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Interaction between the low molecular mass components of blood serum and the vanadium(III)–6-methylpicolinic acid system

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ABSTRACT

The complexes formed between vanadium(III) and 6-methylpicolinic acid (H6Mepic) with small blood serum bioligands: lactic, oxalic, citric and phosphoric acids (HLac), (H_2Ox), (H_3Cit) and (H_3PO_4) 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 analysed using the least-squares computational program LETAGROP, obtaining the complexes $[V(6Mepic)(Lac)]^+$, V(OH)(6Mepic)(Lac), $[V(OH)_2(6Mepic)(Lac)]^-$, $[V(OH)_3(6Mepic)(Lac)]^{2-}$ in the vanadium(III)–6Mepic-Lac system. In the case of the vanadium(III)–6Mepic-Ox system the complexes V(6Mepic)(Ox) and $[V(6Mepic)_2(Ox)]^-$ were observed , in the vanadium(III)–6Mepic–H_3PO_4 system the complexes $[V(6Mepic)(H_2PO_4)]^+$ and V(6Mepic)(HPO_4) were detected, and finally in the vanadium(III)–6Mepic-Cit system the complexes V(6Mepic)(HCit), $[V(6Mepic)(Cit)]^-$ and $[V(OH)(6Mepic)(Cit)]^{2-}$ were observed . The respective stability constants of the complexes formed in aqueous solution were determined.

1. Introduction

Interest on the study of vanadium(III) complexes is growing [1–4]. The vanadium (III) cysteine complexes have some antitumoral activity [1,2], and the vanadium(III) maltolate [3], and vanadium(III) dipicolinate complexes [4], have shown some insulinomimetic activity.

The bis(picolinato)oxovanadium(IV) ($VO(Pic)_2$) may exert hypoglycemic activity when administered orally and bis(6-methylpicolinato)oxovanadium(IV) $VO(6Mepic)_2$), which has a relatively high n-octanol/water partition coefficient (suggesting higher lipophilicity), was found to be an effective inhibitor of the in vitro release of free fatty acid from isolated rat adipocytes, similar to $VO(Pic)_2$, and to normalise the serum glucose level without loss in body weight. It displays a long-acting character: the normal serum glucose level was maintained for at least 80 days after the cessation of complex administration. These features of $VO(6Mepic)_2$ might be dependent on its relatively high lipid solubility. Accordingly, these complexes ($VO(Pic)_2$ and especially $VO(6Mepic)_2$) may be useful agents in the treatment of insulin-dependent diabetes mellitus [5].

After oral administration of these complexes, they may encounter many other potential vanadium(III) binding molecules present in extracellular or intracellular biological fluids. These latter ligands may partially or completely displace the original vanadium carrier molecules from the coordination sphere of the metal. Accordingly, ternary complex formation should be taken into account in a speciation description of these complexes in biological fluids. Such ternary complexes might be of great importance in the absorption and transport process of the vanadium complexes and even in their physiological activity [5].

The study of the vanadium(III) speciation has been limited, because the facility of oxidation of the vanadium(III) and the high tendency to the hydrolysis of this metal ion [6]. The vanadium(III)–6Mepicolinic acid [7], and vanadium(III)–oxalic acid complexes [8] were previously studied by us. Until now, there are no reports on the speciation of ternary Vanadium(III)–6Mepicolinic acid complexes with lactic, oxalic, phosphoric and citric acids [9,10].

In this work we report the results on mixed ligand complex formation in the V(III)–6-methylpicolinic acid–ligand B systems, where ligand Bs were the most important low molecular mass (l.m.m.) V(III) binders present in blood serum: oxalate, lactate, citrate and monophosphate. The pH-potentiometry technique was used to determine the stoichiometries and stability constants of the complexes formed in aqueous solution.

