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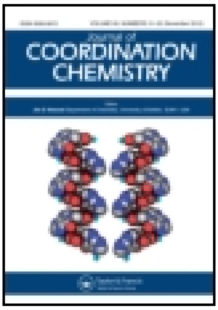

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Solution studies of vanadium(IV), vanadium(V), and vanadium(IV,V) complexes with methionine in 3.0 mol L^{-1} KCl ionic medium at 25°C

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A study of the H^+–VO^{2+}-methionine, H^+–VO_2^+–methionine, and H^+–$V_2O_3^{3+}$–methionine (ligand, HL) systems by *emf*(H) measurements in 3.0 mol L^{-1} KCl ionic medium at 25°C is presented here. Data analysis using the LETAGROP program indicate formation of vanadium(IV) species $[HVOL]^{2+}$, $[VOL]^+$, and $[H_2VOL_2]^{2+}$; vanadium(V) species $[HVO_2L]^+$ and VO_2L; and the mix-valence vanadium(IV,V) species $[H_2V_2O_3L]^{4+}$, $[V_2O_3L]^{2+}$, $[OHV_2O_3L]^+$, $(OH)_2V_2O_3L$, $(OH)_3V_2O_3L$, $[HV_2O_3L_2]^{2+}$, $[V_2O_3L_2]^+$, and $OHV_2O_3L_2$, whose stability constants β_{pqrs} were determined according to the general reaction $p\ H^+ + q\ VO^{2+} + r\ VO_2^+ + s\ L^- \rightleftarrows H_p(VO)_q(VO_2)_q L_r^{(p+2q+r-s)}$. Selected structural parameters of some complexes formed in solution were determined using *ab initio* methods.

Keywords: Solution equilibria; Vanadium complexes; Stability constants; LETAGROP program; Theoretical calculations

1. Introduction

Coordination chemistry of vanadium plays a significant role in its interaction with biomolecules [1]. An important issue on vanadium complexes is the observation in nature that certain marine animals known as *ascidians* have cellular vanadium content more than one million times larger than that of the seawater in which they live. Vanadium also is extracted from the soil and accumulated by the *Amanita muscaria*, or fly agaric mushroom as a low molecular weight complex known as *amavadin*. It can be concentrated by up to 400 ppm against background levels of less than 0.1 ppm [2].

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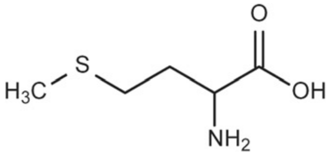

Figure 1. Structure of methionine.

Vanadium is believed to inhibit cholesterol synthesis in mammals and it is also a possible pollutant that could cause pulmonary illnesses due to its presence in industrial smoke [3].

Methionine is a principle supplier of sulfur which prevents hair, skin, and nail disorders, helps lower cholesterol levels by increasing the liver's production of lecithin, reduces liver fat, and protects the kidneys. It is a natural chelating agent for heavy metals, regulates the formation of ammonia, and creates ammonia-free urine, which reduces bladder irritation, influences hair follicles, and promotes hair growth [4].

Methionine (figure 1) besides the two standard positions whose acidity is reflected in the average values $pK_{\mathrm{COOH}} = 2.23$ and $pK_{\mathrm{NH3}} = 9.12$ [5] has the thioether (–SMe) group which would be protonated in very acidic solutions [6]. Nevertheless, for the large negative inductive effect that this group has making the groups lightly more acidic, metallic complexes of methionine are less stable than those formed by amino acids like glycine, unless the formation of chelates through the –SMe compensates for this effect [7].

Methionine possesses three potential donors, which can alternately participate in coordination, relying on the individual character of the metal cation studied.

We did not find any references on the vanadium(IV)–methionine, vanadium(V)–methionine, and vanadium(IV,V)–methionine systems. The vanadium(III)–methionine system leads to formation of $[HVL]^{3+}$, $[VL]^{2+}$, $[VL_2]^{+}$, VL_3, and $[(OH)_4V_2L]^{+}$ [8].

In this article, we report results on a study of the vanadium(IV)–methionine, vanadium(IV)–methionine, and vanadium(IV,V)–methionine conducted by *emf*(*H*) measurements in 3.0 mol L^{-1} KCl ionic medium at 25°C. Selected structural parameters on some of the complexes found in solution were determined using *ab initio* methods.

2. Experimental

2.1. *Materials and solutions*

Reagents included HCl and KOH Fixanal Riedel–de Haën ampoules, $VOSO_4 \cdot 5H_2O$ Merck (99.99%), V_2O_5 LKB (99.93%), methionine Merck (99.0%), KCl Merck (99.0%), O_2 and CO_2 free nitrogen, and triply distilled water.

V(IV) and methionine were employed for weighing of the respective reagents. V(V) solution was prepared in 3.0 mol L^{-1} KCl ionic medium as described [9]. The analytical methods are the same as detailed [9, 10] and the *emf*(*H*) titration method described [11] was used.

2.2. *Mass balance and symbols*

The symbols used in this work are the same as those adopted in previous publications, chemical symbols are in Roman, and concentrations in italic font [12].

In acid medium, VO^{2+} and VO_2^+ hydrolyze, forming $[VOOH]^+$, $[(VO)_2(OH)_2]^{2+}$, and $VO(OH)_2$ [13], and the decavanadate series $H_{3-n}V_{10}O_{28}^{(n+3)}$ ($n = 0$–3) [14], respectively.

