

# Multicomponent Polyanions. 40. A Potentiometric and $^{51}\text{V}$ NMR Study of Equilibria in the $\text{H}^+ - \text{H}_2\text{VO}_4^- - \text{C}_2\text{O}_4^{2-}$ System in 0.6 M Na(Cl) Medium

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The speciation in the  $\text{H}^+ - \text{H}_2\text{VO}_4^- - \text{C}_2\text{O}_4^{2-}$  system was determined from potentiometric (glass electrode) and  $^{51}\text{V}$  NMR measurements. The study was performed in 0.6 M Na(Cl) medium at 25 °C. The potentiometric data cover the range  $2 \leq -\lg[\text{H}^+] \leq 8$ , and were evaluated with the computer program LE-TAGROPVRID. The NMR data collected were recorded in the region  $1 \leq -\lg[\text{H}^+] \leq 7$  and used qualitatively to find the number of complexes and quantitatively to find whether the complexes and formation constants from the potentiometric data were in accordance with the NMR data. Two ternary complexes,  $(\text{H}^+)_p(\text{H}_2\text{VO}_4^-)_q(\text{C}_2\text{O}_4^{2-})_r$ , having the  $(p, q, r)$  values (2,1,2) and (2,1,1) with  $\lg \beta_{2,1,2} = 17.11 \pm 0.01$  and  $\lg \beta_{2,1,1} = 13.07 \pm 0.02$  explained all potentiometric and NMR data within the  $-\lg[\text{H}^+]$  range covered. The errors given are  $3\sigma$ . The equilibrium conditions are illustrated in distribution and predominance diagrams and possible structures discussed.

When fossil fuels are burnt, vanadium pentoxide is released to the environment. A Swedish study has shown that vanadium is enriched in the neighbourhood of a power station.<sup>1</sup> To understand how this vanadium reacts in nature, it is necessary to know the complex chemistry of pentavalent vanadium, V(V). One of the most abundant organic ligands in nature is oxalic acid.<sup>2,3</sup> It is therefore of vital interest to know what complexes form between vanadate and oxalate and how strong they are. In the literature, the most frequently reported species have the oxalate/vanadate ratios one and two. In some of the studies, the formation constants of the vanadoolxalate complexes have been given.<sup>4-7</sup> These studies have however been flawed by the lack of accurate knowledge of the hydrolysis of V(V). This is clearly demonstrated by the fact that the value of the formation constant obtained by different authors can differ by as much as four logarithmic units. The hydrolysis of V(V) is very complicated but has recently been determined at our department in the two media 0.6 M Na(Cl)<sup>8</sup> and 3.0 M

Na(ClO<sub>4</sub>).<sup>9</sup> With these results as a firm basis, we have started a project to study the complexation of vanadate with both inorganic and organic ligands. In the present study of the vanadoolxalate system, 0.6 M Na(Cl) was chosen as constant ionic medium to resemble the conditions prevailing in seawater.

## Experimental

The study was carried out in fundamentally the same manner as an earlier work on the binary vanadate system.<sup>8</sup>

*Chemicals and analyses.* Disodium oxalate (Merck *p.a.*) was dried at 120 °C and used without further purification. The other chemicals used were treated and analysed as described in Ref. 8. Boiled distilled water was used in the preparation of solutions. The concentration of  $\text{H}^+$ -consuming impurities in the titration solutions was found to be  $2 \cdot 10^{-5}$  M.

Table 1. Species and hydrolysis constants used in LETAGROP calculations (0.6 M NaCl), 25 °C).

$(p, q, r)$	$\lg \beta_{par}$	Formula	NMR assignments
1,0,0	—	H <sup>+</sup>	—
-1,1,0	-7.92	HVO <sub>4</sub> <sup>2-</sup>	} A
0,1,0	—	H <sub>2</sub> VO <sub>4</sub> <sup>-</sup>	
0,2,0	2.77	H <sub>2</sub> V <sub>2</sub> O <sub>7</sub> <sup>2-</sup>	B
0,4,0	10.0	V <sub>5</sub> O <sub>12</sub> <sup>4-</sup>	D
0,5,0	12.4	V <sub>5</sub> O <sub>15</sub> <sup>5-</sup>	E
4,10,0	52.1	V <sub>10</sub> O <sub>28</sub> <sup>6-</sup>	} F, F', F''
5,10,0	58.1	HV <sub>10</sub> O <sub>28</sub> <sup>5-</sup>	
6,10,0	61.9	H <sub>2</sub> V <sub>10</sub> O <sub>28</sub> <sup>4-</sup>	
7,10,0	63.5	H <sub>3</sub> V <sub>10</sub> O <sub>28</sub> <sup>3-</sup>	
2,1,0	6.96	VO <sub>2</sub> <sup>+</sup>	
0,0,1	—	C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	—
1,0,1	3.57	HC <sub>2</sub> O <sub>4</sub> <sup>-</sup>	—
2,0,1	4.54	H <sub>2</sub> C <sub>2</sub> O <sub>4</sub>	—

**Potentiometric measurements.** The measurements were carried out as a series of potentiometric titrations in 0.6 M NaCl medium at 25 °C. In the present system, anion equilibria were studied in which some of the ions formed are highly charged (i.e. V<sub>10</sub>O<sub>28</sub><sup>6-</sup>). We therefore chose to maintain the counterions in the medium, Na<sup>+</sup>, at a constant concentration. The measurements were made with an automated potentiometric titrator, somewhat modified from the description given in Ref. 10. The solution in the titration vessel was protected from atmospheric carbon dioxide by an argon or nitrogen gas stream. The glass electrode used was of the general purpose type, Ingold 201-NS. The free hydrogen ion concentration was calculated from the measured emf using the equation  $E = E_o + 59.157 \lg[H^+] + E_j$ .

