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Dimerization of Aquadioxovanadium(V) Ion in Concentrated Perchloric and Sulfuric Acid Media[1a]

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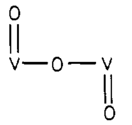
The aquadioxovanadium(V) ion was found to give a dimer with a central $V_2O_3^{4+}$ group in concentrated $HClO_4$ and H_2SO_4 media. Evidence for dimerization was obtained by UV-visible, Raman, and NMR spectroscopy, X-ray scattering, and cyclic voltammetry. The mass action law constant of the dimerization reaction is equal to 1.54 M^{-1} for 11.8 M $HClO_4$ and 83 M^{-1} for 10 M H_2SO_4. Vanadium(V) exists in the pure dimeric form for a H_2SO_4 concentration range of 13-16 M. Raman and X-ray scattering indicate the dimer structure is of the type



with a nonlinear oxygen bridge and a V-V distance of 3.25 Å. ^{51}V NMR is also consistent with this formulation. The vanadium(V) dimer in H_2SO_4 medium exhibits a reversible redox behavior on polished platinum and glassy carbon electrodes. In 13-16 M H_2SO_4 media, a large increase in vanadium concentration or an increase in temperature leads to a further polymerization step to form a soluble species with a long V-O-V-O-V- chain. Vanadium(V) and neptunium(V) dimers are compared.

Introduction

It has been recently demonstrated that aquadioxovanadium(V) and aquaoxovanadium(IV) ions are able to form a mixed-valence "cation-cation" complex, $V_2O_3^{3+}$, in perchloric, sulfuric, and hydrochloric acid media.[2] This "cation-cation" complex involving vanadium ions exhibits properties similar to those for the "cation-cation" complexes involving actinide(V) MO_2^+ ions.

In order to compare the ability of vanadium(V) and actinide(V) ions to form "cation-cation" complexes, two kinds of studies were undertaken. In the first work a comparison was made by electronic and Raman spectroscopy[3] of the reactivity of $VO_2(aq)^+$ and $NpO_2(aq)^+$ ions with $VO(aq)^{2+}$. In the present work, we report the study of the dimerization of aquadioxovanadium(V) ion in concentrated perchloric and sulfuric acid solution by electronic, Raman, and NMR spectroscopy and by X-ray scattering and cyclic voltammetry. This study was initiated in order to compare $VO_2(aq)^+$ with $NpO_2(aq)^+$, which, as has been recently demonstrated,[4] possesses the ability to form a dimer and even higher polymers in perchlorate solutions.

Experimental Section

Chemicals. The chemicals NH_4VO_3, H_2SO_4(d = 1.84), $HClO_4$ (70% by weight), $KMnO_4$, and $Fe(NH_4)_2(SO_4)_2{\cdot}5H_2O$ were analytical grade reagents meeting ACS specifications. They were used without additional purification.

Vanadium(V) Solutions. Preparation. Vanadium(V) stock solutions were prepared by dissolving weighed amounts of NH_4VO_3 in $HClO_4$ or H_2SO_4 solutions of the desired concentration with vigorous shaking. For the yellow solutions of vanadium(V), no particular problems occurred. The preparation of concentrated vanadium(V) solutions in concentrated $HClO_4$ required a special procedure. It was noted that warming the concentrated $HClO_4$ solution in order to improve the rate of dissolution of NH_4VO_3 always converted the NH_4VO_3 solid into another solid, the red-brown hydrated vanadium pentoxide $V_2O_5{\cdot}nH_2O$.[5] In these attempts, solutions of low vanadium(V) concentrations were obtained. However, NH_4VO_3 was found to dissolve in cold (≃ 0 °C) concentrated $HClO_4$, giving a dark red solution that is stable for months without the precipitation of $V_2O_5{\cdot}nH_2O$ when stored at -5 °C, and is stable for hours at room temperature. By the use of this procedure a 1 M vanadium(V) solution in concentrated $HClO_4$ medium was easily obtained. The preparation of concentrated vanadium(V) solutions in 12-14 M H_2SO_4 was accomplished by the slow addition of fine NH_4VO_3 powder to concentrated H_2SO_4 solutions with vigorous shaking to prevent the formation of a vanadium(V) solid compound (polymeric vanadium(V) sulfate). A dark red 1 M vanadium(V) solution so prepared was stable for months at room temperature (for $[H_2SO_4]$ = 12 M). It was observed that the darkness of the solution increased with increasing temperature. This process was reversible, and cooling the warm solution to room temperature restored the initial color.

Analytical Determinations. The concentration of vanadium(V) in the stock solutions was checked by potentiometric titrations using saturated calomel and platinum wire electrodes connected to a potentiometer. Titrations were performed on aliquots diluted in 6 M H_2SO_4 solution with 0.1 M Fe^{2+} solution as titrant.[6]

Spectrometric Measurements. Electronic Spectra. A Cary 14 spectrophotometer was used for measurements of electronic spectra in the visible and UV regions. One-centimeter quartz cells were used, and the patthlength was varied from 1 to 0.02 cm by using quartz spacers in order to adjust the measured absorbance at selected wavelengths to the range 0.05-1. For dilute vanadium(V) solutions a pair of 5-cm quartz cells was used. Prior to recording a spectrum the temperature of the solution was measured. Temperatures were in the range 22 ± 1 °C. A special thermostated 1-cm cell equipped with an electrical heater, a water circulation temperature adjustment, and a thermocouple for temperature measurements was used for the study of the influence of temperature on the electronic spectrum of vanadium(V) in H_2SO_4 medium.

Raman Spectra. Raman spectra were recorded with a Ramanor HG-2S spectrophotometer (Jobin Yvon-Instruments SA). Spectra were accumulated with a Nicolet 1170 signal analyzer, which permitted repetitive scanning for enhanced signal to noise ratio. Excitation was with the 632.8-nm line of a Spectra-Physics Model 125 helium-neon

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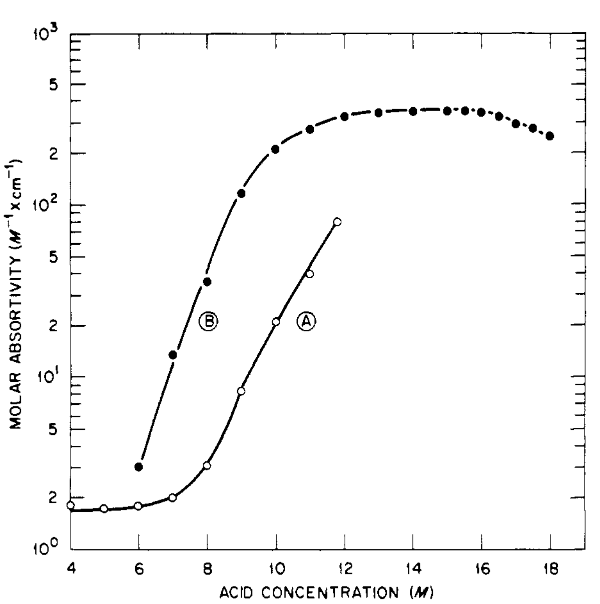

Figure 1. Influence of acid concentration on the molar absorptivity (λ = 470 nm) of vanadium(V) solutions in $HClO_4$ (A) and H_2SO_4 (B) media. Total vanadium(V) concentration $C^T_{V(V)}$ = 0.1 M (A), 0.02 M (B); path length = 0.1 and 1 cm; T = 22 °C.

laser. A spike filter was used to eliminate plasma lines. Slit widths were in the range 4–8 cm^{-1}. Samples were placed in small (4 mm square) glass cells. For measurements of Raman spectra above room temperature the sample cells were placed in a Pyrex glass resistance heated "furnace" equipped with a thermocouple for temperature measurement. Raman spectra were observed at 90° to the exciting light. The monochromator slits were parallel to the plane formed by the exciting laser light and the observed Raman light. Polarization measurements were made by rotating the plane of polarization of the exciting laser light by 90°. A polarization scrambler was used in the light path just before entry into the monochromator.

