entire series and electrons are added to or taken from the ligands. The results of our calculations are in good agreement with the qualitative and quantitative aspects of the UV-visible spectra of tris(*o*-quinone)iron complexes considering the approximate nature of the Fenske-Hall method.

In a comparison of the iron series to the related chromium series, we have found that in complexes with the same overall charge but different metals the 3d orbitals of iron are more stable than the 3d orbitals or chromium. The iron-ligand interactions appear to be slightly weaker than the chromium-ligand interactions, which is probably due to the longer Fe-O bond lengths. When isoelectronic complexes of iron and chromium are compared, the greater stability of the 3d orbitals of iron is even more pronounced. The MOs for the isoelectronic iron 1- and chromium 3- complexes are much lower in energy for the iron complex than for the chromium complex and such a comparison provides no support for any supposed lesser stability of the iron 1- compound as compared to the chromium 1- compound. The inability to obtain evidence for the existence of an iron 1- complex may very well be related to a kinetic as opposed to a thermodynamic instability, as has been previously suggested.[3] Comparison of our calculations on the 3- complexes of iron and chromium provides convincing evidence for the presence and lack of an intense transition in the visible region of the spectrum assignable to a ligand to metal charge-transfer transition for the iron and chromium complexes, respectively. The iron system is analogous in many ways to the chromium system presented earlier. However, it has been pointed out that from a bonding and energetic point of view a given iron complex most closely resembles a chromium complex containing 4 fewer electrons rather than the isoelectronic chromium complex. As in the chromium series, the dramatic changes in the bonding over the entire seven-membered redox series are directly attributable to the dramatic destabilization of the 3d orbitals of iron as the complexes are reduced.

Acknowledgment. We gratefully acknowledge Professor K. N. Raymond for communicating his results to us prior to publication. We also wish to thank Professor C. G. Pierpont for many helpful discussions about *o*-quinone compounds. This research was supported by National Science Foundation Grant CHE78-24882.

Registry No. $Fe(BQ)_3^{3+}$, 81875-94-7; $Fe(BQ)_2(SQ)^{2+}$, 81875-95-8; $Fe(SQ)_2(BQ)^+$, 81875-96-9; $Fe(SQ)_3$, 81857-50-3; $Fe(SQ)_2(CAT)^-$, 81875-92-5; $Fe(CAT)_2(SQ)^{2-}$, 81875-93-6; $Fe(CAT)_3^{3-}$, 67966-15-8.

Contribution from the Commissariat à l'Energie Atomique, Centre d'Etudes Nucléaires,
Section des Transuraniens, 92260 Fontenay-aux-roses, France,
and Laboratoire de Chimie des Métaux de Transition, Université Pierre et Marie Curie, 75230 Paris Cedex 05, France

Spectrophotometric Identification of a Mixed-Valence Cation-Cation Complex between Aquadioxovanadium(V) and Aquaoxovanadium(IV) Ions in Perchloric, Sulfuric, and Hydrochloric Acid Media

P. BLANC,[1a] C. MADIC,*[1a] and J. P. LAUNAY[1b]

Received August 27, 1981

The mixture of aquadioxovanadium(V) and aquaoxovanadium(IV) ions in perchloric, sulfuric, and hydrochloric acid media gives a mixed-valence cation-cation 1/1 complex, $V_2O_3^{3+}$(aq), which was studied by absorption spectrophotometry. The order of stability of $V_2O_3^{3+}$(aq) vs. the nature of the medium is $H_2SO_4 > HClO_4 > HCl$ for acid concentrations lower than 8 M. In perchloric acid (8.7 M) the formation constant is found, $K = 8.1$ M^{-1} ($\sigma_K = 1.3\%$), whereas in 5 N $HClO_4$, K is lower and estimated to be about 0.8 M^{-1}; for this medium the thermodynamic parameters $\Delta H = -10.0 \pm 0.8$ kJ mol^{-1} and $\Delta S = -35.5 \pm 4.2$ J mol^{-1} K^{-1}. These characteristics are very close to those of cation-cation complexes involving actinide(V) ions (MO_2^+). The electronic spectrum of $V_2O_3^{3+}$(aq) presents an intense absorption for the whole visible range characterized by four transitions (17 500, 15 150, 12 300, and 10 100 cm^{-1}). The transition located at $\nu = 10\,100$ cm^{-1} can be attributed to intervalence band transition.

Introduction

A special feature of the chemistry of pentavalent actinides is the property of MO_2^+ ions (where M = actinide) to form "cation-cation" complexes with certain cations in acidic noncomplexing (ClO_4^-) or slightly complexing (Cl^-, NO_3^-) aqueous solutions. The first term of the series, Np(V)-U(VI), was identified by Sullivan[2] by means of spectrophotometric and potentiometric measurements, and since then, it has been shown that U(V), Pu(V), and Am(V) possessed the same property.[3] The nature of these "cation-cation" complexes is a subject of controversy. Sullivan and most workers consider them as true complexes, while Rykov and others feel that these species correspond rather to "long-range" interactions of the "aborted" redox reaction type, involving solvent molecules.[3a] However additional proofs of the existence of these complexes were provided recently: (1) It was confirmed by absorption spectrophotometry that the formation of the complexes Np(V)-U(VI), Np(V)-Np(VI), and Am(V)-U(VI) obeys the law of mass action.[3b,4] (2) Raman spectrometry has revealed a modification in the M-O bond (of the MO_2^+ ion) during complexation of NpO_2^+ by U(VI) and Np(V) and that of AmO_2^+ by U(VI).[5] (3) X-ray diffraction was used to measure the distance between metallic nuclei in solutions containing the complexes Np(V)-U(VI) and Np(V)-Np(V).[6]

---

(1) (a) Centre d'Etudes Nucléaires. (b) Université Pierre et Marie Curie.