As V(V) takes part in proton equilibria in the whole pH region studied, the calibration of the glass electrode (i.e. the determination of the constant  $E_o$ ) had to be performed separately in solutions with known [H<sup>+</sup>]. To check any variation,  $E_o$  was determined before and after each titration. For the liquid junction potential,  $E_j = -76[H^+]$  was used.

**NMR measurements.** <sup>51</sup>V NMR spectra were recorded at 65.76 MHz (5.9T) using a Bruker WM-250 FT spectrometer. The probe temperature was 24 ± 1 °C throughout. The field frequency sta-

bilization was established by inserting a D<sub>2</sub>O-filled capillary tube (i.d. = 1.5 mm) coaxially inside the 10 mm NMR tubes. Capillary liquid VOCl<sub>3</sub> was used as external <sup>51</sup>V standard with a positive chemical shift ( $\delta$ ) corresponding to higher frequency. Spectral widths of 20 kHz were used, described by 4 K input data points. The spectra were obtained from the accumulation of 6400–25 600 transients at acquisition times 10<sup>-1</sup> s. The free induction decays were in most cases multiplied with an exponential line-broadening (3 Hz) function in order to improve the signal-to-noise ratio. As <sup>51</sup>V is a quadrupolar nucleus, the relaxation times are short. The  $T_1$  values were found to be shorter than 10<sup>-3</sup> s, so that peak areas gave a reliable measure of relative concentration.

**Notations.** The equilibria studied are written with H<sup>+</sup>, H<sub>2</sub>VO<sub>4</sub><sup>-</sup> and C<sub>2</sub>O<sub>4</sub><sup>2-</sup> as components and thus the complexes are formed according to

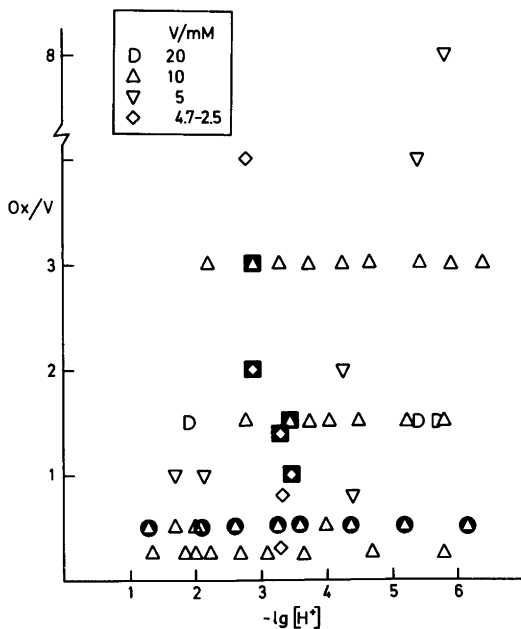
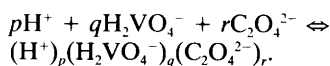


Fig. 1. Points, Ox/V ( $-\lg[H^+]$ ), where NMR spectra have been recorded. The filled circles and squares mark the NMR spectra shown in Figs. 2 and 3, respectively.

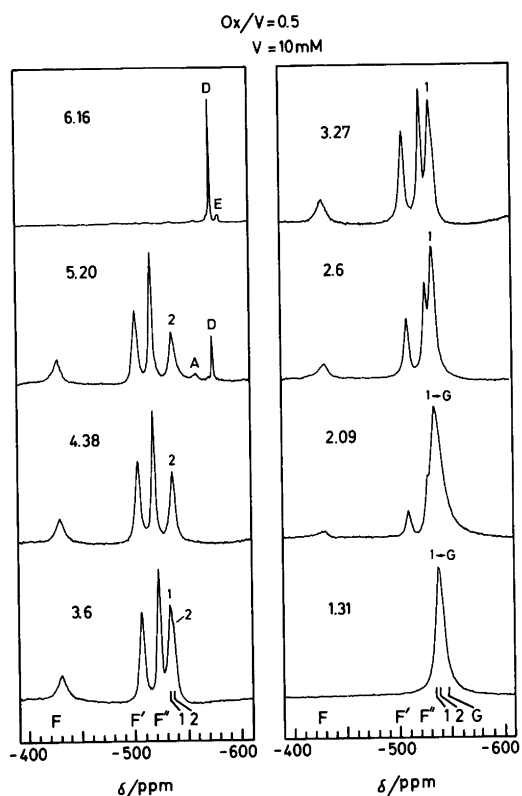


Fig. 2. Some  $^{51}\text{V}$  NMR spectra from a  $-\lg[\text{H}^+]$  titration at  $V = 10$  mM,  $\text{Ox} = 5$  mM. On the left, is given the  $-\lg[\text{H}^+]$  value for each solution. Letters refer to binary vanadates (see Table 1) and figures to ternary species.

Equilibrium constants are denoted  $\beta_{p,q,r}$  and complexes are, for brevity, often given the notation  $(p,q,r)$ . The symbols  $V$  and  $\text{Ox}$  stand for the total concentrations of vanadate and oxalate, respectively;  $H$  the excess concentration of hydrogen ions over the zero level  $\text{H}_2\text{O}$ ,  $\text{H}_2\text{VO}_4^-$  and  $\text{C}_2\text{O}_4^{2-}$ . The free concentration of  $\text{H}^+$  is denoted  $h$ . The  $\text{H}^+$  bound per  $\text{H}_2\text{VO}_4^-$  and  $\text{C}_2\text{O}_4^{2-}$  is denoted  $Z_v$  and  $Z_{\text{Ox}}$ . Thus,  $Z_v = (H-h)/V$  and  $Z_{\text{Ox}} = (H-h)/\text{Ox}$ . The deviation between  $H$  calculated from potentiometric data,  $H_{\text{calc}}$  and  $H$  calculated from analytical concentrations,  $H_{\text{top}}$  is denoted  $\Delta H$ .

