Inorganica Chimica Acta, 17 (1976) 167–173

Spectrophotometric Investigation of Vanadyl Phosphate Equilibria in Acid Media*

W. C. COPENHAFER, M. W. KENDIG,** T. P. RUSSELL,*** and P. H. RIEGER****
Department of Chemistry, Brown University, Providence, Rhode Island 02912, U.S.A.
Received June 6, 1975

The formation of vanadyl phosphate complexes in acidic 1.0M $NaClO_4$ solution was studied by spectrophotometry in the charge-transfer region of the optical spectrum. In the $[H^+]$ range studied, 0.4–13mM, the principal species appear to be $VO(H_2PO_4)^+$ and $VO(H_2PO_4)_2$, formed with logarithmic stepwise formation constants of approximately 3.2 and 2.0, respectively. Both species are weakly acidic, ionizing to give $VO(HPO_4)$ and $VO(H_2PO_4)(HPO_4)^-$ with pK_a values on the order of 3–4. Results obtained for $[H^+]$ = 13 mM are anomalous and are not explained by these equilibrium constants.

Introduction

Complex formation in the oxovanadium(IV) orthophosphate system at low pH was studied several years ago by Salmon and Whyman.[1] These authors used ion exchange techniques to demonstrate the existence of both 1:1 and 1:2 vanadyl phosphate complexes; convincing evidence for at least one anionic species was obtained. More recently Kriss and Yatsimirski[2] studied the formation of vanadyl complexes with orthophosphate and several other phosphate ligands. Ivakin *et al.*[3] have very recently published a more complete spectrophotometric study of the system at 25°C in media maintained at 1.0*M* ionic strength with sodium perchlorate.

As Salmon and Whyman point out, an anionic 1:2 complex implies coordinated HPO_4^{2-}. A general equilibrium model for the vanadyl phosphate system, limited to monomeric complexes, thus includes a total of five complex species, coupled by the following equilibria:

$$VO^{2+} + H_2PO_4^- \rightleftarrows VO(H_2PO_4)^+ \quad (1)$$

$$VO(H_2PO_4)^+ + H_2PO_4^- \rightleftarrows VO(H_2PO_4)_2 \quad (2)$$

$$VO(H_2PO_4)^+ \rightleftarrows VO(HPO_4) + H^+ \quad (3)$$

$$VO(H_2PO_4)_2 \rightleftarrows VO(H_2PO_4)(HPO_4)^- + H^+ \quad (4)$$

$$VO(H_2PO_4)(HPO_4)^- \rightleftarrows VO(HPO_4)_2^{2-} + H^+ \quad (5)$$

Although Salmon and Whyman[1] did not determine equilibrium constants, they concluded that the only 1:1 complex present in the pH range 0–3 was VO (HPO_4). They also neglect the neutral 1:2 species, $VO(H_2PO_4)_2$. In terms of the above model, this would imply that pK_3 and pK_4 are both small, on the order of or less than zero. Ivakin and co-workers,[3] on the other hand, found that their data require both 1:1 species, but only $VO(HPO_4)_2^{2-}$ among the possible 1:2 species. Equilibrium constants determined by these workers, in terms of the above model, are $K_1 = 31$, $pK_3 = 4.35$, and $K_2K_4K_5 = 2.4 \times 10^{-8}$. Since the 1:2 complex is expected from these equilibrium constants to become significant above pH 2, pK_4 and pK_5 must apparently be less than 2.

There is evidence in the literature that the pK_a of coordinated $H_2PO_4^-$ is often substantially less than that of the free ion; Table I lists several results. It would appear that the pK_a of coordinated $H_2PO_4^-$ is usually somewhat less than that of coordinated water in the corresponding aquo ions. Based on the results given in Table I, however, one would not expect the pK_a of coordinated $H_2PO_4^-$ in the vanadyl complex to be much less than 3. It seems probable, therefore, that the cationic 1:1 complex was present in the acidic solutions studied by Salmon and Whyman, but that experiments to detect it were not performed. Ivakin's value of pK_3 seems plausible, but the implied values of pK_4 and pK_5 are unlikely.

Preliminary experiments in our laboratory on the vanadyl phosphate system[4] demonstrated that the esr spectrum of vanadium(IV) was sensitive to complexation by phosphate. The vanadium nuclear hyperfine splitting constant decreased from 116 G in 1*M* $NaClO_4$ at pH 2 to 113 G in 1*M* NaH_2PO_4 at the

---

* Taken in part from the Ph. D. Thesis of M.W.K., Brown University, 1973.

