

# Speciation of the Ternary Complexes of Vanadium(III)–Dipicolinic Acid with the Amino Acids Glycine, Proline, $\alpha$ -Alanine and $\beta$ -Alanine Studied in 3.0 mol·dm<sup>-3</sup> KCl at 25 °C

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Received: 25 August 2010 / Accepted: 11 November 2010 / Published online: 25 May 2011  
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**Abstract** In this paper we present speciation results for the ternary vanadium(III)–dipicolinic acid (H<sub>2</sub>dipic) systems with the amino acids glycine (Hgly), proline (Hpro),  $\alpha$ -alanine (H $\alpha$ -ala), and  $\beta$ -alanine (H $\beta$ -ala), obtained by means of electromotive forces measurements emf(H) using 3.0 mol·dm<sup>-3</sup> KCl as the ionic medium and a temperature of 25 °C. The experimental data were analyzed by means of the computational least-squares program LETAGROP, taking into account hydrolysis of the vanadium(III) cation, the respective stability constants of the binary complexes, and the acid base reactions of the ligands, which were kept fixed during the analysis. In the vanadium(III)–dipicolinic acid–glycine system, formation of the ternary [V(Hdipic)(Hgly)]<sup>2+</sup>, [V(dipic)(Hgly)]<sup>+</sup>, [V(dipic)(gly)], [V(dipic)(gly)(OH)]<sup>-</sup> and [V(dipic)(gly)(OH)<sub>2</sub>]<sup>2-</sup> was observed; in the case of the vanadium(III)–dipicolinic acid–proline system the ternary complexes [V(Hdipic)(Hpro)]<sup>2+</sup>, [V(dipic)(Hpro)]<sup>+</sup>, [V(dipic)(pro)] and [V(dipic)(pro)(OH)]<sup>-</sup> were observed; in the vanadium(III)–picolinic acid– $\alpha$ -alanine were observed [V(Hdipic)(H $\alpha$ -ala)]<sup>2+</sup>, [V(dipic)(H $\alpha$ -ala)]<sup>+</sup>, [V(dipic)( $\alpha$ -ala)], [V(dipic)( $\alpha$ -ala)(OH)]<sup>-</sup> and [V(dipic)( $\alpha$ -ala)(OH)<sub>2</sub>]<sup>2-</sup>; and in the vanadium(III)–dipicolinic acid– $\beta$ -ala system the complexes [V(dipic)(H $\beta$ -ala)]<sup>+</sup>, [V(dipic)( $\beta$ -ala)], [V(dipic)( $\beta$ -ala)(OH)]<sup>-</sup> and [V(dipic)( $\beta$ -ala)(OH)<sub>2</sub>]<sup>2-</sup> were observed. Their respective stability constants were determined, and we evaluated values of  $\Delta \log_{10} K''$  in order to understand the relative stability of the ternary complexes compared to the corresponding binary ones. The species distribution diagrams are briefly discussed as a function of pH.

**Keywords** Vanadium(III) · Dipicolinic acid · Amino acid · Potentiometric studies · Ternary complexes

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## 1 Introduction

Research on the chemistry of vanadium has increased in the last 30 years, basically because of the insulinomimetic activity and some anticancer activity shown by complexes of this metal [1, 2]. Research on vanadium has focused on V(IV) and V(V) chemistry. However, V(III) has not been studied as extensively because of the ease of oxidation of this ion and the high level of hydrolysis observed for the vanadium(III) cation. In 1997 the tris(picolinato)vanadium(III) complex was synthesized that is very stable in air [3]. Orvig et al. [4] studied the tris(maltolato)vanadium(III) complex and reported that it showed insulinomimetic activity, this being the first report on insulinomimetic activity of a vanadium(III) complex. Crans et al. [5] studied the insulinomimetic activity of vanadium complexes with dipicolinic acid at different oxidation states (III, IV and V). They observed a major insulinomimetic activity for the vanadium(V) complex, and considered that the oxidation state and the ligand both play important roles in the insulinomimetic activity of the vanadium complexes.

Sakurai et al. [6] studied *in vivo* coordination structural changes of a potent insulinomimetic agent, bis(picolinato)oxovanadium(IV), by electron spin-echo envelope modulation spectroscopy, and observed that the original binary complex was transformed into a ternary complex with a composition VO(pic)(X), where X represents an amino acid. They reported that the insulinomimetic activity was changed substantially by formation of this ternary complex. Thus, taking into account the possible application of vanadium(III) dipicolinic acid complexes in medicine, we considered it necessary to investigate formation of ternary complexes in the vanadium(III)–dipicolinic acid–amino acid system as a contribution to the knowledge of the speciation of vanadium(III)–dipicolinic acid in biofluids.

Until now, there are no reports on the speciation of ternary vanadium(III)–dipicolinic acid complexes with the amino acids glycine (Hgly), proline (Hpro),  $\alpha$ -alanine (H $\alpha$ -ala) and  $\beta$ -alanine (H $\beta$ -ala) [7, 8].

