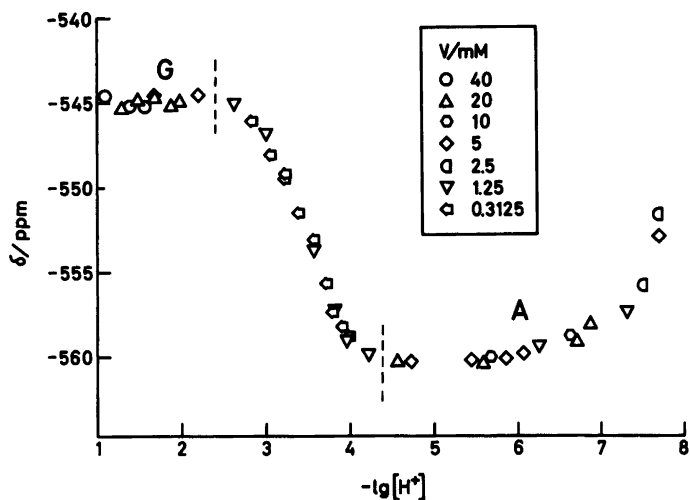
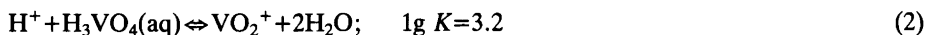
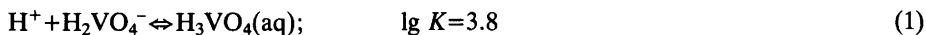


Fig. 2. Chemical shifts, δ , as a function of $-\lg[\text{H}^+]$. Letters refer to the assignments in Fig. 1. The data points collected in the present investigation are between the dashed lines.

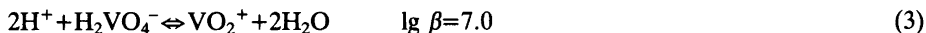
is estimated to be at most 3 units. No experimental point is outside this limit (Table 1). The experimental values are somewhat lower than the calculated. This is in accordance with earlier findings that small peak areas often become slightly underestimated. Thus, from our experimental NMR data there is no sign of any uncharged monomer, although we have studied a vanadium concentration as low as 0.3 mM.

Although we considered NMR data to be much more reliable than emf data at the present low vanadium concentrations ($[\text{V}] = 1.25$ and 0.3125 mM) we found it worthwhile to perform a LETAGROP calculation on the emf data. Besides 14 of the 16 experimental points in the $-\lg[\text{H}^+]$ region 2.6–4.3 (shown in Fig. 2 between the bars), 39 points from 5 titrations at $[\text{V}] = 5$ and 1.25 mM in the $-\lg[\text{H}^+]$ range 2.1–5.6 were included in the data set. In a first calculation (2,1) was varied. (From now on species and formation constants will often be given in (p,q) notation with H^+ and HVO_4^{2-} as components. Thus (2,1) stands for H_3VO_4 .) The formation value $\lg \beta_{2,1} = 11.2 \pm 1.1$ was obtained. The very high 3σ value shows that the uncharged monomer is not consistent with the experimental data. In a second calculation (2,1) was varied together with (1,1) and (3,1) and obtained the value 11.6 ± 0.5 . The 3σ value is still far too high and $\lg \beta_{1,1}$ came out with the value 7.98 which is somewhat too high to be consistent with emf and NMR data in the more alkaline region. Thus, the uncharged monomer cannot be established from the emf data, nor can it be definitely ruled out.

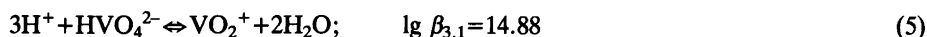
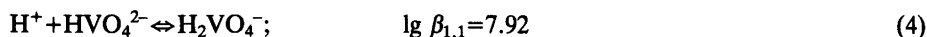
In the earlier mentioned distribution study by Dyrssen and Sekine⁴ (0.5 M $\text{Na}(\text{ClO}_4)$ medium) the acidity constants of the monomers were found to be



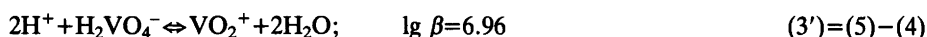
giving



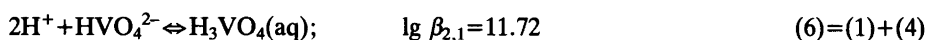
In our previous study¹ (0.6 M NaCl) medium) we established the following monomeric equilibria



giving



Thus, the β values of equilibrium (3)/(3') differ by only 0.04 lg-units, an excellent agreement. Including the uncharged monomer and the formation constant of reaction (1) into our equilibrium model gives



