

# POTENTIOMETRIC MONITORING OF SODIUM BOROHYDRIDE IN AQUEOUS SOLUTIONS

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**ABSTRACT:** Platinum, palladium, gold, cadmium, nickel and niobium immersed in sodium borohydride alkaline solutions are characterised by electrode responses that allow monitoring the borohydride present in aqueous media. A simple and relatively precise potentiometric titration technique is described and applied for the analysis of borohydride solutions.

**Keywords:** Sodium borohydride; Potentiometry; Thermodynamic data.

**RESUMO:** Platina, paládio, ouro, cádmio, níquel e nióbio imersos em soluções alcalinas de borohidreto de sódio são caracterizados por respostas de eléctrodo que permitem monitorizar o conteúdo em borohidreto presente num dado meio aquoso. Descreve-se uma técnica de titulação potenciométrica relativamente simples e precisa que pode ser aplicada para a análise de soluções de borohidreto.

**Palavras chave:** Borohidreto de sódio; Potenciometria; Dados termodinâmicos.

## 1. INTRODUCTION

Sodium borohydride,  $\text{NaBH}_4$ , has several applications in chemical and electrochemical synthesis, electroless deposition of metals, energy systems, etc. [1]. Aqueous borohydride solutions are generally kept strongly alkaline to prevent hydrolysis that occurs at lower pH. Quantitative determination of borohydride anions,  $\text{BH}_4^-$ , in aqueous alkaline solutions can be obtained by numerous methods including hydrogen evolution [2], acid-base titration [3], iodate [4], hypochlorite [5], and voltammetric procedures [6]. These methods, however, are not very simple and/or rapid. In 1999, Amendola and co-workers [7] reported the non-destructive, in-situ detection of relatively low  $\text{BH}_4^-$  concentrations by a simple method that is basically a potentiometric titration technique. For the majority of chemists and, in fact, many non-chemists, potentiometry is one of the first instrumental analytical procedures they encounter. The use of glass electrodes in pH measurement is the most common application of potentiometry [8,9]. As an analytical method, potentiometry gained popularity in the 1920s, mainly as a result of the activities of Müller [10] and Kolthoff and Furman [11], and has been gaining momentum ever since [12,13]. Potentiometry is an extremely versatile analytical method and, as the name suggests, involves measuring the potential of a galvanic cell. Such cells contain two electrodes and we can use the Nernst equation to calculate the potential of each. In the majority of potentiometric measurements the potential of one electrode is kept constant, being this electrode referred to as the reference electrode. The second electrode responds to the activity or concentration of the species contained in the solution under investigation and is referred to as an indicator

electrode. Amendola *et al.* [7] used a saturated calomel electrode (SCE) as reference electrode, and platinum, rhodium, and cobalt as metal indicator electrodes. The recommended reference electrode for highly alkaline media is the mercury/mercury oxide (Hg/HgO) electrode [14], but since the concentrated NaOH electrolyte is extremely corrosive for the glass material of the reference electrode, we have selected the Hg/HgO electrode with 1 M NaOH inner electrolyte solution:



The reaction for this electrode is:



It has a potential of 0.098 V against the standard hydrogen electrode (SHE), and of -0.144 V relative to the SCE at 25 °C. A detailed analysis of the Amendola data is described by one of us [15], and lack of space does not allow further consideration on their work.

In our titration studies, we have observed that any metal/alloy (*e.g.* Au, Pt, Pd, Ni, Co, Cd, Cr, Cu, Zn, Fe, Al, Mo, Nb, Rh, AISI 312, AISI 316) whose open-circuit potential (OCP) is significantly different when immersed in NaOH supporting electrolyte with or without  $\text{NaBH}_4$  may be a candidate indicator electrode for  $\text{BH}_4^-$  estimation. In this paper we report data on 6 metals whose OCPs were monitored in alkaline solutions for various  $\text{BH}_4^-$  concentrations. Available thermodynamic data [16-18] helped in the analysis of the obtained OCP –  $[\text{BH}_4^-]$  plots.

