

NIOBIUM AS A POTENTIOMETRIC SENSOR IN REDOX TITRATIONS WITH AND WITHOUT PASSIVATION BY AMMONIUM MOLYBDATE.

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ABSTRACT

The Pt indicator electrode has been commonly used for redox potentiometric titrations. In this work the Nb indicator electrode is suggested as an alternative for the Pt indicator electrode for the redox potentiometric titrations of the system Fe(II)/K₂Cr₂O₇. The utilization of proposed electrode has been studied with and without passivation. The passivation is made by electrode immersion in oxidising anodic inhibitor of NH₄MoO₄. The result was an observed increase of the potentiometric leap from 30 mV to 60 mV, allowing a better visualization of the equivalence point. The same equivalence point was observed with the conventional and proposed electrode. With the Nb electrode an inverse potentiometric leap was also obtained.

RESUMO

O eletrodo indicador de platina tem sido usado nas titulações potenciométricas de oxi-redução convencionalmente. Neste trabalho, o eletrodo indicador de nióbio é considerado como uma alternativa ao eletrodo indicador de platina nas titulações potenciométricas de oxi-redução para o sistema Fe(II)/K₂Cr₂O₄. A utilização do eletrodo foi estudada com e sem passivação. A passivação foi feita com a imersão do eletrodo num inibidor oxidante anódico de NH₄MoO₄. Como consequência ocorreu um aumento do salto potenciométrico de 30 mV para 60 mV (ECS), permitindo uma melhor visualização do ponto de equivalência. Foi observado o mesmo ponto de equivalência para o eletrodo proposto em relação ao convencional. Além disso, com o eletrodo de nióbio foi obtido um salto potenciométrico invertido.

Keywords: potentiometric sensor; redox titrations; niobium; passivation; ammonium molybdate

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INTRODUCTION

The indicator electrodes used in potentiometric titrations depend on the type of reaction that is being investigated. In an acid-base titration it may be a hydrogen electrode or any other electrode that responds to hydrogen ions. The equivalence point of the reaction is revealed by a sudden change of potential in the e.m.f. curve vs the volume of the titrant solution.

Many pure metals are resistant to corrosion and have the common characteristic of forming oxides very adherent to the surface that repress the corrosion and are suitable as proton sensors¹.

The metal-oxides. xH_2O indicator electrodes have been used as sensors because of their low price and easy handling.

Some metals, such as Ti, Ni, Ta and alloys such as chromium-cobalt and stainless steel tend to become passive due to the formation of a thin, adherent layer of oxide or another compound that protects them from oxidation².

The sensibility of metal-oxide. xH_2O electrodes in redox titration was studied by Sayed³. Redox titrations were made and appreciable potential leaps were observed in the equivalence point.

The Nb is covered by a Nb_2O_5 film that can be dissolved by fusion with hydroxide but is not attacked by the hydrogen ion⁴.

Chromium-Nickel alloys, used as potentiometric sensor in redox titrations, show well determined potentiometric leaps, and usually in the same potential range of platinum electrodes. These potentiometric leaps are usually 50% of the value of the leaps obtained when platinum electrode are used⁵.

The first studies carried out to verify the response of metallic-oxide films used hastelloy alloys and have shown that the film can respond to protons in solution. Systematic studies in acid-base reactions and the Nernst type behavior extends to the range of pH 1,0 to pH 13,0⁶.

In this work, Nb was used as indicator electrode in redox potentiometric titration for the system $Fe(II)/K_2Cr_2O_7$. The passivation was made to increase the potentiometric leap.

MATERIALS AND METHODS

Potentiometric titrations of 0,01N $FeSO_4 \cdot 7H_2O$ (in H_2SO_4 solution) with 0,1N $K_2Cr_2O_7$ solution were done, with stirring at room temperature using the calomel electrode as reference and a Nb electrode as indicator, instead of the Pt electrode. The Nb electrode was sanded with granulometry 280, 320, 400 and 600 a paper and then polished with Al_2O_3 .

In some cases, the Nb electrodes were treated chemically and the passivation was achieved by immersion in 0,01 N NH_4MoO_4 solution for thirty minutes and for one hour.

The titrations were conducted at $25 \pm 1^\circ\text{C}$, with a PW 9409 Phillips potentiometer using a Shott Mainz B281 calomel electrode of simple junction, as reference. In order to achieve a better resolution a 274 microburette Methrohm was used. A 702 Fisaton magnetic stirrer, was used to ensure adequate mixing.

RESULTS AND DISCUSSION

Figures 2 and 3 show that the equivalence points in the titrations coincide exactly with that verified when the Pt electrode is used (Figure 1), although the potential leap is reversed and smaller.

The Nb electrode passivated by immersion in oxidizing anodic inhibitor solution of NH_4MoO_4 for thirty minutes and one hour presented a potentiometric leap of about 60 mV, that is twice that observed without passivation in the Fe(II) titration by $\text{K}_2\text{Cr}_2\text{O}_7$ (30 mV). The passivated electrode allows a better detection of the equivalence point.

When the Nb is exposed to the air, it has the characteristic of formation of a film mainly of Nb_2O_5 .

The oxidizing anodic inhibitor of NH_4MoO_4 , probably makes this layer thicker and the redox potential becomes higher than the original one.