^{51}V NMR Spectra. ^{51}V NMR spectra were recorded with a Bruker WM 400 spectrometer in the pulse (Fourier transform) mode. The frequency was 100.5 MHz, and nonspinning samples were used. Chemical shifts were measured with respect to a solution of $NaVO_3$ in 1 M NaOH contained in a coaxial tube. This yielded a very sharp signal due to VO_4^{3-}. The shifts were then converted with respect to $VOCl_3$ by using δ $VOCl_3$ = δ VO_4^{3-} – 536.[7] The reference solution was prepared with D_2O, which provided the lock.

X-ray Scattering. The wide-angle X-ray scattering apparatus and its use have been extensively described previously.[8] The variation with angle of the intensity of the scattered Mo Kα X-radiation (λ = 0.7107 Å) was measured in reflection geometry in four angular ranges, extending from 2 to 130°. This angular interval is equivalent to the variation of k from 0.3 to 16.0, where $k = (4\pi/\lambda) \sin \theta$ and 2θ is the scattering angle; data were taken in steps of Δk = 0.1.

Four different solutions were investigated by X-ray scattering—a sample containing only 13.5 M H_2SO_4, and three samples that contained very different concentrations of vanadium(V), namely 0.9, 2.02, and 2.97 M in strong H_2SO_4 (9.6–11 M).

Cyclic Voltammetry. Cyclic voltammetry experiments were performed with Tacussel equipment consisting of a PRT 30-01 Potentiostat, a GSATP linear scan generator, and an X–Y recorder. The scan rate was generally 0.05 V s^{-1}. The working electrode was a nonplatinized platinum wire or a glassy carbon rod. Potentials were measured with respect to a saturated calomel electrode (SCE). Relatively high (about 10^{-2} M) vanadium concentrations were used in order to minimize the influence of residual currents.

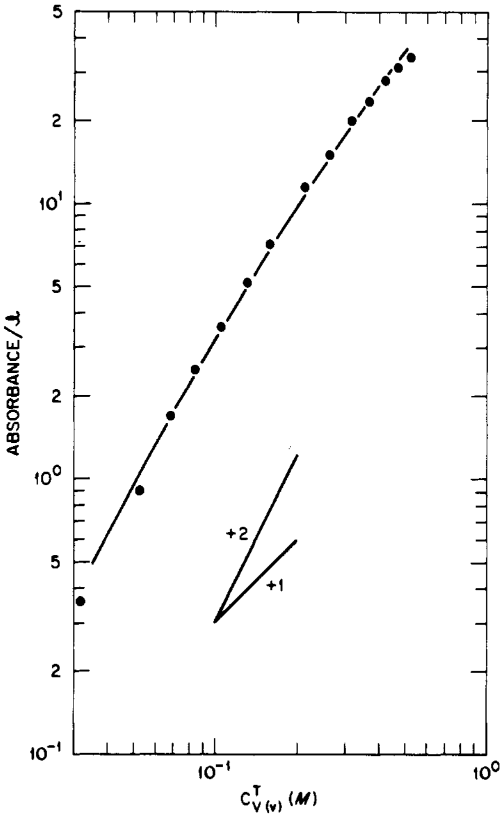

Figure 2. Variations of the absorbance at λ = 500 nm of vanadium(V) solutions in 11.8 M $HClO_4$ medium vs. total vanadium(V) concentration ($C^T_{V(V)}$). Absorbances are normalized for a 1-cm path length; T = 22 °C; (●) experimental data; curve calculated with ϵ^{500}_{dimer} = 320 M^{-1} cm^{-1} and K_D = 1.54 M^{-1}.

Results

Identification of Vanadium(V) Dimer and Equilibrium Study. Electronic Spectra. Vanadium(V) solutions in diluted $HClO_4$ or H_2SO_4 acid media possess the yellow color corresponding to the $VO_2(aq)^+$ ion; as the acid concentration is increased the color of the solutions gradually turns to orange and red. This effect, while well-known for a long time for H_2SO_4 solutions,[9] has not been satisfactorily explained until now. This corresponds in the visible spectra to the shifting toward higher wavelengths of an intense band located in the UV region.

The variations of the molar absorptivity of vanadium(V) solutions at 470 nm vs. the concentration of acid are shown in Figure 1 for $HClO_4$ and H_2SO_4 media. For $HClO_4$ solutions the molar absorptivity increases monotonically for $[HClO_4] \geq 7$ M. The molar absorptivities for all the H_2SO_4 solutions are higher than those corresponding to the $HClO_4$ media. The regular increase observed in the range 6–13 M H_2SO_4 is followed by a plateau from 13–16 M H_2SO_4. For H_2SO_4 concentrations >16 M a net decrease in the molar absorptivity was noted. We have studied at constant acid concentration ($HClO_4$ or H_2SO_4) the variation of the absorbance of vanadium(V) solutions vs. the total vanadium(V) concentration, [V(V)], at a selected wavelength corresponding to a low VO_2^+ monomeric ion absorptivity. The variations of absorbances at λ = 500 nm ($HClO_4$ medium) or λ = 470 nm (H_2SO_4 medium) of vanadium(V) solutions vs. [V(V)] are shown in log/log plots in Figures 2 for $HClO_4$ and H_2SO_4 media, respectively. For the $HClO_4$ medium the experimental data obtained for low total vanadium(V) concentrations are close to a straight line with a slope equal to 2; for higher vanadium(V) concentrations some curvature is observed and the curve tends toward a straight line with a slope of 1. For the sulfuric acid medium at low concentrations the experi-

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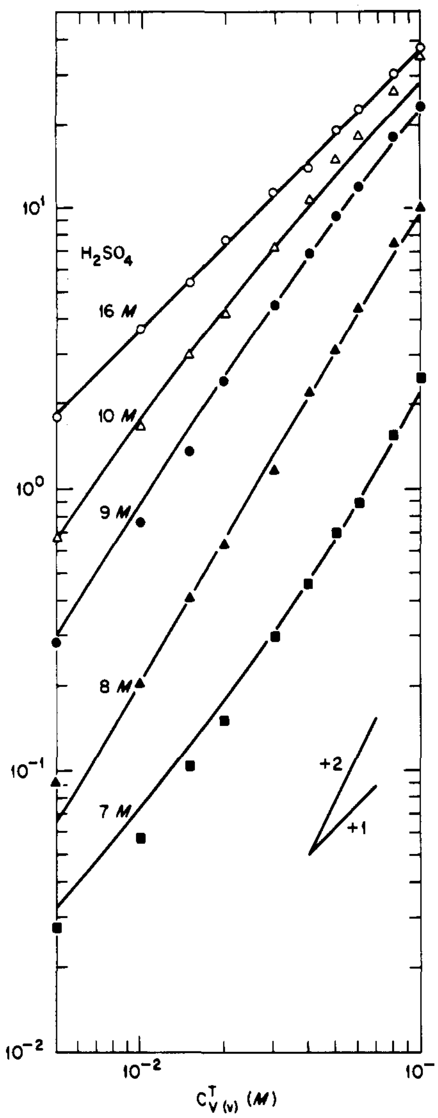