## 2 Experimental

### 2.1 Reagents

VCl<sub>3</sub> (Merck p.a.), dipicolinic acid (H<sub>2</sub>dipic) (Merck 99%), and the amino acids Hgly, Hpro, H $\alpha$ -ala and H $\beta$ -ala (all Merck p.a.), were used. Also, sodium oxalate, potassium permanganate and Mohr's salt (Merck p.a.) were used to standardize the VCl<sub>3</sub> stock solution. All of the reagents were used without purification. The HCl and KOH solutions were prepared using 100.0 mmol·dm<sup>-3</sup> Titrisol™ Merck ampoules. The KOH solution was standardized against potassium hydrogen phthalate (Merck p.a.) that had been re-crystallized and dried at 120 °C, using phenolphthalein as indicator, and the HCl solution was standardized with this KOH solution of known concentration [9]. The solutions were prepared using triple glass-distilled water, boiled before preparation of the solutions in order to remove dissolved CO<sub>2</sub>.

To prevent hydrolysis of the VCl<sub>3</sub> stock solution, it also contained 200 mmol·dm<sup>-3</sup> HCl and was maintained under a H<sub>2</sub> atmosphere in the presence of a Pt platinated net in order to avoid oxidation of vanadium(III) to vanadium(IV) [10]. It is important to mention that VCl<sub>3</sub> is hygroscopic and it must be weighed as fast as possible, and for that reason it is necessary to standardize the VCl<sub>3</sub> stock solution. We used a method reported by Mateo and Brito [11]. First, the vanadium(III) was oxidized with a KMnO<sub>4</sub> solution to vanadium(V) in acidic

medium (the  $\text{KMnO}_4$  was standardized with  $\text{Na}_2\text{oxalate}$ ). After oxidation, the vanadium solution standardized with a Mohr's salt solution  $\{\text{Fe(II)}\}$  solution previously standardized with  $\text{KMnO}_4$  using DAS as indicator. The acidity of the  $\text{VCl}_3$  stock solution was determined by the Gran method [12].

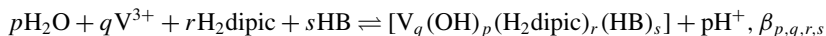
The stability of the vanadium(III) stock solution was checked periodically by spectrophotometric measurements and it was found to be stable for several weeks. The potentiometric measurements were carried out in aqueous solution using  $3.0 \text{ mol}\cdot\text{dm}^{-3}$  KCl as the ionic medium. Nitrogen-free  $\text{O}_2$  and  $\text{CO}_2$  was used.

## 2.2 Methods

The potentiometric measurements were done 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  $(25.0 \pm 0.1)^\circ\text{C}$  by constant circulation of water from the thermostatic bath.

The emf(H) measurements were carried out by means of a REF||S|IGE cell, where REF denotes  $\text{Ag}|\text{AgCl}| 3.0 \text{ mol}\cdot\text{dm}^{-3} \text{ KCl}$ , S is the equilibrium solution being studied, and GE denotes the glass electrode. At  $25^\circ\text{C}$  the emf (mV) of this cell follows the Nernst equation,  $E = E^0 + jh + 59.16 \log_{10} h$ , where  $h$  represents the free hydrogen ion concentration,  $E^0$  is the standard potential, and  $j$  is a constant that takes into account the liquid junction potential [13]. The experiments were carried out as follows: a fixed volume of  $0.100 \text{ mol}\cdot\text{dm}^{-3}$  HCl was titrated with successive additions of  $0.100 \text{ mol}\cdot\text{dm}^{-3}$  KOH, until near neutrality, in order to obtain the parameters  $E^0$  and  $j$ . Then, aliquots of dipicolinic acid and the amino acid under study were added, and finally aliquots of the vanadium(III) stock solution were added sequentially. The titration was then continued with  $0.100 \text{ mol}\cdot\text{dm}^{-3}$  KOH. The measurements were done using total V(III) concentrations of  $M_T = 2\text{--}3 \text{ mmol}\cdot\text{dm}^{-3}$  and vanadium(III):dipicolinic acid:amino acid molar ratios of  $R = 1:1:1$  and  $1:1:2$ .

Reactions in the systems  $\text{V}^{3+}$ – $\text{H}_2\text{dipic}$ –amino acids (HB) occur according to the reaction scheme:



where HB represents the amino acids Hgly, Hpro, H $\alpha$ -ala and H $\beta$ -ala, and  $[\text{V}_q(\text{OH})_p(\text{H}_2\text{dipic})_r(\text{HB})_s]$  is the ternary  $(p, q, r, s)$  complex (the charges are omitted), and  $\beta_{p,q,r,s}$  is the respective stability constant.

