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Potentiometric studies on the formation equilibria of ternary complexes of vanadium(III) with cysteine and some amino acids

Eduis Guerra^a, Yendry Martínez^a, José Daniel Martínez^a, Mary Lorena Araujo^a, Felipe Brito^a, Edgar del Carpio^b, Lino Hernández^b and Vito Lubes^{b*}

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In this work, we present the results of the speciation of the ternary vanadium(III)–cysteine (H₂Cys) complexes with the amino acids glycine (HGly), proline (HPro), α -alanine (H α Ala), β -alanine (H β Ala), histidine (HHis), aspartic acid (H₂Asp), and glutamic acid (H₂Glu), studied by the measurements of electromotive forces, emf(H), using 3.0 mol dm⁻³ KCl as the ionic medium at 25 °C. The experimental data were analyzed by means of the computational least-squares program LETAGROP, taking into account the hydrolysis of the vanadium(III) cation, the respective stability constants of the binary complexes, and the acid base reactions of the amino acids, which were kept fixed during the analysis. In the vanadium(III)–cysteine-amino acid (HB) systems, where HB represents the bidentate ligands, the formations of the ternary complexes [V(Cys)(HB)]⁺, V(Cys)(B), [V(Cys)(B)(OH)]⁻, and [V(Cys)(B)(OH)₂]²⁻ were observed. In the vanadium(III)-H₂Cys-HHis system, the formations of the complexes [V(HCys)(HHis)]²⁺, [V(HCys)(His)]⁺, V(Cys)(His), and [V(Cys)(His)(OH)]⁻ were detected; in the vanadium(III)-H₂Cys-H₂Asp system, the complexes [V(H₂Cys)(HAsp)]²⁺, [V(HCys)(HAsp)]⁺, V(HCys)(Asp), [V(Cys)(Asp)]⁻, and [V(Cys)(Asp)(OH)]²⁻ were detected; and finally, in the vanadium(III)-H₂Cys-H₂Glu system, the complexes [V(H₂Cys)(HGlu)]²⁺, [V(HCys)(HGlu)]⁺, V(Cys)(HGlu), and [V(Cys)(HGlu)(OH)]⁻ were observed. The species distribution diagrams as a function of pH are briefly discussed.

Keywords: vanadium(III) complexes; cysteine; potentiometric studies; speciation; ternary complexes

1. Introduction

Interest of the study of vanadium complexes has been centered on vanadium(IV) and vanadium(V) chemistry since the discovery of the insulinomimetic activity of those complexes.[1] The chemistry of the vanadium(III) complexes is difficult to study because vanadium(III) easily oxidizes to vanadium(IV), which has a strong hydrolysis reaction. The insulinomimetic activity of the vanadium(III) maltolato system was first reported in [2].

The investigation of application of vanadium(III) complexes in medicine is growing; some antitumoral activity has been reported, and Papaioannou et al. [3] demonstrated the activity of the vanadium(III)–cysteine complexes as antimetastatic, antioxidant, and the inhibition of neutral endopeptidase activities.[3] The effect on actin in hepatoma Morris 5123 cell lines of the vanadium(III)–cysteine complexes was observed.[4]

In vivo coordination structural changes of a potent insulinomimetic agent, bis(picinato)oxovanadium(IV), were studied by electron spin-echo envelope modulation spectroscopy,[5] and these authors observed that the original binary complex is transformed to a ternary complex with a composition VO(pic)(X), where X represents an amino acid, and suggested that the activity changed substantially by the formation of this ternary complex. Taking into account the possible application of the vanadium(III)-H₂Cys complexes, the aim of this work was to

investigate the formation of the ternary complexes in the vanadium(III)-H₂Cys-amino acid systems as a contribution to the knowledge of the speciation of the vanadium(III)-H₂Cys in biofluids.

To the present, there are no reports on the speciation of the ternary complexes of vanadium(III)-H₂Cys and the amino acids studied in this work.[6,7]

2. Experimental

2.1. Reagents

The VCl₃ (Merck p.a.); the cysteine (H₂Cys) (Merck 99%); and the amino acids glycine (HGly), proline (HPro), α -alanine (H α Ala), β -alanine (H β Ala), histidine (HHis), aspartic acid (H₂Asp), and glutamic acid (H₂Glu) (Merck p.a.) were used also sodium oxalate, potassium permanganate, and Mohr's salt (Merck p.a.) to standardize the VCl₃ stock solution. All the reagents were used without more purification. The HCl and KOH solutions were prepared using 100.0 mmol dm⁻³ Titrisol Merck ampoules. The KOH solution was standardized against potassium hydrogen phthalate (Merck p.a.), recrystallized, and dried at 120 °C using phenolphthalein as indicator, and the HCl solution was standardized with the KOH solution of known concentration.[8] The solutions were prepared using triple glass-distilled water and boiled before the preparation of the solutions in order to

