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Multicomponent Polyanions. 47. The Aqueous Vanadophosphate System

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Equilibrium and metastable speciations in the aqueous vanadophosphate system in 0.6 M Na(Cl) medium at 25 °C have been characterized by pH-potentiometry and high-field ^{31}P and ^{51}V NMR spectrometry. Equilibrations are slow at 25 °C, requiring months to years to reach equilibrium. The simultaneous analysis of $[H^+]$–emf data with ^{31}P and ^{51}V NMR shift and integral data was required to establish the speciation in aged, equilibrated solutions. Vanadophosphate species exist at equilibrium in solutions at $1.3 < pH < 4.0$ with centimolar to decimolar vanadium and have the formula $[H_xPV_{14}O_{42}]^{(9-x)-}$. The predominant equilibrium species is $[H_4PV_{14}O_{42}]^{5-}$ ($\log \beta = 94.84 \pm 0.07$ (3σ) from H^+, $H_2VO_4^-$, and $H_2PO_4^-$). Its conjugate acid, $[H_5PV_{14}O_{42}]^{4-}$ ($\log \beta = 96.41 \pm 0.09$), and its conjugate base, $[H_3PV_{14}O_{42}]^{6-}$ ($\log \beta = 90.7 \pm 0.6$), are minor species at equilibrium, especially the latter. Fresh solutions of dissolved $Na_5[H_4PV_{14}O_{42}]$ salt were examined to find metastable species. Rapid pH-titrations and ^{31}P and ^{51}V NMR shift data over $0 < pH < 8.5$ established $[H_xPV_{14}O_{42}]^{(9-x)-}$ species having $x = 1$–6, and their pK_a values for $x = 2$–6. All observed $[H_xPV_{14}O_{42}]^{(9-x)-}$ species exhibited solution NMR spectra corresponding to the trans-bicapped Keggin structure. Transient, metastable $[H_xPV_{13}O_{41}]^{(12-x)-}$ species were observed in fresh solutions of $Na_5[H_4PV_{14}O_{42}]$ salt dissolved at $pH < \sim 1.3$, during its decomposition to H_3PO_4 and VO_2^+. The pK_a values of H_3PO_4, $H_2PO_4^-$, and HPO_4^{2-} in the 0.6 M Na(Cl) medium at 25 °C were determined to be 1.772, 6.418, and 11.232, respectively.

Introduction

At Umeå University, we are studying the speciation and structures in aqueous heteropoly- and isopolyoxometalate systems using potentiometric $[H^+]$ titration as a fundamental tool, complemented with other methods, especially multinuclear NMR spectrometry. We are presently studying the quaternary molybdovanadophosphate system ($H^+ - MoO_4^{2-}$–$HVO_4^{2-} - HPO_4^{2-}$ components forming $[PMo_{(12-x)}V_xO_{40}]^{(3+x)-}$ species)[1] to complement research conducted at Catalytica on its catalytic applications.[2]

A prerequisite to determining the speciation in a complicated multicomponent system is to have the subsystems well characterized at the same temperature and ionic strength. As the binary H^+–MoO_4^{2-} system,[3] the binary H^+–HVO_4^{2-} system,[4,5] and the extremely complicated ternary H^+–MoO_4^{2-}–HVO_4^{2-} system[6,7] were previously characterized in 0.6 M Na(Cl) medium at 25 °C, these conditions were also chosen for characterization of the quaternary molybdovanadophosphate system and its other subsystems. The simple binary H^+–HPO_4^{2-} system and the complicated ternary H^+–MoO_4^{2-}–HPO_4^{2-} system were thoroughly studied previously at this temperature but in a higher concentration medium, 3.0 M $Na(ClO_4)$.[8a] These systems have now been reinvestigated in 0.6 M Na(Cl).[8] The pK_a's of H_3PO_4, $H_2PO_4^-$, and HPO_4^{2-} in this medium are reported herein. The speciation in the ternary H^+–MoO_4^{2-}–HPO_4^{2-} system in this medium was found to be essentially the same as in 3.0 M $Na(ClO_4)$ and will be reported separately.[8b] The remaining ternary subsystem, H^+–HVO_4^{2-}–HPO_4^{2-}, is the subject of this paper.

Vanadophosphate polyanions have been studied previously by other investigators.[9–13] Most notably, Sasaki and co-workers[10] obtained the guanidinium salt $(CN_3H_6)_8[HPV_{14}O_{42}]\cdot 7H_2O$ from

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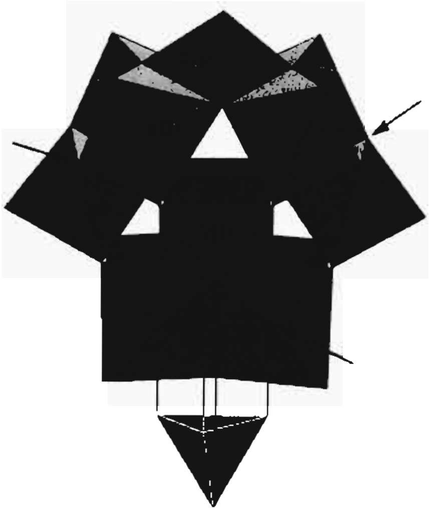

Figure 1. Idealized polyhedral representation of the trans-bicapped α-Keggin structure of tetradecavanadophosphates. Adapted from ref 10. The arrows on oxygen vertices show three of the four symmetrically arranged (S_4 axis) protonation sites located for a $[H_4PV_{14}O_{42}]^{5-}$ polyanion in ref 13. The distorted trigonal bipyramid of the lower cap is shown exploded from the structure for visibility.

solutions of $NaVO_3$ and H_3PO_4 (V:P = 4) at pH = 2–3 (HNO_3) and determined the crystal structure of the polyanion to be the trans-bicapped Keggin structure shown in Figure 1. Two capping VO^{3+} units are added to the α-Keggin framework, decreasing the otherwise very high negative charge of the hypothetical Keggin polyanion, $[PV_{12}O_{40}]^{15-}$. (Stable Keggin heteropolyanions typically have a predominance of hexavalent component metals (e.g. Mo^{VI}, W^{VI}) and hence a lower negative charge, for example $[PMo_{10}V_2O_{40}]^{5-}$.) Each capping vanadium(V) is pentacoordinated to oxygen, in contrast to the 12 others which are each hexacoordinated.

Sasaki and co-workers[10] also demonstrated by ^{31}P and ^{51}V NMR that trans-bicapped Keggin species, $[H_xPV_{14}O_{42}]^{(9-x)-}$ (collectively, PV_{14}), exist in solutions of freshly redissolved ammonium salt (formulated as $(NH_4)_{6.5}[H_{2.5}PV_{14}O_{42}]\cdot nH_2O$) and in freshly mixed solutions of NaH_2PO_4, $NaVO_3$, and H_2SO_4. Their NMR spectra (23.5 MHz ^{51}V, 24.2 MHz ^{31}P) did not reveal the existence of any other vanadophosphate structures in solution over a wide range of V:P ratios ($^1/_2$–14) and pH (1–6), leading the authors to specifically rule out noncapped (PV_{12}), monocapped (PV_{13}), and cis-bicapped (PV_{14}) species. They reinterpreted the earlier reports[9] of PV_{12} and PV_{13} polyanion salts as actually pertaining to the PV_{14} polyanion.

Harrison and Howarth[11] extended the multinuclear NMR characterization of the PV_{14} species to higher field, including ^{17}O as well as ^{31}P and ^{51}V NMR data (54.2, 162.0, and 105.2 MHz, respectively), over the range 0.5 < pH < 8 in 2.0 M $Na(ClO_4)$. This study used a sodium salt crystallized from solutions of $NaVO_3$ and H_3PO_4 (V:P = 2–12) at pH = 2–3 ($HClO_4$) and formulated as $Na_8[HPV_{14}O_{42}]\cdot 9H_2O$. (The balance between Na^+ and H^+ countercations was assigned by analogy to Sasaki and co-workers' octaguanidinium salt.[11b]) The ^{17}O NMR spectrum further confirmed the trans-bicapped α-Keggin PV_{14} structure in solution. Again, no other vanadophosphate species were noted. The reported chemical shift vs pH data indicated protonations of the polyanion occuring over the entire pH range studied.

Recently Zubieta and co-workers[13] reported the crystal structure of the salt[13b] $(Me_3NH)_4(NH_4)[H_4PV_{14}O_{42}]$ in which the four protonated sites in the polyanion were identified by locating the hydrogen atoms. They are in a symmetrically arranged set (S_4 axis) of four of the eight edge-shared oxygens, V(1)–O_e–V(2), where indicated in Figure 1.

In view of the literature precedent, we expected the equilibrium analysis of the H^+–$H_2VO_4^-$–$H_2PO_4^-$ system would be straightforward, involving a simple determination of the $[H_xPV_{14}O_{42}]^{(9-x)-}$ formation constants, and hence pK_a values, in the 0.6 M Na(Cl) medium. However, this study proved substantially more troublesome than expected. Equilibrations were found to be extremely slow at 25 °C, requiring months to years. The equilibration time could not be shortened by interim heating, as the PV_{14} species proved markedly less stable at higher temperature. Moreover, the emf effects in [H^+]-potentiometry were small. The equilbrium speciation could be established only by simultaneously considering high-field ^{31}P and ^{51}V NMR chemical shift and integral data in combination with the potentiometric data. To our advantage, $[H_xPV_{14}O_{42}]^{(9-x)-}$ species decompose sufficiently slowly outside the [H^+] range in which they are stable to allow the observation of several metastable members of the series and the determination of their pK_a values by rapid titrations. Moreover, the monocapped Keggin PV_{13} could be observed as a transient, metastable intermediate in acid decompositions.

