

Niobium Oxide Solution Chemistry

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The solution chemistry of niobium oxide in alkaline and acidic oxalate solutions was investigated by Raman spectroscopy in order to determine the molecular structures of the various aqueous niobium oxide species. The aqueous potassium niobate species were studied as a function of pH from 14.5 to 0.55. Different types of niobium oxide ionic species such as $H_xNb_6O_{19}^{(8-x)-}$ ($x = 0-3$), $Nb_{12}O_{36}^{12-}$ and $Nb_2O_5 \cdot nH_2O$ exist in aqueous solutions, and both the solution pH and niobium oxide concentration determine the different niobium oxide ionic species. The aqueous niobium oxide ionic species are unstable at $pH < 6.5$, and hydrolyze and polymerize to form $Nb_2O_5 \cdot nH_2O$ precipitate. In acidic solutions containing oxalic acid two niobium oxalate ionic species are present, $[NbO(C_2O_4)_2(H_2O)_2]^-$ and $[NbO(C_2O_4)_3]^-$, and the equilibrium between these species is dependent on the solution pH, oxalic acid concentration, niobium concentration and H^+ concentration. The niobium oxalate ionic species are stable in the pH range 0.5-3.0, and also form the $Nb_2O_5 \cdot nH_2O$ precipitate at $pH > 3.0$. This study demonstrates the ability of Raman spectroscopy to determine directly the solution chemistry and molecular structures of niobium oxide species in aqueous solutions.

INTRODUCTION

The aqueous solution chemistry of the oxides of vanadium, molybdenum and tungsten has been studied by modern x-ray crystallographic and nuclear magnetic resonance spectroscopic techniques in order to determine the relationships between structure, bonding and reactivity.^{1,2} The molecular structures of these metal oxides in aqueous solutions depend on the solution pH and metal oxide concentration.^{2,3} In general, the small ionic species VO_4^{3-} , MoO_4^{2-} and WO_4^{2-} are present in aqueous solutions in the most basic environment and at dilute concentrations. The small metal ionic species start to hydrolyze and polymerize to form larger ionic species ($V_{10}O_{28}^{8-}$, $Mo_7O_{24}^{6-}$ and $W_{12}O_{39}^{9-}$) at moderate acidities and metal oxide concentrations.³ The nature of the niobium oxide species in aqueous solutions has not received as much attention as the corresponding oxides of vanadium, molybdenum and tungsten because of the difficulty in preparing pure, stable niobium ionic species in aqueous solutions and the inability to obtain good ^{93}Nb NMR data. No magnetic resonances have yet been observed for ^{93}Nb in the solid state or solutions owing to the excessive line widths which result from the large quadrupole coupling constant.¹

Nb^{5+} complexes can exist in both alkaline and acidic solutions owing to the amphoteric character of niobium oxide. These complexes also exhibit an unusually pronounced tendency to hydrolyze owing to their low stability in aqueous solutions and high affinity for oxygen ligands. Consequently, niobium oxide aqueous solutions tend to polymerize into a colloidal state. The alkali metal niobates in aqueous solutions contain the hexaniobate ionic species, $[H_xNb_6O_{19}]^{(8-x)-}$ ($x = 0-3$), at a solution $pH > 7$. Raman spectroscopy^{4,5} and ^{17}O nuclear magnetic resonance⁶ studies suggest that the

hexaniobate ionic species consists of three types of Nb—O bonds: six Nb=O terminal bonds, twelve Nb—O—Nb bridging bonds and one Nb_6O sixfold bridging bond. The hexaniobate ionic species, $Nb_6O_{19}^{8-}$, starts to degrade into tetrameric, $Nb_4O_{16}^{12-}$, and monomeric, $NbO_2(OH)_4^{3-}$, species in very basic solutions ($pH \approx 14$).^{7,8} The alkali metal niobates in aqueous solutions form a hydrated Nb_2O_5 precipitate at a solution $pH < 7.9$.⁹ Hence the presence of various niobate ionic species in aqueous solutions primarily depends on the solution pH and the coordination number of the Nb atom appears to be 6 for the soluble niobium oxide ionic species. The tetrahedral NbO_4^{3-} species does not exist in aqueous solutions owing to the high electronegativity of niobium and the relatively small size of the oxygen ligands.¹⁰

Acidic solutions of niobium oxide are prepared by reacting the hydrated niobium oxide with an oxalic acid aqueous solution. The presence of oxalic acid stabilizes the niobium oxide in aqueous solutions by forming niobium oxalate ionic species such as $NbO(C_2O_4)_3^{3-}$, $NbO(C_2O_4)_2(H_2O)_2^-$ and $NbO(C_2O_4)(OH)_2(H_2O)_2^-$.^{9,11} For the niobium oxalate species in aqueous solutions, $NbO(C_2O_4)_3^{3-}$ and $NbO(C_2O_4)_2(H_2O)_2^-$, the coordination number of the Nb atom appears to be 7.¹⁰ Mechanisms for the hydrolysis and polymerization of the niobium oxide ionic species in aqueous solutions have been proposed.^{9,12-14} However, no studies have been performed to determine the chemistry and structure of the niobium oxalate ionic species in acidic aqueous solutions.

