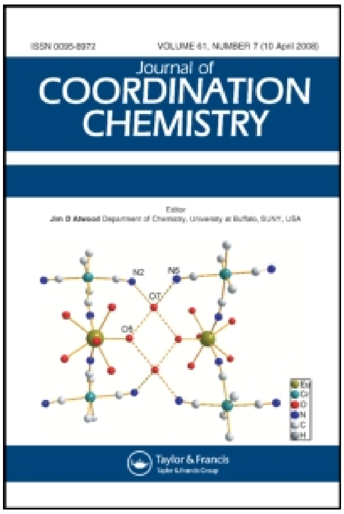

Journal of Coordination Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Solution studies of vanadium(IV) complexes with nitrilotriacetic acid (NTA) and other aminopolycarboxylic acids (NDAP, NDPA, and NTP)

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To cite this Article Araujo, ML , Brito, F. , Cecarello, I. , Guilarte, C. , Martinez, JD , Monsalve, G. , Oliveri, V. , Rodriguez, I. and Salazar, A.(2009) 'Solution studies of vanadium(IV) complexes with nitrilotriacetic acid (NTA) and other aminopolycarboxylic acids (NDAP, NDPA, and NTP)', Journal of Coordination Chemistry, 62: 1, 75 — 81

To link to this Article: DOI: 10.1080/00958970802474813

URL: http://dx.doi.org/10.1080/00958970802474813

Journal of Coordination Chemistry
Vol. 62, No. 1, 10 January 2009, 75–81

Solution studies of vanadium(IV) complexes with nitrilotriacetic acid (NTA) and other aminopolycarboxylic acids (NDAP, NDPA, and NTP)

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(*Received 10 June 2008; in final form 21 July 2008*)

Complexes of vanadium(IV) with aminopolycarboxylic acids, nitrilotriacetic (NTA), nitrilodiaceticpropionic (NDAP), nitrilodipropionicacetic (NDPA), and nitrilotripropionic (NTP) acids were studied by electromotrice force measurements [emf(H)] in 3.0 M KCl ionic medium at 25°C. Data analysis using the least-squares program LETAGROP, according to the general reaction $p\ \mathrm{H}^{+} + q\ \mathrm{VO}^{2+} + r\ \mathrm{C}^{3-} \leftrightarrows \mathrm{H}_p(\mathrm{VO})_q\mathrm{C}_r^{\,p+2q-3r}$, indicates that the following complexes are formed (H_3C ligands): NTA ($[\mathrm{VOC}]^{-}$ and $[\mathrm{OHVOC}]^{2-}$); NDAP ($[\mathrm{VOC}]^{-}$ and $[\mathrm{OHVOC}]^{2-}$); NDPA ($[\mathrm{VOC}]^{-}$ and $[\mathrm{OHVOC}]^{2-}$); and NTP ($[\mathrm{H_2VOC}]^{+}$, HVOC, $[\mathrm{VOC}]^{-}$, and $[\mathrm{OHVOC}]^{2-}$). The following order of coordination capacity NTA > NDAP > NDPA > NTP is suggested, based on values of stability constants and is attributed to the increase in propionic groups in the sequence. The study confirms that five-membered ring chelates are the most stable for V^{IV}, like $\mathrm{Cu}^{\mathrm{II}}$, $\mathrm{Ni}^{\mathrm{II}}$, lanthanides, and other heavier elements.

Keywords: Solution equilibria; Vanadium(IV) complexes; Aminopolycarboxylic acids; Stability constants; LETAGROP program

1. Introduction

The coordination chemistry of vanadium plays an important role in the interaction with biomolecules [1]. Among the biological functions attributed to vanadium are therapeutic, hormonal, cardiovascular effects and anticarcinogen activity [2–6].

Several studies have been reported on complexes of nitrilotriacetic (NTA), nitrilodiaceticpropionic (NDAP), nitrilodipropionicacetic (NDPA), and nitrilotripropionic (NTP) acids (figure 1) with ions like Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Cd^{2+}, and Mg^{2+} [7].

The present work reports the results of the study of the complexes of vanadium(IV) with these ligands by electromotrice force measurements [emf(H)], in 3.0 M KCl ionic medium at 25°C.