The potentiometric data were analyzed using the program LETAGROP [14, 15] in order to minimize the function  $Z_B = (h - H)/M_T$ , where  $Z_B$  is the average number of moles of  $\text{H}^+$  dissociated per mole of metal,  $H$  is the total (analytical) concentration of  $\text{H}^+$ ,  $h$  represents the equilibrium concentration of  $\text{H}^+$ , and  $M_T$  represents the total (analytical) concentration of vanadium(III).

Equilibria corresponding to the formation of hydroxo-complexes of vanadium(III) were considered in the calculation of the stability constants of ternary complexes. The following species were assumed:  $[\text{V}(\text{OH})]^{2+}$  with  $\log_{10} \beta_{1,-1} = -3.13$  (8);  $[\text{V}_2\text{O}]^{4+}$  with  $\log_{10} \beta_{2,-2} = -3.76$  (6);  $[\text{V}(\text{OH})_2]^+$  with  $\log_{10} \beta_{1,-2} = -6.86$  (2); and  $[\text{V}_3(\text{OH})_8]^+$  with  $\log_{10} \beta_{3,-8} = -27.47$  (4) [16]. The binary vanadium(III)–dipicolinic acid [17], vanadium(III)–gly [18], vanadium(III)–pro [19], vanadium(III)– $\alpha$ -ala [20], and vanadium(III)– $\beta$ -ala systems [20] were previously studied by us.

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 errors squared,  $U = \sum (Z_B^{\text{exp}} - Z_B^{\text{calc}})^2$ , and the fittings were done while testing different  $(p, q, r, s)$  combinations.

The species distribution diagrams were done with the computer program HYSS [21] yielding the  $\beta_{pqrs}$  values that are summarized in Tables 2, 3, 4, 5.

### 3 Results

#### 3.1 Ionization Constants of the Studied Ligands

The ionization constants (Table 1) in the 3.0 mol·dm<sup>-3</sup> KCl ionic medium are in good agreement with literature values, considering the differences in ionic strength and ionic medium [7, 8].

#### 3.2 Ternary Vanadium(III) Complexes

##### 3.2.1 Vanadium(III)–H<sub>2</sub>dipic–Hgly System

The  $Z_B(\text{pH})$  results are shown in Fig. 1 and Fig. 2 shows the species distribution diagram for this system under the following conditions:  $M_T = 3$  mmol·dm<sup>-3</sup> and molar ratio  $R = 1:1:1$ , using the stability constants summarized in Table 2.

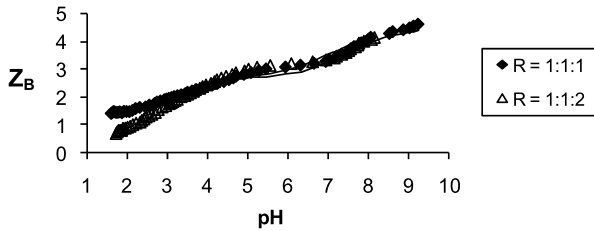
##### 3.2.2 Vanadium(III)–H<sub>2</sub>dipic–Hpro System

Figure 3 shows the results of the  $Z_B(\text{pH})$  analysis performed with LETAGROP and Fig. 4 presents the species distribution diagram under the following conditions:  $M_T = 3$  mmol·dm<sup>-3</sup> and molar ratio  $R = 1:1:1$ , using the stability constants summarized in Table 3.

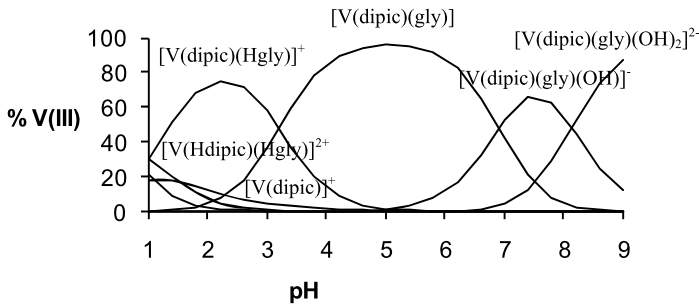
**Table 1** Values of  $\log_{10} \beta_{pr}$  and  $\text{p}K_i$  for the ligands studied (25 °C,  $I = 3.0$  mol·dm<sup>-3</sup> KCl ionic medium)

Equilibrium	H <sub>2</sub> dipic $\log_{10} \beta_{pr}$	H $\alpha$ -ala $\log_{10} \beta_{pr}$	H $\beta$ -ala $\log_{10} \beta_{pr}$	Hgly $\log_{10} \beta_{pr}$	Hpro $\log_{10} \beta_{pr}$
$\text{HL} + \text{H}^+ \rightleftharpoons \text{H}_2\text{L}^+$		2.81 (2) <sup>a</sup>	4.18 (6)	3.10 (2)	2.48 (4)
$\text{HL} \rightleftharpoons \text{L}^- + \text{H}^+$		-10.01 (3)	-10.05 (7)	-9.37 (2)	-11.04 (9)
$\text{H}_2\text{L} \rightleftharpoons \text{HL}^- + \text{H}^+$	-2.28 (2)				
$\text{H}_2\text{L} \rightleftharpoons \text{L}^{2-} + 2\text{H}^+$	-6.92 (3)				
Dispersion( $\sigma$ )	0.018	0.018	0.035	0.047	0.026
Titrations	2	2	2	2	2
Ligands (mmol·dm <sup>-3</sup> )	3	3	3	3	3
$\text{p}K_i$					
$\text{p}K_{a1}$	2.28 (2)	2.81 (1)	4.18 (6)	3.10 (2)	2.48 (4)
$\text{p}K_{a2}$	4.64 (3)	10.01 (3)	10.05 (7)	9.37 (2)	11.04 (9)

