for the Np(VIII)–Np(VI) couple is considerably more positive than that of the other reactants considered and the rate of oxidation of VO^{2+} by Np(VII) is also greater.

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Depolarized Light-Scattering Study of Isopolyvanadates in Alkaline Aqueous Solution

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Rayleigh depolarized scattering intensities have been measured at 6328 Å over a range of vanadate concentrations in alkaline aqueous salt solutions at 20°. Vanadates have been found to be highly anisotropic. On the basis of the scattering data it is possible to ascribe tetrahedral coordination to a HVO_4^{2-} monomer, a linear $V_2O_7^{4-}$ dimer, and a planar metavanadate species in agreement with Raman and nmr assignments. Evidence for association of HVO_4^{2-} ions has been presented and a polymerization mechanism involving the formation of hydrogen-bonded intermediates has been proposed.

Introduction

The pH-dependent polymerization of vanadium(V) in aqueous solution has been the subject of numerous chemical investigations[1-13] ranging from applications of cryoscopy[1] and diffusion[2] to more recent emf,[3,4] ^{51}V nmr,[9,10] and Raman spectroscopic studies.[11-13] The aggregation process has been described in some detail,[3,4] pointing clearly to the stability of monomer and dimer species. There seems to be some doubt on the basis of emf work though, concerning whether or not the dimer condenses to form a trimer or a tetramer, or a mixture of the two.

Raman and ^{51}V nmr studies have provided strong evidence for a VO_4^{3-} ion in strongly alkaline solution followed in succession at lower pH by HVO_4^{2-}, $H_2VO_4^-$, $V_2O_7^{3-}$, and $V_3O_9^{3-}$ or $V_4O_{12}^{4-}$. Spectroscopic data do not support the existence of mixtures of trimeric and tetrameric metavanadates. As the pH is lowered from 14 to 8, VO_4^{3-}, HVO_4^{2-}, $V_2O_7^{4-}$, and the metavanadate appear to predominate in turn. Fundamental Raman vibrational frequencies for postulated VO_4^{3-}, $V_2O_7^{4-}$, and the metavanadate do not shift in heavy water even though oxygen and hydrogen exchange is rapid indicating that these species are not protonated.

Seemingly in contrast, crystal studies[14,15] have shown the importance of the VO_6 octahedron in the solid state, although a number of solids show coordination numbers 4 and 5[16,17] as well. Because of the marked tendency of vanadium to expand its coordination number from 4 to 5 or 6 there has been a lingering concern that vanadates could be present in aqueous solution as five-coordinate $(VO_2)(OH)_3^{2-}$ rather than HVO_4^{2-} or even $(VO_2)O(OH)_4^{4-}$ rather than $V_2O_7^{4-}$, etc. Uncertainty has been heightened because emf results cannot distinguish between such species and because kinetic results[18] have been used as a basis for suggesting the existence of five-coordinate species.

This light-scattering depolarization study has been undertaken to choose between the postulated four- and five-coordinate structures. A choice should be possible on the basis of predicted substantially different molecular polarizability tensor components calculated for structures of given degree of polymerization. The assignments will be especially credible if calculations based on the optical bond model can be shown to explain the scattering data for all species present. Results will be valuable since they will complement extensive nmr and Raman data already available.

Experimental Section

Light-Scattering Photometer. Intensities of Rayleigh-scattered light were measured by means of a specially constructed photometer described elsewhere.[19] A Spectra-Physics Model 122 cw laser was used to provide a vertically polarized light source of wavelength 6328 Å. All depolarization measurements were made using a 30 × 30 mm glass cell. The cell was painted on the outside, except for the entrance and exit slits, with a flat black paint to minimize reflection. The calibration of the photometer and a secondary glass standard was accomplished using aqueous solutions of 12-tungstosilicic acid. The procedure has been described elsewhere.[20] Solution refractive indices were measured by means of a Brice-Phoenix differential refractometer, Model BP-2000V.

