STUDIES ON FORMATION OF CHROMIUM NIOBATES

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Studies on formation of chromium niobates. The precise nature of the reaction between chromium chloride and potassium niobate at specific pH levels 12.0, 10.8 and 7.6 has been studied by means of electrometric techniques involving pH and conductometric titrations. The well defined breaks and inflections in the titration curves provide cogent evidence for the formation and precipitation of chromium *ortho*-$Cr_2O_3.3Nb_2O_5$, *hexa*-$4Cr_2O_3.9Nb_2O_5$ and *meta*-$Cr_2O_3.3Nb_2O_5$ niobates in the vicinity of pH 7.5, 6.8 and 5.6, respectively. Analytical investigations of the precipitates have also been carried out which substantiate the results of the electrometric study.

Keywords: niobates; chromium niobates; electrometry.

INTRODUCTION

An outstanding character of niobates is their strong tendency to form condensed ions in solutions[1,2] and from these polyniobates crystallize, depending upon the H^+ concentration which plays an important role on the aggregation process. It has been reported[3] that sodium ortho-niobate, Na_3NbO_4, dissolves in water giving a strongly alkaline solution due to its hydrolysis to form $Nb_6O_{19}^{8-}$ which upon decreasing the pH may successively change to $HNb_6O_{19}^{7-}$ and $(Nb_6O_{18}^{6-})n$. The value of about 3 for *n*, has been suggested but Conard and Land[4] concluded that the value of *n* should be about 6. A large number of niobates with conflicting reports have been described[5] in which the ratio of alkali metal to acid (M_2O/Nb_2O_5) is given variously as 5/1, 4/1, 3/1, 2/1, 16/5, 3/2, 4/3, 4/5, 1/1, 6/7, 3/4, 2/3, 1/2, 1/3, and 1/4. There is no doubt, however, that the study of niobates is complicated by the fact that many of the hydrated salts do not exist in anhydrous state, nor do they form congruently saturated solutions, while in both anhydrous and hydrated systems, metastability and slowness to attain equilibrium contribute to the variability of composition. Some of these compounds have ferroelectric and piezoelectric properties and have been found to be attractive alternatives to quartz as *frequency filters* in communications devices. A number of nonstoichiometric *bronzes* are also known[6] which like tungsten bronzes, are characterized by high electrical conductivity and characteristic colors.

There has also been a rapid increase in recent years in the use of niobium in steel industry. Small amounts of niobium markedly increase the yield strength of mild steel plates and prevent weld decay and intergranular corrosion in stainless steel[7]. In addition to its continued use in the production of chrome and stainless steel, it is now being used as a component for nonferrous superalloys, generally nickel-based[8,9], which have been developed for the manufacture of jet engines, turbines, and missiles. It has also been found that certain niobium alloys, especially with tin and zirconium, become superconducting at easily available temperatures, and retain their superconductivity in magnetic fields[10,11]. Some work has appeared on the electrodeposition of niobium alloys using niobate solutions in baths[12,13]. The literature surveyed clearly reflects the usefulness of niobium alloys in imparting specific properties, but almost no electrolytic bath has been developed until now which can deposit an alloy of good quality of some commercial value. Adequate control of the baths and complicated chemistry of niobates seem to be the main sources of the problem.

Niobium compounds are also employed as catalyst in many reactions (dehydrogenation, oxidation-reduction, etc) of industrial importance. Recently, interest in dehydrogenation processes has increased due to high demand for production of oxygenated compounds in reformulated gasoline and C_9-C_{14} mono-olefines to obtain biodegradable detergents[14,15] . The catalysts Pt/Nb_2O_5 and $Pt\text{-}Sn/Nb_2O_5$ have been reported to be excellent and highly selective catalysts in dehydrogenation reactions[16-18]. Structure of the metal oxide catalysts may have a profound effect on catalytic processes[19,20]. The study of chemistry of niobate polyanions may help in unfolding some structural aspects of the oxides. Due to their high charge and large size niobate polyanions exhibit many of the properties of infinite lattices[21]. For such reasons these polyanions can be used to examine the catalytic properties of the metal oxides by methods which are inapplicable to solids, such as absorption spectroscopy and polarography. Further these anions can be used as convenient models for testing theories of bonding and metal-metal interactions in oxide lattices[21].