<sup>a</sup> Values in parentheses are three times the standard deviations [ $3\sigma(\log_{10} \beta)$ ] on the last significant figure



**Fig. 1** Plot of  $Z_B$ , the average number of moles of  $H^+$  dissociated per mole of vanadium(III), versus pH for the vanadium(III)– $H_2$ dipic–Hgly system in  $3.0 \text{ mol}\cdot\text{dm}^{-3}$  KCl at  $25^\circ\text{C}$ . The lines represent theoretical curves calculated with the equilibrium constants of Table 2



**Fig. 2** Species distribution diagram as a function of pH for the V(III)– $H_2$ dipic–Hgly system in  $3.0 \text{ mol}\cdot\text{dm}^{-3}$  KCl at  $25^\circ\text{C}$  with the conditions  $M_T = 3 \text{ mmol}\cdot\text{dm}^{-3}$  and molar ratio  $R = 1:1:1$

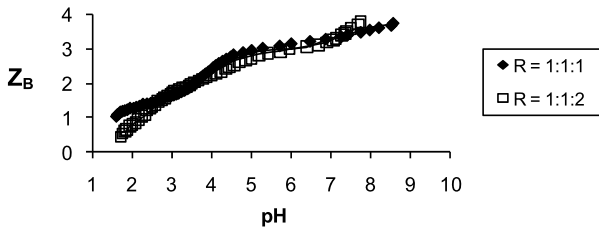
**Table 2** Equilibrium constants ( $\log_{10} \beta_{pqrs}$ ) for the V(III)–dipicolinic acid–glycine system ( $25^\circ\text{C}$ ,  $I = 3.0 \text{ mol}\cdot\text{dm}^{-3}$  KCl ionic medium)

Equilibrium	$\log_{10} \beta_{pqrs}$ $Z_B$
$V^{3+} + H_2\text{dipic} + \text{Hgly} \rightleftharpoons [V(\text{Hdipic})(\text{Hgly})]^{2+} + H^+$	7.4 (4) <sup>a</sup>
$V^{3+} + H_2\text{dipic} + \text{Hgly} \rightleftharpoons [V(\text{dipic})(\text{Hgly})]^+ + 2H^+$	6.4 (1)
$V^{3+} + H_2\text{dipic} + \text{Hgly} \rightleftharpoons [V(\text{dipic})(\text{gly})] + 3H^+$	3.2 (1)
$V^{3+} + H_2\text{dipic} + \text{Hgly} + H_2O \rightleftharpoons [V(\text{dipic})(\text{gly})(\text{OH})]^- + 4H^+$	−3.7 (2)
$V^{3+} + H_2\text{dipic} + \text{Hgly} + 2H_2O \rightleftharpoons [V(\text{dipic})(\text{gly})(\text{OH})_2]^{2-} + 5H^+$	−13.83 (5)
Dispersion ( $\sigma$ )	0.096

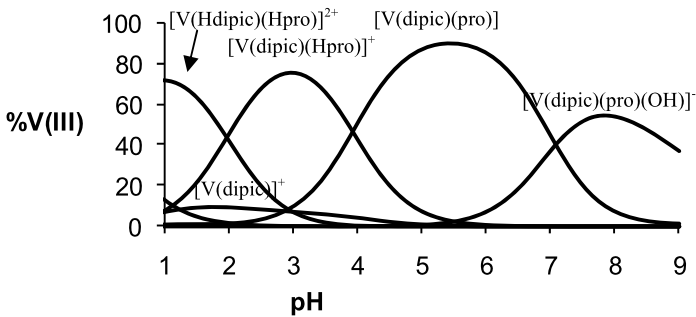
<sup>a</sup> Values in parentheses are three times the standard deviations [ $3\sigma(\log_{10} \beta_{pqrs})$ ] on the last significant figure

### 3.2.3 Vanadium(III)– $H_2$ dipic–H $\alpha$ -ala System

Figure 5 shows the  $Z_B(\text{pH})$  analysis of this system. Figure 6 shows the species distribution diagram, using the stability constants summarized in Table 4, under the following conditions:  $M_T = 3 \text{ mmol}\cdot\text{dm}^{-3}$  and molar ratio  $R = 1:1:1$ .