Solution Clarification. Dust-free solutions were obtained by

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pressure ultrafiltration. A Millipore stainless steel funnel equipped with the Millipore Type VCWPO4700 filter of pore size 100 nm freed solutions of colloidal material after three to five filtrations even under alkaline conditions. However, pressure could not be raised above 2 psi without the passage of particles through the filter. Intensity minima were reproducible to ±(3–10)% depending upon solution concentrations.

Reagents. Sodium vanadate was purchased from Fisher Scientific Co. and used without purification, or it was prepared from V_2O_5 and stoichiometric amounts of NaOH and recrystallized from alkaline aqueous solution. Vanadium was determined as mercurous vanadate and ignited to vanadium pentoxide. Supporting electrolyte was prepared using "reagent grade" chemicals without further purification. Silicotungstic acid purchased from Alfa Inorganics Inc. or Baker and Adamson, Inc., could also be used without further purification. Water of hydration was variable and determined by heating to constant weight at 500°. Tungstosilicic acid was analyzed independently by Galbraith Laboratories, Inc., Knoxville, Tenn. 37921. *Anal.* Calcd for $SiO_2 \cdot 12WO_3 \cdot 20.4H_2O$: Si, 0.906; W, 68.8. Found: Si, 0.91; W, 69.4.

Measurement of the Molecular Polarizability Anisotropy, γ^2. According to Bothorel[21] the optical anisotropy of a solute molecule, γ^2, can be determined by measurement of the intensity increments of depolarized scattered light from solutions as in

$$\gamma^2 = \frac{135\lambda^4}{16\pi^4 p(n^2+2)^2}\left[R_{\mathrm{i(soln)}} - R_{\mathrm{i(solv)}}\frac{C_0}{d_0}\left(\frac{n^2+2}{n_0{}^2+2}\right)^2\right]$$

If the molecular polarizability tensor is diagonalized, we have

$$\gamma^2 = {}^1/_2\,[(\alpha_{xx}-\alpha_{yy})^2 + (\alpha_{xx}-\alpha_{zz})^2 + (\alpha_{yy}-\alpha_{zz})^2]$$

λ is the wavelength of incident radiation in centimeters, p is the number of solute molecules per milliliter, n is the refractive index of the solution, n_0 is the refractive index of the pure solvent, c_0 is the number of grams solvent per milliliter of solution, and d_0 is the density of the pure solvent. $R_{\mathrm{i(soln)}}$ and $R_{\mathrm{i(soln)}}$ are respectively the Rayleigh constants of the solution and pure solvent which are proportional to corresponding depolarized scattering intensities at 90° to the incident beam.

In this study the Rayleigh constant of a solution was obtained by comparing depolarized scattered light intensities of the solution with the depolarized scattering intensity of a glass standard calibrated previously by comparison with polarized scattered light intensities from 12-tungstosilicic acid solutions. Simply

$$R_{\mathrm{i(soln)}} = \frac{I_{\mathrm{soln}}}{I_{\mathrm{std}}}R_{\mathrm{i(std)}}$$

I_{soln} and I_{std} are relative intensities of scattered light associated with the solution and the standard, respectively. Because

$$\frac{C_0}{d_0}\left(\frac{n_2+2}{n_0+2}\right)^2$$

was very nearly 1.00 in all instances, typically

$$\gamma^2 = \frac{135\lambda^4}{16\pi^4 p(n^2+2)^2}[R_{\mathrm{i(soln)}} - R_{\mathrm{i(solv)}}]$$

It was assumed that both measured "R values" contained a small and equal contribution from parasitic light which canceled. Elimination of parasitic light was accomplished in standardization by taking advantage of that fact. That is, the increment in scattered light $[(R_{\mathrm{i(soln)}} - R_{\mathrm{i(solv)}}]$ of standard solution scattering over pure solvent scattering was used to calibrate the instrument rather than the scattering from a pure liquid which it was feared would contain an unknown amount of parasitic light.

