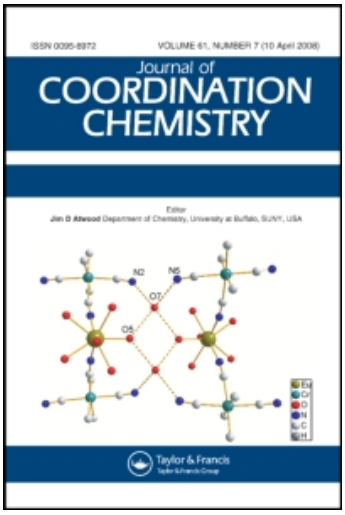

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FORMATION OF A TRIS COMPLEX IN THE VANADIUM(IV)–TIRON SYSTEM

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The formation of a tris complex, VA_3, was detected pH-metrically in the oxovanadium(IV)–tiron (1,2-dihydroxybenzene-3,5-disulphonate) system, and its draft stability constant was determined. The slow formation of the tris complex in both acidic and basic solutions was studied in detail *via* a combined pH-spectrophotometric method. Spectrophotometric titration at 25.0 ± 0.1°C and ionic strength 0.2 mol dm^{-3} (KCl) yielded a log K value of 2.01 ± 0.03 for the formation process $VOA_2 + H_2A \rightleftharpoons VA_3 + H_2O$.

Keywords: Tiron, vanadium(IV), tris complex, stability constant

INTRODUCTION

The formation of an octahedral tris(catecholato) complex of vanadium(IV) was reported long ago by Henry *et al.*[1] This system was subsequently studied in detail by Raymond *et al.*,[2] the existence of such species being unambiguously proved for catechol derivatives as well, both in the solid state and in solution. The displacement of the oxovanadium(IV) oxygen by phenolate oxygen was attributed to the exceptional chelating ability of *o*-diphenolates and their great affinity for highly charged metal ions. Bayer *et al.*,[3] recently assumed a similar oxygen displacement in naturally occurring amavadin (a vanadium(IV) complex of *N*-hydroxy-2,2′-iminodipropionate). In a kinetic study of the oxovanadium(IV)-catalysed autoxidation of the catechol derivative adrenaline in slightly acidic solution, Jameson and Kiss[4] obtained kinetic evidence and reported equilibrium constants for the formation of this (O,O)-coordinated tris complex. In a very recent paper, Micera and coworkers[5] published firm e.s.r. evidence for the formation of the complex $V(cat)_3^{2-}$ in aqueous solution. As Raymond *et al.*[2] clearly pointed out, the pH-potentiometric indetectability of such species is due to the fact that no protons are liberated or consumed in the pH range of their formation (pH ~ 3.5–6), the equilibrium involved being

$$VO(O,O)_2 + H_2(O,O) \rightleftharpoons V(O,O)_3 + H_2O$$

where $H_2(O,O)$ symbolizes any catechol derivative protonated on both phenolic groups.

We report here the results of efforts to detect, pH-metrically, the formation of the tris complex $V(IV)A_3$ in the VO^{2+}-tiron (1,2-dihydroxybenzene-3,5-disulphonate) system and to describe its formation equilibria quantitatively by means of visible spectrophotometry.

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EXPERIMENTAL

Reagents

The tiron used was a Fluke product of puriss quality. Its purity was checked and the exact concentrations of its solutions were determined by the Gran method.[6] The VO^{2+} stock solution was prepared as described in Ref. 7, and its metal ion concentration was determined by permanganate titration and standardized potentiometrically for hydrogen ion concentration by using the appropriate Gran function. The ionic strength of all solutions studied was adjusted to 0.2 mol dm^{-3} (KCl). In all cases, the temperature was 25.0 ± 0.1°C.

pH-metry

The stability constants of the proton and vanadium(IV) complexes of tiron were determined by pH-metric titration of 25 cm^3 samples. The concentration of the ligand was 0.008 mol dm^{-3}, and the metal ion-to-ligand molar ratio was 0 : 2, 1 : 2, 1 : 3.3 or 1 : 4. The titrations were performed over the pH range 2.2–11.4 with KOH solution (normal titration) or with HCl solution (back-titration) of known concentrations (*ca* 0.2 mol dm^{-3}) under a purified argon atmosphere to avoid oxidation of the ligand. In all cases, duplicate or triplicate titrations were performed. In acidic solution of pH < 6, about 1 minute was required for pH equilibrium to be reached, but in basic solution a much longer time was necessary (up to 1 hour). Because of the danger of partial oxidation of the ligand during such a very long titration time, "*quasi*-equilibrium" titrations were performed in the basic pH range, the waiting time before the recording of pH readings never being more than 15 minutes. The reproducibility of the titration curves was within 0.005 pH units in the acidic pH range, and within 0.02 pH units in the basic pH range.