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remove dissolved CO₂. To prevent the hydrolysis of the VCl₃ stock solution, it contained 200 mmol dm⁻³ HCl and was maintained under a H₂ atmosphere in the presence of a Pt platinized net in order to avoid oxidation of the vanadium(III) stock solution to vanadium(IV).[9] It is important to mention that the VCl₃ is hygroscopic and it must be weighed as fast as possible, and for that reason, it is necessary to standardize the VCl₃ stock solution. First, the vanadium(III) is oxidized with a KMnO₄ solution to vanadium(V) in acidic medium, and the KMnO₄ was standardized with Na₂Oxalate, and after the oxidation of the vanadium solution, it was standardized with a Mohr's salt solution (Fe(II) solution previously standardized with KMnO₄) using diphenylamine sulfonic acid as indicator.[10] The acidity of the VCl₃ stock solution was determined by the Gran method.[11]

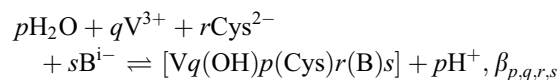
The stability of the vanadium(III) stock solution was checked periodically by spectrophotometric measurements, and it was shown to be stable for several weeks. The potentiometric measurements were carried out in aqueous solution using 3.0 mol dm⁻³ KCl as ionic medium. Nitrogen-free O₂ and CO₂ were used.

2.2. Methods

The potentiometric measurements were carried out using the following instruments: Thermo Orion model 520A pH meter, Metrohm EA 876-20 titration vessel, and Lauda Brikmann RM6 thermostat bath. The sealed 100-mL thermostatted double-walled glass titration vessel was fitted with a combined Orion Ross 8102BN pH electrode with a titrant inlet, magnetic stirrer, and an inert nitrogen atmosphere inlet with outlet tubes. The temperature was maintained at (25.0 ± 0.1) °C by constant circulation of water from the thermostat bath.

The emf (H) measurements were carried out by means of the REF//S/GE cell, where REF = Ag/AgCl/ 3.0 mol dm⁻³ KCl; S = equilibrium solution; and GE = glass electrode. At 25 °C, the emf (mV) of this cell follows the Nernst equation, $E = E^0 + jh + 59.16 \log h$, where h represents the free hydrogen ion concentration, E^0 is the standard potential, and j is a constant which takes into account the liquid junction potential.[12] The experiments were carried out as follows: A fixed volume of 0.100 mol dm⁻³ HCl was titrated with successive additions of 0.100 mol dm⁻³ KOH until near neutrality in order to get the parameters E^0 and j . Then, aliquots of the cysteine and the amino acid under study were added, and finally, an aliquot of the vanadium(III) stock solution was added sequentially. And, the titration was continued with 0.100 mol dm⁻³ KOH. The measurements were done using a total metal concentration, $M_T = 2-3$ mmol dm⁻³, and vanadium(III):H₂Cys:amino acid molar ratios $R = 1:1:1, 1:1:2, \text{ and } 1:2:1$.

The systems V³⁺-H₂Cys-Amino Acids (H_iB) were studied according to the reaction scheme:



where H_iB represents the amino acids studied, [Vq(OH)p(Cys)r(B)s] is the ternary (p, q, r, s) complex (the charges were omitted), and $\beta_{p,q,r,s}$ is the respective stability constant.

The potentiometric data were analyzed using the program LETAGROP,[13,14] in order to minimize the function $Z_B = (h - H)/M_T$, where Z_B is the average number of mole of H⁺ dissociates per mole of metal, H is the total (analytical) concentration of H⁺, h represents the concentration in equilibrium of H⁺, and M_T represents the total (analytical) concentration of vanadium(III).

Equilibria corresponding to the formation of the hydroxo complexes of vanadium(III) were considered in the calculation of the stability constants of ternary complexes. The following species were assumed: [V(OH)]²⁺, $\log \beta_{1,-1} = -3.13(8)$; [V₂O]⁴⁺, $\log \beta_{2,-2} = -3.76(6)$; [V(OH)₂]⁺, $\log \beta_{1,-2} = -6.86(2)$; and [V₃(OH)₈]⁺, $\log \beta_{3,-8} = -27.47(4)$. [15] The binary vanadium(III)-H₂Cys,[16] vanadium(III)-glycine,[17] vanadium(III)-proline,[18,19] vanadium(III)- α -alanine and vanadium(III)- β -alanine systems,[20] the vanadium(III)-HHis system,[18,19] the vanadium(III)-H₂Asp system,[20] and finally for the vanadium(III)-H₂Glu system [17] were previously studied by us.

The stability constants of the vanadium(III) hydroxo complexes, the acidity constants of the ligands, and the stability constants of the binary complexes were kept fixed during the analysis. The aim was to find a complex or complexes giving the lowest sum of the errors squared, $U = \sum (Z_B^{\text{exp}} - Z_B^{\text{calc}})^2$, the fittings were done by testing different (p, q, r, s) combinations.

The species distribution diagrams were obtained using the computer program HYSS,[21] yielding the $\beta_{p,q,r,s}$ values, which are summarized in Tables 2 and 3.