Raman spectroscopy is a very powerful technique for determining the molecular structures of metal oxides, not only in the solid state but also in aqueous solutions because of the weak Raman scattering of water. It can discriminate between different types of metal—oxygen bonds such as Nb=O ($850-1000\text{ cm}^{-1}$), Nb—O ($500-700\text{ cm}^{-1}$) and Nb—O—Nb ($200-300\text{ cm}^{-1}$). In this study, aqueous potassium niobate solutions were inves-

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tigated by Raman spectroscopy to determine the molecular structures of the niobium oxide ionic species in alkaline solutions, particularly in the pH range 0.55–6.50 where very few data are available. The chemistry and structure of niobium oxalate in acidic solutions were also studied by Raman spectroscopy as a function of the solution pH, the oxalic acid concentration, the niobium concentration and the H^+ concentration. The aqueous solution chemistry of niobium oxide needs to be understood better in order to determine the molecular structures of the surface niobium oxide phases on oxide supports under ambient conditions where the surfaces are hydrated.

EXPERIMENTAL

Materials and preparations

Potassium niobate, $K_8Nb_6O_{19} \cdot xH_2O$, was obtained from Pfaltz & Bauer (Waterbury, CT). Niobium oxalate, $Nb(HC_2O_4)_5$, was provided by Niobium Products Company (Pittsburgh, PA) with the chemical analysis of 20.5% Nb_2O_5 , 790 ppm Fe, 680 ppm Si and 0.1% insoluble solid. Oxalic acid, potassium chloride, potassium hydroxide, nitric acid and hydrochloric acid were obtained from Fisher Scientific (Fair Lawn, NJ) with a minimum purity of 99.9%. Ammonia solution was purchased from J. T. Baker Chemical (Phillipsburg, NJ).

The alkaline solutions were prepared as follows: 0.5 g of potassium niobate was dissolved in 10 M potassium hydroxide solution and the pH of solution was varied from 14.5 to 0.5 by adding hydrochloric acid. The pH of the resulting solution was measured with a Beckman Φ 34 pH meter (Model 123141) and a Beckman combination electrode (Model 39838). The pH of the initial aqueous potassium niobate solution was found to be 14.5. The acidic solutions were prepared as follows: 3 g niobium oxalate were dissolved in 1.2 M oxalic acid solution and the pH of the solution was varied from 0.50 to 5.00 by the addition of ammonia solution.

Raman spectroscopy

Raman spectroscopic measurements were obtained with a Spex Triplemate spectrometer (Model 1877) couple to an EG&G intensified photodiode-array detector, cooled thermoelectrically to $-35^\circ C$, and interfaced with an EG&G OMA III optical multi-channel analyzer (Model 1463). The liquid sample was placed in a 0.8–1.10 \times 90 mm capillary tube (Kimax-51) and excited by the 514.5-nm line of an Ar^+ laser with 100-mW power. The laser beam was focused on the sample illuminator, where the capillary tube was held by a V-shaped cell mount in the liquid sample holder. The indirect scattered laser beam and the Raman scattering were reflected into the spectrometer by a 90° angle with the incident light. The scattered Raman light was collected by the spectrometer at room temperature and analyzed with an OMA III software package. The overall spectral resolution of the spectra was determined to be better than 2 cm^{-1} .

RESULTS

Niobium oxide in alkaline solutions

The Raman spectra of aqueous potassium niobate solutions in the pH range 14.5–0.55 are shown in Fig. 1. At high pH (ca. 14.5), the potassium niobate solution possesses Raman bands at ca. 1060, 865, 815, 520, 290 and 230 cm^{-1} . On decreasing the pH to 11.50 by adding hydrochloric acid, the major Raman band at ca. 865 cm^{-1} shifts to ca. 880 cm^{-1} , the Raman band at ca. 290 cm^{-1} decreases in intensity and an additional Raman band appears at ca. 380 cm^{-1} . A further decreasing in the pH of the solution to 6.5 causes the Raman band at ca. 880 cm^{-1} to shift to ca. 901 cm^{-1} , the Raman bands at ca. 520 and 290 cm^{-1} to disappear completely and an additional Raman band at ca. 480 cm^{-1} to appear. At low pH (<3.65), the Raman band at ca. 630 cm^{-1} becomes dominant and the Raman band at ca. 901 cm^{-1} becomes broad and weak. The aqueous potassium niobate solution prepared at pH 0.55 was further evacuated at $120^\circ C$ to remove the excess of water, and the resulting precipitate possessed Raman bands at ca. 900, 650 and 250 cm^{-1} , which are similar to those for $Nb_2O_5 \cdot nH_2O$.¹⁵

Niobium oxide in acidic oxalate solutions

Niobium oxalate solubility. The solubility of niobium oxalate in aqueous solutions is low, but it can be dramatically increased by the addition of oxalic acid. The solubility curve of niobium oxalate in aqueous solutions is shown in Fig. 2 as a function of oxalic acid concentration. At high oxalic acid concentrations, however, the niobium oxalate and oxalic acid precipitate from solution.

