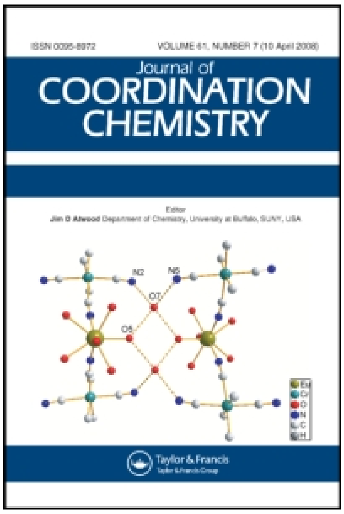

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Speciation of the vanadium(III)-acetylacetone system in 3.0 M KCl ionic medium at 25°C

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

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A study of the H^+-acetylacetone (acac, HC) and H^+–V^{3+}-acetylacetone 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 acetylacetone 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+}-acetylacetone 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}-acetylacetone complexes were obtained by *ab initio* calculations.

Keywords: Acetylacetone; 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 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^+-acetylacetone and H^+-vanadium(III)-acetylacetone 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 acetylacetone pK_a value and compare it with one previously determined under similar experimental conditions [5]; subsequently, we study the H^+–V^{3+}-acetylacetone system as the fundamental objective of this work, which will supplement previous investigations on H^+–V^{2+}-acetylacetone [6] and H^+–VO^{2+}-acetylacetone [5, 7] systems, as well as recent work on the H^+–VO_2^+ -acetylacetone 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 ε 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, acetylacetone (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) $HE \leftrightarrows HQ$ 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+}-acetylacetone 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 acetylacetone 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 acetylacetone 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 acetylacetone 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 intermerdiates. $VO(acac)_3$ 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+}-acetylacetone 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 acetylacetone should form *nk* complexes $H_pV_qC_r^{p+3q-r}$. 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).

$$p\,H^+ + q\,V^{3+} + r\,C^- \rightleftarrows H_pV_qC_r^{p+3q-r} \tag{1}$$

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

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

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) **H**, **B**, and **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, $\Sigma\Sigma\, p\, c_{pqo}$, and the equilibrium concentration of the HC species, c_{101}, from the total number of associate H^+, $\mathbf{C}Z_C$, and from the total concentration **C**, and we also use the *reduced* formation function Z_{Cf} (3),

$$Z_{Cf} = (\mathbf{C}Z_C - \Sigma\Sigma\, p\, c_{pqo} - c_{101})/(\mathbf{C} - c_{101}) \tag{3}$$

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 $[\mathbf{H}, \mathbf{B}, \mathbf{C}, E_o, J, (v, E)_{np}]_{ns}$ (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,

$$U_1 = \Sigma(E - E^*)^2, \tag{4}$$

$$U_2 = \Sigma\left(Z_C - Z_C^*\right)^2, \tag{5}$$

$$U_3 = \Sigma\left(Z_{Cf} - Z_{Cf}^*\right)^2, \tag{6}$$

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 $[-\log h, \mathbf{B}, \mathbf{C}, (D(\lambda)_{n\lambda}]_{n\mathrm{sol}}$ (D_λ = absorptivity values for n_λ 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),

$$D = \Sigma\, \varepsilon_i\, c_i, \tag{7}$$

where c_i is the equilibrium concentration of the ith species in this solution, ε_i is its molar absorptivity for wavelength λ, 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.

$$\mathrm{U}_3 = \Sigma(D - D^*)^2 \tag{8}$$

2.4. *Materials, solutions, and methods*

The reagents HCl and KOH, KCl, acetylacetone and $VOSO_4 \cdot 5H_2O$ (Merck), free O_2 and 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 H^+ and 3.0 M K(OH, Cl), Ao M in OH^- solutions were prepared by weighing dry KCl, adding HCl and KOH (0.100 M ampoules) in the presence of nitrogen, and standardized *versus* $KHCO_3$ and $KHC_8H_4O_4$, respectively. V(III) solutions were prepared by reducing a V(IV) solution, in turn prepared starting with $VOSO_4 \cdot 5H_2O$, with hydrogen in the presence of platinized-Pt according to reaction (9) [11, 12, 32],

$$\mathrm{qVO^{2+} + (q-p)H^+ + q/2\ H_2 \rightleftarrows V_q(OH)_p^{3q-p} + (q-p)H_2O}, \tag{9}$$

through which the value of the total concentration **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 H^+/H_2 system [11, 12]. In effect, the standard potential of the VO^{2+}/V^{3+} system is 363.0 mV (3.0 KCl 3.0, 25°C) [32]. Finally, acetylacetone solutions were prepared starting with the commercial product, which is then purified and distilled [17]. It was analyzed by adding excess Ca^{2+} to form the $[CaC^+]$ complex according to reaction (10) [33], leaving off one H^+ per mol of HC, which was later on potentiometrically titrated, figure 1.