(2) Sullivan, J. C.; Hindman, J. C.; Zielen, A. J. *J. Am. Chem. Soc.* **1961**, *83*, 3373.

(3) For further information, see: (a) Frolov, A. A.; Rykov, A. G. *Radiokhimiya* **1979**, *3*, 329. (b) Madic, C.; Guillaume, B.; Morisseau, J.-C.; Moulin, J.-P. *J. Inorg. Nucl. Chem.* **1979**, *41*, 1027.

(4) Guillaume, B.; Hobart, D.; Hahn, R. L.; Bourges, J. *J. Inorg. Nucl. Chem.*, in press.

(5) Guillaume, B.; Begun, G. M.; Hahn, R. L.; Narten, A. H. "11 èmes Journées des Actinides"; Jesolo Lido: Venice, Italy, 1981.

0020-1669/82/1321-2923$01.25/0

In the course of a research work involving the V(V)–V(IV) couple, it was observed[7] that perchloric solutions containing VO_2^+(aq) and VO^{2+}(aq) ions exhibited abnormally high absorbance, which appeared to reflect an interaction of the "cation–cation" type between the two vanadium ions. Hence a spectrophotometric study was undertaken with the double aim of interpreting this important property of vanadium ions[8] and making a comparison with the better known properties of "cation–cation" complexes involving the MO_2^+ ions of actinides.

Experimental Section

Reagents. The reagents $VOSO_4 \cdot 3.5H_2O$, PbO_2, $BaCl_2 \cdot 2H_2O$, HCl, $HClO_4$, H_2SO_4, CH_3COCH_3, and CH_3CN were Prolabo products of Normapur grade. The barium perchlorate ($Ba(ClO_4)_2$) was supplied by BDH (Laboratory Chemical Groups). These reagents were used without additional purification. The Np(V) stock solution was prepared as described earlier.[3b]

Preparation of Solutions. Vanadium(IV) Solutions. The V(IV) mother solutions were prepared by dissolving vanadyl sulfate in the appropriate medium, namely, the desired type and normality of the acid. For nonsulfuric acid media, sulfates were eliminated by precipitation of $BaSO_4$ upon addition of the corresponding barium salt ($Ba(ClO_4)_2$ or $BaCl_2$). These solutions were standardized by determining vanadium by a solution of Fe^{2+} ions in H_2SO_4–H_3PO_4.[9] After the Beer–Lambert law was determined for V(IV) solutions at $\lambda = 750$ nm ($\epsilon^{750}_{VO^{2+}} = 17.7$, $\sigma_\epsilon = 1\%$, $C_{HClO_4} = 5$ N), the V(IV) concentrations in the solutions were then analyzed by spectrophotometry.

Vanadium(V) Solutions. Preliminary results showed the necessity of using V(IV) and V(V) mother solutions of strictly identical concentrations, so that the V(V) solutions were prepared by chemical oxidation of V(IV) solutions by PbO_2. The oxidation proceeds as

$$2VO^{2+} + PbO_2(s) \rightleftarrows 2VO_2^+ + Pb^{2+}$$

As proved by complementary experiments, most of the Pb^{2+} was eliminated as $PbSO_4$ and no difference was observed with such solutions and V(V) solutions prepared by dissolving sodium metavanadate in the appropriate medium.

Vanadium(IV) and Vanadium(V) Solutions. These solutions were obtained by only mixing the V(IV) and V(V) mother solutions. The acidity of the solutions was checked by pH meter determination with 1 N sodium hydroxide.

Spectrophotometric Measurements. All the measurements were taken with use of Hellma Q.S. cells with optical path lengths of 1 and 10 mm. The experiments at different temperatures were performed by the use of a Haake apparatus. The spectrophotometer was a Hewlett-Packard 8450 A instrument designed to measure absorption spectra in the 200–800-nm wavelength range. The advantages of this instrument are its high measurement speed (0.1 s for the overall spectrum) and also its information storage in an internal memory and on a cassette, allowing rapid and easy processing of the collected data. In addition, some measurements up to $\lambda = 1300$ nm were performed on a Beckman 5270 spectrophotometer.

Results and Discussion

Identification of $V_2O_3^{3+}$(aq) and Equilibrium Study. While the V(IV) and V(V) solutions were respectively blue and yellow, their mixtures displayed a green color that was much darker than expected. A rapid comparison between the spectra of the mixtures and those of the pure constituents showed a sharp increase in absorbance for wavelengths ranging from 400 to 800 nm (measurement limit of the Hewlett-Packard spectrophotometer), which appears to reflect an interaction between the two species VO_2^+(aq) and VO^{2+}(aq) present in solution for acidities exceeding 3 N.[10] Figure 1 shows the spectra of perchloric acid solutions ($C_{HClO_4} = 5$ N) for which the sum of the concentrations

$$C_{V(IV)}{}^T + C_{V(V)}{}^T = C_0$$

was constant and equal to 0.24 M. It may be noted that the spectra for $X = 0$ and $X = 1$, which are respectively characteristic of V(V) and V(IV) solutions, intersect for $\lambda = 490$ nm. If no interaction occurs between the V(V) and V(IV) species, all the other spectra corresponding to the V(IV) + V(V) mixtures should give an isosbestic point. Actually, this is not observed (see Figure 1). Hence one can conclude that an interaction exists between the chromophoric species. For this type of experiment, the spectra of the solutions of V(IV) and V(V) alone in concentrations identical with those used in the mixtures were measured, allowing the determination of the excess spectra by simple subtraction. The excess spectra $\Delta OD = f(\lambda)$ are shown in Figure 2 (same experimental conditions as for Figure 1).