Notations and Designations. The polyanion formation constants are reported with H^+, $H_2VO_4^-$, and $H_2PO_4^-$ as the components, according to eq 1. The resulting polyanions are, for brevity, often

$$pH^+ + qH_2VO_4^- + rH_2PO_4^- \leftrightarrow [(H^+)_p(H_2VO_4^-)_q(H_2PO_4^-)_r]^{p-q-r} \quad (1)$$

designated by (*p,q,r*) and formation constants are reported as $\beta_{p,q,r}$. The potentiometric [H^+]-titration data establish only the (*p,q,r*) identities of the polyanions. Their actual ionic formulas are related to their (*p,q,r*) values by loss of water, eq 2, and must

$$[(H^+)_p(H_2VO_4^-)_q(H_2PO_4^-)_r]^{p-q-r} \leftrightarrow [H_{(p+2q+2r-2w)}P_rV_qO_{(4q+4r-w)}]^{p-q-r} + wH_2O \quad (2)$$

be established by complementary structural information, such as NMR spectrometric data. Accordingly, for $[H_xPV_{14}O_{42}]^{(9-x)-}$ species, $(p,q,r) = (x+6,14,1)$.

The 0.6 M Na(Cl) ionic medium is 0.600 M Na^+ with Cl^- providing the counteranion balance not provided by the oxoanions present. The acidity measurements are on the concentration scale, where pH = –log[H^+], *not* on the activity scale, where pH = –log(a_{H^+}). From now on we will for simplicity use pH insted of –log[H^+]. For brevity, the total concentration of phosphorus present in solution is often denoted by *P* and the total concentration of vanadium by *V*.

Experimental Section

Solid Sodium Tetradecavanadophosphate Salt Syntheses and Elemental Analyses. Solid sodium salts of the tetradecavanadophosphate polyanion were prepared by the general method reported for other salts,[10] adapted by using HCl for acidification and NaCl for common Na^+ ions for crystallization. HCl and NaCl were employed so that the product could not be potentially contaminated by any ions other than those used as the ionic medium in the equilibrium analysis. Starting materials were $NaVO_3$ (Alfa) and H_3PO_4 (Mallincrodt 85% AR).

For elemental analyses, salt samples were redissolved in water. Sodium, phosphorus, and vanadium were analyzed by inductively coupled plasma atomic emission spectrometry using an ARL Model 3510 spectrometer, calibrated with bracketing standards diluted from commercial 1000 ppm standard solutions (Spectrum). Chloride was analyzed by ion chromatography using a Dionex DX100 ion chromatograph, a HPIC AS4A column (standard conditions), and suppressed conductivity detection, calibrated with standards prepared from reagent grade sodium chloride.

$Na_{4.75}[H_{4.25}PV_{14}O_{42}]\cdot NaCl\cdot 12H_2O$. A suspension of $NaVO_3$ (61.0 g, 0.500 mol) in 700 mL distilled water was boiled to dissolve the salt. 30% H_2O_2 solution was added dropwise (~50 drops) to the hot solution to oxidize any V^{IV} present in the $NaVO_3$ to V^V. The solution was boiled an additional hour to ensure decomposition of excess peroxide, and cooled to room temperature. Small amounts of heavy solids and turbidity, containing iron and silica impurities in the $NaVO_3$, were removed by vacuum filtration through 5.0 μm cellulose acetate/nitrate filters. 85.4% (w/w) H_3PO_4 (14.3 g, 0.125 mol) was added to the sodium metavanadate solution, and the pH of the resulting solution was adjusted to 2.3 with concentrated HCl. (ORION Research 81–03 ROSS combination electrode, calibrated with pH 2.0 and 7.0 phosphate buffers.) After 64 and 70 h stirring at room temperature, the solution pH was readjusted to 2.3 with additional HCl. After an additional 48 h, the pH was still ~2.3 and ^{51}V NMR showed essentially complete formation of the $[H_xPV_{14}O_{42}]^{(9-x)-}$ anion. NaCl (175 g, 3 mol) was added to the solution and dissolved to give a visually homogeneous solution. The solution was cooled to 4 °C overnight and then further cooled briefly to ice-cold temperature. Crystals were harvested by rapid vacuum filtration of the ice-cold mixture through a course fritted glass filter. The dark, reddish purple crystals were dried with ambient air drawn through the filter cake by vacuum for 5 h and then *in vacuo* over $CaCl_2$ desiccant overnight, yielding 55.6 g (87% yield on V; see below) of dried powder.

Samples of the salt redissolved rapidly and completely in water to give solutions whose ^{31}P and ^{51}V NMR spectra showed only the resonances of the $[H_xPV_{14}O_{42}]^{(9-x)-}$ anions. (See below.) The composition of the solid was assigned based on the ideal mole ratios (countercations:P:V:O = 9:1:14:42) and the average of the analyzed equivalent weights for P and V_{14} (1804 g/polyanion). The number of proton countercations was, at first, assigned by difference ($9PV_{14}$–Na) based on the sodium analysis. The water content was calculated as the difference between the equivalent weight and the formula weight for anhydrous salt. On this basis the salt was initially assigned the formulation $Na_{5.7}[H_{3.3}PV_{14}O_{42}]\cdot 14H_2O$. However, the equilibrium analysis study and titrations determined unambiguously 4.25 H$^+$ per PV_{14} in this salt, essentially one more proton per polyanion than indicated by the sodium analysis. Solutions of the salt were then found to give a precipitate with Ag$^+$, and ion chromatography showed an elution peak at the retention time for chloride corresponding to nearly one (0.83) Cl$^-$ per PV_{14}. Giving precedence to the H$^+$ determination and then to the Na analysis (both of which are more important to the equilibrium analysis than the chloride content), the salt was reassigned the formulation $Na_{4.75}[H_{4.25}PV_{14}O_{42}]\cdot NaCl\cdot 12H_2O$. Anal. Calcd: P, 1.72; V, 39.53; Na, 7.33; Cl, 1.96. Found (σ): P, 1.73-(0.03); V, 39.3(0.5); Na, 7.29(0.07); Cl, 1.63(0.04).

$Na_5[H_4PV_{14}O_{42}]\cdot 28H_2O$. This material was prepared similarly and prior to that above, with the following significant differences: The polyanion synthesis was conducted in half the volume of water (350 mL) and the NaCl was added as 350 mL of saturated solution. The filtered crystals were washed one time with ice-cold water. Although this washing was conducted as quickly as possible, a significant amount of material appeared to dissolve in the wash (by color). The recovered salt crystals (71% yield on V) were dried in air only and not *in vacuo*. The material was analyzed and its formulation assigned as described above. The equilibrium analysis study and titrations confirmed 4.0 H$^+$ per PV_{14} in this salt. Anal. Calcd for $Na_5[H_4PV_{14}O_{42}]\cdot 28H_2O$: P, 1.52; V, 34.97, Na, 5.64. Found (σ): P, 1.51(0.01); V, 35.9(0.4); Na, 5.67(0.04).

Solutions for Potentiometric and Quantitative NMR Studies. Solutions were mixed from stock solutions of the components (HCl, V_2O_5, or $NaVO_3$, and NaH_2PO_4), or from the solid sodium salts (usually $Na_{4.75}[H_{4.25}PV_{14}O_{42}]\cdot NaCl\cdot 12H_2O$). Boiled distilled water was used to prepare all the solutions. All solutions for potentiometric and NMR study were prepared to contain 0.6 M Na(Cl) at 25 °C. Sodium chloride (E. Merck, p.a.) was dried at 180 °C and used without any further purification. Diluted solutions of hydrochloric acid (E. Merck p.a.) were standardized against tris(hydroxymethyl)aminomethane, TRIS (Sigma Chemical Co.). Dilute sodium hydroxide was prepared from "oljelut" (50% NaOH and 50% H_2O) and standardized against hydrochloric acid. Vanadium pentoxide (Fischer Scientific Company, p.a.) was dried at 100 °C and used without any further purification. Acidic stock solutions of vanadium (VO_2^+) were prepared by dissolving the V_2O_5 in aqueous HCl of known molarity. Due to the low solubility of VO_2^+ (in equilibrium with insoluble V_2O_5), the highest vanadium concentration obtainable in moderately acid solutions (HCl ~ 0.2 M) is about 40 mM. Sodium metavanadate (E. Merck p.a.) was used for preparing vanadium stock solutions of higher concentration in neutral solutions. After dissolving the sodium metavanadate in hot water, the solution was cooled to room temperature, filtered through porous glass G4, and standardized by evaporation to solid. Sodium dihydrogenphosphate monohydrate (E. Merck p.a.) was used as received and solutions were standardized by evaporation to anhydrous solid.

Ionic Medium. The pH-potentiometry and NMR studies were performed at 25 °C using a 0.6 M Na(Cl) ionic medium to maintain constant activity coefficients. As anion equilibria were being studied, the countercation ion in the medium, Na$^+$, was held at a constant concentration (0.6 M) and the Cl$^-$ concentration was varied to provide the balance of counteranions not provided by the phosphate and vanadate species.

pH Potentiometry. For determining the pK_a values of $H_xPO_4^{(3-x)-}$ and metastable $[H_xPV_{14}O_{42}]^{(9-x)-}$ species, titrations were conducted at 25.0 ± 0.1 °C using an automated potentiometric titrator. Free H$^+$ concentrations were determined by measuring the emf of the following cell, using an Ingold type 201-NS glass electrode, an Ag/AgCl electrode prepared according to Brown,[14] and a Wilhelm bridge.[15] A hydrogen electrode must be used for determination of the pK_a value for HPO_4^{2-} because a glass electrode is not reliable at such alkaline solutions. The free H$^+$ concentration was calculated from the measured emf, E (in mV), by eq 3, where the two last terms are the liquid junction potentials for

$$-\ \mathrm{Ag, AgCl}|0.6\ \mathrm{M\ NaCl}||\mathrm{test\ soln}|\mathrm{measuring\ electr}\ +$$

$$E = E_0 + 59.157 \log[\mathrm{H}^+] - 76[\mathrm{H}^+] + 42[\mathrm{OH}^-] \qquad (3)$$

0.6 M Na(Cl) medium and Wilhelm-type bridge. The constant E_0 was determined before and after each titration using separate solutions of known [H$^+$]. A fluoropolymer-encased magnetic bar was used to stir the solution in the titration vessel. The solution was protected from atmospheric carbon dioxide by a stream of argon gas (hydrogen gas when the hydrogen electrode was used). The argon was sparged through 10% NaOH solution to remove any acid impurities, 10% H_2SO_4 solution to remove any alkaline impurities, and, finally, 0.6 M NaCl medium before introduction to the titration vessel.