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Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online
DOI: 10.1080/00958970802474813

In water solution the oxovanadium(IV) ion, $[VO(H_2O)_5]^{2+}$, briefly VO^{2+}, hydrolyzes at $-\log h > 2.5$ forming $[OHVO]^+$, $[(OH)_2(VO)_2]^{2+}$, and $(OH)_2VO$ [8]. For $-\log h > 4$ $(OH)_2VO$ precipitates, but re-dissolves above $-\log h = 10$ to give clear brown solutions from which brown-black salts such as $K_{12}[V_{18}O_{42}] \cdot 24\ H_2O$ can be isolated [9].

In connection with vanadium(IV) complexes with the aforementioned ligands, there is only information on complexes with NTA acid, as shown in table 1 [10–14].

In the present investigation the VO^{2+} ion and NTA, NDAP, NDPA and NTP (H_3C) in aqueous solution form *nk* complexes $H_p(VO)_qC_r{}^{p+2q-3r}$, denoted by (p, q, r), each with a formation constant β_{pqr}, according to the general reaction (1).

$$pH^+ + qVO^{2+} + rC^{3-} \rightleftarrows H_p(VO)_qC_r^{p+2q-3r} \tag{1}$$

2. Experimental

2.1. *Mass balance equations and symbols*

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

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

The symbols used are the same as in a previous work, chemicals are in roman and concentrations in italic font [15]. **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^+, VO^{2+} and C^{3-}, respectively; K_w is the water dissociation constant, and the formation functions Z_B and Z_C are defined as the average number of H^+ bonds per metal and ligand, respectively.

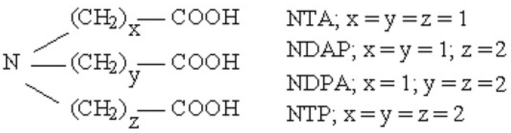

Figure 1. Structural formula of NTA, NDAP, NDPA, and NTP acids.

Table 1. Stability constant values β_{p11} for the vanadium(IV) complexes with NTA acid according to the general reaction (1).

Species	*pqr*	$\log \beta_{p11}$				
HVOC	111					15.69
$[VOC]^-$	011	10.82	15.34	12.30	11.47	13.18/12.6 (UV–Vis)
$[OHVOC]^{2-}$	−111	7.23		7.15	7.06	6.07
Ionic medium		0.1 M KNO_3	1.0 M $(NH_4)_2SO_4$	0.5 M $NaClO_4$	0.1 M KNO_3	0.2 M KCl
°C		25				
Method		Emf(H)				
References		[10]	[11]	[12]	[13]	[14]

Using the FONDO concept [16], which consists of subtracting from the total number of associated H^+, $\mathbf{B}Z_B$, or $\mathbf{C}Z_C$, and from the total concentrations **C** and **B**, the contribution of the equilibrium concentration of the products of the hydrolysis of VO^{2+} ion, $\Sigma\Sigma pc_{pq0}$, and the equilibrium concentration of the H_pC^{3-p} ($p = 1$–4) ligand acid species, $\Sigma\Sigma pc_{p01}$, and $\Sigma\Sigma c_{p01}$, respectively. We use instead of Z_B and Z_c, the *reduced* formation functions Z_{Bf} and Z_{Cf} (3), where

$$\begin{aligned} Z_{Bf} &= (\mathbf{B}Z_B - \Sigma\Sigma pc_{pq0} - \Sigma\Sigma pc_{p01})/(\mathbf{B} - \Sigma\Sigma qc_{pq0}) \\ Z_{Cf} &= (\mathbf{C}Z_C - \Sigma\Sigma pc_{pq0} - \Sigma\Sigma pc_{p01})/(\mathbf{C} - \Sigma\Sigma c_{p01}) \end{aligned} \tag{3}$$

we only observe the contribution of the species of 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 equation parameters [17], $ns =$ experiments number, $np =$ number of points in each experiment) for the H^+–VO^{2+} – ligand systems were analyzed by means of the NERNST [18] and FONDO [16] versions of LETAGROP [19]. For this purpose, functions (4)–(8) were minimized with Z^*_B,Z^*_C,Z^*_{Cf},Z^*_{Cf},

$$U_1 = \Sigma(Z_B - Z^*_B)^2 \tag{4}$$

$$U_2 = \Sigma(Z_C - Z^*_C)^2 \tag{5}$$

$$U_3 = \Sigma(Z_{Bf} - Z^*_{Bf})^2 \tag{6}$$

$$U_4 = \Sigma(Z_{Cf} - Z^*_{Cf})^2 \tag{7}$$

$$U_5 = \Sigma(\mathrm{E} - E^*)^2 \tag{8}$$

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

Similarly, the equilibrium emf(H) data $[\mathbf{H}, \mathbf{C}, E_o, J, (v, E)_{np}]_{ns}$ for the H^+ – ligand systems were treated by means of the NERNST version [18], according to reaction (9).