** Metcalf Fellow, 1970–71; present address: The Center for Surface and Coatings Research, Lehigh University, Bethlehem, Pennsylvania.

*** Undergraduate research participant, summer 1973.

**** To whom correspondence should be addressed.

TABLE I. Acidity Constants for Coordinated H_2O and $H_2PO_4^-$.

Species	pK_a	Ref.	Species	pK_a	Ref.
$Fe(H_2O)_6^{3+}$	2.7	a	$Fe(H_2PO_4)^{2+}$	1.7	b
$Al(H_2O)_6^{3+}$	4.3	c	$Al(H_2PO_4)^{2+}$	2.1	d
$Cr(H_2O)_6^{3+}$	4.1	e	$Cr(H_2PO_4)^{2+}$	4.0	f
$Coen_2(H_2O)_2^{3+}$	6.0	g	$Coen_2(H_2PO_4)^{2+}$	3.1	h
$VO(H_2O)_5^{2+}$	6.0	i	–		

[a] D.D. Perrin, *J. Chem. Soc., 1959,* 1710 (measured in 1*M* $NaClO_4$ at 20°C). [b] H. Galal-Gorchev and W. Stumm, *J. Inorg. Nucl. Chem., 25,* 567 (1963) (0.4*M* $NaClO_4$, 25°C). [c] K. Srinivasan and G.A. Rechnitz, *Anal. Chem., 40,* 1818 (1968) (1*M* $NaClO_4$, 25°C). [d] N. Bjerrum and C.R. Dahm, *Z. phys. Chem., Bodenstein Festband,* 627 (1931) (ionic strength, *ca.* 0.04*M*, 18°C). [e] G. Schwartzenbach, *Pure Appl. Chem., 5,* 377 (1962) (0.1*M* $NaClO_4$, 20°C). [f] J.H. Walsh and J.E. Earley, *Inorg. Chem., 3,* 343 (1964) (0.1*M* $NaClO_4$, 25°C). [g] R.D. Cannon and J.E. Earley, *J. Am. Chem. Soc., 88,* 1872 (1966) (1*M* $NaClO_4$, 25°C). [h] S.F. Lincoln and D.R. Stranks, *Aust. J. Chem., 21,* 37 (1968) (1*M* $NaClO_4$, 25° C). [i] F.J.C. Rossotti and H.S. Rossotti, *Acta Chem. Scand., 9,* 1177 (1955) (3*M* $NaClO_4$, 25° C).

same pH. The change is too small, however, to accurately determine complex formation constants.

Small extinction coefficient decreases were observed[4] in the 700–800 nm range of the optical spectrum as the *d–d* band centered at 760 nm appeared to shift to lower energy on the addition of phosphate at pH 2. The band at 625 nm, which appears as a shoulder in the spectrum of the aquo ion, appeared to shift to somewhat higher energy, causing small increases in extinction coefficients in the 550–650 nm range. The shifts, though real, are small and the changes in extinction coefficient, ranging up to $4M^{-1}cm^{-1}$, would require a total metal concentration on the order of 10 m*M* to obtain reliable spectrophotometric data, even in a 10 cm cell. Such a concentration would severely limit the phosphate-to-metal ratios accessible without causing the ionic strength and the overall character of the medium to vary widely. Thus, after preliminary work convinced us that complexes were formed, attention was focussed on the first charge-transfer band in the uv region where much larger extinction coefficient shifts were observed on the addition of phosphate.

Experimental

Solutions

A stock $VO(ClO_4)_2$ solution, 0.195*M* by permanganate titration, was prepared as described elsewhere.[5] A secondary stock solution, 1.95 m*M* in VO^{2+}, was prepared by dilution of the first solution with 1.00*M* $NaClO_4$, keeping the pH at about 2 by the addition of 70% perchloric acid. Sample solutions for determination of difference spectra were prepared by dilution of the 1.95 m*M* VO^{2+} 1:10 with 1.00*M* $NaClO_4$. The pH was adjusted to the desired value by addition of 70% $HClO_4$ or 1*M* Na_2CO_3 just before completion of the dilution.