## 2. EXPERIMENTAL DETAILS

Platinum, palladium, gold, cadmium, nickel and niobium wires/flags of specpure grade were supplied by Goodfellow Metals (UK). Stock solutions of 4 M NaOH, and of 2 M NaBO<sub>2</sub> in 1 M NaOH were prepared from analytical grade chemicals and deionised water (Millipore). These base solutions were used for the preparation of standards with a wide range of NaBH<sub>4</sub> concentrations. Potentiometric titrations were performed using a titration apparatus consisting of a Metrohm 725 Dosimat titrator and an automatic potentiometric recorder. The 100 ml titration vessel was thermostatically controlled at 25 ± 0.1 °C, and the electrode pair consisted of a metal indicator electrode and a Radiometer Analytical XR 440 Hg/HgO/NaOH, 1M reference electrode. OCPs were monitored as a function of added BH<sub>4</sub><sup>-</sup> solution with the help of a computer interface linked to a Pentium IV microprocessor which allowed automatic data collection at constant time intervals.

## 3. RESULTS AND DISCUSSION

**Platinum.** Simulating approximately the conditions used by Amendola [7], rest potentials of Pt in NaBO<sub>2</sub> 2 M + NaOH 1 M were investigated. Starting at an initial value of about 0.02 V, the OCP gradually became more negative as [BH<sub>4</sub><sup>-</sup>] increased (Figure 1), remaining relatively invariant with time at about -0.65 V, even for [BH<sub>4</sub><sup>-</sup>] as high as 0.012 M.

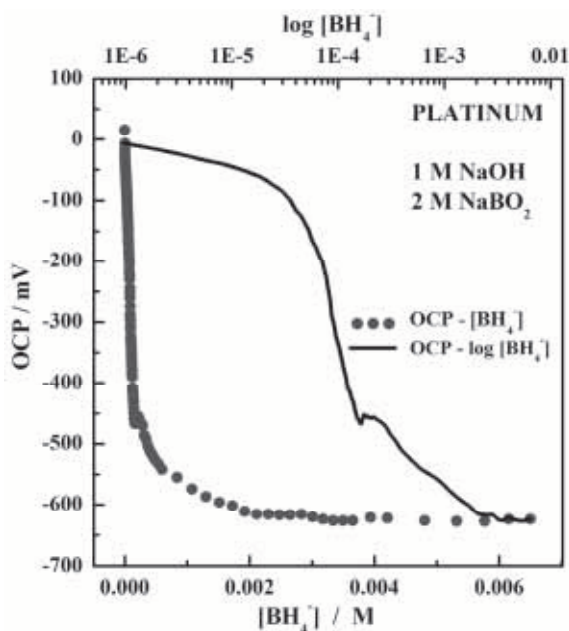


Fig. 1. OCP versus borohydride concentration for Pt.

These results confirmed those of Amendola, but we did not observe the step-potential change at [BH<sub>4</sub><sup>-</sup>] = 3 × 10<sup>-4</sup> M; in our case, there was always a gradual change of potential that, in fact, was more abrupt for [BH<sub>4</sub><sup>-</sup>] between 5 × 10<sup>-5</sup> and 6 × 10<sup>-4</sup> M.

**Cadmium.** When a cadmium foil was immersed in NaBO<sub>2</sub> 2 M + NaOH 1 M large potential oscillations were observed, being necessary to wait some time for a stable potential to be reached. The influence of [BH<sub>4</sub><sup>-</sup>] on the Cd potential is shown in Figure 2.

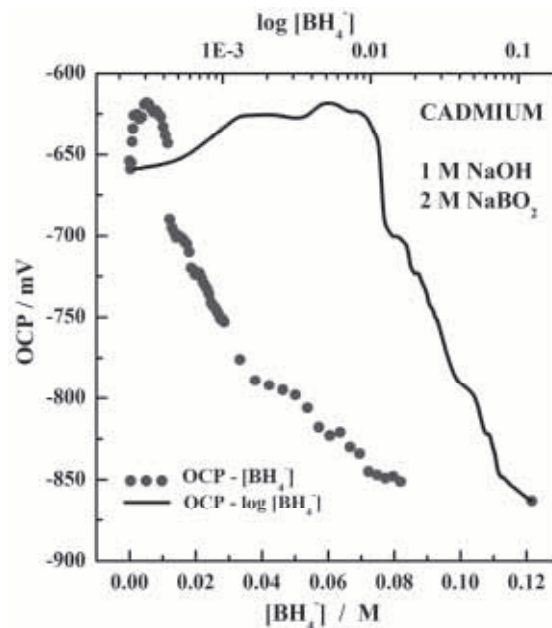
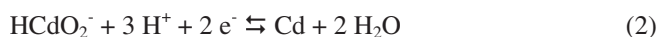


Fig. 2. OCP versus borohydride concentration for Cd.