Figure 3. Variations of the absorbance at λ = 470 nm of vanadium(V) solutions in H_2SO_4 medium vs. total vanadium(V) concentration ($C^T_{V(V)}$). Absorbances are normalized for a 1-cm path length; H_2SO_4 concentrations are noted on the curves; T = 22 °C. Points are experimental data; curves were calculated with $\epsilon^{470}_{VO_2^+} = 4.2$ M^{-1} cm^{-1}, $\epsilon^{470}_{dimer} = 747$ M^{-1} cm^{-1}, and K_D values presented in Table I.

mental data fit a straight line with a slope of 2. The slope gradually decreases with the increase of [H_2SO_4]. For [H_2SO_4] = 16 M, the experimental data lie on a straight line with a slope of 1. It should be noted that the contribution of the monomeric VO_2^+ ion to the absorbances measured ($\epsilon^{470}_{VO_2^+}$ = 4.2 M^{-1} cm^{-1}) explains the deviations from linearity observed for the data corresponding to 7 and 8 M H_2SO_4 for [V(V)] ≤ 0.02 M.

These patterns show the occurrence of a dimerization reaction in both $HClO_4$ and H_2SO_4 media, instead of a reaction involving only monomeric species, as claimed by Lukachina et al.[10] The dimerization reaction can be written in two different ways:

$$2VO_2^+ \rightleftarrows V_2O_4^{2+} \qquad (1)$$

or

$$2VO_2^+ + 2H^+ \rightleftarrows V_2O_3^{4+} + H_2O \qquad (2)$$

with the elimination of a water molecule from the first hydration shell of one $VO_2(aq)^+$ ion in the case of reaction 1 or of one oxygen atom from one VO_2^+ ion in the case of reaction 2 and the possible complexation of $V_2O_4^{2+}$ or $V_2O_3^{4+}$ by HSO_4^- ions for the sulfuric acid solutions.

Table I. Mass Action Law Constant for the Dimerization of Aquadioxovanadium(V) Ion in Sulfuric Acid Media

[H_2SO_4], M	K_D, M^{-1}	% σ_{K_D}
7	0.26	±13.8
8	2.3	±8.3
9	19	±13.4
10	83	±16.9

To test these conclusions, quantitative tests of the general hypothesis of dimerization were performed; the possibility of distinguishing between reactions 1 and 2 will be considered in the Discussion.

(1) Since quantitative conversion of vanadium(V) into the dimeric form was not obtained in $HClO_4$ medium (i.e., no straight line with slope 1 was obtained for the [V(V)] range investigated), ϵ^{500}_{dimer} was not directly accessible from the experimental data; thus a least-squares adjustment method was used to interpret the data, with the adjustable parameters = ϵ^{500}_{dimer} and K_D. The best pair of values obtained was ϵ^{500}_{dimer} = 320 M^{-1} cm^{-1} and K_D = 1.54 M^{-1} with a relative standard deviation equal to σ_{K_D} = 14.2%. The good agreement between experimental data and calculated values is shown in Figure 2.

(2) For the sulfuric acid medium, ϵ^{470}_{dimer} can be calculated from the data corresponding to [H_2SO_4] = 16 M. A straight line of slope equal to 1 was obtained, indicating that vanadium(V) was totally converted into the dimeric form for the range of total vanadium(V) concentration investigated. The mean value of ϵ^{470}_{dimer} obtained was = 747 M^{-1} cm^{-1} with a relative standard deviation equal to $\bar{\sigma}$ = 3.2%. On the assumption that the same new vanadium(V) species was responsible for the increase of absorbance for the entire range of H_2SO_4 concentration investigated, ϵ^{470}_{dimer} was determined for all these solutions. The concentration stability constants from the experimental data corresponding to 7–10 M H_2SO_4 solutions (Figure 3) were calculated and are reported in Table I with their relative standard deviations. The good agreement between experimental data and calculated curves is shown in Figuure 3.

For sulfuric acid concentrations in the range 13–16 M the vanadium(V) was totally converted into the dimeric form even for total vanadium(V) concentrations as low as 10^{-2} M. Thus the entire spectrum of the vanadium(V) dimer was readily obtained by using a very short pathlength equal to 0.02 cm. The spectrum of the vanadium(V) dimer in 13.5 M H_2SO_4 acid solution and that of $VO_2(aq)^+$ ion present in 0.5 M H_2SO_4 solution shown in Figure 4 are clearly different. The spectrum of vanadium(V) dimer in H_2SO_4 medium shows a strong band at wavelengths ≤550 nm with a peak located in the UV region at 340 nm possessing a molar extinction coefficient equal to 8200 M^{-1} cm^{-1}. The pure spectrum of vanadium(V) dimer present in concentrated $HClO_4$ acid solution was not observed because of the low stability of that species. A mixture of monomer and dimer was always obtained even for the best experimental conditions used, [$HClO_4$] = 11.8 M and [V(V)] = 0.52 M.

Raman Spectra. In order to obtain structural information for the vanadium(V) dimer formed in concentrated $HClO_4$ and H_2SO_4 solutions, the Raman spectra of these solutions were recorded. Since the anions (ClO_4^- or HSO_4^- and SO_4^{2-}) were present in these media at very high concentrations and gave interfering Raman spectra, a reasonably high concentration of solute was required to obtain a Raman spectrum. The total vanadium(V) concentration range investigated was 0.21–0.525 M for the $HClO_4$ medium and 0.12–0.6 M for the H_2SO_4 solution. The corresponding Raman spectra in the

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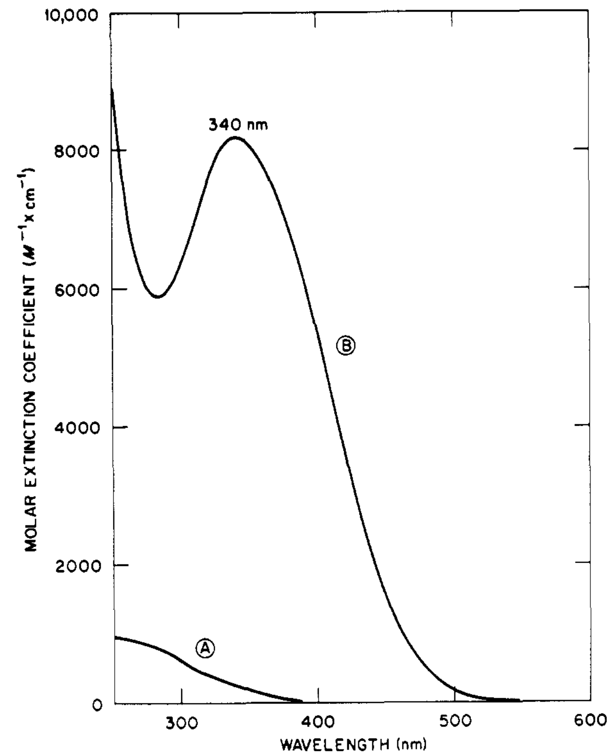

Figure 4. Electronic spectra of vanadium(V) monomer VO_2^+ (A) and dimer $V_2O_3^{4+}$ (B) in H_2SO_4 medium: $[H_2SO_4]$ = 0.5 M (A), 13.5 M (B).