The pH was measured with a Radiometer PHM 84 instrument with a GK-2322C combined glass electrode, which was calibrated for hydrogen ion concentration according to the method of Irving *et al.*[8]

The concentration stability constants $\beta_{pqr} = [M_pA_qH_r]/[M]^p[A]^q[H]^r$ were calculated with the aid of the computer program PSEQUAD.[9]

Spectrophotometry

The time dependence of the visible spectra of solutions with similar compositions to those used in pH-metry was recorded at different pH values in the range 3–11 on a Varian DMS 100 double-beam recording spectrophotometer.

The formation constant of the complex VA_3 was determined spectrophotometrically by titrating solutions of the ligand adjusted to given pH values (pH 4.0, 4.5 and 5.0) with a metal ion solution. The samples were circulated in a closed system by means of a peristaltic pump between the spectrophotometer flow-cell and the titration vessel used for measurements and to keep the pH of the solution constant with the aid of a pH-stat apparatus consisting of a pHM84 pH-meter, a TTA60 titrator unit and an ABU80 automatic burette. At each titration point in the metal ion-to-ligand ratio range 1:460–1:40, the visible spectra of the solutions were recorded with a Beckman ACTA MIV instrument. The time dependences of the spectral changes in the sample solutions were followed.

RESULTS AND DISCUSSION

As the formation of the tris complex $V(IV)A_3$ takes place without a direct pH effect in the acidic pH range and is expected to be a rather slow reaction, a detailed pH-metric study was made in a wide pH range and at various metal ion-to-ligand ratios in three different ways, as follows.

Sample 1

Normal titration with base solution started at pH ~ 2.2 and continued up to pH ~ 11.5. Stable pH-meter readings were attained rapidly in the acidic pH range (~20 seconds), but much more slowly above pH ~ 7. The colour of the solution was pale blue at first. It became a very intense blue by pH ~ 5, and did not change significantly during the rest of the titration.

Sample 2

Sample 1 was back-titrated with an acid solution immediately. The colour of the solution remained deep blue to pH ~ 3.