The $NaClO_4$ solution was prepared using G.F. Smith $NaClO_4 \cdot H_2O$ and was filtered through a fritted glass funnel before use. This reagent proved to be quite critical to the success of the experiments. Anhydrous $NaClO_4$ or $NaClO_4 \cdot H_2O$ from other suppliers apparently contained impurities which either oxidize vanadium(IV) or catalyse the oxidation by perchlorate. Vanadyl perchlorate solutions, prepared using the G.F. Smith material, were stable for at least several days, as judged by the absence of the greenish cast which appeared rapidly in the case of solutions prepared with other $NaClO_4$ samples.

A stock phosphate solution, 0.990*M* by pH titration, was prepared using J.T. Baker reagent grade $NaH_2PO_4 \cdot H_2O$ and sufficient 70% $HClO_4$ to adjust the pH to the desired value. A 0.099*M* solution was prepared by 1:10 dilution of the stock solution with the pH readjusted just before completion of the dilution.

Two phosphate solutions were prepared as titrants, both containing 0.195 m*M* $VO(ClO_4)_2$. The first (solution A) was prepared by diluting the 1.95 m*M* VO^{2+} solution 1:10 with 0.099*M* phosphate, adjusting the pH just before completion of the dilution. The second (solution B) was prepared similarly, but using the 0.99*M* stock phosphate solution.

Difference Spectra

Spectra were recorded in the UV region using a Cary 15 spectrophotometer and 10 cm cylindrical absorption cells. In any series of measurements, the reference and sample solutions were initially identical solutions containing 0.195 m*M* $VO(ClO_4)_2$ and 1.00*M* $NaClO_4$, adjusted to the desired pH. The sample cell was connected through a flow system to a titration vessel where aliquots of a phosphate solution could be added. The flow system was originally deoxygenated with nitrogen gas and kept under nitrogen pressure during the experiment. After each addition of phosphate solution to the titration vessel, the contents of the spectrophotometer cell were flushed back and forth between the cell and the titration vessel at least three times to ensure homogeneity of the solution. Mixing efficiency was checked by measuring the absorbance of a standard chromate solution before and after dilution in the flow system. The sample cell in the spectrophotometer was held at 25.0 ± 0.1 °C through use of a cell mounting block through which thermostatted water was pumped.

In determining the difference spectra, aliquots of phosphate solution A were first added using a 5 ml Hamilton repeating dispenser which delivered 0.10 ml per addition. After about 2.5 ml of solution A had been added and about nine difference spectra recorded for phosphate concentrations ranging up to about 2.2 m*M*, the syringe was refilled with solution B and the titration continued for an additional 13–14 spectra with phosphate concentrations ranging up to about 0.2*M*.

The absorbance due to free phosphate was determined by measuring the absorbance of the 0.99*M* stock phosphate solutions at each of the pH values, using distilled water as a reference.

pH Measurements

Solution pH values were determined using a Coleman pH meter and a combination pH electrode. Calibration was with commercial buffer solution at pH 1.68 and 4.0. pH values determined in this way are of questionable significance because of the variable reference electrode liquid junction potential. For this reason, the experimental pH scale was converted to hydrogen ion concentration using a calibration curve constructed by measuring the pH of solutions of $HClO_4$ of known concentration in 1.0*M* $NaClO_4$.

Data Analysis

Absorbances measured in the experimental spectra are the difference between the absorbance of the sample solution and that of the reference solution. It is assumed that the only species which absorb in the wavelength region 235–300 nm are the aquo vanadyl ion, the various vanadyl phosphate complexes, and (to a much smaller degree) free phosphate. The absorbance of the reference solution, where VO^{2+} is the only absorbing species, is

$$A_{ref} = \varepsilon_0 C_M b \qquad (6)$$

where ε_0 is the extinction coefficient of VO^{2+}, C_M is the metal concentration, and b is the path length. The absorbance of the sample solution is

$$A_{sam} = \varepsilon_l C_l b + \varepsilon_0 C_0 b + \sum_i \varepsilon_i C_i b \qquad (7)$$

where ε_l and C_l are the extinction coefficient and concentration of the free phosphate ligand, C_0 is the concentration of uncomplexed VO^{2+}, and ε_i and C_i are the extinction coefficient and concentration of vanadyl phosphate complex i. The experimental quantity ΔA is thus the difference of eqs (6) and (7). Defining an effective metal extinction coefficient difference by

$$\Delta\varepsilon = (\Delta A - \varepsilon_l C_l b)/C_M b, \qquad (8)$$

we find that $\Delta\varepsilon$ is given by

$$\Delta\varepsilon = \sum_i \Delta\varepsilon_i x_i \qquad (9)$$

where x_i is the mol fraction of total metal in the *i*th form and $\Delta\varepsilon_i = \varepsilon_i - e_0$.