In an earlier publication[22] the author has shown that the solution containing the species NbO_4^{3-} on treatment with dilute acid decomposes into Nb_2O_5.aq via formation of various intermediate anions depending upon the hydrogen ion concentration of the medium. In view of the interesting results obtained and the importance of niobium poly-compounds, it was considered worthwhile to investigate precisely the composition of chromium niobates obtained by the interaction of chromium chloride on various niobate species at different pH levels by employing electrometric techniques which have provided more conclusive evidences on the composition of these and related compounds[22-25]. There is, however, no reference available in the literature on the study of chromium niobates as a function of pH.

EXPERIMENTAL

$NbCl_5$, $CrCl_3.6H_2O$, KOH, HNO_3 and acetic acid of extra-pure grade were used, and their solutions were prepared in

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carbonate-free conductivity water. The solution of potassium ortho-niobate was prepared by digesting $NbCl_5$ in KOH solution of the required strength. The concentration of K_3NbO_4 solution was further verified by determining niobium as pentoxide[26]. Calculated amounts of acetic acid were then added to K_3NbO_4 solutions in definite molar proportions to vary the pH.

The pH and conductometric measurements were carried out as usual[22]. Using different concentrations of chromium chloride and the alkali niobates at specific pH levels 12.0, 10.8 and 7.6, a series of pH and conductometric titrations was performed. Twenty five mL of the titre solution was taken in the cell each time. A standardized transfer pipette of 25.00±0.03 mL capacity which conforms to Class A test of National Physical Laboratory[26a] was used to take the titre solution in the cell. A micro-pipette of 5 mL capacity graduated to 0.01 mL was used for addition of the titrant solution. Identical concentrations of the reactants were taken in the two techniques for the sake of comparison of the results. All the values of pH and conductance were noted under the state of chemical equilibrium. The titrations were performed in presence of 20% ethanol. The titration curves were plotted between pH and corrected conductance and the volume of titrant used. Typical curves of only one dilution of each system are demonstrated in the Figures. The shape of titration curves with the other dilutions were similar to those demonstrated in the diagrams.

The precipitates obtained at the end-points of titrations between chromium chloride and potassium niobates were also analyzed to substantiate the electrometric results. The different chromium niobates were prepared by mixing stoichiometric amounts of chromium chloride solution with potassium niobate solutions at specific pH levels. The precipitates obtained were washed several times with 20% ethanolic water and dried in a vacuum desiccator for 40 h. A known amount (ca. 2 g) of each of the precipitates was treated with hydrochloric acid to extract chromium. Niobium was determined as oxide[27] and chromium spectrophotometrically[26b] and oxygen by difference. From the proportions of chromium, niobium and oxygen in the compounds thus obtained their composition was established.

RESULTS AND DISCUSSION

Potassium niobate solution was prepared by digesting $NbCl_5$ in a KOH solution in 1:8 molar ratio.

$$NbCl_5 + 8KOH = K_3NbO_4 + 5KCl + 4H_2O$$

When acid (HNO_3, HCl or CH_3COOH) is gradually added to K_3NbO_4 solution, it changes to hexa-niobate $Nb_6O_{19}^{8-}$, meta-niobate NbO_3^- and finally to the oxide Nb_2O_5.aq around pH 10.8, 7.6 and 3.8 corresponding to the ratios 3Nb:5H, 3Nb:6H and 3Nb:9H, respectively[22]. This studies[22] did not evidence the existence of the other forms, such as $HNb_6O_{19}^{7-}$ and $Nb_2O_7^{4-}$, as reported in the literature[2,28]. The behavior of K_3NbO_4 with HNO_3 is shown in Fig. 1. Similar curves were obtained when K_3NbO_4 was treated with the other acids. Curve 1 illustrates the pH titration results showing three inflections at 3Nb:5H, 3Nb:6H and 3Nb:9H corresponding to the formation of $Nb_6O_{19}^{8-}$, NbO_3^- and Nb_2O_5.aq, respectively. The position of the inflections is further checked by dpH/dV (curve 2). Similar results are obtained by conductometric titrations (curve 3). The stepwise degradation of ortho-niobate anion by the gradual addition of acid can be represented[22] by the following set of equations:

