

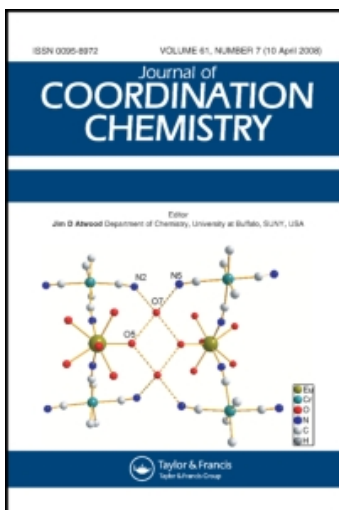
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## Speciation of the vanadium(III)–acetylacetonone system in 3.0 M KCl ionic medium at 25°C

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A study of the  $H^+$ -acetylacetonone (acac, HC) and  $H^+-V^{3+}$ -acetylacetonone systems using emf(H) and UV–Vis measurements in 3.0 M KCl ionic medium at 25°C is presented here. As the initial case, the acetylacetonone  $pK_a$  value was determined under similar experimental conditions as reported a few years ago, finding very similar values. Subsequently, in the study of the  $H^+-V^{3+}$ -acetylacetonone system, the stability constants of  $[VC]^{2+}$ ,  $[VC_2]^+$ ,  $VC_3$ ,  $[OHVC]^+$ ,  $OHVC_2$ ,  $[(OH)_2V_2C]^{3+}$  and  $[(OH)_2V_2C_2]^{2+}$  complexes were determined by emf(H) measurements, and by means of UV–Vis measurements the respective values of  $[VC]^{2+}$ ,  $[VC_2]^+$ ,  $VC_3$  and  $[OHVC]^+$  species, which are the most abundant in this system. The data analysis was carried out using the NERNST, FONDO, and SPEFO versions of the least-squares program LETAGROP. Some extra-thermodynamic relationships about the stability order of the  $V^{II}$ ,  $V^{III}$ , and  $V^{IV}$ -acetylacetonone complexes were obtained by *ab initio* calculations.

**Keywords:** Acetylacetonone; Vanadium(III) complexes; Emf(H) and UV–Vis measurements; Stability constants; LETAGROP program

### 1. Introduction

Research on vanadium(III) complexes has gained relevance due to their applications as mimetic agents of insulin, anti-inflammatories and anticarcinogenic agents [1, 2].

An important issue on vanadium(III) complexes is the observation in nature that certain marine animals, known as *ascidians*, have cellular vanadium contents more than one million times larger than that of the seawater in which they live. In *ascidians* the vanadium is captured from the seawater as  $V^V$  and incorporated into the *vacuoles* of the blood cells through the phosphate channel taking advantage of the similarity between  $VO_4^{3-}$  and  $PO_4^{3-}$ . Inside the *vacuoles* the vanadium is reduced to  $V^{IV}$  and  $V^{III}$ . However, in spite of the efforts of many researchers, the role of vanadium in the physiologic functions of these animals is still not clear [3, 4].

In this article, we report results on a study of the  $H^+$ -acetylacetonone and  $H^+$ -vanadium(III)-acetylacetonone systems performed by electromotive force, emf(H),

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and spectrophotometric UV-Vis measurements in 3.0 M KCl ionic medium at 25.0°C.

We first verify the acetylacetonone  $pK_a$  value and compare it with one previously determined under similar experimental conditions [5]; subsequently, we study the  $H^+-V^{3+}$ -acetylacetonone system as the fundamental objective of this work, which will supplement previous investigations on  $H^+-V^{2+}$ -acetylacetonone [6] and  $H^+-VO^{2+}$ -acetylacetonone [5, 7] systems, as well as recent work on the  $H^+-VO_2^+$ -acetylacetonone system [8]. We are primarily interested in stability of the complexes of these systems (*vide infra*), which may be involved in vanadium physiological function [1, 2].

The  $[V(H_2O)_6]^{3+}$  ion hydrolyzes at  $pH > 1$  forming  $[OHV]^{2+}$ ,  $[(OH)_2V_2]^{4+}$  [9–12],  $[(OH)_2V]^+$  [9],  $[(OH)_3V_2]^{3+}$  [11, 12],  $[(OH)_5V_3]^{4+}$  [13] and/or  $(OH)_{12}V_4$  [14] species, all octahedral [12]. The spectrum of the  $[V(H_2O)_6]^{3+}$  ion has very weak absorption bands at 400 and 580 nm. However, it undergoes a fundamental change on hydrolysis. A new strong band at 436 nm appears at  $pH > 2$  instead of the two bands in acid solution. The molar absorptivity  $\epsilon$  of this new band and, partially, also its position are dependent on the total concentration of vanadium [9, 10]. Likewise, spectra of considerable number of vanadium(III) complexes with a wide variety of ligands have been reported [15].

In water, acetylacetonone (Hacac, HC) is present in the *enolic* form  $CH_3-CO-CH=COH-CH_3$  (HE, 80%). It loses the  $H^+$  of the  $-COH$  group to give its conjugate base, which is a bidentate ligand. We have the *keto*(HQ)–*enolic*(HE)  $HE \rightleftharpoons HQ$  equilibrium ( $[HE] = K [HQ]$ ,  $\log K = -0.69$  (25°C)) [16], which has been the object of a great number of investigations [17]. It is a weak acid ( $pK_a = 9.36$ ) [5] and forms complexes with many transition metals ions.