We assume that the data may be understood in terms of chemical equilibria,

$$M + iL \rightleftarrows ML_i, \qquad (10)$$

with conditional formation constants

$$\beta_i' = x_i/x_0 C_l^i. \qquad (11)$$

Combining eqs (9) and (11), we have

$$\Delta\varepsilon = \frac{\Sigma \Delta\varepsilon_i \beta_i' C_l^i}{1 + \Sigma \beta_i' C_l^i}. \qquad (12)$$

The ΔA data were first converted to $\Delta\varepsilon$, using eq (8), and then fitted to eq (12), using a non-linear least-squares procedure.[6,7] After initial attempts to fit the data assuming the formation of only a 1 : 1 vanadyl phosphate complex showed that good agreement could not be obtained,[4] successive data analysis assumed the formation of both 1 : 1 and 1 : 2 complexes. In the final analyses, absorbances measured at eight different wavelengths, ranging from 235 to 300 nm, were fitted simultaneously, yielding a total of 18 parameters, *i.e.*, eight values of $\Delta\varepsilon_1$, eight values of $\Delta\varepsilon_2$, and the equilibrium constants β_1' and β_2'.

The non-linear least-squares calculation was programmed in APL and run on an IBM 360/67 computer. Starting with reasonable parameter estimates, convergence was usually relatively rapid with at most about 10 cycles of iteration required before the parameters became effectively constant.

To ensure that only one least-squares minimum was possible in the 18-dimensional parameter space, an auxiliary linear least-squares program was used which fitted the data to the sixteen values of $\Delta\varepsilon_i$, given values of β_1' and β_2'. Searching over a wide range of values of β_1' and β_2' invariably led to the same minimum error point found by the non-linear program.

Results

Difference spectra were obtained for 0.2 m*M* solutions of vanadium(IV) containing concentrations of phosphate ranging from 0.2 m*M* up to about 0.2*M*. Beyond a large number of preliminary experiments which served to refine techniques, a total of eleven sets of data were collected. Reproducibility among the runs at the same acidity was only fair, and, of the experimental runs, we have a degree of confidence in two runs with $[H^+] = 13$ mM, two of those with $[H^+] = 4$ mM, and one each with $[H^+] = 1.3$ mM and 0.4 mM. The most common problems which caused experimental runs to be rejected in the final analysis were drift of the spectrophotometer baseline over the several hours of a run and apparent oxidation of vanadium(IV) in solutions of high phosphate concentration.

A typical "good" set of data – absorbance differences obtained in two runs with $[H^+] = 4$ mM at wavelengths of 240, 270, and 300 nm – is plotted in Figure 1 as a function of the concentration of total phosphate in solution.

The absorbances plotted in Figure 1 are corrected for absorbance of free phosphate; this correction is small, but significant toward the upper end of the concentration range plotted. Above 0.1M, the absorbance of free phosphate is a sizable factor, rendering the corrected absorbances less reliable; furthermore, the nature of the medium is significantly altered when the phosphate-to-perchlorate ratio exceeds 0.1. For these reasons only data for phosphate concentrations up to 0.1M were included in the least-squares fitting procedures.

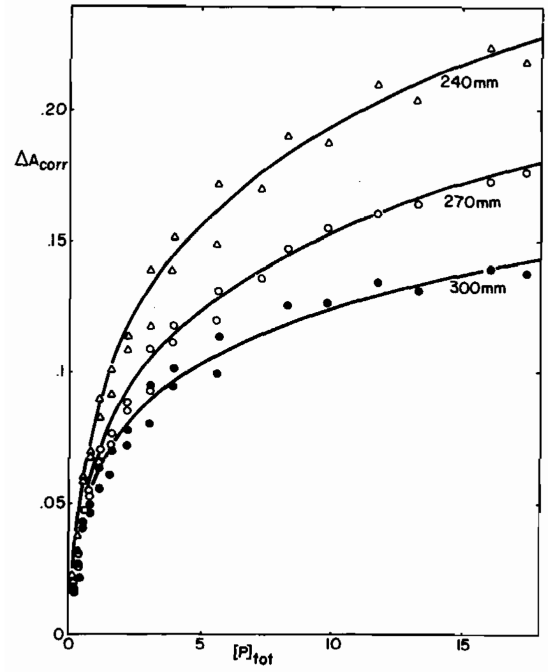

Figure 1. Differential absorbances, measured at 240 nm (triangles), 270 nm (open circles), and 300 nm (closed circles) for solutions 0.195 mM in VO^{2+}, 4 mM in $[H^+]$ as functions of total phosphate concentration, expressed in mM.