$$6NbO_4^{3-} + 10H^+ = Nb_6O_{19}^{8-} + 5H_2O$$

$$Nb_6O_{19}^{8-} + 2H^+ = 6NbO_3^- + H_2O$$

$$2NbO_3^- + 2H^+ = Nb_2O_5 + H_2O$$

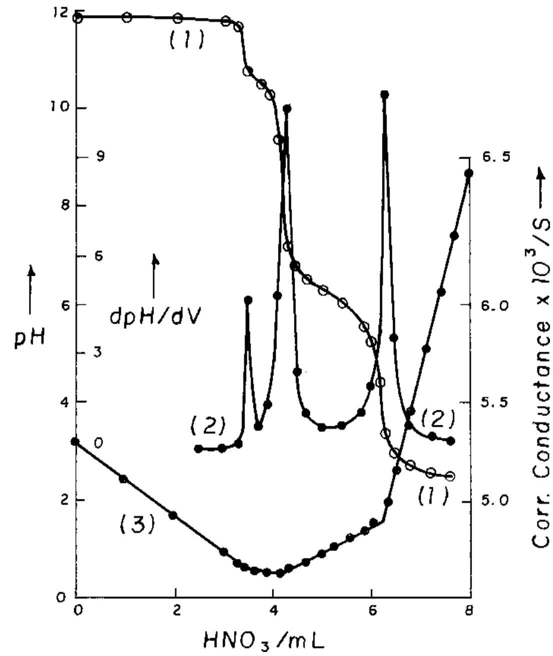

Figure 1. *pH and conductometric titrations. 25.00 mL of 8.33 x 10^{-3} M K_3NbO_4 titrated with 1.00 x 10^{-1} M HNO_3. Volume of HNO_3 vs. (1) pH, (2) dpH/dV, (3) Corrected conductance.*

Ortho-niobate Titrations. Using different concentrations of chromium chloride (pH 3.5) and K_3NbO_4 (pH 12.0) a series of pH titrations was carried out. Fig. 2 (curve 1) shows the changes occurring in H^+ ion concentration when the solution of chromium chloride was titrated with K_3NbO_4 solution. It may be noted that the first addition of the alkaline niobate solution to chromium chloride, results in gradual increase in pH to about 5.0. Further addition of the titrant brings about steep rise in pH value at a point where the molar ratio of Cr^{3+}:NbO_4^{3-} is 1:1 (see Table 1), corresponding to the stoichiometry for the precipitation of chromium ortho-niobate $Cr_2O_3.Nb_2O_5$ in the vicinity of pH 7.5. The reaction can be represented as follows:

$$2CrCl_3 + 2K_3NbO_4 = Cr_2O_3.Nb_2O_5 + 6KCl$$

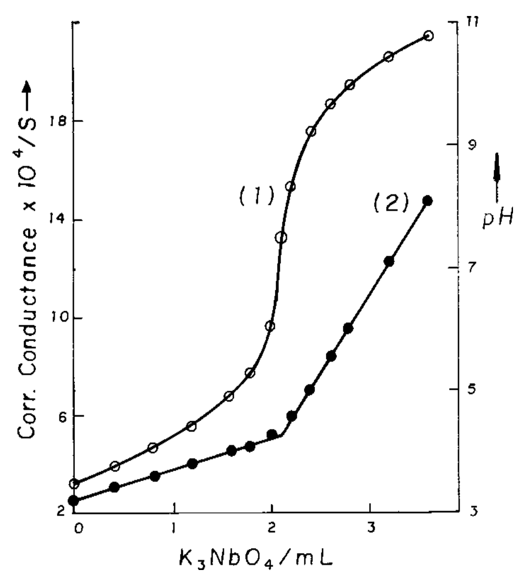

Figure 2. *Ortho-niobate titrations. 25 mL of 1.667 x 10^{-3} M $CrCl_3$ titrated with 2.00 x 10^{-2} M K_3NbO_4.*

Table 1. Summary of results of electrometric study on formation of chromium niobates. Volume of titre solution taken in the cell = 25.00 ± 0.03 mL.