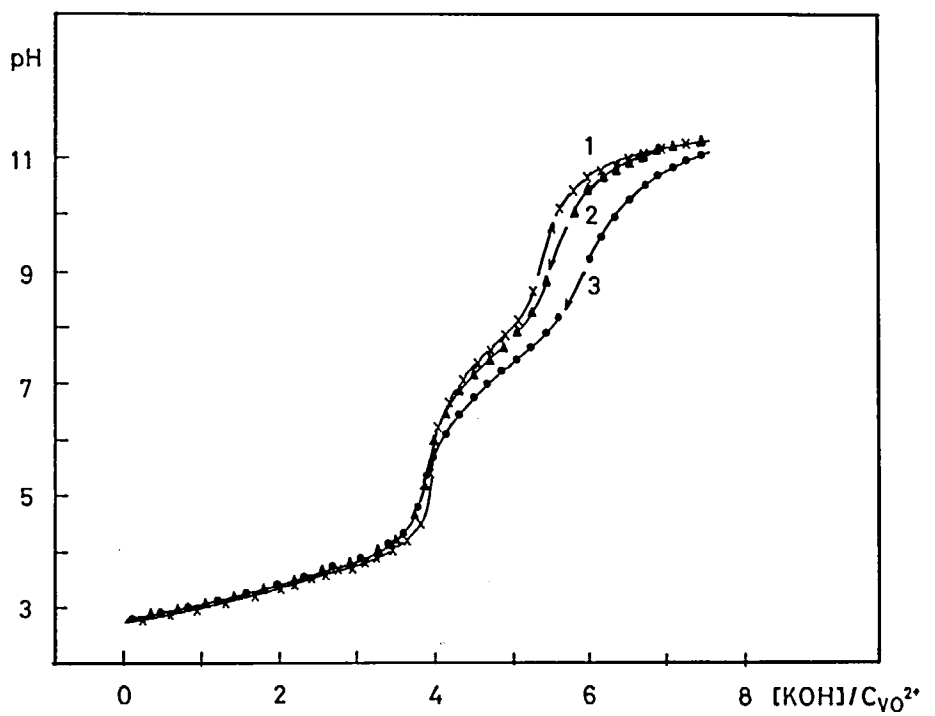

FIGURE 1 pH-metric titration curves for the oxovanadium(IV)–tiron system at a metal ion-to-ligand ratio of 1:3.3 ($C_{VO^{2+}} = 1.4 \times 10^{-3}$ mol dm^{-3}) obtained in three different ways; (1): normal titration with base; (2): back titration with acid; (3): normal titration with acid (see text)

Sample 3

The amount of base necessary for pH ~ 11 was added to sample 1 in one portion and the resulting sample was titrated with strong acid solution. The basic sample prepared in this way remained pale blue, started to deepen only at pH ~ 5, and it became almost colourless again (the colour of the uncomplexed oxovanadium(IV) ion) by pH ~ 2.5.

The titration curves recorded at a metal ion-to-ligand ratio of 1:3.3 are given in Figure 1, which clearly shows that the titration curves of samples 1 and 2 differ from each other in the basic pH range, even if the samples were back-titrated immediately. The small difference in the acidic pH range originates from the dilution of the sample during titration (see curves 1 and 2). Curve 3 starts from a significantly lower pH and displays a significantly different shape from that of curve 2 in the basic pH range (in spite of the fact that the same amount of base was added to both samples). This indicates some slow base-consuming process, presumably associated with mixed hydroxo complex formation. Below pH ~ 5, the two curves again agree within experimental error. This strongly suggests that practically no oxidation of the ligand occurs during the titration time. The differences in curves 1–3 in the basic pH range, however, indicate some further time-dependent reaction(s).

The spectral changes in samples 1–3 during titration were recorded spectrophotometrically at 550 nm (the absorption maximum of the deep blue solution); the apparatus involved a spectrophotometric flow-cell and a pH-metric titration vessel connected *via* a peristaltic pump, whereby the pH and the spectrum of the solution could be recorded simultaneously (see Figure 2).