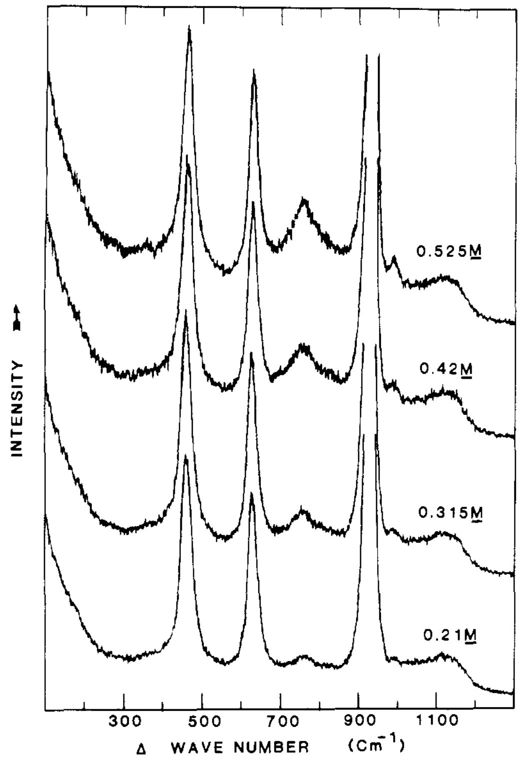

Figure 5. Raman spectra of vanadium(V) dimer in 11.8 M $HClO_4$ medium. The total vanadium(V) concentrations are noted on the spectra. Excitation = 632.8 nm.

range 100–1300 cm^{-1} are shown in Figures 5 and 6 for $HClO_4$ and H_2SO_4 media, respectively. The $VO_2(aq)^+$ ion is known to give a strong symmetrical stretching ν_1 band at 940 cm^{-1} and an antisymmetrical one at 917 cm^{-1};[11] thus, that species

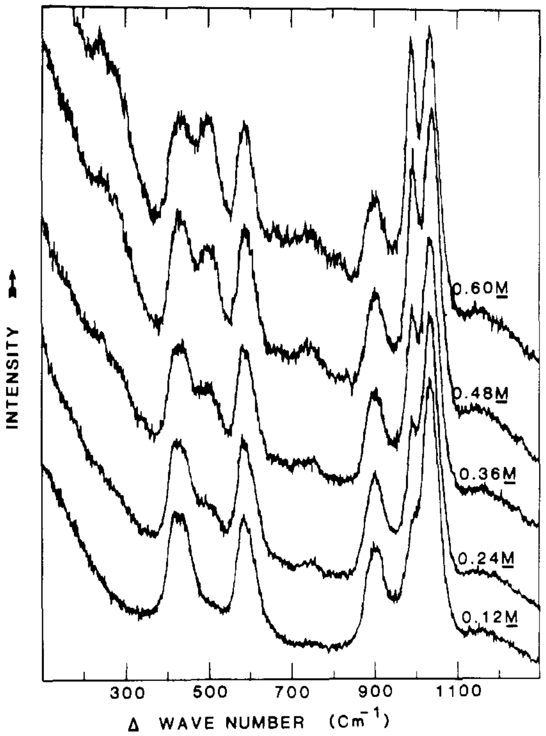

Figure 6. Raman spectra of vanadium(V) dimer in 12 M H_2SO_4 medium. The total vanadium(V) concentrations are noted on the spectra. Excitation = 632.8 nm.

was not observable in $HClO_4$ medium due to strong interference with the band of ClO_4^- (ν_1 located at 936 cm^{-1}).[12] Similarly in H_2SO_4 solutions, overlap can occur between the $VO_2(aq)^+$ bands and the HSO_4^- peaks (902 and 1036 cm^{-1} for S–OH and SO_3 symmetrical stretches, respectively)[13,14] and SO_4^{2-} bands (983 cm^{-1} for ν_1 symmetrical stretch).[12] At constant $HClO_4$ or H_2SO_4 concentration equal to 11.8 and 12 M, respectively, the increase of vanadium(V) concentration leads to the appearance of new bands located at 757 and 988 cm^{-1} for $HClO_4$ medium and 242, 500, 750, and 988 cm^{-1} for H_2SO_4 medium. These bands appear in the "windows" present in the Raman spectra of ClO_4^-, HSO_4^-, and SO_4^{2-} (Figures 5 and 6). A broadening of the 460-cm^{-1} ν_2 band of ClO_4^- ion was also observed with the increase of vanadium(V) concentration; this broadening may be due to the possible presence of a band corresponding to the new vanadium(V) species.

The relative intensities of these new bands, normalized to the 627-cm^{-1} band (ν_4 band of ClO_4^-) and 585-cm^{-1} band (bending band of HSO_4^-) for $HClO_4$ and H_2SO_4 media, respectively, were found to be linearly related to the absorbances measured with the same solutions at $\lambda > 500$ nm. It can thus be concluded that the dimer responsible for the absorbances measured was also responsible for the appearance of the new Raman bands.

Polarization measurements on the Raman bands of vanadium(V) dimer present in $HClO_4$ and H_2SO_4 media were made. The 757- and 988-cm^{-1} bands of vanadium(V) dimer present in $HClO_4$ medium were both found to be polarized. In H_2SO_4 medium the 500- and 988-cm^{-1} bands were polarized and the 242- and 750-cm^{-1} bands were depolarized.

NMR Spectra. The ^{51}V NMR spectrum of an 0.05 M vanadium(V) solution in 13 M H_2SO_4 was recorded. Under these conditions, dimer formation was quantitative on the basis

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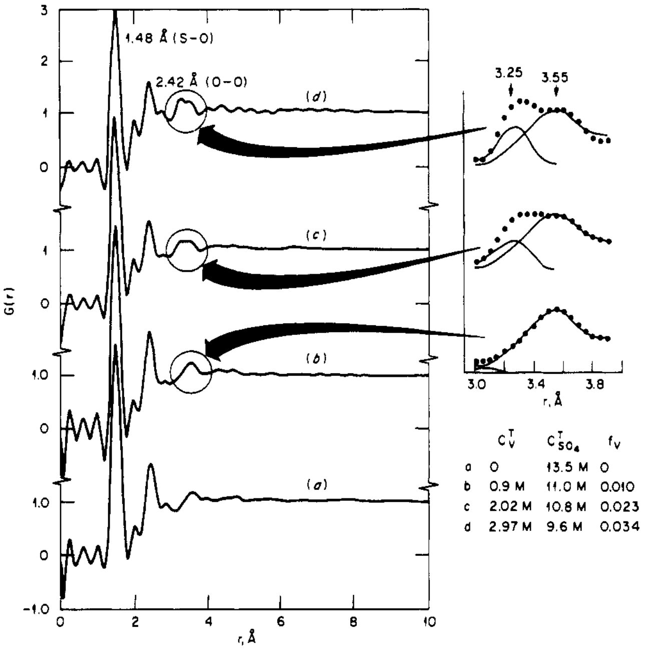

Figure 7. Radial distribution functions of vanadium(V) in strong sulfuric acid solutions compared to sulfuric acid alone. C^T_i is the total concentration of species i, and f_v is the atom fraction of vanadium. Inset shows deconvolution of peaks >3 Å, assuming the constant shape of the 3.55-Å peak from solution a.

of the disappearance of the VO_2^+ signal. Careful scanning from −250 to −820 ppm with respect to $VOCl_3$ revealed only one broad signal at −640 ppm which was 5000 Hz wide. A solution in 1 M $HClO_4$ gave the usual signal of VO_2^+ at −540 ppm[7] (480 Hz wide).