Vanadium(III) forms a number of complexes, mostly anionic [15, 18], but there is little information on the  $H^+-V^{3+}$ -acetylacetonone system. Only electrochemical information in acetonitrile and dimethyl sulfoxide, and a study of liquid-liquid extraction in nonpolar solvents, are available.

Kitamura *et al.* [19] found that acetylacetonone was catalytically reduced in the course of electrolytic reduction of  $VO(acac)_2$  at a mercury electrode. In acetonitrile solutions, the catalytic reduction proceeded at  $-2.1$  V *versus*  $Ag/0.01$  M  $AgClO_4$  electrode and the reduction products were hydrogen and  $C^-$  anions, while direct electrolysis of acetylacetonone at  $-2.5$  V gave a product with vicinal hydroxyl groups. A reaction mechanism involving regeneration of  $V^{III}$  by the coupled chemical reaction of  $V^{II}$  with acetylacetonone was proposed by these authors.

Nawi and Riechel [20] studied the electrochemistry of  $V(acac)_3$  and  $VO(acac)_2$  by cyclic voltammetry and controlled-potential coulometry in DMSO at a platinum electrode.  $VO(acac)_2$  was irreversibly reduced by one electron at  $-1.9$  V *versus* SCE to a stable V(III) product. In the presence of excess ligand,  $VO(acac)_2$  is reduced by two electrons to  $[V(acac)_3]^-$ , with the  $V^{III}$  species mentioned above and  $V(acac)_3$  as intermediates.  $VO(acac)_3$  is reversibly reduced to  $[V(acac)_3]^-$  at  $-1.42$  V. The one-electron oxidation of  $VO(acac)_2$  and the two-electron oxidation of  $V(acac)_3$  give the same vanadium(V) product.

Imura and Suzuki [21] studied the  $H^+-V^{3+}$ -acetylacetonone system by liquid-liquid partition (0.1 M  $NaClO_4$ -heptane,  $-chloroform$ , and  $-benzene$ , 25°C), reporting  $[V(acac)]^{2+}$ ,  $[V(acac)_2]^+$ , and  $V(acac)_3$ .

## 2. Experimental

### 2.1. Mass balance and symbols

In the present investigation carried out in aqueous solution, the  $V^{III}$  ion and acetylacetonate should form  $nk$  complexes  $H_p V_q C_r^{p+3q-r}$ . In what follows we denote such complexes for brevity by the set  $(p, q, r)$ . We treat the data according to the general reaction of equation (1).



We have for hydrogen ions, vanadium and ligand concentrations the mass balance equations (2).

$$\begin{aligned} CZ_C (= H - h + K_w h^{-1}) &= \sum \sum \sum p \beta_{pqr} h^p b^q c^r \\ \mathbf{B} &= b + \sum \sum \sum q \beta_{pqr} h^p b^q c^r \\ \mathbf{C} &= c + \sum \sum \sum r \beta_{pqr} h^p b^q c^r \end{aligned} \quad (2)$$

The symbols used in the present article are the same as those adopted in the previous work, chemical symbols are in roman and concentrations in *italic* type [22, 23]. In equations (2)  $\mathbf{H}$ ,  $\mathbf{B}$ , and  $\mathbf{C}$  represent the total (analytical) concentrations of  $H^+$ , metal and ligand, and  $h$ ,  $b$ , and  $c$  are the equilibrium concentrations of  $H^+$ ,  $V^{3+}$ , and  $C^-$ , respectively;  $K_w$  is the water dissociation constant and the formation function  $Z_C$  is defined as the average number of  $H^+$  bound per ligand [24],  $h$  being measured by means of emf(H) measurements [25].

Furthermore, using the FONDO concept [25], we take away the contribution of the equilibrium concentration of the products of the hydrolysis of the  $V^{III}$  ion,  $\sum \sum p c_{pqr}$ , and the equilibrium concentration of the HC species,  $c_{101}$ , from the total number of associate  $H^+$ ,  $CZ_C$ , and from the total concentration  $\mathbf{C}$ , and we also use the *reduced* formation function  $Z_{Cr}$  (3),

$$Z_{Cr} = (CZ_C - \sum \sum p c_{pqr} - c_{101}) / (\mathbf{C} - c_{101}) \quad (3)$$

instead of  $Z_C$ . In this way, we only observe the contribution of the species of the reaction (1) of interest.

### 2.2. Emf(H) measurements

The equilibrium emf(H) data  $[H, B, C, E_o, J, (v, E)_{np}]_{ns}$  ( $E_o$  and  $J$  = Nernst's equation parameters [26],  $ns$  = number of experiments,  $np$  = number of points in each experiment,  $v$  = reagent's aliquot,  $E$  = potential measured) were analyzed by means of the NERNST [27, 28] and FONDO [25] versions of LETAGROP [23]. For this purpose, functions listed in equations (4–6) were minimized,

$$U_1 = \sum (E - E^*)^2, \quad (4)$$

$$U_2 = \sum (Z_C - Z_C^*)^2, \quad (5)$$

$$U_3 = \sum (Z_{Cr} - Z_{Cr}^*)^2, \quad (6)$$

where  $E^*$ ,  $Z_C^*$ , and  $Z_{Cf}^*$  are the respective calculated values, according to the probable model of species  $(p, q, r, \beta_{pqr})_{nk}$ .