2. Experimental

2.1. Reagents

The VCl_3 (Merck p.a) and the pyridinecarboxylic acid, 6-Mepicolinic acid (H6Mepic) (Merck p.a.) were used without purification. The HCl

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

Equilibrium	$\log \beta_{pr}$				
	H6Mepic	HLac	H_2Ox	H_3Cit	H_3PO_4
$HL + H^+ \rightleftharpoons H_2L^+$	1.51(2)				
$H_nL \rightleftharpoons H_{n-1}L^- + H^+$	−5.57(2)	−3.75(1)	−1.47(2)	−2.97(2)	−1.67(3)
$H_nL \rightleftharpoons H_{n-2}L^{2-} + 2H^+$			−5.11(2)	−7.20(2)	−8.08(3)
$H_nL \rightleftharpoons H_{n-3}L^{3-} + 3H^+$				−12.48(2)	−19.12(4)
Dispersion σ (Z)	0.020	0.013	0.022	0.019	0.030
Ligand concentration (mmol dm^{-3})	3.0	3.0	3.0	3.0	3.0
pK_i					
H_2L^+–HL	1.51				
HL–L^-	5.57	3.75			
H_3L–H_2L				2.97	1.67
H_2L–HL			1.47	4.23	6.41
HL–L			3.64	5.28	11.04

Values in parentheses are standard deviations [$3\sigma(\log_{10}\beta)$] on the last significant figure.

and KOH solutions were prepared using 100.0 mmol dm^{-3} Titrisol Merck ampoules. The KOH solution was standardised against potassium hydrogen phthalate. The solutions were prepared using triple glass-distilled water, boiled before the preparation of the solutions in order to remove dissolved CO_2. To prevent the hydrolysis of the VCl_3 stock solution, it contained 200 mmol dm^{-3} HCl and was maintained under a H_2 atmosphere in the presence of a Pt platinized net in order to avoid oxidation of the V(III) solution to V(IV) [11]. In this case, the H_2 cannot induce reduction to V(II), because the V(III)/V(II) standard potential is negative ($E^0 = -0.26$ V) [12]. 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,

$$VO^{2+} + H^+ + 1/2H_2(g) \rightleftharpoons V^{3+} + H_2O \quad (1)$$

which is 366.3(3) mV [13]. 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 O_2 and CO_2 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.

Table 2
Stability constants ($\log \beta_{pqrs}$) of the V(III)-H6Mepic-HLac system (KCl 3.0 mol.dm^{-3}, 25 °C).

Equilibrium	Species	$\log \beta_{pqrs}$
$V^{3+} + 6Mepic^- + HLac^- \rightleftharpoons [V(6Mepic)(Lac)]^+$	(0,1,1,1)	13.81(4)
$V^{3+} + 6Mepic^- + HLac^- + H_2O \rightleftharpoons V(6Mepic)(Lac)(OH) + H^+$	(−1,1,1,1)	9.81(4)
$V^{3+} + 6Mepic^- + HLac^- + 2H_2O \rightleftharpoons [V(6Mepic)(Lac)(OH)_2]^- + 2H^+$	(−2,1,1,1)	4.25(7)
$V^{3+} + 6Mepic^- + HLac + 3H_2O \rightleftharpoons [V(6Mepic)(Lac)(OH)_3]^{2-} + 3H^+$	(−3,1,1,1)	−8.1(1)
Dispersion (σ)		0.066

Values in parentheses are standard deviations [$3\sigma(\log \beta_{pqrs})$] on the last significant figure.

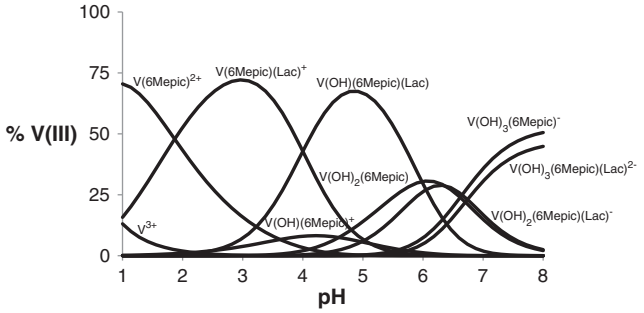

Fig. 1. Species distribution diagram of the V(III)-H6Mepic-HLac system. Considering M_T = 3 mM and V^{3+}–H6Mepic–HLac ratio R = 1:1:1.

