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

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

\textsuperscript{a}Facultad de Ciencias. Centro de Equilibrios en Solución, Escuela de Química, Universidad Central de Venezuela (UCV), Caracas, Venezuela; \textsuperscript{b}Departamento de Química, Universidad Simón Bolívar (USB), Caracas, Venezuela

In this work, we present the results of the speciation of the ternary vanadium(III)-cysteine (H\textsubscript{2}Cys) complexes with the amino acids glycine (HGly), proline (HPro), α-alanine (H\textsubscript{2}Ala), β-alanine (H\textsubscript{2}Bala), histidine (HHis), aspartic acid (H\textsubscript{2}Asp), and glutamic acid (H\textsubscript{2}Glu), studied by the measurements of electromotive forces, emf(H), using 3.0 mol dm\textsuperscript{-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 systems, where HB represents the bidentate ligands, the formations of the ternary complexes [V(Cys)(HB)]\textsuperscript{2+}, [V(Cys)(B)(OH)]\textsuperscript{+}, and [V(Cys)(B)(OH)]\textsuperscript{2+} were observed. In the vanadium(III)-H\textsubscript{2}Cys-HHis system, the formations of the complexes [V(HCys)(HHis)]\textsuperscript{+}, [V(HCys)(HHis)]\textsuperscript{2+}, [V(Cys)(HHis)], and [V(Cys)(HHis)(OH)] were detected; in the vanadium(III)-H\textsubscript{2}Cys-H\textsubscript{2}Asp system, the complexes [V(HCys)(HAsp)]\textsuperscript{+}, [V(HCys)(HAsp)]\textsuperscript{2+}, [V(Cys)(HAsp)], [V(Cys)(Asp)]\textsuperscript{+}, and [V(Cys)(Asp)(OH)]\textsuperscript{2+} were detected; and finally, in the vanadium(III)-H\textsubscript{2}Cys-H\textsubscript{2}Glu system, the complexes [V(H\textsubscript{2}Cys)(HGlu)]\textsuperscript{2+}, [V(HCys)(HGlu)]\textsuperscript{+}, 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 vanadium(III)-H\textsubscript{2}Cys complexes, the aim of this work was to investigate the formation of the ternary complexes in the vanadium(III)-H\textsubscript{2}Cys-amino acid systems as a contribution to the knowledge of the speciation of the vanadium(III)-H\textsubscript{2}Cys in biofluids.

To the present, there are no reports on the speciation of the ternary complexes of vanadium(III)-H\textsubscript{2}Cys and the amino acids studied in this work.[6,7]

2. Experimental

2.1. Reagents

The VCl\textsubscript{3} (Merck p.a.); the cysteine (H\textsubscript{2}Cys) (Merck 99%); and the amino acids glycine (HGly), proline (HPro), α-alanine (H\textsubscript{2}Ala), β-alanine (H\textsubscript{2}Bala), histidine (HHis), aspartic acid (H\textsubscript{2}Asp), and glutamic acid (H\textsubscript{2}Glu) (Merck p.a.) were used also sodium oxalate, potassium permanganate, and Mohr’s salt (Merck p.a.) to standardize the VCl\textsubscript{3} stock solution. All the reagents were used without more purification. The HCl and KOH solutions were prepared using 100.0 mmol dm\textsuperscript{-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

\[\text{Corresponding author. Email: lubesv@usb.ve}\]
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 Laura 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 \( R = 1:1:1, 1:1:2, \) and 1:2:1.

The systems V³⁺-H₂Cys-Amino Acids (H₂B) were studied according to the reaction scheme:

\[
pH_2O + qV^{3+} + rCys^{2-} + sB^{+} \rightarrow [V_q(OH)_p(Cys)_r(B)_s] + pH^+ + p\beta_{p,q,r,s}
\]

where H₂B represents the amino acids studied, \([V_q(OH)_p(Cys)_r(B)_s])\) is the ternary \((p, q, r, s)\) complex (the charges were omitted), and \(p\beta_{p,q,r,s}\) 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 \( H^+ \), 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: \([V(OH)]^{2+}\), \( \log \beta_{-1} = -5.13(8) \); \([V_2O]^4\), \( \log \beta_{-2} = -7.36(6) \); \([V(OH)]^2\), \( \log \beta_{-1} = -6.86(2) \); and \([V_3(OH)_3]^+\), \( \log \beta_{-3} = -27.47(4) \).[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)-H₂Glu 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, \( U = \sum (Z_{\exp} - Z_{calc})^2 \), 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 ion strength and ion medium.[6,7]