The long times needed to reach equilibria in vanadophosphate solutions at 25 °C when starting from the components, $H_2VO_4^-$ and $H_2PO_4^-$, prohibited using the pH titration method for determining the formation constants of stable $[H_xPV_{14}O_{42}]^{(9-x)-}$ species. Instead, many individual "point solutions", corresponding to points in a hypothetical pH titration, were mixed and allowed to equilibrate at 25 °C. The pH values in these aged solutions were measured using an ORION Research 81-03 ROSS combination electrode. The electrode was calibrated using solutions of known [H$^+$] in the 0.6 M Na(Cl) medium.

NMR Spectrometry. The ^{31}P and ^{51}V NMR measurements were obtained (at Umeå University) using a Bruker WM250 spectrometer at 101.3 and 65.8 MHz, respectively, and a Bruker AM500 spectrometer at 202.5 and 131.55 MHz, respectively. The probe temperature was thermostated at 25.0 ± 0.5 °C. The field frequency stabilization was locked to deuterium by placing the 8-mm sample tubes into 10-mm tubes containing D_2O. The samples were spinning in all experiments.

The spin–lattice relaxation times (T_1) were evaluated using the inversion recovery method and the relaxation delay was at least $5T_1$. The free induction decay (FID) was multiplied by an exponential line-broadening function (LB = 1), using the Bruker software, to impove the signal/noise ratio. A Gaussian–Lorentzian double apotization was applied to the FID, using the Bruker software, to enhance resolution to obtain more accurate chemical shift values of overlapping resonances. $VOCl_3$ and 85% H_3PO_4 were used as external chemical shift standards. Positive chemical shifts (δ) correspond to higher frequency.

Routine ^{31}P and ^{51}V NMR solution spectra and ^{31}P and ^{51}V MAS NMR spectra of solid salts, to support the synthesis and stability studies at Catalytica, were obtained using a Bruker MSL400 spectrometer at 162.0 and 105.2 MHz, respectively, and standard Bruker probes. For the solid-state spectra, samples were spun in 4-mm rotors at 15 kHz for the ^{51}V spectra and at 6–8 kHz for the ^{31}P spectra.

Mathematical Analyses by Computer Programs. Resonance intensities were computed by integration using the Bruker software, or, for overlapping resonances, by line shape analysis using the program NMRi,[16] inputting the chemical shifts determined by resolution enhancement (see above). The mathematical analysis of combined [H$^+$]–emf data and ^{31}P and ^{51}V NMR shift and integral data was accomplished using the least-squares program LAKE,[17] which is a new program, still under development. The greatest advantage of this program is that multimethod data can be treated simultaneously, which considerably refines the equilibrium analysis. [H$^+$]-emf data from the rapid titrations were evaluated with another least-squares program, LETAGROPVRID[18] version ETITR.[19]

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Calculations and plots of distribution and predominance diagrams were performed using the program SOLGASWATER.[20]

Results

Preparations of Sodium Tetradecavanadophosphate Salt. A sodium salt of the tetradecavanadophosphate polyanion—the sole definitively known isolable vanadophosphate polyanion[10]—was required for the equilibrium analysis and titration studies in the Na(Cl) ionic medium. The literature[9–12] teaches that sodium salt solutions are prepared by acidification of solutions of metavanadate (or, less commonly, decavanadate) and orthophosphate with mineral acids other than phosphoric acid, optimally to pH 2–3.[10] The sodium salt is highly soluble in water, and such synthetic solutions have previously been used directly for solution studies[10,12bd] and for preparing less soluble salts by cation metathesis.[10,12cf] Solid sodium salts have been recovered from such synthetic solutions in low or unreported yields.[9af,10,11]

We used hydrochloric acid to acidify solutions of 4:1 metavanadate:orthophosphate (~0.7 or ~1.4 M vanadium) to pH ~ 2.3. After several days at room temperature with interim reacidifications, the homogeneous solution stabilized at this pH and ^{51}V NMR indicated essentially complete incorporation of the vanadium into the tetradecavanadophosphate polyanion. NaCl was then added to ~4 M concentration to decrease the solubility of the polyanion salt, which was then crystallized out of solution at 4 °C, in high yield. Samples of the recovered salts redissolved rapidly and completely in water to give solutions whose immediate NMR spectra showed only the single ^{31}P resonance and three ^{51}V resonances of the $[H_xPV_{14}O_{42}]^{(9-x)-}$ anions. (See below.) ^{51}V MAS NMR spectra of the solid salts were consistent with the solution ^{51}V NMR spectra of $[H_xPV_{14}O_{42}]^{(9-x)-}$ anions.

HCl and NaCl were employed in our preparations so that the recovered polyanion salt could not potentially be contaminated by any ions other than those used for the ionic medium in the equilibrium analysis and titration studies. Indeed, the product of one such preparation contained NaCl in analytically significant amounts. (See $Na_{4.75}[H_{4.25}PV_{14}O_{42}]\cdot NaCl\cdot 12H_2O$ in the Experimental Section.) This was learned only after, and as a result of, collecting equilibrium analysis data using this material. However, since this material was employed based on its analyzed PV_{14} equivalent weight and $Na^+:PV_{14}$ content, its contribution to the 0.6 M Na^+ ionic medium had been correctly predetermined. Consequently, the NaCl present in this material did not compromise the integrity of the equilibrium analysis and titration data. (We believe the NaCl was present in a physical mixture with the hydrous polyanion salt in this *unwashed* product, as a similarly prepared product that was washed with cold water, with concomitant yield loss, did not evidence any corecovered NaCl.)

An attempt was made to expedite the synthesis by heating the acidified solution. At the boil, a brownish purple solid rapidly deposited from the solution. Elemental analysis of the solid recovered from the mixture at room temperature (yellow supernatant, pH ~ 2) and dried *in vacuo* gave 43.5% V with V:P ~ 55 and Na:V ~ 0.3, suggesting it was substantially some combination of V_2O_5 and sodium decavanadate salt. In a related experiment, sodium tetradecavanadophosphate salt was dissolved in D_2O and the solution was heated in a boiling water bath. Over several hours, a brown solid deposited from the solution. The supernatant remaining after 9 h contained orthophosphate as the only significant phosphorus species (^{31}P NMR) and essentially no dissolved vanadium (^{51}V NMR). Previous workers have noted that higher temperature promotes the decomposition the vanadophosphate polyanion.[9f,10]

An attempt was made to instead use phosphoric acid for the acidification of the metavanadate–orthophosphate solution. To a 4:1 sodium metavanadate–phosphoric acid solution (~0.7 M V, mixed 1–2 days earlier), additional 85% phosphoric acid was added to a total concentration of ~0.85 M to obtain pH 2.3. When the mixture was next examined after stirring overnight, a yellow solid had begun separating from the solution, which remained at pH 2.3. After serveral more days, ^{51}V NMR showed predominant, but far from complete, incorporation of the dissolved vanadium into the tetradecavanadophosphate polyanion. One other dissolved vanadium species, with a single resolved resonance at ~563 ppm (between the V(2) and V(3) resonances of the polyanion—see below), presumed to be VO_2^+, persisted in the solution. ^{31}P NMR showed an unusually broad orthophosphate resonance in addition to the normal tetradecavanadophosphate resonance. These observations are discussed in more detail in the section Pervanadyl Cation—Phosphoric Acid Interactions, below. The yellow solid, after separation, proved insoluble in water. It was not further characterized at the time (and unfortunately was not retained), but we now believe it to have been a $VOPO_4\cdot xH_2O$ material,[9b,12d,21] based on its color and the reported preparations of $VOPO_4\cdot xH_2O$ under similar conditions.[12d,21ce]

Stability of Solid Sodium Tetradecavanadophosphate Salts. Two and one-half years after its preparation, a sample of the air-dried material $Na_5[H_4PV_{14}O_{42}]\cdot 28H_2O$ (described in the Experimental Section) that had been stored at 25 °C in a sealed colorless glass vial in a dark cabinet in Umeå was found to no longer dissolve in water. On closer inspection, the material was seen to contain islands of yellowish material in the brown-red bulk. Another sample from the same batch of original material that was stored similarly at Catalytica was found to be still homogeneous in color and mostly, though not completely, soluble. Comparison of the powder X-ray diffraction patterns of the two samples revealed that the Umeå sample was morphologically distinct and much less crystalline. ^{31}P MAS NMR of the samples showed them to contain similar, but not the same, phosphorus environments. In the 4 years since these observations, the yellow islands in the unmixed metamorphic sample have slowly expanded. At the surface of the material in the vial, where physical mixing occurs with handling of the vial, the material is a salt-and-pepper-like mixture of yellow and brown-red particles.

These findings prompted the production of the second batch of salt, the material $Na_{4.75}[H_{4.25}PV_{14}O_{42}]\cdot NaCl\cdot 12H_2O$ (see Experimental Section). This material was dried *in vacuo* based on the speculation that waters of crystallization might facilitate unwanted phase changes. The powder X-ray diffraction pattern of this material, shortly after its production, showed it to have very low crystallinity, suggesting that its dehydration led to crystal collapse. Its ^{31}P and ^{51}V MAS NMR spectra were similar to those of the unchanged (or, less changed) sample of the earlier, more hydrous material. This material has remained visually homogeneous in color and completely dissolvable in water for over 4 years since its production.

We have no explanation to offer for the instability of the one salt sample, nor have we attempted to characterize its metamorphic product any further. We report these results to alert and inform future investigators.[22]

Equilibrium Analysis. Binary Subsystems. Formation constants and pK_a values of the monomeric orthophosphate species (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-}) that comprise the binary H^+–$H_2PO_4^-$ system in 0.6 M Na(Cl) at 25 °C were calculated from 185 experimental [H^+]-emf titration data points and 43 ^{31}P NMR chemical shift values in the ranges $1.4 < pH < 11.4$ and $5 < [H_xPO_4^{(3-x)-}] < 40$ mM. See Table 1.

The ^{31}P NMR chemical shift vs pH profile for these orthophosphate species in this ionic medium was characterized from

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(20) Eriksson, G. *Anal. Chim. Acta* **1979**, *112*, 375.

(21) (a) Ladwig, G. *Z. Anorg. Allg. Chem.* **1965**, *338*, 266. (b) Bordes, E.; Courtine, P. *C. R. Acad. Sci., Ser. C* **1972**, *274*, 1365. (c) Preuss, F.; Schug, H. *Z. Naturforsch.* **1975**, *30B*, 334. (d) Tietze, H. R. *Aust. J. Chem.* **1981**, *34*, 2035. (e) Casañ, N.; Amorós, P.; Ibañez, R.; Martinez-Tamayo, E.; Beltrán-Porter, A.; Beltrán-Porter, D. *J. Inclusion Phenom.* **1988**, *6*, 193.