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 [14]. 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 ligand Bs 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): 6Mepic: Ligand B ratios R = 1:1:1, 1:2:1 and 1:1:2.

The systems V^{3+}–6Mepic–Ligand B were studied according to the reaction scheme:

$$pH_2O + qV^{3+} + r6Mepic^- + sB^{j-} \rightleftharpoons [Vq(OH)p(6Mepic)r(B)s] + pH^+$$

where ligand B represents the ligands: Lac^-, Ox^{2-}, PO_4^{3-} and Cit^{3-}, and [Vq(OH)p(6Mepic)r(B)s] is the ternary (p, q, r, s) complex and $\beta_{p,q,r,s}$ is the respective stability constant.

The potentiometric data were analysed using the program LETAGROP [15,16], in order to minimise 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 V^{3+}. 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: $[V(OH)]^{2+}$, $\log \beta_{1,-1} = -3.07(3)$; $[V_2O]^{4+}$, $\log \beta_{2,-2} = -3.94(2)$; and $[V_2O(OH)]^{3+}$, $\log \beta_{2,-3} = -7.87(9)$ [13]. In the Binary V(III)-HLac [17] system the following complexes were considered: $[V(Lac)]^{2+}$, $\log \beta_{1,1,-1} = 0.11(4)$; $[V(Lac)(OH)]^+$, $\log \beta_{1,1,-2} = -2.29(2)$; $[V(Lac)(OH)_2]$, $\log \beta_{1,1,-3} = -7.74(3)$. In the V(III)-$H_2$Ox [8] system

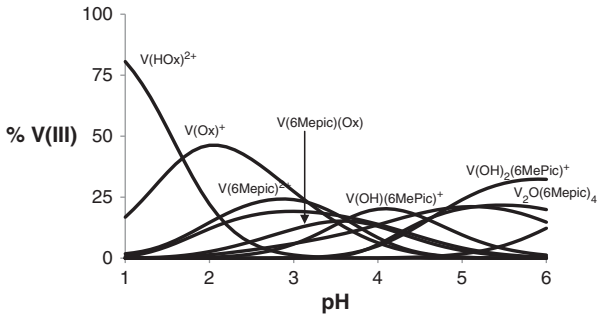

Fig. 2. Species distribution diagram of the V(III)–H6Mepic–H_2Ox system. Considering M_T = 3 mM and V^{3+}–H6Mepic–H_2Ox ratio R = 1:1:1.

Table 3
Stability constants (log β_{pqrs}) of the V(III)–H6Mepic–H_2Ox system (KCl 3.0 mol dm^{-3}, 25 °C).

Equilibrium	Species	log β_{pqrs}
$V^{3+} + 6Mepic^- + Ox^{2-} \rightleftharpoons V(6Mepic)(Ox)$	(0,1,1,1)	15.3 (2)
$V^{3+} + 26Mepic^- + Ox^{2-} \rightleftharpoons [V(6Mepic)_2(Ox)]^- + H^+$	(−1,1,2,1)	19.3 (1)
Dispersion (σ)		0.085

Values in parentheses are standard deviations [3σ(log β_{pqrs})] on the last significant figure.