3. Results

3.1. Ionization constants of the studied ligands

The ionization constants (Table 1) in the ionic medium 3.0 mol dm⁻³ KCl are in good agreement with the literature values, considering the differences in ionic strength and ionic medium.[6,7]

3.2. Ternary vanadium(III) complexes

3.2.1. Vanadium(III)-H₂Cys-HB systems

Figure 1 shows the $Z_B(\text{pH})$ data, and in Figures 2–8 are shown the species distribution diagrams for these systems for the following conditions: $M_T = 3$ mmol dm⁻³ and molar ratio $R = 1:1:1$; the stability constants are summarized in Tables 2 and 3.

Table 1. Values of $\log \beta_{pr}$ for the ligands studied (25 °C, $I = 3.0 \text{ mol dm}^{-3}$ KCl ionic medium).

Equilibrium	H ₂ Cys $\log \beta_{pr}$	Ha-Ala $\log \beta_{pr}$	H β -Ala $\log \beta_{pr}$	HGly $\log \beta_{pr}$	HPro $\log \beta_{pr}$
$\text{HL} + \text{H} \rightleftharpoons \text{H}_2\text{L}^+$		2.784(6)	4.05(1)	2.77(1)	2.349(7)
$\text{HL} \rightleftharpoons \text{L}^- + \text{H}^+$		-10.18(1)	-10.54(2)	-10.12(1)	-11.10(2)
$\text{H}_2\text{L} + \text{H}^+ \rightleftharpoons \text{H}_3\text{L}^+$	2.28(3)				
$\text{H}_2\text{L} \rightleftharpoons \text{HL}^- + \text{H}^+$	-8.81(3)				
$\text{H}_2\text{L} \rightleftharpoons \text{L}^{2-} + 2\text{H}^+$	-20.4(2)				
Dispersion (σ)	0.033	0.007	0.014	0.047	0.009
Equilibriums	H ₂ Asp	$\log \beta_{pr}$ H ₂ Glu	HHis		
$\text{H}_2\text{L} + \text{H}^+ \rightleftharpoons \text{H}_3\text{L}^+$	2.60(4)	2.72(4)			
$\text{H}_2\text{L} \rightleftharpoons \text{HL}^- + \text{H}^+$	-4.08(2)	-4.58(2)			
$\text{H}_2\text{L} \rightleftharpoons \text{L}^{2-} + 2\text{H}^+$	-13.86(3)	-14.23(3)			
Dispersion (σ)	0.022	0.028			
$\text{HL} + \text{H}^+ \rightleftharpoons \text{H}_2\text{L}^+$			6.67(4)		
$\text{HL} + 2\text{H}^+ \rightleftharpoons \text{H}_3\text{L}^{2+} + \text{H}^+$			9.32(7)		
$\text{HL} \rightleftharpoons \text{L}^- + \text{H}^+$			-9.40(5)		
Dispersion (σ)			0.035		

Note: Values in parentheses are standard deviations [$3\sigma(\log \beta)$] on the last significant figure.

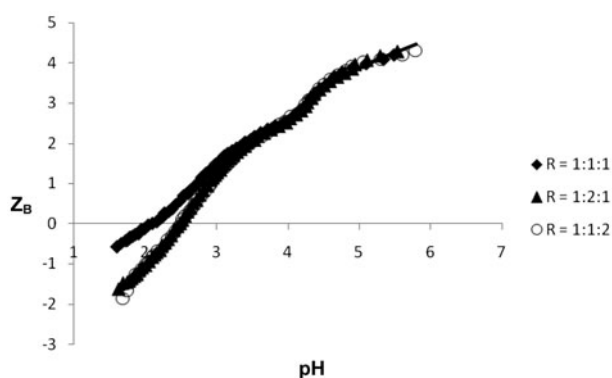


Figure 1. Z_B , average number of mole of H^+ dissociate per mole of vanadium(III) vs. pH of the Vanadium(III)-H₂Cys-HGly system, in 3.0 mol dm^{-3} KCl at 25 °C. The lines represent theoretical curves calculated with the equilibrium constants of Table 2.

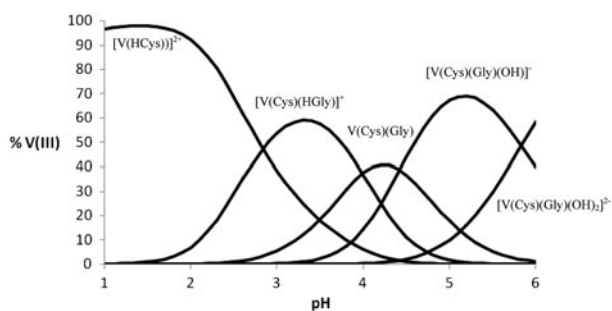


Figure 2. Species distribution diagram as a function of pH for the V(III)-H₂Cys-HGly system in 3.0 mol dm^{-3} KCl at 25 °C considering the conditions $M_T = 3 \text{ mmol dm}^{-3}$ and molar ratio $R = 1:1:1$.

3.2.2. Vanadium(III)-H₂Cys-HHis system

Figure 6 shows the species distribution diagrams for this system for the following conditions: $M_T = 3 \text{ mmol dm}^{-3}$ and molar ratio $R = 1:1:1$, considering the stability constants summarized in Table 2.