X-ray Scattering. The intensity of scattered radiation was corrected for contributions from background radiation, polarization, absorption, the Compton effect, and multiple scattering.[8] From the corrected angular distribution, a structure function was derived

$$H(k) = [S(k) - \sum_\alpha f_\alpha^2(k)]/[\sum_\alpha f_\alpha(k)]^2 \qquad (3)$$

where $S(k)$ is the coherent scattering function and $f_\alpha(k)$ is the coherent scattering length[15] of atom α. The structure function was then Fourier transformed to give

$$G(r) = 1 + (2\pi^2\rho_0 r)^{-1} \int_0^{k_{\max}} kH(k) \sin(kr)\, dk \qquad (4)$$

where ρ_0 is the number density per Å^3 of scattering centers in the solution and $G(r)$ is the radial distribution function (RDF). The RDF was corrected (a) for truncation errors in the Fourier transform that are caused by $k_{\max}$ not extending to ∞ but cutting off at $k = 16/$Å and (b) for the presence of any peaks at small separation distances that are less than ionic radii values.

The RDF curves for the solutions studied are shown in Figure 7. Two prominent peaks are seen in all of the curves at 1.48 and 2.42 Å. These have been previously identified as the S–O and O–O nearest neighbor distances in the SO_4^{2-} (or HSO_4^-) ion,[16] and these distances indicate that SO_4^{2-} retains its tetrahedral symmetry in concentrated aqueous solution. A third peak is seen in the RDF of H_2SO_4 at 3.55 Å. A peak at about this distance (3.79 Å) has been attributed to the hydration of SO_4^{2-} in 3.6 M H_2SO_4, i.e., to the distance between S and H_2O in the inner hydration sphere.[16] It is also possible that in a solution as concentrated as 13.5 M H_2SO_4, this peak simply corresponds to the average nearest distance of the solution constituents, since there are too few water molecules available to act as the bulk solvent.

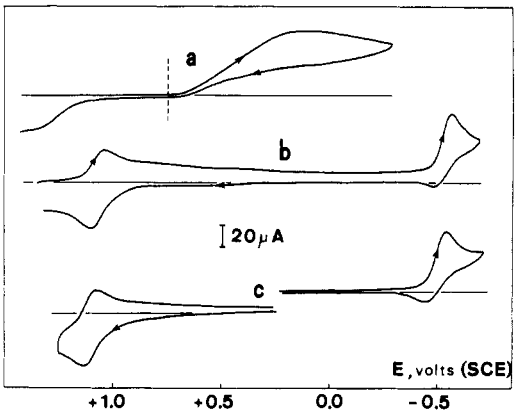

Figure 8. Voltammograms on a glassy carbon electrode: (a) VO_2^+ in 1 M $HClO_4$ (the dotted line shows the position of the standard electrode potential VO_2^+/VO^{2+}); (b) vanadium(V) dimer in 13 M H_2SO_4; (c) vanadium(IV) in 13 M H_2SO_4—(right) cathodic scan followed by an anodic scan, (left) anodic scan followed by a cathodic scan. Concentrations = 2×10^{-2} M; scan rate = 0.02 V s^{-1}.

Crystal structure determinations of compounds containing V(IV) or V(V) have found the characteristic V–O distances to be 1.56–1.63 Å in VO^{2+} and 1.62–1.66 Å in VO_2^+.[17] Such peaks are not evident in the RDF's of solutions b–d, because of the very large intensity of the S-O peak at 1.48 Å. We draw attention to the fact that, while the peak at 3.55 Å observed for solution a (13.5 M H_2SO_4) changes only slightly for solution b (0.9 M V(V) in 11 M H_2SO_4), it becomes much broader for solutions c and d (2.02 M and 2.97 M of V(V) in 10.8 and 9.6 M H_2SO_4, respectively), indicating the presence of another peak at shorter distances.

The peaks above 3 Å have been resolved in the RDF's of solutions b–d by normalizing the shape of the 3.55-Å peak in solution a (H_2SO_4 alone) to the data. The results are shown in the inset in Figure 7. It is seen that both solutions c and d exhibit a new peak centered at 3.25 Å, whose intensity increases with V(V) concentration. The fact that the appearance of this peak is the only change that occurs in solutions of approximately constant H_2SO_4 concentration and strongly increasing V(V) concentration leads us to conclude that it is a direct indication of the formation of the vanadium(V) dimer (or polymer). This increase in peak intensity is qualitatively in agreement with the increase in K_D noted in Table I. We attribute this peak at 3.25 Å to the V–V distance in the dimer.

Cyclic Voltammetry. A solution of vanadium(V) 10^{-2} M in 13 M H_2SO_4 exhibited a reversible behavior near 1.1 V vs. SCE (see Figure 8b). The difference between cathodic and anodic peak potentials was found to be 50 mV for this process. With the glassy carbon electrode, a second cathodic peak was observed at −0.57 V. The general shape of the voltammogram remained unchanged when the scan rate varied from 2×10^{-3} to 0.1 V s^{-1}. For scan rates in the range 1–2 V s^{-1}, the second cathodic peak began to decrease.

Controlled potential electrolysis at +0.7 V corresponding to the descending part of the first peak quantitatively yielded vanadium(IV) according to the overall process

$$V_2O_3^{4+} + 2e^- + 2H^+ \rightleftarrows 2VO^{2+} + H_2O \qquad (5)$$

Several observations suggest that this is also the reaction occurring on the voltammetry time scale. The second peak

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[15] Scattering factors and dispersion lengths were taken from: "International Tables for X-ray Crystallography"; Ibers, J. A., Hamilton, W. C., Eds.; Kynoch Press: Birmingham, England, 1974; Vol. IV.

[16] Caminiti, R.; Pashina, G.; Pinna, G.; Magini, M. *Chem. Phys. Lett.* **1979**, *64*, 391.

[17] Nishizawa, M.; Hirotsu, K.; Shun'ichino, O.; Satio, K. *J. Chem. Soc., Chem. Commun.* **1979**, 707.