3.2. Ternary vanadium(III) complexes

3.2.1. Vanadium(III)-H₂Cys-HB systems

Figure 1 shows the \(Z_B(pH)\) 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.
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.

| Equilibrium | H2Cys log \( \beta_{pr} \) | Hu-Ala log \( \beta_{pr} \) | Hβ-Ala log \( \beta_{pr} \) | HGlly log \( \beta_{pr} \) | HPro log \( \beta_{pr} \) |
|-------------|----------------|----------------|----------------|----------------|----------------|
| \( \text{HL} + \text{H} = \text{H}_2\text{L}^+ \) | 2.78(6) | 4.05(1) | 2.77(1) | 2.349(7) |
| \( \text{HL} = \text{L}^+ + \text{H}^- \) | -10.18(1) | -10.54(2) | -10.12(1) | -11.10(2) |
| \( \text{H}_2\text{L} + \text{H}^+ = \text{H}_3\text{L}^+ \) | 2.28(3) |
| \( \text{H}_2\text{L} = \text{HL}^- + \text{H}^+ \) | -8.81(3) |
| \( \text{H}_2\text{L} = \text{L}^2+ + 2\text{H}^+ \) | -20.4(2) |
| Dispersion \( (\sigma) \) | 0.033 | 0.007 | 0.014 | 0.047 | 0.009 |
| Equilibriums | H2Asp log \( \beta_{pr} \) | HGlly log \( \beta_{pr} \) | HHis |
| \( \text{HL} + \text{H} = \text{H}_2\text{L}^+ \) | 2.60(4) | 2.72(4) |
| \( \text{H}_2\text{L} + \text{H}_2\text{L}^+ + \text{H}^+ \) | -4.08(2) | -4.58(2) |
| \( \text{H}_2\text{L} = \text{L}^2+ + 2\text{H}^+ \) | -13.86(3) | -14.23(3) |
| Dispersion \( (\sigma) \) | 0.022 | 0.028 |
| \( \text{HL} + \text{H}^+ = \text{H}_2\text{L}^+ \) | 6.67(4) |
| \( \text{HL} + 2\text{H}^+ = \text{H}_3\text{L}^2+ + \text{H}^+ \) | 9.32(7) |
| \( \text{HL} = \text{L}^+ + \text{H}^- \) | -9.40(5) |
| Dispersion \( (\sigma) \) | 0.035 |

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

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 \( [\text{V(Cys)(HB)}]^+, [\text{V(Cys)(B)}], [\text{V(Cys)(B)(OH)}]^- \), and \( [\text{V(Cys)(B)(OH)}_2]^{2-} \), with the bidentate amino acids glycine, proline, \( \alpha \)-alanine, and \( \beta \)-alanine. The good agreement between the experimental data (dotted curve)
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 $M_r = 3$ mmol dm$^{-3}$ and a molar ratio $R = 1:1:1$ are given in Figures 2–5. The binary $[\text{V(Cys)}]^2+$ is formed in an important proportion between $1 < \text{pH} < 2.5$, the complex $[\text{V(Cys)}^2+]^2+$ is formed in a $60\%$ in the range $2.5 < \text{pH} < 4$, the complex $\text{V(Cys)(B)}$ is formed in a $50\%$ between $4 < \text{pH} < 4.4$, the ternary complex $[\text{V(Cys)(B)(OH)}]$ is important in the range $4.4 < \text{pH} < 5.8$, and the species $[\text{V(Cys)(B)(OH)}]^2$ is important at $\text{pH} > 5.8$.