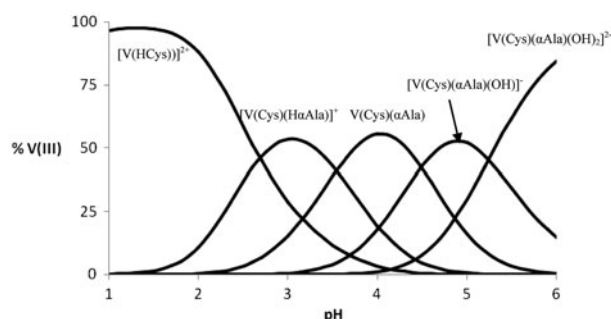


Figure 3. Species distribution diagram as a function of pH for the V(III)-H₂Cys-HaAla system in 3.0 mol dm^{-3} KCl at 25 °C considering the conditions $M_T = 3 \text{ mmol dm}^{-3}$ and molar ratio $R = 1:1:1$.

3.2.3. Vanadium(III)-H₂Cys-H₂Asp system

In Figure 7, the species distribution diagrams are presented for the following conditions: $M_T = 3 \text{ mmol dm}^{-3}$ and molar ratio $R = 1:1:1$ for this system, considering the stability constants summarized in Table 3.

3.2.4. Vanadium(III)-H₂Cys-H₂Glu system

The species distribution diagrams for this system are given in Figure 8, and the stability constants are summarized in Table 3, under the following conditions: $M_T = 3 \text{ mmol dm}^{-3}$ and molar ratio $R = 1:1:1$.

4. Discussion

The potentiometric data analysis of the vanadium(III)-H₂Cys-Amino acids systems performed with LETA-GROP indicate the formation of the mononuclear complexes $[\text{V}(\text{Cys})(\text{HB})]^+$, $\text{V}(\text{Cys})(\text{B})$, $[\text{V}(\text{Cys})(\text{B})(\text{OH})]^-$, and $[\text{V}(\text{Cys})(\text{B})(\text{OH})_2]^{2-}$, with the bidentate amino acids glycine, proline, α -alanine, and β -alanine. The good agreement between the experimental data (dotted curve)

Table 2. Equilibrium constants ($\log \beta_{p,q,r,s}$) for the V(III)-Cys-B⁻ systems (25 °C, $I = 3.0 \text{ mol dm}^{-3}$ KCl ionic medium). Studied according to the equilibrium: $p\text{H}_2\text{O} + q\text{V}^{3+} + r\text{Cys}^{2-} + s\text{B}^- \rightleftharpoons [\text{V}q(\text{OH})p(\text{Cys})r(\text{B})s] + p\text{H}^+$, $\beta_{p,q,r,s}$.

Species	$\log \beta_{p,q,r,s}$ Gly	$\log \beta_{p,q,r,s}$ α -Ala	$\log \beta_{p,q,r,s}$ β -Ala	$\log \beta_{p,q,r,s}$ Pro	$\log \beta_{p,q,r,s}$ His
$[\text{V}(\text{HCys})(\text{HB})]^{2+}$					47.67(7)
$[\text{V}(\text{HCys})(\text{B})]^{+}$					44.24(5)
$[\text{V}(\text{Cys})(\text{HB})]^{+}$	36.96(2)	37.27(2)	37.96(3)	37.81(3)	
$\text{V}(\text{Cys})(\text{B})$	32.97(5)	33.73(3)	33.1(1)	34.01(5)	39.67(8)
$[\text{V}(\text{Cys})(\text{B})(\text{OH})]^{-}$	28.55(4)	29.24(5)	29.15(4)	-29.35(7)	34.85(6)
$[\text{V}(\text{Cys})(\text{B})(\text{OH})_2]^{2-}$	22.7(1)	24.00(9)	23.1(1)	23.3(3)	
Dispersion (σ)	0.067	0.065	0.099	0.071	0.090

Note: Values in parentheses are standard deviations [$3\sigma(\log \beta_{p,q,r,s})$] on the last significant figure.

Table 3. Equilibrium constants ($\log \beta_{p,q,r,s}$) for the V(III)-Cys-B²⁻ systems (25 °C, $I = 3.0 \text{ mol dm}^{-3}$ KCl ionic medium). Studied according to the equilibrium: $p\text{H}_2\text{O} + q\text{V}^{3+} + r\text{Cys}^{2-} + s\text{B}^{2-} \rightleftharpoons [\text{V}q(\text{OH})p(\text{Cys})r(\text{B})s] + p\text{H}^+$, $\beta_{p,q,r,s}$.