The -0.87 V open-circuit potential observed for Cd, once it is immersed in the free NaBH<sub>4</sub> solution, could be due to the establishment of the reaction between Cd and the bicadmite ion HCdO<sub>2</sub><sup>-</sup> that is the predominant dissolved form of Cd at pH ~ 14:



The Nernst potential for this reaction can be written as:

$$\begin{aligned} E &= 0.583 + 0.0295 \log \{ [\text{HCdO}_2^-][\text{H}^+]^3 \} \\ &= 0.583 - 0.0886 \text{pH} + 0.0295 \log [\text{HCdO}_2^-] \\ &= 0.583 - 0.0886 \text{pH} + 0.0295 (-17.59 + \text{pH}) \end{aligned}$$

For pH = 14, E = -0.762 V vs. SHE, which translates into -0.860 V versus the Hg/HgO reference electrode.

Given that our working solutions are aerated, the presence of the O<sub>2</sub>/OH<sup>-</sup> couple must be considered, and the Cd potential variations observed for the first hour of immersion between -0.87 V and -0.58 V reflect necessarily its oxidising action:



For this reaction E ~ 0.4 V vs. SHE, at pH = 14, which translates into 0.30 V versus our reference electrode. The mixed potential resulting from the joint intervention of the HCdO<sub>2</sub><sup>-</sup>/Cd and the O<sub>2</sub>/OH<sup>-</sup> redox couples tends to a stationary value of about -0.65 V and then, the Cd potential steadily decreases with the additions of BH<sub>4</sub><sup>-</sup> ions. The reduction action of the BO<sub>2</sub><sup>-</sup>/BH<sub>4</sub><sup>-</sup> couple may suppress the dominant role of the HCdO<sub>2</sub><sup>-</sup>/Cd couple leading to a reaction of the type:



Appearance of a rose scale on the Cd foil surface was also observed, evidencing the involvement of the boron-cadmium system in the reaction products of process (4).

**Palladium.** Palladium has similar properties to platinum, and therefore it was anticipated to behave approximately as platinum in borohydride aqueous solutions. When immersed in NaBH<sub>4</sub> free solutions a rest potential of 0.022 V was measured. As borohydride concentration increased, Pd OCPs gradually became more negative. For [BH<sub>4</sub><sup>-</sup>] = 6 × 10<sup>-4</sup> M, the Pd potential was -0.45 V; for further BH<sub>4</sub><sup>-</sup> additions, the OCP decrease was slower, remaining practically invariant with time for [BH<sub>4</sub><sup>-</sup>] ≥ 10<sup>-2</sup> M, for which a value of -0.80 V was measured (Figure 3).

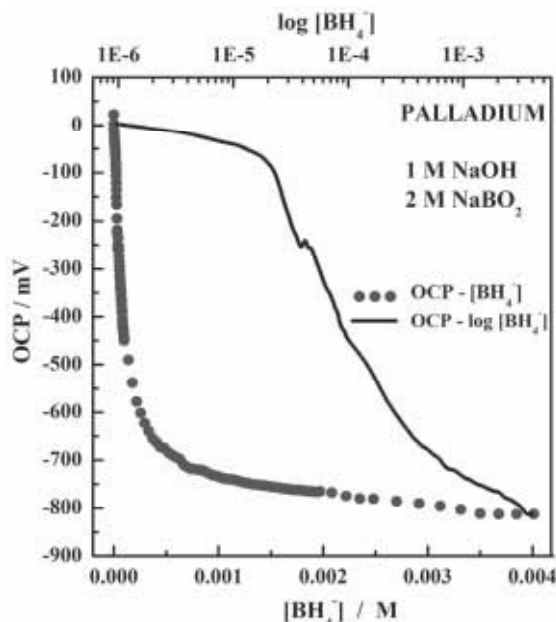


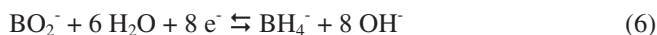
Fig. 3. OCP versus borohydride concentration for Pd.