Molarity of solutions		Equivalence points (mL)			Formula supported
(x 10^3)	(x 10^4)	Calculated	Observed from		
			pH	Conductance	
K_3NbO_4	$CrCl_3$	Ortho-niobate titrations. Fig. 2.			
33.33	33.33	2.50	2.50	2.50	$Cr_2O_3.Nb_2O_5$
20.00	16.67	2.08	2.10	2.10	
10.00	9.09	2.27	2.28	2.25	
$K_8Nb_6O_{19}$	$CrCl_3$	Hexa-niobate titrations. Fig. 3.			
6.67	15.38	2.16	2.15	2.15	$4Cr_2O_3.9Nb_2O_5$
3.33	7.14	2.01	2.00	2.00	
2.00	5.00	2.34	2.32	2.32	
$KNbO_3$	$CrCl_3$	Meta-niobate titrations. Fig. 4.			
3.33	10.00	2.25	2.25	2.23	$Cr_2O_3.3Nb_2O_5$
20.00	5.56	2.08	2.10	2.05	
10.00	2.86	2.14	2.12	2.10	

In the case of conductometric titrations of chromium chloride with the alkali ortho-niobate (Fig. 2, curve 2) the conductance value increases gradually in the beginning of the titration, but after completion of the reaction, conductance rises sharply at the ratio $Cr^{3+}:NbO_4^{3-}$ as 1:1 which coincides with the stoichiometry indicated by the pH study.

Hexa-niobate Titrations. The solution of potassium hexa-niobate $K_8Nb_6O_{19}$ was prepared by addition of acetic acid to K_3NbO_4 in the molar ratio 5:3. Fig. 3 (curve 1) illustrates the changes occurring in H^+ concentration when potassium hexa-niobate solution (pH 10.8) was added from the microburette to the solution of chromium chloride (pH 3.5). The titration curve shows a well-defined inflection at the equivalence point, where the molar ratio $Cr^{3+}:Nb_6O_{19}^{8-}$ is 8:3, corresponding to the stoichiometry for the formation chromium hexa-niobate $4Cr_2O_3.9Nb_2O_5$, in the neighborhood of pH 6.8. The reaction can be represented by the following equation:

$$8CrCl_3 + 3K_8Nb_6O_{19} = (4Cr_2O_3.9Nb_2O_5) + 24KCl$$

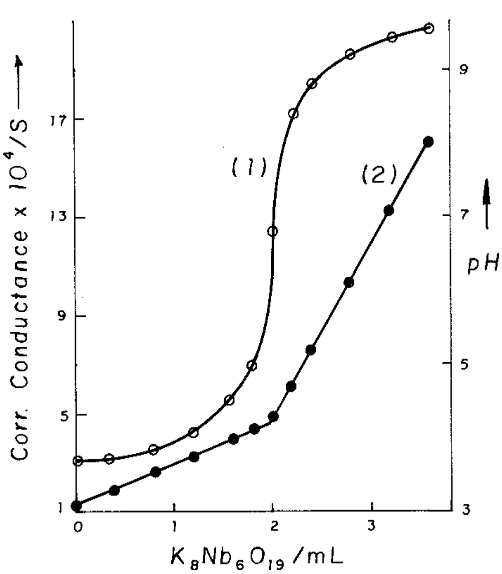

Figure 3. *Hexa-niobate titrations. 25 mL of 7.14 x 10^{-4} M $CrCl_3$ titrated with 3.33 x 10^{-3} M $K_8Nb_6O_{19}$.*

Employing similar concentrations of the reactants a series of conductometric titrations between the solutions of chromium chloride and potassium hexa-niobate was also carried out. Well defined breaks in the titration curves (Fig. 3, curve 2) were obtained at 8:3 molar ratio of $Cr^{3+}:Nb_6O_{19}^{8-}$, which confirm the formation of the identical compound, chromium hexa-niobate $4Cr_2O_3.9Nb_2O_5$. In these titrations, when alkaline hexaniobate solution was added from the microburette to chromium chloride solution in the titration cell, a gradual increase in conductance value was observed (due to removal of chromium ions in the form of precipitate by more mobile potassium ions) until the stoichiometric end-point, after which the conductance increased sharply with the increase in ionic concentration.