Solution pH. A series of Raman spectra of niobium oxalate in aqueous oxalic acid solutions are shown in Fig. 3. The solution pH was varied from 0.50 to 5.00 by the addition of ammonia solution. At low pH (0.50), the niobium oxalate aqueous solution possesses Raman bands at ca. 940 and 920 cm^{-1} in the high-wavenumber

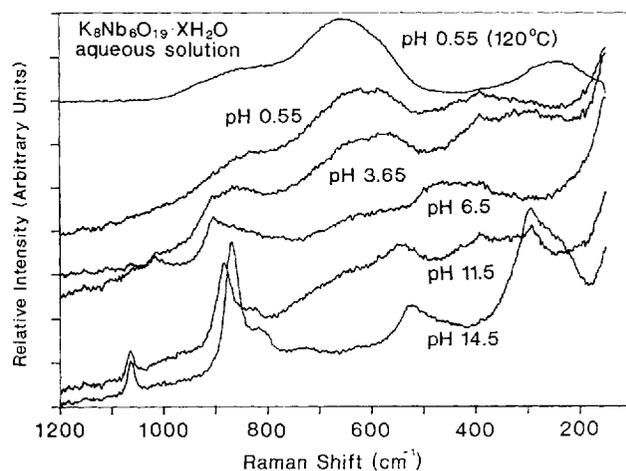


Figure 1. Raman spectrum of $K_8Nb_6O_{19} \cdot xH_2O$ in 10 M KOH aqueous solution as a function of pH.

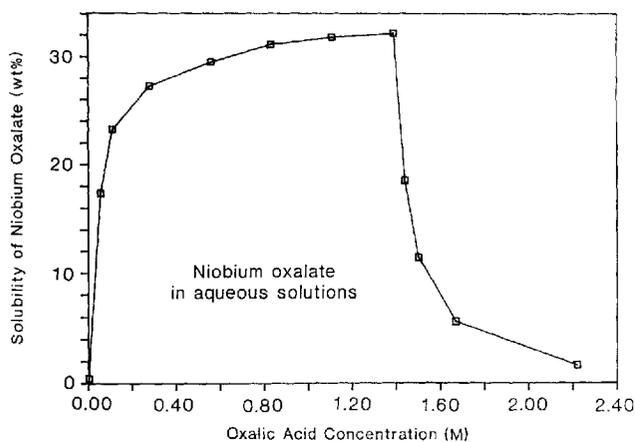


Figure 2. Solubility of niobium oxalate in aqueous oxalic acid solutions.

region ($900\text{--}1000\text{ cm}^{-1}$), which are characteristic of $\text{Nb}=\text{O}$ terminal stretching modes.¹¹ After the addition of ammonia solution to increase the pH to 3.00, the Raman bands at *ca.* 940 and 920 cm^{-1} shift to *ca.* 932 and 914 cm^{-1} , respectively, and their relative intensities change. In the intermediate wavenumber region ($500\text{--}800\text{ cm}^{-1}$), Raman bands are present at *ca.* 570 , 545 and 522 cm^{-1} . In the low-wavenumber region ($200\text{--}400\text{ cm}^{-1}$), the relative intensities of the *ca.* 305 and 275 cm^{-1} Raman bands also change with increasing solution pH. The Raman bands at *ca.* 845 and 460 cm^{-1} are due to the vibrational modes of the free $\text{C}_2\text{O}_4^{2-}$ ionic species in aqueous solutions (see Fig. 4). At high pH (>5.00), two additional Raman bands appear at *ca.* 675 and 230 cm^{-1} which are characteristic of hydrated niobium oxide.¹⁵

Oxalic acid concentration. The Raman spectra of niobium oxalate in aqueous solutions with different oxalic acid concentrations are shown in Fig. 5. The Raman bands at *ca.* 940 and 920 cm^{-1} are characteristic of $\text{Nb}=\text{O}$ terminal stretching modes, and their relative intensities change with increasing $\text{C}_2\text{O}_4^{2-}$ concentration. The intensity of the $\text{C}_2\text{O}_4^{2-}$ Raman bands at *ca.* 845 and 460 cm^{-1} increases with increasing $\text{C}_2\text{O}_4^{2-}$ concentration, as expected (see Fig. 4). In the intermediate region ($500\text{--}800\text{ cm}^{-1}$), weak Raman bands appear at *ca.* 795 , 569 , 545 and 517 cm^{-1} , and the intensity of *ca.* 517 cm^{-1} Raman band increases with increasing $\text{C}_2\text{O}_4^{2-}$ concen-

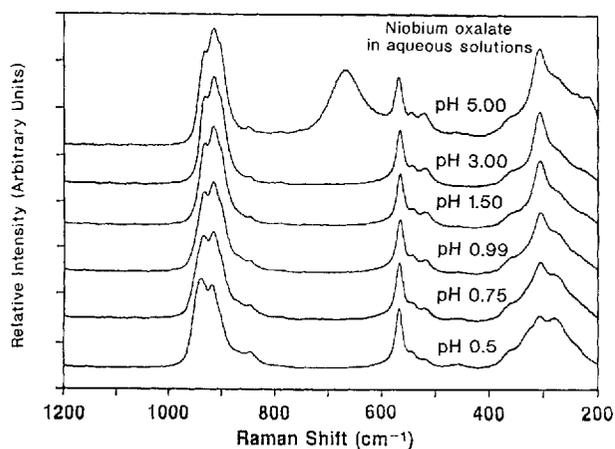


Figure 3. Raman spectra of niobium oxalate in aqueous solutions as a function of solution pH.