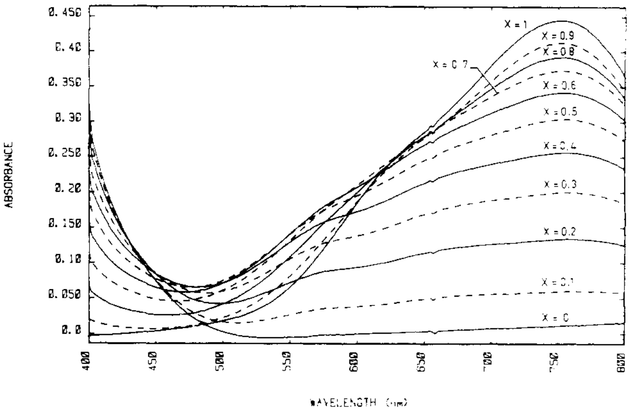


Figure 1. Continuous-variations-method spectra of V(IV) and V(V) solutions. Experimental conditions: total vanadium concentration = 0.24 M; X = V(IV) molar fraction; medium = 5 N $HClO_4$; cell path length = 0.1 cm.

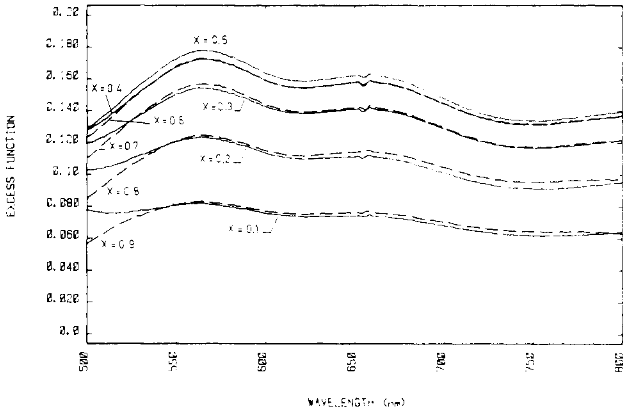


Figure 2. Continuous-variations-method excess spectra of V(IV) and V(V) solutions (same experimental conditions as in Figure 1).

As the excess spectra show an identical morphology for the entire range of molar fractions investigated, namely, $X = 0.1$–0.9, this indicates that a unique species is certainly responsible for the excess absorbance. Figure 3 shows the excess functions ΔOD^λ vs. molar fraction of V(IV) in the mixtures for three wavelengths: $\lambda = 570$, 662, and 750 nm (same experimental conditions as for Figure 1). The obtained curves

---

(6) Guillaume, B.; Narten, A. H.; Hahn, R. L., manuscript in preparation.

(7) Blanc, P., thesis in preparation.

(8) To our knowledge, the only "cation–cation" complex involving VO_2^+ found in the literature is $VNpO_2^{5+}$, which is formed as a reaction intermediate in the reaction $VO_2^+ + Np^{4+} + H_2O \rightarrow VO^{2+} + NpO_2^+ + 2H^+$ investigated by: Koltunov, V. S.; Marchenko, V. I.; Shapovalov, M. P. *Radiokhimiya* **1977**, *19*, 56.

(9) Charlot, G. "Les Méthodes de la Chimie Analytique. L'analyse Quantitative Minérale"; Masson et Cie: Paris, 1961.

(10) (a) Pourbaix, M. "Atlas d'Équilibres Électrochimiques à 25 °C"; Gauthier-Villars: Paris, 1963. (b) Baes, C. F.; Messmer, R. E. "The Hydrolysis of Cations"; Wiley-Interscience: New York, 1976.

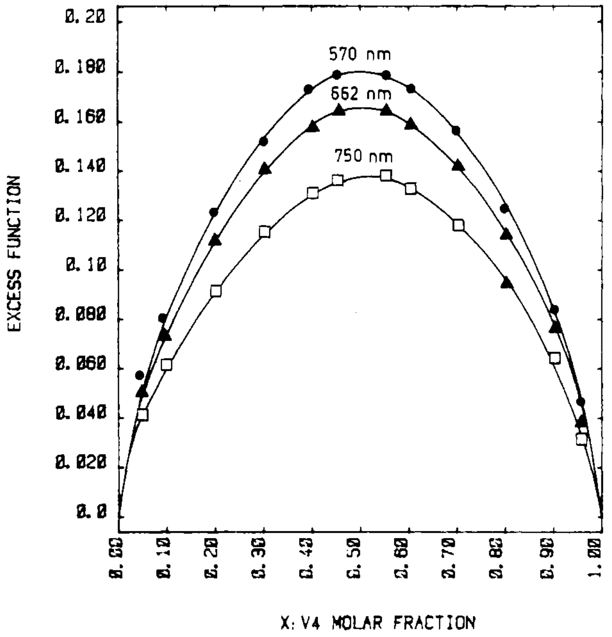


Figure 3. Continuous-variations-method excess functions of V(IV) and V(V) solutions vs. V(IV) molar fraction (X) (same experimental conditions as in Figure 1).

all exhibit a maximum for $X = 0.5$ and are all symmetrical about the axis of equation $X = 0.5$, suggesting that the formed complex has 1/1 stoichiometry, so that the reaction equation can be written

$$VO^{2+} + VO_2^+ \rightleftarrows V_2O_3^{3+} \qquad (1)$$

characterized by the constant

$$K = C_{V_2O_3^{3+}}(C_{VO^{2+}}C_{VO_2^+})^{-1} \qquad (2)$$

The continuous-variations method is based on the equations

$$C_0 = C_{V(IV)}{}^T + C_{V(V)}{}^T \qquad (3)$$

$$C_{V(IV)}{}^T = XC_0 \qquad (4)$$

$$C_{V(V)}{}^T = (1 - X)C_0 \qquad (5)$$

In addition, the excess functions for any wavelength are expressed by

$$\Delta OD^\lambda = l(\epsilon^\lambda{}_{V_2O_3^{3+}} - \epsilon^\lambda{}_{VO^{2+}} - \epsilon^\lambda{}_{VO_2^+})C_{V_2O_3^{3+}} \qquad (6)$$