**Fig. 3** Plot of  $Z_B$ , the average number of moles of  $H^+$  dissociated per mole of vanadium(III), versus pH for the vanadium(III)– $H_2dipic$ – $Hpro$  system in  $3.0\text{ mol}\cdot\text{dm}^{-3}$  KCl at  $25^\circ\text{C}$ . The lines represent theoretical curves calculated with the equilibrium constants of Table 3



**Fig. 4** Species distribution diagram as a function of pH for the V(III)– $H_2dipic$ – $Hpro$  system in  $3.0\text{ mol}\cdot\text{dm}^{-3}$  KCl at  $25^\circ\text{C}$  with the conditions  $M_T = 3\text{ mmol}\cdot\text{dm}^{-3}$  and molar ratio  $R = 1:1:1$

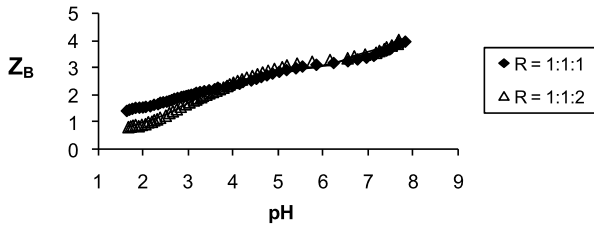
**Table 3** Equilibrium constants ( $\log_{10} \beta_{pqrs}$ ) for the V(III)–dipicolinic acid–proline system ( $25^\circ\text{C}$ ,  $I = 3.0\text{ mol}\cdot\text{dm}^{-3}$  KCl ionic medium)

Equilibrium	$\log_{10} \beta_{pqrs}$	$Z_B$
$V^{3+} + H_2dipic + Hpro \rightleftharpoons [V(Hdipic)(Hpro)]^{2+} + H^+$	7.9 (1) <sup>a</sup>	
$V^{3+} + H_2dipic + Hpro \rightleftharpoons [V(dipic)(Hpro)]^+ + 2H^+$	5.92 (7)	
$V^{3+} + H_2dipic + Hpro \rightleftharpoons [V(dipic)(pro)] + 3H^+$	1.98 (9)	
$V^{3+} + H_2dipic + Hpro + H_2O \rightleftharpoons [V(dipic)(pro)(OH)]^- + 4H^+$	–5.1 (2)	
Dispersion ( $\sigma$ )	0.079	

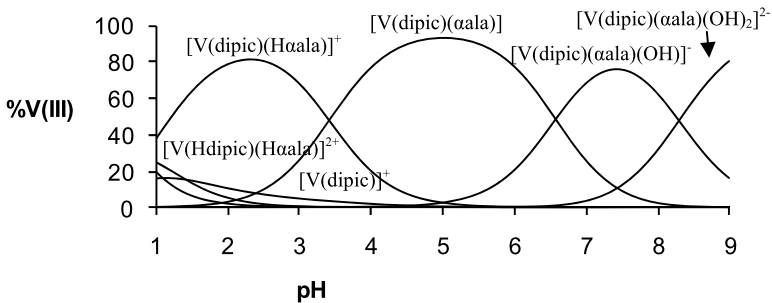
<sup>a</sup> Values in parentheses are three times the standard deviations [ $3\sigma(\log_{10} \beta_{pqrs})$ ] on the last significant figure

### 3.2.4 Vanadium(III)– $H_2dipic$ – $H\beta$ -ala System

Figure 7 presents the  $Z_B(\text{pH})$  results and Fig. 8 shows the species distribution diagram for this system, using the stability constants summarized in Table 5, with the conditions:  $M_T = 3\text{ mmol}\cdot\text{dm}^{-3}$  and molar ratio  $R = 1:1:1$ .



**Fig. 5**  $Z_B$ , the average number of moles of  $H^+$  dissociated per mole of vanadium(III), versus pH of the vanadium(III)– $H_2$ dipic– $H\alpha$ -ala system in  $3.0 \text{ mol}\cdot\text{dm}^{-3}$  KCl at  $25^\circ\text{C}$ . The lines represent theoretical curves calculated with the equilibrium constants of Table 4



**Fig. 6** Species distribution diagram as a function of pH for the V(III)– $H_2$ dipic– $H\alpha$ -ala system in  $3.0 \text{ mol}\cdot\text{dm}^{-3}$  KCl at  $25^\circ\text{C}$  with the conditions  $M_T = 3 \text{ mmol}\cdot\text{dm}^{-3}$  and molar ratio  $R = 1:1:1$

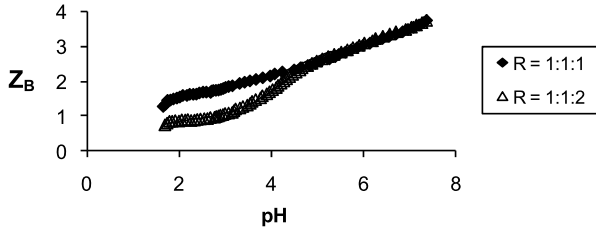
**Table 4** Equilibrium constants ( $\log_{10} \beta_{pqrs}$ ) for the V(III)–dipicolinic acid– $\alpha$ -alanine system ( $25^\circ\text{C}$ ,  $I = 3.0 \text{ mol}\cdot\text{dm}^{-3}$  KCl ionic medium)

