



## Carbonate complexes of vanadate

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### ABSTRACT

The interaction of vanadate with bicarbonate has been investigated using a combination of  $^{51}\text{V}$  NMR and potentiometric titrations. While such an interaction has long been suspected, little evidence and no information on the stability of the resulting complexes has previously been available. A global analysis of the results enabled the identification of two species, a mono-carbonato and a di-carbonato complex. The equilibrium constants of both species were determined between 1 and 56 °C, facilitating the calculation of the corresponding thermodynamic parameters.

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### 1. Introduction

The coordination chemistry of vanadium (V) is a topic that has generated and received a lot of interest in recent years. One reason for this is the significant role of vanadates in biological systems [1–5]. The vanadate anion ( $\text{VO}_4^{3-}$ ) is structurally analogous to the biologically important phosphate anion ( $\text{PO}_4^{3-}$ ), and it has been postulated that many of the biological functions of vanadate are derived from its similarity to phosphate [6,7]. Indeed, vanadate and vanadate complexes have been found to both activate and inhibit phosphate metabolising enzymes [8]. In recent years, attention has been focused on the medicinal applications of vanadates [9], particularly their potential as insulin mimetics in the treatment of diabetes [10–12].

A wide range of different types of vanadate complexes have been investigated to date, including those with amino alcohols, alcohols and amino acids, amongst others [10,13–20]. These studies focused primarily on the determination of equilibrium constants under biologically relevant conditions and the identification of structural features which influence the stability of the complexes. Much of this work is summarised in a review (see [21]).

While there are many studies investigating the interaction between vanadates and small ligands, the interaction with the simple bicarbonate ligand has not been studied to date. The bicarbonate ligand presents a good model system for understanding the fundamental interactions of vanadate with carboxylate containing ligands. It has been acknowledged for some time that vanadate complexes of some form of carbonate most likely occur under mild

conditions [22,23], yet until now, little evidence for, or investigation into such an interaction has been published. To our knowledge, the only reported investigation is a voltammetric and spectroscopic study into bicarbonate containing  $\text{V}^{\text{IV}}/\text{V}^{\text{V}}$  solutions [24]. This study suggested the presence of a non-protonated dicarbonato–vanadate complex in which the vanadate is 6-coordinate, with two bidentate carbonate ligands. The structure of this complex was based on the earlier reported crystal structure of a diperoxovanadate complex of carbonate [25]. Both mono- and bi-dentate coordination of carboxylate ligands have been reported in a number of transition metal complexes involving metal centres other than vanadate [26–29].

In addition to its potential as a model system, the vanadate–bicarbonate system is interesting for a number of different reasons: bicarbonate is a relatively commonly used buffer and complexation of vanadate by the buffer system will significantly affect the outcomes of such studies. Bicarbonate is also often used in competition binding studies where it is thought to competitively bind to vanadate receptors [22]. An understanding of the direct interaction between bicarbonate and vanadate is vital to understanding and interpreting these experiments. From a biological perspective, bicarbonate is present within the human body. Vanadium, in oxidation states (III) to (V) binds to blood proteins and the role of bicarbonate in this binding has been extensively investigated [30–33]. It is highly likely that interactions with bicarbonate also influence other biological and medicinal properties of vanadium.

Finally, in recent years, the use of vanadate as an additive to potassium carbonate (potash) solutions used for the selective removal of  $\text{CO}_2$  from gas streams has received increasing interest [34]. Although it is generally accepted that vanadates increase the kinetics of  $\text{CO}_2$  absorption, little is known about the mechanism associated with this process [35].

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Both we [36] and others [37] have shown that a combination of  $^{51}\text{V}$  NMR spectroscopy and potentiometric titrations are ideal for investigating the equilibria associated with the complex vanadate system. Here, we extend this work to incorporate the interaction of bicarbonate with the vanadate system.

## 2. Experimental

Vanadium pentoxide ( $\text{V}_2\text{O}_5$ ) and tetraethylammonium bicarbonate ( $\text{Et}_4\text{NHCO}_3$ ) were purchased from Sigma Aldrich, 35% w/w aqueous tetraethylammonium hydroxide ( $\text{Et}_4\text{NOH}$ ) solution was purchased from Alfa Aesar and standardised against potassium hydrogen phthalate (KHP), purchased from Sigma Aldrich. All chemicals were used without further purification. All solutions were prepared under a nitrogen atmosphere using ultra-pure water. Vanadate solutions were prepared by adding 1 equivalent of  $\text{V}_2\text{O}_5$  to 2 equivalents of  $\text{Et}_4\text{NOH}$  in aqueous solution and were typically heated to approximately  $40\text{ }^\circ\text{C}$  and left to stand at least overnight to ensure complete equilibration prior to use. All solution compositions are expressed in molarities at  $25\text{ }^\circ\text{C}$ .

Three types of titration were conducted: (1) 2.5 M hydroxide solution was titrated into a solution containing 0.005 M vanadate and 0.3 M bicarbonate; (2) 2.5 M hydroxide solution was titrated into a solution containing 0.02 M vanadate and 0.15 M bicarbonate and (3) 2.0 M bicarbonate solution was titrated into a solution containing 0.01 M vanadate. Measurements of all titrations were taken at approximately  $14\text{ }^\circ\text{C}$  intervals from 1 to  $84\text{ }^\circ\text{C}$ . All titrations were followed by  $^{51}\text{V}$  NMR, titrations (1) and (2) were also followed potentiometrically.