**Niobium.** Figure 4 shows measured OCPs of Nb as a function of NaBH<sub>4</sub> concentrations in 4 M NaOH. OCPs were independent of [BH<sub>4</sub><sup>-</sup>] and approximately equal to -1.13 V; a slight decrease of -1.13 to -1.18 V was observed for [BH<sub>4</sub><sup>-</sup>] ≥ 10<sup>-1</sup> M. Niobium is a base metal, whose domain of stability lies at potentials well below those which correspond to the stability of water. For all pHs it tends to cover itself with a layer of niobium oxide. Consequently, the response of Nb to BH<sub>4</sub><sup>-</sup> would depend of its oxide stability with respect to the BH<sub>4</sub><sup>-</sup> solutions considered. For the Nb<sub>2</sub>O<sub>5</sub>/Nb couple at pH = 14, we have:



$$E = -0.601 - 0.0591 \text{pH} = -1.428 \text{ V (vs. SHE)}$$

For the BO<sub>2</sub><sup>-</sup>/BH<sub>4</sub><sup>-</sup> couple, at pH = 14, we have:



$$E = -1.24 + 0.0074 \log \left\{ \frac{[\text{BO}_2^-][\text{OH}^-]^8}{[\text{BH}_4^-]} \right\} \\ = -1.24 + 0.0074 \log [\text{BO}_2^-]/[\text{BH}_4^-] \text{ (V vs. SHE)}$$

A thermodynamic instability of Nb<sub>2</sub>O<sub>5</sub> in the presence of BH<sub>4</sub><sup>-</sup> is shown by these values, but it is clear that voltage differences in the order of 0.2 V, apart from the fact that we have observed a white thin film of good quality, strongly suggest that the coated Nb electrode is stable in NaBH<sub>4</sub> aqueous alkaline solutions.

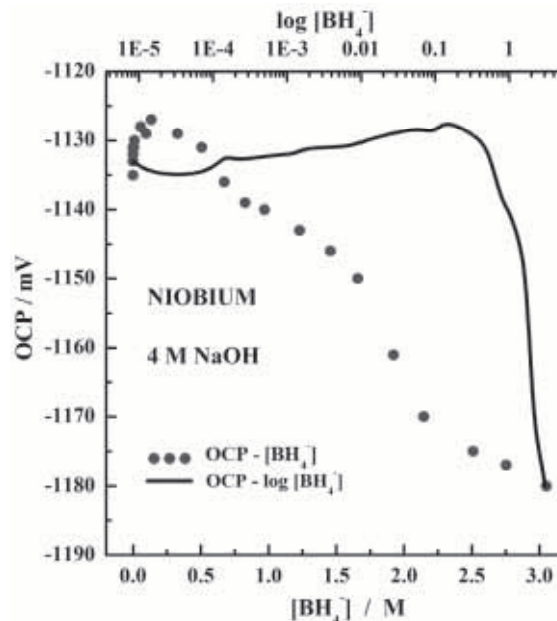


Fig. 4. OCP versus borohydride concentration for Nb.

**Gold.** Open circuit-potentials for Au were relatively constant at approximately -0.06 V for [BH<sub>4</sub><sup>-</sup>] < 10<sup>-1</sup> M. For higher BH<sub>4</sub><sup>-</sup> concentrations there was a steadily decrease of the OCP to approximately -0.66 V, and this value remained relatively constant even for very high BH<sub>4</sub><sup>-</sup> concentrations. The behaviour displayed by Au was very similar to that shown by Pt (compare Figs. 1 and 5).