**Computer programs.** The mathematical analysis of data was performed with the least-squares program LETAGROPVRID<sup>11</sup> version ETITR<sup>12</sup> and the error-squares sums  $U = \sum(\Delta H)^2$ ,  $U = \sum(\Delta H/$

$V)^2$  and  $U = \sum(\Delta H/\text{Ox})^2$  were minimized. The standard deviations were defined and calculated according to Sillén.<sup>13,14</sup> Calculation and plotting of distribution and predominance diagrams were performed with the program SOLGASWATER.<sup>15</sup> The computations were all carried out on a CD Cyber 730 computer.

**Binary equilibria.** The equilibrium conditions in the vanadate system are well known from a previous study in 0.6 M Na(Cl) medium.<sup>8</sup> Since  $\text{HVO}_4^{2-}$  was used as component in that study, we recalculated the formation constants with  $\text{H}_2\text{VO}_4^-$  as component. These recalculated values are given in Table 1. The formation constants in the oxalate system (0.6 M Na(Cl) medium) have also been determined at our department<sup>16</sup> and are given in the table as well.

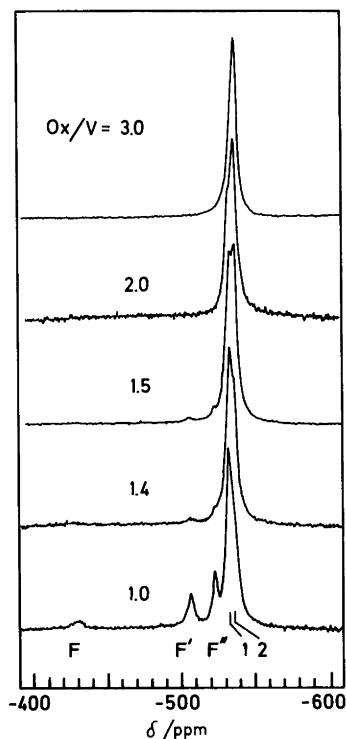


Fig. 3.  $^{51}\text{V}$  NMR spectra from solutions with similar  $-\lg[\text{H}^+]$  values (2.9–3.5) but different  $\text{Ox}/V$  ratios (1–3). The  $V$  and  $-\lg[\text{H}^+]$  values for each solution can be found in Fig. 1 (filled squares). Letters refer to binary vanadates and figures to ternary species.

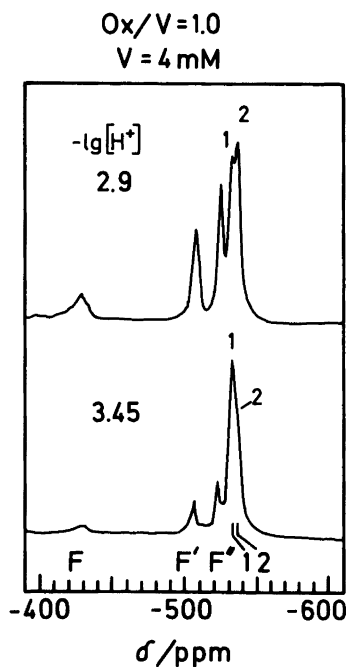


Fig. 4.  $^{51}\text{V}$  NMR spectra from a time-dependent study on an  $\text{Ox}/V = 4$  mM,  $V = 4$  mM solution. The upper spectrum is recorded 2 h and the lower 24 h after mixing.

### Description of data

**NMR data.** In total, NMR spectra were recorded from 56 vanadate solutions in the ranges  $1 < -\lg h < 7$ ,  $2.5 \leq V \leq 20$  and  $0.25 \leq \text{Ox}/V \leq 8$  (see Fig. 1). Representative solutions were selected both from titrations with constant  $\text{Ox}/V$  at different  $h$  and from ratio titrations at almost constant  $h$ . Spectra from such titrations are shown in Figs. 2 and 3. A time-dependent study on a solution from a slow equilibrium region was also made in order to follow the speciation changes until equilibrium was reached (see Fig. 4).

For most solutions, the  $-\lg h$  value was measured in close connection to the recording of the spectrum. In some cases, the  $-\lg h$  value was evaluated from the chemical shift values of the decavanadate peaks. In the previous studies on the binary vanadate system,<sup>8,9</sup> the different peaks were assigned letters. Thus, F, F' and F'' are the three peaks from the structurally different vanadium atoms in the decavanadate ions and G the

$\text{VO}_2^+$  cation. In Fig. 5, all chemical shift values of the vanadate peaks are plotted as a function of  $-\lg h$ . For comparison, shifts of the G peak from the previous study<sup>8</sup> are plotted as well. Just two peaks were found, labelled 1 and 2. Peak 2 originated from the first vanadate complex formed and shows no  $-\lg h$ -dependence, which indicates no protonation equilibria. At  $\text{Ox}/V \leq 2$  and  $-\lg h < 4$ , peak 1 appeared. When  $\text{Ox}/V = 1/4$  and  $-\lg h$  is lowered, this peak moved towards the shift expected for the  $\text{VO}_2^+$  peak (G), the limiting value being 3/4 of the way to G. When  $\text{Ox}/V = 1/2$  the corresponding limit is half-way. This behaviour indicates that there is rapid exchange between the ternary complex 1 and the  $\text{VO}_2^+$  cation, so that they cannot be individually detected on the NMR time scale. A strong complex with an  $\text{Ox}/V = 1$  ratio is in accordance with the change in the chemical shift values. Thus, in solutions with  $\text{Ox}/V = 1/2$ , 50% of the vanadium is present as species 1 and 50% as  $\text{VO}_2^+$  when the solutions are sufficiently acidic. With equal amounts of  $\text{VO}_2^+$  and 1, the  $\delta$  values of such a solution will then be the arithmetic mean value of the  $\text{VO}_2^+$  and 1 peaks.