With use of eq 2–5, eq 6 becomes

$$\Delta OD = l(\epsilon^\lambda{}_{V_2O_3^{3+}} - \epsilon^\lambda{}_{VO^{2+}} - \epsilon^\lambda{}_{VO_2^+})\{(KC_0 + 1) - [(KC_0 + 1)^2 - 4K^2X(1 - X)C_0{}^2]^{1/2}\}(2K)^{-1} \qquad (7)$$

where l is the optical path length and $\epsilon^\lambda{}_{V_2O_3^{3+}}$, $\epsilon^\lambda{}_{VO^{2+}}$, and $\epsilon^\lambda{}_{VO_2^+}$ are the molar extinction coefficients of the complex, of vanadium(IV), and of vanadium(V), respectively.

Since it was not possible to obtain the spectrum of the complex alone, $\epsilon^\lambda{}_{V_2O_3^{3+}}$ could not be measured directly. Hence the method employed to calculate K consists of the determination of the best pair of ($\epsilon^\lambda{}_{V_2O_3^{3+}}$, K) values that minimizes the sum of the error squares:

$$\sum(\Delta OD^\lambda{}_{\text{exptl}} - \Delta OD^\lambda{}_{\text{calcd}})^2$$

The results obtained by processing the experimental data corresponding to the chemical conditions $C_0 = 0.07$ M, $C_{HClO_4} = 8.7$ M, $X = 0.1$–0.9, $T = 25$ °C, and $l = 1$ cm are compiled in Table I.

Table I. Results of Calculations Relative to Determination of the Constant of Formation K of the $V_2O_3^{3+}$ Complex[a]

λ, nm	$\epsilon^\lambda{}_{VO^{2+}}$, M^{-1} cm^{-1}	K, M^{-1}	$\epsilon^\lambda{}_{V_2O_3^{3+}}$, M^{-1} cm^{-1}	K, M^{-1} (% σ_K)
570	4.0	8.05	130	
662	12.1	8.06	127	8.13 (1.4)
800	14.2	8.30	131	

[a] $\epsilon^\lambda{}_{VO_2^+}$ at 570, 662, and 800 nm ~0; uncertainty of $\epsilon^\lambda{}_{VO^{2+}}$ = 1%. Chemical conditions: $C_{HClO_4} = 8.7$ M; $C_0 = 0.07$ M; $X = 0.1$–0.9; $\Theta \simeq 25$ °C; $l = 1$ cm.

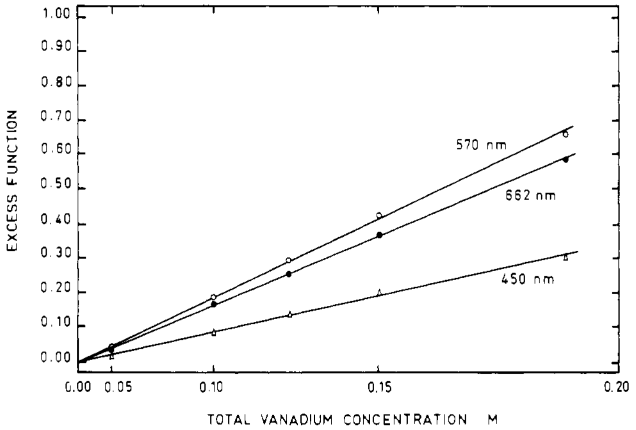


Figure 4. Excess functions of V(IV) and V(V) solutions vs. the square of vanadium concentration. Experimental conditions: V(IV) molar fraction $X = 0.5$; cell path length = 1 cm; medium = 5 N $HClO_4$.

The low value of K can be confirmed by examining the effect of dilution on ΔOD^λ. In fact, with the assumption that K is low, the concentrations of V(IV) and V(V) at equilibrium are substantially equal to $C_{V(IV)}{}^T$ and $C_{V(V)}{}^T$. The law of mass action can then be written:

$$K = C_{V_2O_3^{3+}}[X(1 - X)C_0{}^2]^{-1} \qquad (8)$$

Equations 6 and 8 give

$$\Delta OD^\lambda = l(\epsilon^\lambda{}_{V_2O_3^{3+}} - \epsilon^\lambda{}_{VO^{2+}} - \epsilon^\lambda{}_{VO_2^+})[KX(1 - X)C_0{}^2] \qquad (9)$$

Consequently, ΔOD^λ is proportional to $C_0{}^2$ for a given molar fraction X. The variations of ΔOD^λ as a function of $C_0{}^2$ in 5 M perchloric acid are shown in Figure 4. It can be seen that eq 9 is satisfied, thus confirming the low value of K for the medium considered and also indicating that this complex is a monomer. It should be noted that the equilibrium is instantaneously established during the mixture of solutions of V(V) and V(IV) and during the dilution of these mixtures the complex disappears quickly, thus showing the kinetic lability of the complex formed.

The effects of acid concentration and type on the intensity of interaction between V(V) and V(IV) were investigated with perchloric, sulfuric, and hydrochloric acid media. The obtained results, all corresponding to the conditions $C_0 = 0.1$ M, $X = 0.5$, and $T \simeq 25$ °C are given in Figure 5 in the form of ΔOD^λ vs. C_{A^-}.

The amount of complex formed increases with the concentration of acid for $HClO_4$, H_2SO_4, and HCl up to a value of about 8 M. In addition, for this concentration range, the order of stability of the complex as a function of the medium varies as $H_2SO_4 > HClO_4 > HCl$. Nevertheless, the case of hydrochloric acid medium is certainly a special one because, contrary to the excess spectra obtained for the two other media, the excess spectrum relative to the HCl medium exhibits a single maximum only, for $\lambda = 570$ nm, indicating a change in the identity of the complex (see below).