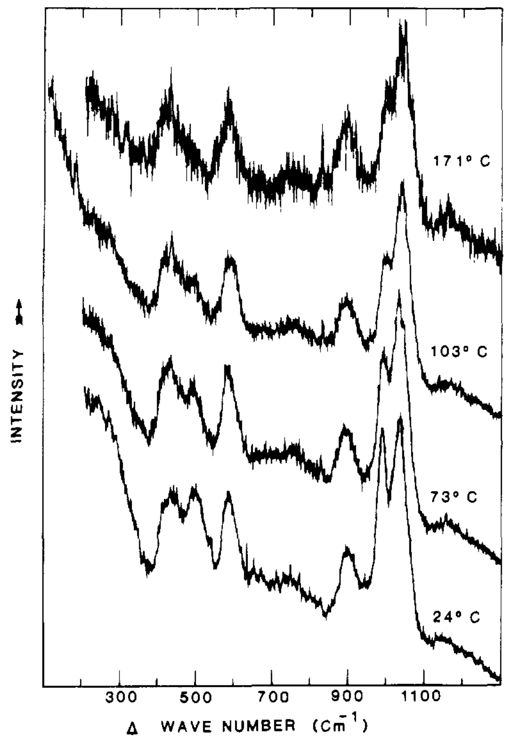

Figure 9. Influence of temperature on the Raman spectra of vanadium(V) dimer in 12 M H_2SO_4. Total vanadium(V) concentration = 0.6 M; excitation = 632.8 nm.

of vanadium(V) is identical with the reduction peak of vanadium(IV) (see Figure 8c), showing that vanadium(IV) has been effectively generated in the first step. Moreover, if we assume that this second peak corresponds to a 2-electron process, as usual in acidic medium,[18a] then the height of the first peak corresponds to 1 electron per vanadium atom. Finally, the difference between cathodic and anodic peak potentials is slightly less than 60 mV.

The reversibility of the vanadium(V)/vanadium(IV) couple in 13 M H_2SO_4 contrasts with the situation in 1 M $HClO_4$. In this medium, VO_2^+ exhibited only ill-defined curves (Figure 8a), showing that the VO_2^+/VO^{2+} couple is slow at these electrodes.[18b]

Influence of Temperature on the Vanadium(V) Dimer in H_2SO_4 Medium. For vanadium(V) in 12–16 M H_2SO_4 solutions an increase in temperature causes an increase in the intensity of the red color. Consistent with the visual observations, a regular shift of the spectrum towards higher wavelengths was obtained with increasing temperature. The modification of the spectrum was rapid and reversible. Cooling the warm solution to 21 °C restored the initial spectrum.

At constant temperature (21 °C) an investigation of the Beer-Lambert Law for vanadium(V) solutions in 13.5 M H_2SO_4 medium in a concentration range that was not investigated in the experiments presented in Figure 3, i.e., 0.05–1 M V(V), showed that a satisfactory linearity was obtained up to 0.2 M V(V). For higher vanadium(V) concentrations a positive deviation was observed, indicating that as in the temperature experiment, vanadium(V) dimer is involved in a new reaction at higher concentrations.

The influence of temperature on the Raman spectrum of vanadium(V) dimer was also studied, and the results for a 0.6 M vanadium(V) solution in 12 M H_2SO_4 medium are presented in Figure 9. The increase of temperature in the range 24–171 °C induces a decrease of the three vanadium(V) dimer bands located at 242, 500, and 988 cm^{-1}, while the 750-cm^{-1} band remains approximately constant in intensity. It should be noted that the signal/noise ratio of the Raman spectra became poorer at high temperature, due to the increasing opacity of the solution with temperature. The effect of temperature on the vanadium(V) dimer in $HClO_4$ acid medium was not investigated because, as described in the Experimental Section, the increase of temperature induces a precipitation of $V_2O_5{\cdot}nH_2O$ solid compound.

Discussion

Mechanism of Formation and Structures of Vanadium(V) Polymers. The ability of $VO_2(aq)^+$ ion to form a dimer depends greatly on the concentration of the acid for both media studied. It should be noted that for these concentrated acidic solutions the activity of water is low,[19a] which means that elimination of water molecules is involved in the dimerization process. The stability of the dimeric species is greater in H_2SO_4 than in $HClO_4$ medium, implying that the stabilization of the new structure is obtained by complexation with HSO_4^- and/or SO_4^{2-} ligands. Moreover the molar absorptivities of the dimer for $HClO_4$ and H_2SO_4 media are different (ϵ^{500}_{dimer} = 320 and 186 M^{-1} cm^{-1}, respectively), indicating that HSO_4^- or SO_4^{2-} ions are involved in the formation of the dimeric species in H_2SO_4 medium. The large variations of the mass action law constant with acid concentration allows us to distinguish between reactions 1 and 2. (See Table I for H_2SO_4 medium. For $HClO_4$ medium these variations can be estimated from the data presented in Figure 1; i.e., K_D increases by a factor of 10 between 9 and 11.8 M.) In the case of H_2SO_4, K_D increases by a factor of 320 between 7 and 10 M. This large variation cannot be accounted for by the variation in water activity alone, since it drops by only a factor of 3.6 (from 0.36 in 7 M H_2SO_4 to 0.10 in 10 M H_2SO_4[19b]). Thus the intervention of protons as in reaction 2 appears necessary. However a quantitative check of reaction 2 is not possible, due to the probable intervention of HSO_4^- ions and to the lack of the proper acidity function in concentrated H_2SO_4. Since the vanadium(V) monomeric species is known to exist in acidic aqueous solutions as the aqua ion, $VO_2(H_2O)_4^+$, the dimerization reactions can be written as follows:

For reaction 1:

$$2VO_2(H_2O)_4^+ \rightleftarrows V_2O_4(H_2O)_7^{2+} + H_2O \qquad (6)$$

for $HClO_4$ medium;

$$2VO_2(H_2O)_4^+ + xHSO_4^- \rightleftarrows V_2O_4(H_2O)_{(7-2x)}(SO_4)_x^{(2-2x)} + xH^+ + (2x + 1)H_2O \qquad (7)$$

for H_2SO_4 medium.

For reaction 2:

$$2VO_2(H_2O)_4^+ + 2H^+ \rightleftarrows V_2O_3(H_2O)_8^{4+} + H_2O \qquad (8)$$

for $HClO_4$ medium;

$$2VO_2(H_2O)_4^+ + xHSO_4^- \rightleftarrows V_2O_3(H_2O)_{(8-2x)}(SO_4)_x^{(4-2x)} + (x - 2)H^+ + (2x + 1)H_2O \qquad (9)$$

for H_2SO_4 medium.

For reactions 7 and 9, HSO_4^- was used in the left part of the equations because this species is known to predominate in H_2SO_4 solutions in the range 9 to 16 M;[14] moreover it was

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(18) (a) "Encyclopedia of Electrochemistry of the Elements"; Bard, A. J., Ed.; Marcel Dekker: New York, 1976; Vol. 7, p 336. (b) The observation of a reversible behavior for the VO_2^+/VO^{2+} couple required the use of *platinized* electrodes. See for instance: Nucci, L.; Raspi, G. *J. Electroanal. Chem. Interfacial Electrochem.* **1972**, *36*, 499.

(19) (a) Robinson, R. A.; Stokes, R. H. "Electrolyte Solutions", 2nd ed.; Butterworths: London, 1965; p 216. (b) Coussemant, A.; Hellin, M.; Torck, B. "Les fonctions d'acidité et leurs utilisations en catalyse acido-basique"; Gordon and Breach: Paris, 1969; p 46.

assumed that SO_4^{2-} acts as a bidentate ligand in forming inner-sphere complexes.