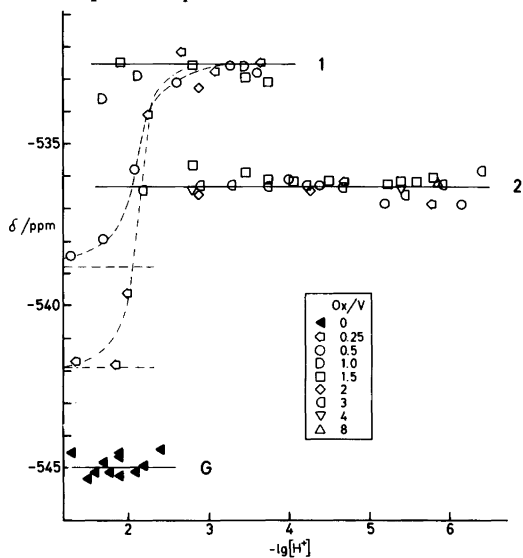


Fig. 5. Chemical shifts,  $\delta$ , as a function of  $-\lg[\text{H}^+]$ . The figures refer to vanadate species and G to the  $\text{VO}_2^+$  cation. The barred horizontal line marks half the distance from 1 to G and the barred curve shows the  $\delta$  change of the ternary peak in acid  $\text{Ox}/V = 0.5$  solutions. The bar-dotted horizontal line marks three-quarters of the distance; the curve the  $\delta$  change in acid  $\text{Ox}/V = 0.25$  solutions.

As shown in Fig. 5, both peak 1 and 2 coexist around  $-\lg h = 3$  when  $1 < Ox/V < 3$ . Spectra of solutions from a ratio titration in this region are given in Fig. 3. When  $Ox/V = 1$ , peak 2 cannot be detected but, when the ratio is increased, peak 2 shows up first as a small shoulder then turns to a peak which increases at the expense of peak 1 to become predominant. At  $Ox/V = 1.5$ , the two peaks are equal in size. This behaviour strongly indicates that peak 2 originates from a complex having  $Ox/V = 2$ . The linewidth at half-height is about  $3.5 \cdot 10^{-2}$  Hz (5.3 ppm) for either peak.

**Potentiometric data.** Data cover the ranges  $2 < -\lg h < 8$ ,  $1.25 \leq V \leq 20$  mM,  $1 \leq Ox \leq 40$  mM; the oxalate to vanadate ratio was varied between the limits  $0.25 \leq Ox/V \leq 16$ . Some additional acidic data ( $-\lg h < 2$ ) were also collected from the combined emf-NMR experiments. They have not, however, been included in the final calculations on emf data. In total, about 600 experimental titration data points were collected. However, many points had to be excluded as there was a drift in the emf values. These slow equilibria were for most points caused by the spontaneous reduction of V(V) at high  $Ox/V$  ratios in acid solutions. In some cases, the reason was that full equilibrium was not attained in the instability range of the  $H^+ - H_2VO_4^-$  system. After the exclusion, 206 points remained and these were used for the final calculations. In order to check the reversibility of data two types of titrations were carried out: titrations at constant  $Ox$  and  $V$  varying  $H$ ; and titrations varying the  $Ox/V$  ratio in a restricted  $-\lg h$  area. As a further check, all titra-

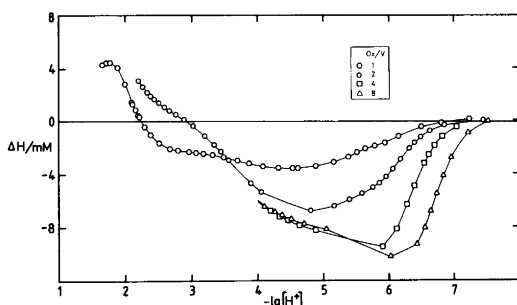


Fig. 6. Residual plot  $\Delta H(-\lg[H^+])$  with  $V = 5$  mM at different  $Ox/V$  ratios. Each symbol represents a titration point. Points below  $-\lg[H^+] = 4$  have been omitted for the titrations with  $Ox/V = 4$  and  $8$  due to reduction.

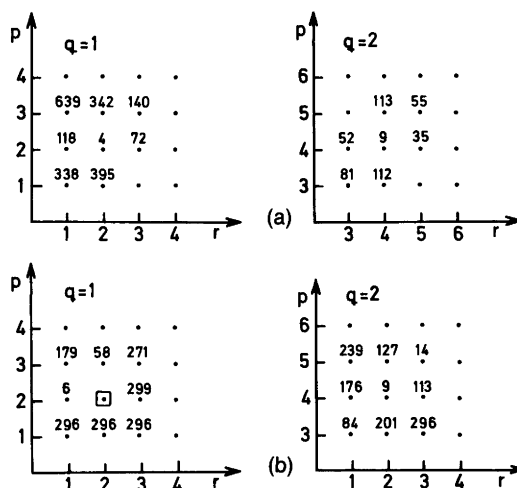


Fig. 7. Results from preliminary  $(p, q, r)$  analyses. Error-squares sums  $U(H)$  are plotted as a function of various  $(p, r)$  sets at  $q = 1$  and  $q = 2$ . (a) Data consist of 36 experimental points with  $Ox/V \geq 2$  and  $4.6 < -\lg[H^+] < 8$ . (b) Data consist of 103 experimental points with  $Ox/V \leq 1$  and  $-\lg[H^+] > 2$ .

tions were performed in both increasing and decreasing  $-\lg h$  and  $Ox/V$  directions, giving excellent agreement. In the binary  $H^+ - H_2VO_4^-$  system, the solubility of  $V_2O_5(s)$  is approximately 2 mM at  $-\lg h \sim 2.5$ . The supersaturation is, however, considerable. Therefore, the concentration ranges are restricted mainly by the reduction of V(V) and not by precipitation.