$$\mathrm{Ca^{2+} + HC \rightleftarrows CaC^+ + H^+} \tag{10}$$

3. Results and discussion

3.1. *Emf(H) measurements*

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

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

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

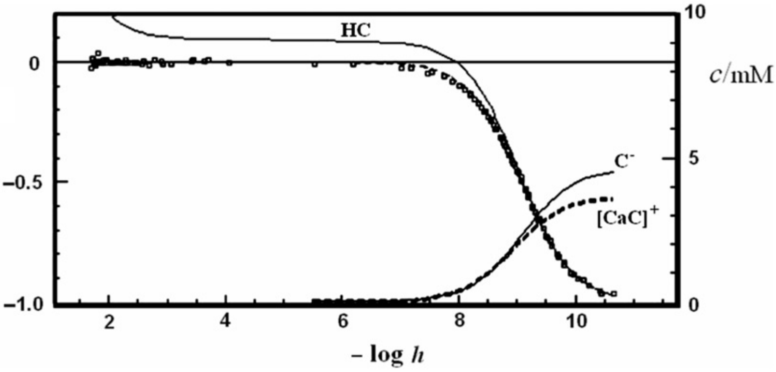

Figure 1. Z_C, average number of H^+ associated per mole of ligand and species distribution diagram *vs.* $-\log h$ for the H^+–Ca^{2+}-acetylacetone (HC) system in 3.0 M KCl ionic medium at 25°C, for $\mathbf{C} = 10$ mM and $[Ca^{2+}] = 30$ mM. The lines represent theoretical curves calculated with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

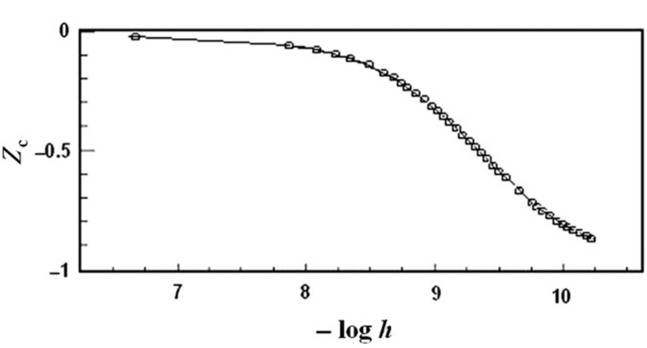

Figure 2. Z_C *vs.* $-\log h$ for the H^+-acetylacetone (HC) system in 3.0 M KCl ionic medium at 25°C. The line represents theoretical curve calculated with $pK_{HC} = 9.33(2)$.

$Z_{Cf}(\log h)$, assuming that FONDO = $[OHV]^{2+}$, $[(OH)_2V_2]^{4+}$, $[(OH)_2V]^{+}$, $(OH)_{12}V_4$ and HC species [25].