the complexes: $[V(HOx)]^{2+}$, log $\beta_{1,1,-1} = 6.83(3)$; $[V(Ox)]^{2+}$, log $\beta_{1,1,-2} = 5.16(3)$; $[V(Ox)(OH)]$, log $\beta_{1,1,-3} = 0.97(5)$; $[V(Ox)(OH)_2]^-$, $\log_{10} \beta_{1,1,-4} = -4.76(7)$; $[V(Ox)_2]^-$, log $\beta_{1,2,-4} = 6.37(8)$; $[V(Ox)_2(OH)]^{2-}$, log $\beta_{1,2,-5} = 1.6(1)$; $[V(Ox)_3]^{3-}$, log $\beta_{1,3,-6} = 7.23(6)$; $[V(Ox)_3(OH)]^{4-}$, log $\beta_{1,3,-7} = 1.15(7)$. In the V(III)-H_3PO_4 [17] system the following complexes were considered: $[V(H_2PO_4)]^{2+}$, log $\beta_{1,1,-1} = 1.17(4)$; $[V(HPO_4)]^+$, log $\beta_{1,1,-2} = -1.08(7)$; $[V(HPO_4)(H_2PO_4)]$, log $\beta_{1,2,-3} = 0.06(6)$; $[V(HPO_4)_2]^-$, log $\beta_{1,2,-4} = -2.69(6)$. And in the V(III)-$H_3$Cit system [17] the following complexes were considered: $[V(HCit)]^+$, log $\beta_{1,1,-2} = -1.24(1)$; $[V(Cit)]$, log $\beta_{1,1,-3} = -4.66(3)$; $[V(HCit)_2]^-$, log $\beta_{1,2,-4} = -5.53(9)$; $[V(HCit)(Cit)]^{2-}$, log $\beta_{1,2,-5} = -8.50(2)$; $[V(Cit)_2]^{3-}$, log $\beta_{1,2,-6} = -13.26(2)$; $[V(Cit)_2(OH)]^{4-}$, log $\beta_{1,2,-7} = -19.24(3)$. All the system given have been study in 3.0 mol dm^{-3} KCl at 25 °C.

The stability constant of the V(III) hydroxo complexes, the stability constants of the ligands and 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, $U = \sum (Z_B^{exp} - Z_B^{calc})^2$, the fittings were done by testing different (p, q, r, s) combinations.

The species distribution diagrams were done with the computer program HYSS [18], yielding the β_{pqrs} values, which are summarised in Tables 2–5.

3. Results and discussion

3.1. Ionisation constants of ligands studied

The ionisation 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 [9,10]. For 6Mepicolinic acid, the pK_1 corresponds to the deprotonation of the carboxylic group in the species H_2L^+ and the pK_2 corresponds to the deprotonation of the pyridine in the HL species, because this pK_a value is in close agreement with that for pyridine pK_a (pK_a = 5.24) [9,10]. This permits us to assume that the HL species corresponds to the zwitterionic form of the 6Mepicolinic acid. For lactic acid (HLac), only one pK_a was obtained, because the hydroxyl group has a pK_a > 14, and it is not possible to measure it in aqueous solution with a glass electrode. For the oxalic acid (H_2Ox) two pK_a values were obtained, because this ligand has two dissociable protons in the studied pH range. In ortophosphoric acid (H_3PO_4), and citric acid (H_3Cit), three pK_a values were measured. In the case of the H_3Cit, the hidroxyl group has a pK_a > 14, it is not possible to measure it with a glass electrode.

Table 4
Stability constants (log β_{pqrs}) of the V(III)-H6Mepic-H_3PO_4 system (KCl 3.0 mol dm^{-3}, 25 °C).

(KCl 3.0 mol dm^{-3}, 25 °C).Equilibrium	Species	log β_{pqrs}
$V^{3+} + 6Mepic^- + PO_4^{3-} + 2H^+ \rightleftharpoons [V(6Mepic)(H_2PO_4)]^+$	(2,1,1,1)	30.83 (7)
$V^{3+} + 6Mepic^- + PO_4^{3-} + H^+ \rightleftharpoons V(6Mepic)(HPO_4)$	(1,1,1,1)	27.07
Dispersion (σ)		0.057

Values in parentheses are standard deviations [3σ(log β_{pqrs})] on the last significant figure.

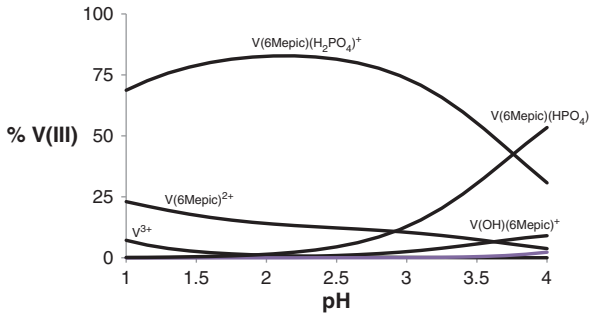

Fig. 3. Species distribution diagram of the V(III)–H6Mepic–H_3PO_4 system. Considering M_T = 3 mM and V^{3+}–H6Mepic–H_3PO_4 ratio R = 1:1:1.