Meta-niobate Titrations. The solution of potassium meta-niobate was prepared by addition of acetic acid to K_3NbO_4 in the molar ratio 2:1. Using different concentrations of chromium chloride (pH 3.5) and potassium meta-niobate (pH 7.6) a series of pH and conductometric titrations (Fig. 4) was carried out. The breaks and inflections in the titration curves at the stoichiometric end-point corresponding to the molar ratio $Cr^{3+}:NbO_3^-$ as 1:3, suggest the formation of chromium meta-niobate $Cr_2O_3.3Nb_2O_5$ in the neighborhood of pH 5.6., according to the equation:

$$2CrCl_3 + 6KNbO_3 = Cr_2O_3.3Nb_2O_5 + 6KCl$$

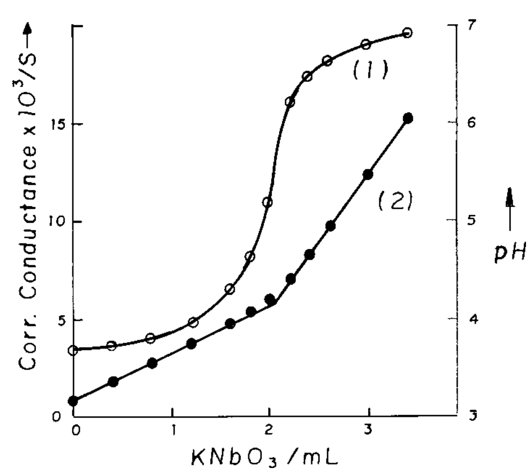

Figure 4. *Meta-niobate titrations. 25 mL of 5.56 x 10^{-4} M $CrCl_3$ titrated with 2.00 x 10^{-2} M $KNbO_3$.*

The feeble break obtained in the conductometric titration curves may be ascribed to the presence of potassium acetate in appreciable amount in meta-niobate solution.

Table 2. Summary of analytical results of the precipitates of chromium niobates.

Proposed formula of the compound	Percentage of Cr		Percentage of Nb	
	Found	Theoretical	Found	Theoretical
	Analysis of ortho-niobate precipitates.			
$Cr_2O_3.Nb_2O_5$	24.83	24.89	44.54	44.47
	Analysis of hexa-niobate precipitates.			
$4Cr_2O_3.9Nb_2O_5$	13.85	13.87	55.79	55.74
	Analysis of meta-niobate precipitates.			
$Cr_2O_3.3Nb_2O_5$	10.91	10.95	58.77	58.71

Similar studies using chromium chloride solution as titrant was also realized, but the curves did not exhibit conclusive results for the formation of chromium niobates which may be ascribed to probable parallel reactions due to high pH values of the alkaline niobate solutions present in the cell.

It was noted that, after each addition of the titrant, the pH and conductance values required a little time to become steady. A thorough stirring in the neighborhood of the end-point had a favorable effect. The presence of ethanol (20%) increases the magnitude of the jump in pH curves as it decreases the solubility of the precipitates formed and minimizes hydrolysis and adsorption. For this reason all the titrations were performed in presence of 20% ethanol. Higher than this percentage of the alcohol was of no advantage. The results obtained were precise. The relative standard deviation of the results reported in Table 1 was <1%.

The precipitates of chromium niobates obtained at the end-points of the titrations were also analyzed by classical methods. The results obtained (Table 2) confirm those obtained by the electrometric study.

CONCLUSIONS

The present electrometric and analytical investigations on interaction of chromium chloride with potassium niobate at specific pH levels 12.0, 10.8 and 7.6 provide definite evidence for the formation of chromium *ortho*-$Cr_2O_3.Nb_2O_5$, *hexa*-$4Cr_2O_39Nb_2O_5$ and *meta*-$Cr_2O_3.3Nb_2O_5$ niobates in the vicinity of pH 7.5, 6.8 and 5.6, respectively. As the structure of these compounds are not known they are represented in the form of double oxides[29,30].