The rapid rise in absorbance when the phosphate concentration was increased from zero to 2 mM suggests the formation of a 1:1 complex with a formation constant on the order of 1000. If only a 1:1 complex were formed, however, the equilibrium would be essentially saturated by the time the total phosphate concentration reached 10 mM, and no further increase in absorbance would be expected at higher concentrations. The observed slow increase in absorbance above 10 mM (which continues with decreasing slope up to the limit of the experiment) suggests the formation of a 1:2 complex as well.

Analysis of these data, together with absorbances measured at 235, 250, 260, 280, and 290 nm, by the non-linear least-squares procedure described above gave a good fit at all wavelengths. The standard deviation of the experimental absorbances from those calculated was 0.0055, very close to the anticipated random error in the experimental measurements. The formation constants β_1' and β_2', obtained from the least-squares fit, are given in Table II, and the fitted extinction coefficient differences, $\Delta\varepsilon_1$ and $\Delta\varepsilon_2$, are given in Table III. The smooth curves shown in Figure 1 correspond to the absorbances calculated from the parameters of Tables II and III. The qualitatively similar results obtained for solutions of other acidities are also given in Tables II and III.

Discussion

The conditional formation constants, β_1' and β_2', defined by eq (11) and given in Table II, refer to total free phosphate in solution. Assuming that $H_2PO_4^-$ is the only form of free phosphate which forms complexes with VO^{2+}, these values may be converted to conditional stepwise constants and corrected for undissociated H_3PO_4 in solution by the following expressions:

$$K_1' = \beta_1'(1 + \frac{[H_3PO_4]}{[H_2PO_4^-]}) \qquad (13)$$

$$K_2' = \frac{\beta_2'}{\beta_1'}(1 + \frac{[H_3PO_4]}{[H_2PO_4^-]}) \qquad (14)$$

where the phosphate concentration ratio may be computed from $[H^+]$ and the concentration ionization constant of phosphoric acid at 25° C in 1M $NaClO_4$, $K_a = 0.020$.[8] Values of K_1' and K_2' thus computed are given in Table II.

If the results were interpretable in terms of the general equilibrium model, eqs (1)–(5), the conditional formation constants K_1' and K_2' should be related to the equilibrium constants of reactions (1) to (5) by:

$$K_1' = K_1(1 + K_3/[H^+]) \qquad (15)$$

TABLE II. Formation Constants.

$[H^+]$	No. of Points	Standard Deviation[a]	β_1' [b]	$\beta_2'/1000$ [b]	K_1' [c]	K_2' [d]
13 m*M*	344	0.0048	3600 ± 200	241 ± 92	5900 ± 400	110 ± 40
4 m*M*	320	0.0055	1440 ± 100	79 ± 4	1730 ± 130	66 ± 6
1.3 m*M*	168	0.0030	2290 ± 90	205 ± 6	2430 ± 100	95 ± 5
0.4 m*M*	168	0.0037	3890 ± 170	232 ± 16	3970 ± 170	61 ± 5

[a] Standard deviation of experimental absorbances from those calculated in least-squares fit. [b] Least-squares parameters with uncertainties estimated from the fit. [c] Calculated using eq (13). [d] Calculated using eq (14).

TABLE III. Extinction Coefficient Differences[a].

	Wavelength (nm)							
	300	*290*	*280*	*270*	*260*	*250*	*240*	*235*
$[H^+]$ = 13 m*M*								
$\Delta\varepsilon_1$	40	45	47	48	50	54	60	62
$\Delta\varepsilon_2$	79	93	104	111	117	125	143	155
$[H^+]$ = 4 m*M*								
$\Delta\varepsilon_1$	47	50	51	52	54	58	65	68
$\Delta\varepsilon_2$	103	118	128	137	145	157	175	192
$[H^+]$ = 1.3 m*M*								
$\Delta\varepsilon_1$	59	65	68	68	72	77	91	96
$\Delta\varepsilon_2$	94	110	124	133	145	161	190	214
$[H^+]$ = 0.4 m*M*								
$\Delta\varepsilon_1$	63	69	71	70	73	79	88	97
$\Delta\varepsilon_2$	125	145	164	170	195	229	283	334

