THE DETERMINATION OF THE STOICHIOMETRY OF THE MIXED COMPLEX OF VANADIUM WITH HYDROGEN PEROXIDE AND WITH 4-(2-PYRIDILAZO) RESORCINOL

Xiwen He
Department of Chemistry - Nankai University - Weijin Road - Tianjin 300071 - China
Matthieu Tubino [*] **and Adriana Vitorino Rossi**
Instituto de Química - UNICAMP - CP 6154 - 13083-970 Campinas - SP

The present study reports details of the stoichiometric characterization of the mixed complex system, $V(H_2O_2)PAR$, formed when vanadium adequately reacts with hydrogen peroxide and with 4-(2-Pyridilazo)Resorcinol. Also the presence of polynuclear species was investigated in order to elucidate about unambiguous assignment of the molar absorptivity, stability constant and composition of the complex. Two mathematical treatments methods of the experimental results were employed. From the results it can be concluded that this system corresponds to a mononuclear complex with 1:1:1 stoichiometry.

Keywords: vanadium; PAR; H_2O_2; complex stoichiometry.

INTRODUCTION

Vanadium forms a very pale complex with H_2O_2 in acid medium ($\varepsilon_{450-455\,nm}$ = 25 to 280 L mol^{-1} cm^{-1}, $\varepsilon_{350\,nm}$ = 610 L mol^{-1} cm^{-1})[1,2]. Therefore this reaction is not sensitive enough to be used for the determination of small amounts of vanadium. On the other hand, PAR, 4-(2-Pyridylazo) Resorcinol, is known as a spectrophotometric reagent that produces a sensitive color reaction with vanadium, a red complex (λ_{max} = 545 nm), with a 1:1 stoichoimetry, which maximum color intensity is observed at pH from 5 to 6.5[3]. Its high molar absorptivity ($\varepsilon_{545\,nm}$ = 3.45ξ10^4 L mol^{-1} cm^{-1})[4-6] permits the determination of low concentrations of vanadium from 0.1 to 1.2 µg mL^{-1}. However several ions interfere and must be carefully removed [4].

An efficient way for increasing selectivity and sensitivity of vanadium quantitative analysis is the formation of a mixed ligand complex as it was applied for the spectrophotometric determination of total vanadium using the V / H_2O_2 / PAR system[3, 7-10]. When vanadium ions are treated with PAR in the presence of H_2O_2 in H_2SO_4 0.5 mol L^{-1}, a new red colored species with absorption maximum at 542 nm is formed. Although the good analytical performance of this system, it is not clear what kind of species is formed in this reaction but for analytical purposes it can be considered as a mixed complex $V(H_2O_2)PAR$[5, 8-10].

The present study reports details of the stoichiometric characterization of the system V / H_2O_2 / PAR and the investigation of the presence of polynulear species in order to elucidate about unambiguous assignment of the molar absorptivity, stability constant and composition of the complex. The successful selective and sensitive analytical determination of total amount of vanadium in steels using this complex has been already reported[10].

In this work, two mathematical models were used to investigate the stoichiometry and the possible presence of polynuclear complex species in order to obtain the true molecular formula, the true molar absorptivity and the true formation constant.

The reaction of hydrogen peroxide with vanadium(**V**) leads to a species that can be represented as $VO(O_2)^{+2}$. Therefore, the reaction of this species with PAR is supposed to form a complex that could be represented as $VO(O_2)PAR$. For simplification purposes, the following representations will be used $V(H_2O_2)$, $V(PAR)$ and $V(PAR)H_2O_2$. Also, for simplicity the vanadium(**V**), V(**V**), will be represented only as vanadium or V in this text.

EXPERIMENTAL

Equipments and reagents

Absorbance measurements were made with a Hewlett Packard HP 8452A diode array spectrophotometer and a Micronal B 382 spectrophotometer, using glass cells with a 1.00 cm optical path length.

All reagents used were of analytical grade. Standardization was used when recommended. Water was distilled in glass equipment and deionized in a Milli Qplus Ultra Pure Water System.

A 1.00x10^{-1} mol L^{-1} vanadium solution was prepared by dissolving 1.1688 g of NH_4VO_3 (Merck) and boiling with a slight excess of NaOH (Nuclear). The solution was cooled to room temperature and diluted to 100.0 mL with water. Working solutions were obtained by appropriate dilutions of this stock solution. The PAR solutions were prepared daily by dissolving the right amount of 4-(2-Pyridylazo) Resorcinol monosodium salt hydrate (Aldrich) in water. The H_2O_2 solutions were prepared by dilution of the 30% w/v H_2O_2 (Merck) with water. The H_2SO_4 solutions were prepared by appropriate dilutions of the acid (Carlo Erba) with water.