It has been reported that at $-\log h < 2$, VO^{2+} and VO_2^+ interact to form $V_2O_3^{3+}$, which successively hydrolyzes to form the homonuclear V(V)–V(V) mixed species $[V_2O_3(OH)]^{2+}$, $[V_2O_3(OH)_2]^+$, $V_2O_3(OH)_3$, and $[V_2O_3(OH)_4]^-$ [15].

In the present investigation, VO^{2+}, VO_2^+, $V_2O_3^{3+}$, and methionine (HL) should form vanadium(IV)–methionine, vanadium(V)–methionine, and vanadium(IV,V)–methionine complexes, giving systems of three and four components, respectively.

In a generalized four component-system H, B, C, and L to form complexes $H_pB_qC_rL_s$ (p, q, r, s), in brief, according to reaction (1), have the mass balances

$$pH + qB + rC + sL \rightleftarrows H_pB_qC_rL_s \tag{1}$$

In equations (2)–(5), **H**, **B**, **C** and **L** represent the total (analytical) concentrations of H^+, V(IV), V(V), and ligand; *h*, *b*, *c*, and *l* are the equilibrium concentrations of H^+, VO^{2+}, VO_2^+, and L^- ions; Z_B, Z_C, and Z_L stand for the average number of H^+ bound per mol of B, C, and L, respectively, c_{pqrs} is the equilibrium concentration of the complex (p, q, r, s), and K_w is the water dissociation constant.

$$\mathbf{H} - h + K_w h^{-1} = \mathbf{B}Z_B = \mathbf{C}Z_C = \mathbf{L}Z_L = \Sigma_p \Sigma_q \Sigma_r \Sigma_s p\, c_{pqrs}, \tag{2}$$

$$\mathbf{B} = b + \Sigma_p \Sigma_q \Sigma_r \Sigma_s q\, c_{pqrs}, \tag{3}$$

$$\mathbf{C} = c + \Sigma_p \Sigma_q \Sigma_r \Sigma_s r\, c_{pqrs}, \tag{4}$$

$$\mathbf{L} = l + \Sigma_p \Sigma_q \Sigma_r \Sigma_s s\, c_{pqrs} \tag{5}$$

Knowledge of the total concentrations **H**, **B**, **C,** and **L** by analysis and determining *h* by electromotive force measurements, *emf*(*H*), the primary experimental data (emfs, analysis, volumes, etc.) can be given in terms of the formation functions (6)–(8), as $Z_B(\log h, \mathbf{B}, \mathbf{C}, \mathbf{L})$, $Z_C(\log h, \mathbf{B}, \mathbf{C}, \mathbf{L})$, or $Z_L(\log h, \mathbf{B}, \mathbf{C}, \mathbf{L})$, more suitable for mathematical treatment.

$$Z_B = (\mathbf{H} - h + K_w h^{-1})/\mathbf{B} = \Sigma_p \Sigma_q \Sigma_r \Sigma_s p\, c_{pqrs}/(b + \Sigma_p \Sigma_q \Sigma_r \Sigma_s q\, c_{pqrs}), \tag{6}$$

$$Z_C = (\mathbf{H} - h)/\mathbf{C} = \Sigma_p \Sigma_q \Sigma_r \Sigma_s p\, c_{pqrs}/(c + \Sigma_p \Sigma_q \Sigma_r \Sigma_s r\, c_{pqrs}), \tag{7}$$

$$Z_L = (H - h)/\mathbf{L} = \Sigma_p \Sigma_q \Sigma_r \Sigma_s p\, c_{pqrs}/(l + \Sigma_p \Sigma_q \Sigma_r \Sigma_s s\, c_{pqrs}). \tag{8}$$

Sometimes it is possible to achieve a more efficient approach to the problem using instead of these relationships, the reduced formation functions (9)–(11), where c_{pq00},

Table 1. Levels of reference, stoichiometric coefficients, concentrations of reagents, and formation functions used.

Reagents	H^+	VO^{2+}	VO_2^+	L^-
Stoichiometric coefficients	p	q	r	s
Total (analytical) concentrations	$\mathbf{H}$	$\mathbf{B}$	$\mathbf{C}$	$\mathbf{L}$
Equilibrium concentrations	h	b	c	l
Formation functions		Z_B/Z_{Bf}	Z_C/Z_{Cf}	Z_L/Z_{Lf}

Table 2. Stability constants for *two*, *three,* and *four* component systems.

Species	Stability constants
$H_pL^{(p-1}$	β_{p001}
$H_p(VO)_qL_s^{(p+2q-s)}$	β_{pq0s}
$H_p(VO_2)_rL_s^{(p+r-s)}$	β_{p0rs}
$H_p(V_2O_3)L_s^{(p+3-s)}$	β_{p11s}

c_{p0r0}, and c_{p110} denote the equilibrium concentrations of the products of hydrolysis of V(IV), V(V), and V(IV,V), respectively, and c_{p001} the equilibrium concentration of ligand acid species, the stability constants of which are known under identical experimental conditions [15].