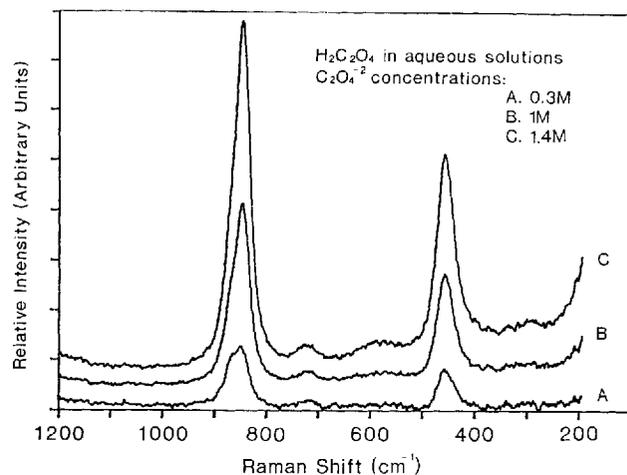


Figure 4. Raman spectra of the aqueous oxalic acid solutions. A, 0.3; B, 1.0; C, 1.4 M $\text{C}_2\text{O}_4^{2-}$.

tration. In the low-wavenumber region ($200\text{--}400\text{ cm}^{-1}$), Raman bands are present at *ca.* 365 , 325 , 305 and 275 cm^{-1} , and their relative intensities also change with increasing $\text{C}_2\text{O}_4^{2-}$ concentration.

Nb concentration. The Raman spectra of niobium oxalate aqueous solutions with different Nb concentrations are shown in Fig. 6. At low Nb concentration (0.08 M), Raman bands appear at *ca.* 932 and 918 cm^{-1} , which are characteristic of $\text{Nb}=\text{O}$ terminal stretching modes and the Raman bands at *ca.* 845 and 460 cm^{-1} are due to the free $\text{C}_2\text{O}_4^{2-}$ ionic species. On increasing the Nb concentration in the aqueous solution, the Raman band at *ca.* 932 cm^{-1} shifts to *ca.* 943 cm^{-1} , and the relative intensities of two $\text{Nb}=\text{O}$ terminal bands at *ca.* 940 and 918 cm^{-1} change. In the intermediate region ($500\text{--}800\text{ cm}^{-1}$), Raman bands appear at *ca.* 795 , 569 , 545 and 517 cm^{-1} . In the low-wavenumber region ($200\text{--}400\text{ cm}^{-1}$), Raman bands are present at *ca.* 365 , 325 , 305 and 275 cm^{-1} , and their relative intensities also change. At high Nb concentration ($>0.7\text{ M}$), an additional broad and weak Raman band appears at *ca.* 870 cm^{-1} .

H^+ concentration. The Raman spectra of niobium oxalate in aqueous solutions with different H^+ concentrations

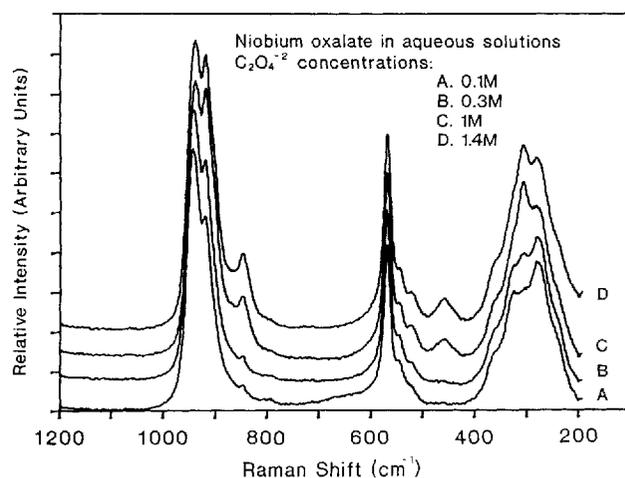


Figure 5. Raman spectra of niobium oxalate in aqueous solutions as a function of $\text{C}_2\text{O}_4^{2-}$ concentration. A, 0.1; B, 0.3; C, 1.0; D, 1.4 M $\text{C}_2\text{O}_4^{2-}$.

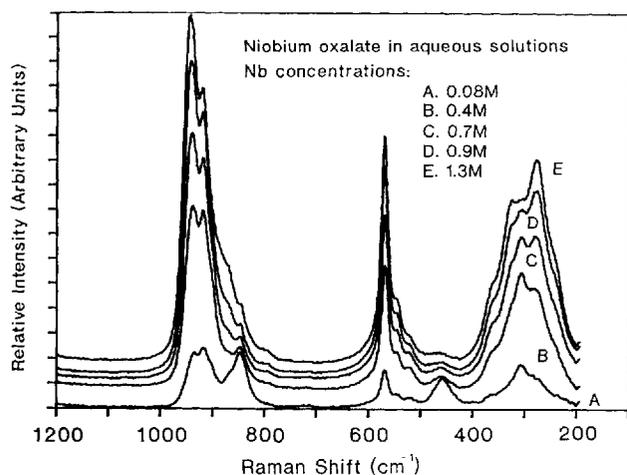


Figure 6. Raman spectra of niobium oxalate in aqueous solutions as a function of Nb concentration. A, 0.08; B, 0.4; C, 0.7; D, 0.9; E, 1.3 M Nb.

are shown in Fig. 7. The H^+ concentrations were determined by the addition of nitric acid to the aqueous solution. The Raman bands at *ca.* 1045 and 715 cm^{-1} are due to the free NO_3^- ionic species,¹⁶ and those at *ca.* 847 and 460 cm^{-1} are due to the free $C_2O_4^{2-}$ ionic species. The relative intensities of the two Nb=O terminal bands at *ca.* 941 and 919 cm^{-1} change with increasing H^+ concentration. In the intermediate region (500–800 cm^{-1}), Raman bands appear at *ca.* 795, 569, 545 and 517 cm^{-1} , and the intensity of the *ca.* 517 cm^{-1} Raman band decreases with increasing H^+ concentration. In the low-wavenumber region (200–400 cm^{-1}), Raman bands are present at *ca.* 365, 325, 305 and 275 cm^{-1} , and their relative intensities also change with increasing H^+ concentration.