**Analysis of data.** In the potentiometric titrations,  $h$  is accurately measured. From  $h$ ,  $V$ ,  $Ox$  and the known equilibrium constants of the binary  $H^+ - H_2VO_4^-$  and  $H^+ - C_2O_4^{2-}$  complexes,  $H$  can be calculated. If this  $H_{calc}$  value then deviates from the analytically known  $H$  value, ternary vanadooxalate species must be formed. Inspection of the deviations  $\Delta H = H_{calc} - H_{tot}$  at different  $Ox/V$  ratios gives valuable hints of the stoichiometry of these complexes. From a  $(p, q, r)$  search in restricted  $-\lg h$  ranges and/or  $Ox/V$  ratios, that  $(p, q, r)$  set which gives the lowest error-squares sum is considered to represent the predominant complex. It should, however, be borne in mind that the found  $p$ ,  $q$  and  $r$  figures can be the mean values from coexisting species. Consequently, combinations of two or more complexes must be tested as well. The search tends to swell and often many

combinations explain the data almost equally well. A complementary method such as NMR, which identifies the number of complexes present, thus greatly facilitates the  $(p,q,r)$  analysis. Moreover, the results obtained are considered to be much more reliable if the NMR data are collected in a quantitative way and the proposed complexes and formation constants are in accordance with both emf and NMR data.

The potentiometric study was started with some titrations at  $V = 5$  mM and with the different  $Ox/V$  ratios 1, 2, 4 and 8. The deviations,  $\Delta H$ , as a function of  $-\lg h$  were calculated and are plotted in Fig. 6. For the highest  $Ox/V$  ratio, the  $\Delta H$  curve has a minimum at  $-\lg h \sim 6$ , where the binary systems have consumed no  $H^+$  over the zero points,  $H_2VO_4^-$  and  $C_2O_4^{2-}$ . As the  $\Delta H$  value is  $\sim -10$  mM, which is twice the concentration of vanadium, one can conclude that a vanadooxalate complex was formed having a  $H/V$  ratio of about 2. When going from the ratio 8 to 4, small changes in the deviations occurred. At still lower ratios, 2 and 1,  $\Delta H$  was greatly changed, indicating that the  $Ox/V$  ratio in the complex was somewhere between 1 and 4 and most probably around 2. Thus  $(H^+)_2(H_2VO_4^-)(C_2O_4^{2-})_2$  is a very plausible composition, although multiples such as  $(4,2,4)$ ,  $(6,3,6)$  and so on must be considered as well.

In acid solutions ( $-\lg h \leq 2.5$ )  $\Delta H$  changed sign to plus. This means that the vanadooxalate complex(es) consumed fewer protons than the binary systems. For  $V = 5$  mM,  $Z_v$  reaches the value 2 at  $-\lg h \sim 1.8$  and the reaction  $H_2VO_4^- + 2H^+ \rightleftharpoons VO_2^+ + 2H_2O$  is completed. The  $pK_a$  values in the oxalate system are 0.97 and 3.57. Thus at  $-\lg h \sim 1.8$ ,  $Z_{ox}$  is very close to 1. The NMR data strongly indicated a  $Ox/V = 1/1$  complex. If this complex has the composition  $(H^+)_2(H_2VO_4^-)(C_2O_4^{2-})$  it consumes one proton fewer than the binary systems, which is in accordance with the  $+5$  mM  $\Delta H$  value for the  $Ox/V = 1$  titration in Fig. 6.

By combining the information obtained from NMR data with the behaviour of the  $\Delta H$  curves, it was possible to postulate the existence of two vanadooxalate complexes with probable compositions  $(2,1,2)$  and  $(2,1,1)$ . To ascertain these species, a  $(p,q,r)$  search was performed. This search was much facilitated by means of information from NMR spectra which enabled proper  $-\lg h$  and  $Ox/V$  regions to be chosen. The data were divided into two groups, one with  $Ox/V \geq 2$  and  $-\lg h > 4.6$ , to establish the complex which gave rise to peak 2. As seen in Fig. 7a,  $(2,1,2)$  had the lowest  $U$  value. This complex was then considered as known in the  $(p,q,r)$  search for the complex which gave rise to peak 1. The data used for

Table 2. Results from the final LETAGROP calculations. Data consist of 20 titrations and 206 experimental points in the range  $2.1 \leq -\lg[H^+] \leq 7.4$ . The binary constants used are compiled in Table 1 (0.6 M Na(Cl), 25°C).

Calc. No.	$(p,q,r)$ combination	$\lg \beta_{p,q,r} \pm 3\sigma$	Error	$U$	$\sigma$
1	2,1,2	17.11±0.01	$\Delta H$	2.0	0.099
	2,1,1	13.07±0.02			
2	2,1,2	17.14±0.02	$\Delta H$	7.3	0.189
	4,2,2	28.50±0.07			
3	4,2,4	36.58±0.09	$\Delta H$	24.6	0.347
	2,1,1	13.01±0.08			
4	4,2,4	36.61±0.10	$\Delta H$	30.2	0.385
	4,2,2	28.45±0.15			
5	2,1,2	17.10±0.01	$\Delta H/V$	$8.6 \cdot 10^{-2}$	0.020
	2,1,1	13.12±0.02			
6	2,1,2	17.10±0.02	$\Delta H/Ox$	$3.5 \cdot 10^{-2}$	0.013
	2,1,1	13.06±0.02			

this search were restricted to  $Ox/V \leq 1$  and  $-\lg h > 2$  in order to avoid points where reduction had occurred. The  $U$  values for the different  $(p, q, r)$  sets tested are given in Fig. 7b. Even in this search, the expected answer was obtained: (2,1,1) was found to give the lowest  $U$  value.

In order to make an accurate determination of the formation constants, complementary titrations were performed. Data were then once more examined to finally exclude all the points where reduction had occurred or equilibria had not been attained. Results from some LETAGROP calculations on this final data set are given in Table 2.

