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-Cr2O3.3Nb2O5, hexa-4Cr2O3.9Nb2O4 and meta-Cr2O3.3Nb2O4 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 solutions1-3 and from these polyniobates crystallize, depending upon the H+ concentration which plays an important role on the aggregation process. It has been reported1 that sodium ortho-niobate, Na3NbO4, dissolves in water giving a strongly alkaline solution due to its hydrolysis to form Nb6O198− which upon decreasing the pH may successively change to HNb6O197− and (Nb6O186−)n. The value of about 3 for n, has been suggested but Conard and Land4 concluded that the value of n should be about 6. A large number of niobates with conflicting reports have been described5 in which the ratio of alkali metal to acid (M2O/Nb2O5) 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 known6 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 steel7. 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-chrome and stainless steel8. In addition to its continued use in the production of these and related compounds9-11. Some work has appeared on the electrodeposition of niobium alloys using niobate solutions in baths12,13. 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 C7-C14 mono-olefines to obtain biodegradable detergents14-15. The catalysts Pt/Nb2O5 and Pt-Sn/Nb2O4 have been reported to be excellent and highly selective catalysts in dehydrogenation reactions16-18. Structure of the metal oxide catalysts may have a profound effect on catalytic processes19,20. 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 lattices21. 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 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 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 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 to examine the catalytic properties of the metal oxides by methods which are inapplicable to solids, such as absorption spectroscopy and polarography.

In an earlier publication22 the author has shown that the solution containing the species NbO4− on treatment with dilute acid decomposes into Nb2O5,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 compounds22-25. There is, however, no reference available in the literature on the study of chromium niobates as a function of pH.

EXPERIMENTAL

NaCl, CrCl3.6H2O, KOH, HNO3 and acetic acid of extra-pure grade were used, and their solutions were prepared in
carbonate-free conductivity water. The solution of potassium ortho-niobate was prepared by digesting NbCl₅ in KOH solution of the required strength. The concentration of K₃NbO₄ solution was further verified by determining niobium as pentoxide²⁶. Calculated amounts of acetic acid were then added to K₃NbO₄ solutions in definite molar proportions to vary the pH.

The pH and conductometric measurements were carried out as usual²². 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 Laboratory²⁶a 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 oxide²⁷ and chromium spectrophotometrically²⁶b 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 NbCl₅ in a KOH solution in 1:8 molar ratio.

\[
\text{NbCl}_5 + 8\text{KOH} = \text{K}_3\text{NbO}_4 + 5\text{KCl} + 4\text{H}_2\text{O}
\]

When acid (HNO₃, HCl or CH₃COOH) is gradually added to K₃NbO₄ solution, it changes to hexa-niobate Nb₆O₁₉⁻²⁻, meta-niobate NbO₃⁻ and finally to the oxide Nb₂O₅ around pH 10.8, 7.6 and 3.8 corresponding to the ratios 3Nb:5H, 3Nb:6H and 3Nb:9H, respectively²². This studies²² did not evidence the existence of the other forms, such as HNb₆O₁₉⁻⁷⁻ and Nb₂O₇⁴⁻, as reported in the literature²,²⁸. The behavior of K₃NbO₄ with HNO₃ is shown in Fig. 1. Similar curves were obtained when K₃NbO₄ 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 Nb₆O₁₉⁻²⁻, NbO₃⁻ and Nb₂O₅aq, 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 represented²² by the following set of equations:

\[
\begin{align*}
6\text{NbO}_4^{3-} + 10\text{H}^+ &= \text{Nb}_6\text{O}_{19}^{8-} + 5\text{H}_2\text{O} \\
\text{Nb}_6\text{O}_{19}^{8-} + 2\text{H}^+ &= 6\text{NbO}_3^- + \text{H}_2\text{O} \\
2\text{NbO}_3^- + 2\text{H}^+ &= \text{Nb}_2\text{O}_5^- + \text{H}_2\text{O}
\end{align*}
\]

**Ortho-niobate Titrations.** Using different concentrations of chromium chloride (pH 3.5) and K₃NbO₄ (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 K₃NbO₄ 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 Cr³⁺:NbO₄³⁻ is 1:1 (see Table 1), corresponding to the stoichiometry for the precipitation of chromium ortho-niobate Cr₂O₃.Nb₂O₅ in the vicinity of pH 7.5. The reaction can be represented as follows:

\[
2\text{CrCl}_3 + 2\text{K}_3\text{NbO}_4 = \text{Cr}_2\text{O}_3\cdot\text{Nb}_2\text{O}_5 + 6\text{KCl}
\]

Figure 1. pH and conductometric titrations. 25.00 mL of 8.33 x 10⁻³ M K₃NbO₄ titrated with 1.00 x 10⁻¹ M HNO₃. Volume of HNO₃ vs. (1) pH, (2) dpH/dV, (3) Corrected conductance.