DISCUSSION

Raman studies of the aqueous potassium niobate solution at pH 14.5 (see Fig. 1) and the corresponding $K_8Nb_6O_{19}$ crystalline solid⁵ suggest that the $Nb_6O_{19}^{8-}$ ionic species in the liquid and solid states possess similar structures. The presence of $Nb_6O_{19}^{8-}$ ionic species in the aqueous potassium niobate solution was also concluded from light-scattering,¹⁷ ultracentrifugation^{18,19} and potentiometric measurements.²⁰ In the high-wavenumber region (800–1200 cm^{-1}), a strong and sharp Raman band at *ca.* 865 cm^{-1} for the aqueous $Nb_6O_{19}^{8-}$ ionic species indicates that unequal Nb=O bond lengths do not exist in the aqueous $Nb_6O_{19}^{8-}$ structure. The Raman band appearing at *ca.* 1060 cm^{-1} is due to the vibrational mode of KOH.¹⁶ In the intermediate wavenumber region (400–800 cm^{-1}), the Raman band appearing at *ca.* 810 cm^{-1} is characteristic of the Nb=O antisymmetric stretching mode and the Raman bands at *ca.* 735 and 520 cm^{-1} are characteristic of the Nb–O–Nb antisymmetric and symmetric stretching modes, respectively. In the low-wavenumber region (200–400 cm^{-1}), Raman bands appearing at *ca.* 290 and 240 cm^{-1} are due to the Nb–O (central oxygen) stretching mode and the Nb–O–Nb bending mode, respectively. The existence of the Raman band at *ca.* 290 cm^{-1} indicates that the $Nb_6O_{19}^{8-}$ structure is still retained at a solution pH of 14.5.

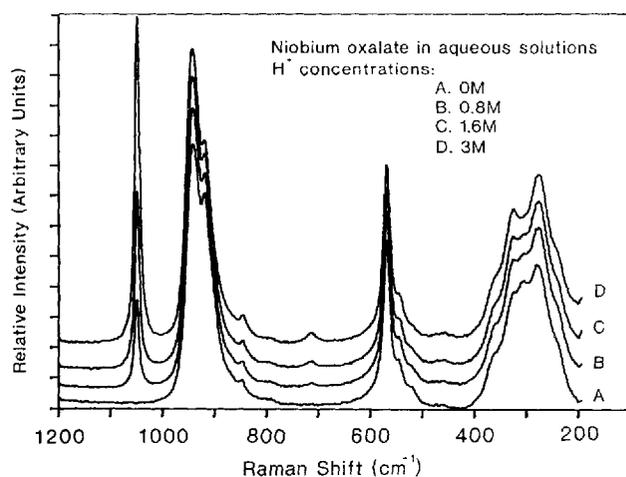


Figure 7. Raman spectra of niobium oxalate in aqueous solutions as a function of H^+ concentration. A, 0; B, 0.8; C, 1.6; D, 3 M H^+ .

On decreasing the solution pH to 11.5, the equilibria between $Nb_6O_{19}^{8-}$, hexaniobate ionic species and $H_xNb_6O_{19}^{(8-x)-}$ ($x = 1-3$), protonated hexaniobate ionic species, exist in aqueous solutions.²¹ The Raman band at *ca.* 865 cm^{-1} shifts to *ca.* 880 cm^{-1} owing to an increase in the Nb=O bond order resulting from protonation of the $Nb_6O_{19}^{8-}$ species with decreasing solution pH. This is consistent with Griffith and Lesniak's results²² that the V=O Raman band of aqueous $V_{10}O_{28}^{6-}$ species increases by about 15 cm^{-1} owing to the increased distortion of the $V_{10}O_{28}^{6-}$ structure with decreasing solution pH.

A further decrease in the solution pH to 6.5 causes the major Raman band to shift to *ca.* 901 cm^{-1} owing to the formation of a polymeric $Nb_{12}O_{36}^{12-}$ species in the aqueous solution.²¹ The Raman band at *ca.* 290 cm^{-1} disappears for the aqueous potassium niobate solution at pH 6.5, indicating that the aqueous $H_xNb_6O_{19}^{(8-x)-}$ ($x = 0-3$) species are not present at a solution pH of 6.5 and below. An additional Raman band appears at *ca.* 480 cm^{-1} which is assigned to the symmetric stretching of Nb–O–Nb bridging bonds in the polymeric $Nb_{12}O_{36}^{12-}$ species. The Raman band at *ca.* 630 cm^{-1} becomes dominant at a solution pH of 3.65 and below owing to the formation of a hydrated Nb_2O_5 precipitate which is similar to $Nb_2O_5 \cdot nH_2O$.¹⁵ The Raman band at *ca.* 901 cm^{-1} also becomes broad and weak on further decreasing the solution pH below 6.5 and indicates that hydrolysis and polymerization of the Nb=O bonds occur extensively at pH < 6.5. After evacuating the aqueous potassium niobate solution (pH 0.55) at 120 °C, the hydrated Nb_2O_5 precipitate possesses broad Raman bands at *ca.* 900 (very weak), 650 (strong) and 250 cm^{-1} (medium), characteristic of $Nb_2O_5 \cdot nH_2O$.