$$pH^+ + C^{3-} \rightleftharpoons H_pC^{3-p} \tag{9}$$

2.3. *Materials, solutions, and methods*

Used reagents included HCl and KOH, Titrisol, $KHCO_3$, KCl, NTA, $VOSO_4 \cdot 5H_2O$ Merck, cation exchange Dowex 50 W-X8(H) 50 mesh, O_2 and CO_2 free nitrogen, and triply-distilled water. The analytical methods are the same as detailed in reference [8a] and the emf(H) titration method described in [20] was used.

The ligands NDAP, NDPA, and NTP were synthesized [21], 3.0 M $(H^+, K^+)Cl$ $(=\{\mathbf{H^+}\})$, H_o mM in H^+, and 3.0 M $K(OH^-, Cl^-)$ $(=\{\mathbf{OH^-}\})$, A_o mM in OH^- solutions were prepared by weighing dry KCl, adding HCl and KOH (0.100 M ampoules), in the presence of nitrogen, and standardized the first one *versus* Na_2CO_3 [22] and the second *versus* this last one, using the Gran method [23], respectively.

Vanadium(IV) 3.0 M (½VO^{2+}, H^+, K^+) Cl (={$\mathbf{VO^{2+}}$}) solution was prepared by extracting the VO^{2+} ion with 3.0 M KCl from a cationic exchange resin saturated with VO^{2+} and H^+ ions, followed by dilution, gauging, and finally titration in H^+ and vanadium(IV) [24].

Potentiometric titrations were carried out in a Metrohm BT 8-02 reaction cell of about 100 mL, with double walls and several mouths for inserting tubes for gas charge and discharge, measuring electrodes and a burette for the addition of reagents. The measurements were performed with bubbling nitrogen and under magnetic agitation.

The concentration of H^+ in equilibrium h was determined by means of the cell REF// S/EV, where EV denotes the glass electrode, S is the equilibrium solution, and REF (=KCl 3.0 M/KCl 3.0 M, Hg_2Cl_2/Hg, Pt), the reference half-cell. The potential (mV) of the cell at 25°C is given by the Nernst equation $E = E_0 + J\,h + 59.16\log h$, with E_0 as its normal potential and J a constant related to the potential at the liquid junction [17].

The experiments were carried out in two successive stages. The first stage consists of a strong acid–base titration to determine the parameters E_0 and J of the Nernst equation and the second stage is the experiment.

After determination of acidity constants of the ligands in the first stage, the second consisted of adding a weighed quantity of H_3C, and later titrating with {$\mathbf{H^+}$} and/or {$\mathbf{OH^-}$} solutions. For determination of the stability constants of the complexes, the second stage consisted of adding an aliquot of the {$\mathbf{VO^{2+}}$} solution, a weighed quantity of ligand H_3C using the ligand: metal ratios $R = 1$ and 2, and then titrated with {$\mathbf{H^+}$} and/or {$\mathbf{OH^-}$} solutions.

3. Results and discussion

3.1. *Ionization constants of the acids*

The pK_i values presented in table 2 were calculated from the values of β_{p01} defined in the equilibrium reactions (9).

The validity of the values found is proven by the good fit between the experimental $Z_c(\log h)$ curve (dotted curve) and the $Z_c^*(\log h)$ calculated curve (continuous line), as can be observed in figure 2 for NTA, NDPA, NDAP, and NTP acids.