(22) The metamorphic sample can be made available to suitable, interested investigators.

Table 1. Formation Constants, pK_a Values, and ^{31}P NMR Chemical Shifts of the Monomeric Orthophosphate Species in 0.6 M Na(Cl) at 25 °C

(*p*,*q*,*r*)	log β ($\pm 3\sigma$)	pK_a value	δ_P ($\pm 3\sigma$)	formula
−2,0,1	−17.650(5)		5.73(6)	PO_4^{3-}
−1,0,1	−6.418(3)	11.232	3.22(2)	HPO_4^{2-}
0,0,1		6.418	0.70(2)	$H_2PO_4^-$
1,0,1	1.772(2)	1.772	0.48(3)	H_3PO_4

Table 2. Formation Constants, pK_a Values, and ^{51}V NMR Resonance Assignments of Binary Vanadate Species in 0.6 M Na(Cl) at 25 °C[a]

(*p*,*q*,*r*)	log $\beta_{p,q,r}$	pK_a value	formula	NMR assignts
1,0,0			H^+	
−1,1,0	−7.92		HVO_4^{2-}	A
0,1,0		7.92	$H_2VO_4^-$	
−2,2,0	−15.17		$V_2O_7^{4-}$	B
−1,2,0	−5.25	9.92	$HV_2O_7^{3-}$	
0,2,0	2.77	8.02	$H_2V_2O_7^{2-}$	
−2,4,0	−8.88		$V_4O_{13}^{6-}$	C
−1,4,0	0.22	9.10	$HV_4O_{13}^{5-}$	
0,4,0	10.00		$V_4O_{12}^{4-}$	D
0,5,0	12.38		$V_5O_{15}^{5-}$	E
4,10,0	52.13		$V_{10}O_{28}^{6-}$	F, F′, F″
5,10,0	58.13	6.00	$HV_{10}O_{28}^{5-}$	
6,10,0	61.87	3.74	$H_2V_{10}O_{28}^{4-}$	
7,10,0	63.47	1.60	$H_3V_{10}O_{28}^{3-}$	
2,1,0	6.96		VO_2^+	G

[a] Data are taken from Pettersson et al.,[4] and the formation constants are recalculated for $H_2VO_4^-$ as the vanadium component.

the spectra of individual "point solutions", mixed to correspond to points in a pH titration (a simulated spectrometric titration). Additional ^{31}P NMR chemical shift vs pH data for the orthophosphate species were collected during the rapid spectrometric titrations of freshly dissolved sodium tetradecavanadophosphate salt, and are shown in Figure 7. The calculated chemical shifts of the individual H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, and PO_4^{3-} species are included in Table 1.

The orthophosphate ^{31}P NMR chemical shift vs pH dependence was frequently used as an internal pH probe for vanadophosphate solutions at pH > 5, where the chemical shift has a marked pH-dependence. (See Figure 7.) In the range 2 < pH < 6, the decavanadate ^{51}V resonance F″ (see Table 2 and Figure 2) could also be used to determine pH in vanadophosphate solutions.

The formation constants of the binary vanadate species, H^+–$H_2VO_4^-$, in 0.6 M Na(Cl) at 25 °C were taken from Pettersson et al.[4] Since that study used HVO_4^{2-} as the vanadium(V) component, the formation constants were recalculated for $H_2VO_4^-$, the vanadium(V) component used in the present study. The binary vanadate species and their formation constants, $\beta_{p,q,r}$ ($r = 0$), are given in Table 2.

Equilibrium Analysis. Ternary System. Equilibrations in the ternary vanadophosphate system were monitored by comparing NMR spectra recorded at increasing times after solutions were mixed. The mixed components (H^+, $H_2VO_4^-$, and $H_2PO_4^-$) take up to 4 months at 25 °C to reach equilibrium, forming tetradecavanadophosphate species (collectively, PV_{14}). Dissolved sodium tetradecavanadophosphate salt takes up to several years at 25 °C to reach equilibrium when decomposing partly or wholely to decavanadate at pH > ~2. Accordingly, most solutions in the present equilibrium study were prepared as individual "point" solutions from the components in order to reach equilibrium in minimal time. The formation and decomposition of PV_{14} species is relatively rapid only at pH < ~2, where "free" vanadium exists predominantly as the pervanadyl cation, VO_2^+.

Figure 2 shows a representative set of ^{51}V NMR spectra from equilibrated "point" solutions, having 8 mM phosphorus and 24 mM vanadium, in the pH range in which PV_{14} species exist at equilibrium. The three resonances, V(1), V(2), and V(3) (4:8:2 intensity ratio), of trans-bicapped Keggin PV_{14} species, having D_{2d} symmetry, appear in addition to the resonances of the binary vanadate species,[4,5] decavanadate (F, F′, F″) and the pervanadyl cation (G). As previously noted by Sasaki and co-workers,[10] the PV_{14} polyanion is unstable toward decavanadate at higher pH and toward pervanadyl at lower pH.

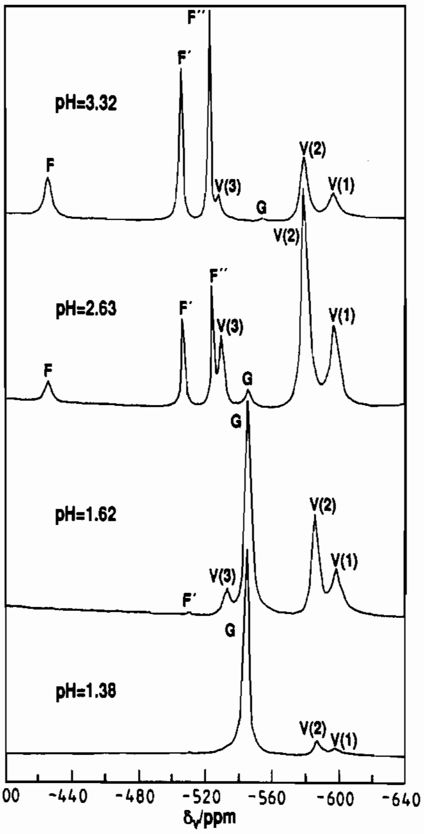

Figure 2. ^{51}V NMR spectra of equilibrated solutions having 8 mM phosphorous and 24 mM vanadium in 0.6 M Na(Cl) at 25 °C, in the pH range in which tetradecavanadophosphate species exist at equilibrium. The resonances labeled V(1), V(2), and V(3) are of $[H_xPV_{14}O_{42}]^{(9-x)-}$, as assigned in Figure 1. The resonances labeled F, F′, and F″ are of decavanadate, $[H_xV_{10}O_{28}]^{(6-x)-}$. The resonance labeled G is of pervanadyl, VO_2^+.

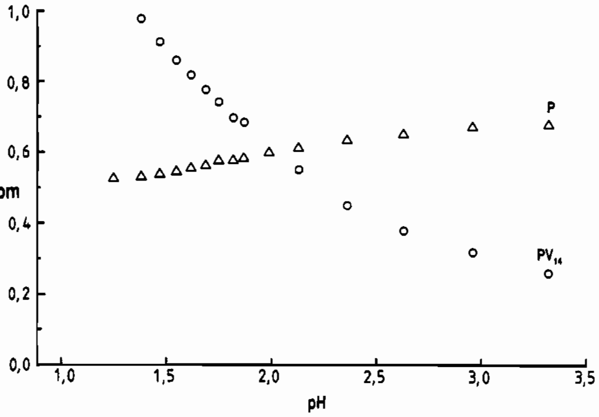

Figure 3. ^{31}P NMR chemical shifts of orthophosphate (triangles) and tetradecavanadophosphate (circles) plotted vs pH, in equilibrated solutions, containing 0.6 M Na(Cl), at 25 °C.

Both the ^{31}P and the ^{51}V NMR spectra of equilibrated "point" solutions were recorded. Figures 3 and 4 plot ^{31}P and ^{51}V chemical shifts, respectively, vs pH, at equilibrium.

The equilibrium speciation could be established only by simultaneous least-squares evaluation of [H^+]-emf data with the ^{31}P and ^{51}V NMR integral and shift data. The [H^+]-emf data alone were not definitive since decavanadates and PV_{14} species coexist at equilibrium in the PV_{14} pH-stability range and have similiar proton consumptions for their formations from the components, $H_2VO_4^-$ and $H_2PO_4^-$. ^{31}P and ^{51}V NMR are

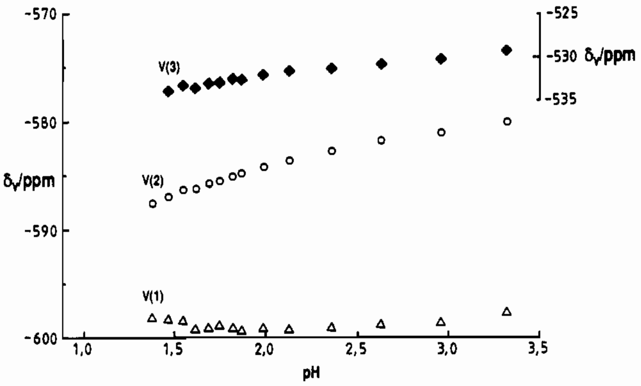

Figure 4. ^{51}V NMR chemical shifts of the three tetradecavanadophosphate resonances plotted vs pH, in equilibrated solutions, containing 0.6 M Na(Cl), at 25 °C. The open symbols for V(1) (triangles) and V(2) (circles) are plotted on the left-hand axis. The filled diamonds for V(3) are plotted on the right-hand axis.