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

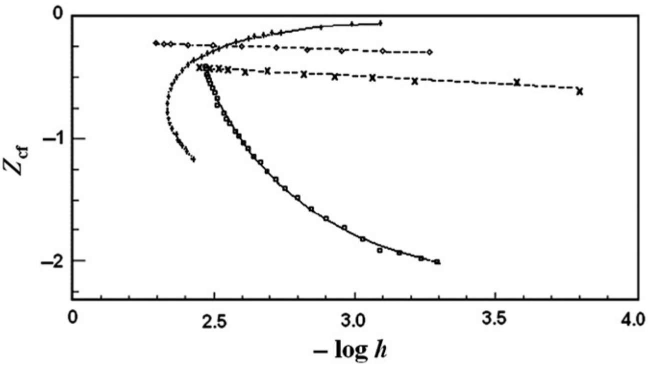

Figure 3. Z_{Cf} *vs.* $-\log h$ for the H^+–V^{3+}-acetylacetone (HC) system in 3.0 M KCl ionic medium at 25°C, for Experiment 1: (×): $\mathbf{B} = 5.1$–4.8 mM, $R = 4.1$; Experiment 2: (◇): $\mathbf{B} = 6.1$–5.7 mM, $R = 8.2$; Experiment 3: (+): $\mathbf{B} = 0.7$–15.5 mM, $R = 41.0$–1.0; and Experiment 4: (□): $\mathbf{B} = 7.6$–5.1 mM, $R = 0.1$–4.1, according to reaction (1) and assuming that FONDO = $[VOH]^{2+}$, $[V_2(OH)_2]^{4+}$, $[V(OH)_2]^{+}$, $[V_4(OH)_{12}]$, and [HC] species. The lines represent theoretical curves calculated with equilibrium constants of table 1 (column 4).

Table 1. Equilibrium constants β_{pqr} for the H^+–V^{3+}-acetylacetone (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[a]	9.33[a]	9.33[a]		
$[VOH]^+$	−3.13[a]	−3.13[a]	−3.13[a]		
$[V_2(OH)_2]^{2+}$	−3.76[a]	−3.76[a]	−3.76[a]		
$[V(OH)_2]^+$	−6.59(1)	−6.59(1)	−6.59(1)		
$V_4(OH)_{12}$	−32.61(7)	−32.71(7)	−32.61(7)		
$[VC]^{2+}$	9.64(5)	9.57(2)	9.59(2)	9.5(<9.8)[b]	10.19
$[VC_2]^+$	18.56(6)	18.49(6)	18.53(5)	18.9(2)	19.18
VC_3	26.17(5)	26.1(1)	26.10(9)	26.7(<26.9)[b]	26.10
$[VOHC]^+$	7.19(4)	7.21(1)	7.20(1)	6.7(2)	
$[V_2(OH)_2C]^{3+}$	6.2(<6.5)[b]	5.9(1)	6.1(1)		
$VOHC_2$	14.5(2)	14.2(<14.5)[b]	14.3(4)		
$[V_2(OH)_2C_2]^{2+}$	15.2(<15.8)[b]				
$\sigma(E)$	1.34 mV				
$\sigma(\theta_C)$		0.0079			
$\sigma(\theta_{Cf})$			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 $NaClO_4$/25
Method	Emf(H)	Emf(H)	Emf(H)	UV–Vis	Liquid–liquid partition
References	This work	This work	This work	This work	[18]

Notes: [a]Equilibrium constants kept invariable.
[b]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 $[VC]^{2+}$, $[VC_2]^+$, VC_3, and $[OHVC]^+$ are the most significant, $[OHVC]^+$ is less abundant, and $[(OH)_2V_2C]^{3+}$ is scarce.

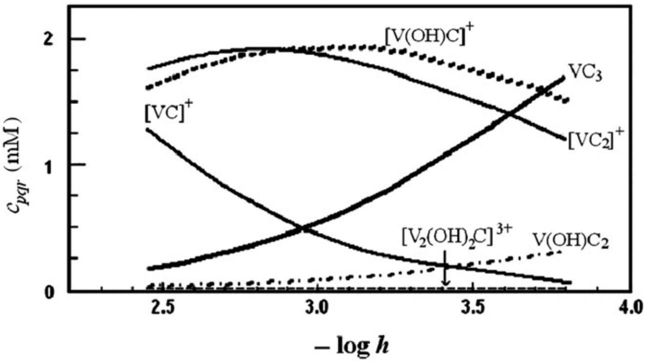

Figure 4. Species distribution diagram for the H^+–V^{3+}-acetylacetone (HC) system in 3.0 M KCl ionic medium at 25°C for, Experiment 1.