Procedure

The solutions of vanadium, PAR, H_2O_2 and H_2SO_4, in different concentrations were mixed and the absorbance of the complex solution obtained was monitored spectrophotometrically, using as blank a mixture containing all the reagents solutions except vanadium, at the correspondant concentrations.

RESULTS AND DISCUSSION

Complex formation

It has been observed that the $V(H_2O_2)$ complex, at pH = 1 (sulfuric acid medium), can be converted into a new colored

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[*] e-mail: tubino@iqm.unicamp.br, adriana@iqm.unicamp.br

species assumed as a mixed complex with good selectivity by adding a complexing agent as PAR [8], that can be represented as $V(PAR)H_2O_2$.

The maximum molar absorptivity, ε, of the red colored species formed when vanadium ions are treated with PAR in the presence of H_2O_2 in H_2SO_4 0.5 mol L^{-1} is 1.85×10^4 L mol^{-1} cm^{-1} at 542 nm. The Fig. 1 shows the spectra of $V(PAR)H_2O$, $V(H_2O_2)$ and $V(PAR)$ complexes in pH = 1.0 where it can be observed the higher molar absorptivity of the mixed complex.
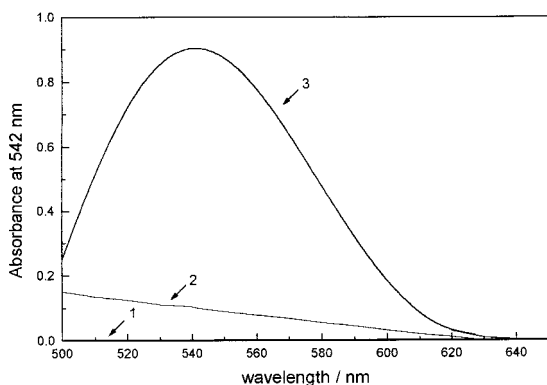

Figure 1. *Visible absorption spectra of the systems: (1) V/H_2O_2; (2) V/PAR; (3) $V/PAR/H_2O_2$. [Vanadium] = 5.0×10^{-5} mol L^{-1}; [PAR] = 2.5×10^{-4} mol L^{-1}; concentration of H_2O_2 = 0.15 % w/v. All solutions were prepared in $[H_2SO_4]$ = 0.5 mol L^{-1}.*

In a previous work[8] it has been reported the existence of a single complex for this system 1:1:1 stoichiometry as ratio of $V(PAR)H_2O_2$. Although the methods of the mole ratio, the continuous variation and of the triangular diagram can yield combining ratio of vanadium to ligands, they do not indicate the true composition of the molecular formula and if polynuclear species are present. In order to determine the composition formula, two mathematical model methods were applied for differentiating mononuclear and polynuclear complexes from where it can be deduced the molecular formula.

(1) First mathematical treatment for yielding the total number of units of the vanadium and of the ligand in the complex[11]

A known aliquot of vanadium solution was treated preliminary with an excess of hydrogen peroxide to form the $V(H_2O_2)$ complex[1,2]. Under these conditions, upon the addition of the third reagent, PAR, a red complex is formed. The reaction producing the mixed ligand is assumed to be the general equilibrium:

$$\mathbf{m} \; V(H_2O_2) + \mathbf{m} \; PAR \rightleftharpoons V_m(PAR)_m(H_2O_2)_m \qquad (1)$$

The combining ratio of the components V, H_2O_2 and PAR in the complex were determined in a previous work[12] as (1 : 1 : 1).

Let **a** and **b** be the initial concentrations of vanadium and PAR respectively, chosen so that **a** / **b** =1.

If an optical path of 1.00 cm is considered, the complex reagent concentrations at equilibrium will be:

$$V_m \; (PAR) \; _m(H_2O_2)_m = \mathbf{A}/\varepsilon$$

$$[V(H_2O_2)] = \mathbf{a} - \mathbf{m}.(\mathbf{A}/\varepsilon)$$

As $\mathbf{b} = \mathbf{a}$: $\quad [PAR] = \mathbf{b} - \mathbf{m}.(\mathbf{A}/\varepsilon) = \mathbf{a} - \mathbf{m} \; (\mathbf{A}/\varepsilon) = [V(H_2O_2)]$

where **A** is the absorbance and ε is the molar absorptivity of the complex $V_m(PAR)_m(H_2O_2)_m$.