$$Z_{Bf} = (\mathbf{B}Z_B - \Sigma_p\Sigma_q p\, c_{pq00} - \Sigma_p\Sigma_r p\, c_{p0}r_0 - \Sigma_p p\, c_{p110} - \Sigma_p p\, c_{p001})/(\mathbf{B} - \Sigma_p\Sigma_q q\, c_{pq00}), \tag{9}$$

$$Z_{Cf} = (\mathbf{C}Z_C - \Sigma_p\Sigma_q p\, c_{pq00} - \Sigma_p\Sigma_r p\, c_{p_0}r_0 - \Sigma_p p\, c_{p110} - \Sigma_p p\, c_{p001})/(\mathbf{C} - \Sigma_r\, c_{p_0}r_0), \tag{10}$$

$$Z_{Lf} = (\mathbf{L}Z_L - \Sigma_p\Sigma_q p\, c_{pq00} - \Sigma_p\Sigma_r p\, c_{p0}r_0 - \Sigma_p p\, c_{p110} - \Sigma_p p\, c_{p001})/(\mathbf{L} - \Sigma\, c_{s001}). \tag{11}$$

The situation is reduced then to fitting of the experimental data to the model of *nx* $H_pB_qC_rL_s$ species that through equations (6)–(11) better satisfy the system.

In this work, in order to appropriately present the stability constant β_{pqrs} of a particular complex $H_pB_qC_rL_s$, we use the nomenclature given in table 1 for levels of reference, stoichiometric coefficients, concentrations of the reagents, and formation functions used.

For methionine, the species are L^-, HL, and H_2L^+. In the *three* component systems species of general formula $H_p(VO)_qL_s^{(p+2q-s)}$ and $H_p(VO_2)_rL_s^{(p+r-s)}$, and for *four* component systems complexes of general formula $H_p(VO)(VO_2)L_s^{(p+3-s)}$ or $H_pV_2O_3L_s^{(p+3-s)}$ would be present. The respective stability constants are defined in table 2.

2.3. *Electronic structure calculations*

Ground-state electronic structure calculations were performed using *ab initio* method by means of HyperChem 7.5 software package [16] in a Pentium® PC computer [17].

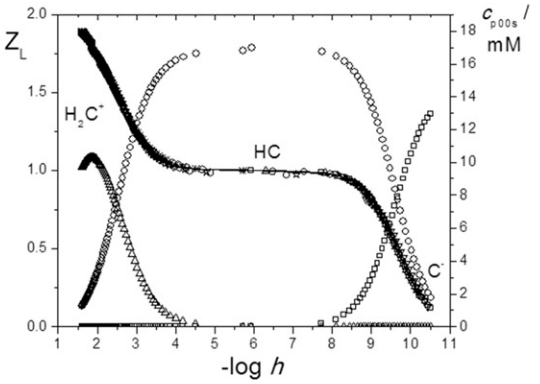

Figure 2. Z_L, average number of H^+ associated per mol of ligand and species distribution diagram *vs.* $-\log h$ for the H^+–methionine (HL) system in 3.0 mol L^{-1} KCl ionic medium at 25°C, for **L** = 10 mmol L^{-1}. The lines represent theoretical curves calculated with the acidity constants of table 3.

Table 3. Acidity constants ($\log \beta_{p001}$) and pK_i values for the H^+–methionine (HL) system in 3.0 mol L^{-1} KCl ionic medium at 25°C.

Reaction	$\log \beta_{p001}$	Equilibria	pK_i (HL)
$2\,H^+ + L^- \rightleftarrows H_2L^+$	12.02(3)	(2) H_2L^+/HL	2.48(2)
$H^+ + L^- \rightleftarrows HL$	9.54(1)	(1) HL/L^-	9.54(1)
$\sigma(Z_L)$	0.011		
Number of experiments = 7, number of points = 283.			

3. Results and discussion

3.1. *Ionization constants of the ligand*

Figure 2 shows the experimental data for the H^+–methionine (HL) system in terms of the formation function $Z_L(\log h)$ as well as the species distribution diagram $c_{p001}(-\log h)$. The lines represent theoretical curves calculated with the β_{p001} constants of table 3.

As observed from the dispersion $\sigma(Z_L)$, there is a good fit between the experimental data and the model of species $H_pL^{(1-p)}$ ($p = 0$–2). Formation of the different species go from $Z_L = 0$ ($-\log h > 10$) where the anion L^- dominates, to $Z_L = 2$ ($-\log h \approx 1$) where the acid ion is H_2L^+. In the interval $4 \le -\log h \le 8$ where $Z_L = 1$, the neutral species HL prevails in the form of the dipolar-ion (*zwitterion*) $HL^{\pm}$.

3.2. *H^+–VO^{2+}–methionine system*

Figure 3 shows the experimental data for the H^+–VO^{2+}–methionine system in terms of the formation function $Z_B(\log h)$, for **B** = 5.0 mmol $L^{-1}$and ligand:V(IV) $R = 5$–10 ratios. The lines represent theoretical curves calculated with equilibrium constants β_{pq0s} from table 4 (column 2).

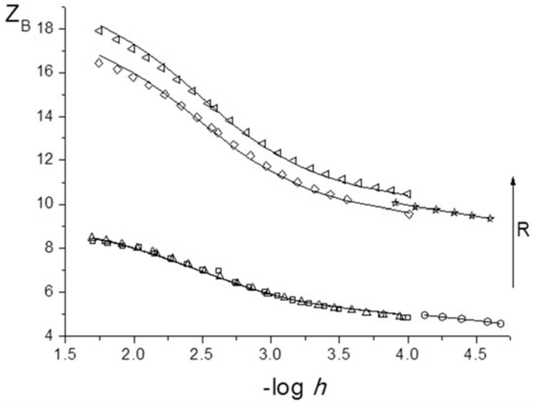

Figure 3. Z_B, average number of H^+ associated per mol of V(IV) *vs.* $-\log h$ for the H^+–VO^{2+}–methionine (HL) system in $3.0\,mol\,L^{-1}$ KCl ionic medium at 25°C, for $\mathbf{B} = 5.0\,mmol\,L^{-1}$ and $R = 5$–10 ratios. The lines represent theoretical curves calculated with the equilibrium constants β_{pq0s} of table 4 (column 6).