The results relative to $HClO_4$ medium have been studied by plotting log (ΔOD^λ) vs. log ($C_{ClO_4^-}$). A straight line with slope +3 is obtained, suggesting that three ClO_4^- ions participate in the reaction, which may therefore be written

$$VO^{2+} + VO_2^+ + 3ClO_4^- \rightleftarrows (V_2O_3)(ClO_4)_3 \qquad (10)$$

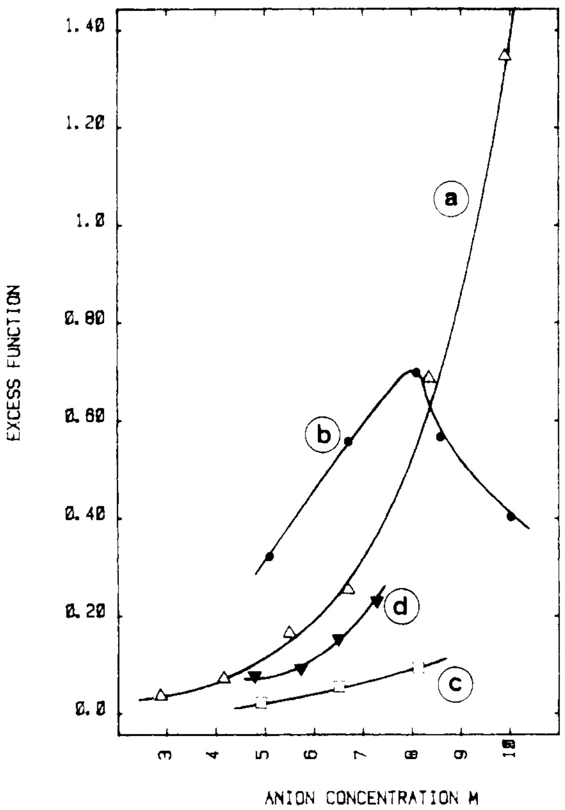


Figure 5. Excess functions of V(IV) and V(V) solutions (for λ = 570 nm) vs. medium. Experimental conditions: total vanadium concentration = 0.1 M; V(IV) molar fraction $X = 0.5$; λ = 570 nm; cell path length = 1 cm; medium = (a) $HClO_4$, (b) H_2SO_4, (c) HCl, (d) $NaClO_4$ (2.3 N $HClO_4$).

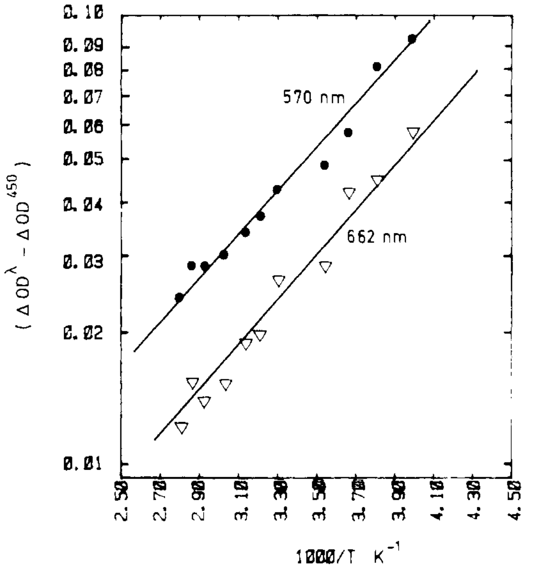


Figure 6. Excess function of V(IV) and V(V) solutions vs. temperature. Experimental conditions: total vanadium concentration = 0.1 M; V(IV) molar fraction = 0.5; medium = 5 N $HClO_4$; cell path length = 1 cm.

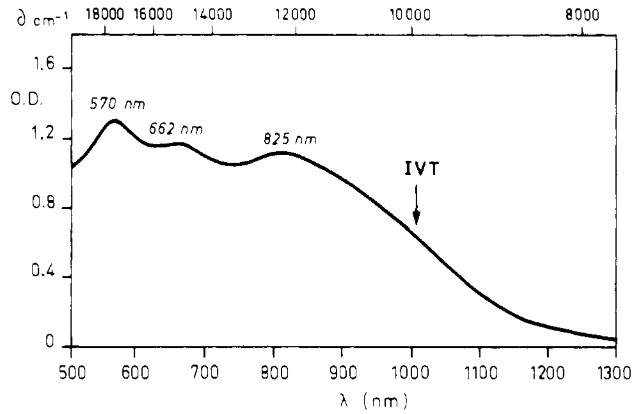


Figure 7. Electronic spectrum of $V_2O_3^{3+}$(aq). Experimental conditions: concentration V(IV) = 5×10^{-2} M, V(V) = 5×10^{-2} M; medium = 9.9 N $HClO_4$; cell path length = 1 cm; T = 25 °C (note that IVT stands for intervalence transition).

Table II. Electronic Spectra of $V_2O_3^{3+}$(aq) and VO^{2+}(aq)[a]

	ν			
$V_2O_3^{3+}$	17 500 (130)	15 150 (118)	12 300 (112)	10 100 (sh)
VO^{2+}	15 600 (sh)	13 300 (18)		

[a] Energy in cm^{-1}, molar extinction coefficient in parentheses in mol^{-1} cm^{-1}; sh = shoulder.

However, the results obtained for media of constant $HClO_4$ acidity and increasing $NaClO_4$ concentration (Figure 5, curve d), while reflecting the reinforcement of the stability of the complex with increasing $C_{ClO_4^-}$, are not identical with those related to the $HClO_4$ medium alone. It would be obviously necessary to take account of the real activities of the ClO_4^- ions for these different media, in order to invalidate or confirm eq 10. Since these values are not available, only the qualitative aspect of the equilibrium should be discussed. In the case of H_2SO_4 medium, a clear decrease in the stability of the complex appears for acidities above ≃8 M.