For reactions 6 and 7, the only factor that shifts the reaction toward the right as the concentration of the acid is increased is the decrease of the activity of water in these media. For reactions 8 and 9, two effects, namely the increase of acid concentration and the decrease in activity of water, favor the formation of the vanadium(V) dimer. Thus reactions 8 and 9 seem preferable to account for the dimerization process in both media.

The involvement of HSO_4^- ion in the formation of vanadium(V) dimer in H_2SO_4 medium is also suggested if we consider the decrease of the stability of that species for $[H_2SO_4] > 16$ M (Figure 1). Young et al.[14] in their Raman study of H_2SO_4 acid solutions showed that for these H_2SO_4 concentrations, the HSO_4^- concentration decreases and the concentration of free H_2SO_4 undissociated molecules increases.

Lukachina et al.[10] in their study of the distribution coefficients (K_D) of vanadium(V) between aqueous $HClO_4$ solutions and a cationic acid resin interpreted the increase of K_D values for $[HClO_4] > 2$ M as proof of the existence of VO^{3+} species in these solutions. Their estimate of the 3+ charge of the new vanadium(V) species was based on the comparison of the K_D values of vanadium(V) with the ones obtained for doubly and quadruply charged cations ($Ti(OH)_2^{2+}$ and Th^{4+}, respectively): the following order was obtained: $K_D^{Ti(OH)_2^{2+}} < K_D^{V(V)} < K_D^{Th^{4+}}$. If we instead consider that the vanadium(V) exists as a dimeric species, we must compare the charge density rather than the effective charge. It can thus be concluded that the formation of the quadruply charged dimer $V_2O_3(H_2O)_8^{4+}$ in $HClO_4$ medium is compatible with the distribution coefficients obtained by Lukachina et al.[10] A strong case for the formation of $V_2O_3(H_2O)_8^{4+}$ rather than $V_2O_4(H_2O)_7^{2+}$ is also obtained by comparison with the stoichiometry of the mixed-valence (V(IV), V(V)) dimer $V_2O_3(H_2O)_8^{3+}$, recently discovered.[2]

The Raman spectrum of the vanadium(V) dimer in H_2SO_4 medium is characteristic of an oxygen-bridged structure containing the V–O–V group. The following assignments can be made by comparison with other oxygen bridged M—O—M dimers described in the literature,[20] especially $V_2O_7^{4-}$[20d] and $Cr_2O_7^{2-}$;[20a] for the V—O—V bridge 500 cm^{-1} (polarized, symmetrical stretch), 750 cm^{-1} (depolarized, asymetrical stretch), and 242 cm^{-1} (depolarized, bending); for the V═O (terminal) 988 cm^{-1} (polarized stretch). The appearance of all three modes of vibration for the V–O–V bridge in the Raman spectrum of the vanadium(V) dimer in H_2SO_4 medium indicates that the bridge is not linear. The high value of the frequency (988 cm^{-1}) attributed to the vibration of the V═O (terminal) group is to be compared with the value of 1001 cm^{-1} noted for the V═O vibration in the aquavanadium(IV) ion $VO(H_2O)_5^{2+}$[21] rather than those obtained for the aquavanadium(V) ion $VO_2(H_2O)_4^+ = 940$ and 917 cm^{-1}.[11] The high $[H_2SO_4]/[V(V)]$ ratio in the experimental solutions used in the Raman experiments explains why modified bands of complexed SO_4^{2-} ions were not observed.

The V–V distance in the vanadium(V) dimer, determined by X-ray scattering, was found to be 3.25 Å, approximately double that of the V═O bond length in either VO_2^+ or VO^{2+}. However, we note that the recent crystal structure determination of the V(IV)–V(V) nitrilotriacetate compound[17] containing two equivalent vanadium ions in the $V_2O_3^{3+}$ group (which differs only by one electron from the proposed V(V) dimeric species, $V_2O_3^{4+}$) showed that the V–O distance in the linear V—O—V bridge is 1.81 Å, which is considerably longer than the V═O distance. If we use this information, we conclude that the V—O—V bridge of the V(V) dimer in solution is bent with an angle of ~128°, a result that is consistent with that arrived at in the Raman measurements described above.

The NMR results gave some additional information about the detailed structure of the vanadium(V) dimer in H_2SO_4 solutions. Generally speaking, broad signals are observed when the ^{51}V nucleus is in an unsymmetrical (e.g., distorted octahedral) environment as a result of quadrupole relaxation. This explains the difference in width between $VO_2(H_2O)_4^+$ (480 Hz) and the more symmetrical VO_4^{3-} (16 Hz). However, in the case of the vanadium(V) dimer, an additional source of broadening is provided by the high viscosity of the medium which prevents a fast tumbling of the molecules. This would explain the particularly large width observed (5000 Hz).

The position of the resonance peak (−640 ppm) is unusual for a vanadium(V) compound in an oxygen environment, since most reported chemical shifts range from −400 to −580 ppm.[22] More negative chemical shifts have only been obtained with fluoride complexes such as $VOF_4{\cdot}CH_3CN^-$ ($\delta = -778.3$)[23] of VOF_3 in different solvents ($\delta \simeq -780$).[24] According to Howarth and Richards,[25] there is a correlation between the chemical shift and the charge per vanadium atom. A very negative chemical shift would imply a high positive charge of the species greater than that for VO_2^+. Thus the NMR results suggest that an important rearrangement with respect to VO_2^+ has occurred and are more consistent with the formulation $V_2O_3^{4+}$ rather than $V_2O_4^{2+}$ for the central group.

For the $HClO_4$ medium, the Raman spectrum of vanadium(V) dimer showed only two bands located at 757 and 988 cm^{-1} (both polarized). These correspond fairly well with those observed in H_2SO_4 medium that have been attributed, respectively, to the V—O—V asymmetrical stretching and V═O (terminal) stretching vibrations. However if the assignments are the same for the 988-cm^{-1} bands, the polarized character of the 757-cm^{-1} band excludes its attribution to a V–O–V asymmetrical stretch. No simple explanation was found to explain this particular phenomenon. Thus, the structure of the vanadium(V) dimer in $HClO_4$ medium is still unclear.

The effect of increasing temperature on the Raman spectrum of vanadium(V) dimer (Figure 9) leads to the disappearance of the V═O (terminal, 988 cm^{-1}) band and to the suppression of the symmetrical stretching and the bending vibrations of the V–O–V group present in the vanadium(V) dimer. The only band unaffected by the increase in temperature is the 750-cm^{-1} vibration corresponding to the asymmetrical vibration of the bridge. The persistence of the 750-cm^{-1} band in the Raman spectrum of the hot vanadium(V) H_2SO_4 solution is consistent with the presence of a polymeric species,[26] i.e., with the further polymerization of the vanadium(V) dimer giving a polymeric species with a -V–O–V–O–V- chain. It must be noted that Berzelius,[9a] in his pioneering work on vanadium chemistry in 1831, described two vanadium(V) sulfate solid compounds isolated from vanadium(V) solutions in concentrated H_2SO_4. Their empirical formulas possess the groups $V_2O_3^{4+}$ and $V_2O_2^{6+}$ in the compounds $V_2O_3(SO_4)_2$ and $V_2O_2(SO_4)_3$, identical with the formulas proposed in the present paper for the vanadium(V) dimer and higher polymers in H_2SO_4 solutions.