Table 4. Equilibrium constants ($\log \beta_{pq0s}$) for the H^+–VO^{2+}–methionine system in $3.0\,mol\,L^{-1}$ KCl ionic medium at 25°C.

Species	$\log \beta_{pq0s}$				
$[HVOL]^{2+}$	14.6(2)	14.5(1)	14.6(1)	14.5(3)	14.39(4)
$[VOL]^{+}$	9.9(2)	9.9(1)	9.9(2)	9.9(2)	9.95(3)
$[H_2VOL_2]^{2+}$	(<25.1)	(<24.9)	(<25.0)	25.3(3)	24.9(2)
VOL_2	15.7(<16.1)		15.3(<15.9)	15.4(<16.0)	15.2(4)
$\sigma(Z_B)$	0.107				
$\sigma(Z_c)$		0.014			
$\sigma(Z_{Bf})$			0.107		
$\sigma(Z_{cf})$				0.098	
$\sigma(E)$ (mV)					1.5
Number of experiments = 10, number of points = 152.					

The group of species that better fit the data includes $[HVOL]^{2+}$, $[VOL]^{+}$, $[H_2VOL_2]^{2+}$, and VOL_2 for almost all the minimized functions. Figure 4 shows the species distribution diagram for $\mathbf{B} = 5\,mmol\,L^{-1}$ and $R = 5$ ratio. In these conditions the most abundant species is $[HVOL]^{2+}$.

As deduced from values of dispersions $\sigma(Z_B)$, $\sigma(Z_L)$, $\sigma(Z_{Bf})$, $\sigma(Z_{Lf})$, and $\sigma(E)$, there is a good fit between the experimental data and this model, as one could conclude from the small amount of VO^{2+} ion still present at $-\log h < 2$, according to the species distribution diagram.

3.3. *H^+–VO_2^+–methionine system*

Figure 5 shows the experimental data for the H^+–VO_2^+–methionine system in terms of the formation function $Z_C(\log h)$ for $\mathbf{C} = 5.0\,mmol\,L^{-1}$ and $R = 1$–4 ratios. Table 5 summarizes the analysis through the model formed by $[HVO_2L]^+$ and VO_2L, and figures 6 and 7 show the species distribution diagram for $R = 1$ and 4 ratios, respectively.

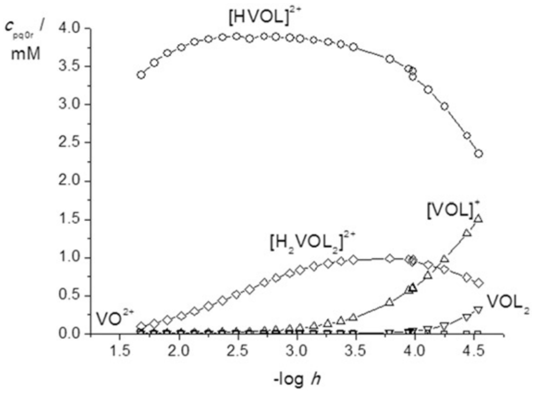

Figure 4. Species distribution diagram *vs.* $-\log h$ for the H^+–VO^{2+}–methionine (HL) system in 3.0 mol L^{-1} KCl ionic medium at 25°C, for $\mathbf{B} = 5$ mmol L^{-1} and $R = 5$ ratio.

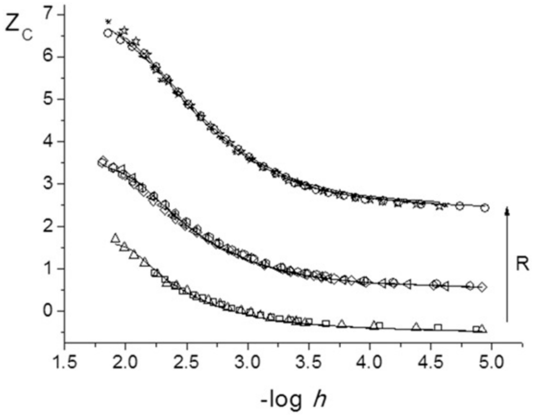

Figure 5. Z_C, average number of H^+ associated per mol of V(V) *vs.* $-\log h$ for the H^+–VO_2^+–methionine (HL) system in 3.0 mol L^{-1} KCl at 25°C, for $\mathbf{C} = 5.0$ mmol L^{-1} and $R = 1$, 2, and 4 ratios.

Table 5. Equilibrium constants ($\log \beta_{p0rs}$) for the H^+–VO_2^+–methionine (HL) system in 3.0 mol L^{-1} KCl at 25°C.

Species	$\log \beta_{p0rs}$				
$[HVO_2L]^+$	11.77(7)	11.81(8)	11.75(7)	11.9(1)	11.9(2)
VO_2L	9.34(7)	9.51(7)	9.43(8)	9.61(6)	9.20(7)
$\sigma(Z_B)$	0.052				
$\sigma(Z_C)$		0.023			
$\sigma(Z_{Bf})$			0.041		
$\sigma(Z_{Cf})$				0.168	
$\sigma(E)$ (mV)					3.5
Number of experiments = 9, number of points = 228.					