Equilibrium	$\log_{10} \beta_{pqrs}$	$Z_B$
$V^{3+} + H_2\text{dipic} + H\alpha\text{-ala} \rightleftharpoons [V(\text{Hdipic})(H\alpha\text{-ala})]^+ + H^+$	7.1 (3) <sup>a</sup>	
$V^{3+} + H_2\text{dipic} + H\alpha\text{-ala} \rightleftharpoons [V(\text{dipic})(H\alpha\text{-ala})]^+ + 2H^+$	6.29 (6)	
$V^{3+} + H_2\text{dipic} + H\alpha\text{-ala} \rightleftharpoons [V(\text{dipic})(\alpha\text{-ala})] + 3H^+$	2.88 (5)	
$V^{3+} + H_2\text{dipic} + H\alpha\text{-ala} + H_2O \rightleftharpoons [V(\text{dipic})(\alpha\text{-ala})(OH)]^- + 4H^+$	−3.7 (1)	
$V^{3+} + H_2\text{dipic} + H\alpha\text{-ala} + 2H_2O \rightleftharpoons [V(\text{dipic})(\alpha\text{-ala})(OH)_2]^{2-} + 5H^+$	−12.0 (1)	
Dispersión ( $\sigma$ )	0.069	

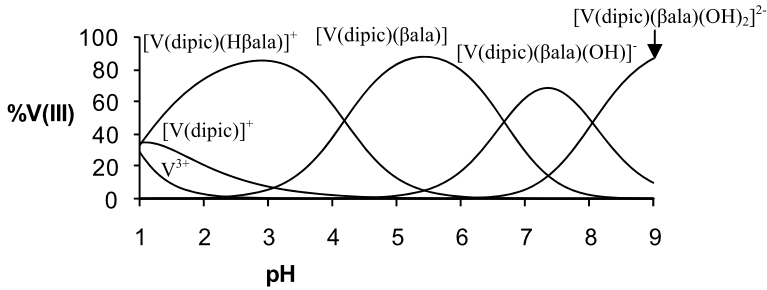
<sup>a</sup> Values in parentheses are three times the standard deviations [ $3\sigma(\log_{10} \beta_{pqrs})$ ] on the last significant figure

## 4 Discussion

The analysis of potentiometric data of the vanadium(III)–dipicolinic acid–glycine system performed with LETAGROP [14, 15] indicated formation of the following mononuclear complexes  $[V(\text{Hdipic})(\text{Hgly})]^{2+}$ ,  $[V(\text{dipic})(\text{Hgly})]^+$ ,  $[V(\text{dipic})(\text{gly})]$ ,  $[V(\text{dipic})(\text{gly})(\text{OH})]^-$  and  $[V(\text{dipic})(\text{gly})(\text{OH})_2]^{2-}$ . As usual, good agreement between the experimental data (dotted curve) and the model (continuous line) can be observed as shown in Fig. 1, and the stability constants are summarized in Table 2. The species distribution diagram for this system under the experimental conditions  $M_T = 3 \text{ mmol}\cdot\text{dm}^{-3}$  and molar ratio  $R = 1:1:1$  is



**Fig. 7** Plot of  $Z_B$ , the average number of moles of  $H^+$  dissociated per mole of vanadium(III), versus pH of the V(III)– $H_2dipic$ – $H\beta$ -ala system in  $3.0\text{ mol}\cdot\text{dm}^{-3}$  KCl at  $25^\circ\text{C}$ . The lines represent theoretical curves calculated with the equilibrium constants of Table 5



**Fig. 8** Species distribution diagram as a function of pH for the V(III)– $H_2dipic$ – $H\beta$ -ala system in  $3.0\text{ mol}\cdot\text{dm}^{-3}$  KCl at  $25^\circ\text{C}$  with the conditions  $M_T = 3\text{ mmol}\cdot\text{dm}^{-3}$  and molar ratio  $R = 1:1:1$

**Table 5** Equilibrium constants ( $\log_{10} \beta_{pqrs}$ ) for the V(III)–dipicolinic acid– $\beta$ -alanine system ( $25^\circ\text{C}$ ,  $I = 3.0\text{ mol}\cdot\text{dm}^{-3}$  KCl ionic medium)