### 2.3. UV-Vis measurements

For the equilibrium UV-Vis data  $[-\log h, \mathbf{B}, \mathbf{C}, (D(\lambda)_{n\lambda})_{n_{sol}}]$  ( $D_\lambda$  = absorptivity values for  $n_\lambda$  wavelengths in each  $n_{sol}$  equilibrium solutions of known analytical composition), we assume that Beer's law is valid and that for each solution and wavelength,  $D$  may be expressed by equation (7),

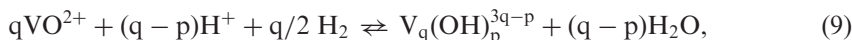
$$D = \sum \varepsilon_i c_i, \quad (7)$$

where  $c_i$  is the equilibrium concentration of the  $i$ th species in this solution,  $\varepsilon_i$  is its molar absorptivity for wavelength  $\lambda$ , and the sum is taken over all absorbing species. The UV-Vis data were analyzed using the SPEFO version [29] of LETAGROP [23], minimizing the function (8), where  $D^*$  are the corresponding calculated values of absorptivity.

$$U_3 = \sum (D - D^*)^2 \quad (8)$$

### 2.4. Materials, solutions, and methods

The reagents HCl and KOH, KCl, acetylacetonone and  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$  (Merck), free  $\text{O}_2$  and  $\text{CO}_2$  nitrogen and triply-distilled water were used as detailed in references [12] and [30]. The emf(H) titration method is described in reference [31], and the UV-Vis titration method outlined in reference [24]. 3.0 M (K, H)Cl, Ho M in  $\text{H}^+$  and 3.0 M K(OH, Cl), Ao M in  $\text{OH}^-$  solutions were prepared by weighing dry KCl, adding HCl and KOH (0.100 M ampoules) in the presence of nitrogen, and standardized *versus*  $\text{KHCO}_3$  and  $\text{KHC}_8\text{H}_4\text{O}_4$ , respectively. V(III) solutions were prepared by reducing a V(IV) solution, in turn prepared starting with  $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ , with hydrogen in the presence of platinized-Pt according to reaction (9) [11, 12, 32],



through which the value of the total concentration  $\mathbf{H}$  of those solutions was calculated [32] by means of the NERNST [27, 28] version of LETAGROP [23]. Under these conditions hydrogen is an excellent electron source for obtaining low oxidation states of ions having a standard potential at least 0.2 V greater than the  $\text{H}^+/\text{H}_2$  system [11, 12]. In effect, the standard potential of the  $\text{VO}^{2+}/\text{V}^{3+}$  system is 363.0 mV (3.0 KCl 3.0, 25°C) [32]. Finally, acetylacetonone solutions were prepared starting with the commercial product, which is then purified and distilled [17]. It was analyzed by adding excess  $\text{Ca}^{2+}$  to form the  $[\text{CaC}^+]$  complex according to reaction (10) [33], leaving off one  $\text{H}^+$  per mol of HC, which was later on potentiometrically titrated, figure 1.



### 3. Results and discussion

#### 3.1. *Emf(H)* measurements

The determination of the acidity constant  $pK_{\text{HC}}$  of acetylacetonate in terms of the formation function  $Z_c(\log h)$  is shown in figure 2.

The continuous line was generated using the value  $pK_{\text{HC}}=9.33(2)$  ( $\sigma(Z_c)=0.012$ ), which is very near to the one reported previously,  $pK_{\text{HC}}=9.36(1)$  ( $\sigma(Z_c)=0.010$ ), under similar experimental conditions [5]. For  $-\log h < 6$  the species HC prevail, whereas as the  $-\log h$  increases, the base  $\text{C}^-$  is formed, which predominates for  $-\log h > 10$ .

To study the  $\text{H}^+ - \text{V}^{3+}$ -acetylacetonate system by *emf(H)* measurements, four experiments with different ligand/metal ratio  $R$  are presented, namely, Experiment 1: ( $\text{V}^{\text{III}}$  and HC solution titrated with KOH solution):  $\text{B}=5.1\text{--}4.8\text{ mM}$ ,  $R=4.1$ ; Experiment 2: (*idem*):  $\text{B}=6.1\text{--}5.7\text{ mM}$ ,  $R=8.3$ ; Experiment 3: (HC solution titrated with  $\text{V}^{\text{III}}$  solution):  $\text{B}=0.7\text{--}15.5$ ,  $R=41.0\text{--}1.0$ ; and Experiment 4:  $\text{V}^{\text{III}}$  solution titrated with HC solution):  $\text{B}=7.6\text{--}5.1$ ,  $R=0.1\text{--}4$ . Figure 3 shows these experiments in terms of