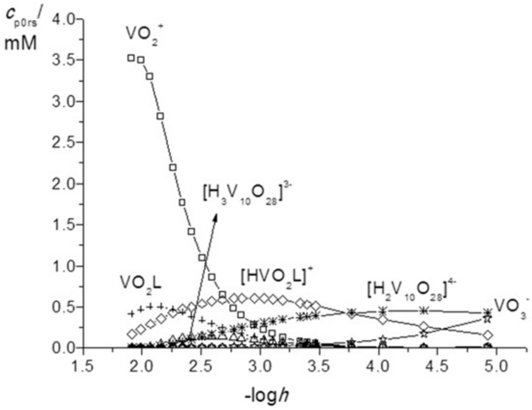

Figure 6. Species distribution diagram *vs.* $-\log h$ for the H^+–VO_2^+–methionine (HL) system in 3.0 mol L^{-1} KCl ionic medium at 25°C, for $\mathbf{C} = 5$ mmol L^{-1} and $R = 1$ ratio.

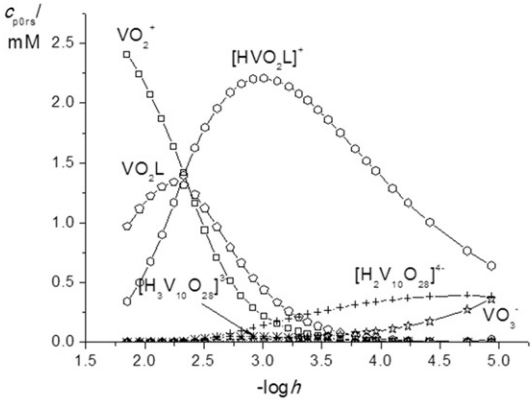

Figure 7. Species distribution diagram *vs.* $-\log h$ for the H^+–VO_2^+–methionine system in 3.0 mol L^{-1} KCl ionic medium at 25°C, for $\mathbf{C} = 5.0$ mmol L^{-1} and $R = 4$ ratio.

In this case, it can be concluded from the dispersions $\sigma(Z_C)$, $\sigma(Z_L)$, $\sigma(Z_{Cf})$, $\sigma(Z_{Lf})$, and $\sigma(E)$ values that there is a good fit between the experimental data and this model. The complexes are quite weak whose concentration grows as the R ratio increases, competing favorably with the *decavanadate* species, product of the hydrolysis of VO_2^+, whose concentration lightly diminishes as R increases.

3.4. H^+–VO^{2+}–VO_2^+–methionine system

Figure 8 shows the experimental data for the H^+–VO^{2+}–VO_2^+–methionine system in terms of the formation function $Z_L(\log h)$ for $\mathbf{B} = 5.0$ mmol L^{-1}, $\mathbf{C} = 5.0$ mmol L^{-1}, and ligand:V(V):V(V) $R = 2$, 4, and 8 ratios, and table 6 contains the results of the analysis

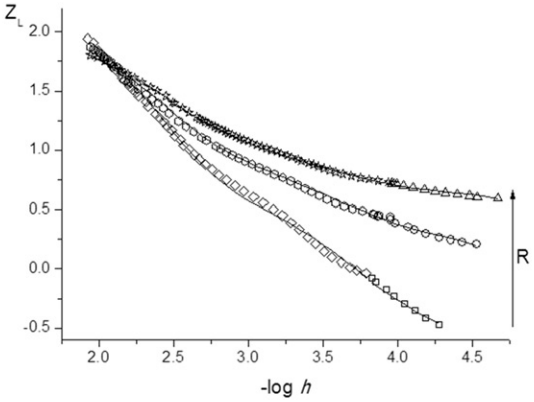

Figure 8. Z_L, average number of H^+ associated per mol f ligand as a function of $-\log h$ for the H^+–VO^{2+}–VO_2^+–methionine system in 3.0 mol L^{-1} KCl ionic medium at 25°C, for $\mathbf{B} = 5.0$ mmol L^{-1}, $\mathbf{C} = 5.0$ mmol L^{-1} and $R = 2$, 4, and 8 ratios.

Table 6. Equilibrium constants ($\log \beta_{pqrs}$) for the H^+–VO^{2+}–VO_2^+–methionine system in 3.0 mol L^{-1} KCl ionic medium at 25°C.

Species	$\log \beta_{pqrs}$				
$[H_2V_2O_3L]^{4+}$	37.25(3)	37.29(3)	37.29(3)	37.30(3)	37.30(5)
$[V_2O_3L]^{2+}$	32.34(3)	32.38(3)	32.37(4)	32.39(3)	32.33(3)
$[OHV_2O_3L]^+$	28.3(2)	28.5(2)	28.4(2)	28.5(2)	28.4(1)
$(OH)_2V_2O_3L$	24.82(6)	24.86(8)	24.85(9)	24.87(7)	24.83(4)
$[(OH)_3V_2O_3L]^-$	19.5(<19.8)	19.6(<19.9)	19.6(<19.9)	19.6(<19.9)	18.9(<19.3)
$[HV_2O_3L_2]^{2+}$	43.2(<43.4)	43.2(2)	43.3(2)	43.2(2)	43.4(1)
$[V_2O_3L_2]^+$	39.7(<40.0)	39.4(<39.7)	39.5(<39.8)	39.4(<39.7)	39.7(2)
$OHV_2O_3L_2$	36.0(2)	36.0(1)	36.1(2)	36.0(1)	35.99(7)
$\sigma(Z_L)$	0.029				
$\sigma(Z_B)$		0.085			
$\sigma(Z_{Lf})$			0.083		
$\sigma(Z_{Bf})$				0.085	
$\sigma(E)$ (mV)					1.5
Number of experiments = 6, number of points = 185.					