Species	$\log \beta_{p,q,r,s}$ Asp	$\log \beta_{p,q,r,s}$ Glu
$[\text{V}(\text{H}_2\text{Cys})(\text{HB})]^{2+}$	48.67(9)	49.18(6)
$[\text{V}(\text{HCys})(\text{HB})]^{+}$	46.0(2)	46.42(8)
$\text{V}(\text{HCys})(\text{B})$	43.29(8)	43.12(6)
$[\text{V}(\text{Cys})(\text{B})]^{-}$	39.4(1)	38.59(7)
$[\text{V}(\text{Cys})(\text{B})(\text{OH})]^{2-}$	35.0(1)	-
Dispersion (σ)	0.094	0.090

Note: Values in parentheses are standard deviations [$3\sigma(\log \beta_{p,q,r,s})$] on the last significant figure.

and the model (continuous line) is observed in Figure 1, and the stability constants are summarized in Table 2. The species distribution diagrams for these systems considering the experimental conditions $M_T = 3 \text{ mmol dm}^{-3}$ and a molar ratio $R = 1:1:1$ are given in Figures 2–5. The binary $[\text{V}(\text{HCys})]^{2+}$ is formed in a important proportion between $1 < \text{pH} < 2.5$, the complex $[\text{V}(\text{Cys})(\text{HB})]^{+}$ is formed in a 60% in the range $2.5 < \text{pH} < 4$, the complex $\text{V}(\text{Cys})(\text{B})$ is formed in a 50% between $4 < \text{pH} < 4.4$, the ternary complex $[\text{V}(\text{Cys})(\text{B})(\text{OH})]^{-}$ is important in the range $4.4 < \text{pH} < 5.8$, and the species $[\text{V}(\text{Cys})(\text{B})(\text{OH})_2]^{2-}$ is important at $\text{pH} > 5.8$.

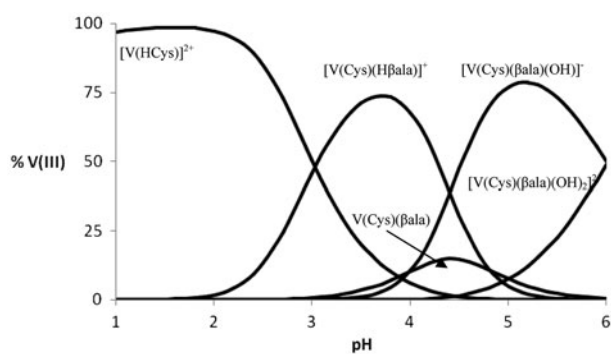


Figure 4. Species distribution diagram as a function of pH for the V(III)-H₂Cys-H β ala system in 3.0 mol dm^{-3} KCl at 25 °C considering the conditions $M_T = 3 \text{ mmol dm}^{-3}$ and molar ratio $R = 1:1:1$.

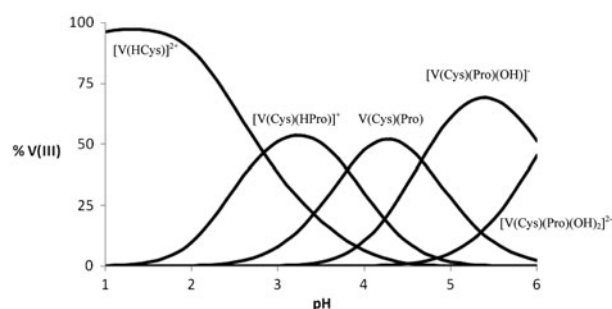
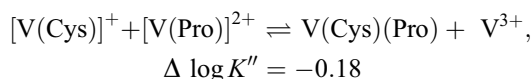
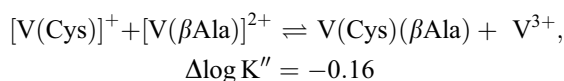
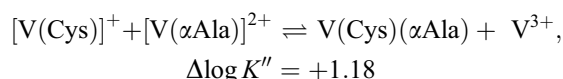
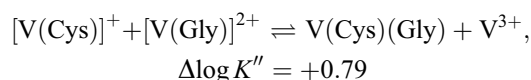


Figure 5. Species distribution diagram as a function of pH for the V(III)-H₂Cys-HPro system in 3.0 mol dm^{-3} KCl at 25 °C considering the conditions $M_T = 3 \text{ mmol dm}^{-3}$ and molar ratio $R = 1:1:1$.

The relative stability of the ternary complexes comparing to the binary complexes is measured with the $\Delta \log K''$ [22] that is given by the reactions:



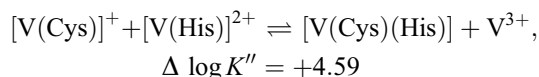
The positive values for HGly and H α Ala indicate that the ternary complexes are more stable than the binary complexes. In the case of the ternary complexes with H β Ala and HPro have negative $\Delta \log K''$ values, this can be explained because the HGly and H α Ala form five-membered chelated rings, the H β Ala forms a six-membered chelated ring, and the HPro has a different structure and is possible that this causes some steric

effect that made unfavorable the formation of the ternary complex.