Hence the aqueous potassium niobate species are stabilized in the pH range 6.5–14.5, and start to form a hydrated Nb_2O_5 precipitate at pH \approx 6.5 and below. The relationships between the aqueous potassium niobate species and the corresponding Raman bands over the entire pH range are shown in Table 1. At high pH (>6.5), the aqueous potassium niobate species possess their major Raman band in the 850–1000 cm^{-1} region owing to the presence of Nb=O bonds. At low

Table 1. Aqueous potassium niobate species and Raman bands in the pH range 14.5–0.55

Solution pH	Species	Raman bands (cm ⁻¹)
14.4	Nb ₆ O ₁₉ ⁸⁻	865 (s), 815 (w), 730 (w), 520 (m), 290 (s), 230 (w)
11.5	H _x Nb ₆ O ₁₉ ^{(8-x)-} (x = 1, 2, 3)	880 (s), 820 (w), 520 (m), 420 (w), 290 (w)
6.5	Nb ₁₂ O ₃₆ ¹²⁻	901 (s), 480 (m), 420 (w),
	Nb ₂ O ₅ · nH ₂ O	880 (vw), 630 (w)
3.65	Nb ₁₂ O ₃₆ ¹²⁻	901 (w), 420 (w)
	Nb ₂ O ₅ · nH ₂ O	880 (w), 630 (m), 280 (w)
0.55	Nb ₂ O ₅ · nH ₂ O	880 (w), 630 (s), 420 (w), 280 (w)

pH (<6.5), the major Raman band shifts from 850–1000 to *ca.* 630 cm⁻¹, indicating that Nb–O bonds form in the structures owing to hydrolysis and polymerization of the aqueous potassium niobate species. The solution chemistry of potassium niobate at pH > 6.5 is in agreement with prior Raman studies in which the presence of different niobate ionic species in aqueous solutions was found to depend on the solution pH and the NbO₂(OH)₄³⁻ monomer only exists in very basic and dilute solutions.²²

Niobium oxide complexes can also dissolve in oxalic acid aqueous solutions and form stable niobium oxide ionic species containing one, two or three oxalate groups.^{10,23,24} The equilibria between these niobium oxide ionic species depend on the solution pH, the oxalic acid concentration and the Nb concentration. The presence of oxalic acid in the aqueous solutions has a pronounced effect on the niobium oxalate solubility (see Fig. 2) because the oxalic acid concentration controls the formation of the stable aqueous niobium oxide ionic species. For oxalic acid concentrations less than 0.4 M, the free oxalate ionic species break the Nb–O–Nb linkages and chelates to the Nb atom to form isolated niobium oxide ionic species with a 3:1 and 2:1 coordinated oxalate to Nb ratio in the aqueous solutions. The chelating effect is stronger for the 3:1 than for the 2:1 complex owing to the high electronegativity of the C₂O₄²⁻ ligands,^{25–27} and results in an increase in the niobium oxalate solubility in aqueous solutions. For oxalic acid concentrations between 0.4 and 1.4 M, the niobium oxalate solubility curve starts to level off and reaches its saturation point. For oxalic acid concentrations greater than 1.4 M, the niobium oxalate solubility decreases to its initial low value because the total concentration of the C₂O₄²⁻ species (free and chelated) reaches its solubility limit.

The crystal structure of niobium oxalate complexes was determined from x-ray diffraction data to consist of either [NbO(OH)(C₂O₄)₂H₂O] or [NbO(C₂O₄)₃] units and water molecules connected by hydrogen bonds.^{28–31} The [NbO(OH)(C₂O₄)₂H₂O] unit has a pentagonal bipyramidal structure with a short Nb=O terminal double bond and a long Nb–OH₂ bond nearly perpendicular to the pentagonal equatorial plane which consists of two bidentate oxalate ligands and a hydroxyl group. The [NbO(C₂O₄)₃] unit also has a pentagonal bipyramidal structure with a short Nb=O terminal double bond and three bidentate oxalate ligands coordinated to the pentagonal equatorial plane.

The Na[NbO(C₂O₄)₂H₂O] · 4H₂O, the 2:1 complex and Na₃[NbO(C₂O₄)₃] · 4H₂O, the 3:1 complex, crystal structures were investigated by Muller *et al.*

using Raman and IR spectroscopy.¹¹ The 2:1 and 3:1 complexes exhibit strong, sharp Raman bands at *ca.* 960 and 940 cm⁻¹, respectively, in addition to a weak Raman band at *ca.* 930 cm⁻¹, which are characteristic of Nb=O bonds. For the 2:1 complex, the Raman bands at *ca.* 570 and 545 cm⁻¹ arise from the two bidentate oxalate ligands coordinated to the Nb atom and are characteristic of the stretching modes of the Nb–O₂–C₂ bridging bonds. For the 3:1 complex, the Raman bands at *ca.* 575 and 525 cm⁻¹ arise from the three bidentate oxalate ligands coordinated to the Nb atom and are characteristic of the stretching modes of the Nb–O₂–C₂ bridging bonds. The 2:1 complex also possesses a Raman band at *ca.* 290 cm⁻¹ which is characteristic of the Nb–OH₂ stretching mode and, as expected, this Raman band is not observed for the 3:1 complex.