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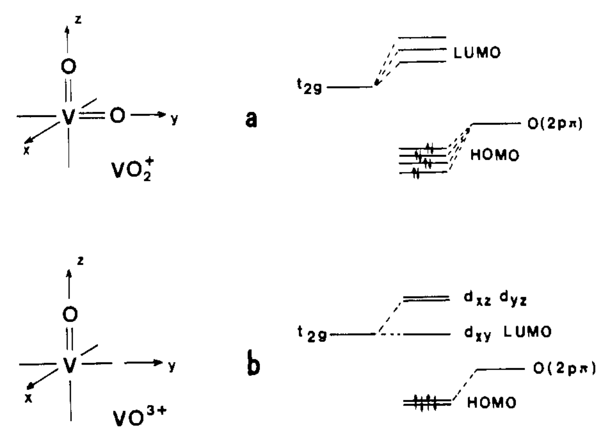

Figure 10. Schematic energy level diagram for the molecular orbitals obtained by interaction between t_{2g} vanadium orbitals and oxygen $2p\pi$ orbitals. In VO_2^+ (a) *all* three t_{2g} orbitals interact while in VO^{3+} (b) the d_{xy} remains nonbonding. Note that in (a) the symmetry is C_{2v} so that the actual d levels are combinations of t_{2g} orbitals.

In $HClO_4$ solutions, the vanadium(V) dimer is also involved in a further polymerization process leading finally to the percipitation of the polymer $V_2O_5 \cdot nH_2O$ compound. As in the case of the H_2SO_4 medium the reaction seems endothermic. The main difference between the phenomena observed in the two media is that the higher vanadium(V) polymer is soluble in H_2SO_4 solution, certainly due to complexation by SO_4^{2-} ions.

Possible Bonding Mode in the Vanadium(V) Dimer and Origin of the Red Color. It is well established that the bent structure of the VO_2^+ group (either aqueous or in complexes) results from the maximum use of vacant d orbitals for d_π–p_π bonding with terminal oxygens[27] (see Figure 10a). This gives a relatively high HOMO–LUMO (highest occupied molecular orbital–lowest unoccupied molecular orbital) separation with a resultant high-energy charge-transfer transition. Thus VO_2^+ is pale yellow (see Figure 4). Moreover, the electrochemical reduction is irreversible, since the added electron must enter an antibonding orbital with subsequent rearrangement of the structure to give a monooxovanadium(IV) species.

In view of the large HOMO–LUMO separation, the interaction of two VO_2^+ units giving $V_2O_4(aq)^{2+}$ is not expected to give a very stable product. On the contrary, the interaction between VO_2^+ and VO^{3+} should be more favorable, as a result of the decreased frontier orbitals gap between VO_2^+ HOMO and VO^{3+} LUMO (nonbonding d_{xy}, see Figure 10b). Thus the stability of $V_2O_3^{4+}$ with respect to the fragments VO_2^+ and VO^{3+} (the latter being generated by the strongly acidic medium) can be explained.

It is also easier to explain the red color of the vanadium(V) dimer in terms of the species $V_2O_3^{4+}$ rather than $V_2O_4^{2+}$. In the former, the vanadium atoms are of the monooxo type (VO^{3+}). This makes possible a low-energy charge-transfer transition from O(2p) levels to $V(d_{xy})$ orbitals. Also, as shown by Pope,[28] this generally implies an easy and reversible reduction (see below).

Implications of the Dimerization for Homogeneous and Heterogeneous Electron Transfer. The existence of a vanadium(V) dimer in very acidic solutions explains nicely the results of Giuliano and McConnell, who measured the rate of the homogeneous exchange reaction between vanadium(V) and vanadium(IV) in a mixture of HCl and $HClO_4$.[29] They found a rate law of the form $k[V^{IV}][V^V]^2$, which they interpreted as being evidence for the existence of a vanadium(V) dimer. The rate-determining step would thus be the reaction between dimeric vanadium(V) and monomeric vanadium(IV). Furthermore, in view of the strong influence of H^+ ions on the rate, they proposed the formula $V_2O_3^{4+}$.

A similar involvement of the vanadium(V) dimer in the electrochemical process appears likely since the V^{IV}/V^V couple, which is slow in 1 M $HClO_4$, becomes rapid in concentrated sulfuric acid. It is tempting to invoke the mixed-valence $V_2O_3^{3+}$ species in this process. Thus the first step could be

$$V_2O_3^{4+} + e^- \rightleftarrows V_2O_3^{3+}$$

followed by a rapid decomposition of the mixed valence species, since its equilibrium concentration is very low in this medium.[2] In cyclic voltammetry, only the overall process, i.e., complete reduction to vanadium(IV), is observed. For scan rates near 1–2 V s^{-1}, the decrease of the second peak at −0.57 V could mean that the chemical reaction begins to be "frozen", so that the reduction proceeds to $V_2O_3^{3+}$ only. Unfortunately a more thorough study of this mechanism is precluded by the difficulty of using fast scan rates on solid electrodes.

Comparison with the Polymers of Neptunium(V). Guillaume et al.[4a] recently discovered that the $NpO_2(aq)^+$ ion forms dimeric and polymeric species in aqueous perchlorate solutions for the range of total neptunium(V) concentration of 0.1–1 M and >1 M, respectively. The equilibrium constant of the dimerization reaction was found to be 0.82 M^{-1} for 4.26 M (Na^+, H^+)ClO_4^- medium. At similar ClO_4^- concentrations, no vanadium(V) dimer was detected.

The stability of "cation–cation" complexes involving actinide(V) ions is known to increase as the ionic strength of the medium is increased;[30] this would certainly be the case for the neptunium(V) dimer. Consequently we expect that the dimerization constant for Np(V) will be high for 11.8 M ClO_4^- medium; for that concentration the dimerization constant of vanadium(V) is only 1.54 M^{-1}. The ability of neptunium(V) to dimerize is thus higher than that of vanadium(V). Moreover, at constant ionic strength, the dimerization of the $NpO_2(aq)^+$ ion was found to be independent of the acid concentration. The empirical formula of the neptunium(V) dimer can thus be written as $Np_2O_4(H_2O)_x^{2+}$, different from that proposed in this paper for the vanadium(V) dimer, $V_2O_3(H_2O)_8^{4+}$.

In the study of the dimerization of neptunium(V),[4a] the Raman spectra showed the appearance of a new band located at 738 cm^{-1}, characteristic of the neptunium(V) dimer. This band was assigned to the symmetrical stretching frequency of the linear O=Np=O group shifted from 767 cm^{-1} (ν_1 for the NpO_2^+ monomer) to 738 cm^{-1} due to the complexation. No other bands were found in the Raman spectrum of the neptunium(V) dimer; it can thus be concluded that the existence of a Np–O–Np bridge in the neptunium(V) dimer is highly improbable. Although the present study does not give an unequivocal answer to the question of the structure of the vanadium(V) dimer in $HClO_4$ medium, it is totally different from that of the monomer. Thus the dimerization process certainly involves a greater structural modification in the case of vanadium(V) than in that of the neptunium(V) species.

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