Another important aspect is that in the ternary complex $[V(Cys)(B)(OH)_2]^{2-}$, we suggest that the Cys^{2-} is acting as a tridentate ligand by (COO⁻, N, S⁻) coordination, the B^- is acting as a bidentate ligand by (N, COO⁻) coordination, and the two OH^- occupy two coordination positions, so these ternary complexes must be heptacoordinated. This agrees with the observation in the literature of the heptacoordinated complex $[V(dipic)(pic)(H_2O)_2] \cdot H_2O$, [23] where pic^- corresponds to the picolinate ligand, which is coordinated to the vanadium(III) ion by (N, COO⁻) and forms a five-membered chelated ring, similar to the amino acids studied in this work, and it was reported that systems forming five-membered chelated ring tend to be heptacoordinated complexes. [24]

The analysis of the data performed in the vanadium(III)-H₂Cys-HHis system indicates the formation of the species $[V(HCys)(HHis)]^{2+}$, $[V(HCys)(His)]^+$, $V(Cys)(His)$, and $[V(Cys)(His)(OH)]^-$. The species distribution diagram, Figure 6, indicates that the ternary complex $[V(HCys)(HHis)]^{2+}$ is the most important species in the range $1 < pH < 3.2$; between $3.2 < pH < 4.5$ is observed the species $[V(HCys)(His)]^+$; in the range $4 < pH < 6$ is formed in low extension the complex $V(Cys)(His)$; and the species $[V(Cys)(His)(OH)]^-$ is very important at $pH > 5$.

The relative stability of the ternary complex, compared with the binary complexes, can be obtained considering the $\Delta \log K''$ value, where $\Delta \log K''$ is calculated considering the reaction:



This indicates that the ternary complex is more stable than the binary complexes.

In the vanadium(III)-H₂Cys-H₂Asp system, the complexes $[V(H_2Cys)(HAsp)]^{2+}$, $[V(HCys)(HAsp)]^+$, $V(HCys)(Asp)$, $[V(Cys)(Asp)]^-$, and $[V(Cys)(Asp)(OH)]^{2-}$

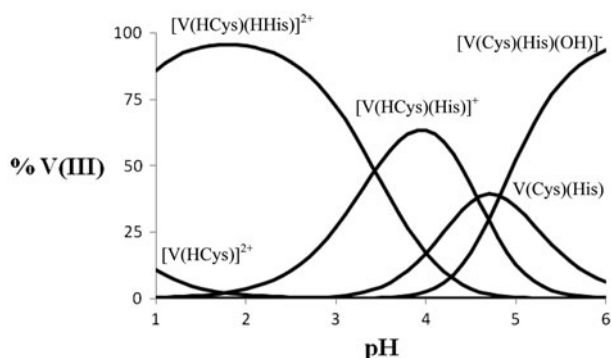


Figure 6. Species distribution diagram for the vanadium(III)-H₂Cys-HHis system, for the experimental conditions $M_T = 3 \text{ mmol dm}^{-3}$ and molar ratio $R = 1:1:1$.

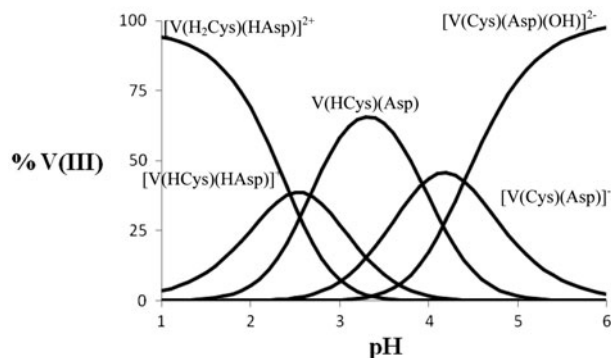
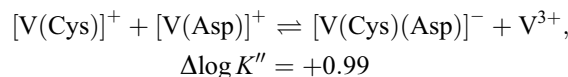


Figure 7. Species distribution diagram for the vanadium(III)-H₂Cys-H₂Asp system, for the experimental conditions $M_T = 3 \text{ mmol dm}^{-3}$ and molar ratio $R = 1:1:1$.

were detected. The species distribution diagram, Figure 7, for this system indicates that between $1 < pH < 2.5$, the most important species is the complex $[V(H_2Cys)(HAsp)]^{2+}$. Between $1 < pH < 4$ is formed in low extension the ternary complex $[V(HCys)(HAsp)]^+$; in the range $2.5 < pH < 4$ is formed the complex $V(HCys)(Asp)$; the species $[V(Cys)(Asp)]^-$ is formed in low extension in the range $3 < pH < 6$; and finally, at $pH > 4.5$, the species $[V(Cys)(Asp)(OH)]^{2-}$ is abundant.

The relative stability of the ternary complex $\Delta \log K''$ value for this system is +0.99:



which means that the ternary complex is more stable than the binary complexes.