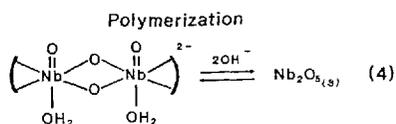
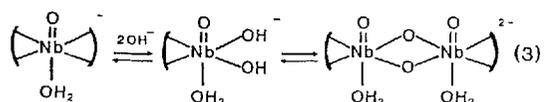
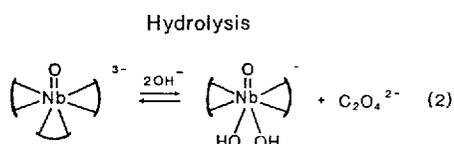
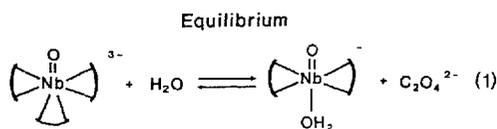
The Raman spectrum of the solid niobium oxalate complex, Nb(HC₂O₄)₅,¹⁵ employed in this study possesses Raman bands at *ca.* 960, 930, 575, 550 and 285 cm⁻¹. This suggests that the structure of the niobium oxalate complex possesses the same [NbO(C₂O₄)₂H₂O] unit as that of the Na[NbO(C₂O₄)₂H₂O] · 4H₂O complex because of their similar Raman spectra. On dissolving the niobium oxalate complex in aqueous solution, two Nb=O terminal bonds appear in the aqueous Raman spectra (see Fig. 3), indicating that two niobium oxalate ionic species, [NbO(C₂O₄)₂H₂O] (Nb=O band at *ca.* 940 cm⁻¹) and [NbO(C₂O₄)₃] (Nb=O band at *ca.* 920 cm⁻¹), coexist in the solution. The two aqueous niobium oxalate ionic species exhibit their Nb=O Raman bands about 20 cm⁻¹ lower than found in the solid state because hydrogen bonding in the aqueous environment decreases the Nb=O bond order.

The Raman spectra also reveal that the relative intensities of two Nb=O bands at *ca.* 940 and 920 cm⁻¹ change with increasing pH (see Fig. 3) owing to the shift of the equilibrium point between these two aqueous niobium oxalate ionic species on addition of ammonia to the solution. The hydrolysis of [NbO(C₂O₄)₃] ionic species occurs as one of the oxalate groups is replaced with OH groups, and forms the [NbO(C₂O₄)₂(OH)₂] ionic species. The change in the relative intensities of two Raman bands at *ca.* 275 and 305 cm⁻¹, which are assigned to the bending modes of the two Nb=O terminal bonds, *ca.* 940 and 920 cm⁻¹, respectively, also suggests that the [NbO(C₂O₄)₃] ionic species tend to hydrolyze at higher pH. Similarly, the [NbO(C₂O₄)₂H₂O] ionic species tend to hydrolyze at higher pH.

On increasing the solution pH to 3.00 by further

addition of ammonia, a very weak Raman band appearing at *ca.* 900 cm^{-1} increases in intensity, suggesting the formation of an additional niobium ionic species in the aqueous solution. This is consistent with Muller and Dehand's IR studies,¹¹ which showed that a dimeric $[\text{Nb}_2\text{O}_4(\text{OH})_2(\text{C}_2\text{O}_4)_2]$ ionic species is present and possesses IR bands at *ca.* 890 and 630 cm^{-1} due to $\text{Nb}=\text{O}$ and $\text{Nb}-\text{O}-\text{Nb}$ bonds, respectively. The equilibria between these niobium oxalate ionic species are reached because of the absence of changes in the relative Raman intensity in the 900–1000 cm^{-1} region. The increase in Raman intensity at *ca.* 520 cm^{-1} with increasing pH is due to the formation of $\text{Nb}-\text{O}-\text{Nb}$ bonds in the aqueous niobium oxalate species. This is also consistent with the conclusion that the dimeric $[\text{Nb}_2\text{O}_4(\text{OH})_2(\text{C}_2\text{O}_4)_2]$ ionic species is present in the aqueous solution. At $\text{pH} > 3.00$, the addition of ammonia causes the dimeric $[\text{Nb}_2\text{O}_4(\text{OH})_2(\text{C}_2\text{O}_4)_2]$ ionic species to hydrolyze and coagulate to a hydrated Nb_2O_5 precipitate possessing Raman bands at *ca.* 675 and 230 cm^{-1} , which is similar to those for TT- Nb_2O_5 possessing a pseudohexagonal unit cell.¹⁵

The aqueous solution chemistry of niobium oxalate is proposed to be as shown in Eqns (1)–(4).

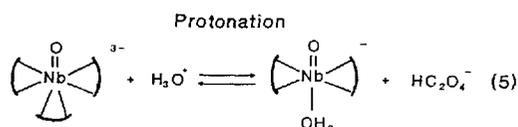


Equation (1) is the equilibrium between the $[\text{NbO}(\text{C}_2\text{O}_4)_2\text{H}_2\text{O}]$ and $[\text{NbO}(\text{C}_2\text{O}_4)_3]$ ionic species, Eqns (2) and (3) are the hydrolysis of these two ionic species to form the dimeric $[\text{Nb}_2\text{O}_4(\text{OH})_2(\text{C}_2\text{O}_4)_2]$ ionic species on addition of ammonia and Eqn (4) is the polymerization of the dimeric $[\text{Nb}_2\text{O}_4(\text{OH})_2(\text{C}_2\text{O}_4)_2]$ ionic species to form a hydrated Nb_2O_5 precipitate on further addition of ammonia.