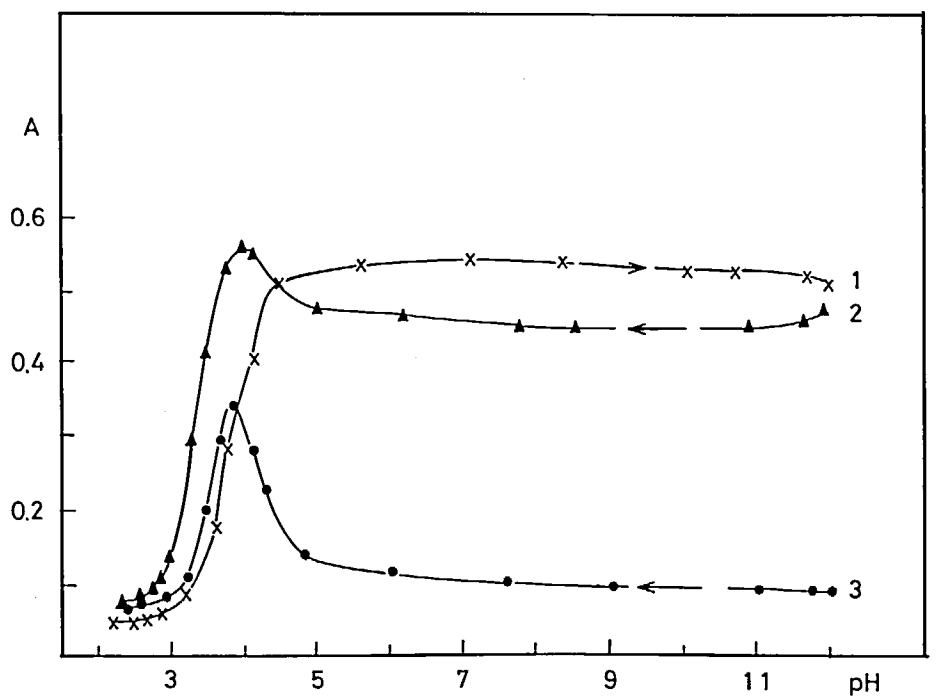

FIGURE 2 Spectrophotometric titration curves (λ_{max} = 550 nm) for the oxovanadium(IV)–tiron system at a metal ion-to-ligand ratio of 1:3.3. Details as in Figure 1.

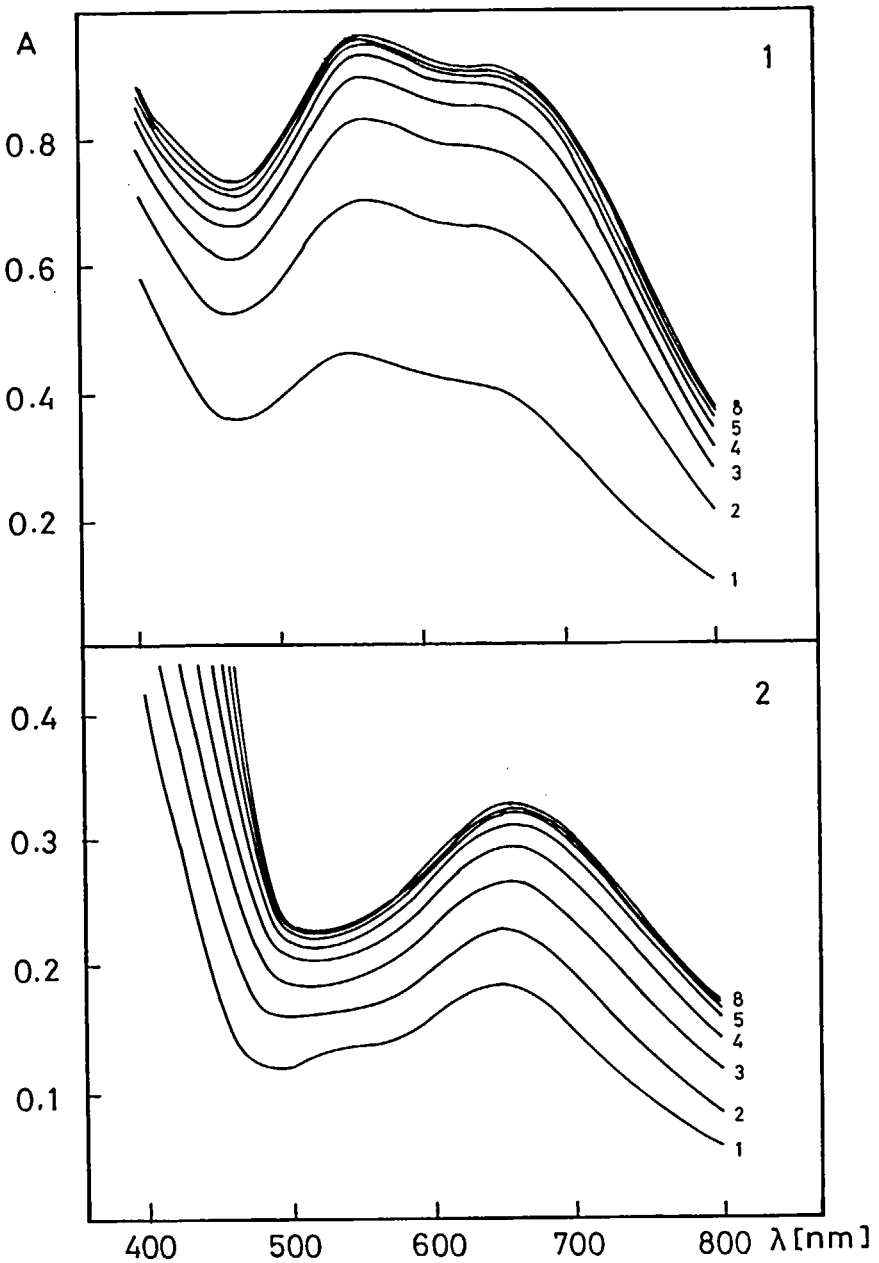

FIGURE 3 Time dependence of the visible absorption spectra of the oxovanadium(IV)-tiron 1:3.3 system; (1): pH = 4.5; (2): pH = 8.0; $C_{VO}^{2+} = 1.4 \times 10^{-3}$ mol dm^{-3}.