3.2. Ternary vanadium(III) complexes

3.2.1. V(III)-H6Mepic-HLac system

Summarised in Table 2 are the respective stability constants of this system and the species distribution diagrams are represented in Fig. 1.

In this system four complexes were detected: $[V(6Mepic)(Lac)]^+$, V(OH)(6Mepic)(Lac), $[V(OH)_2(6Mepic)(Lac)]^-$, $[V(OH)_3(6Mepic)(Lac)]^{2-}$. Given in Fig. 2 is the species distribution diagram for this system taking into account the molar ratio V^{3+}:H6Mepic:HLac R = 1:1:1 and M_T = 3 mmol dm^{-3}, the complex $[V(Lac)]^{2+}$ is formed at pH < 1.8. Between the pH range 1.8 and 4, the ternary complex $[V(6Mepic)(Lac)]^+$ is the most important species, and the complex V(OH)(6Mepic)(Lac) is predominant in the range 4 < pH < 6, the other two complexes $[V(OH)_2(6Mepic)(Lac)]^-$ and $[V(OH)_3(6Mepic)(Lac)]^{2-}$ are formed in less extension at pH > 6.

The relative stability of the ternary complex, compared with the binary complexes, can be obtained considering the Δlog K″ value, where Δlog K″ is calculated considering the reaction:

$$[V(6Mepic)]^{2+} + [V(Lac)]^{2+} \rightleftharpoons [V(6Mepic)(Lac)]^+ + V^{3+}, \Delta \log K'' = +0.84$$

For the $[V(6Mepic)(Lac)]^+$ complex the Δlog K″ is +0,84, which means that the ternary complex is more stable than the binary complexes [19].

3.2.2. V(III)-H6Mepic-H_2Ox system

Results of the analysis are shown considering the formation of the complexes V(6Mepic)(Ox) and $[V(6Mepic)_2(Ox)]^-$, with the stability constants given in Table 3. The respective species distribution diagrams are presented in Fig. 2.

The formation of two complexes V(6Mepic)(Ox) and $[V(6Mepic)_2(Ox)]^-$ was observed. We tried to include the complex $[V(6Mepic)(Ox)_2]^{2-}$, but the fitting obtained was worse, for this reason the formation of two ternary complexes is considered. In Fig. 4 the species distribution diagram for the conditions R = 1:1:1 and M_T = 3 mmol dm^{-3} is presented. A very complicated diagram is observed, where the ternary complex V(6Mepic)(Ox) is formed in 20% in the range 2 < pH < 5, the other complex cannot be observed under this experimental condition.

Table 5
Stability constants (log β_{pqrs}) of the V(III)-H6Mepic-H_3Cit system (KCl 3.0 mol dm^{-3}, 25 °C).

Equilibrium	Species	log β_{pqrs}
$V^{3+} + 6Mepic^- + Cit^{3-} + 3H^+ \rightleftharpoons V(6Mepic)(HCit)$	(1,1,1,1)	21.15 (6)
$V^{3+} + 6Mepic^- + Cit^{3-} \rightleftharpoons [V(6Mepic)(Cit)]^-$	(0,1,1,1)	18.19 (6)
$V^{3+} + 6Mepic^- + Cit^{3-} \rightleftharpoons [V(6Mepic)(Cit)(OH)]^{2-} + H^+$	(−1,1,1,1)	11.8 (2)
Dispersion (σ)		0.088

Values in parentheses are standard deviations [3σ(log β_{pqrs})] on the last significant figure.

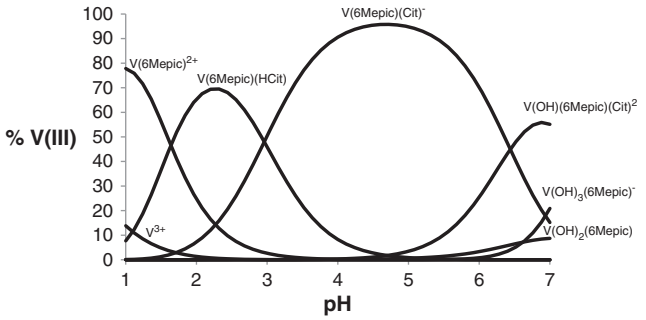

Fig. 4. Species distribution diagram of the V(III)–H6Mepic–H_3Cit system. Considering $M_T = 3$ mM and V^{3+}–H6Mepic–H_3Cit ratio $R = 1{:}1{:}1$.