In the vanadium(III)-H₂Cys-H₂Glu system, the following complexes were observed: $[V(H_2Cys)(HGlu)]^{2+}$, $[V(HCys)(HGlu)]^+$, $V(Cys)(HGlu)$, and $[V(Cys)(Glu)]^-$. The distribution diagrams, Figure 8, indicate that in the range $1 < pH < 2.8$, the most important complex is $[V(H_2Cys)(HGlu)]^{2+}$, and the ternary complex $[V(HCys)(HGlu)]^+$ is formed in low quantity in the range

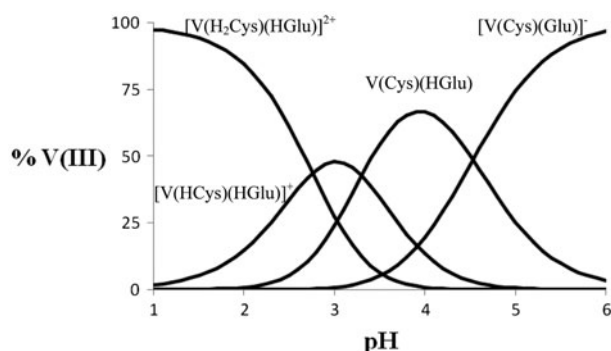


Figure 8. Species distribution diagram for the vanadium(III)-H₂Cys-H₂Glu system, for the experimental conditions $M_T = 3 \text{ mmol dm}^{-3}$ and molar ratio $R = 1:1:1$.

$1 < \text{pH} < 4$. The complex $\text{V}(\text{Cys})(\text{HGlu})$ is presented between $3 < \text{pH} < 4.5$, and at $\text{pH} > 4.5$, the most abundant species is the complex $[\text{V}(\text{Cys})(\text{Glu})]^-$. In this system, the $\Delta \log K''$ value could not be obtained because the formation of the binary $[\text{V}(\text{Glu})]^+$ complex was not observed.

5. Conclusions

The analysis of the potentiometric data shows the formation of mononuclear ternary complexes with the composition 1:1:1. In the vanadium(III)- H_2Cys - HHis system, the formation of the complexes $[\text{V}(\text{HCys})(\text{HHis})]^{2+}$, $[\text{V}(\text{HCys})(\text{His})]^+$, $\text{V}(\text{Cys})(\text{His})$, and $[\text{V}(\text{Cys})(\text{His})(\text{OH})]^-$ were detected; in the vanadium(III)- H_2Cys - H_2Asp system, the complexes $[\text{V}(\text{H}_2\text{Cys})(\text{HAsp})]^{2+}$, $[\text{V}(\text{HCys})(\text{HAsp})]^+$, $\text{V}(\text{HCys})(\text{Asp})$, $[\text{V}(\text{Cys})(\text{Asp})]^-$, and $[\text{V}(\text{Cys})(\text{Asp})(\text{OH})]^{2-}$ were detected; and in the vanadium(III)- H_2Cys - H_2Glu system, the complexes $[\text{V}(\text{H}_2\text{Cys})(\text{HGlu})]^{2+}$, $[\text{V}(\text{HCys})(\text{HGlu})]^+$, $\text{V}(\text{Cys})(\text{HGlu})$, and $[\text{V}(\text{Cys})(\text{HGlu})(\text{OH})]^-$ were observed. Finally, in the vanadium(III)- H_2Cys - HB system, the complexes $[\text{V}(\text{Cys})(\text{HB})]^+$, $\text{V}(\text{Cys})(\text{B})^-$, $[\text{V}(\text{Cys})(\text{B})(\text{OH})]^-$, and $[\text{V}(\text{Cys})(\text{B})(\text{OH})]^-$ were observed.