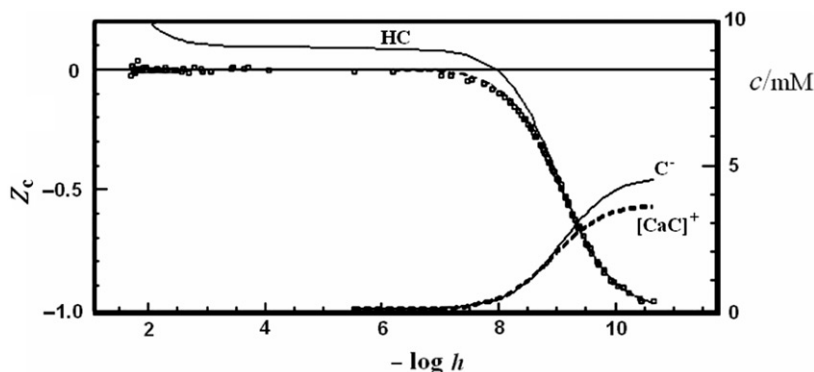


Figure 1.  $Z_c$ , average number of  $\text{H}^+$  associated per mole of ligand and species distribution diagram vs.  $-\log h$  for the  $\text{H}^+ - \text{Ca}^{2+}$ -acetylacetonate (HC) system in 3.0 M KCl ionic medium at 25°C, for  $\text{C}=10\text{ mM}$  and  $[\text{Ca}^{2+}]=30\text{ mM}$ . The lines represent theoretical curves calculated with the equilibrium constant  $\beta = 10^{-7.63(2)}$  for reaction  $\text{HC} + \text{Ca}^{2+} \leftrightarrow \text{CaC}^+ + \text{H}^+$ .

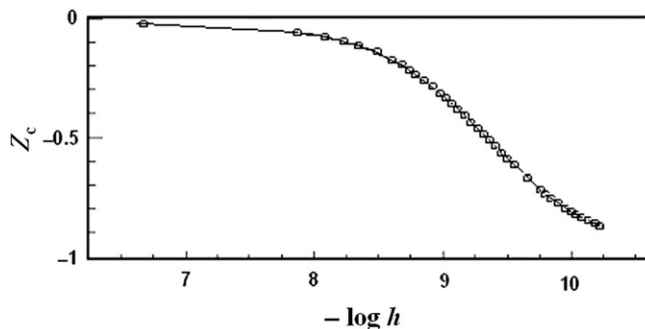


Figure 2.  $Z_c$  vs.  $-\log h$  for the  $\text{H}^+$ -acetylacetonate (HC) system in 3.0 M KCl ionic medium at 25°C. The line represents theoretical curve calculated with  $pK_{\text{HC}}=9.33(2)$ .

$Z_{Cr}(\log h)$ , assuming that FONDO =  $[\text{OHV}]^{2+}$ ,  $[(\text{OH})_2\text{V}_2]^{4+}$ ,  $[(\text{OH})_2\text{V}]^+$ ,  $(\text{OH})_{12}\text{V}_4$  and HC species [25].

Table 1 (columns 1–3) shows the equilibrium constants as well as the SDs.  $\sigma(E)$ ,  $\sigma(Z_C)$ , and  $\sigma(Z_{Cr})$  are determined using LETAGROP [23]. Both the equilibrium constants and the deviations  $\sigma(Z_C)$  and  $\sigma(Z_{Cr})$  are of the same order of magnitude, indicating the goodness of the fit.

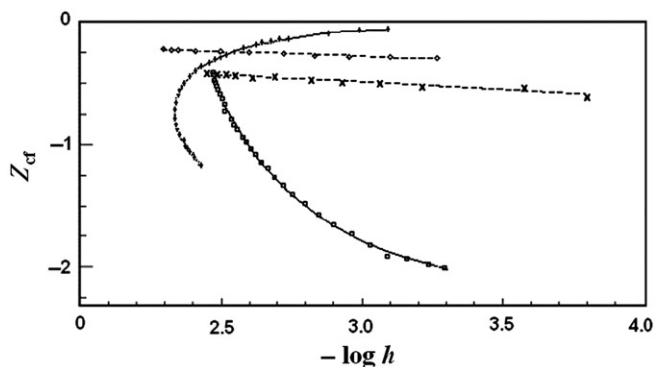


Figure 3.  $Z_{Cr}$  vs.  $-\log h$  for the  $\text{H}^+ - \text{V}^{3+}$ -acetylacetonate (HC) system in 3.0 M KCl ionic medium at 25°C, for Experiment 1: (x);  $\mathbf{B} = 5.1\text{--}4.8$  mM,  $R = 4.1$ ; Experiment 2: ( $\diamond$ );  $\mathbf{B} = 6.1\text{--}5.7$  mM,  $R = 8.2$ ; Experiment 3: (+);  $\mathbf{B} = 0.7\text{--}15.5$  mM,  $R = 41.0\text{--}1.0$ ; and Experiment 4: ( $\square$ );  $\mathbf{B} = 7.6\text{--}5.1$  mM,  $R = 0.1\text{--}4.1$ , according to reaction (1) and assuming that FONDO =  $[\text{VOH}]^{2+}$ ,  $[\text{V}_2(\text{OH})_2]^{4+}$ ,  $[\text{V}(\text{OH})_2]^+$ ,  $[\text{V}_4(\text{OH})_{12}]$ , and [HC] species. The lines represent theoretical curves calculated with equilibrium constants of table 1 (column 4).

Table 1. Equilibrium constants  $\beta_{pqr}$  for the  $\text{H}^+ - \text{V}^{3+}$ -acetylacetonate (HC) system in 3.0 M KCl ionic medium at 25°C, according to reaction (1).