The reaction involving the formation of a very deep blue complex has been suggested to yield a tris(O,O)-coordinated species, $V(IV)A_3$. Figure 2 indicates that this reaction starts at pH > 3 and the concentration of the species reaches a

maximum at around pH ~ 6 and decreases with increasing OH^- concentration. This complex is formed rather slowly (see the differences between curves 1 and 2).

The spectral changes were measured at different times in samples at different pH values. As an illustration, the time dependence of the visible absorption spectrum of the VO(IV)-tiron 1:3.3 system at two different pH values (one in the acidic and one in the basic pH range) is depicted in Figure 3.

It can be seen from Figure 3 that the slow reaction results in an increase in intensity and also a change in the structure of the spectrum for both samples. The time for attainment of a stable absorption (equilibrium state) was 20–60 minutes, strongly depending on the pH of the solution. In acid, the reaction was considerably faster than in neutral or basic solutions. The shape of the spectrum obtained at pH 4.5 strongly resembles that of the species VA_3 formed in the reaction $VOA_2 + H_2A \rightleftharpoons VA_3 + H_2O$.[2] Since no proton is consumed or liberated in this reaction, a stable pH reading can be achieved in a short time during pH titration, without real equilibrium for complex formation being reached. The spectra recorded at pH ~ 8 are of lower intensity and seem to be mixtures of the spectra of VA_3 and VOA_2. According to Raymond *et al.*,[2] the intensities of the visible absorption bands of the VA_3 complex of catechol (9200 and 8200 cm^{-1} at 552 nm and 650 nm, respectively) are much higher than those of the species VOA_2 (69 M cm^{-1} at 656 nm and 30 M cm^{-1} at 540 nm). Thus, the increase in intensity at pH ~ 8 is still due to the slow formation of VA_3 in the reaction $VOA_2 + HA \rightleftharpoons VA_3 + OH^-$, which above pH 8, where the free ligand exists mainly in the monoprotonated form HA, can also be detected by pH-metry (*c.f.* the slow attainment of pH equilibrium in the basic pH range).

The pH range of formation of the complex VA_3 may be determined from Figure 4, which depicts the pH dependence of the equilibrium absorbances at 550 nm, reached 20–60 minutes after preparation of the samples.

It can be seen from Figure 4 that the pH range for optimum formation of the complex VA_3 is between 3.5 and 7.5, *i.e.*, practically the same pH range as that in which the "normal" oxovanadium(IV) complexes VOA and VOA_2 are formed. As the formation of VA_3 does not have a direct pH effect in the pH range 2.3–6.5 (the free ligand exists in the form H_2A), the pH-metric titration curves were evaluated on the assumption of the species VOA and VOA_2. The stability constants calculated separately from the acidic pH range of the titration curves for samples 1, 2 and 3 are listed in Table 1.

The stability data obtained from the normal titration (sample 1), the immediate back-titration (sample 2) and the acidic titration (sample 3) show good agreement and give average values of $\log \beta_{VOA} = 16.50 \pm 0.03$ and $\log \beta_{VOA_2} = 31.22 \pm 0.03$. These values are in reasonable agreement with those of Zelinka and Bartusek:[10] $\log \beta_{VOA} = 16.8$ and $\log \beta_{VOA_2} = 31.2$ ($I = 0.1$ mol dm^{-3} (KNO_3) at 20°C).