### 2.1. Potentiometric titrations

Vanadate/bicarbonate solutions were titrated on a Titrino Plus fully automatic set-up from Metrohm. Titrations were performed under a nitrogen atmosphere (the gas stream was pre-saturated with water) and were fully thermostatted with a water bath to the relevant temperature.

### 2.2. NMR measurement and analysis

NMR titrations were conducted manually and the associated  $^{51}\text{V}$  NMR spectra were measured on a 600 MHz Bruker Avance spectrometer. For each spectrum, 5120 transients were obtained from approximately  $-300$  to  $-700$  ppm with an acquisition time of 0.258 s and a relaxation delay of 0.2 s. The titrations were conducted in  $\text{H}_2\text{O}$  in 5 mm tubes with capillary inserts containing a vanadium(V)–maltol (V–Ma) solution in  $\text{D}_2\text{O}$  as a lock signal and reference. Chemical shifts are reported relative to an external reference standard of  $\text{VOCl}_3$  (0 ppm). In reality, the chemical shifts were determined relative to the V–Ma complex contained within the capillary. This species exhibits a peak at approximately  $-502$  ppm relative to  $\text{VOCl}_3$ , which does not overlap with any other peaks in the system investigated herein. It has been reported that slow reduction of the vanadium has been observed in V–Ma solutions [16]. However, V(IV) is not visible by  $^{51}\text{V}$  NMR, and the capillary solutions were checked regularly to ensure only a single peak was visible in the measured spectra. No degradation or broadening of this peak was visible over the course of the research, although a decrease in the relative intensity was observed over time. Temperature calibration of the spectrometer was performed using methanol and ethylene glycol [38].

For the most part, spectra with overlapping peaks were deconvoluted using a peak fitting procedure developed in house. In cases where the peaks overlapped to such an extent that a reliable deconvolution could not be carried out, the sum of the peaks was

fitted to the sum of the vanadate molarity in the two species involved. In some cases, the peaks could not be deconvoluted to the extent that reliable integrations could be obtained, but peak positions could still be reasonably estimated. In these cases, the summed molarities were used but peak positions were also determined individually for the two peaks.

### 2.3. Data analysis and thermodynamic model

The experimental data in the form of NMR-measured molarities, chemical shifts, and potentiometric titration data were fitted globally. Equilibrium constants were fitted to the data using standard Newton–Raphson techniques [39]. The equilibrium constants used in this work are expressed in terms of molarities. As only dilute conditions were used, water molarities were assumed to be constant and were not considered in the formulation of the equilibrium constants. Activity coefficient corrections were applied based on a simple Debye–Hückel equation (Eq. (1)) where  $\mu$  is the ionic strength (as a molarity) of the solution,  $\gamma_i$  is the molarity based activity coefficient,  $z_i$  the charge on the  $i$ th ion and  $A$  is defined as given in Supplementary Information.

$$\log_{10}\gamma_i = \frac{-Az_i^2\sqrt{\mu}}{1 + \sqrt{\mu}} \quad (1)$$

## 3. Results and discussion

### 3.1. Species identification

$\text{V}_2\text{O}_5$  reacts with aqueous, basic solutions to form vanadate ( $\text{H}_x\text{VO}_4^{(3-x)-}$ , where  $x = 1$  and 2), as well as a number of higher oligomers:  $\text{H}_x\text{V}_2\text{O}_7^{(4-x)-}$ , where  $x = 0-2$ ,  $\text{HV}_3\text{O}_{10}^{4-}$ ,  $\text{V}_4\text{O}_{12}^{4-}$ ,  $\text{V}_4\text{O}_{13}^{6-}$  and  $\text{V}_5\text{O}_{15}^{5-}$ . For clarity, from here on, all  $\text{H}_x\text{VO}_4^{(3-x)-}$  species will be represented as V1, all  $\text{H}_x\text{V}_2\text{O}_7^{(4-x)-}$  as V2,  $\text{HV}_3\text{O}_{10}^{4-}$  as V3,  $\text{V}_4\text{O}_{12}^{4-}$  as V4,  $\text{V}_4\text{O}_{13}^{6-}$  as V4I and  $\text{V}_5\text{O}_{15}^{5-}$  as V5. The interactions between these species and the associated temperature dependent equilibrium constants were taken from our previous work [36]. As shown previously [36], each of these species exhibits an NMR signal at a slightly different chemical shift. The chemical shift of each peak reflects the relative molarity of the different protonation states within each species, according to Eq. 2, where  $i$  is the polymer of interest, and  $j$  represents the different forms of this polymer.  $c$  is the molarity, and  $\delta$  is the chemical shift, either of the individual species,  $j$ , or of the polymer,  $i$ , under the given conditions.

$$\delta_i = \frac{\sum_{j=1} c_j \delta_j}{c_i} \quad (2)$$

Peak assignments for the pure vanadate species were the same as those used by us previously in an investigation of the pure vanadate system [36].

In addition to the vanadate speciation, bicarbonate speciation must also be taken into consideration. Under the conditions used here, only bicarbonate and carbonate are relevant – the equilibrium between these two species is represented by Eq. (3). The associated temperature dependent equilibrium constant was taken from [40].



The  $^{51}\text{V}$  NMR spectra resulting from the titration of a vanadate solution with bicarbonate (titration type 3) are shown in Fig. 1. There are two important features to note in this figure. These two features can be directly linked to the appearance of two new species as discussed below.

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