For the V(6Mepic)(Ox) complex the Δ log K" is −4.1, which means the ternary complex is less stable than the binary complexes.

$$[V(6Mepic)]^{2+} + [V(Ox)]^{+} \rightleftharpoons V(6Mepic)(Ox) + V^{3+},\ \Delta \log K'' = -4.1$$

3.2.3. V(III)-H6Mepic-H_3PO_4 system

The results of the analysis for this system considered the formation of the complexes: $[V(6Mepic)(H_2PO_4)]^{+}$ and $V(6Mepic)(HPO_4)$. The stability constants are summarised in Table 4 and the respective species distribution diagrams are shown in Fig. 3.

In Fig. 3 the species distribution diagrams for $R = 1{:}1{:}1$ and $M_T = 3$ mmol dm^{-3} are presented, where it can be appreciated that the complex $[V(6Mepic)(H_2PO_4)]^{+}$ is the most important species in the range 1<pH<3.7, at pH>3,7 the complex $V(6Mepic)(HPO_4)$ is more abundant.

In this case we could not calculate the Δlog K" because it was not observed in the $[V(6Mepic)(PO_4)]^{-}$ complex.

3.2.4. V(III)-H6Mepic-H_3Cit system

Finally, the analysis performed for this system considered the formation of the three complexes: V(6Mepic)(HCit), $[V(6Mepic)(Cit)]^{-}$ and $[V(OH)(6Mepic)(Cit)]^{2-}$. The stability constants are presented in Table 5 and the species distribution diagrams are given in Fig. 4.

The respective species distribution diagrams are given in Fig. 4 for the conditions $R = 1{:}1{:}1$ and $M_T = 3$ mmol dm^{-3}. At pH<1.5 the species $[V(6Mepic)]^{2+}$ predominates, in the pH range 1.5–3 it formed the V(6Mepic)(Hcit),between 3 and 6.3 pH it is very important the ternary complex $[V(6Mepic)(Cit)]^{-}$, and at pH > 6. is formed in less extension the complex $[V(OH)(6Mepic)(Cit)]^{2-}$.

If we want to see the relative stability of the ternary complex compared to the binary ones, we take into account the following reaction:

$$[V(6Mepic)]^{2+} + VCit \rightleftharpoons [V(6Mepic)(Cit)]^{-} + V^{3+},\ \Delta \log K'' = +1.26$$

this positive value indicates that the ternary complex [V(6Mepic)(Cit)] is more stable than the respective binary ones.

4. Conclusions

In this work we have studied the speciation of the ternary complexes of vanadium(III)–6Mepic–Ligand B, where Ligand B represents the lactic acid, oxalic acid, phosphoric acid and citric acid, which are components of small blood serum bioligand. The data analysed using the least-squares computational program LETAGROP, indicate the formation of the complexes $[V(6Mepic)(Lac)]^{+}$, $V(OH)(6Mepic)(Lac)$, $[V(OH)_2(6Mepic)(Lac)]^{-}$ and $[V(OH)_3(6Mepic)(Lac)]^{2-}$ in the vanadium(III)–6Mepic-Lac system. In the case of the vanadium(III)–6Mepic-Ox system the complexes V(6Mepic)(Ox) and $[V(6Mepic)_2(Ox)]^{-}$ were observed, in the vanadium(III)–6Mepic–H_3PO_4 system the complexes $[V(6Mepic)(H_2PO_4)]^{+}$ and $V(6Mepic)(HPO_4)$ were detected, and finally in the vanadium(III)–6Mepic-Cit system the complexes V(6Mepic)(HCit), $[V(6Mepic)(Cit)]^{-}$ and $[V(OH)(6Mepic)(Cit)]^{2-}$ were observed.

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