Above pH ~ 6.5, *i.e.*, still in the pH range of formation–dissociation of VA_3, the free ligand H_2A starts to dissociate (pK = 7.47). Thus, the formation of VA_3 *via* the process $VOA_2 + HA \rightleftharpoons VA_3 + OH^-$ results in some base liberation, which makes the reaction detectable by pH-metry. However, the long reaction time, the fact that the equilibrium state cannot be detected by pH-metry in the acidic pH range, the enhanced oxygen sensitivity of catecholic ligands in the presence of VO(IV)[4] (which does not permit a long waiting time at each titration point), and the parallel occurrence of a slow base-consuming process (probably to do with mixed hydroxo complex formation), does not allow one to obtain accurate stability constants for species formed in the neutral–basic pH range. Draft stability constants calculated

from the basic range of the titration curves of samples 1–3 are also included in Table I. In the calculation, the tris complex VA_3 had also to be regarded as an associate of VO(IV), A and H; thus, it was defined as $VOA_3H_2 = VA_3 \cdot H_2O$. Besides this complex, two hydroxo complexes VOA_2H_{-1} (or more precisely $VOA_2(OH)$) and $VO_2A_4H_{-1}$ (=$VOA_2(OH)A_2VO$), were also assumed; in these species, the water molecule in the sixth coordination position is ionized and $VOA_2(OH)$ is formed. Alternatively this OH group can behave as a bridging ligand between monomeric VOA_2 species.

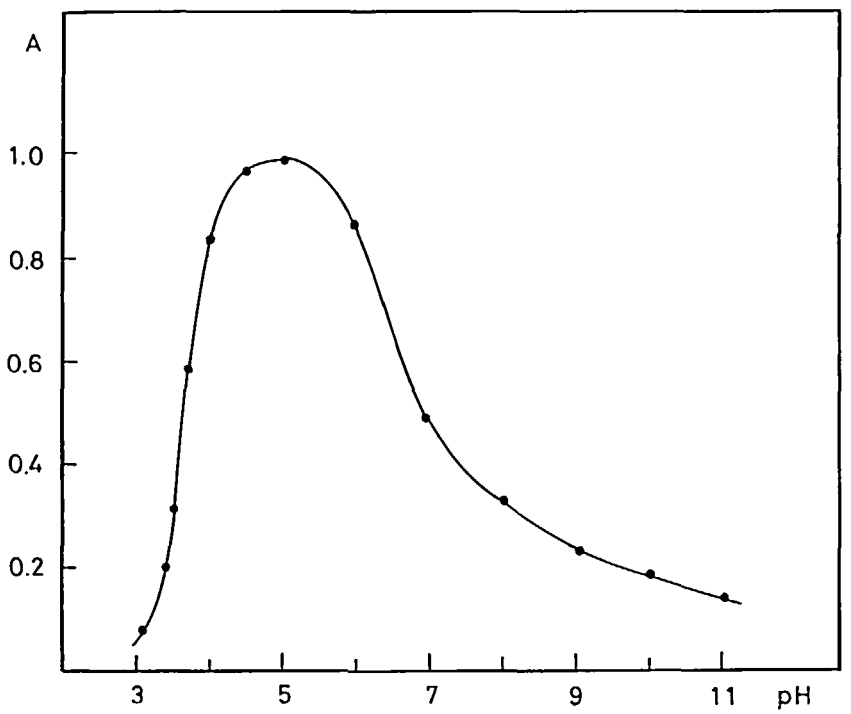

FIGURE 4 Equilibrium absorbances at 550 nm of samples of the oxovanadium(IV)–tiron 1:3.3 system at different pH values; $C_{VO}^{2+} = 1.4 \times 10^{-3}$ mol dm^{-3}.

The complex VOA_3H_2 could be detected only in sample 1; in the case of the other two samples, this species was rejected in the calculation. The longer the solution stood at basic pH, the larger the extent of the base-consuming, hydroxo complex formation that took place. This "concealed" the base-liberating formation of VOA_3H_2.

The two hydroxo complexes $VOA_2(OH)$ and $VO_2A_4(OH)$ could partly substitute for each other in the calculation, although the experimental data were somewhat better fitted by the dimeric species; if both species were assumed in the calculation, $VOA_2(OH)$ was rejected. The increasing formation of the hydroxo complex in the sequence sample 1 < sample 2 < sample 3 (see the stability constants and VO% values in Table I) clearly indicates that the titration was a non-equilibrium one because of the slow reactions. In sample 1 the experimental conditions were favourable for the formation of the tris complex, which greatly hinders the formation

of mixed hydroxo complexes, while in sample 3 the sudden increase of the pH to ~11 suppresses the formation of the tris complex and the high OH^- concentration promotes hydrolytic processes.