For the orthovanadate monomer and the metavanadate it was possible to prepare monodisperse solutions over a range of concentrations. If more than one vanadate species was present, the ratios of solution to standard depolarized scattering intensity could be calculated taking into account that for each solute species

$$I_{\mathrm{soln}} = I_{\mathrm{std}}\frac{\gamma_i{}^2 P_i}{5.66 \times 10^{-26}}$$

Considering the contribution of each structure to the depolarized scattered light intensity, I

$$I_{\mathrm{soln}} = I_{\mathrm{std}}\sum_i^h \frac{\gamma_i{}^2 P_i}{5.66 \times 10^{-26}}$$

Vanadate Solutions. Concentrations of monomers, dimers and trimers or tetramers can be inferred from stability constant data.[3] Table I describes the degrees of aggregation in the solutions studied.

The solutions containing a known amount of sodium orthovanadate were adjusted to the desired pH by addition of a calculated amount of 1 M perchloric acid. Then, enough 3 M $NaClO_4$ to provide a 1 M supporting electrolyte concentration was added

$$(NaClO_4) = 1.0 - \frac{3}{2}\left(\frac{\text{mol of vanadate}}{\text{l. of soln}}\right) - \frac{1}{2}\left(\frac{\text{mol of }HClO_4\text{ added}}{\text{l. of soln}}\right).$$

Following preparation, solutions were decolorized by heating to 80° for 1 hr and were allowed to stand 1 full day before optical measurements were made at 20°. pH was checked before and after filtration. Replacement of $NaClO_4$ by NaCl resulted in no significant changes in scattered light intensities.

Candidate Vanadate Structures. Anisotropies of candidate structures have been calculated using bond polarizabilities calculated according to the method of Lippincott and Stutman[22] (Table II). These bond polarizabilities have been used to estimate optical anisotropies for the molecules listed in Table III.

An Alternate Approach. None of the candidate structures or combinations of them appears to explain the observed scattering data. The high intensities of depolarized scattering of the monomer solutions appear especially remarkable, since Raman and nmr data point rather strongly to a highly symmetrical tetrahedral geometry. In a sense the problem reduces to an explanation of an anisotropy of about the same order of magnitude as that of benzene in terms of a relatively simple tetrahedral monomer unit building up into heavier species. A unique model follows which satisfies all the requirements of the Raman and nmr data and which fits the light-scattering requirements.

The set of structures proposed allows for the transferability of bond polarizabilities but requires that V–OH bonds in solution be slightly longer than the average of those V–O–V bridge bonds observed in unprotonated crystalline vanadates. Specifically, if it is assumed that the V–O bond distance is 2.2 Å instead of the bridge-bond value of 1.9 Å, which is only an average of values varying over a ±0.3 Å range, then the V–O bond as described by the Lippincott–Stutman model will be anisotropic enough to give rise to the large depolarization ratios observed. Crystal data[23] for $VO(OH)_2$ do indicate that protonation lengthens V–O bonds slightly more than does simple bridge formation. However, two other conditions apply. First of all, V–O terminal bonds are assumed to be nearly isotropic. Since it has been observed by us that 0.3 M $VO_2{}^+$ at pH 1.1 produces almost no depolarized scattering from aqueous solution, it is reasonably certain that such bonds are very nearly optically isotropic. In addition, there must be some sort of ordering of molecules in solution to bring the anisotropic bonds on adjacent molecules into a more anisotropic configuration. It is proposed that hydrogen-bonded structure **13** which results in parallel V–O–H groups is the only simple tetrahedral one capable of producing the observed intensity of depolarized scattering. It is expected that coplanar O–H groups will not affect results significantly since the O–H bond is not highly anisotropic.

There is some evidence for hydrogen bonding involving vanadates. Examination of the Raman spectra of all our solutions showed exact agreement with the published work of Griffith, *et al.*[12] It was also noted that rather broad bands were associated with the polarized, highest energy A_1 vibration. In fact that line was observed to be over 100 wave numbers wide at half-height for $HVO_4{}^{2-}$ in contrast to the corresponding $MoO_4{}^{2-}$ peak which was about 15 wave numbers wide observed from aqueous solution with the same spectrometer slit width and solution concentration used in each case.

The similarity of the I/I_{std} values of the monomer and dimer is attributed to a simple tetrahedral structure possessing a linear V–O–V arrangement.