Figure 2. Ortho-niobate titrations. 25 mL of 1.667 x 10⁻³ M CrCl₃ titrated with 2.00 x 10⁻² M K₃NbO₄.
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 hexaniobate K\(_{8}\)Nb\(_{6}\)O\(_{19}\) was prepared by addition of acetic acid to K\(_{3}\)NbO\(_{4}\) in the molar ratio 5:3. Fig. 3 (curve 1) illustrates the changes occurring in H\(^{+}\) concentration when potassium hexaniobate 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\(_{6}\)O\(_{19}^{8-}\) is 8:3, corresponding to the stoichiometry for the formation chromium hexa-niobate 4Cr\(_{2}\)O\(_{3}\).9Nb\(_{2}\)O\(_{5}\) in the neighborhood of pH 6.8. The reaction can be represented by the following equation:

\[
8\text{CrCl}_3 + 3\text{K}_8\text{Nb}_6\text{O}_{19} = (4\text{Cr}_2\text{O}_3.9\text{Nb}_2\text{O}_5) + 24\text{KCl}
\]

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\(_{3}\)NbO\(_{4}\) 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\(_{2}\)O\(_{3}\).3Nb\(_{2}\)O\(_{5}\) in the neighborhood of pH 5.6., according to the equation:

\[
2\text{CrCl}_3 + 6\text{KnBO}_3 = \text{Cr}_2\text{O}_3.3\text{Nb}_2\text{O}_5 + 6\text{KCl}
\]

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\(^{3+}\) : NbO\(_{6}^{3-}\), which confirm the formation of the identical compound, chromium hexa-niobate 4Cr\(_{2}\)O\(_{3}\).9Nb\(_{2}\)O\(_{5}\). 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.

**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.

<table>
<thead>
<tr>
<th>Molarity of solutions (x 10(^{-3}))</th>
<th>Equivalence points (mL)</th>
<th>Formula supported</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Calculated</td>
<td>Observed from</td>
</tr>
<tr>
<td></td>
<td></td>
<td>pH</td>
</tr>
<tr>
<td>K(<em>{3})NbO(</em>{4}) CrCl(_{3})</td>
<td>Ortho-niobate titrations. Fig. 2.</td>
<td></td>
</tr>
<tr>
<td>33.33</td>
<td>2.50</td>
<td>2.50</td>
</tr>
<tr>
<td>20.00</td>
<td>2.08</td>
<td>2.10</td>
</tr>
<tr>
<td>10.00</td>
<td>2.27</td>
<td>2.25</td>
</tr>
<tr>
<td>K(<em>{8})Nb(</em>{6})O(<em>{19}) CrCl(</em>{3})</td>
<td>Hexa-niobate titrations. Fig. 3.</td>
<td></td>
</tr>
<tr>
<td>6.67</td>
<td>2.16</td>
<td>2.15</td>
</tr>
<tr>
<td>3.33</td>
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</tr>
<tr>
<td>2.00</td>
<td>2.34</td>
<td>2.32</td>
</tr>
<tr>
<td>K(<em>{3})NbO(</em>{3}) CrCl(_{3})</td>
<td>Meta-niobate titrations. Fig. 4.</td>
<td></td>
</tr>
<tr>
<td>3.33</td>
<td>2.25</td>
<td>2.25</td>
</tr>
<tr>
<td>20.00</td>
<td>2.08</td>
<td>2.05</td>
</tr>
<tr>
<td>10.00</td>
<td>2.14</td>
<td>2.10</td>
</tr>
</tbody>
</table>

**Figure 3.** Hexa-niobate titrations. 25 mL of 7.14 \(\times\) 10\(^{-4}\) M CrCl\(_{3}\) titrated with 3.33 \(\times\) 10\(^{-4}\) M K\(_{8}\)Nb\(_{6}\)O\(_{19}\).

**Figure 4.** Meta-niobate titrations. 25 mL of 5.56 \(\times\) 10\(^{-4}\) M CrCl\(_{3}\) titrated with 2.00 \(\times\) 10\(^{-5}\) M K\(_{3}\)NbO\(_{3}\). 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.
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$_2$O$_3$Nb$_2$O$_5$, hexa-4Cr$_2$O$_3$9Nb$_2$O$_5$ and meta-Cr$_2$O$_3$3Nb$_2$O$_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$^{29,30}$. 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.

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**ACKNOWLEDGEMENT**

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

<table>
<thead>
<tr>
<th>Proposed formula of the compound</th>
<th>Percentage of Cr</th>
<th>Percentage of Nb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Analysis of ortho-niobate precipitates.</td>
<td>Cr$_2$O$_3$Nb$_2$O$_5$</td>
<td>24.83</td>
</tr>
<tr>
<td>Analysis of hexa-niobate precipitates.</td>
<td>4Cr$_2$O$_3$9Nb$_2$O$_5$</td>
<td>13.85</td>
</tr>
<tr>
<td>Analysis of meta-niobate precipitates.</td>
<td>Cr$_2$O$_3$3Nb$_2$O$_5$</td>
<td>10.91</td>
</tr>
</tbody>
</table>