These results unambiguously show that pH-metry was able only to detect the slow formation of the tris complex VA_3 (=VOA_3H_2) in the basic pH range, but was unable to characterize quantitatively its formation because of the low rate of formation of this species and interfering hydrolytic processes.

TABLE I

Proton (pK) and vanadium(IV) (log β) stability constants for the complexes[a] of tiron at 25.0 ± 0.1°C and I = 0.2 mol dm^{-3}.

Constant	Sample 1	Sample 2	Sample 3
pK(OH)		12.2[b]	
pK(OH)		7.47 ± 0.02	
pH range: 2.3–6.5			
log β_{VOA}	16.47 ± 0.01	16.50 ± 0.01	16.54 ± 0.02
log β_{VOA_2}	31.18 ± 0.01	31.24 ± 0.01	31.24 ± 0.02
pH range: 2.3–11.0			
log β_{VOA}	16.47 ± 0.01	16.50 ± 0.01	16.53 ± 0.02
log β_{VOA_2}	31.22 ± 0.02	31.22 ± 0.02	31.20 ± 0.02
log $\beta_{VOA_2H_2}$	52.5 ± 0.2 (10%)	–	–
log $\beta_{VO_2A_2H_{-1}}$	51.9 ± 0.5 (5%)	53.4 ± 0.3 (20%)	57.4 ± 0.1 (100%)

[a] Maximum concentrations of some complexes at a 1:3.3 metal ion-to-ligand ratio are given in parentheses. [b] Ref. 11.

TABLE II

Spectrophotometrically determined stability constants (K)[a] of the complex VA_3 formed in the vanadium(IV)–tiron system at 25.0 ± 0.1°C and I = 0.2 mol dm^{-3}.

Metal-to-ligand ratio	pH = 4.0	pH = 4.5		pH = 5.0
	550 nm	550 nm	640 nm	550 nm
1:480	93	102	104	101
1:240	93	106	105	104
1:160	93	106	104	102
1:120	90	106	104	100
1:96	88	105	102	98
1:80	85	105	102	101
1:40		104	97	97
mean values	90±3	105±2	103±3	100±2
average K (log K)		103±3 (2.01±0.03)		

[a] K for the reaction $VOA_2 + H_2A \rightleftharpoons VA_3 \cdot H_2O$.

In the acidic pH range, where hydroxo complex formation does not take place, but the formation of the intensely blue VA_3 is favoured, spectrophotometry proved to be a suitable method for following the formation of VA_3 and for determination of its stability constant. In the spectrophotometric titrations, the ligand solution was

titrated with the metal ion and stable absorbance values were recorded at different metal ion-to-ligand ratios high enough for only the single reaction of VA_3 formation to be assumed, *i.e.*, $VOA_2 + H_2A \rightleftharpoons VA_3 + H_2O$. Through determination of the molar absorptivity of VA_3 at an extremely high ligand excess (1:800), the slight absorbance of the complex VOA_2 also being taken into account, the equilibrium concentration of VA_3 and thus the K value characteristic of the above reaction could be calculated at each titration point. The stability constants calculated from each of the individual spectrophotometric titration curves measured at different pH values are listed in Table II.

