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Mixed-ligand complex formation equilibria of vanadium(III) with picolinic and dipicolinic acids with some dicarboxylic acids (oxalic, malonic, and phthalic acids) studied in 3.0 M KCl at 25 °C

Ana Esteves^a, Jessaid Escobar^a, José Daniel Martínez^a, Mary Lorena Araujo^a, Felipe Brito^a, Lino Hernández^b, Edgar Del Carpio^b and Vito Lubes^{b*}

^aFacultad de Ciencias, Escuela de Química, Centro de Equilibrios en Solución, Universidad Central de Venezuela (UCV), Caracas, Venezuela; ^bDepartamento de Química, Universidad Simón Bolívar (USB), Caracas, Venezuela

The ternary complexes formed between vanadium(III) and picolinic acid (Hpic) and dipicolinic acid (H₂dipic) with the dicarboxylic oxalic, malonic, and phthalic acids (H₂ox), (H₂mal), and (H₂phtha) briefly (H₂L) were studied in aqueous solution by means of electromotive forces' measurements emf(H) at 25 °C and 3.0 mol dm⁻³ KCl as ionic medium. The potentiometric data were analyzed using the least-squares computational program LETAGROP, considering the hydrolysis products of the V(III), the acidity constants of the ligands employed, and the formation constants of the binary complexes, obtaining the complexes V(pic)(ox), log β_{1,1,1,-3} = 5.39(7) and [V(pic)₂(ox)]⁻, log β_{1,2,1,-4} = 4.3(1); V(pic)(ma), log β_{1,1,1,-3} = 5.58(5) and [V(pic)₂(ma)]⁻, log β_{1,2,1,-4} = 5.00(8); V(pic)(phtha), log β_{1,1,1,-3} = 5.66(6) and [V(pic)₂(phtha)]⁻, log β_{1,2,1,-4} = 4.5(2) in the vanadium(III)-Hpic-H₂L system. In the case of the vanadium(III)-H₂dipic-H₂L system, the complexes [V(dipic)(ox)]⁻, log β_{1,1,1,-4} = 9.3(2), [V(dipic)(Hox)(ox)]²⁻, log β_{1,1,2,-5} = 11.2(2) and [V(dipic)(ox)₂]³⁻, log β_{1,1,2,6} = 5.7 max 7.0; [V(dipic)(ma)]⁻, log β_{1,1,1,-4} = 8.7(2), [V(dipic)(Hma)(ma)]²⁻, log β_{1,1,2,-5} = 10.3(1) and [V(dipic)(ma)₂]³⁻, log β_{1,1,2,6} = 6.9(1); [V(dipic)(phtha)]⁻, log β_{1,1,1,-4} = 10.9(1), [V(dipic)(Hphtha)(phtha)]²⁻, log β_{1,1,2,-5} = 9.2 max 10.4 and [V(dipic)(phtha)₂]³⁻, log β_{1,1,2,6} = 6.9(3) were observed.

Keywords: vanadium(III) complexes; picolinic acid; dipicolinic acid; dicarboxylic acids; potentiometric studies; speciation; ternary complexes

1. Introduction

Recent studies on the coordination chemistry of vanadium have shown that V complexes have great potential as pharmaceuticals. Studies have been conducted *in vivo* and *in vitro* of these compounds in different oxidation states, and the complete structure of some has been determined. However, there are many vanadium complexes that have not been isolated and studied structurally.[1]

Among the most common biochemical properties that support the study of the coordination chemistry of vanadium are the metabolic enzyme inhibition of ATPase: stimulation of phosphomutases; a required cofactor for a number of haloperoxidases; regulation of anomalies of thyroid; insulinomimetic and anticarcinogenic activity; and in some cases a preventive and therapeutic capacity of the malignancy of certain tumor cell lines.[1,2]

The interest in the study of the aqueous chemistry of vanadium began with the discovery of vanadium in some species of tunicates. Even when high concentrations of vanadium have been found frequently in various tissues of living organisms, few animal organisms are known to accumulate vanadium. However, high levels of vanadium have been reported in ascidians (*Pseudopotamilla acce-lata*), discovered by German M. Henze in 1911 and is so far the second tunicate with high accumulation in the

animal kingdom.[3] At the bottom of the Black Sea bay located in Sevastopol, about 400 kg of vanadium is found per square mile, located in the blood and tissues of these sedentary tunicates.[4] The species *Ascidia gemmata* contains values as high as 0.35 M of vanadium in the blood cells corresponding to 107 times the concentration of the metal in sea water.[5]

In this work, we report the results on mixed-ligand complex formation in the V(III)-picolinic acid-H₂L and V(III)-dipicolinic acid-H₂L systems, where the H₂L were the dicarboxylic oxalic, malonic, and phthalic acids (H₂ox), (H₂mal), and (H₂phtha). The pH-potentiometry technique was used to determine the stoichiometries and stability constants of the complexes formed in aqueous solution, because the study of vanadium(III) complexes gives you an idea of the behavior of these complexes in natural systems.