Equilibrium	$\log_{10} \beta_{pqrs}$	$Z_B$
$V^{3+} + H_2dipic + H\beta\text{-ala} \rightleftharpoons [V(dipic)(H\beta\text{-ala})]^+ + 2H^+$	7.02 (6) <sup>a</sup>	
$V^{3+} + H_2dipic + H\beta\text{-ala} \rightleftharpoons [V(dipic)(\beta\text{-ala})] + 3H^+$	2.83 (5)	
$V^{3+} + H_2dipic + H\beta\text{-ala} + H_2O \rightleftharpoons [V(dipic)(\beta\text{-ala})(OH)]^- + 4H^+$	−3.85 (8)	
$V^{3+} + H_2dipic + H\beta\text{-ala} + 2H_2O \rightleftharpoons [V(dipic)(\beta\text{-ala})(OH)_2]^{2-} + 5H^+$	−11.9 (2)	
Dispersion ( $\sigma$ )	0.068	

<sup>a</sup> Values in parentheses are three times the standard deviations [ $3\sigma(\log_{10} \beta_{pqrs})$ ] on the last significant figure

shown in Fig. 2. The species  $[V(Hdipic)(Hgly)]^{2+}$  and  $[V(dipic)]^+$  are formed in low proportions between  $1 < \text{pH} < 3$ , the complex  $[V(dipic)(Hgly)]^+$  is formed at 80 % in the range  $1 < \text{pH} < 3$ , the complex  $[V(dipic)(gly)]$  is the more abundant species between  $3 < \text{pH} < 7$ , the ternary complex  $[V(dipic)(gly)(OH)]^-$  is important in the range  $7 < \text{pH} < 8$ , while the species  $[V(dipic)(gly)(OH)_2]^{2-}$  is important at  $\text{pH} > 8$ .

The relative stability of a ternary complex compared to its corresponding binary ones is measured by the quantity  $\Delta \log_{10} K''$  [22] that is given for the reaction:





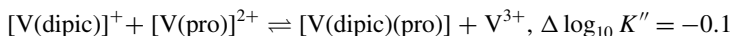
This positive value indicates that the ternary complex is more stable than the corresponding binary ones.

Another aspect that is very important to mention for the ternary complex  $[\text{V}(\text{dipic})(\text{gly})(\text{OH})_2]^{2-}$ , is that we suppose  $\text{dipic}^{2-}$  is acting as a tridentate ligand by ( $\text{COO}^-$ , N,  $\text{COO}^-$ ) coordination, that  $\text{gly}^-$  is acting as a bidentate ligand by (N,  $\text{COO}^-$ ) coordination, and the two  $\text{OH}^-$ s occupy two coordination positions, so this ternary complex must be hepta coordinated. This agrees with the reported hepta-coordinated complex  $[\text{V}(\text{dipic})(\text{pic})(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$  [23], where  $\text{pic}^-$  denotes the picolinate ligand, which is coordinated to the vanadium(III) ion by (N,  $\text{COO}^-$ ) and forms a five membered chelate ring, similar to the amino acids studied in this work. Kanamori [24] stated that systems forming a five membered chelate ring tend to be hepta-coordinated complexes.

Analysis of the potentiometric data for the vanadium(III)– $\text{H}_2\text{dipic}$ –Hpro system shows formation of the species  $[\text{V}(\text{Hdipic})(\text{Hpro})]^{2+}$ ,  $[\text{V}(\text{dipic})(\text{Hpro})]^+$ ,  $[\text{V}(\text{dipic})(\text{pro})]$  and  $[\text{V}(\text{dipic})(\text{pro})(\text{OH})]^-$ . As in the previous case, good agreement between the experimental data (dotted curve) and the model (continuous line) can be observed as shown in Fig. 3. The respective stability constants are summarized in Table 3.

The species distribution diagram for the vanadium(III)– $\text{H}_2\text{dipic}$ –Hpro system under the experimental conditions  $M_T = 3 \text{ mmol}\cdot\text{L}^{-1}$  and  $R = 1:1:1$  is presented in Fig. 4. The complex  $[\text{V}(\text{Hdipic})(\text{Hpro})]^{2+}$  is important at  $1 < \text{pH} < 2$ , while the species  $[\text{V}(\text{dipic})(\text{Hpro})]^+$  is formed, up to 80%, between  $2 < \text{pH} < 4$ . In the pH range 4 to 7 the ternary complex  $[\text{V}(\text{dipic})(\text{pro})]$  is the most abundant species while the complex  $[\text{V}(\text{dipic})(\text{pro})(\text{OH})]^-$  is more abundant at  $\text{pH} > 7$ .

The relative stability of the ternary complex, compared to the corresponding binary ones, is given by the  $\Delta \log_{10} K''$  value:

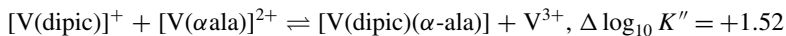


This negative value indicates that the ternary complex is less stable than the corresponding binary ones.