The equilibrium between the $[\text{NbO}(\text{C}_2\text{O}_4)_2\text{H}_2\text{O}]$ and $[\text{NbO}(\text{C}_2\text{O}_4)_3]$ ionic species [see Eqn (1)] is determined by the $\text{C}_2\text{O}_4^{2-}$ concentration in the aqueous niobium oxalate solutions. At low $\text{C}_2\text{O}_4^{2-}$ concentrations (< 0.1 M), the equilibrium is driven to the right-hand side of

the Eqn (1) and the $[\text{NbO}(\text{C}_2\text{O}_4)_2\text{H}_2\text{O}]$ ionic species, Raman band at *ca.* 940 cm^{-1} (see Fig. 5), is the dominant species in the aqueous niobium oxalate solutions. On increasing the $\text{C}_2\text{O}_4^{2-}$ concentration, the equilibrium is driven in the other direction, and an increase in the $[\text{NbO}(\text{C}_2\text{O}_4)_3]$ ionic species, Raman band at *ca.* 920 cm^{-1} , occurs in the aqueous niobium oxalate solutions. The relative intensities of the two niobium oxalate ionic species, $[\text{NbO}(\text{C}_2\text{O}_4)_2\text{H}_2\text{O}]$ and $[\text{NbO}(\text{C}_2\text{O}_4)_3]$, also change with Nb concentration (see Fig. 6). At low Nb concentration (< 0.08 M), the two niobium oxalate ionic species possess similar Raman intensities in the aqueous niobium oxalate solutions. On increasing the Nb concentration, however, the intensity of the $[\text{NbO}(\text{C}_2\text{O}_4)_2\text{H}_2\text{O}]$ ionic species starts to increase. The Nb concentration and the $\text{C}_2\text{O}_4^{2-}$ concentration have an opposite effect on the equilibrium of the aqueous niobium oxalate ionic species.

The relative intensities of the two niobium oxalate ionic species, $[\text{NbO}(\text{C}_2\text{O}_4)_2\text{H}_2\text{O}]$ and $[\text{NbO}(\text{C}_2\text{O}_4)_3]$, also change with the H^+ concentration in the aqueous solution (see Fig. 7). The $[\text{NbO}(\text{C}_2\text{O}_4)_3]$ ionic species in aqueous niobium oxalate solutions reacts with H^+ to form the $[\text{NbO}(\text{C}_2\text{O}_4)_2\text{H}_2\text{O}]$ ionic species as follows:⁹



At high H^+ concentration, the $[\text{NbO}(\text{C}_2\text{O}_4)_2\text{H}_2\text{O}]$ ionic species becomes slightly more dominant in the aqueous niobium oxalate solutions.

This study has demonstrated the ability of Raman spectroscopy to monitor directly the niobium oxide species present in aqueous solutions. Consequently, Raman spectroscopy allows the determination of the various niobium oxide molecular structures present in solution and their aqueous solution chemistry. This aspect of Raman spectroscopy was used to study the niobium oxide solution chemistry in both alkaline and acidic aqueous solutions. In acidic oxalate solutions, the niobium oxalate solution chemistry was shown to depend on the solution pH, oxalic acid concentration, Nb concentration and H^+ concentration.

CONCLUSIONS

Niobium oxide complexes can exist in both alkaline and acidic oxalate solutions. In alkaline solutions, niobium oxide contains different types of niobium oxide ionic species such as $\text{H}_x\text{Nb}_6\text{O}_{19}^{(8-x)-}$ ($x = 0-3$) and $\text{Nb}_{12}\text{O}_{36}^{12-}$ polymer. The presence of the different niobium oxide ionic species is dependent on the solution pH. At high pH (*ca.* 14.5), the hexaniobate ionic species $\text{Nb}_6\text{O}_{19}^{8-}$ exists in aqueous solutions. In the pH range 11.5–14.5, equilibria between the $\text{Nb}_6\text{O}_{19}^{8-}$ and $\text{H}_x\text{Nb}_6\text{O}_{19}^{(8-x)-}$ ($x = 1-3$) hexaniobate ionic species exist in aqueous solutions. At low pH (< 6.5), the hexaniobate ionic species starts to polymerize to form $\text{Nb}_{12}\text{O}_{36}^{12-}$ species, and further forms a hydrated Nb_2O_5 precipitate. In acidic oxalate solutions, niobium oxide contains two niobium oxalate ionic species, $[\text{NbO}(\text{C}_2\text{O}_4)_2\text{H}_2\text{O}]$ and

[$\text{NbO}(\text{C}_2\text{O}_4)_3$], and the equilibria between these species are dependent on the solution pH, oxalic acid concentration, Nb concentration and H^+ concentration. The niobium oxalate ionic species is stable in the pH range 0.5–3.0 and forms a hydrated Nb_2O_5 precipitate at $\text{pH} > 3.0$. This study has demonstrated the ability of Raman spectroscopy to determine directly the solution

chemistry and molecular structures of niobium oxide species in aqueous solutions.

Acknowledgement

Financial support for this work by Niobium Products Company is gratefully acknowledged.

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