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References

- [1] Crans DC, Smeets JJ, Gaidamauskas E, Yang L. The chemistry and biochemistry of vanadium and the biological activities exerted by vanadium compounds. *Chem. Rev.* 2004;104:849–902.
- [2] Melchior M, Rettig SJ, Liboiron BD, Thompson KH, Yuen VG, McNeill JH, Orvig C. Insulin-Enhancing Vanadium(III) Complexes. *Inorg. Chem.* 2001;40:4686–4690.
- [3] Papaioannou A, Manos M, Karkabounas S, Liasko R, Evangelou AM, Correia I, Kalfakakou V, Pessoa J, Kabanos T. Solid state and solution studies of a vanadium (III)-l-cysteine compound and demonstration of its antitastatic, antioxidant and inhibition of neutral endopeptidase activities. *J. Inorg. Biochem.* 2004;98:959–968.
- [4] Osńska-Królicka I, Podsiadły H, Bukietyńska K, Zemanek-Zboch M, Nowak D, Suchoszek-Lukaniuk K, Malicka-Błaszkiwicz M. Vanadium(III) complexes with l-cysteine – stability, speciation and the effect on actin in hepatoma Morris 5123 cells. *J. Inorg. Biochem.* 2004;98:2087–2098.
- [5] Fukui K, Fujisawa Y, Ohya-Nishiguchi H, Kamada H, Sakurai H. In vivo coordination structural changes of a potent insulin-mimetic agent, bis(picolinato)oxovanadium (IV), studied by electron spin-echo envelope modulation spectroscopy. *J. Inorg. Biochem.* 1999;77:215–224.
- [6] Martell AE, Smith RM, Motekaitis RJ. NIST standard reference database [Version 8]. Gaithersburg, MD; 2004.
- [7] Pettit D, Powell K. IUPAC stability constants database. Otley: Academic Software; 1997.
- [8] Kolthoff IM, Stenger VA. Volumetric analysis, Vol. II. Nueva York: Interscience Publishers; 1947. p. 94.
- [9] Brito F, Goncalves JM. Complejos de Vanadio(III) 2. Potencial Normal del Sistema $\text{VO}^{2+}/\text{V}^{3+}$ [25 °C (K)Cl 3 M] [Vanadium(III) complexes. 2. Normal Potential of the $\text{VO}^{2+}/\text{V}^{3+}$ system [25 °C 3 M (K)Cl]]. *An. Fis. Quím.* 1982;78:104–105.
- [10] Mateo S, Brito F. Complejos de vanadio(III). 1. Hidrólisis de V^{3+} en (K)Cl 3.0 M a 25 °C [Vanadium(III) complexes. 1. V^{3+} hydrolysis in 3.0 M (K)Cl at 25 °C]. *An. Fis. Quím.* 1968;64B:115–138.
- [11] Gran G. Determination of the equivalence point in potentiometric titrations. Part II. *Analyst.* 1952;77:661–671.
- [12] Biedermann G, Sillén LS. The hydrolysis of metal ions. IV. Liquid-junction potentials and constancy of activity factors in $\text{NaClO}_4\text{--HClO}_4$ ionic medium. *Ark. Kemi.* 1953;5:425–540.
- [13] Brito F, Araujo ML, Lubes V, D'Ascoli A, Mederos A, Gili P, Domínguez S, Chinae E, Hernández-Molina R, Armas MT, Baran EJ. Emf(H) data analysis of weak metallic complexes using reduced formation functions. *J. Coord. Chem.* 2005;58:501–512.
- [14] Sillén LG, Warnqvist B. High-speed computers as a supplement to graphical methods. VI. A strategy for two-level Letagrop adjustment of common and “group” parameters. Features that avoid divergence. *Arkiv Kemi.* 1969;31:315–339.
- [15] Lubes G, Brito F, Araujo ML, Lubes V. Vanadium(III) ion hydrolysis at pH higher than 3 in 3M KCl at 25 °C. *Avances en Química.* 2010;5:51–55.

- [16] Rosas H, Sarmiento LE, Lubes V, Goncalves M, Araujo ML, Brito F. Study of the ternary complex formation between vanadium(III)-cysteine and small blood serum bioligands. *J. Solution Chem.* 2008;37:701–711.
- [17] Mendoza M. Estudio del sistema vanadio(III)-glutati3n por medio de medidas de emf(H) en KCl 3.0 M a 25 3C [Vanadium(III)- glutathione system study using emf(H) measurements in 3.0 M KCl at 25 3C] [undergraduate thesis]. Facultad de Ciencias. Universidad Central de Venezuela; 2004.
- [18] Rosas H. Estudio del sistema vanadio(III)-prolina por medio de medidas de emf(H) en KCl 3.0 M a 25 3C. Trabajo Dirigido [Vanadium(III)- proline system study using emf(H) measurements in 3.0 M KCl at 25 3C]. Postgrado de Qu3mica. Departamento de Qu3mica. Universidad Sim3n Bol3var; 2008.
- [19] Rosas H. Estudio del sistema vanadio(III)-histidina por medio de medidas de emf(H) en KCl 3.0 M a 25 3C. Trabajo Dirigido [Vanadium(III)- histidine system study using emf(H) measurements in 3.0 M KCl at 25 3C]. Postgrado de Qu3mica. Departamento de Qu3mica. Universidad Sim3n Bol3var; 2008.
- [20] Zambrano N. Complejos de V(III) con los amino3cidos α -alanina, (-alanina y 3cido asp3rtico estudiados mediante medidas de fuerzas electromotrices (KCl 3.0 M, 25 3C) [Vanadium(III) complexes with the amino acids α -alanine, β -alanine and aspartic acid study using emf(H) measurements (3.0 M KCl, 25 3C)] [Undergraduate thesis]. Facultad de Ciencias. Universidad Central de Venezuela; 2004.
- [21] Alderighi L, Gans P, Ienco A, Peters D, Sabatini A, Vacca A. Hyperquad simulation and speciation (HySS): a utility program for the investigation of equilibria involving soluble and partially soluble species. *Coord. Chem. Rev.* 1999;184:311–318.
- [22] Khalil MM, Attia AE. Potentiometric studies on the binary and ternary complexes of copper(II) containing dipicolinic acid and amino acids. *J. Chem. Eng. Data.* 1999;44:180–184.
- [23] Chatterjee M, Maji M, Ghosh S, Mak TCW. Studies of V(III) complexes with selected α -N-heterocyclic carboxylato NO donor ligands: structure of a new seven-coordinated pentagonal bipyramidal complex containing picolinato ligands. *J. Chem. Soc., Dalton Trans.* 1998;3641–3646.
- [24] Kanamori K. Structures and properties of multinuclear vanadium(III) complexes: seeking a clue to understand the role of vanadium(III) in ascidians. *Coord. Chem. Rev.* 2003;237:147–161.