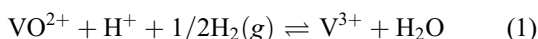
2. Experimental

2.1. Reagents

The VCl₃ (Merck p.a); and the pyridinecarboxylic acids, picolinic acid (Hpic), and dipicolinic acid (H₂dipic) (Merck p.a.); and the dicarboxylic oxalic, malonic and phthalic acids (H₂ox), (H₂mal), and (H₂phtha) briefly (H₂L) also (Merck p.a) were used without purification.

*Corresponding author. Email: lubesv@usb.ve

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. The solutions were prepared using triple glass-distilled water and boiled before the preparation of the solutions in order to 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 V(III) solution to V(IV).[6] In this case, the H₂ cannot induce reduction to V(II), because the V(III)/V(II) standard potential is negative ($E^0 = -0.26$ V).[7] Moreover, if there is any oxidation to V(IV), the solution is immediately reduced to V(III) because of the standard potential of the reaction,



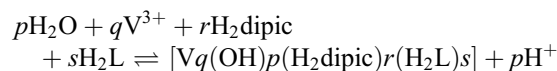
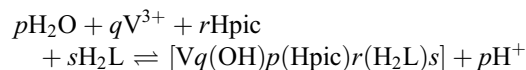
which is 366.3(3) mV.[8] Under these conditions, the V(III) solution can be maintained. The stability of the V(III) solution was checked periodically by spectrophotometric measurements, and it was shown to be stable for several weeks. The emf (H) measurements were carried out in aqueous solution at an ionic strength of 3.0 mol dm⁻³ in KCl. Nitrogen-free O₂ and CO₂ was used to maintain an inert atmosphere.

2.2. Methods

The emf (H) measurements were done using the following instruments: Thermo Orion model 520A pH meter, Metrohm EA 876-20 titration vessel, Lauda Brikmann RM6 thermostat bath, Shimadzu UV-1601 PC spectrophotometer, and a quartz cell with a 10.0-mm path length. 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(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.[9] 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 6Mepic, and the ligands B and an aliquot of the Vanadium(III) stock solution were added sequentially. Finally, 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): Hpic: H₂L and Vanadium(III): H₂dipic: H₂L molar ratios $R = 1:1:1$, $1:2:1$, and $1:1:2$.

The systems Vanadium(III): Hpic: H₂L and Vanadium(III): H₂dipic: H₂L were studied according to the reactions scheme:



where H₂L represents the ligands: H₂ox, H₂mal, and H₂phtha, $[\text{V}q(\text{OH})p(\text{Hpic})r(\text{H}_2\text{L})s]$ and $[\text{V}q(\text{OH})p(\text{H}_2\text{dipic})r(\text{H}_2\text{L})s]$ are the ternary (p, q, r, s) complexes, and $\beta_{p,q,r,s}$ are the respective stability constant.