The values of pK_i for all the acids are in good agreement with literature data [25]. These ligands show an acidity order NTA > NDAP > NDPA > NTP due to the successive substitution of acetic groups by propionic groups, which have a greater

Table 2. pK_i values of NTA, NDAP, NDPA, and NTP acids (H_3C) in 3.0 M KCl ionic medium at 25°C.

	pK_i (3σ)			
Equilibrium	NTA	NDAP	NDPA	NTP
H_4C^+/H_3C	1.33(3)	1.12(4)	1.81(6)	3.14(9)
H_3C/H_2C^-	1.76(1)	2.30(2)	3.42(3)	3.97(5)
H_2C^-/HC^{2-}	2.48(2)	3.83(4)	4.28(5)	4.39(7)
HC^{2-}/C^{3-}	9.45(3)	9.47(5)	9.76(7)	9.72(7)
$\sigma(Z_c)$	0.011	0.018	0.033	0.015

inductive electronic donor effect because of the presence of another CH_2 group [7]. The values of $pK_{H4C/H3C}$, $pK_{H3C/H2C}$, and $pK_{H2C/HC}$ correspond fundamentally to carboxyl protons, and the values of $pK_{HC/C}$ for all ligands are in agreement with the protonation of the *N* atom in aqueous solution. The diagrams of the distribution of species show that mono-protonated HC^{2-} is the most stable and abundant species, and species containing protonated carboxylic groups improve their stability as the number of propionic groups increases [21]. The diagram corresponding to NTA is presented in figure 3. The H_4C^+, H_3C and H_2C^- species prevail to $-\log h \leq 3$. This last one becomes dominant in the interval $4 \leq -\log h \leq 9$, which in turn loses the last H^+ to form the basic species C^{3-}, that prevails for $-\log h \geq 10$.

3.2. *Stability constants of the complexes formed*

Analysis of the experimental data of V(IV) – ligand systems allowed us to calculate the β_{pqr} constants for the complex formed for each ligand, defined by means of equilibrium reaction (1).

Taking into account the species resulting from the ionization of the ligand (*vide supra*) as well as the hydrolytic species of vanadium(IV) existing, i.e., $[OHVO]^+$, $[(OH)_2(VO)_2]^{2+}$, and $(OH)_2VO$, whose formation constants at this temperature and

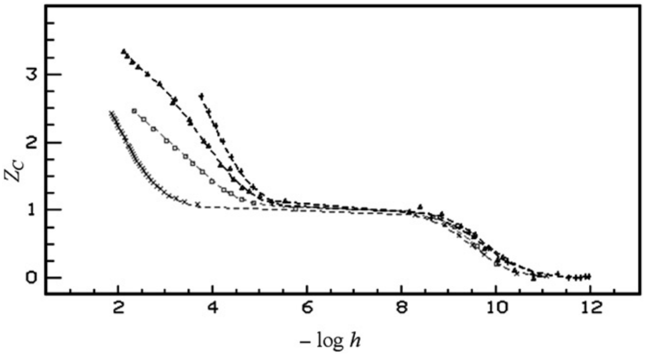

Figure 2. Z_c, average number of H^+ associated per mol of ligand *versus* $-\log h$ for NTA(+), NDAP(Δ), NDPA(□) and NTP(×) acids (H_3C) in 3.0 M KCl ionic medium at 25°C. The lines represent theoretical curves calculated with the pK_i values of table 1.

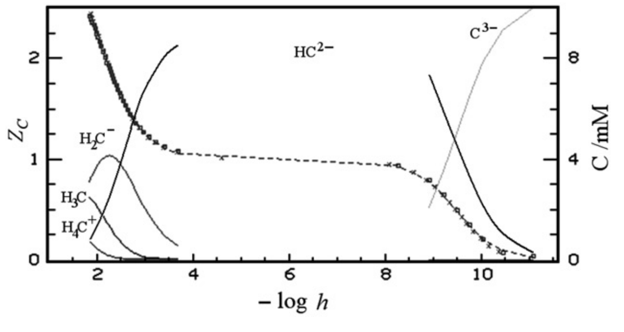

Figure 3. $Z_c(-\log h)$ data and species distribution diagram for NTA acid (H_3C) in 3.0 M KCl ionic medium at 25°C, for **C** = 10 mM.

Table 3. Equilibrium constants β_{pqr} for the system $H^+ - VO^{2+}$ – NTA (H_3C) in 3.0 M KCl ionic medium at 25°C, according to reaction (1).