Species	Log $\beta_{pqr}(3\sigma)$				
HC	9.33 <sup>a</sup>	9.33 <sup>a</sup>	9.33 <sup>a</sup>		
$[\text{VOH}]^+$	-3.13 <sup>a</sup>	-3.13 <sup>a</sup>	-3.13 <sup>a</sup>		
$[\text{V}_2(\text{OH})_2]^{2+}$	-3.76 <sup>a</sup>	-3.76 <sup>a</sup>	-3.76 <sup>a</sup>		
$[\text{V}(\text{OH})_2]^+$	-6.59(1)	-6.59(1)	-6.59(1)		
$\text{V}_4(\text{OH})_{12}$	-32.61(7)	-32.71(7)	-32.61(7)		
$[\text{VC}]^{2+}$	9.64(5)	9.57(2)	9.59(2)	9.5(<9.8) <sup>b</sup>	10.19
$[\text{VC}_2]^+$	18.56(6)	18.49(6)	18.53(5)	18.9(2)	19.18
$\text{VC}_3$	26.17(5)	26.1(1)	26.10(9)	26.7(<26.9) <sup>b</sup>	26.10
$[\text{VOHC}]^+$	7.19(4)	7.21(1)	7.20(1)	6.7(2)	
$[\text{V}_2(\text{OH})_2\text{C}]^{3+}$	6.2(<6.5) <sup>b</sup>	5.9(1)	6.1(1)		
$\text{VOHC}_2$	14.5(2)	14.2(<14.5) <sup>b</sup>	14.3(4)		
$[\text{V}_2(\text{OH})_2\text{C}_2]^{2+}$	15.2(<15.8) <sup>b</sup>				
$\sigma(E)$	1.34 mV				
$\sigma(\theta_C)$		0.0079			
$\sigma(\theta_{Cr})$			0.0075		
$\sigma(D)$				0.005	
Medium (°C)	3.0 KCl/25	3.0 KCl/25	3.0 KCl/25	3.0 KCl/25	0.1 NaClO <sub>4</sub> /25
Method	Emf(H)	Emf(H)	Emf(H)	UV-Vis	Liquid-liquid partition [18]
References	This work	This work	This work	This work	[18]

Notes: <sup>a</sup>Equilibrium constants kept invariable.

<sup>b</sup>Equilibrium constants with  $(100(3\sigma)/\beta_{pqr}) > 20\%$  [23].

Figures 4–7 show the species distribution diagrams for these experiments, which were generated using the equilibrium constant values of table 1 (column 4). It is observed that  $[\text{VC}]^{2+}$ ,  $[\text{VC}_2]^+$ ,  $\text{VC}_3$ , and  $[\text{OHVC}]^+$  are the most significant,  $[\text{OHVC}]^+$  is less abundant, and  $[(\text{OH})_2\text{V}_2\text{C}]^{3+}$  is scarce.

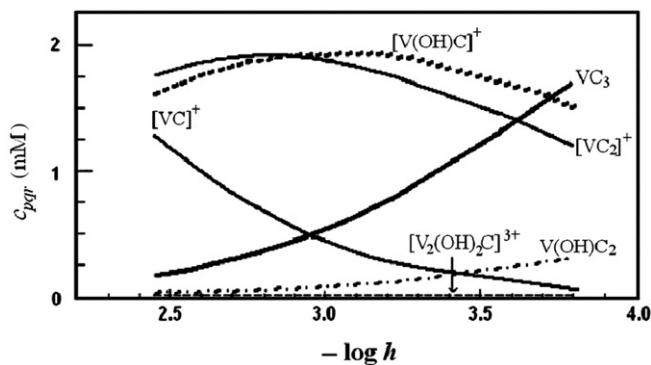


Figure 4. Species distribution diagram for the  $\text{H}^+ - \text{V}^{3+}$ -acetylacetonate (HC) system in 3.0 M KCl ionic medium at 25°C for, Experiment 1.

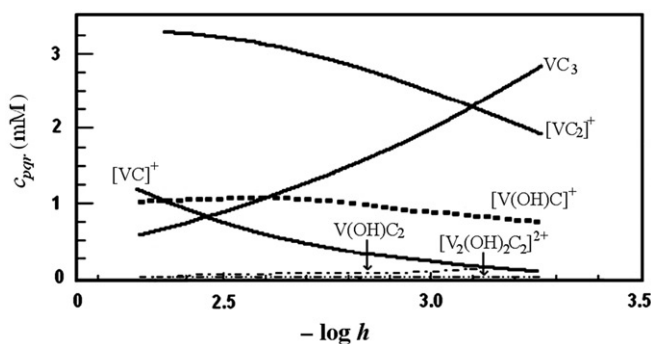


Figure 5. Species distribution diagram for the  $\text{H}^+ - \text{V}^{3+}$ -acetylacetonate (HC) system in 3.0 M KCl ionic medium at 25°C, for Experiment 2.

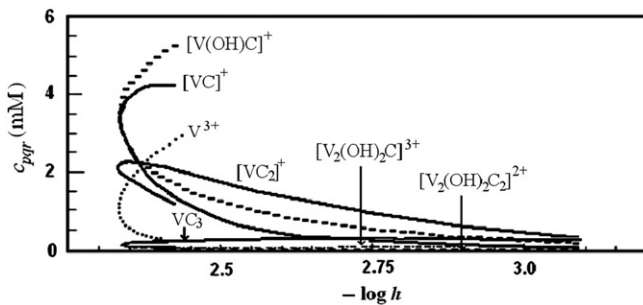


Figure 6. Species distribution diagram for the  $\text{H}^+ - \text{V}^{3+}$ -acetylacetonate (HC) system in 3.0 M KCl ionic medium at 25°C, for Experiment 3.