The potentiometric data were analyzed using the program LETAGROP,[10,11] in order to minimize the function $Z_B = (h - H)/M_T$, where H is the total (analytical) concentration of H⁺, h represents the equilibrium concentration of H⁺, and M_T represents the total (analytical) concentration of V³⁺. Equilibria corresponding to the formation of the hydroxo complexes of V(III) were considered in the calculation of the stability constants of the ternary complexes. The following species were assumed: $[\text{V}(\text{OH})]^{2+}$, $\log \beta_{1,-1} = -3.07(3)$; $[\text{V}_2\text{O}]^{4+}$, $\log \beta_{2,-2} = -3.94(2)$; and $[\text{V}_2\text{O}(\text{OH})]^{3+}$, $\log \beta_{2,-3} = -7.87(9)$. [8] In the Binary V(III)-Hpic [12] system were considered the complexes: $[\text{V}(\text{pic})]^{2+}$, $\log \beta_{1,1,-1} = 0.39(9)$; $[\text{V}(\text{pic})(\text{OH})]^{+}$, $\log \beta_{1,1,-2} = -2.12(7)$; $[\text{V}(\text{pic})_2]$, $\log \beta_{1,1,-2} = 1.68(2)$; $\text{V}(\text{pic})_3$, $\log \beta_{1,1,-3} = 0.68(3)$; $\text{V}_2\text{O}(\text{pic})_4$, $\log \beta_{2,4,-6} = -0.55(4)$; In the V(III)-H₂dipic [12] system were considered the complexes: $[\text{V}(\text{dipic})]^{+}$, $\log \beta_{1,1,-2} = 1.16(2)$; $\text{V}(\text{dipic})(\text{OH})$, $\log \beta_{1,1,-3} = -3.38(3)$; $[\text{V}(\text{dipic})(\text{OH})_2]^{-}$, $\log \beta_{1,1,-4} = -10.36(2)$; $\text{V}(\text{Hdipic})(\text{dipic})$, $\log \beta_{1,2,-3} = 1.85(3)$; $[\text{V}(\text{dipic})_2]^{-}$, $\log \beta_{1,2,-4} = -0.96(2)$. In the V(III)-H₂ox [13] system were the complexes: $[\text{V}(\text{Hox})]^{2+}$, $\log \beta_{1,1,-1} = 6.83(3)$; $[\text{V}(\text{ox})]^{2+}$, $\log \beta_{1,1,-2} = 5.16(3)$; $[\text{V}(\text{ox})(\text{OH})]$, $\log \beta_{1,1,-3} = 0.97(5)$; $[\text{V}(\text{ox})(\text{OH})_2]^{-}$, $\log \beta_{1,1,-4} = -4.76(7)$; $[\text{V}(\text{ox})_2]^{-}$, $\log \beta_{1,2,-4} = 6.37(8)$; $[\text{V}(\text{ox})_2(\text{OH})]^{2-}$, $\log \beta_{1,2,-5} = 1.6(1)$; $[\text{V}(\text{ox})_3]^{3-}$, $\log \beta_{1,3,-6} = 7.23(6)$; $[\text{V}(\text{ox})_3(\text{OH})]^{4-}$, $\log \beta_{1,3,-7} = 1.15(7)$. In the V(III)-H₂mal [13] system were the complexes: $[\text{V}(\text{Hmal})]^{2+}$, $\log \beta_{1,1,-1} = 6.74(3)$; $[\text{V}(\text{mal})]^{2+}$, $\log \beta_{1,1,-2} = 5.04(3)$; $[\text{V}(\text{mal})_2]^{-}$, $\log \beta_{1,2,-4} = 7.11(7)$; $[\text{V}(\text{mal})_2(\text{OH})]^{2-}$, $\log \beta_{1,2,-5} = 4.07(5)$; $[\text{V}(\text{mal})_2(\text{OH})_2]^{-}$, $\log \beta_{1,2,-6} = -1.05(8)$; $[\text{V}(\text{mal})_3]^{3-}$, $\log \beta_{1,3,-6} = 4.09(6)$; $[\text{V}(\text{ox})_3(\text{OH})]^{4-}$, $\log \beta_{1,3,-7} = 0.34(7)$. In the V(III)-H₂phtha [14] system were considered the complexes: $[\text{V}(\text{Hphtha})]^{2+}$, $\log \beta_{1,1,-1} = 7.84(5)$; $[\text{V}(\text{phtha})]^{+}$, $\log \beta_{1,1,-2} = 4.9(1)$; $[\text{V}(\text{phtha})_2]^{-}$, $\log \beta_{1,2,-4} = 8.04(4)$; $\text{V}(\text{OH})(\text{phtha})$, $\log \beta_{1,1,-3} = 1.55(8)$; $\text{V}(\text{Hphtha})(\text{phtha})_2$, $\log \beta_{1,2,-3} = 8.5(1)$; $[\text{V}(\text{OH})(\text{phtha})_2]^{2-}$, $\log \beta_{1,2,-5} = 4.2(2)$; $[\text{V}(\text{OH})_2(\text{phtha})_2]^{2-}$, $\log \beta_{1,2,-6} = 0.8(1)$; $[\text{V}(\text{phtha})_3]^{3-}$, $\log \beta_{1,3,-6} = 4.88(5)$.