In the first calculation, the pair (2,1,2) and (2,1,1), which had given the lowest  $U$  value in the preliminary  $(p, q, r)$  analysis (Fig. 7) was used. The small  $\Delta H$  residuals that remained showed no systematic trend and the standard deviations of the formation constants were low. However, before this pair could be considered as the final model, other pairs should be tested. In the Tables (Nos. 2, 3 and 4) some results from calculations

using species which gave low  $U$  values in the  $(p, q, r)$  search are shown. All these pairs gave much higher error-squares sums and standard deviations when covaried. Thus the pair (2,1,2), (2,1,1) constituted the "best" emf model. So far, the error-squares sums had been calculated using the error  $\Delta H = H_{calc} - H_{tot}$ . It was found worthwhile to test the influence of relative errors on the formation constants. In two calculations on the "best" model (Nos. 5 and 6), the error-squares sums  $\Sigma(\Delta H/V)^2$  and  $\Sigma(\Delta H/Ox)^2$  were minimized. The values of the formation constants did not vary significantly, indicating no large systematic concentration errors in the vanadate and oxalate stock solutions.

As a final check it was tested whether the "best" emf model was in accordance with the experimental NMR data. To obtain accurate quantitative data, the area of each peak was evaluated by multiplying the height and the half-height width values manually measured from expanded plots. The percentage values are compiled in Table 3. As the two ternary peaks severely over-

Table 3. Experimental and calculated percentage of vanadium bound in vanadooxalate species at  $V = 10$  mM. In the calculation, the values from Table 2 with  $\Delta H$  as error were used. The distribution for  $Ox/V = 1.5$  is also illustrated in the upper distribution diagram in Fig. 8.

$Ox/V$	$-\lg[H^+]$	% V in (2,1,1)		% V in (2,1,2)		% V in (2,1,1)+(2,1,2)	
		Exp. NMR data	Emf model	Exp. NMR data	Emf model	Exp. NMR data	Emf model
0.25	2.26	44 <sup>a</sup>	24+19	0	0	44 <sup>a</sup>	24+19
0.25	2.67	29 <sup>a</sup>	24+5	0	0	29 <sup>a</sup>	24+5
0.25	3.09	24	20	0	2	24	22
0.25	3.65	16	12	0	6	16	18
0.25	4.70	0	3	7	9	7	12
0.25	5.79	0	0	0	4	0	4
1.5	1.91	100	68	0	31	100	99
1.5	2.90	50	53	50	46	100	100
1.5	3.46	49	40	51	52	100	92
1.5	3.74	0	28	88	60	88	88
1.5	4.05	0	20	83	63	83	83
1.5	4.51	0	8	77	67	77	75
1.5	5.24	0	3	66	63	66	66
1.5	5.80	0	0	52	47	52	47
3	2-5.5	0	0	100	100	100	100
3	5.92	0	0	94	90	94	90
3	6.42	0	0	30	34	30	34

<sup>a</sup>In these two points, NMR data give the sum of (2,1,1) and  $VO_2^+$ . According to the emf model, 19% at  $-\lg h = 2.26$  and 5% at  $-\lg h = 2.67$  originate from  $VO_2^+$ . These figures have therefore been added to (2,1,1) in the emf column.

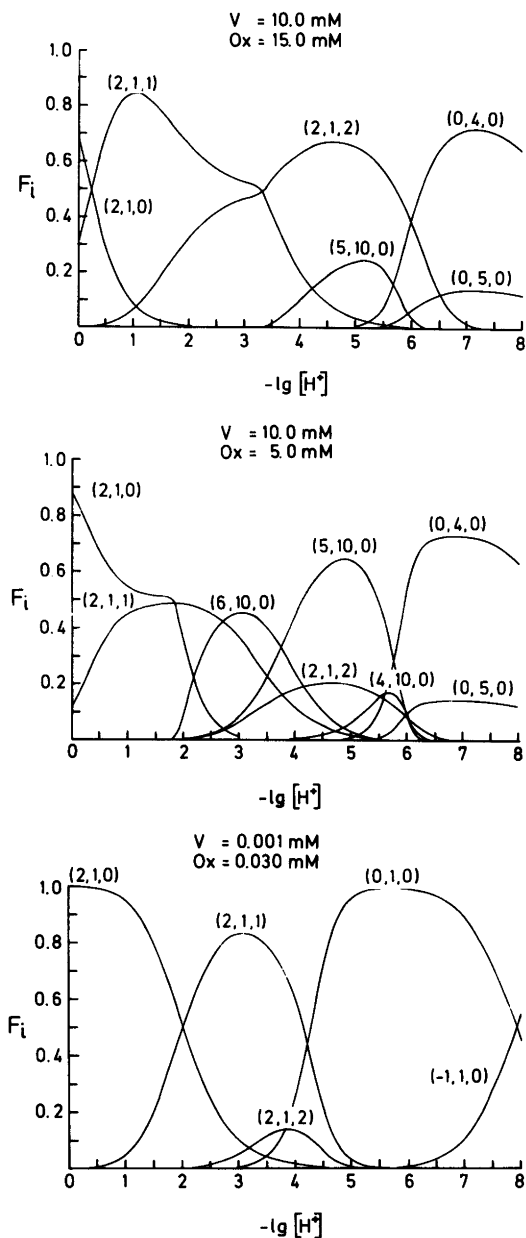


Fig. 8. Diagrams showing the distribution of vanadium in soluble species as a function of  $-\lg[H^+]$ . The quantity  $F_i$  is defined as the ratio between vanadium in a species to total vanadium. In the calculations, the constants given in Table 1 and Table 2 (error  $\Delta H$ ) were used. For clarity, species with  $F_i < 0.10$  have been omitted. Species are given in  $(p,q,r)$  notation. For binary complexes, corresponding formulas are found in Table 1.