The effect of temperature on ΔOD^{λ} was investigated for chemical conditions in which eq 9 is satisfied (C_{HClO_4} = 5 N, C_0 = 0.1 M, X = 0.5), and the results are shown in Figure 6 in the form of graphs of the equation log ($\Delta OD^{\lambda_1} - \Delta OD^{\lambda_2}$) = $f(1/T)$, where λ_2 = 450 nm, λ_1 = 570 and 662 nm, and T is in K.[11]

The mean slope of the straight lines is used to determine the enthalpic variation associated with reaction 1 for 5 N $HClO_4$ medium, which is found to be equal to $\Delta H = -10.0 \pm 0.8$ kJ mol^{-1}. A determination of K according to the previous method yielded a value of about 0.8 M^{-1} in this medium. This is also obtained by considering the variation of ΔOD between 8 N $HClO_4$ and 5 N $HClO_4$, since ΔOD is proportional to K (eq 9). This makes possible an estimation of the associated entropic variation ΔS for the temperature of 298 K. This gives

$$\Delta S = -35.5 \pm 4.2 \text{ J mol}^{-1} \text{ K}^{-1}$$

Qualitative tests were undertaken to determine the effect of the addition of a water-miscible organic solvent on the stability of the complex $V_2O_3^{3+}$. Three solvents were used, acetone, acetonitrile, and hexamethylphosphoramide (HMPA), with dielectric constants of 20.7, 36.2, and 30, respectively.[12] The addition of acetone and acetonitrile considerably reinforces the stability of the interaction, while, on the contrary, HMPA reduces it significantly.

Spectrum of the $V_2O_3^{3+}$(aq) Ion. As noted above, it was impossible to obtain the $V_2O_3^{3+}$(aq) ion quantitatively, owing to the weakness of the interaction between the VO_2^+(aq) and VO^{2+}(aq) ions. Consequently, its spectrum could not be obtained separately. However, with the consideration that the interaction between the ions is low, the species VO_2^+(aq) and VO_2^+(aq) are only slightly consumed during the reaction, so that the excess spectrum corresponds to the spectrum of the

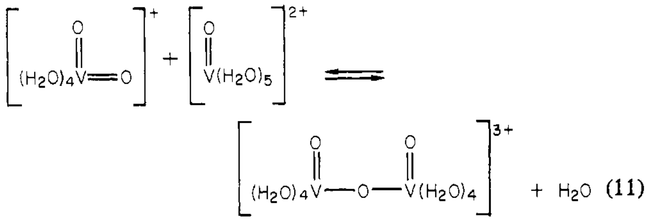
---

(11) The function log ($\Delta OD^{\lambda_1} - \Delta OD^{\lambda_2}$) is preferable to log ΔOD^{λ} because it allows the elimination of certain interference mechanisms such as the condensation of moisture on the walls of spectrophotometer cells during measurements taken at low temperature.

(12) Tremillon, B. "La Chimie en Solvants Non-aqueux"; Presses universitaires de France: Paris, 1971.

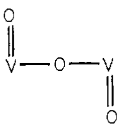
$V_2O_3^{3+}$(aq) ion. It must also be noted that the absorption due to the VO_2^+(aq) ion is nearly zero for $\lambda > 500$ nm. Hence the spectrum of a solution of composition $C_{VO_2^+} = 0.05$ M, $C_{VO^{2+}} = 0.05$ M, and $C_{HClO_4} = 9.9$ M, which was recorded with a solution of composition $C_{VO^{2+}} = 0.05$ M and $C_{HClO_4} = 9.9$ M in the reference compartment, shown in Figure 7, corresponds to the spectrum of the $V_2O_3^{3+}$(aq) ion. The main characteristics of this spectrum, compared to those of the VO^{2+}(aq) ion, are given in Table II.

Mechanism of Formation and Structure of the Mixed-Valence Compound. In acidic aqueous solution, vanadium in the oxidation states IV and V is found in the form of $VO(H_2O)_5^{2+}$ and $VO_2(H_2O)_4^+$ ions, respectively. Several structural studies have shown that the $V^VO_2^+$ group is bent.[13] The overall experimental results show that the formation of the mixed-valence compound can be considered as the substitution of one of the coordinated water molecules of the VO^{2+}(aq) cation by one of the oxygens of the dioxovanadium(V) group playing the role of ligand. The reaction can thus be written



$$[(H_2O)_4V(=O)=O]^+ + [O=V(H_2O)_5]^{2+} \rightleftharpoons [(H_2O)_4V(=O)-O-V(=O)(H_2O)_4]^{3+} + H_2O \qquad (11)$$

A similar reaction exists between the anions $[V^VO_2(NTA)]^{2-}$ and $[V^{IV}O(NTA)(H_2O)]^-$, where NTA denotes the nitrilotriacetate ligand,[14] and also between the species $[V^VO_2(PMIDA)]^-$ and $[V^{IV}O(PMIDA)(H_2O)]$ (PMIDA = pyridyl methyl iminodiacetate).[15] In both cases, the structure of the addition product shows the presence of the moiety



where each terminal oxygen is in the cis position with respect to the bridging oxygen and where the V–O–V bridge is linear.[14,15]

The effect of solvents on the formation reaction can be explained by the competition between the solvent molecules and the VO_2^+(aq) cation for coordination with VO^{2+}. Hence strong donor solvents like HMPA do not favor the formation of the mixed-valence complex, probably by blocking the coordination sites of VO^{2+}. On the other hand, weak donor solvents, especially acetonitrile, favor the formation of the addition product. A similar effect is observed with the complexes of NTA and PMIDA discussed above.[15]