The stability constant of the V(III) hydroxo complexes, the stability constants of the ligands, and the stability constants of binary complexes were kept fixed

during the analysis. The aim of the analysis 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 carried out using the computer program HYSS,[15] yielding the $\beta_{p,q,r,s}$ values, which are summarized in Tables 2 and 3.

3. Results and discussion

3.1. Ionization constants of ligands studied

The analysis of the picolinic acid (Hpic) system was obtained two pka values, being the first pK_a value that

corresponds to the deprotonation of carboxylic group, and the second pK_a corresponds to the deprotonation of the pyridinic group. In the case of the dipicolinic acid (H₂dipic) system, two pka values were also obtained, the first pK_a corresponds to the deprotonation of the first carboxylic group, which has a value of 0.5 and it is not possible to measure it due to the high error made with the glass electrode. The second pK_a value corresponds to the deprotonation of the second carboxylic group, and the last pK_a corresponds to the deprotonation of the pyridinic group.[12] In the case of the dicarboxylic oxalic, malonic, and phthalic acids (H₂ox), (H₂mal), and (H₂phtha) briefly (H₂L), they have two pK_a that correspond to

Table 1. Ligands acidity constants ($\log \beta_{p,r}$) in 3.0 M KCl at 25 °C.

Equilibrium	Hpic	$\log \beta_{p,r}$ H ₂ dipic	H ₂ ox	H ₂ mal	H ₂ phtha
$\text{HL} + \text{H}^+ \rightleftharpoons \text{H}_2\text{L}^+$	1.51(2)				
$\text{H}_n\text{L} \rightleftharpoons \text{H}_{n-1}\text{L}^- + \text{H}^+$	-5.57(2)	2.45(2)	-0.68(3)	-2.87(3)	-2.95(3)
$\text{H}_n\text{L} \rightleftharpoons \text{H}_{n-2}\text{L}^{2-} + 2\text{H}^+$		-7.11(3)	-4.47(3)	-8.15(5)	-7.71(4)
Dispersion σ (Z)	0.020	0.026	0.022	0.026	0.021
Ligand concentration (mmol. dm ⁻³)	3.0	3.0	3.0	3.0	3.0
pK_i					
$\text{H}_2\text{L}^+ - \text{HL}$	1.51	2.45			
$\text{HL} - \text{L}^-$	5.57	4.66			
$\text{H}_2\text{L} - \text{HL}$			0.68	2.87	2.95
$\text{HL} - \text{L}^-$			3.79	5.28	4.76

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

Table 2. Stability constants ($\log \beta_{p,q,r,s}$) of the V(III)-Hpic-H₂L systems (KCl 3.0 mol dm⁻³, 25 °C). Considering the following reaction scheme: $p\text{H}_2\text{O} + q\text{V}^{3+} + r\text{Hpic} + s\text{H}_2\text{L} \rightleftharpoons [\text{V}q(\text{OH})p(\text{Hpic})r(\text{H}_2\text{L})s] + p\text{H}^+$.

Complex	Model (p, q, r, s)	Oxalic acid	$\log \beta_{p,q,r,s}$ Malonic acid	Phthalic acid
V(pic)L	(-3, 1, 1, 1)	5.39(7)	5.58(5)	5.66(6)
$[\text{V}(\text{pic})_2\text{L}]^-$	(-4, 1, 2, 1)	4.3(1)	5.00(8)	4.5(2)
Dispersion (σ)		0.089	0.063	0.088

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

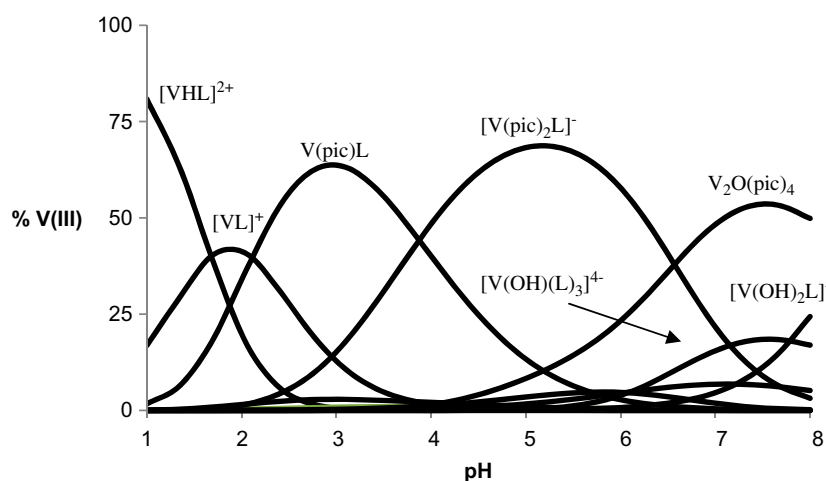


Figure 1. Species distribution diagram of the V(III)-Hpic-H₂ox system. Considering $M_T = 3$ mM and V^{3+} -Hpic-H₂ox ratio $R = 1:2:1$.