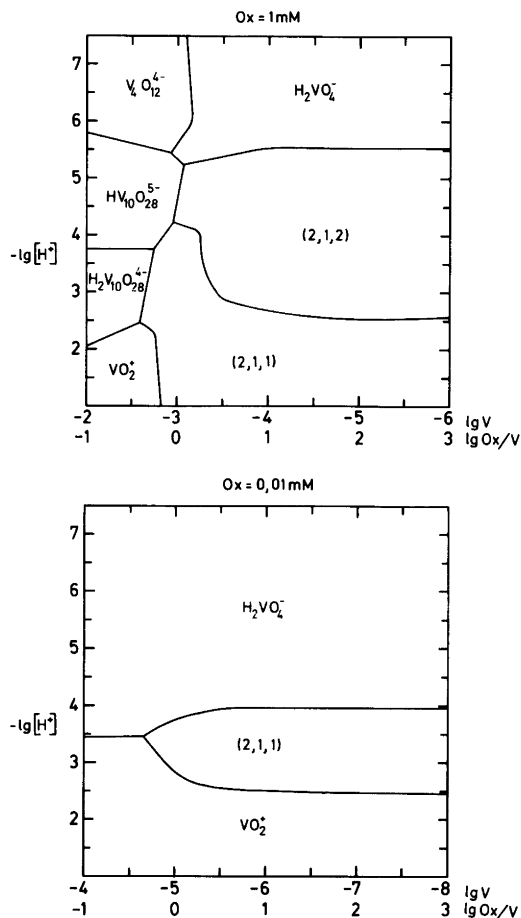


Fig. 9. Diagrams showing predominance areas of vanadium-containing complexes. In each area, the complex which has the highest vanadium content is marked out. On a borderline, the complexes in question contain the same amount of vanadium.

lap each other, it was, in most cases, not possible to evaluate the individual areas but only the sum. This sum shows an excellent fit to the emf model.

### Results and discussion

By means of a combined potentiometric and  $^{51}\text{V}$  NMR study of the vanadooxalate system, we have been able to establish the speciation in the vanadooxalate system. Two strong ternary species  $(\text{H}^+)_2(\text{H}_2\text{VO}_4^-)(\text{C}_2\text{O}_4^{2-})_2$  and  $(\text{H}^+)_2(\text{H}_2\text{VO}_4^-)(\text{C}_2\text{O}_4^{2-})$  are formed with the formation constants  $\lg \beta_{2,1,2} = 17.11 \pm 0.01$  and  $\lg \beta_{2,1,1} = 13.07 \pm 0.02$ .



The errors given are  $3\sigma$ . We feel confident that the constants are of high quality. The somewhat higher error in (2,1,1) is probably due to reduction in some acid titration points.

We found no sign of any additional ternary complex either from emf or from NMR data. The existence of small amounts of the protonated (3,1,2) and (3,1,1) species might, however, be difficult to establish. The (3,1,2) complex should exist in acid solutions ( $-\lg h < 3$ ) having high  $Ox/V$  ratios. Such solutions are spontaneously reduced and have not been included in the present study. Preuss *et al.*<sup>17</sup> have, however, postulated the existence of the monoprotonated species but also stated that salts containing this species cannot be prepared from aqueous solutions. The (3,1,1) species should be formed in even more acid solutions ( $-\lg h < 2$ ) where emf data are not very accurate and where the chemical shift of the NMR peak changes with the amount of  $VO_2^+$  present in the solutions (Fig. 5).

To illustrate the equilibrium conditions, some distribution diagrams have been constructed (Fig. 8). No solid phases have been included in the calculations and, in the middle diagram, the solutions are somewhat supersaturated with respect to  $V_2O_5(s)$  in the range  $1.5 < -\lg h < 2.5$ . The upper diagram exemplifies the conditions in one of the titrations ( $Ox/V = 1.5$ ,  $V = 10$  mM). At this ratio, the two vanadoolxalate complexes coexist in the region  $0.5 \leq -\lg h \leq 5.5$ . Moreover, the binary vanadate complexes are strongly suppressed and, for  $1 < -\lg h < 4$ , more than 90% of the vanadium is bound in ternary complexes. The strength of the  $VO_2^+$  cation is clearly demonstrated by the fact that even the acid (2,1,1) complex starts to decompose at  $-\lg h < 1$  although there is an excess of oxalate present. The middle diagram shows the distribution of complexes at the same  $V = 10$  mM but at  $Ox/V = 0.5$ . Some representative NMR spectra from such solutions are shown in Fig. 2. At this ratio, the (2,1,2) complex binds at most 20% and the (2,1,1) complex 50% of the total vanadium.

In nature, the total concentrations of vanadium and oxalate are much lower. In the Pacific Ocean, where the ionic medium is about the same as in our investigation,  $Ox \sim 2 \cdot 10^{-7}$  M and  $V \sim 3.5 \cdot 10^{-8}$  M. However, much higher concentrations can be found due to biological activity.<sup>2,18</sup> In soils,  $Ox = 1 \cdot 10^{-5}$  M and  $V = 10$   $\mu\text{g/g}$  dry earth have been reported.<sup>1,3</sup> The bottom diagram in

Fig. 8 demonstrates the distribution of species for  $V = 10^{-6}$  M and  $Ox/V = 30$ , conditions which might occur in nature. It is remarkable how dominant (2,1,1) is in the  $-\lg h$  region 2–4.2, and how little of the vanadium is bound as (2,1,2) although  $Ox/V = 30$ . This diagram indicates oxalic acid to be important in the speciation of vanadium in acidic natural waters. This is even better illustrated by the lower predominance diagram in Fig. 9. In this diagram,  $Ox$  is as low as  $10^{-5}$  M. Nevertheless, (2,1,1) is predominant in the  $-\lg h$  region 2.5–4.