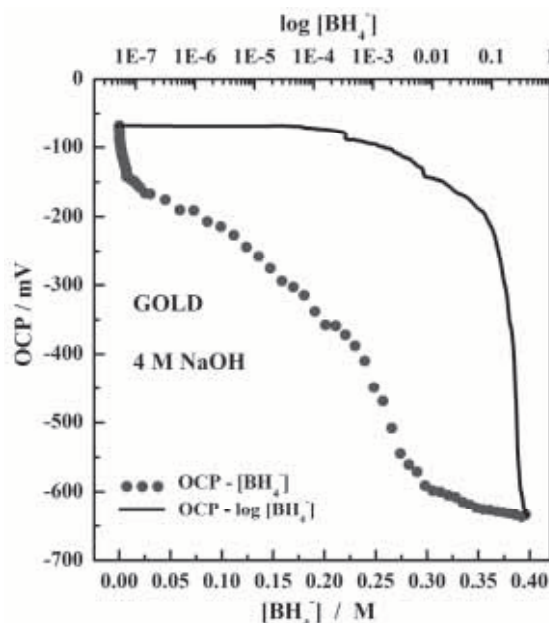
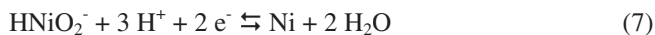


Fig. 5. OCP versus borohydride concentration for Au.

**Nickel.** Figure 6 shows the OCP-[BH<sub>4</sub><sup>-</sup>] plot for Ni at 25 °C in NaOH 4 M solution. The initial OCP for free and very diluted [BH<sub>4</sub><sup>-</sup>] solutions was about 0.0 V and did not change with time. It seems that since the dinickelate ion HNiO<sub>2</sub><sup>-</sup> is the predominant dissolved form of Ni at pH = 14, and the solution is aerated, the stationary measured potential is a mixed potential resulting from the joint action of the O<sub>2</sub>/OH<sup>-</sup> (Eq. 4) and HNiO<sub>2</sub><sup>-</sup>/Ni couples:





$$E = 0.648 - 0.0886 \text{ pH} + 0.0295 \log [\text{HNiO}_2^-]$$

$$E = 0.648 - 0.0886 \text{ pH} + 0.0295 (-17.99 + \text{pH})$$

At pH = 14, E = -0.710 V vs. SHE

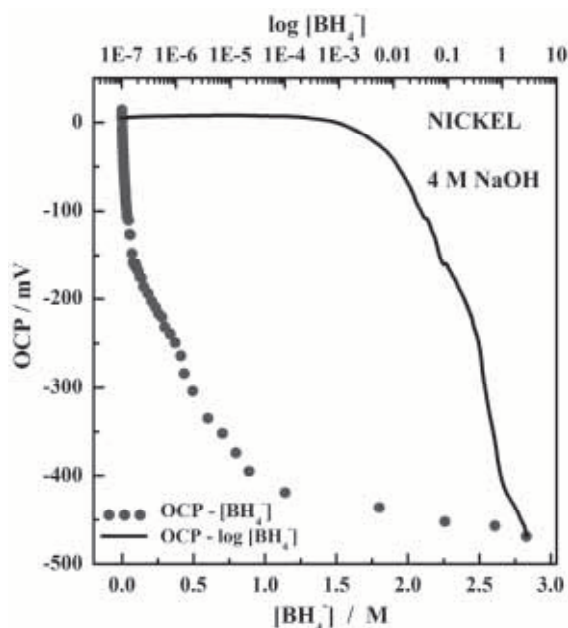


Fig. 6. OCP versus borohydride concentration for Ni.

For  $[\text{BH}_4^-] > 10^{-3} \text{ M}$  the OCP begins to decrease steadily with the  $\text{BH}_4^-$  additions, tending to a value of about -0.46 V that is probably related with the establishment of a reaction of the type:



at the Ni/solution interface.

#### 4. CONCLUDING REMARKS

A simple potentiometric method is described to monitor  $\text{BH}_4^-$  concentrations in alkaline solutions. Metal electrodes are characterised by potential responses that were tentatively explained with the help of available thermodynamic data. Studies on the chemistry/electrochemistry of metal/  $\text{BH}_4^-$  systems are underway to facilitate the analysis of the obtained data and to open up avenues for increasing the applicability and the reproducibility of the technique. The present paper is part of a series of studies [19-22] that our group has been publishing on novel materials for electrochemical energy devices.

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