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Table I. Concentrations of the Various Vanadate Species in Solution

	Concn, *M*				
pH	Vanadate	Monomer	Dimer	Trimer	Tetramer
12.5	0.2	0.1991	4.77×10^{-4}	4.1×10^{-9}	≈0
12.5	0.4	0.3962	1.91×10^{-3}	3.31×10^{-8}	≈0
12.5	0.6	0.5914	4.29×10^{-3}	1.12×10^{-7}	≈0
10.5	0.2	0.1296	3.52×10^{-2}	≈0	≈0
10.5	0.4	0.2062	9.69×10^{-2}	≈0	≈0
10.5	0.6	0.2074	1.963×10^{-1}	≈0	≈0
8.5	0.2	≈0	≈0	0.066	≈0
8.5	0.4	≈0	≈0	0.133	≈0
8.5	0.2	≈0	≈0	≈0	0.05
8.5	0.4	≈0	≈0	≈0	0.1

Table II. Calculated Bond Polarizabilities

Bond	Bond length, Å	$10^{-25}\alpha_{\parallel}$, cm^3	$10^{-25}\alpha_{\perp}$, cm^3
V-O(terminal)	1.6	16.5	7.1
V-O(bridge)	1.9	22.2	3.2

Table III. Calculated Values of γ^2 for the Candidate Vanadate Structures

Structure	$10^{-48}\gamma^2$, cm^6	Structure	$10^{-48}\gamma^2$, cm^6	Structure	$10^{-48}\gamma^2$, cm^6
1	0	**5**	1.60	**9**	49.0
2	1.0	**6**	1.20	**10**	33.0
3	18.6	**7**	2.20	**11**	10.5
4	14.5	**8**	0	**12**	96.0

Table IV. Bond Descriptions for Structures **1-12**

Structure	Bond description	*θ*, deg	*φ*, deg
1	4 terminal	54.73	
2	2 terminal	0	0
2	1 elongated	90	0
2	2 elongated	90	60
3	4 terminal	54	60
3	2 terminal	54	0
3	4 bridged	36	90
4	4 terminal	54	60
4	2 terminal	54	0
4	4 bridged	45	90
5	1 bridged	0	0
5	2 terminal	71	60
5	1 terminal	71	0
6	1 bridged	0	0
6	2 terminal	71	60
6	1 terminal	71	0
7	4 bridged	90	60
7	2 bridged	90	0
7	2 terminal	90	60
7	1 terminal	90	0
7	6 terminal	0	0
8	2 terminal	54	0
8	4 terminal	54	60
8	4 bridged	54	0
8	8 bridged	54	60
9	4 terminal	54	60
9	2 terminal	54	0
9	2 terminal	90	0
9	8 bridged	36	90
10	4 terminal	54	60
10	2 terminal	54	0
10	2 terminal	90	0
10	8 bridged	45	90
11	4 bridged	90	54
11	2 bridged	90	6
11	2 terminal	35	0
11	4 terminal	35	60
12	4 terminal	54	60
12	2 terminal	54	0
12	4 terminal	90	0
12	12 bridged	36	90