The conditional formation constant for the reaction, K_c, is:

$$K_c = [(V_m(PAR)_m \; (H_2O_2)_m) / ([V(H_2O_2)]^m \; [PAR]^m) \qquad (1)$$

Substituting the above values into eq.1 for the complex $V_m(PAR)_m(H_2O_2)_m$ and then simplifying, gives:

$$K_c = (\mathbf{A} / \varepsilon) / [V(H_2O_2)]^{2m} \qquad (2)$$

which on rearrangement and expressing in logarithmic form becomes:

$$\log \mathbf{A} = \log(K_c \; \varepsilon) + \mathbf{2m} \log[V(H_2O_2)] \qquad (3)$$

The first term on the right is a constant, so that a plot of log A *versus* log $[V(H_2O_2)]$ will be a straight line with slope equal to **2m**. The slope gives the total number of ligand units in the complex, from which the true molecular formula can be obtained if the empirical formula is known.

For different values of **a** and **b**, keeping **a** / **b** =1, the $[V(H_2O_2)]$ changes and can be calculated from the equation 4.

$$[V(H_2O_2)] = \mathbf{a} - \mathbf{A} / \varepsilon' \qquad (4)$$

where ε' is the apparent molar absorptivity of the complex.

In a first approximation if **m** is assumed to be 1, ε' becames 1.85×10^4 L mol^{-1} cm^{-1}.

Absorbance data and calculated results for solutions containing equimolar amounts of vanadium and PAR are shown in Table 1. A plot of - log **a** *vs* - log (**a** − **A** / ε') results in a straight line as can be seen in Fig. 2, fitting the equation log **A** = (9.47±0.23) + (2.10±0.05) log$[V(H_2O_2)]$, with a correlation coefficient of 0.9987. As the slope is **2m** and this value is 2.10, the value of **m** is 1.05, or approximately 1.

If in sequence **m** is considered as 2, the slope obtained is 1.60. This value is incoherent because in these case **m** = 0.80,

Table 1. Data of the Vanadium / PAR / H_2O_2 system with 0.50 mol L^{-1} H_2SO_4 and 0.15% w/v H_2O_2 at 28.0±0.5 °C for the first mathematical treatment.

a * (10^{-5} mol L^{-1})	**A** **	- log **A**	- log (**a** - **A**/ε') ***	log K_c ****
1.0	0.050	1.310	5.135	4.70
2.0	0.142	0.848	4.914	4.72
3.0	0.260	0.585	4.804	4.77
4.0	0.385	0.415	4.731	4.79
5.0	0.509	0.293	4.647	4.74
6.0	0.651	0.186	4.606	4.77
7.0	0.768	0.114	4.559	4.75
			average log K_c =	4.75±0.02

* **a** = **b** = [vanadium] = [PAR]; ** **A** = absorbance at 542 nm; *** ε' = molar absorptivity of the complex assuming that it is mononuclear; **** K_c = formation constant of the complex.
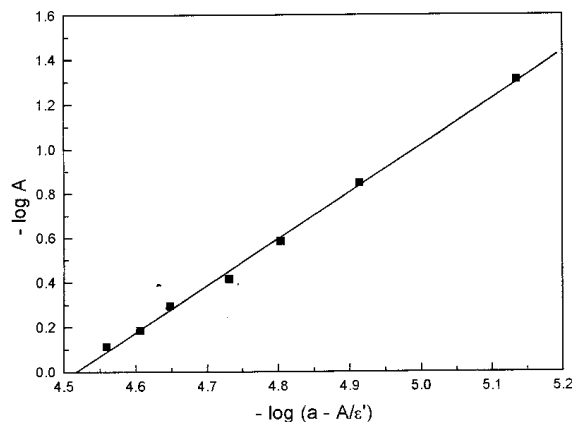
Figure 2. Correlation between the - log A and the - log $(a - A / \varepsilon')$ where a = [vanadium], A is the absorbance at 542 nm and ε' is the molar absorptivity of the complex, assuming m = 1. Concentration of H_2O_2 is 0.15% w/v; $[H_2SO_4]$ = 0.5 mol L^{-1}; ionic strength = 0.01 mol L^{-1} (KCl). Temperature = 28.0 ± 0.5 ^oC.

that is far from an integer number, so it was discarded. Therefore the value **m** = 1 was considered as the true and the specie $V_m(PAR)_m(H_2O_2)_m$ was admitted as mononuclear, i.e. $V(PAR)H_2O_2$.