[a] Extinction coefficients in units of M^{-1} cm^{-1}; uncertainties estimated from the least-squares fits are in the range 1–2 M^{-1} cm^{-1}.

$$K_2' = K_2\left(\frac{1 + K_4/[H^+] + K_4K_5/[H^+]^2}{1 + K_3/[H^+]}\right) \qquad (16)$$

Quantitative fitting of the experimental values of K_1' and K_2' to eqs (15) and (16) is impossible because of the very large values of the constants found for $[H^+] = 13$ m*M*. In particular, eq (15) predicts that K_1' will be a monotonic decreasing function of $[H^+]$. If we ignore the offending result, the remaining data fit eqs (15) and (16) reasonably well, leading to the following equilibrium constants: $K_1 = 1600$, $K_2 = 90$, $K_3 \simeq 6 \times 10^{-4}$, and $K_4 \sim 3 \times 10^{-4}$. K_5 was assumed to be less than 10^{-4} and was neglected. These values give predicted values of $K_1' = 1650$, 1810, 2320, and 4000, and $K_2' = 88$, 84, 76, and 64, respectively, for the four acidities studied.

The value of K_1' predicted for $[H^+] = 13$ m*M* is smaller than the experimental value by nearly a factor of four. The large experimental value found in this case is not an artifact of the data analysis procedure. Examination of the raw data, either from the two experimental runs included in the data analysis or from another run which was rejected (because of apparent baseline drift at higher concentrations), shows that the absorbance increases rapidly at very low phosphate concentrations, more rapidly than in solutions of lower acidity.

One approach to an explanation of the anomaly would be to assume a protonation equilibrium which becomes important at low pH. It is conceivable that VO^{2+} forms a complex with undissociated H_3PO_4, but, in order to explain the results, the formation constant would have to be substantially greater than K_1 which implies that the ionization constant of coordinated H_3PO_4 would have to be somewhat smaller than that of the free acid. This would certainly not be consistent with the notion that ligand pK_a's are reduced on coordination to vanadyl ion.

Alternatively, the vanadyl oxygen atom may be slightly basic in the phosphate complex. This is, of course, thermodynamically equivalent to the previous suggestion and is thus experimentally indistinguishable using the present techniques. There is precedent for protonation of the aquo vanadyl ion in concentrated acid media. Rivkind[9] estimated the equilibrium constant for the process

$$VO^{2+} + H^+ \rightleftarrows VOH^{3+}$$

to be about 0.13 in $HClO_4$ solution, and somewhat larger in H_2SO_4 solution. Protonation of the less positively charged phosphate complexes seems likely to occur with a somewhat larger equilibrium constant. Although it seems unlikely that this effect could be large enough to explain the present results, it remains a possibility. There seem to have been no vanadyl complexes with anionic ligands studied in the pH range 0–2 so that the importance of protonation is hard to assess.

The aquo vanadyl ion is known to dimerize on hydrolysis,

$$2\,VO^{2+} \rightleftarrows (VOOH)_2{}^{2+} + 2\,H^+$$

with an equilibrium constant of about 1.3×10^{-7} at 25 °C in $3M$ $NaClO_4$.[10] Although one would certainly expect phosphate complexes of low charge to polymerize to some degree, the low total metal concentration used in these experiments, 0.2 mM, probably is sufficient insurance against polymerization as a major complication.

There are a number of sources of systematic error in the experiment. Because of the aliquot addition of phosphate titrant, errors in phosphate concentration tend to accumulate and probably amount to ±5% in the more concentrated solutions; this error is small, however, in the context of the results. A more serious problem was baseline drift in the spectrophotometer. This occured to a degree during all runs; an example of the magnitude of the error introduced is apparent in Figure 1, where the data points from the two runs are easily separated into two parallel curves, particularly at 240 nm. The problem probably affects the $\Delta\varepsilon$ values more than it does the β's. For example, one experimental run at pH 2.5 which was not included in the final data analysis gave $\beta_1' = 1820$, $\beta_2' = 108 \times 10^3$, values reasonably close to those given in Table II. The fitted extinction coefficients, however, were about 20% higher than those given in Table III at the long wavelength end of the spectrum while only about 3% different at the short wavelength end.