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REFERENCES

1. Greenwood, N. N.; Earnshaw, A.; *Chemistry of Elements*; Pergamon; New York, 1984; p. 1134.
2. Fairbrother, F.; *The Chemistry of Niobium and Tantalum*, Elsevier, London, 1967; p. 36, 222.
3. Jander, G.; Ertel, D.; *J. Inorg. Nucl. Chem*. **1960**, *14*, 71, 77 and 85.
4. Conard, R. W.; Land, J. E.; *J. Less-Common Met.* **1964**, *7*, 180.
5. Fairbrother, F.; *The Chemistry of Niobium and Tantalum;* Elsevier; London, 1967; p. 36.
6. Hagenmuller, P. In *Comprehensive Inorganic Chemistry*, vol. 4, Trotman-Dickenson, A.F., Ex. Ed.; Pergamon; Oxford, 1975; p. 541.
7. Argent, B. B.; *Sci. Progr. London* **1964**, *52*, 608.
8. Koch, C. C.; Cavin, O. B.; McKamey, C. G.; Scarbrough, J. O.; *Appl. Phys. Lett*. **1983**, *43*, 725.
9. Nasu, T.; *J. Non-cryst. Solids* **1990**, *117/118*, 725.
10. Kunzler, J. E.; Buehler, E.; Hsu, F. S. L.; Wernick, J. H.; *Phys. Rev. Lett.* **1961**, *6*, 89.
11. Martin, D. L.; Benz, M. G.; Bruch, C. A.; Rosner, C. H.; *Cryogenics* **1963**, *3*, 144.
12. Bost, G.; *German Offen.*, 2,064,586 (1971); *Chem. Abstr*. **1971**, *107*, 70757.
13. Baker, D. H.; Ramlsdell, J. D.; *J. Electrochem. Soc.* **1960**, *107*, 985.
14. Cortright, R. D.; Dumesic, J. A.; *Appl. Catal*. **1995**, *129*, 101.
15. Devis, B. H. In *Selectivity in Catalysis*, ACS Symposium Series, vol. 517, Devis, M.E.; Suib, S. L., Eds.; Am. Chem. Soc.; Washington, DC, 1993.
16. Aranda, D. A. G.; Noronha, F. B.; Passos, F. B.; Schmal, M.; *Appl.Catal.* **1993**, *100*, 77.
17. Aranda, D. A. G.; Passos, F. B.; Noronha, F. B.; Schmal, M.; *Catal. Today* **1993**, *16*, 397.
18. Aranda, D. A. G.; Ramos, A. L. D.; Passos, F. B.; Schmal, M.; *Catal. Today* **1996**, *28*, 119.
19. Sullivan, D. H.; Harold, M. P.; Conner Jr.; W. C.; *J. Catal*. **1998**, *178*, 108.
20. Arora, N.; Deo, G.; Wachs, I. E.; Hirt, A. M.; *J. Catal*. **1996**, *159*, 1.
21. Pope, M. T.; Dale, W. B.; *Q. Revs*. **1968**, *22*, 527.
22. Prasad, S.; *J. Braz. Chem. Soc.* **1995**, *6*, 7.
23. Prasad, S.; *Quím. Nova* **1994**, *17*, 31.
24. Prasad, S.; *Can. J. Chem*. **1981**, *59*, 563.
25. Prasad, S.; Guimarães, T. L. M.; *J. Braz. Chem. Soc*. **1998**, *9*, 253.
26. Vogel, A. I.; *A Textbook of Quantitative Inorganic Analysis*, 3rd ed.; Longmans; London, 1968; p. (a) 199, (b) 791.
27. Moshier, R. W.; *Analytical Chemistry of Niobium and Tantalum*; Macmillan; New York, 1964; p. 27.
28. Cotton, F. A.; Wilkinson, G.; *Advanced Inorganic Chemistry*; Interscience; New York, 1962, p. 770.
29. Standen, A.; Ex. Ed.; *Kirk-Othmer Encyclopedia of Chemical Technology*, 2nd. ed.; Interscience; New York, 1967; p. 782, vol. 13.
30. Brauer, G., Ed.; *Handbook of Preparative Inorganic Chemistry*, 2nd. ed.; Academic Press; New York, 1965, p. 1705, vol. 2.