### 3.2. UV-Vis measurements

We now discuss the results of the  $H^+-V^{3+}$ -acetylacetonone system by UV-Vis measurements. Figure 8 shows the absorption spectra  $[(D(\lambda)_{n\lambda}]_{n_{sol}}$  for  $n_{sol}=10$ ,  $n\lambda=14$ ,  $B=2.0$  mM,  $C=10.0$  mM, and for the wavelength intervals  $400 \leq \lambda \leq 650$  nm and  $2.950 \leq -\log h \leq 3.635$ . The intensity of the band increases as  $-\log h$  diminishes, due to formation of the products of reaction (1).

Table 1 (column 5) contains the equilibrium constants for the four most abundant complexes of this system,  $[VC]^{2+}$ ,  $[VC_2]^+$ ,  $VC_3$ , and  $[OHVC]^+$ . In figure 9 there are five representative experimental (points) and calculated spectra (trace-line), for  $-\log h=2.956, 3.180, 2.350, 3.272$ , and  $3.631$ , with the best fit.

Figure 10 presents the present data in terms of absorptivity  $D$  versus the molar ratio  $R$  (the so-called mole-ratio method [34]) for four wavelengths in the interval  $400 \leq \lambda \leq 460$  nm, with best fit. The dotted lines were calculated using the stability constants of column 5 of table 1.

The stability constant values determined through UV-Vis measurements (column 5) are of the same order of magnitude as determined by emf(H) measurements

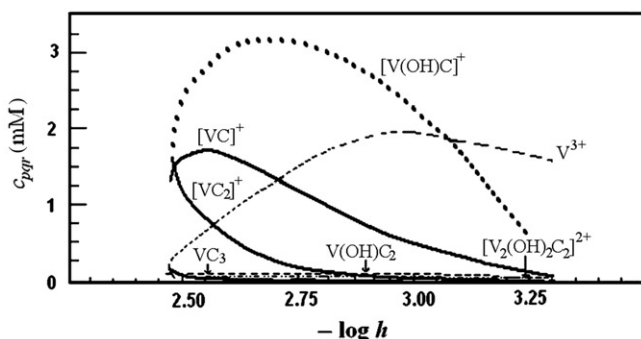


Figure 7. Species distribution diagram for the  $H^+-V^{3+}$ -acetylacetonone (HC) system in 3.0 M KCl ionic medium at 25°C, for Experiment 4.

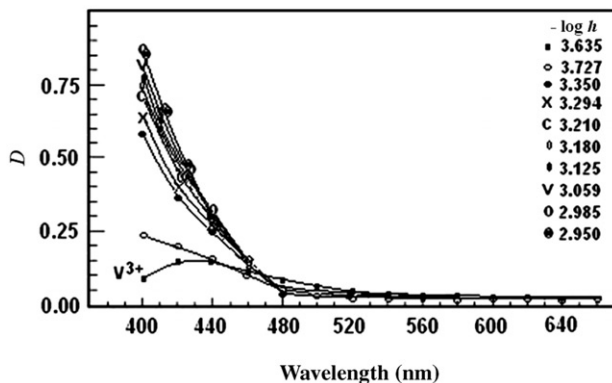


Figure 8. Absorption spectra for the  $H^+-vanadium(III)-acetylacetonone$  (HC) system in 3.0 M KCl ionic medium at 25°C, and for the ranges  $400 \leq \lambda \leq 650$  nm and  $2.950 \leq -\log h \leq 3.635$ .

(columns 2–4), but have larger dispersions, indicating that emf(H) measurements are more reliable than those of UV–Vis.

### 3.3. Linear free energy relationship $\Delta G_{pqr}(E_{\text{periodicbox}})$

Finally, for comparative purposes, the stability constants  $\beta_{pqr}$  for  $V^{2+}$ -acetylacetonate [6],  $V^{3+}$ -acetylacetonate (this work), and  $V^{IV}$ -acetylacetonate [5] complexes are summarized in table 2 showing the stability order  $V^{II} < V^{III} > V^{IV}$ , agreeing with that predicted in the linear free energy relationship [35] of figure 11, where the corresponding free energy  $\Delta G_{pqr}$  ( $= -1.3642 RT \log \beta_{pqr}$ ) values versus the structural energy calculations  $E_{\text{periodic box}}$  using the program HyperChem (*ab initio*, STO-3G, MM+, periodic box) [36, 37] for species  $V^{III}C_3$  and  $[V^{II}C_3]^-$  (bottom curve);  $[V^{III}C_2]^+$ ,  $V^{IV}OC_2$  and  $V^{II}C_2$  (intermediate curve 1);  $[V^{III}C]^{2+}$ ,  $[VO^{IV}C]^+$  and  $[V^{II}C]^+$  (intermediate curve 2); and hydroxyl species  $[OHV^{III}C]^+$  and  $[OHV^{IV}OC]$  (top curve) were plotted. This program places the molecular system in a periodic box containing water molecules, which imposes periodic boundary conditions on calculations. For this purpose, molecules can move in a constant density environment, similar to being in a liquid.