The effect of acid concentration and nature appears to be more complex. In the case of $HClO_4$, a very clear reinforcement of the interaction occurs with increasing concentration. This may be explained by the formation of ion pairs, which would decrease the total charge of the species formed, according to reaction 10. Moreover, for very strong acidities, a drop in the activity of water must occur, thus favoring substitution. In the presence of chloride ions, however, competition occurs between the ligands Cl^- and VO_2^+(aq) for coordination with VO^{2+}(aq), giving rise to an especially weak interaction. Species such as $VO(H_2O)_3Cl^+$ and $VO(H_2O)_2Cl_2$ have been identified in hydrochloric solutions of VO^{2+}.[16] Besides, the mixed-valence compound itself is probably a chloride complex. This is suggested by its excess spectrum, which is different from the case of $HClO_4$, as already mentioned. In the case of sulfuric acid, it appears that the charge neutralization effect is predominant for concentrations between 5 and 8 M. Above this concentration, the decrease in the excess function (Figure 5) can be explained by the extensive complexation of VO^{2+} ions with occupation of most of the available coordination sites. Very little information is available about species existing in H_2SO_4 medium, but the especially stable complex $VO(SO_4(H_2O)_n)$ is known.[17]

As for the thermodynamic aspect of reaction 11, it is noteworthy that the value of ΔS is negative, while reactions leading to the loss of a water molecule generally show a positive ΔS of about 70 J mol^{-1} K^{-1}.[18] The negative value is certainly due to the fact that the reaction occurs between two species with the same charge sign, yielding a strongly charged cation. The structural effect on the solvent is thus reinforced, leading to a higher ordering of the solvation layers. It may be noted that the value of ΔS (−35.5 J mol^{-1} K^{-1}) closely approaches that obtained by Saito et al. (−40 J mol^{-1} K^{-1})[14] for the reaction between the two anions:

$$[V^VO_2(NTA)]^{2-} + [V^{IV}O(NTA)(H_2O)]^- \rightleftharpoons [V_2O_3(NTA)_2]^{3-} + H_2O$$

Furthermore, many reactions of the cation–cation type also lead to negative values of ΔS (see below).

An examination of the spectrum of the mixed-valence compound provides some additional information concerning its structure. In fact, four bands are observed as compared with only two for the VO^{2+}(aq) cation (Table II and Figure 7). For $VO(H_2O)_5^{2+}$, the two transitions observed at 13 300 and 15 600 cm^{-1} are assigned to the excitations $b_2(d_{xy}) \rightarrow e(d_{xz},d_{yz})$ and $b_2(d_{xy}) \rightarrow b_1(d_{x^2-y^2})$, respectively, in C_{4v} symmetry.[19]

By comparison with the spectra of $[V_2O_3(NTA)_2]^{3-}$ and $[V_2O_3(PMIDA)_2]^-$, in $V_2O_3^{3+}$(aq) the shoulder around 10 000 cm^{-1} can be assigned to an intervalence transition (IVT) between V(IV) and V(V), this energy being outside the usual range of d–d transitions. On the other hand, the three remaining bands appear to correspond to d–d transitions. Their number may be explained by a low symmetry of the V(IV) site, leading to a splitting of the e level. In effect, it is known that the spectra of complexes with very low symmetry such as $[(V^{IV}O)_2(d\text{-tartrate})_2]^{4-}$ sometimes display three bands in the 11 000–19 000-cm^{-1} range.[20]

This behavior contrasts with that of the complexes $[V_2O_3(NTA)_2]^{3-}$ and $[V_2O_3(PMIDA)_2]^-$, for which only two d–d bands are observed. In the latter compounds, moreover, the intervalence band appears as a very clearly distinct peak with an intensity much greater than that for $V_2O_3^{3+}$(aq). Hence for this band $\epsilon = 610$ in $[V_2O_3(NTA)_2]^{3-}$ and $\epsilon = 1050$ in $[V_2O_3(PMIDA)_2]^-$ are observed,[15] whereas in $V_2O_3^{3+}$(aq), the intervalence band appears as a shoulder on the side of a transition for which ϵ is about 110. This difference in behavior may be explained by a different geometry of the V–O–V bridge

---

(13) (a) Scheidt, W. R.; Tsui, C.; Hoard, J. L. *J. Am. Chem. Soc.* **1971**, *93*, 3867. (b) Scheidt, W. R.; Collins, D. M.; Hoard, J. L. *Ibid.* **1971**, *93*, 3873. (c) Scheidt, W. R.; Countryman, R.; Hoard, J. L. *Ibid.* **1971**, *93*, 3878. (d) Drew, R. E.; Einstein, F. W. B.; Gransden, S. E. *Can. J. Chem.* **1974**, *52*, 2184. (e) Rieskamp, M.; Mattes, R. *Z. Anorg. Allg. Chem.* **1976**, *419*, 193.

(14) (a) Nishizawa, M.; Hirotsu, S.; Ooi, S.; Saito, K. *J. Chem. Soc., Chem. Commun.* **1979**, 707. (b) Nishizawa, M.; Saito, K. *Inorg. Chem.* **1980**, *19*, 2284.

(15) Launay, J.-P.; Daoudi, M.; Jeannin, Y., manuscript in preparation.

(16) (a) Zeltmann, A. H.; Morgan, L. O. *Inorg. Chem.* **1971**, *10*, 2739. (b) Kalinichenko, N. B.; Marov, I. N.; Ermakov, A. N. *Zh. Neorg. Khim.* **1972**, *17*, 3250.

(17) Strehlow, H.; Wendt, H. *Inorg. Chem.* **1963**, *2*, 6.

(18) Lewis, J.; Wilkins, R. G. "Modern Coordination Chemistry"; Interscience: New York, 1960; Chapter 1.