Species	$\log \beta_{pqr}(3\sigma)$				
HVOC	12.8(3)	12.9(2)	13.0(2)	13.1(2)	13.9(<14.2)
$[VOC]^-$	12.74(2)	12.74(1)	12.76(1)	12.76(1)	12.77(2)
$[OHVOC]^{2-}$	5.59(2)	5.60(1)	5.61(2)	5.62(2)	5.62(2)
$[(OH)_2VOC]^{3-}$	−5.4(1)	−5.40(7)	−5.4(1)	−5.4(1)	−5.3(1)
$\sigma(Z_B)$	0.18				
$\sigma(Z_C)$		0.009			
$\sigma(Z_{Bf})$			0.017		
$\sigma(Z_{Cf})$				0.016	
$\sigma(E)$(mV)					2.3

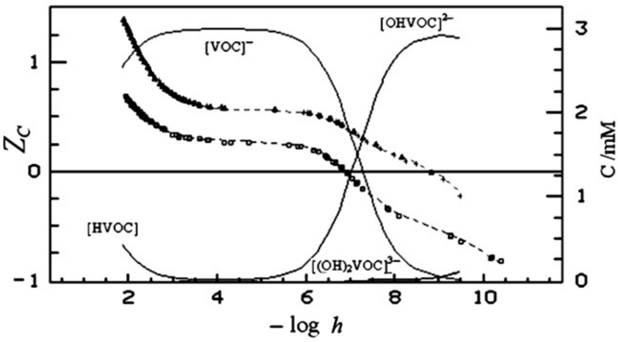

Figure 4. (a) Z_C *versus* $-\log h$ for the system $H^+ - VO^{2+}$ – NTA (H_3C) in 3.0 M KCl ionic medium at 25°C, for $\mathbf{B} = 3.0$ mM and ratios $R = 1.37$(□), 2.25(+) and 2.30(Δ), according to reaction (1). The lines represent theoretical curves calculated with the equilibrium constants of table 3 (column 3). (b) Species distribution diagram $C_{pqr}(-\log h)$ for $\mathbf{B} = 3.0$ mM and ratio $R = 2.0$ (right ordinate).

ionic medium were determined in previous work [8], the results of this analysis for the $H^+–VO^{2+}$ – NTA system are given in table 3, with equilibrium constants and standard deviations $\sigma(Z_B)$, $\sigma(Z_C)$, $\sigma(Z_{Bf})$, $\sigma(Z_{Cf})$, and $\sigma(E)$ determined with NERNST [18] and FONDO [16], versions of LETAGROP [19]. The values obtained are of the same order of magnitude.

The validity of these results are displayed in figure 4, where an excellent fit can be observed between the experimental Z_C *versus* $-\log h$ curves and those calculated. This figure also shows the species distribution diagram for $\mathbf{B} = 3.0$ mM and ratio $R = 2.0$. The most abundant complexes are $[VOC]^-$ and $[OHVOC]^{2-}$, but for $-\log h < 2$ and $-\log h > 9$ small quantities of HVOC and $[(OH)_2VOC]^{3-}$, respectively, are formed.

Finally, table 4 contains a summary of the equilibrium constants for the other three systems studied, i.e., $H^+–VO^{2+}$ – NDAP, $H^+–VO^{2+}$ – NDPA, and $H^+–VO^{2+}$ – NTP. In none is $[(OH)_2VOC]^{3-}$ formed, although $[H_2VOC]^+$ is observed in small quantities for the $H^+–VO^{2+}$ – NDPA and $H^+–VO^{2+}$ – NTP systems. Analogous curves to figure 4 are obtained for these three systems.

Usually an increase of chelate ring size leads to a decrease in complex stability [26]. In our case, the order of stability of the vanadium(IV) complexes with the aminopolycarboxylic acids studied is NTA > NDAP > NDPA > NTP. With NTA vanadium(IV) can form five-membered ring chelates, while NTP could form only six-

Table 4. Equilibrium constants β_{pqr} $H^+ - VO^{2+} - H_3C$ ($H_3C = $ NDAP, NDPA, and NTP) in 3.0 M KCl ionic medium at 25°C, according to reaction (1).

	$\text{Log}\,\beta_{pqr}(3\sigma)$		
Species	NDAP	NDPA	NTP
$[H_2VOC]^+$		15.9(4)	16.7(1)
HVOC	14.1(1)	13.5(2)	12.7(1)
$[VOC]^-$	12.60(7)	11.19(1)	8.60(5)
$[OHVOC]^{2-}$	5.4(1)	4.01(3)	3.17(9)

membered ring chelates. That is, as the acetic groups are replaced by propionic groups they diminish the stability of the complexes with six-membered ring chelates.

Therefore, it has been confirmed that five-membered ring chelates are most stable for V(IV), like Cu(II), Ni(II), lanthanides and other heavier elements, while Be(II) and other elements of the first short period prefer six-membered ring chelates [21].

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