Figure 4. Species distribution diagram as a function of pH for the V(III)-H$_2$Cys-My system in 3.0 mol dm$^{-3}$ KCl at 25 °C considering the conditions $M_r = 3$ mmol dm$^{-3}$ and molar ratio $R = 1:1:1$.

Figure 5. Species distribution diagram as a function of pH for the V(III)-H$_2$Cys-HPro system in 3.0 mol dm$^{-3}$ KCl at 25 °C considering the conditions $M_r = 3$ 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:

\[
[\text{V(Cys)}]^+ + [\text{V(Gly)}]^2+ \rightleftharpoons [\text{V(Cys)(Gly)}]^+ + \text{V}^{3+},
\]

$\Delta \log K'' = +0.79$

\[
[\text{V(Cys)}]^+ + [\text{V(zAla)}]^2+ \rightleftharpoons [\text{V(Cys)(zAla)}] + \text{V}^{3+},
\]

$\Delta \log K'' = +1.18$

\[
[\text{V(Cys)}]^+ + [\text{V(bAla)}]^2+ \rightleftharpoons [\text{V(Cys)(bAla)}] + \text{V}^{3+},
\]

$\Delta \log K'' = -0.16$

\[
[\text{V(Cys)}]^+ + [\text{V(Pro)}]^2+ \rightleftharpoons [\text{V(Cys)(Pro)}] + \text{V}^{3+},
\]

$\Delta \log K'' = -0.18$

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

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

| Species | $b_p$ (Gly) | $b_p$ α-Ala | $b_p$ β-Ala | $b_p$ Pro | $b_p$ His |
|---------|-------------|-------------|-------------|-----------|-----------|
| $[\text{V(Cys)}^2+]^2$ | 36.96(2) | 37.27(2) | 37.96(3) | 37.81(3) | 47.67(7) |
| $[\text{V(Cys)}]^+$ | 44.24(3) | 45.24(4) | 46.15(4) | 46.0(2) | 46.42(8) |
| $[\text{V(HCys)(B)}]^{-}$ | 28.55(4) | 29.24(5) | 29.15(4) | 29.15(4) | 38.59(7) |
| $[\text{V(HCys)(B)(OH)}]^{-}$ | 22.7(1) | 24.0(9) | 23.1(1) | 23.3(1) | 39.4(1) |
| Dispersion ($\sigma$) | 0.067 | 0.065 | 0.099 | 0.071 | 0.090 |

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

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

| Species | $b_p$ Asp | $b_p$ Glu |
|---------|-----------|-----------|
| $[\text{V(HCys)}^2+]^2$ | 48.67(9) | 49.18(6) |
| $[\text{V(HCys)}]^+$ | 46.0(2) | 46.42(8) |
| $[\text{V(Cys)}]^+$ | 43.29(8) | 43.12(6) |
| $[\text{V(HCys)}]^+$ | 39.4(1) | 38.59(7) |
| $[\text{V(Cys)}^2+]^2$ | 35.0(1) | 34.85(6) |
| Dispersion ($\sigma$) | 0.094 | 0.090 |

Note: Values in parentheses are standard deviations $[3\sigma(b_p)]$ on the last significant figure.
effect that made unfavorable the formation of the ternary complex.

Another important aspect is that in the ternary complex \([\text{V(Cys)}(\text{B})(\text{OH})_2]^{2-}\), 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 \([\text{V(dipic)}(\text{pic})(\text{H}_2\text{O})_2]^{2-}\) [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)-H\(_2\)Cys-HHIs system indicates the formation of the species \([\text{V(HCys)(HHis)}]^{2+}\), \([\text{V(HCys)(His)}]^+\), V(Cys)(His), and \([\text{V(Cys)(His)}(\text{OH})]^\text{-}\). The species distribution diagram, Figure 6, indicates that the ternary complex \([\text{V(HCys)(HHis)}]^{2+}\) is the most important species in the range 1 < pH < 3.2; between 3.2 < pH < 4.5 is observed the species \([\text{V(HCys)(His)}]^+\); in the range 4 < pH < 6 is formed in low extension the complex V(Cys)(His); and the species \([\text{V(Cys)(His)}(\text{OH})]^\text{-}\) 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:

\[
\text{[V(Cys)]}^+ + [\text{V(His)}]^{2+} = [\text{V(Cys)(His)}] + V^{3+},
\]