This value of the formation constant is, however, much too high to comply with our experimental NMR data (see Table 1). In order to find the highest value, which can be considered consistent with our data, we stepwise decreased the $\lg \beta_{2,1}$ -value until we obtained acceptable agreement. We thereby found that if the uncharged monomer exists, $\lg \beta_{2,1}$ must have a value slightly lower than 11 (see Table 1). The experimental data are, however, best reproduced when (2,1) was excluded from the calculations. If then (4) and (5) are combined with (6) using the limit $\lg \beta_{2,1} \lesssim 11$, the following pK_a limits are found:

$$pK_a(\text{H}_3\text{VO}_4) \lesssim 3.08 \quad \text{and} \quad pK_a(\text{VO}_2^+) \gtrsim 3.88.$$

It may thus be concluded that the H_3VO_4 species can never become the predominant species in 0.6 M NaCl. It does not, however, exclude its presence in minor amounts at very low total concentrations of vanadium.

In Fig. 3 the distribution of complexes as a function of $-\lg[\text{H}^+]$ is illustrated for $[\text{V}] = 0.3125$ mM, the lowest vanadium concentration studied. The striking feature in the neutral region is that the monomeric species dominates over the polynuclear species due to the low concentration. At higher acidity, the decavanadates are found to be "squeezed" between the two monomers (3,1) and (1,1). The three-protonated decavanadate (17,10) is not found at all and the unprotonated (14,10) is present only to a very small extent. It may be noted that at pH around 3.5, where the decavanadates are at maximum, as much as 15–20 % of the vanadium is bound in the monomers even though no uncharged species is present. If an uncharged monomer existed, it would certainly appear in this pH -range. The only way to include H_3VO_4 in the equilibrium model is to decrease the formation constants of the other two monomers. Both constants are, however, accurately determined and such a decrease would make it impossible to obtain a good explanation of the experimental data in the neutral and the more acid pH -range.

Redox-pH data. Combined redox- pH data were collected at the two total vanadium (V+IV) concentrations, $[\text{V}]_{\text{tot}}$, 5.00 and 1.25 mM in the $-\lg[\text{H}^+]$ range 1.5–8. In all the experiments argon gas was bubbled through the solutions to prevent contamination by oxygen from the air. Stable redox potentials were obtained when appreciable amounts of the

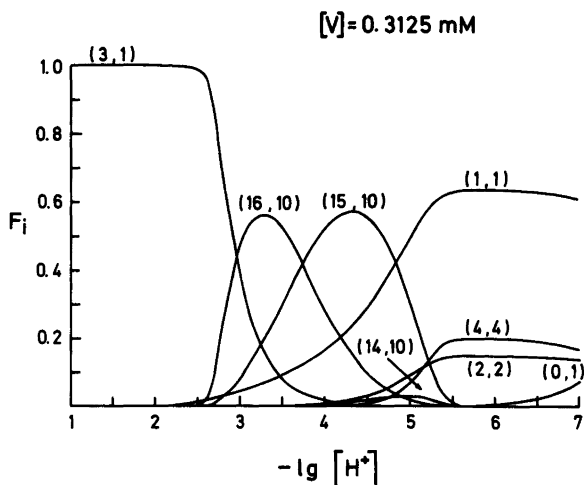


Fig. 3. Distribution diagram $F_i(-\lg[H^+])$ at $[V]=0.3125$ mM. The quantity F_i is defined as the ratio between vanadium in a species to total vanadium. In the calculations, the constants from Ref. 1 were used. For clarity, species with $F_i < 0.02$ have been omitted. Complexes are given in (p, q) notation; $(3,1)=VO_2^+$, $(1,1)=H_2VO_4^-$, $(14,10)=V_{10}O_{28}^{6-}$, $(4,4)=V_4O_{12}^{4-}$, $(2,2)=H_2V_2O_7^{2-}$.

VO_2^+ cation are present ($-\lg[H^+] \leq 3$). In solutions where VO_2^+ is predominant the colour changed from yellow over green ($VO_2^+ + VO^{2+}$) to blue (VO^{2+}) when electrons were added. In slightly acid solutions, $-\lg[H^+] \geq 3$, where the decavanadate species are predominant, the addition of electrons caused a change in colour from orange to green to blue to almost black. The species became increasingly difficult to reduce, and lower and lower potentials had to be applied. No stable redox potentials were obtained and also a slight drift in the pH-value was observed. In our opinion this behaviour indicates formation of partly reduced decavanadate species containing delocalized electrons. The dark colour cannot arise from $V_2O_3^{3+}$, the dimeric mixed-valence V(IV)/V(V) cation described in Ref. 6, as in our experiments the solutions are not acidic enough, and the total vanadium concentrations are too low. In the metavanadate range ($pH \approx 7$), no reduction occurred until such a low potential was applied that hydrogen gas was evolved. Thus, the only redox equilibrium that could be studied by using a potentiostat and a platinum foil as electron mediator, was the assumed cation V(V)/V(IV) reaction