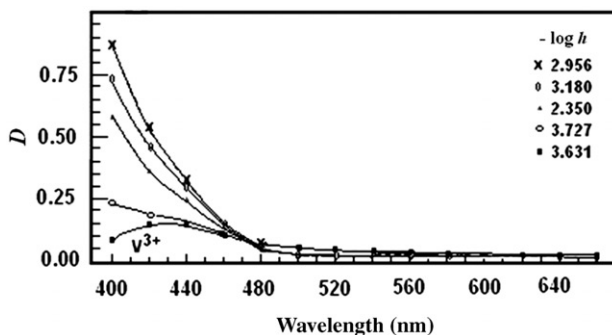


Figure 9. Five representative experimental (points) and calculated (trace-line) absorption spectra for the  $H^+$ –vanadium(III)-acetylacetonate (HC) system in 3.0 M KCl ionic medium at 25°C, for  $-\log h = 2.956$  (+), 3.180 ( $\diamond$ ), 2.350 ( $\Delta$ ), 3.272 ( $\times$ ) and 3.631 ( $\square$ ), and 14 wavelengths in the range  $400 \leq \lambda \leq 660$  nm, in the position of best fit.

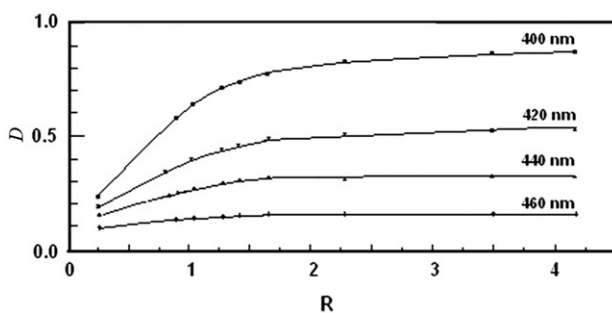


Figure 10. Absorptivity values  $D$  at 460 (+), 440 ( $\Delta$ ), 420 ( $\times$ ), and 400 ( $\square$ ) vs. the molar ratio  $R$ .

Table 2. Stability constants  $\beta_{pqr}$  of  $V^{II}$ -,  $V^{III}$ - and  $V^{IV}$ -acetylacetonone complexes.

V(II)		V(III)		V(IV)	
$[VC]^+$	$10^{5.38(1)}$	$[VC]^{2+}$	$10^{9.36(5)}$	$[VOC]^+$	$10^{8.85(3)}$
$VC_2$	$10^{10.19(3)}$	$[VC_2]^+$	$10^{18.59(6)}$	$VOC_2$	$10^{16.42(5)}$
$[VC_3]^-$	$10^{14.70(1)}$	$VC_3$	$10^{26.21(7)}$	$VOOHC$	$10^{3.6(1)}$
		$[VOHC]^+$	$10^{7.23(2)}$		
		$VOHC_2$	$10^{14.3(2)}$		
Ionic medium ( $^{\circ}C$ )	1.0 M KCl/25		3.0 M KCl/25		3.0 M KCl/25
References	[35]		This work		[5]

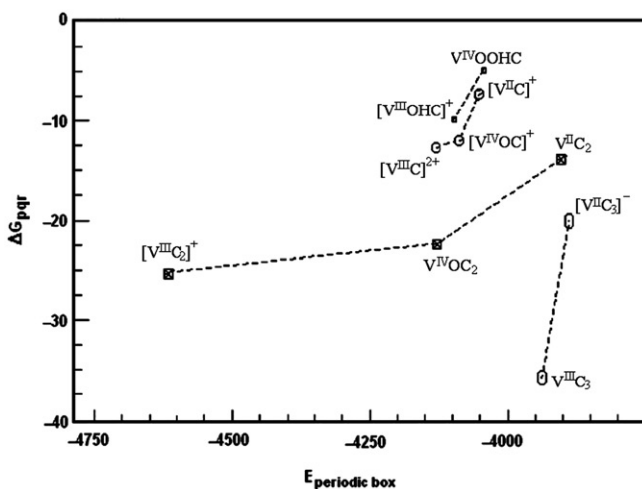


Figure 11. Free energy  $\Delta G_{pqr}$  ( $Kcal\ mol^{-1}$ ) values vs. the result of structural energy calculations (*ab initio*, STOG-3G, MM+, periodic box, 216  $H_2O$  molecules), for  $V^{III}C_3$  and  $[V^{III}C_3]^-$  (bottom curve),  $[V^{III}C_2]^+$ ,  $V^{IV}OC_2$  and  $V^{II}C_2$  (intermediate curve 1),  $[V^{III}C]^{2+}$ ,  $[V^{IV}OC]^+$  and  $[V^{II}C]^+$  (intermediate curve 2) species, and  $[V^{III}OHC]^+$  and  $V^{IV}OOHC$  (top curve) hydroxyl species.

According to this simulation, although  $V^{II}$  does not form OHVC [6], nor  $V^{IV}$ ,  $[VOC_3]^-$  [5]; in each series  $n:1$  ( $n=1-3$ ) the most stable complexes are those of  $V^{III}$ , followed by those of  $V^{IV}O^{2+}$  and of  $V^{II}$ .

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## References

- [1] M. Melchior, S.J. Retting, B. Liboiron, K.H. Thompson, V.G. Yuen, J.H. McNei, C. Orvig. *Inorg. Chem.*, **40**, 4686 (2001).