The values of K_c used in Table 1 were calculated using equation 1 from which was obtained an average value of log K_c = 4.75±0.02 at ionic strength = 0.01 mol L^{-1} (KCl). This value can be also obtained from the intercept of the straight line of the Fig. 2. However, as experimental values of log $[V(H_2O_2)]$ fall in the region from -4 to -5, very far from the intercept of the y axis, graphical extrapolation to log($[V(H_2O_2)]$) = 0 can be expected to yield large error in the value of K_c.

(2) Second mathematical treatment: graphical method[13]

In order to confirm the results of the first mathematical treatment, a second one was performed.

As done in the previous mathematical treatment, in the presence of large amounts of H_2O_2, the general equilibrium (I) can be assumed.

The degree of complex formation, α, can be defined by:

$$\alpha = \{ \mathbf{m} \ [\ V_m(PAR)_m \ (H_2O_2)_m] \} / \mathbf{a} = A / A_{max} \qquad (5)$$

where **a** = total vanadium concentration = total PAR concentration; **A** = absorbance of the complex under the experimental constraints; A_{max} is the absorbance of the complex for 100% complexation of vanadium ion.

Under the experimental constraints, $[V(H_2O_2)]$ = [PAR] and $[V(H_2O_2)]$ = **a** (1-α), the rearrangement of eq.5 gives:

$$[V_m(PAR)_m \ (H_2O_2)_m] = \mathbf{a} \ (\alpha \ / \ \mathbf{m}) \qquad (6)$$

Combination of the above relationships with eq.1 gives:

$$K_c = (\mathbf{a} \ \alpha) \ / \ (\mathbf{m} \ \mathbf{a}^{2m}.(1- \ \alpha)^{2m}) \qquad (7)$$

Rearranging the eq.7 and taking of logarithms the eq.8 is obtained:

$$\log (\ \alpha \ / \ (1- \ \alpha)^{2m}) = \log (\mathbf{m}K_c) + (2\mathbf{m} - 1) \log \mathbf{a} \qquad (8)$$

Thus, a plot of log (α / (1- α)^{2m}) *vs* log **a** yields a straight line with slope 2**m**-1 and linear intercept equal to log(**m**K_c). Selection of different values of **m** will yield straight lines with different slopes, but only the correct value of **m** will yield a slope which is equal to the value predicted by eq.8.

Treatment of the data according to the present approach yields the results shown in Table 2. The predicted and observed slopes agree for **m** = 1, according to Table 3 and Fig. 3, corresponding to the composition $V(PAR)H_2O_2$. The values of log K_c calculated from eq.7 are shown in Table 4 and the average is 4.73±0.04, in agreement with 4.75±0.02 found in the first mathematical treatment done above.

It is interesting to note that if the difference (Δslope) between the observed and the predicted slope is obtained for each **m** value, and the difference between successive Δslope values is than taken,

Table 2. Data of the Vanadium / PAR / H_2O_2 system with 0.50 mol L^{-1} H_2SO_4 and 0.15% w/v H_2O_2 at 28.0±0.5 ^oC for the second mathematical treatment.

a * (10^{-5} mol L^{-1})	log **a**	log (α / (1-2α)$^{2\mathbf{m}}$) **, ***			
		m = 1	**m** = 2	**m** = 3	**m** = 4
1.0	- 5.00	- 0.301	- 0.030	0.241	0.512
2.0	- 4.70	- 0.023	0.457	0.885	1.315
3.0	- 4.52	0.165	0.680	1.194	1.708
4.0	- 4.40	0.396	1.083	1.713	2.397
5.0	- 4.30	0.450	1.156	1.861	2.566
6.0	- 4.22	0.536	1.305	2.073	2.841
7.0	- 4.15	0.592	1.401	2.210	3.019

* **a** = [vanadium] = [PAR]; ** α = degree of complex formation, calculated from eq.5; *** **m** = assumed values, considering $V_m(PAR)_m(H_2O_2)_m$

Table 3. Predicted and observed slope of the curves log **a** *versus* log(α / (1-2α)$^{2\mathbf{m}}$) for different assumed values of **m**.