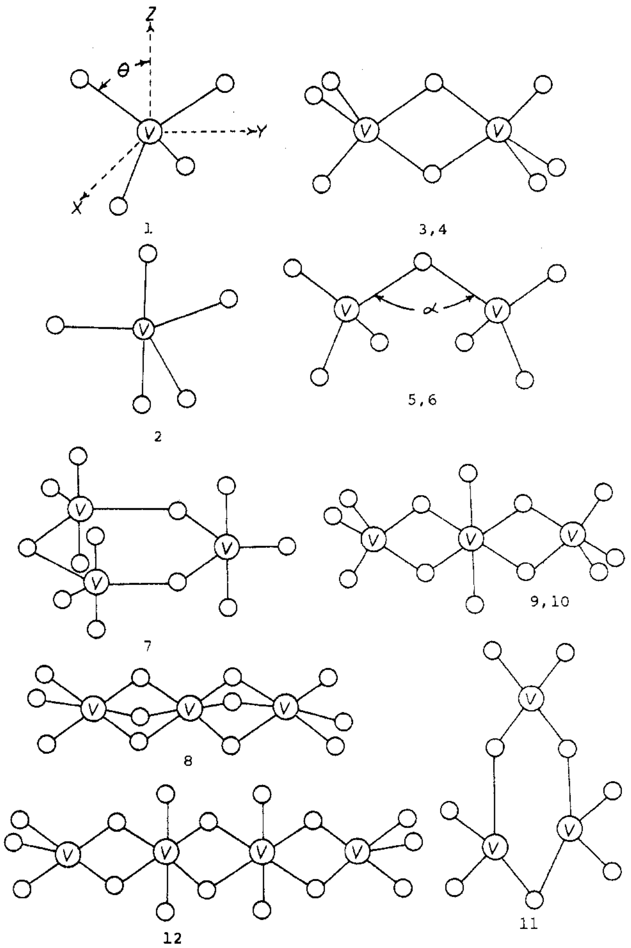

Figure 1. Structures **1-12**.

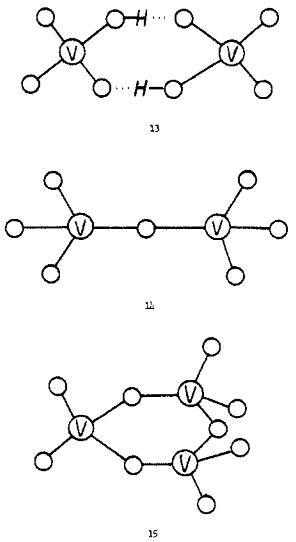

Figure 2. Structures **13-15**.

The trimer which shows a larger depolarization value is described as a six-membered ring composed of three VO_4 tetrahedra sharing corners. The resulting six V-O bridge bonds lying in a single plane will give rise to a large optical anisotropy consistent with the observed data.

The Monomer (Structure 13). The "*Z*" axis has been placed parallel to the V-O bonds which are attached to hydrogen. The "*X*" axis is included in the plane of the hydrogen-bonded species. Thus, since only two bonds will contribute significantly to the optical anisotropy, calculations are especially simple. There will be two V-O bonds each with $\theta = 0°$ and $\phi = 0°$.

The V-O bond polarizability components can be calculated by means of the Lippincott-Stutman model as follows, assuming a bond length of 2.2 Å.

$$\frac{R^2}{4} = \frac{2.2^2}{4} \times 10^{-16}\ \text{cm}^2 = 1.2. \times 10^{-16}\ \text{cm}^2$$

$$\overline{X}^2 = (1.21 + 0.01) \times 10^{-16}\ \text{cm}^2$$

$$\alpha_{\|b} = \frac{4 \times 0.716(1.22 \times 10^{-16})^2}{0.529 \times 10^{-8}} = 8.06 \times 10^{-24}\ \text{cm}^3$$

$$\alpha_{\|}p = \sigma\alpha_{\|b} = 0.441 \times 8.06 \times 10^{-24} = 3.55 \times 10^{-24}\ \text{cm}^3$$

$$\alpha_{\|} = \sigma\alpha_{\|b} + \alpha_{\|}n = 3.55 + 0.2 = 3.75 \times 10^{-24}\ \text{cm}^3$$

$$\alpha_{\perp} = 0.3 \times 10^{-24}\ \text{cm}^3$$

The monomer's optical anisotropy can be calculated as

$$\gamma^2 = (7.5 - 0.6)^2 \times 10^{-48}\ \text{cm}^6 = 47.6 \times 10^{-48}\ \text{cm}^6$$

Perhaps the best approach, considering the fact that the anisotropy of the monomer is not a function of concentration over the range studied, is the one based on the assumption that the molecular anisotropy arises exclusively from the anisotropy of the two parallel V–O bonds, the ones attached to hydrogen. In that case if one defines a bond anisotropy, $\delta = \alpha_{\|} - \alpha_{\perp}$, for this bond, $(2\delta)^2 = \gamma^2$. Since γ^2 has been determined for the monomer experimentally to be 46.2×10^{-48} cm^6, $\delta = 3.4 \times 10^{-24}$ cm^3. This is very slightly lower than the value predicted from the modified Lippincott–Stutman calculations and certainly is within a reasonable range.