Figure 5 shows the  $Z_B(\text{pH})$  results for the vanadium(III)– $\text{H}_2\text{dipic}$ –H $\alpha$ -ala system, the points represents the experimental data, and the continuous line was constructed considering the formation of the complexes  $[\text{V}(\text{Hdipic})(\text{H}\alpha\text{-ala})]^{2+}$ ,  $[\text{V}(\text{dipic})(\text{H}\alpha\text{-ala})]^+$ ,  $[\text{V}(\text{dipic})(\alpha\text{-ala})]$ ,  $[\text{V}(\text{dipic})(\alpha\text{-ala})(\text{OH})]^-$  and  $[\text{V}(\text{dipic})(\alpha\text{-ala})(\text{OH})_2]^{2-}$ , using the stability constants summarized in Table 4.

Figure 6 shows the species distribution diagram of this system for the conditions  $M_T = 3 \text{ mmol}\cdot\text{dm}^{-3}$  and molar ratio  $R = 1:1:1$ . Here we can see that the complex  $[\text{V}(\text{Hdipic})(\text{H}\alpha\text{-ala})]^{2+}$  is formed to a low extent in the range  $1 < \text{pH} < 2$ , between  $1 < \text{pH} < 3.5$  the ternary complex  $[\text{V}(\text{dipic})(\text{H}\alpha\text{-ala})]^+$  is important,  $[\text{V}(\text{dipic})(\alpha\text{-ala})]$  is very important in the range  $3.5 < \text{pH} < 6.5$ , between  $6.5 < \text{pH} < 8.5$  the species  $[\text{V}(\text{dipic})(\alpha\text{-ala})(\text{OH})]^-$  occurs, and at  $\text{pH} > 8.5$  the ternary complex  $[\text{V}(\text{dipic})(\alpha\text{-ala})(\text{OH})_2]^{2-}$  is the most important one.

The relative stability of the ternary complex, compared to the corresponding binary ones, is given by the  $\Delta \log_{10} K''$  value:



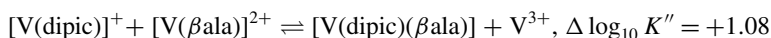
This positive value indicates that the ternary complex is more stable than the corresponding binary ones.

Figure 7 shows the  $Z_B(\text{pH})$  results for the vanadium(III)– $\text{H}_2\text{dipic}$ –H $\beta$ -ala system. As before, the points represents the experimental values and the line was constructed considering the formation of the complexes  $[\text{V}(\text{dipic})(\text{H}\beta\text{-ala})]^+$ ,  $[\text{V}(\text{dipic})(\beta\text{-ala})]$ ,  $[\text{V}(\text{dipic})(\beta\text{-ala})]$ .

ala(OH)]<sup>-</sup> and [V(dipic)(βala)(OH)<sub>2</sub>]<sup>2-</sup> whose respective stability constants are given in Table 5.

The species distribution diagram of this system is shown in Fig. 8 for the condition  $M_T = 3 \text{ mmol} \cdot \text{dm}^{-3}$  and molar ratio  $R = 1:1:1$ . Here we can see that the complex [V(dipic)]<sup>+</sup> and V<sup>3+</sup> are both in low proportion in the range  $1 < \text{pH} < 3$ , between  $1 < \text{pH} < 4$  the complex [V(dipic)(Hβ-ala)]<sup>+</sup> is very important, the ternary complex [V(dipic)(β-ala)] is present in  $4 < \text{pH} < 6.5$ , between  $6.5 < \text{pH} < 8$  the complex [V(dipic)(β-ala)(OH)]<sup>-</sup> is the most important one, and at  $\text{pH} > 8$  the ternary complex [V(dipic)(β-ala)(OH)<sub>2</sub>]<sup>2-</sup> is the most abundant species.

The relative stability of the ternary complex, compared to the binary ones, is given by the  $\Delta \log_{10} K''$  value:



This positive value indicates that the ternary complex is more stable than the corresponding binary ones.

It is very important to mention that the amino acids glycine, α-alanine and β-alanine all have positive  $\Delta \log_{10} K''$  values, whereas proline has a negative  $\Delta \log_{10} K''$  value. This difference is explained because the three amino acids have almost the same structure whereas proline has a different structure, and it is possible that this causes some steric effect that made formation of the ternary complex unfavorable for proline.

## 5 Conclusions

The analysis of potentiometric data shows the formation of mononuclear ternary complexes with composition 1:1:1, protonated forms such as [V(Hdipic)(HB)]<sup>2+</sup> and [V(dipic)(HB)]<sup>+</sup>, neutral forms [V(dipic)(B)], and two hydrolytic forms [V(dipic)(B)(OH)]<sup>-</sup> and [V(dipic)(B)(OH)<sub>2</sub>]<sup>2-</sup>. Even though these amino acids are coordinated by (N, COO<sup>-</sup>) to form five- and six-membered chelated rings, we haven't found any evidence that can explain why they do not speciate in the same way, or why little differences are observed in the speciation of these systems.

**Acknowledgements** We acknowledge the Decanato de Investigación y Desarrollo (DID) from Simón Bolívar University for the financial support (Project S1-IC-CB-003-07). We also acknowledge Professors Antonio Barriola, Antonio Zapata, and Simón López from Simón Bolívar University for their help during this work.

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