the deprotonation of the carboxylic groups. The pK_a values obtained are in good agreement with the values reported in the literature [16,17] (Table 1).

3.2. Ternary vanadium(III) complexes

3.2.1. *V(III)-Hpic-H₂L* system

Table 2 presents the results of the analysis performed with the LETAGROP program in which it were observed the

formation of the complexes $V(pic)(L)$ and $[V(pic)_2(L)]^-$. The respective species distribution diagrams are given in Figures 13.

3.2.2. *V(III)-H₂dipic-H₂L* system

The results of the analysis are shown in Table 3 and were observed the complexes $[V(dipic)(L)]^-$, $[V(dipic)(HL)(L)]^{2-}$, and $[V(dipic)(L)_2]^{3-}$ in all the systems. The

Table 3. Stability constants ($\log \beta_{p,q,r,s}$) of the $V(III)-H_2dipic-H_2L$ systems (KCl 3.0 mol dm⁻³, 25 °C). Considering the following reaction scheme: $pH_2O + qV^{3+} + rH_2dipic + sH_2L \rightleftharpoons [Vq(OH)p(H_2dipic)r(H_2L)s] + pH^+$.

Complex	(<i>p, q, r, s</i>)	Oxalic acid	Malonic acid $\log \beta_{p,q,r,s}$	Phthalic acid
$[V(dipic)L]^-$	(-4, 1, 1, 1)	9.3(2)	8.7(2)	10.9(1)
$[V(dipic)(HL)L]^{2-}$	(-5, 1, 1, 2)	11.2(2)	10.3(1)	9.2 max 10.4
$[V(dipic)L_2]^{3-}$	(-6, 1, 1, 2)	5.7 max 7.0	6.9(1)	6.9(3)
Dispersion (σ)		0.073	0.132	0.096

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

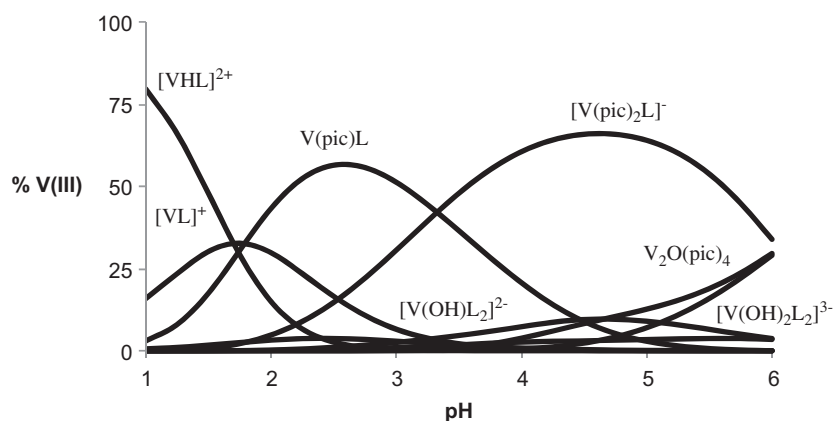


Figure 2. Species distribution diagram of the $V(III)-Hpic-H_2mal$ system. Considering $M_T = 3$ mM and $V^{3+}-Hpic-H_2mal$ ratio $R = 1:2:1$.