\(\Delta \log K'' = +4.59\)

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

In the vanadium(III)-H\(_2\)Cys-H\(_2\)Asp system, the complexes \([\text{V(H\(_2\)Cys)(HAsp)}]^{2+}\), \([\text{V(HCys)(HAsp)}]^+\), V(HCys)(Asp), \([\text{V(Cys)(Asp)}]^{-}\), and \([\text{V(Cys)(Asp)(OH)}]^{2-}\) 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 \([\text{V(H\(_2\)Cys)(HAsp)}]^{2+}\); between 1 < pH < 4 is formed in low extension the ternary complex \([\text{V(HCys)(HAsp)}]^+\); in the range 2.5 < pH < 4 is formed the complex V(HCys)(Asp); the species \([\text{V(Cys)(Asp)}]^{-}\) is formed in low extension in the range 3 < pH < 6; and finally, at pH > 4.5, the species \([\text{V(Cys)(Asp)(OH)}]^{2-}\) is abundant.

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

\[
[V(\text{Cys})]^+ + [\text{V(Asp)}]^+ \rightleftharpoons [\text{V(Cys)(Asp)}]^{-} + V^{3+},
\]

\(\Delta \log K'' = +0.99\)

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

In the vanadium(III)-H\(_2\)Cys-H\(_2\)Glu system, the following complexes were observed: \([\text{V(H\(_2\)Cys)(HGlu)}]^{2+}\), \([\text{V(HCys)(HGlu)}]^+\), V(Cys)(Glu), and \([\text{V(Cys)(Glu)}]^{2-}\). The distribution diagrams, Figure 8, indicate that in the range 1 < pH < 2.8, the most important complex is \([\text{V(H\(_2\)Cys)(HGlu)}]^{2+}\), and the ternary complex \([\text{V(HCys)(HGlu)}]^{2-}\) is formed in low quantity in the range...
1 < pH < 4. The complex V(Cys)(HGlu) is presented between 3 < pH < 4.5, and at pH > 4.5, the most abundant species is the complex [V(Cys)(Glu)]^+. In this system, the Δ log K^+ value could not be obtained because the formation of the binary [V(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)-H2Cys-H2Asp system, the formation 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)]^- were detected; and 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. Finally, in the vanadium(III)-H2Cys-HB system, the complexes [V(Cys)(HB)]^+, [V(Cys)(B)]^+, [V(Cys)(B)(OH)]^-, and [V(Cys)(B)(OH)]^+ were observed.

Acknowledgments

We acknowledge the Decanato de Investigación y Desarrollo (DID) from Simón Bolívar University for the financial support.

Notes on contributors

Eduis Guerra got his bachelor degree from the Universidad Central de Venezuela. It is his first paper in blind-reviewed journals. At this moment, he is working in a Bank.

Yendry Martínez got her bachelor degree from the Universidad Central de Venezuela. It is her first paper in blind-reviewed journals.

José Daniel Martínez got his PhD degree from the Universidad Central de Venezuela. He has to his credit over 25 publications in local and international blind-reviewed journals. His research interest includes solution equilibria, electrochemistry, and the synthesis of nanoparticles.

Mary Lorena Araujo got her PhD degree from the Universidad Central de Venezuela. She has to her credit over 25 publications in local and international blind-reviewed journals. Her research interest includes solution equilibria and electrochemistry.

Felipe Brito got his PhD degree from the Universidad de la Laguna. He has to his credit over 100 publications in local and international blind-reviewed journals. His research interest includes solution equilibria, emulsions, and asphalthenes.

Lino Hernández is a PhD student from the Universidad Simón Bolívar. He has to his credit over 15 publications in local and international blind-reviewed journals. His research interest includes solution equilibria and electrochemistry.

Vito Lubes got his PhD degree from the Universidad Central de Venezuela. He has to his credit over 50 publications in local and international blind-reviewed journals. His research interest includes solution equilibria and electrochemistry.

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