through the model formed by $[H_2V_2O_3L]^{4+}$, $[V_2O_3L]^{2+}$, $[OHV_2O_3L]^+$, $(OH)_2V_2O_3L$, $[(OH)_3V_2O_3L]^-$, $[HV_2O_3L_2]^{2+}$, $[V_2O_3L_2]^+$, and $[OHV_2O_3L_2]^+$. The lines in the figure represent theoretical curves calculated with the respective equilibrium constants.

As deduced from the values of dispersions $\sigma(Z_B)$, $\sigma(Z_L)$, $\sigma(Z_{Bf})$, $\sigma(Z_{Cf})$, and $\sigma(E)$, there is a good fit between the experimental data and this model.

Figures 9 and 10 show the species distribution diagram for ratios $R = 2$ and 8, respectively. According to this diagram, for all R values species of the formula $[H_nV_2O_3L]^{(2+n)}$ ($n = 2, 0, -1, -2, -3$) exist. At $-\log h < 2.5$ the $[H_2V_2O_3L]^{4+}$ prevails; in the interval $2.5 \le -\log h \le 3.5$ $[V_2O_3L]^{2+}$ dominates and as soon as $-\log h$ grows the formation of $[OHV_2O_3L]^+$, $(OH)_2V_2O_3L$, and $[(OH)_3V_2O_3L]^-$ is favored. All these species are strong complexes capable of displacing the two and three component complexes that share the system with the exception of the VO_2L species.

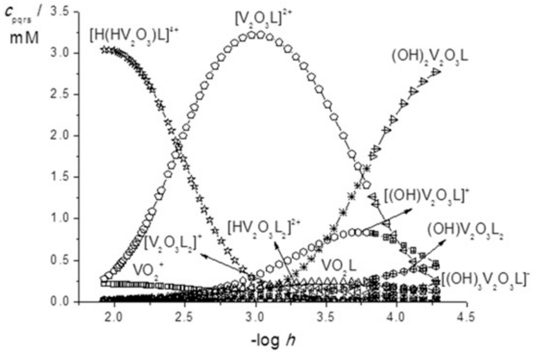

Figure 9. Species distribution diagram *vs.* $-\log h$ for the H^+–VO^{2+}–VO_2^+–methionine system in 3.0 mol L^{-1} KCl ionic medium at 25°C, for $\mathbf{B} = 5.0$ mmol L^{-1}, $\mathbf{C} = 5.0$ mmol L^{-1} and ratio $R = 2$.

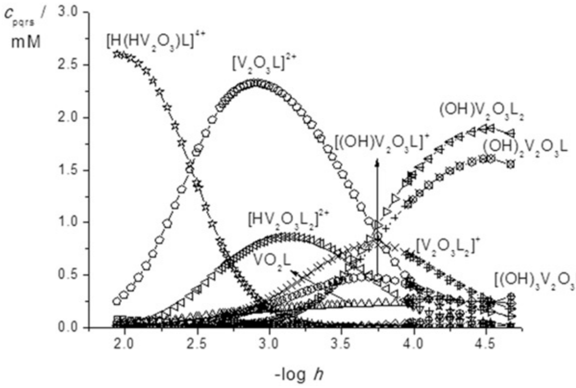

Figure 10. Species distribution diagram *vs.* $-\log h$ for the H^+–VO^{2+}–VO_2^+–methionine system in 3.0 mol L^{-1} KCl ionic medium at 25°C, for $\mathbf{B} = 5.0$ mmol L^{-1}, $\mathbf{C} = 5.0$ mmol L^{-1} and ratio $R = 8$.

Complexes $H_nV_2O_3L_2^{(1+n)}$ $(n = 1, 0, -1)$ only are formed for $-\log h > 3.0$ and their concentration grows with R ratio.

In this system four complexes of *two* components, two complexes of *three* components, and eight complexes of *four* components intervene, and despite the accumulation of experimental errors with an increasing number of components, the model gives a good explanation of the behavior of the H^+–VO^{2+}–VO_2^+–methionine system.

3.5. *Theoretical calculations*

In tables 7–9 selected calculated structural parameters for the H^+–VO^{2+}–*methionine*, H^+–VO_2^+–*methionine*, and H^+–VO^{2+}–VO_2^+–*methionine* systems, involving (a) $[VO(H_2O)_5]^{2+}$ and $[HVOL(H_2O)_2]^{2+}$, (b) $[VO_2(H_2O)_4]^+$ and $[HVO_2L(H_2O)_4]^+$,

Table 7. Selected experimental and calculated bond distances and angles of $VOSO_4{\cdot}5H_2O$ [18], $[VO(H_2O)_5]^{2+}$, and $[HVOL(H_2O)_3]^{2+}$ (HL = methionine), together with the corresponding energy values (kcal mol^{-1}).