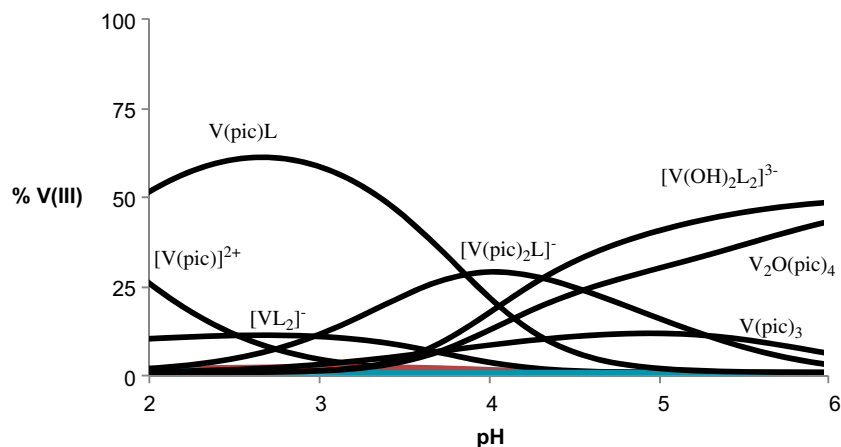


Figure 3. Species distribution diagram of the $V(III)-Hpic-H_2phtha$ system. Considering $M_T = 3$ mM and $V^{3+}-Hpic-H_2phtha$ ratio $R = 1:2:1$.

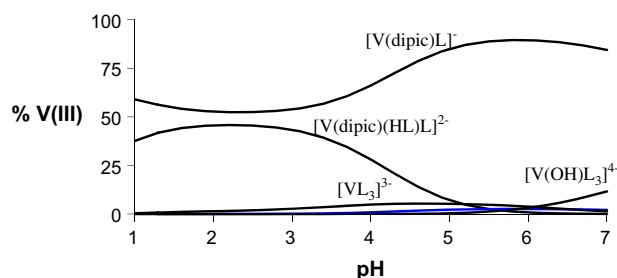


Figure 4. Species distribution diagram of the V(III)-H₂dipic-H₂ox system. Considering $M_T = 3$ mM and V^{3+} -H₂dipic-H₂ox ratio $R = 1:1:2$.

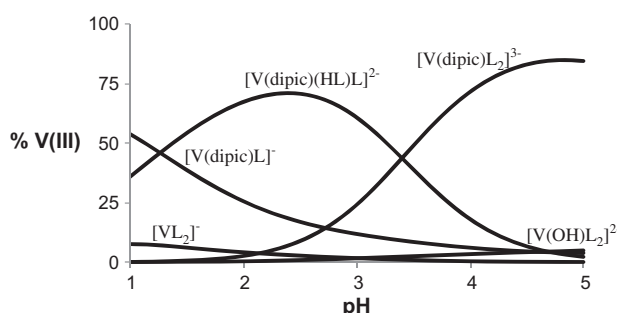


Figure 5. Species distribution diagram of the V(III)-H₂dipic-H₂mal system. Considering $M_T = 3$ mM and V^{3+} -H₂dipic-H₂mal ratio $R = 1:1:2$.

stability constants given and the respective species distribution diagrams are presented in Figures 4–6.

In the V(III)-pic-H₂L ternary system, two complexes were detected: V(pic)(L) and [V(pic)₂(L)][−]. In Figure 1 shows the species distribution diagram for the V(III)-pic-H₂ox system, taking into account the molar ratio V^{3+} :Hpic:H₂ox $R = 1:2:1$ and $M_T = 3$ mmol dm^{−3}. The results

show that the ternary complex is more abundant, V(pic)(L) predominates over a wide pH range ($pH \leq 1 \leq 7$), while the complex [V(pic)₂(L)][−] is in low proportion. In the acid region, the binary complex [VL]^{2−} dominates in the range $1 \leq pH \leq 4$. At $pH > 6.5$, the dimeric complex V₂OL₄ predominates. Figure 2 shows the species distribution diagrams for the V(III)-pic-H₂mal system taking into account the molar ratio V^{3+} :Hpic:H₂mal $R = 1:2:1$ and $M_T = 3$ mmol dm^{−3}. This system has the same behavior as the V(III)-pic-H₂ox, but in this case, the complexes V(pic)(L) and [V(pic)₂(L)][−] are formed in a higher proportion and the dimeric complex V₂OL₄ is formed in less proportion. In Figure 3 is given the species distribution diagram for the V(III)-pic-H₂phtha system taking into account the molar ratio V^{3+} :Hpic:H₂mal $R = 1:2:1$ and $M_T = 3$ mmol dm^{−3}, but in this case, the complex V(pic)(L) is the predominant species in the pH range 2–3.8, the [V(pic)₂(L)][−] in formed in low quantities and the species V₂OL₄, [V(OH)₂L₂]^{3−}, and [VL₃]^{3−} predominates at $pH > 4.4$.