If it is assumed that the bond anisotropy is a large and transferable quantity and that terminal V=O bonds are nearly isotropic, the molecular optical anisotropies of dimer and trimer molecules can be calculated in a very simple way. For example, the dimer (structure **14**) can be drawn so that the "*Z*" axis passes through the vanadium–oxygen bonds. There will be two V–O bonds with $\theta = 0°$, $\phi = 0°$. The net V–O bond contributions to the molecular polarizability semiaxes are $\alpha_{xx} = 7.4 \times 10^{-24}$ cm^3, $\alpha_{yy} = 0.6 \times 10^{-24}$ cm^3, and $\alpha_{zz} = 7.4 \times 10^{-24}$ cm^3, which give a γ^2 value of 46.2×10^{-48} cm^6.

Likewise the molecular anisotropy of the trimer (structure **15**) can be calculated. In this case a simplification can be made by noting that the anisotropic bonds will lie in a plane defined by two coordinate axes. The molecular *Z* axis is chosen to be perpendicular to the plane of the molecule and the *X* axis is chosen to be collinear with one of the molecular C_2 axes. In this manner the angles θ and ϕ for every bond can be obtained easily. Using these molecular axes, two V–O bond types were generated: type I, four bridged O–V–O bonds with $\theta = 90°$, $\phi = 54°$; type II, two bridged V–O bonds with $\theta = 90°$, $\phi = 6°$. Assuming additivity of bond polarizabilities the net V–O bond contributions to the molecular polarizability semiaxes are $\alpha_{xx} = 12.5 \times 10^{-24}$ cm^3, $\alpha_{yy} = 11.5 \times 10^{-24}$ cm^3, and $\alpha_{zz} = 1.8 \times 10^{-24}$ cm^3, which give a γ^2 value of 104.7×10^{-48} cm^6.

Regardless of bond anisotropy values, a tetramer composed of tetrahedra sharing corners with all bond angles 109° 28′ should have a molecular anisotropy of exactly zero. In fact slight distortions would create small anisotropies, but certainly these would not be large enough to produce intense depolarized scattering.

Values of I/I_{std} can be calculated easily on the basis of calculated molecular anisotropies associated with the various structures. Obviously, the values calculated for the monomer unit must agree with experimental values since depolarization ratios of 0.6 *M* HVO_4^{2-} solutions were used to derive the bond polarizability anisotropy value in the first place.

The comparison of calculated *vs.* experimental values can be made most conveniently by means of Table V.

Discussion

The results of this light-scattering investigation are consistent with the formation, successively, of the following dominant species in aqueous solution as the pH is lowered from 14 to 8.5: VO_4^{3-}, HVO_4^{2-}, $V_2O_7^{4-}$ or $(VO_3)_2(OH)_2^{4-}$, and $(VO_2)_3O_3^{3-}$. Other species such as $H_2VO_4^-$ and $V_2O_5(OH)_3^{3-}$ may exist in low concentrations, but there is no new positive evidence for them on the basis of this study. Concentrations of any simple tetramer species must be low if any exist at all at equilibrium. It appears likely that all stable molecules above pH 8.5 have structures based essentially upon the VO_4 tetrahedron. All structures proposed are entirely consistent with the results of Raman, nmr, and "Sillen-type" stability constant investigations with minor differences.