Species	V–O (apical oxygen)	V–O (oxygen of water trans to V–O bond)	V–O (oxygen of equatorial water)	V–O (oxygen of carboxylate)	O–V–OH$_2$ (equatorial water) and O–V–O (carb) angles	E (kcal mol^{-1})
$VOSO_4 \cdot 5H_2O$[a]	1.591	2.218	2.714, 2.714, 2.772, 2.772 (2.74)		96.3, 96.3, 99.7, 99.7 (98)	
$[VO(H_2O)_5]^{2+,b}$	1.474	2.109	1.990, 1.992, 1.990, 1.991 (1.991)		98.60, 96.3, 100.15, 100.21 (99)	−867183.71(1)
$[HVOL(H_2O)_4]^{2+,c}$	1.477	2.136	1.950, 2.001, 2.000 (1.98)	1.966	102.98, 99.63, 97.22 (100) 100.61 (carb)	−1314699.04(1)
$[HVOL(H_2O)_4]^{2+,d}$	1.476		1.994, 1.936, 2.000, 2.008 (1.99)	2.129	99.598.67, 103.39, 98.45, 97.55 (100)	−1314694.44(1)

Bond distances and angles in Å and degrees, respectively (mean values in parentheses).

[a] Single-crystal X-ray diffraction [18].

[b] HyperChem calculation.

[c] HyperChem calculation (oxygen atom of carboxylate (carb) group in the same equatorial water molecules level).

[d] HyperChem calculation (oxygen atom of carboxylate (carb) group bound in position *trans* V–O bond).

Table 8. Selected experimental and calculated bond distances and angles of Na_3VO_2EDTA [19], $[VO_2(H_2O)_4]^+$, and $[HVO_2L(H_2O)_3]^+$ (HL = methionine), together with the corresponding energy values (kcal mol^{-1}).

Species	V–O (apical oxygen)	O–V–O angle	V–N (nitrogen of amine)	V–O (oxygen of equatorial water)	V–O (oxygen of carboxylate)	E (kcal.mol^{-1})
$Na_3VO_2(EDTA)$[a]	1.657, 1.639 (1.65)	106.96	2.359, 2.366	1.999, 2.001 (2.000)	1.999, 2.001 (2.000)	
$[VO_2(EDTA)]^{3-}$[b]	1.516,1.524 (1.520)	105.32	2.224, 2.476		1.858, 1.982 (1.92)	−1355322.10(1)
$[VO_2(H_2O)_4]^{+}$[b]	1.501, 1501 (1.501)	107.58		1.997, 1.997 (1.977)		−866586.72(1)
$[HVO_2L(H_2O)_3]^{+}$[c]	1,501, 1502 (1.52)	107.53		2.019	1.958	−1314079.64(1)
$[HVO_2L(H_2O)_3]^{+}$[d]	1.502, 1.500 (1.51)	106.56		2.001, 2.093, 1.992 (2.03)	2.207	−1314077.44(1)
$VO_2L(H_2O)_2$[e]	1.687, 1.757 (1.72)	92.65	2.182	1.495, 3.366 (2.4)	1.758	−1266677.33(1)

Bond distances and angles in Å and degrees, respectively (mean values in parentheses).

[a] Single-crystal X-ray diffraction [19].

[b] HyperChem calculation.

[c] HyperChem calculation (oxygen atom of carboxylate (carb) group initially bound to 90 degrees *vs.* O=V=O angle, before running the *ab initio* STO-3 G* geometric optimization).

[d] HyperChem calculation (oxygen atom of carboxylate (carb) group initially bound in position *trans* V=O bond, before running the *ab initio* STO-3 G* geometric optimization).

[e] HyperChem calculation (O–VO_2–N chelate).

Table 9. Selected experimental and calculated bond distances and angles for $(NH_4)_3V_2O_3(NTA)_2 \bullet 3H_2O$ [20], $[V_2O_3(H_2O)_8]^{3+}$, $[V_2O_3L(H_2O)_6]^{2+}$, and $[V_2O_3L_2(H_2O)_4]^{+}$ (L = methionine), together with the corresponding energy values (kcal mol^{-1}).

Species	V–O (apical oxygen)	V–O (oxygen of carboxylate)	V–N (nitrogen of amine)	V–O–V (oxygen of bridge)	V–O–V (angle)	O–V–N (angle)	*E* (kcal mol^{-1})
$(NH_4)_3V_2O_3(NTA)_2 \cdot 3H_2O$[a]	1.607	2.041, 1.970, 1.982 (2.000)	2.297	1.810	Linear		
$[V_2O_3(NTA)_2]^{3+,b}$	V_1 1.503 V_2 1.510 (1.507)	V_1 1.972, 2.043, 1.971 (1.995) V_2 1.902, 2.007, 1.899 (1.936)	2.178	V_1 1.899 V_2 1.884 (1.892)	159.87		−2,219,822.71(1)
$[V_2O_3(H_2O)_8]^{3+,b}$	V_1 1.657 V_2 1.667 (1.662)			V_1 1.589 V_2 1.982 (1.786)	84.02		−1,686,862.40(1)
$[V_2O_3L(H_2O)_6]^{2+,c}$	V_1 1.823 V_2 1.533 (1.687)	V_1 1.755	V_1 2.103	V_1 1.668 V_2 1.819 (1.743)	129.00	81.89	−2,086,949.99(1)
$[V_2O_3L_2(H_2O)_4]^{+,d}$	V_1 1.577 V_2 1.683 (1.64)	V_1 1.811 V_2 1.965 (1.90)	V_1 2.087 V_2 2.102 (2.09)	V_1 1.887 V^V 1.606 (1.74)	131.06	V_1 84.33 V_2 81.81 (83.1)	−2,487,147.37(1)

Bond distances and angles in Å and degrees, respectively (mean values in parentheses).