The evaluation of the redox equilibrium constant, K_{red} , is easily performed in solutions of such acidity that VO_2^+ does not hydrolyze. Some of these data are illustrated in Fig. 4. The data points can be described by the expression $-(2\lg[H^+] + \lg\{e^-\}) = \lg([VO_2^+]/[VO^{2+}]) + \lg K_{red}$. Thus reaction (7) is valid. A graphical evaluation of the plot gave $\lg K_{red} \approx 17.4$. As can be seen from the stoichiometry of the reaction the formation of VO^{2+} consumes H^+ . This means that the pH value increases during the titrations and in most cases the decavanadate region was reached. Such titration points could not easily be evaluated graphically. To determine the constant more accurately and to be able to include also these data points the least-squares computer program LETAGROPVRID¹³ version ETITR¹⁴

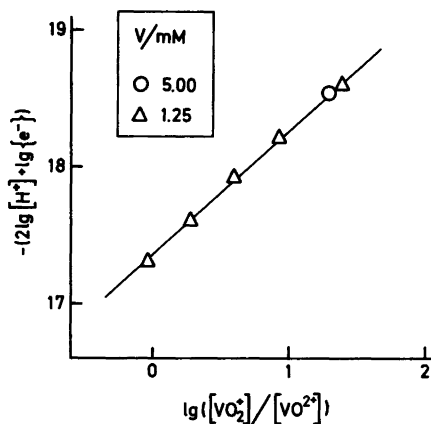


Fig. 4. The experimental data used in a graphical evaluation of the redox equilibrium constant, K_{red} . The data points can be described by the expression $-(2 \lg[\text{H}^+] + \lg\{e^-\}) = \lg([\text{VO}_2^+]/[\text{VO}^{2+}]) + \lg K_{\text{red}}$. For $[V] = 5 \text{ mM}$ only the most acid point has been plotted as all the other titration points are from the hydrolysis range.

was used. Having added such data points the set then consisted of 24 experimental points from four titrations with $[V]_{\text{tot}} = 1.25$ and 5 mM . The speciation and formation constants established in the previous study¹ were used but recalculated with VO_2^+ instead of HVO_4^{2-} as reacting species. In the first calculation the error squares sum $U = \sum (H_{\text{calc.}} - H)^2$ was minimized and in the second calculation $U = \sum (\{e^-\}_{\text{calc.}} - \{e^-\})^2$. The value obtained for $\lg(K_{\text{red}} \pm 3\sigma)$ was 17.373 ± 0.008 and 17.367 ± 0.007 , respectively, with a mean value of 17.37 ± 0.01 ($E^\circ = 1027.6 \pm 0.6 \text{ mV}$).

The solutions from the redox experiments were also investigated by ^{51}V NMR. As V(IV) was NMR silent, as expected for a paramagnetic nucleus, the only detectable resonance was that from VO_2^+ . It showed no shift in δ and the peak was gradually diminished until finally disappearing when all V(V) had been reduced to V(IV).

CONCLUSIONS

We have found that the uncharged monomer H_3VO_4 is not present in the acidity range $2.5 \leq -\lg[\text{H}^+] \leq 4.5$ at $[V] > 0.3 \text{ mM}$. The observed gradual δ -change with $-\lg[\text{H}^+]$ in the ^{51}V NMR data stems from the formally two-proton conversion of H_2VO_4^- to VO_2^+ , giving a change in geometry from a protonated tetrahedron to a presumably five- or six-coordination environment¹⁵ with a bent VO_2^+ moiety.¹⁶ A lower symmetry environment is also indicated by the increased full-width half-maximum value of the G-peak.

The absence of the H_3VO_4 monomer at $[V] \approx 0.3 \text{ mM}$ further indicates that previously published values for the formation constant of this complex are too high. If H_3VO_4 exists at all, its pK_a -value must be less than 3.1 giving $pK_a(\text{VO}_2^+)$ a value greater than 3.9. This implies that H_3VO_4 never becomes dominant, irrespective of dilution.

Furthermore, through combined redox and pH measurements, we have established the redox reaction in acid solutions ($\text{pH} < 3$) to be $\text{VO}_2^+ + 2\text{H}^+ + e^- \rightleftharpoons \text{VO}^{2+} + \text{H}_2\text{O}$ and determined the $\lg K_{\text{red}}$ value to be 17.37 ± 0.01 in 0.6 M NaCl medium. This value is in good accordance with previously accepted values at zero ionic strength (*cf.* Introduction).

The results of our studies of the binary $\text{H}^+ - \text{HVO}_4^{2-}$ system in 3.0 M NaClO_4 medium,¹⁷ of speciation changes in the slow equilibrium region between deca- and metavanadates through a time-dependent ^{51}V NMR study, and of the speciation dependence of ionic media, will all be published shortly.

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