Table 3. Formation Constants, pK_a Values, and ^{31}P NMR Chemical Shifts of the Equilibrium Tetradecavanadophosphate Species in 0.6 M Na(Cl) at 25 °C

(p,q,r)	log β ($\pm 3\sigma$)	pK_a value	δ_P ($\pm 3\sigma$)	formula
11,14,1	96.41(9)	1.57	1.40(6)	$H_5PV_{14}O_{42}^{4-}$
10,14,1	94.84(7)	4.1	0.31(2)	$H_4PV_{14}O_{42}^{5-}$
9,14,1	90.7(6)		-0.2(7)	$H_3PV_{14}O_{42}^{6-}$

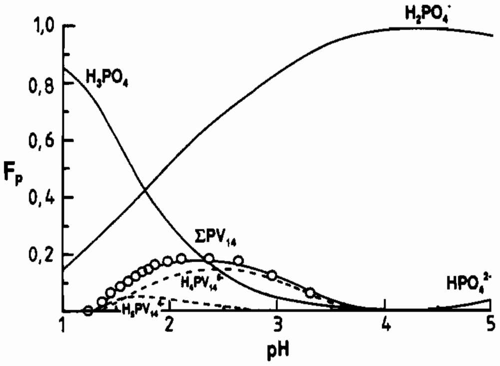

Figure 5. Distribution of phosphorus species at equilibrium plotted vs pH, in solutions of 8 mM P, 24 mM V, and 0.6 M Na(Cl), at 25 °C. F_P is the fraction of the total phosphorus. The circles represent NMR integral data from equilibrated solutions. Species less than 2% are omitted.

complementary to the [H$^+$]-emf data as they distinguish between the decavanadates and PV_{14} species, and the integral data measure the relative amounts of all the species present. Reliable ^{31}P integral data could not be obtained at pH ~ 2 where the chemical shifts of the H_3PO_4 and PV_{14} resonances cross. The deconvolution and integration of resonances in the ^{51}V spectra was complicated by severe overlap of the "capping" V(3) resonance with the decavanadate F″ resonance at higher pH and with the VO_2^+ resonance (G) at lower pH. (See Figure 2.) Combined [H$^+$]-emf, ^{31}P and ^{51}V integral data gave a satisfactory determination of the formation constant of the predominant PV_{14} equilibrium species, $[H_4PV_{14}O_{42}]^{5-}$. However, the full speciation could be established only by also including the ^{31}P and ^{51}V chemical shifts vs pH data in the least-squares calculations. The results are given in Table 3. Only a small fraction of $[H_3PV_{14}O_{42}]^{6-}$ was needed to explain the data, which is why the uncertainties in the formation constant and chemicals shift are greater for this species.

Distribution diagrams of P and V in equilibrated solutions (8 mM P, 24 mM V) are shown in Figures 5 and 6, respectively. The curves in the distribution diagrams were calculated using the formation constants of phosphates, vanadates, and vanadophosphates reported in Tables 1–3. The individual circles for ΣPV_{14} data represent the most reliable of the ^{31}P or ^{51}V NMR integral data, or in some cases a subjective compromise between them.

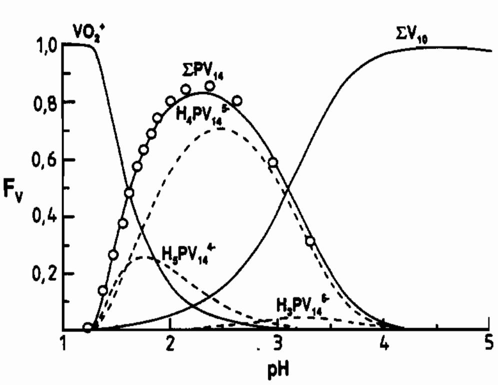

Figure 6. Distribution of vanadium species at equilibrium plotted vs pH, in solutions of 8 mM P, 24 mM V, 0.6 M Na(Cl), at 25 °C. F_V is the fraction of the total vanadium. The circles represent NMR integral data from equilibrated solutions.

The pH range for the existence of PV_{14} species at equilibrium, with 24 mM V and a sufficient excess of P (V:P = 3 in solution), is $1.3 < \text{pH} < 4.0$, with the maximum fraction of PV_{14} at pH ~ 2.3. $[H_4PV_{14}O_{42}]^{5-}$ is the predominant PV_{14} species over most of this pH-stability range. $[H_5PV_{14}O_{42}]^{4-}$ is comparably abundant at the acidic end of the pH-stability range, where, however, <~50% of the vanadium is present in the PV_{14} species. At the basic end of the pH-stability range $[H_3PV_{14}O_{42}]^{6-}$ appears as a minor species, whose existence was detected mainly in the chemical shift vs pH data.

No more than about 85% of the total V in these equilibrated solutions was incorporated into PV_{14} anions. (See Figure 6.) Excess P, compared to the V:P = 14 ratio, is required to incorporate most of V into PV_{14}. When an insufficient fraction of V is incorporated into PV_{14} at equilibrium, the binary vanadate species can saturate the solution, and V_2O_5 is precipitated. Indeed, solutions of dissolved sodium PV_{14} salt (V:P = 14 in solution) eventually precipitate V_2O_5, although this equilibration can take months to years.

Metastable $[H_xPV_{14}O_{42}]^{(9-x)-}$ Species. The decomposition of solution PV_{14} from dissolved sodium PV_{14} salt is so slow that it is possible to observe metastable species in the series $[H_xPV_{14}O_{42}]^{(9-x)-}$ outside the pH range $1.3 < \text{pH} < 4.0$ in which PV_{14} species (x = 3–5) exist in equilibrium. It proved possible to titrate solutions of freshly dissolved sodium PV_{14} salt (10 mM) immediately with H_3PO_4 (10 and 40 mM), HPO_4^{2-} (40 mM), or PO_4^{3-} (40 mM) without significant simultaneous decomposition. All titrations were performed in 0.6 M NaCl and 25 °C. A total of 45 data points were collected over the range $1.5 < \text{pH} < 6.5$ and used for determination of the pK_a values for the metastable species. ^{31}P and ^{51}V NMR spectra of freshly prepared "point" solutions of the salt were recorded to observe the PV_{14} species over a still wider range, $0 < \text{pH} < 8.5$. Below pH = 0, the PV_{14} decomposes to VO_2^+ too rapidly to record a PV_{14} spectrum at 25 °C. Above pH = 8.5 it decomposes too quickly to a mixture of meta- and orthovanadates, mainly HVO_4^{2-}.

The ^{31}P and ^{51}V chemical shifts vs pH data are plotted in Figures 7 and 8, respectively. As previously indicated by the data of Harrison and Howarth,[11] these data show that protonations of the PV_{14} polyanions occur over the entire range $0 < \text{pH} < 8.5$. No chemical shift plateau is reached at either extreme of this pH range, indicating that neither the fully protonated $H_9PV_{14}O_{42}$ nor the fully deprotonated $[PV_{14}O_{42}]^{9-}$ has been observed as a dominant species. Least squares evaluation of the titration data ($1.5 < \text{pH} < 6.5$) and the ^{31}P and ^{51}V NMR chemical shift data ($0 < \text{pH} < 8.5$) revealed six $[H_xPV_{14}O_{42}]^{(9-x)-}$ species. On the basis of the formulas (x = 4 and 5) and corresponding pK_a values established by the equilibrium analysis (Table 3), the six species observed were those with x = 1–6. Table 4 gives their pK_a values (x = 2–6) and their individual chemical shifts determined by the least-squares analysis. The pK_a values for the x = 4 and 5 species

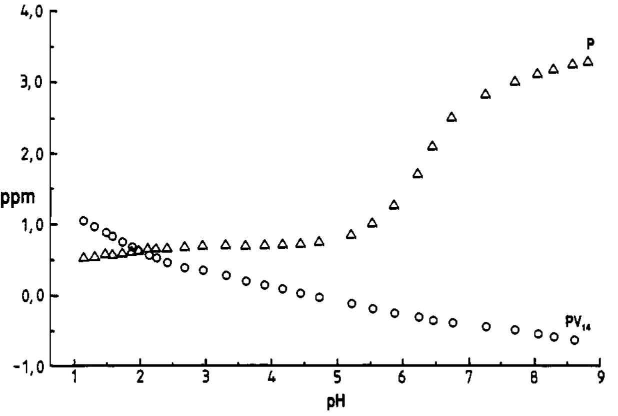

Figure 7. ^{31}P NMR chemical shifts of orthophosphate (triangles) and tetradecavanadophosphate (circles) plotted vs pH, in freshly prepared "point" solutions, containing 0.6 M Na(Cl), at 25 °C.

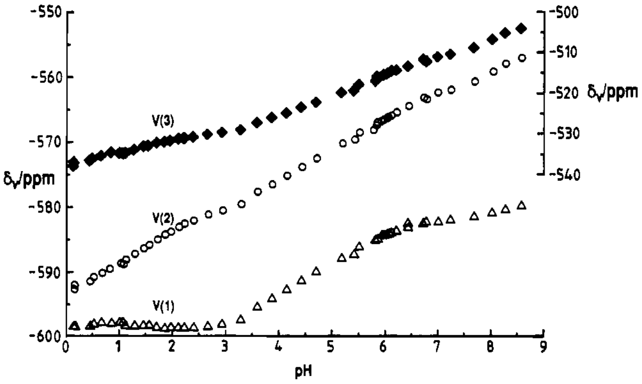

Figure 8. ^{51}V NMR chemical shifts of the three tetradecavanadophosphate resonances plotted vs pH, in freshly prepared "point" solutions, containing 0.6 M Na(Cl), at 25 °C. The open symbols for V(1) (triangles) and V(2) (circles) are plotted on the left-hand axis. The filled diamonds for V(3) are plotted on the right-hand axis.

Table 4. pK_a Values and ^{31}P and ^{51}V NMR Chemical Shifts of Tetradecavanadophosphate Species Determined from Rapid pH-Titrations and Chemical Shift vs pH Data from Freshly Prepared "Point" Solutions, in 0.6 M Na(Cl) at 25 °C

(p,q,r)	pK_a ($\pm 3\sigma$)	δ_P ($\pm 3\sigma$)	$\delta_{V(1)}$ ($\pm 3\sigma$)	$\delta_{V(2)}$ ($\pm 3\sigma$)	$\delta_{V(3)}$ ($\pm 3\sigma$)	formula
12,14,1	1.22(5)	1.2(2)	–598.2(5)	–592.4(6)	–537.3(7)	$H_6PV_{14}O_{42}^{3-}$
11,14,1	1.82(2)	1.0(1)	–598.2(9)	–585(1)	–532(1)	$H_5PV_{14}O_{42}^{4-}$
10,14,1	3.89(2)	0.34(4)	–599.1(5)	–581.2(6)	–530.6(8)	$H_4PV_{14}O_{42}^{5-}$
9,14,1	5.37(2)	–0.03(5)	–590.3(6)	–572.5(7)	–522(1)	$H_3PV_{14}O_{42}^{6-}$
8,14,1	6.88(4)	–0.28(5)	–583.9(4)	–566.5(4)	–515.8(6)	$H_2PV_{14}O_{42}^{7-}$
7,14,1		–0.58(3)	–580.6(4)	–558.5(5)	–506.2(6)	$HPV_{14}O_{42}^{8-}$

reasonably agree with the less precise values determined by the equilibrium analysis.