The speciation at very low vanadium concentrations might be changed somewhat if the uncharged vanadate monomer,  $H_3VO_4$ , is included in the model. In 0.6 M Na(Cl) medium, we have established that  $H_3VO_4$  can never become predominant, irrespective of dilution.<sup>19</sup> However, at the low ionic strengths prevailing in most natural waters, one would expect  $H_3VO_4$  to increase at the expense of  $VO_2^+$  and  $H_2VO_4^-$ .

The speciation is very dependent on the concentration and the two diagrams in Fig. 9 have been constructed so that the upper diagram reflects the conditions when the total concentrations of vanadate and oxalate are increased by a factor  $10^2$ . In the upper diagram, the (2,1,2) complex also shows a large predominance area; at a ten-fold excess of oxalate, it is the predominant species at  $-\lg h$  2.5–5.5.  $V_2O_5(s)$  has not been included in the calculations and the system is supersaturated with respect to  $V_2O_5(s)$  at a small  $-\lg h$  region for the highest  $V$ .

The slow equilibria in parts of the concentration ranges originate from the slow decomposition of decavanadates. This is clearly demonstrated in Fig. 4. Spectra from an  $Ox/V = 1$  solution at  $-\lg h \sim 3$  were recorded 2 and 24 h after mixing. In the first spectrum, much of the vanadate is still bound in decavanadates (peaks F, F' and F'') and not accessible to oxalate and the "real"  $Ox/V$  is then greater than one. Thus peak 2 (2,1,2) is greater than peak 1 (2,1,1). In the equilibrated solution, very little of the decavanadates remains, peak 1 is dominant and  $-\lg[H^+]$  has increased. As a check that there are only two ternary complexes even at high concentrations, we prepared a solution with  $Ox/V = 120/60$  at  $-\lg h = 8.81$  and titrated it with HCl to  $-\lg h = 2.69$ . This titration showed no deviation in the neutral region but reduction already occurred at  $-\lg h \sim 5$ . This reduction of V(V) in acid van-

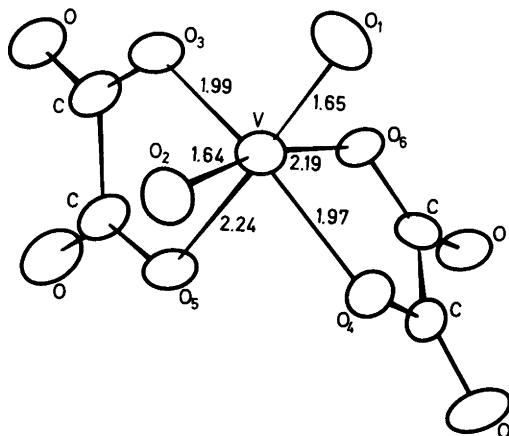


Fig. 10. The structure of the  $\text{VO}_2(\text{C}_2\text{O}_4)_2^{3-}$  anion as given in Ref. 19 but redrawn and somewhat simplified.

adooxalate solution when there is excess of oxalate is interesting from a bioinorganic point of view. Therefore, we have recently started some redox experiments where both  $\{e^-\}$  and  $[\text{H}^+]$  are being measured.

**Structural comments.** It is difficult to determine the structures of aqueous complexes. If, from single-crystal determinations, discrete polyanions are found with compositions corresponding to anions established in the equilibrium analysis, tentative structures can be given. Crystal structures of the two compounds  $(\text{NH}_4)_3[\text{VO}_2(\text{C}_2\text{O}_4)_2]$  and  $\text{K}_3[\text{VO}_2(\text{C}_2\text{O}_4)_2]$  have been published<sup>20,21</sup> and found to contain the discrete anion shown in Fig. 10. As this anion corresponds to our (2,1,2) complex, we propose that the aqueous species has this structure. In the  $\text{VO}_2(\text{C}_2\text{O}_4)_2^{3-}$  anion (Fig. 10) the two short V-O (terminal) bonds are  $\sim 1.64 \text{ \AA}$  with an O-V-O angle of  $\sim 104^\circ$ . The two medium length V-O bonds *cis* to those are  $\sim 2.0 \text{ \AA}$ ; the two long V-O bonds in *trans* position are  $\sim 2.2 \text{ \AA}$ . Each oxalate group is bound to V through one long and one medium length V-O bond. The two positions occupied by terminal oxygen are not available for complexation to ligands and no sign of any complex with  $\text{Ox}/\text{V} = 3$  could be detected in the present study.

As described in Ref. 20, a  $\text{VO}_2$  configuration similar to that in Fig. 10 has also been found in several oxovanadate(V) compounds where the vanadium has a tetrahedral, trigonal-bipyramidal

or octahedral array of oxygen donors (V-O distances 1.65–1.71 Å, O-V-O angles 106–109°). This arrangement seems to be very stable and is likely to exist in aqueous solution as well. The high stability of the  $\text{VO}_2^+$  cation in acid solution supports this hypothesis. Most probably water molecules are attached forming  $\text{VO}_2(\text{H}_2\text{O})_n^+$ , where a total coordination number of five or six has been suggested.<sup>22</sup>

From the NMR measurements, a rapid exchange between the  $\text{VO}_2^+$  cation (2,1,0) and the ternary complex (2,1,1) was found. In comparison, the addition of the second oxalate was slow. This is consistent with ligand exchange kinetics dominated by outer sphere association. To our knowledge, no complete structure determination of the (2,1,1) species has been reported. However, a related dioxofluorooxalatovanadate structure, where vanadium is pentacoordinated, has been published.<sup>23</sup> If the fluoride ligand in the  $\text{VO}_2\text{F}(\text{C}_2\text{O}_4)_2^{2-}$  anion is replaced by a water molecule, a  $\text{VO}_2(\text{H}_2\text{O})(\text{C}_2\text{O}_4)_2^-$  complex corresponding to (2,1,1) is obtained. This hypothetical formula has to be proved and crystallisation experiments are in progress. Besides slow evaporation of equilibrium solutions at 25 °C, we are also using the recipes given in Ref. 24.

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