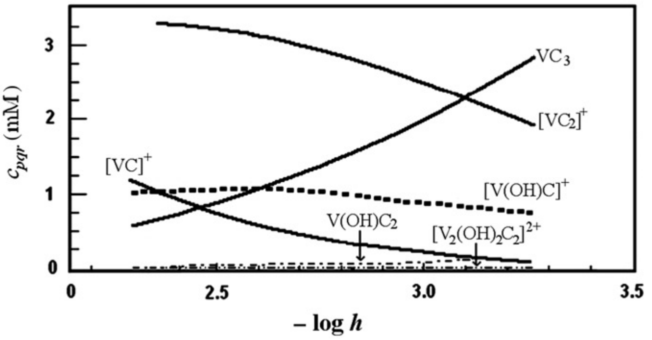

Figure 5. Species distribution diagram for the H^+–V^{3+}-acetylacetone (HC) system in 3.0 M KCl ionic medium at 25°C, for Experiment 2.

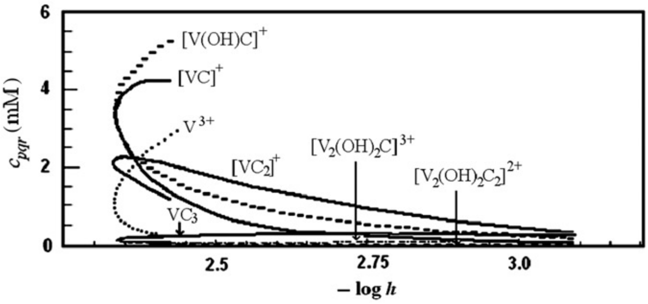

Figure 6. Species distribution diagram for the H^+–V^{3+}-acetylacetone (HC) system in 3.0 M KCl ionic medium at 25°C, for Experiment 3.

3.2. *UV–Vis measurements*

We now discuss the results of the H^+–V^{3+}-acetylacetone system by UV–Vis measurements. Figure 8 shows the absorption spectra $[(D(\lambda)_{n\lambda}]_{n\mathrm{sol}}$ for $n_{\mathrm{sol}} = 10$, $n\lambda = 14$, $\mathbf{B} = 2.0\,\mathrm{mM}$, $\mathbf{C} = 10.0\,\mathrm{mM}$, and for the wavelength intervals $400 \le \lambda \le 650\,\mathrm{nm}$ and $2.950 \le -\log h \le 3.635$. 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 $400 \le \lambda \le 460\,\mathrm{nm}$, 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

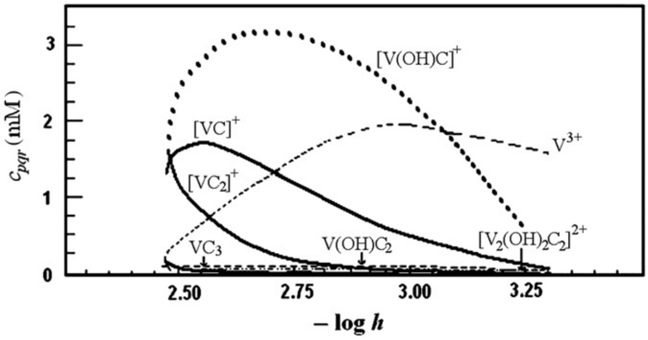

Figure 7. Species distribution diagram for the H^+–V^{3+}-acetylacetone (HC) system in 3.0 M KCl ionic medium at 25°C, for Experiment 4.

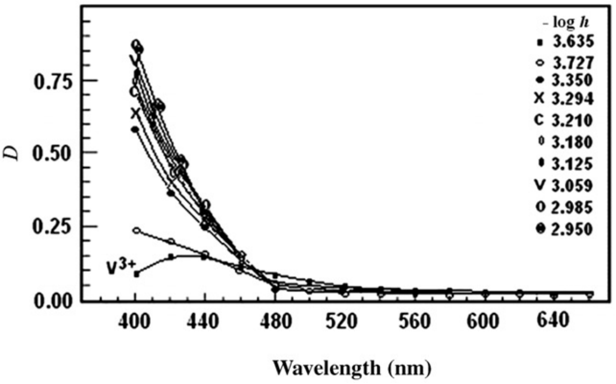

Figure 8. Absorption spectra for the H^+–vanadium(III)-acetylacetone (HC) system in 3.0 M KCl ionic medium at 25°C, and for the ranges $400 \le \lambda \le 650\,\mathrm{nm}$ and $2.950 \le -\log h \le 3.635$.