Observation of PV_{13} Species. While freshly dissolved sodium tetradecavanadophosphate salt is rapidly decomposing to VO_2^+ at high acidity (pH < 1.5) a transient species appears having three observable ^{51}V NMR resonances of near equal intensity (by deconvolution). A ^{51}V NMR spectrum, at pH ~ 0.2, is shown in Figure 9. A corresponding additional, transient resonance appears in the ^{31}P NMR spectrum at ~3.6 ppm. By about 30 min after dissolution, both the original PV_{14} and the transient species are completely decomposed to phosphoric acid and VO_2^+. The additional resonances in both the ^{31}P and ^{51}V NMR spectra are pH dependent over the entire pH range in which they were observed (0 < pH < 1.5), indicating protonation of the transient species within this pH range.

The observed ^{51}V and ^{31}P resonances of the transient species are consistent with a monocapped Keggin PV_{13} species, formed by dissociation of one "capping VO^{3+}" (VO_2^+ after dissociation) from a $[H_xPV_{14}O_{42}]^{(9-x)-}$, and probably having the formula $[H_xPV_{13}O_{41}]^{(12-x)-}$. ($x$ value need not be that of its PV_{14} parent.) The PV_{13} species, of ideal C_{2v} symmetry, would have five

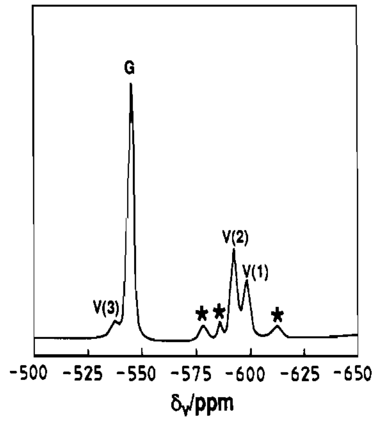

Figure 9. ^{51}V NMR spectrum of sodium tetradecavanadophosphate salt freshly dissolved in 0.6 M Na(Cl) at pH 0.2. V(1), V(2), and V(3) are the tetradecavanadophosphate resonances. G is the resonance of the pervanadyl cation, the final acidic decomposition product. The asterisks show the resonances of a transient intermediate species, assigned as a PV_{13} species.

potentially resolvable ^{51}V NMR resonances in the intensity ratios 2:2:4:4:1, related to the V(n) in the parent PV_{14} (Figure 1) as follows: V(1′):V(1″):V(2′):V(2″):V(3′), respectively. (The removal of the "cap" from one pole of D_{2d} PV_{14} cancels the improper rotation axis S_4 that intertransforms the V(2) sets at the two poles and intertransforms the V(1) sets oriented along orthogonal axes in the equatorial plane.) The "capped" V(2′) set and the "uncapped" V(2″) set are now in substantially different structural environments and their resonances appear resolved. The equitorial V(1′) and V(1″) sets, although no longer equivalent by symmetry, are still in very similar environments and their resonances appear unresolved as the third observable resonance of equal intensity. The least intense resonance of V(3′), the remaining "capping VO^{3+}", is presumed to be overlapped by either the "capping" V(3) resonance of the always more abundant PV_{14} or the adjacent resonance of the even more abundant VO_2^+, and so is not detected.

No transient, intermediate species could be detected when PV_{14} species was decomposed in alkaline solutions.

Pervanadyl Cation–Phosphoric Acid Interactions. In acidic solutions, pH < 1.5, containing high concentrations of *both* phosphoric acid and the pervanadyl cation, VO_2^+, their respective ^{31}P and ^{51}V NMR resonances are each shifted and substantially broadened compared to their normal chemical shifts and line widths in this ionic medium at this acidity. For example, in solution prepared from 50 mM sodium PV_{14} salt (700 mM V) and 300 mM H_3PO_4 at pH ~ 0.2, after complete decomposition of the PV_{14} anion, the phosphoric acid and pervanadyl cation resonances appeared as follows: The ^{31}P NMR resonance for phosphoric acid appeared at 0.78 ppm with a half-height line width of 58 Hz, compared to the normal 0.48 ppm and 1.6 Hz in this medium at this pH. The ^{51}V NMR resonance for VO_2^+ in the same solution appeared at –549.7 ppm with a half-height line width of 790 Hz, compared to the normal –545 ppm and 510 Hz in this medium at this pH.

Importantly, when PV_{14} is also present in such solutions, as when freshly dissolved sodium PV_{14} salt is decomposing in a pH < 1.3 solution containing additional H_3PO_4 (V:P ratio ~2, for example), the ^{31}P and ^{51}V NMR resonances of the PV_{14} species are completely normal, while those of phosphoric acid and VO_2^+ are each both shifted and broadened from normal. As the PV_{14} decomposes, increasing the VO_2^+ concentration, the phosphoric acid resonance is increasingly shifted and broadened. Similarly, the shift and breadth of the pervanadyl resonance appear to increase with increasing phosphoric acid concentration provided in the initial solution. Over longer times after the PV_{14} is fully

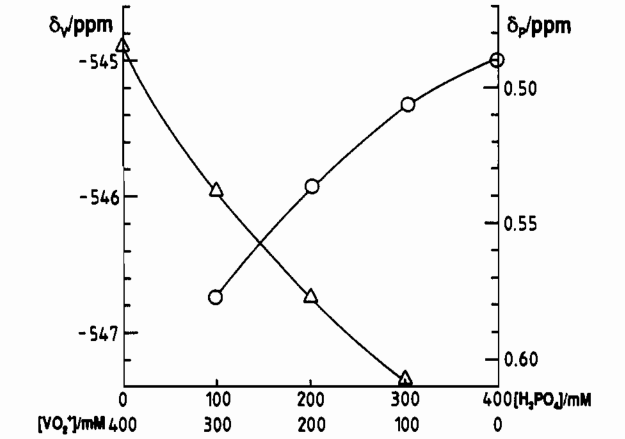

Figure 10. ^{31}P and ^{51}V NMR chemical shifts of phosphoric acid (circles) and pervanadyl cation (triangles), respectively, in solutions prepared by mixing a solution of 400 mM H_3PO_4 and a solution of 400 mM VO_2^+, each in 0.6 M Na(Cl) at pH 0.2, in varying proportions, plotted against the resulting phosphoric acid and vanadyl cation concentrations in the solutions.

decomposed, both the phosphoric acid and pervanadyl resonances return toward normal while a solid phase is slowly precipitated. These observations, in all, indicate that the shifted and broadened resonances are intrinsic to the VO_2^+ and H_3PO_4 species present and apparently interacting under these conditions and are not attributable to adventitious paramagnetic components in these solutions.

In our unsuccessful attempted synthesis of sodium PV_{14} salt by acidification to pH = 2.3 by a large excess of H_3PO_4 (see above), a remarkably broad ^{31}P NMR resonance (10–20 Hz half-height line width) for the orthophosphate in the solution was observed along with the normal resonance of PV_{14}. ^{51}V NMR of the solution showed substantial concentrations of VO_2^+ persisting in this solution. (We cannot assess the extent to which this resonance may have been shifted or broadened compared to "normal" for VO_2^+ in the absence of orthophosphate in the medium of this synthesis milieu, since the medium itself is substantially orthophosphate. Also, this resonance overlapped the V(2) resonance of the polyanion. Likewise, we do not know what chemical shift might be "normal" for orthophosphate hypothetically by itself in this medium.) This solution, held at room temperature, deposited a solid phase that, after separation, proved insoluble in water. In contrast, the successful syntheses of sodium PV_{14} salts using HCl for the acidifying mineral acid showed no significant VO_2^+ persisting in the solution and unremarkable ^{31}P NMR resonance line widths for the (much lesser) excess of orthophosphate in the solution and did not deposit a solid phase until refrigerated to crystallize the desired sodium PV_{14} salt. The undissolvable solid deposited from the high concentration phosphoric acid solution is now thought to have been a $VOPO_4{\cdot}xH_2O$ material,[9b,12d,21] based on its yellow color and the reported preparations of $VOPO_4{\cdot}xH_2O$ under similar conditions.[12d,21c,e]

To further confirm and characterize the apparent interaction between H_3PO_4 and VO_2^+ in solution, we recorded the ^{31}P and ^{51}V NMR spectra of solutions prepared by mixing a solution of 400 mM H_3PO_4 and a solution of 400 mM VO_2^+, each at pH ~ 0.2, in varying proportions. Figure 10 shows the ^{31}P and ^{51}V chemical shifts plotted against the H_3PO_4 and VO_2^+ concentrations in the solutions. The resonance of each species is seen to shift in response to the concentration of the other. Curiously, the resonance line widths were almost unchanged among these solutions. However, neither of the species experiences as high a concentration of the other in these solutions as in the solutions discussed above (and the product $[H_3PO_4][VO_2^+]$ is substantially less), nor are their resonances shifted as far from normal.

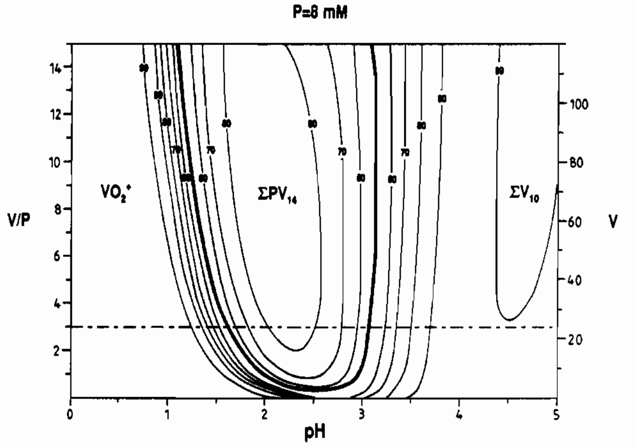

Figure 11. Vanadium predominance diagram over vanadium concentration and pH, with contour lines showing the fraction of the vanadium in the predominant species, summing over each protonation series ($[H_xPV_{14}O_{42}]^{(9-x)-}$ and $[H_xV_{10}O_{28}]^{(6-x)-}$), in solutions with 8 mM P in 0.6 M Na(Cl) at 25 °C. The dashed line at 24 mM V (V:P = 3) indicates to the vertical slice shown as the distribution diagram in Figure 6.