In the V(III)-dipic-H₂L ternary system, three complexes were detected: [V(dipic)(L)][−], [V(dipic)(HL)(L)]^{2−}, and [V(dipic)(L)₂]^{3−}. Figure 4 shows the species distribution diagrams for the V(III)-H₂dipic-H₂ox system under the experimental conditions: molar ratio V^{3+} :H₂dipic:H₂ox $R = 1:1:2$ and $M_T = 3$ mmol dm^{−3} and shows that the complex [V(dipic)L][−] is present in the pH range 1–7, and in less proportion, it is formed the acidic complex [V(dipic)(HL)L]^{2−} in the range $1 < pH < 4$, and the complexes [VL₃]^{3−} and [V(OH)L₃]^{4−} are formed in low proportions. The species distribution diagrams for the system V(III)-H₂dipic-H₂mal are given in Figure 5 for the conditions molar ratio V^{3+} :H₂dipic:H₂mal $R = 1:1:2$ and $M_T = 3$ mmol dm^{−3}, show the formation in less than 50% of the [V(dipic)(L)][−] complex in the pH range 1–4, the complex [V(dipic)(HL)(L)]^{2−} predominates between 1.2 and 3.3 pH range, and the [V(dipic)(L)₂]^{3−} complex is the most important species at $pH > 3.2$. Finally,

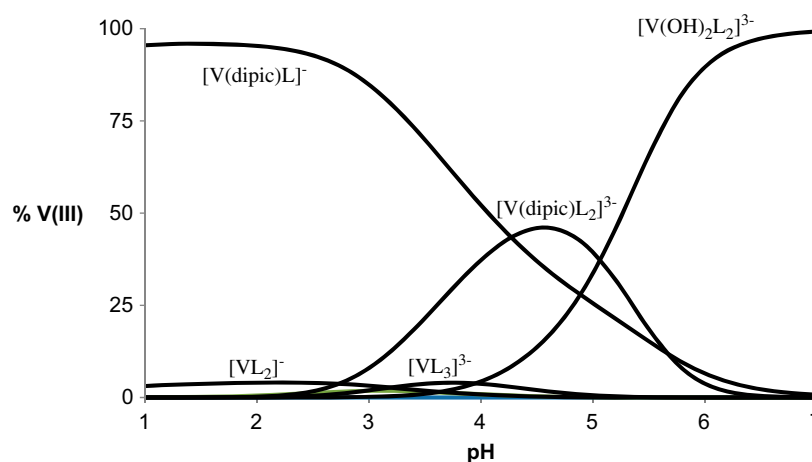


Figure 6. Species distribution diagram of the V(III)-H₂dipic-H₂phtha system. Considering $M_T = 3$ mM and V^{3+} -H₂dipic-H₂phtha ratio $R = 1:1:2$.

Figure 6 shows the species distribution diagrams for the V(III)-H₂dipic-H₂phtha system taking into account the conditions molar ratio V³⁺:H₂dipic:H₂mal $R = 1:1:2$ and $M_T = 3 \text{ mmol dm}^{-3}$, the [V(dipic)(L)]⁻ complex is very important in the pH range 1–4 and is formed in less extension the complex the [V(dipic)(L)₂]³⁻ and the most important species at pH > 5 is the complex [V(OH)₂(L)₂]³⁻.

4. Conclusions

In this work, we have studied the speciation of the ternary complexes of Vanadium(III)-Hpic and Vanadium(III)-H₂dipic with the dicarboxylic oxalic, malonic, and phthalic acids (H₂ox), (H₂mal) and (H₂phtha). The data analyzed using the least-squares computational program LETAGROP indicate the formation of the complexes V(pic)(L) and [V(pic)₂(L)]⁻ in the vanadium(III)-Hpic-H₂L system. In the case of the vanadium(III)-H₂dipic-H₂L system were observed the complexes [V(dipic)(L)]⁻, [V(dipic)(HL)(L)]²⁻ and [V(dipic)(L)₂]³⁻.

Disclosure statement

No potential conflict of interest was reported by the authors.

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Notes on contributors

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

Jessaid Escobar 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 and electrochemistry.

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.

Edgar Del Carpio is a PhD student from the Universidad Simón Bolívar. He has to his credit over 17 publications in local and international blind-reviewed journals. His research interest includes solution equilibria, emulsions, and asphaltenes.

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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