- [2] A. Evangelou, S. Karkabounas, G. Malamas, R. Liasko, D. Stefanou, A.T. Vlahos. *Cancer Lett.*, **119**, 221 (1997).
- [3] F.E. Fenton. *Biocoordination Chemistry*, p. 19, Oxford Science Publications, Oxford (1995).
- [4] D.C. Crans, J.J. Smee, E. Gaidamauskas, L. Yang. *Chem. Rev.*, **104**, 849 (2004).
- [5] J.M. Goncalves. Termodinámica del sistema vanadio(IV)-acetilacetona, Undergraduate thesis, Escuela de Química, Facultad de Ciencias, UCV (1973).
- [6] W. Shaefer. *Inorg. Chem.*, **4**, 642 (1965).
- [7] R. Trujillo, F. Brito. *An. Fis. Quím.*, **52B**, 407 (1956) and **53B**, 441 (1957).
- [8] M.V. Medina. Complejos de vanadio(V) y acetilacetona, Undergraduate thesis, Escuela de Química, Facultad de Ciencias, UCV (2008).
- [9] L. Pajdowski. *J. Inorg. Nucl. Chem.*, **28**, 433 (1966).
- [10] D.T. Richens, C. Chem. *The Chemistry of Aqua Ions*, p. 232, John Wiley & Sons, Chichester (1997).
- [11] F. Brito. *An. Fis. Quím.*, **62**, 193 (1966).
- [12] S. Mateo, F. Brito. *An. Fis. Quím.*, **64**, 115 (1968).
- [13] R. Meier, M. Boldin, S. Mitzenhein, K. Kanamori. *Metal Ions Biol. Syst.*, **31**, 45 (1995).
- [14] P. Buglyo, D. Crans, E. Nagy, R. Lindo, L. Smee, W. Jin, M. Godzala, G. Willsky. *Inorg. Chem.*, **44**, 5416 (2005).
- [15] A.B. Lever. *Inorganic Electronic Spectroscopy*, 2nd Edn, p. 400, Elsevier, Amsterdam (1984).
- [16] M. Eidinoff. *J. Am. Chem. Soc.*, **67**, 2073 (1945).
- [17] J. Rydberg. *Svensk Kemisk Tidskrift*, **62**, 179 (1950).
- [18] F.A. Cotton, G. Wilinsson. *Advanced Inorganic Chemistry*, 5th Edn, p. 674, John Wiley & Sons, New York (1988).
- [19] M. Kitamura, K. Sasaki, H. Imai. *Bull. Chem Soc. Jpn.*, **50**, 3199 (1977).
- [20] M.A. Nawi, T.L. Riechel. *Inorg. Chem.*, **20**, 1974 (1981).
- [21] H. Imura, N. Suzuki. *Bull. Chem. Soc. Jpn.*, **59**, 2779 (1986).
- [22] F. Brito, J. Ascanio, S. Mateo, C. Hernández, M.L. Araujo, P. Gili, P. Martín, S. Domínguez, A. Mederos. *Polyhedron*, **16**, 3835 (1997).
- [23] L.G. Sillén, R. Arnek, O. Wahlberg, P. Brauner, R. Whiteker. *Arkiv Kemi*, **31**, 315, 341, 353, 365, and 377 (1969).
- [24] M.T. Armas, R. Hernández, A. Mederos, P. Gili, S. Domínguez, P. Lorenzo, E. Baran, M.L. Araujo, F. Brito. *Polyhedron*, **20**, 799 (2001).
- [25] F. Brito, M.L. Araujo, V. Lubes, A. D'Ascoli, A. Mederos, P. Gili, S. Domínguez, E. Chinaea, R. Hernández, M.T. Armas, E. Baran. *J. Coord. Chem.*, **58**, 501 (2005).
- [26] G. Biedermann, L.G. Sillén. *Arkiv Kemi*, **5**, 425 (1953).
- [27] F. Brito, J.M. Goncalves. Project S1-1228, CONICIT, Caracas (1981).
- [28] F. Brito, A. Mederos, P. Gili, S. Domínguez, P. Martín. *J. Coord. Chem.*, **17**, 311 (1988).
- [29] L.G. Sillén, B. Warnqvist. *Arkiv Kemi*, **31**, 377 (1969).
- [30] S. Mateo, F. Brito. *An. Quím.*, **68**, 37 (1972).
- [31] Y. Goncalves. Automatización de un sistema de adquisición de datos potenciométricos, Master thesis, CES and Postgrado en Instrumentación, Facultad de Ciencias, UCV (2006).
- [32] F. Brito, J.M. Goncalves. *An. Quím.*, **78**, 104 (1982).
- [33] R. Trujillo, F. Brito. *An. Fis. Quím.*, **52B**, 417 (1956).
- [34] M.T. Beck, I. Nagypál. *Chemistry of Complex Equilibria*, p. 118, Ellis Horwood Limited, Chichester (1990).
- [35] A. Martell, R. Hancock. *Metal Complexes in Aqueous Solutions*, p. 26, Plenum Press, Nueva Cork (1996).
- [36] HyperChem 5.0. Reference Manual, Hypercube, Inc., Gainesville, Florida, p. 219 (1996).
- [37] W.L. Jorgensen, J. Chandrasekhar, D. Madura. *J. Chem. Phys.*, **79**, 926 (1983).