Table V. Comparison of Calculated and Experimental Values of I/I_{std} for Structures **1-12**

pH 12.5, Monomer Structures

[V], *M*	Calcd I/I_{std} 1	Calcd I/I_{std} 2	Obsd I/I_{std}
0.20	0.0	0.0018	0.046
0.40	0.0	0.0036	0.109
0.60	0.0	0.0054	0.147

pH 10.5, Monomer and Dimer Structures

[V], *M*	Calcd I/I_{std} 3	Calcd I/I_{std} 4	Calcd I/I_{std} 5	Calcd I/I_{std} 6	Obsd I/I_{std}
0.20	0.0069	0.0054	0.0006	0.0004	0.046
0.40	0.0190	0.0149	0.0016	0.0012	0.110
0.60	0.0387	0.0302	0.0033	0.0025	0.160

pH 8.5, Trimer Structures

[V], *M*	Calcd I/I_{std} 7	Calcd I/I_{std} 8	Calcd I/I_{std} 9	Calcd I/I_{std} 10	Obsd I/I_{std}
0.20	0.0015	0.0	0.034	0.023	0.074
0.40	0.0031	0.0	0.069	0.047	0.151

pH 8.5, Tetramer Structures

[V], *M*	Calcd I/I_{std} 11	Calcd I/I_{std} 12	Obsd I/I_{std}
0.20	0.0072	0.051	0.074
0.40	0.0148	0.102	0.151

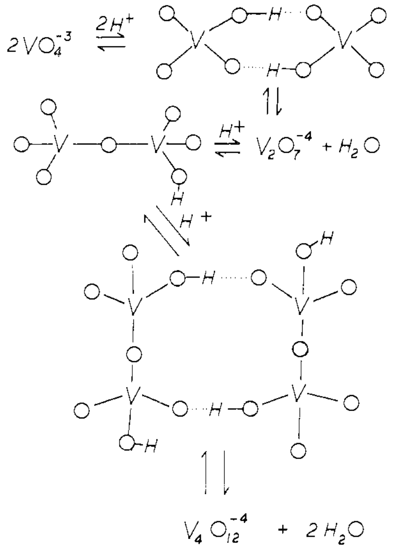

Figure 3. The proposed mechanism.

For example, assignments of Ingri and Brito[3] based on potentiometric work are in complete agreement with those of this study with respect to the monomer and dimer species. In their original report a trimer identical with the one proposed on the basis of this study was assigned. Several years later a change[4] was made in the interpretation of data and the claim was made that arguments invoking a tetramer explained the data better. It is believed that the present study has clearly established the predominance of a cyclic structure. The linear tetramer of high optical anisotropy must be ruled out on the basis of Raman and nmr results and a cyclic tetramer should have a very low anisotropy unless it is planar.

Nmr results[9,10] are in complete accord with the assignment of a cyclic trimer or tetramer, but not a mixture of the two, since there is only one sharp ^{51}V resonance at pH 8.5.

Furthermore, the observed equilibria between the monomer and dimer, on the one hand, and the dimer and trimer, on the other, are in complete accord with the assumption of a hydrogen-bonded monomer, and perhaps analogous association of the dimer and monomer to form a trimer *via* a similar but less stable hydrogen bonded intermediate. Acid catalysis of dimer formation which was suggested on the basis of earlier nmr data[9] seems quite reasonable in connection with these assignments as well.

Raman data[10-12] are in complete agreement with the new structural assignments, but like the nmr results the Raman data do not allow a choice to be made between the trimer and tetramer. The upward shift in vanadium-oxygen symmetrical stretching frequencies associated with each successive degree of polymerization and protonation, as well as the marked similarity between spectra of the trimer and VO_2^+, are entirely consistent with this study's proposed polymerization scheme. Raman data included in this study also provide a measure of evidence for hydrogen bonding between monomers in solution. A comparison of the spectra observed at pH 15, 12.5, 10.5, and 8.5 shows that the peaks associated with the polarized A_1 vibration are markedly broadened at pH 12.5. As a matter of fact, the peak width at half-height of the vanadate, VO_4^{3-}, was only one-fifth the peak width of the corresponding hydrogen vanadate ions studied at pH 12.5. This evidence cannot be considered as conclusive, but it does support the notion of hydrogen bonding between HVO_4^{2-} ions.

The fast-kinetics work[18] demonstrates rather definitely that there are facile equilibria involved in dimer and trimer formation and, most importantly, that the rate constant for dimer formation is much greater for vanadate than for chromate. This again is evidence consistent with the proposed formation of a hydrogen-bonded "monomer."