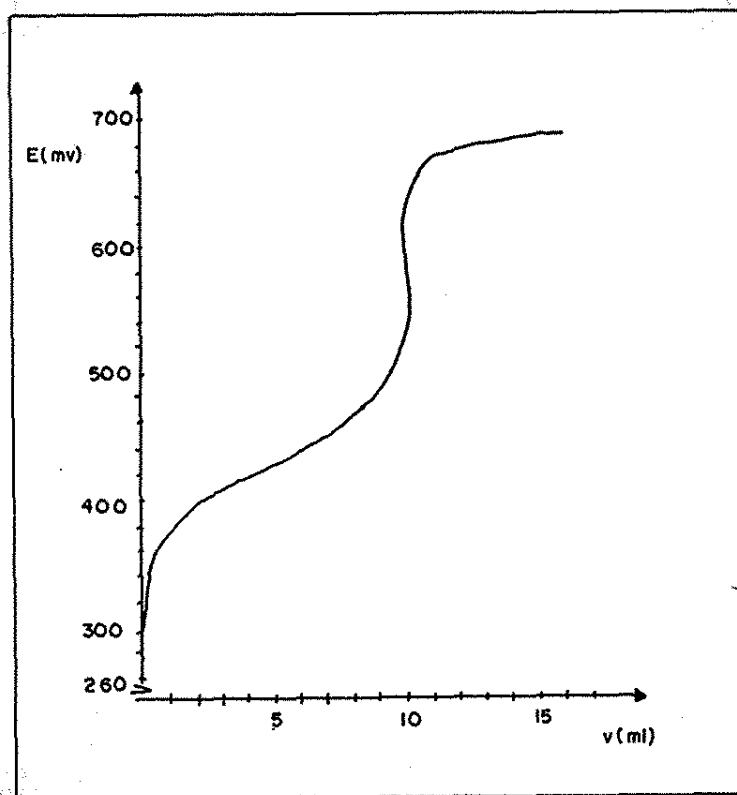


Figure 1. Titration curve using Pt indicator electrode for the system Fe (II)/Cr (VI).

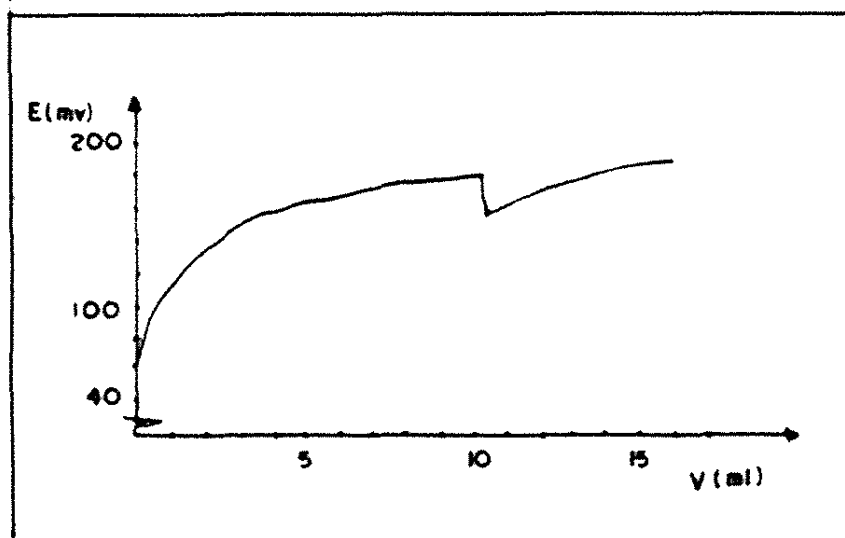
Niobium as Potentiometric Sensor

Figure 2. Titration curve using Nb indicator electrode without passivation for the system Fe(II)/Cr (VI).

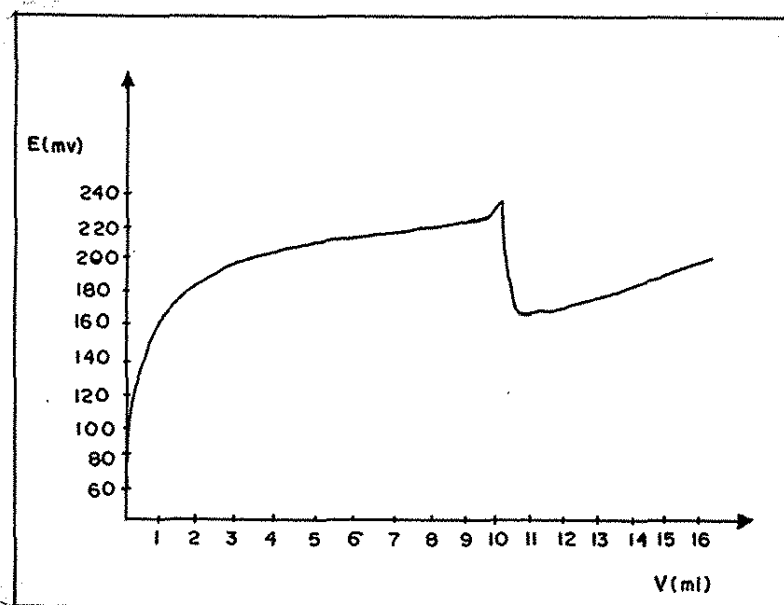


Figure 3. Titration curve using Nb indicator electrode with passivation for the system Fe (II)/Cr (VI).

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