Discussion

Aqueous Vanadophosphate Equilibrium Speciation. The equilibrium speciation in the aqueous vanadophosphate system proved more challenging to establish than expected, in part due to extremely slow equilibrations in the pH range in which tetradecavanadophosphate species, $[H_xPV_{14}O_{42}]^{(9-x)-}$, and decavanadate species, $[H_xV_{10}O_{28}]^{(6-x)-}$, coexist at equilibrium. When vanadate and phosphate solutions are acidified, PV_{14}-forming equilibrations are relatively rapid only at pH < 2 where free vanadium exists predominantly as VO_2^+. In higher pH solutions, where free vanadium exists predominantly as decavanadates, PV_{14}-forming equilibrations can take up to 4 months at 25 °C. A higher temperature could not be used to accelerate the formation of PV_{14}, as it shifts the equilibrium away from the heteropolyanion. When presynthesized sodium PV_{14} salt is dissolved in solutions within the decavanadate pH-stability range, up to several years at 25 °C can be required to reach equilibrium.

No vanadophosphate species other than the tetradecavanadophosphate protonation series was detected in equilibrated solutions. Although this equilibrium speciation is rather simple, the complete compositions (including protonation states) of the thermodynamically stable species and their formation constants were not easily determined. This was not accomplished until the pH-titrimetric data and the ^{31}P and ^{51}V NMR integral and chemical shift data were simultaneously evaluated using the least-squares computer program LAKE.

At centimolar to decimolar vanadium concentrations, the $[H_xPV_{14}O_{42}]^{(9-x)-}$ species with $x = 3$–5 exist at equilibrium in the range ~1.3 < pH < 4.0. See Figures 5 and 6. At these vanadium concentrations, an excess of phosphate is required in the solution to keep enough of the vanadium bound in PV_{14} to avoid eventual precipitation of V_2O_5.

To further illustrate equilibrium conditions, not taking any solid phases into account, Figure 11 presents a vanadium predominance diagram with contour lines showing the vanadium fraction in the predominant species, summing over each protonation series ($[H_xPV_{14}O_{42}]^{(9-x)-}$ and $[H_xV_{10}O_{28}]^{(6-x)-}$), in solutions with 8 mM phosphorus. The horizontal dashed line at 24 mM vanadium (V:P = 3) corresponds to the conditions in Figure 6. The predominance diagram shows that less than 90% of V is bound in PV_{14} at its maximum. The range where greater than 80% of V is bound in PV_{14}, however, is considerable (~1 pH unit) and not very sensitive to total V concentration.

Tetradecavanadophosphate Syntheses. The equilibrium speciation nicely rationalizes the conditions reported in the literature[9-12] and herein for syntheses of tetradecavanadophosphate solutions and salts. Synthesis conditions are typically pH

2–3 with an excess of phosphorus over vanadium (relative to the PV_{14} ratio), just the conditions that favor the formation of tetradecavanadophosphates as the predominant vanadium species at equilibrium.

Moreover, when redissolvable salts, like the sodium salts in this study ($Na_5[H_4PV_{14}O_{42}]\cdot 28H_2O$ and $Na_{4.75}[H_{4.25}PV_{14}O_{42}]\cdot NaCl\cdot 12H_2O$), are crystallized from these solutions, the protonation state of the polyanion in the salt closely reflects the predominant protonation state in the parent solution, $[H_4PV_{14}O_{42}]^{5-}$ at pH = 2–3. (Harrison and Howarth[11] reported an octasodium salt, but that assignment was made solely by analogy to the octaguanidinium salt characterized by Sasaki and co-workers,[10] and was not analytically confirmed.[11b] Sasaki and co-workers also reported a soluble ammonium salt, whose formulation "was taken" as $(NH_4)_{6.5}[H_{2.5}PV_{14}O_{42}]\cdot nH_2O$, seemingly by proportioning to the $(NH_4)_6$:PV_{13} formulation reported by Preuss and Schug.[9f])

Sasaki and co-workers[10] obtained the only slightly soluble octaguanidinium salt, $(CN_3H_6)_8[HPV_{14}O_{42}]\cdot 7H_2O$, with only one proton bound by the polyanion, by addition of guanidinium chloride to a pH 2–3 solution. Apparently, guanidinium preferentially precipitates tetradecavanadophosphate anions which are more highly charged (less protonated) than those predominant in the parent solution. This is not an unusual behavior for guanidinium salts.

The absence of any vanadophosphate species other than tetradecavanadophosphates in the *equilibrium* speciation reinforces the skepticism expressed by Sasaki and co-workers[10] about earlier reports[9] of PV_{12} and PV_{13} polyanion salts. (Not noted by Sasaki and co-workers, solid vanadophosphates with still lower V:P ratios had been reported.[9b]) The observation of the tridecavanadophosphates as very short-lived solution species in this study still further reinforces that skepticism. Sasaki and co-workers reinterpreted the earlier reports of PV_{12} and PV_{13} polyanion salts as actually pertaining to the PV_{14} polyanion. On the basis of our findings, we are inclined to agree, with the following additional speculative elaboration. The solids reported to analyze for V:P < 14 may have contained coprecipitated $VOPO_4\cdot xH_2O$. Preuss and Schug[9f] took their results (from recrystallization and ultracentrifugation experiments) to indicate that PV_{14} ions seem to be stable species over a wide range of pH, while their purported PV_{13} ions were only stabilized in highly acidified solutions containing excess of phosphate. These are conditions that favor the formation of $VOPO_4\cdot xH_2O$ solids.[12d,21c]

Metastable Tetradecavanadophosphate Speciation. Due to the very slow decomposition of tetradecavanadophosphate to decavanadate, supersaturated solutions of PV_{14} can be long-lived, even without excess phosphate. The sodium PV_{14} salts prepared for this study could be dissolved up to ~50 mM concentration (700 mM V), giving solutions whose initial ^{31}P and ^{51}V NMR spectra showed no resonances other than those of PV_{14}. Such solutions, when in the PV_{14} pH-stability range (optimally pH 2–3), could be stored for months before significant PV_{14} decomposition to decavanadate was discerned in the NMR spectra. Over longer times with further decomposition, V_2O_5 precipitation occurred.

PV_{14} species could be observed (^{31}P and ^{51}V NMR) in fresh solutions well outside the pH range in which any exist at equilibrium, covering the broader range 0 < pH < 8.5. Taking advantage of the slow decomposition of the PV_{14} polyanion and the reasonably high solubility of the sodium salts, the six $[H_xPV_{14}O_{42}]^{(9-x)-}$ species having x = 1–6 and their intermediary pK_a values (for the x = 2–6 species) were established from rapid pH-titration data and the ^{31}P and ^{51}V NMR chemical shift vs pH data recorded with freshly prepared "point" solutions. (Figures 7 and 8 and Table 4.)

Deprotonation as far as $[HPV_{14}O_{42}]^{8-}$ was observed (pK_a of $[H_2PV_{14}O_{42}]^{7-}$ at pH = 6.9). Above pH = 8–9, the alkaline decomposition of the polyanion to meta- and orthovanadates became too fast to observe the fully deprotonated polyanion (at 25 °C, at least). Protonation as far as $[H_6PV_{14}O_{42}]^{3-}$ (pK_a = 1.2) was observed. Below pH = 0–1, acidic decomposition of the polyanion to VO_2^+ became too fast to observe still further protonated species (at 25 °C, at least).

Metastable Tridecavanadophosphate Species. When $[H_xPV_{14}O_{42}]^{(9-x)-}$ species are decomposing to phosphoric acid and VO_2^+ in acidic solutions, an intermediate appears in the ^{31}P and ^{51}V NMR spectra, whose ^{51}V NMR spectrum accords with a PV_{13} species formed by dissociation of one "capping VO^{3+}". A polyhedral representation of the monocapped α-Keggin structure can be visualized in Figure 1 by ignoring the cap of PV_{14} that is shown separate in the exploded view.

The chemical shifts of the PV_{13} resonances show a pH dependence over the entire pH range in which they were observed, 0 < pH < 1.5, indicating a protonation step within this pH range. The PV_{14} species observed in this pH range, prior to their decomposition, are $[H_6PV_{14}O_{42}]^{3-}$ (pK_a = 1.2) and $[H_5PV_{14}O_{42}]^{4-}$. To maintain the polyanion charge—typical for polyoxoanion equilibrations at unchanged pH—three protons must be bound to compensate for dissociation of the "capping VO^{3+}". Accordingly, we tentatively suggest that the observed transient PV_{13} species are $[H_9PV_{13}O_{41}]^{3-}$ and $[H_8PV_{13}O_{41}]^{4-}$.

Tetradecavanadophosphate Protonation Sites. Zubieta and co-workers[13] located the four polyanion-bound protons in a crystal of the salt $(Me_3NH)_4(NH_4)[H_4PV_{14}O_{42}]$ in a symmetrically arranged set (S_4 axis) of four of the eight "uncapped" surface edge-shared oxygens, V(1)–O_e–V(2), where indicated in Figure 1. Protonation appears at one of the two "uncapped" edge-shared oxygens in each of the four edge-sharing V_3O_{13} groups of the hypothetical parent α-Keggin $PV_{12}O_{40}$ structure. These eight edge-shared oxygens are expected to provide the first four protonation sites[23] (in solution, at least), and it is not surprising that the four protons are distributed one each over the four edge-sharing V_3O_{13} groups. It is noteworthy, however, that the protons do not appear as equally distributed, on average, over all eight of these oxygens, half each. Curiously, the crystal is ordered not only with respect to the symmetry of the polyanion's tetraprotonation but also with respect to its chirality. Only one of the enantiomers having this symmetry occupies the single polyanion site in the structure. That is, this salt crystallizes as a conglomerate rather than a racemate.