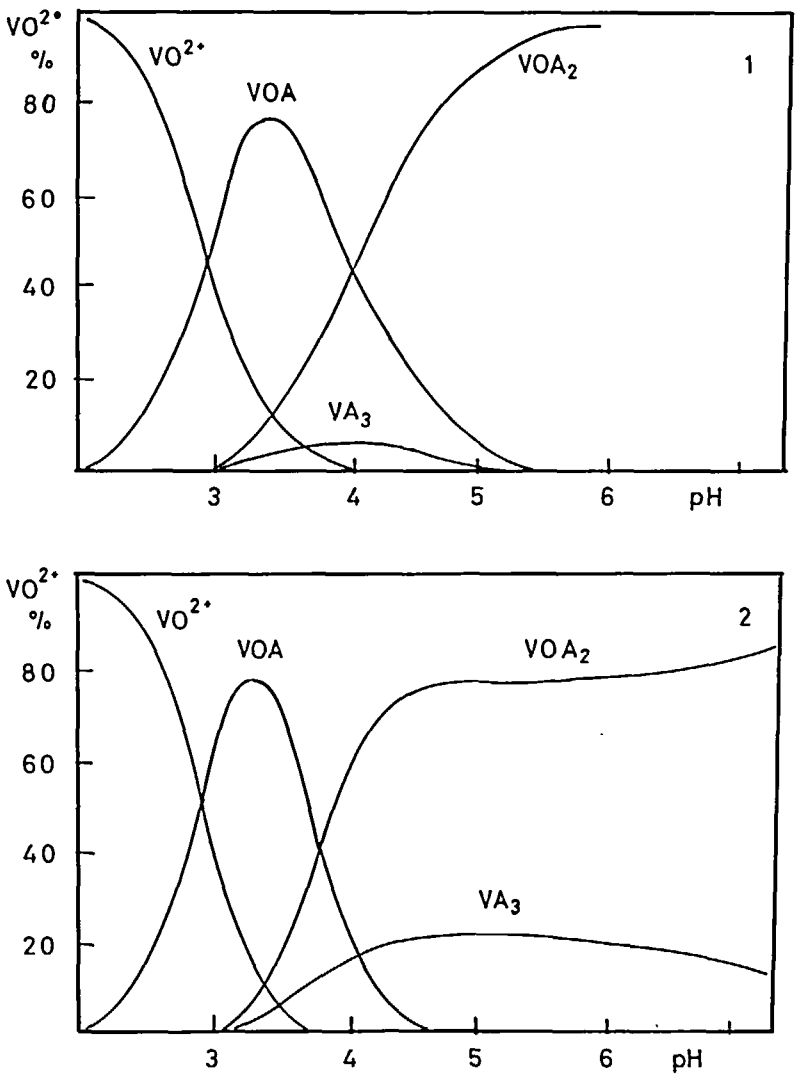

FIGURE 5 Concentration distribution curves for the complexes formed in the oxovanadium(IV)–tiron system, $C_{VO^{2+}} = 0.002\ mol\ dm^{-3}$; (1): 1:2 metal ion-to-ligand ratio; (2): 1:5 ratio.

The average value of log K = 2.01 ± 0.03 is somewhat larger than that obtained from the "*quasi*-equilibrium" pH-metric titration data: log K = log $\beta_{VOA_3H_2}$ − log β_{VOA_2} − log β_{H_2A} = 52.5 − 31.27 − 19.67 = 1.61 (see Table I). In the latter case, however, the equilibrium formation of the tris complex has not been achieved during titration and this may result in the lower log K value. The agreement with the stability constant determined from kinetic measurement (log K = 1.67)[4] for the VA_3 complex of andrenaline is reasonable. This catechol derivative is likewise capable of tris(O,O)-coordination.[4] In the comparison, it has to be taken into account that, due to the presence of the sulphonate groups, tiron is the strongest metal ion binder among the catechol derivatives.[11] Thus, the somewhat higher stability obtained for the tiron complex is in accordance with expectations. Concentration distribution diagrams of the complexes present in 2:1 and 5:1 solutions containing tiron and VO(IV) are illustrated as a function of pH in Figure 5.

It can be seen from the figure 5 that in the absence of sufficient excess ligand (1:2 ratio) the complex VA_3 is formed only in negligible amounts. At a higher ligand excess it is present in considerable concentration. In the basic pH range, hydroxo complexes may also be present.

It should be pointed out that the description of the solution equilibria of VO(IV)–3,4-dihydroxybenzene derivatives in acidic solution in terms of formation of the complexes VO(O,O) and $VO(O,O)_2$ alone is not truly correct. These must be supplemented with the species VA_3, which may modify the relative concentrations of the species considerably, depending largely on the metal ion-to-ligand ratio. For a "draft" description of any VO(IV)-catecholic systems the species VA_3 with a log K ($VOA_2 + H_2A \rightleftharpoons VA_3 \cdot H_2O$) value of 1.8 should be included in the equilibria besides the 1:1 and 1:2 (O,O)-coordinated complexes of the oxovanadium(IV) ion.

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