(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* $\Delta G_{pqr}(E_{periodicbox})$

Finally, for comparative purposes, the stability constants β_{pqr} for V^{2+}-acetylacetone [6], V^{3+}-acetylacetone (this work), and V^{IV}-acetylacetone [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 ΔG_{pqr} ($= -1.3642\ RT\ \log \beta_{pqr}$) values *versus* the structural energy calculations $E_{\text{periodic box}}$ using the program HyperChem (*ab initio*, STOG-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.

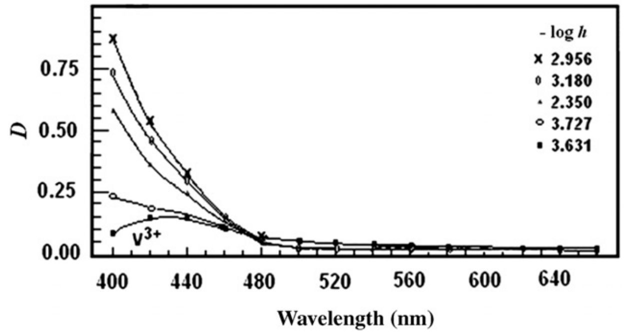

Figure 9. Five representative experimental (points) and calculated (trace-line) absorption spectra for the H^+–vanadium(III)-acetylacetone (HC) system in 3.0 M KCl ionic medium at 25°C, for $-\log h = 2.956$ (+), 3.180 (◇), 2.350(Δ), 3.272 (×) and 3.631 (□), and 14 wavelengths in the range $400 \le \lambda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

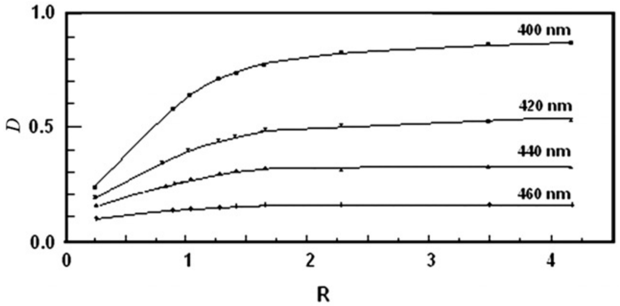

Figure 10. Absorptivity values D at 460 (+), 440 (Δ), 420 (×), and 400 (□) *vs.* the molar ratio R.

Table 2. Stability constants β_{pqr} of V^{II}-, V^{III}- and V^{IV}-acetylacetone 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	$10^{26.21(7)}$		
		$[VOHC]^+$	$10^{7.23(2)}$	VOOHC	$10^{3.6(1)}$
		$VOHC_2$	$10^{14.3(2)}$		
Ionic medium (°C)	1.0 M KCl/25		3.0 M KCl/25		3.0 M KCl/25
References	[35]		This work		[5]

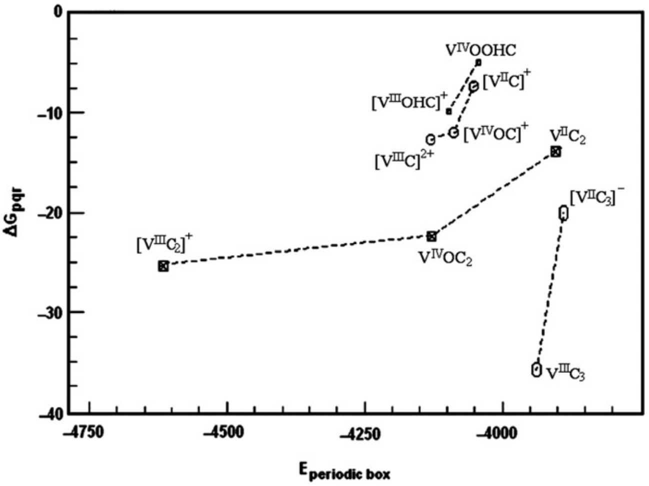

Figure 11. Free energy ΔG_{Pqr} (Kcal mol^{-1}) values *vs*. the result of structural energy calculations (*ab initio*, STOG-3G, MM+, periodic box, 216 H_2O molecules), for $V^{III}C_3$ and $[V^{II}C_3]^-$ (bottom curve), $[V^{III}C_2]^+$, $V^{IV}OC_2$ and $V^{II}C_2$ (intermediate curve 1), $[V^{III}C]^{2+}$,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