Other possible explanations for the large values of the depolarized scattering at pH 12.5 have been explored. Fluorescence has been eliminated as a possible cause by examination of Rayleigh scattering line shapes in the laser Raman spectrometer. The observation that Rayleigh scattering was not reduced appreciably upon insertion of a narrow band interference filter (0.7 nm) also was made. Such experiments also eliminated the possibility of important Raman contributions to the observed Rayleigh scattering intensities. So-called "pseudo Raman rotational scattering" contributions must be small for systems of the type studied since concentrated solutions of perchlorate and molybdate showed anisotropies which were very nearly zero as expected.

Experimental errors lay primarily in the measurement of light-scattering intensities themselves. (See Table VI.) Naturally, since differences between I/I_{std}(solution) and I/I_{std}(solvent) were smallest for solutions of the monomer, the experimental error was greatest for the monomer's anisotropy value. Uncertainty might be as large as 10%. However, such an error would in no way affect the conclusions. Measured anisotropies for the dimer and trimer were subject to uncertainties no greater than 10% and perhaps less. Actually, in a study of this type one has to be very much more concerned with systematic errors than random ones. Errors due to instrument instability, internal reflection, and dirty solutions were considered. Large errors in calibration were eliminated by use of the 12-tungstosilicic acid standard, as well as $NaClO_4$ and Na_2MoO_4 solutions, and the frequent use of a secondary glass standard as a check on instument stability. Observation of reproducibility of scattering minima from day to day was an excellent means of ensuring that there was no large systematic increase in turbidity due to dust or other colloidal material. Careful visual inspection of the laser beam proved to be an excellent means of judging the efficiency of solution filtration.

Table VI. Comparison of Calculated and Experimental Values of I/I_{std} for Structures **13-15**

pH	Analytical V concn, *M*	I/I_{std} Calcd	I/I_{std} Measd
12.5	0.2	0.049	0.046
12.5	0.4	0.098	0.109
12.5	0.6	0.147	0.147
10.5	0.2	0.049	0.046
10.5	0.4	0.098	0.110
10.5	0.6	0.147	0.160
8.5	0.2	0.073	0.074
8.5	0.4	0.148	0.151

The experimental results inspire confidence in the semiempirical model used to calculate bond polarizabilities. Calculated values of the bond polarizability appear to be in excellent agreement with experimental values inasmuch as molecular anisotropies calculated on the basis of the model can explain the observed scattering results through adjustment of only one parameter, the bond length. It appears that a choice between four- and five-coordinate structures based on a simple comparison of calculated and measured scattering intensities is not possible. However, when the entire system is considered, it is quite clear that the data support the four-coordinate structures only.

In conclusion it can be asserted that vanadate ions in the alkaline range are surprisingly optically anisotropic. As a result these species cannot have "alkane-like" tetrahedral structures. Specifically, the V-O-V moiety of the dimer must be linear and the bridging V-O-V bonds in metavanadate must lie very nearly in one plane. Evidence for association of HVO_4^{2-} ions has been presented. However, further study of those ions is needed to determine why they do not behave like hydrogen phosphate or hydrogen sulfate. Even though the data appear to support a planar trimeric metavanadate, they are consistent with the existence of a slightly puckered tetramer as well. It is notable that an earlier light-scattering study[24] has shown the metavanadate to be tetrameric and that it has been claimed that emf data[4] are best explained by a tetramer also. Rapid equilibrium[9] between the dimer and the metavanadate also is good circumstantial evidence for the tetramer.

The suggested polymerization mechanism is highly speculative. Limitations inherent in the use of the δ-function potential model for the calculation of bond polarizabilities have been noted, but it must be recognized that the model can be used effectively with appropriate allowances for differences between bond lengths in solution and in the solid state.

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Registry No. VO_4^{3-}, 14333-18-7; HVO_4^{2-}, 26450-38-4; $V_2O_7^{4-}$, 22466-30-4; $(VO_2)_3O_3^{3-}$, 51194-33-3.

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