One of the more important sources of error is in the adjustment and control of $[H^+]$. All solutions were adjusted to the same pH meter reading before mixing, but variations in liquid junction potential from one solution to another could lead to differences in $[H^+]$. The acidity of the sample solution might then change during the course of a run as phosphate at a different acidity was added. The magnitude of the effect no doubt varies as the nominal $[H^+]$ is changed, but one would not expect the variation to be sufficiently great to explain the present anomaly.

The ionic strength of the medium varied slightly during the course of an experimental run. We estimate that the variation ranges from about 6% at the highest acidity to less than 2% for the less acidic solutions. These are small differences, however, which should have only second-order effects on the results.

Finally, there is the possibility that outer-sphere effects play a role in the observed absorbance variations. Such effects as ion-pairing or just changes in the nature of the medium can have major importance in determining the intensity of charge-transfer bands.[11] It is hoped that, by working with solutions of very low metal concentration and in a medium where the (presumably non-complexing) perchlorate ions outnumber the ligand phosphate ions by at least 10:1, these problems were avoided. Some results obtained for phosphate concentrations above $0.1M$ suggest that outer-sphere effects do eventually become important. The role played in the results reported here is probably small, however.

Although the failure of the results to completely fit the general model is disappointing, the general conclusions of Salmon and Whyman[1] are confirmed. Both 1:1 and 1:2 vanadyl phosphate complexes are formed in solutions of low pH and moderate phosphate concentration. The tendency of values of K_1' to increase with decreasing $[H^+]$ supports the notion that coordinated $H_2PO_4^-$ is significantly more acidic than is the free ion. The values of K_2' obtained, on the other hand, suggest that the dianion, $VO(HPO_4)_2{}^{2-}$, is not an important species at high acidity.

Despite the superficial similarity of the experiments, our results are in substantial disagreement with those reported by Ivakin *et al.*[3] The reason for the disagreement almost certainly lies in an important difference in experimental detail: our phosphate concentration range, 0.2–100 mM, was both much wider and lower than that used by the Russian workers, 0.1–0.5M. They would thus have missed the rapid absorbance increase at low phosphate concentration which determines β_1' in the data analysis. Furthermore, they apparently did not correct for absorbance due to free phosphate. Thus the absorbance changes which they analysed to obtain the reported equilibrium constants probably reflected changes in free ligand concentration and may have been affected by outer-sphere effects as well. Ivakin and co-workers used a vanadium(IV) concentration of 0.6 mM; if polymerization is a problem in this system, their results would be more affected than would ours. Our spectrophotometric data was collected in the wavelength range 235–300 nm whereas the Russian workers used the range 205–240 nm; the shorter wavelengths and resultant increased extinction coefficients allowed them to work with a 1 cm absorption cell, but in our experiments, absorbance data at wavelengths shorter than 235 nm were generally found to be less reliable.

Acknowledgments

The authors are indebted to Professor J.O. Edwards for many stimulating discussions and to the referee of this paper for several helpful comments. The work was supported in part by the National Institute of Environmental Health Sciences.

References

1 J.E. Salmon and D. Whyman, *J. Chem. Soc., 1966,* 980.

2 E.E. Kriss and K.B. Yatsimirski, *Zh. Neorg. Khim., 16,* 386 (1971).

3 A.A. Ivakin, Z.M. Voronova and L.D. Koorbatova, *ibid., 20,* 1246 (1975).

4 W.M. Kendig, *Ph. D. Thesis,* Brown University, 1973.

5 R.R. Reeder and P.H. Rieger, *Inorg. Chem., 10,* 1258 (1971); R.R. Reeder, *Ph. D. Thesis,* Brown University, 1970.

6 W.C. Hamilton, "Statistics in Physical Science", Ronald Press, New York, N.Y. (1964).

7 T.O. Maier and R.S. Drago, *Inorg. Chem., 11,* 8 (1972).

8 B.J. Thamer, *J. Am. Chem. Soc., 79,* 9298 (1957); C.F. Baes, Jr., *J. Phys. Chem., 60,* 878 (1956).

9 A.I. Rivkind, *Dokl. Akad. Nauk SSSR, 142,* 137 (1962).

10 F.J.C. Rossotti and H.S. Rossotti, *Acta Chem. Scand., 9,* 1177 (1955).

11 J.M. Smithson and R.J.P. Williams, *J. Chem. Soc., 1958,* 457.