Assumed **m** *	predicted slope	Observed slope	Δ slope	Δ^2 slope **
1	1	1.09	-0.09	-
2	3	1.72	1.28	1.37
3	5	2.38	2.62	1.34
4	7	3.03	3.97	1.35

* m = assumed values, considering $V_m(PAR)_m(H_2O_2)_m$; ** Δ^2slope = Δ(slope)$_{m+1}$ - Δ(slope)$_m$
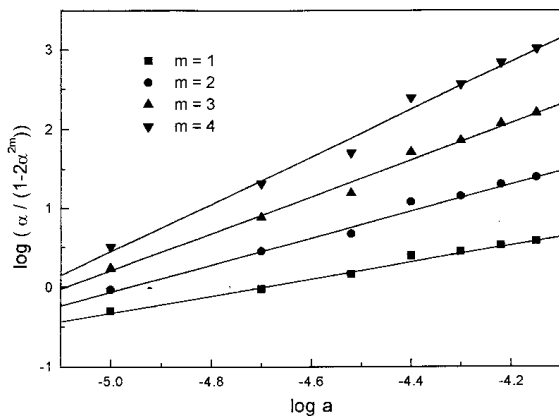
Figure 3. *Correlation between the log (α / (1 - α)^{2m}) and log **a**, where α is the absorbance due the complex for 100 % complexation of vanadium. For **m** = 1, the complex is assumed as mononuclear. For **m** > 1 the complex is assumed as polynuclear. Concentration of H_2O_2 is 0.15% w/v; [H_2SO_4] = 0.5 mol L^{-1}; ionic strength = 0.01 mol L^{-1} (KCl). Temperature = 28.0 ± 0.5 ^oC.*

Table 4. K_c values for the Vanadium / PAR / H_2O_2 system with 0.50 mol L^{-1} H_2SO_4 and 0.15% w/v H_2O_2 at 28.0±0.5 ^oC from the second mathematical treatment.

a * (10^{-5} mol L^{-1})	**A** **	α ***	log K_c (**m** = 1)****
1.0	0.050	0.268	4.70
2.0	0.142	0.391	4.68
3.0	0.260	0.477	4.77
4.0	0.385	0.536	4.80
5.0	0.509	0.556	4.75
6.0	0.651	0.587	4.76
7.0	0.768	0.606	4.74
		Average log K_c =	4.73±0.02

*   **a** = [vanadium] = [PAR]
**   **A** = absorbance at 542 nm
*** α = degree of complex formation, calculated from eq.5
**** **m** = assumed values, considering $V_m(PAR)_m(H_2O_2)_m$

$$\Delta^2 slope = \Delta(slope)_{m+1} - \Delta(slope)_m \qquad (9)$$

the values of Δ^2slope are constant (Table 3). A plot of observed slope *vs.* assumed **m** values must therefore yield a straight line of the general form

$$y = ix + j \qquad (10)$$

where y = observed slope, x = assumed **m** values, i and j are the slope and the linear coefficients respectively. There can be only one correct pair of x and y values for this system, given by the equation for the predicted slope line

$$y = 2x - 1 \qquad (11)$$

where in this case x = true **m** value and y is the correct predicted slope. In Fig. 4, the point of intersection of the two equations can be estimated from the graph, or calculated exactly by solving eq.10 and eq.11 for x. For the V(PAR)H_2O_2 system, eq.10 is y = 0.632x + 0.460, which yields x = 1.06 = **m** .
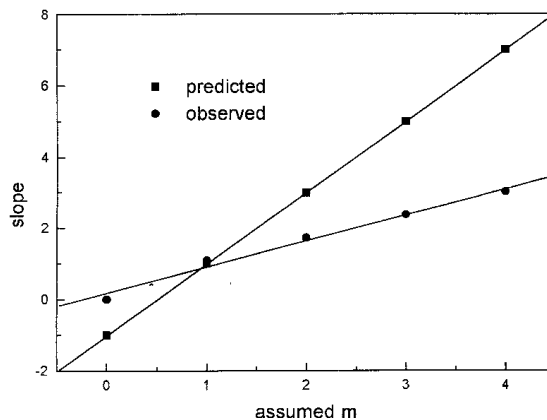

Figure 4. *Correlation of observed and predicted slope values with the assumed **m** values. For **m** = 1, the complex is assumed as mononuclear. For **m** > 1 the complex is assumed as polynuclear.*

CONCLUSION

From the above results, it is possible to conclude that a 1:1:1 mixed mononuclear complex is formed as result of the reaction of vanadium with PAR and hydrogen peroxide in sulfuric acid medium. Therefore, the true formula of the complex can be considered as V(H_2O_2)PAR. The logarithm of the equilibrium constant was found to be 4.73±0.04 or 4.75±0.02 by two different mathematical treatments. As a consequence of the stoichiometry of the complex, the true molar absorptivity is 1.85×10^4 L mol^{-1} cm^{-1} at 542 nm.

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