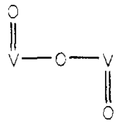
(19) Ballhausen, C. J.; Djurinskij, B. F.; Watson, K. J. *J. Am. Chem. Soc.* **1968**, *90*, 3305.

(20) Wood, J. S. *Prog. Inorg. Chem.* **1972**, *16*, 227 and references therein.

Table III. Comparison of Properties of the $V_2O_3^{3+}$(aq) Complex with Those of "Cation–Cation" Complexes Involving MO_2^+ Ions of Actinides

complex in ClO_4^- medium	μ	$C_{ClO_4^-}$, M	K, M^{-1}	ΔH, kJ mol^{-1}	ΔS, J mol^{-1} K^{-1}	kinetics of formation–dissociation	ref
U(V)-U(VI)	2	variable	16.6	−7.9 ± 1.2	−4.2 ± 4.2	labile	22
Np(V)-U(VI)	7	4.6	3.7			labile	3b
Np(V)-Np(VI)	7	4.7	3.0			labile	3b
Np(V)-Rh(III)	8	variable	3.31	−15.0 ± 3.7	−42 ± 12	nonlabile	23
Np(V)-Cr(III)	8	variable	2.62	−13.8 ± 2.0	−37.6 ± 7.9	nonlabile	24
V(V)-V(IV)	5.3	5.2	0.8	−10.0 ± 0.8	−35.5 ± 4.2	labile	this work

with, in particular, a lower electronic interaction in $V_2O_3^{3+}$(aq). The structure of the moiety



existing in $[V_2O_3(NTA)_2]^{3-}$ is specially favorable to electronic interaction, as the d_{xy} orbitals (each one perpendicular to the V═O bond) are coplanar. The structure of the $V_2O_3^{3+}$(aq) complex may be derived from the foregoing by rotation about the V–O–V axis or by bending of this bridge, these modifications leading to a decrease in symmetry and to a lower electronic interaction.[21]

Comparison with Cation–Cation Complexes of Pentavalent Actinides. A comparison of the properties of the $V_2O_3^{3+}$(aq) complex with those of cation–cation complexes involving MO_2^+ ions of pentavalent actinides is shown in Table III. Although the experimental conditions are not the same for the different complexes discussed, it can nevertheless be noted that they all display low stability.

The thermodynamic characteristics relative to the formation of $V_2O_3^{3+}$(aq) closely approach those of the $NpCrO_2^{4+}$(aq) and $NpRhO_2^{4+}$(aq) complexes, and particularly the values of ΔS are respectively equal to −35.5, −37.5, and −42 J mol^{-1} K^{-1}. This fact supports the identical formation mechanisms of the different complexes. Sullivan[23,24] demonstrated that the formation of the $NpCrO_2^{4+}$(aq) and $NpRhO_2^{4+}$(aq) complexes occurred by the elimination of a water molecule from the $Cr(H_2O)_6^{3+}$ and $Rh(H_2O)_6^{3+}$ ions, respectively, according to a reaction of the type

$$NpO_2^+ + M(H_2O)_6^{3+} \rightleftarrows (NpO_2M(H_2O)_5)^{4+} + H_2O$$

This is similar to the one proposed for the formation of the $V_2O_3^{3+}$(aq) ion (eq 11).

It should also be noted that the $NpCrO_2^{4+}$(aq) and $NpRhO_2^{4+}$(aq) complexes are nonlabile, whereas $V_2O_3^{3+}$(aq) is labile. This can be explained by the slowness (in the cases of $Cr(H_2O)_6^{3+}$ and $Rh(H_2O)_6^{3+}$) or velocity (in the case of $VO(H_2O)_5^{2+}$) of exchange of the water molecule of the coordination site of the "active" cation considered. The similar behavior of these species is also observed with respect to the action of different factors on the formation of the complexes. Hence Rykov et al.[25,26] describe a reinforcement of the stability of the complexes Np(V)–U(VI) with an increase in the concentration of ClO_4^- ions and of Np(V)–Fe(III) on the addition of solvents such as methanol, ethanol, and acetone.

The similarity in the behavior of the pentavalent MO_2^+ ions of vanadium and the actinides is further supported by the identification of an $NpVO_3^+$(aq) complex formed upon addition of neptunium(V) to a concentrated solution of vanadium(IV) ($C_{VO^{2+}}$ = 0.95 M) in 5 N $HClO_4$ medium. The formation of the complex is characterized by a significant decrease in absorbance of the main absorption band of the NpO_2^+(aq) ion (λ = 980 nm) and the appearance of a new band at 988.5 nm, characteristic of the $NpVO_3^{3+}$ complex.

Registry No. $VO_2(H_2O)_4^+$, 81738-79-6; $VO(H_2O)_5^{2+}$, 15391-95-4; V_2O_3(aq), 81768-75-4.

---

(21) A structure in which the bridging oxygen is "trans" in relation to one of the terminal oxygens appears highly improbable. The "trans" position is very weakly bonding, and coordination by this site generally leads to very slightly stable species. In this case, moreover, the electronic interaction would be strictly zero and the spectrum would not display an intervalence band. See: Jeannin, Y.; Launay, J.-P.; Sanchez, C.; Livage, J.; Fournier, M. *Nouv. J. Chim.* **1980**, *4*, 587.

(22) Newton, T. W.; Baker, F. B. *Inorg. Chem.* **1965**, *4*, 1166.

(23) Murmann, R. K.; Sullivan, J. C. *Inorg. Chem.* **1967**, *6*, 892.

(24) Sullivan, J. C. *Inorg. Chem.* **1964**, *3*, 315.

(25) Rykov, A. G.; Frolov, A. A. *Radiokhimiya* **1972**, *15*, 709.

(26) Rykov, A. G.; Frolov, A. A. *Radiokhimiya* **1972**, *14*, 717.