[a] Single-crystal X-ray diffraction [20].

[b] HyperChem calculation.

[c] HyperChem calculation (oxygen atom of carboxylate group in *cis* position to V–O bond).

[d] HyperChem calculation (oxygen atom of carboxylate group, respectively, in *cis* and *trans* positions to V_1–O and V_2–O bonds).

and (c) $[V_2O_3(H_2O)_8]^{3+}$, $[V_2O_3L(H_2O)_7]^{2+}$, and $[V_2O_3L_2(H_2O)_4]^{+}$, are computed *in vacuo* at the STO-3 G* basis set level of theory.

For each system, we compare each species with the corresponding structure of the central ion, i.e. VO^{2+}, VO_2^+, and $V_2O_3^{3+}$, taking experimental information on interatomic distances and bond angles from X-ray diffraction values for $VOSO_4 \cdot 5H_2O$ [18], $Na_3VO_2(EDTA)$ [19], and $(NH_4)_3V_2O_3(NTA)_2 \cdot 3H_2O$ [20], respectively. For each structure, first the *molecular builder* and then *the molecular mechanics force field MM+* were run to get close to the optimized geometry, as a starting point before running the *ab initio* STO-3 G* geometric optimization of the HyperChem software package.

3.5.1. H^+–VO^{2+}–methionine system.

For $[HVOL(H_2O)_2]^{2+}$ the obtained average values for V–O (*apical O*) and V–O (*oxygen* of *equatorial water*) bond distances, and O–V–OH_2 (*equatorial water*) angles are in agreement with the corresponding values for $[VO(H_2O)_5]^{2+}$, but slightly smaller than the experimental X-ray diffraction values for $VOSO_4 \cdot 5H_2O$. Its conformation with oxygen of carboxylate bound in the same equatorial water level has a lower energy than the corresponding configuration with oxygen of carboxylate bound *trans* to the V–O bond (table 7).

3.5.2. H^+–VO_2^+–methionine system.

For $[HVO_2L(H_2O)_3]^{+}$ the calculated mean values for V–O (*apical O*) and V–O (*oxygen* of *equatorial water molecules*) bond distances, and O–V–O angle are in agreement with the corresponding values for $[VO_2(H_2O)_4]^{+}$, but the bond distances are smaller than the experimental X-ray diffraction values in $Na_3VO_2(EDTA)$ [19] (table 8). Its conformation with oxygen from carboxylate initially (*molecular mechanics force field MM+*) bound to 90° *versus* the O–V–O angle has a lower energy than the corresponding configuration with oxygen of carboxylate initially (*molecular mechanics force field MM+*) bound *trans* to the V–O bond.

For the chelated framework of $[VO_2L(H_2O)_2]$ the obtained values for the V–O (*apical O*) bond distances are slightly larger than those in $Na_3VO_2(EDTA)$, whereas V–N (*nitrogen of amine*) and V–O (*oxygen of carboxylate*) bond distances and the O–V–O angle are smaller.

3.5.3. H^+–VO^{2+}–VO_2^+–methionine system.

For $[V_2O_3L(H_2O)_6]^{2+}$ the calculated average value for the V–O (*apical O*) bond distance (table 9) is larger than the corresponding value for $(NH_4)_3V_2O_3(NTA)_2 \cdot 3H_2O$ and $[V_2O_3(NTA)_2]^{3+}$, but almost the same as for $[V_2O_3(H_2O)_8]^{3+}$; the V–O–V (*oxygen of bridge*) bond distance is smaller than the corresponding value for $(NH_4)_3V_2O(NTA)_2 \cdot 3H_2O$ [20] and $[V_2O_3(NTA)_2]^{3+}$, and almost the same as for $[V_2O_3(H_2O)_8^{3+}$; the V–O (*oxygen of carboxylate*) bond distance is smaller than corresponding values for $(NH_4)_3V_2O_3(NTA)_2 \cdot 3H_2O$, $[V_2O_3(NTA)_2]^{3+}$ and $V_2O_3(H_2O)_8^{3+}$; the V–N (*nitrogen of amine*) bond distance is slightly smaller than that for $(NH_4)_3V_2O_3(NTA)_2 \cdot 3H_2O$ and $[V_2O_3(NTA)_2]^{3+}$; lastly, the V–O–V angles are smaller than corresponding values for $(NH_4)_3V_2O_3(NTA)_2 \cdot 3H_2O$ and $[V_2O_3(NTA)_2]^{3+}$, and larger than for $V_2O_3(H_2O)_8^{3+}$.

For $[V_2O_3L_2(H_2O)_4]^{+}$ the calculated average values for V–O (*apical O*) and V–O–V (*oxygen of bridge*) bond distances are almost the same as corresponding values for $[V_2O_3(NTA)_2]^{3+}$, $[V_2O_3(H_2O)_8]^{3+}$, and $(NH_4)_3V_2O_3(NTA)_2 \cdot 3H_2O$. Although the V–O (*oxygen of carboxylate*) bond distance is somewhat smaller, the V–N (*nitrogen of amine*) bond distance and V–O–V angles are nearly the same as corresponding values for $[V_2O_3(NTA)_2]^{3+}$ and $(NH_4)_3V_2O_3(NTA)_2 \cdot 3H_2O$.

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