We attempted to identify the polyanion's protonation sites in solution by natural abundance ^{17}O NMR, but weak signal intensity and long data acquisition times limited the pH range over which spectra containing PV_{14} resonances above baseline could be obtained, and in that range, pH changes across pK_a values did not appear to uniquely shift individual resonances. The enriched abundance ^{17}O NMR shift vs pH data of Harrison and Howarth[11] likewise show resonances shifting simultaneously with pH.

The pH-dependencies of the ^{51}V NMR resonances' chemical shifts (Figure 8) can be taken as consistent with $[H_4PV_{14}O_{42}]^{5-}$ in solution also being protonated at four of the eight "uncapped" surface edge-shared oxygens, V(1)–O_e–V(2), where expected.[23] The shift of V(1) changes continuously with decreasing pH from the highest pH, where the polyanion is $[HPV_{14}O_{42}]^{8-}$ until pH ~ 3, where it is predominantly $[H_4PV_{14}O_{42}]^{5-}$ (pK_a = 3.9). It then remains essentially unchanged as the pH is further decreased and the polyanion is protonated as far as $[H_6PV_{14}O_{42}]^{3-}$, indicating that these two further protonations do not occur at oxygens bound to V(1). The shift of V(2) changes continuously with pH over the entire pH range, no doubt reflecting that all the protonations must occur at oxygens bound to V(2). (Polyoxoanions protonate at bridging oxygens, not terminal oxygens. All the bridging oxygens in the tetradecavanadophosphate structure are bound to V(2) vanadiums.) The shift of V(3) similarly changes continuously with pH over the entire pH range. To account for the shift of the V(3) resonance at pH > 3, we can suggest that it is not unreasonable that the strength of the bonding of the "capping VO^{3+}" by the V(2)–O–V(2) oxygens responds to the anionic

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[23] See footnote 22 (and references cited therein) in ref 1a.

charge neutralization of the polyanion by nearby protonation at the V(1)–O_e–V(2) sites.

The unchanging ^{51}V NMR shift of V(1) and the changing shifts of V(2) and V(3) as the polyanion is protonated from $[H_4PV_{14}O_{42}]^{5-}$ to $[H_6PV_{14}O_{42}]^{3-}$ at pH < 3 indicate that these two additional protonations occur at oxygens shared by V(2) and V(3). These are oxygens that bind the "capping VO^{3+}" units to the polyanion. It seems reasonable to propose that these two additional protonations occur one at each cap. Indeed, the measured pK_a values (1.8 and 1.2) suggest that the two protonation sites are remote and insulated from each other. The difference between them ($K_6/K_5 = 4$) is exactly that predicted by statistical factors for noninteracting, equivalent protonation sites. (The higher pK_a corresponds to each site being one-fourth protonated. The lower pK_a corresponds to each site being three-fourths protonated.) The unchanging chemical shift of the equatorial V(1) set over these protonations accords with these protonation sites being insulated from each other.

The protonation of these oxygens must weaken their bonding to the "capping VO^{3+}" units. Indeed, the polyanion is unstable toward hydrolytic dissociation (to free VO_2^+ and phosphoric acid) in the acidic solutions where these protonations occur. The observation of transient "monocapped" PV_{13} species during these acidic decompositions of PV_{14} corroborates the theory that the decomposition begins with the loss of a "VO^{3+} cap", no doubt initiated by the protonation of an oxygen that binds it.

From this perspective, we can rationalize why $[H_4PV_{14}O_{42}]^{5-}$ is the most stable of the tetradecavanadophosphates. This degree of protonation provides the highest degree of polyanionic charge neutralization possible without destabilizing the polyoxoanion's structure. Further protonations mainly just compete with the "capping VO^{3+}" for anionic charge neutralization and destabilize the trans-bicapped α-Keggin structure. Moreover, this degree of protonation, to $[H_4PV_{14}O_{42}]^{5-}$, happens to occur in the crevice between the stability ranges of decavanadates and pervanadyl, where otherwise V_2O_5 precipitates.

Comments on Pentadecavanadate and Tridecavanadate. Hill and co-workers[24] have recently prepared a pentadecavanadate ion by oxidation of aqueous $V^{IV}O^{2+}$ with H_2O_2, and isolated and characterized (X-ray structure) the salt $(Me_4N)_3H_6V_{15}O_{42}\cdot 2.5H_2O$. The $[H_6V_{15}O_{42}]^{3-}$ ion has a trans-bicapped α-Keggin structure essentially isostructural with the tetradecavanadophosphate anion, with a central tetrahedral vanadium(V) instead of a phosphorus(V). The chemical behaviors of the V_{15} and PV_{14} anions also appear very similar. On redissolution in weakly acidic solution, both are kinetically quite robust. Hill and co-workers report no decomposition of V_{15} in pH = 3.5 solution over one week at 25 °C. Both ultimately decompose to decavanadate, the stable isovanadium(V) species in weakly acidic solution. However, the PV_{14} anion can be at least partially stabilized at equilibrium by sufficient free phosphate concentration. For both, their decomposition is greatly accelerated by increasing temperature.

Both anions are multiply protonated to reduce the high anionic charge of the hypothetical $[MV_{14}O_{42}]^{9-}$ ions (M = P, V). In the weakly acidic solutions in which V_{15} and PV_{14} species can kinetically persist, the most stable PV_{14} species is the *tetra*protonated ion, $[H_4PV_{14}O_{42}]^{5-}$. $[H_5PV_{14}O_{42}]^{4-}$ is at best a minor equilibrium species and $[H_6PV_{14}O_{42}]^{3-}$, having $pK_a = 1.2$, is labile toward rapid decomposition to VO_2^+. Thus, it is somewhat curious to see the *hexa*protonated $[H_6V_{15}O_{42}]^{3-}$ ion found by Hill and co-workers.[24] Perhaps the tetramethylammonium salt's crystal structure selects and stabilizes this higher protonation state preferentially over the *tetra*protonated state that is expected to predominate in its parent solution. Alternatively, the ion's synthesis from vanadium(IV), the black color of the crystals, and the high degree of protonation lead to a *speculation* that the crystals *possibly* contain a vanadium(IV) somewhere in the polyanion.[25] The assembly of these V_{15} ions from, in part, vanadium(IV) components before their oxidation *appears* reasonable since they have not been observed as yet in solutions prepared solely from vanadium(V) components. (See comments on tridecavanadate, below.)

Hill and co-workers[24] presented convincing data (EPR, NMR, UV–vis) indicating that the V_{15} ion is both intact and fully oxidized (all vanadium(V)) when redissolved in aqueous solution—presumably, in *aerobic* aqueous solution. The reported ^{51}V NMR spectrum in pH 3.5 solution (V(1) −597 ppm; V(2) −584 ppm; V(3) −531 ppm) is very similar to that of $[H_4PV_{14}O_{42}]^{5-}$, supporting the expectation that fully oxidized V_{15} exists predominantly as the tetraprotonated ion $[H_4V_{15}O_{42}]^{5-}$ in solution at this pH, where it is kinetically robust.

The only nonequilibrium isovanadate(V) species observed to date in solutions prepared solely from vanadium(V) components is a tridecavanadate ion, $[H_xV_{13}O_{40}]^{(15-x)-}$, also having a central tetrahedral vanadium (V).[26] Its protonation state in its pH-formation range, pH = 1–2, was proposed to be $[H_{12}V_{13}O_{40}]^{3-}$ based on the typical charge of aqueous polyoxoanions of this size at this pH. Note that hypothetical replacement of six H^+ in this ionic formula with two "capping VO^{3+}" leads to the composition $[H_6V_{15}O_{42}]^{3-}$. However, $[H_xV_{13}O_{40}]^{(15-x)-}$ may have the ε-Keggin structure,[26] rather than the α-Keggin structure underlying the structurally characterized $[H_6V_{15}O_{42}]^{3-}$ ion.[24] Indeed, the apparent predilection of the α-Keggin structures underlying PV_{14} and V_{15} to have bound "capping VO^{3+}" units, rather than a compensating number of protons, supports the alternative assignment of the ε-Keggin structure to the metastable $[H_xV_{13}O_{40}]^{(15-x)-}$ species.

Pervanadyl Phosphate Solution Species. The shifted and broadened NMR resonances of phosphoric acid and VO_2^+ in acidic solutions containing both indicate exchange broadening via a rapid equilbrium association/dissociation of these species, as represented by eq 4. In (*p*,*q*,*r*) notation, the resulting complex

$$xH^+ + VO_2^+ + H_2PO_4^- = (H^+)_x(VO_2^+)(H_2PO_4^-) \quad (4)$$

is (x + 2,1,1). (VO_2^+ is (2,1,0) using $H_2VO_4^-$ as the reference vanadium component. See Experimental Section.) We do not know x in this equilbrium. If no free hydrogen ions are involved ($x = 0$), relative to $H_2PO_4^-$ as component, then a neutral (2,1,1) complex results. Such a neutral complex could be pervanadyl ligated by dihydrogen phosphate, $VO_2(H_2PO_4)$(aq), or, with loss of water, $VOPO_4$(aq). Both these neutral formulations appear reasonable as solution precursors to the solid $VOPO_4\cdot xH_2O$ that appears to form from such solutions. We favor the $VO_2(H_2PO_4)$(aq) formulation in view of the rapid rate of exchange and the similarity of the chemical shifts to those of free phosphoric acid and VO_2^+.

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(25) Björnberg, A.; Hedman, B. *Acta Crystallogr.* **1980**, *B36*, 1018. These authors have reported a one-electron-reduced heteropolyanion with an α-Keggin structure and a central V^VO_4 unit, $[V^V(V^{IV}V^VMo_{10})O_{40}]^{6-}$—a "one-electron heteropoly blue". The dark brown crystals were formed from a fully oxidized molybdovanadate solution. This seems to indicate that V(V) in a surrounding octahedron is easily reduced when V(V) is present in the center of the Keggin structure. The crystals are sparingly soluble in water, so it is not known if this species is reoxidized in aerobic aqueous solution. Such reoxidation has, however, been observed in Umeå when reduced molybdovanadophosphates are dissolved in aqueous solution. The at first green-blue solutions turn yellow/orange when exposed to air.

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