

This could be explained in terms of displacement in the equilibrium conditions, promoted by the addition of KCl, with consequent increasing of the buffer ratio $\frac{m_A}{m_{H_3A}}$, not previously accounted for.

Evaluation of pH values for KH_2Cit buffer system eventually contaminated with H_3Cit is, therefore, bound to suffer from unprecise extrapolation. Nevertheless, comparison of calculated and experimental results proved to be a good indication of acid contamination and has led to the development of a methodology for the purification of the solid reagent [4].

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ANODIC OXIDATION OF DMAB AND INFLUENCE OF ADDITIVES IN ELECTROLESS PLATING

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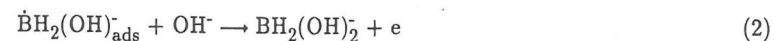
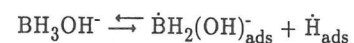
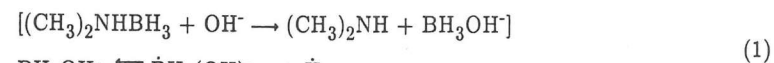
The electrochemical nature of electroless plating is widely accepted [1,2]. The electrode processes involve simultaneously the anodic oxidation of a reductant and the cathodic metal deposition and these partial reactions may proceed by several steps.

In connection with the catalytic activity of the substrates there is experimental evidence for considering the reductant oxidation the dominant factor in electroless process [3,4].

In this work specpure nickel and cobalt were used to study the electrochemical behaviour of dimethylamine borane (DMAB) in acetate containing solutions of slightly alkaline pH. The effect associated to the presence in the electrolyte of thiourea and N-methylthiourea was also considered.

At a given concentration of the reductant, Ni and Co present different behaviours, as can be seen by the evolution of the electrode open-circuit potential with time, illustrated in figure 1. However, as the concentration of DMAB increases the "induction" period is shorter for Co and Ni substrate can present catalytic activity, which suggests an interaction between the substrate and the reducing agent - e. g. adsorption as a first step.

A subsequent formation of radicals is likely to occur as well as its oxidation, reactions 1 and 2.



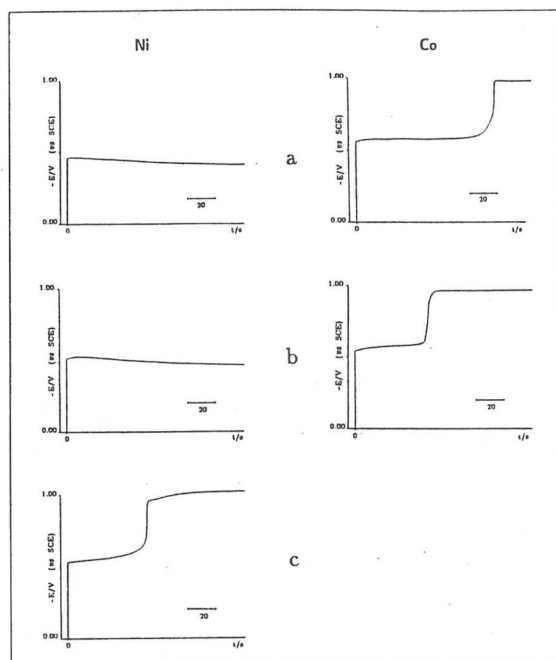
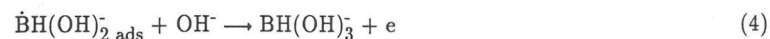


Fig. 1 : Open circuit potential evolution of Ni and Co electrodes in NaCH₃COO 0.50 M + DMAB (a) 0.05 M (b) 0.10 M (c) 0.20 M (pH = 8.7, T = 25 °C)

Additional support and information can be obtained from the analysis of potentiodynamic experiments. During the cathodic scan an anodic current peak is observed - figure 2 - which occurs at more negative potentials as the sweep rate increases, showing that the interaction between substrate and reductant is potential and time dependent.

Further dehydrogenation and oxidation may take place,



and



Reactions 4 and 5, along with 7, contribute for the current response to the anodic potential sweep,

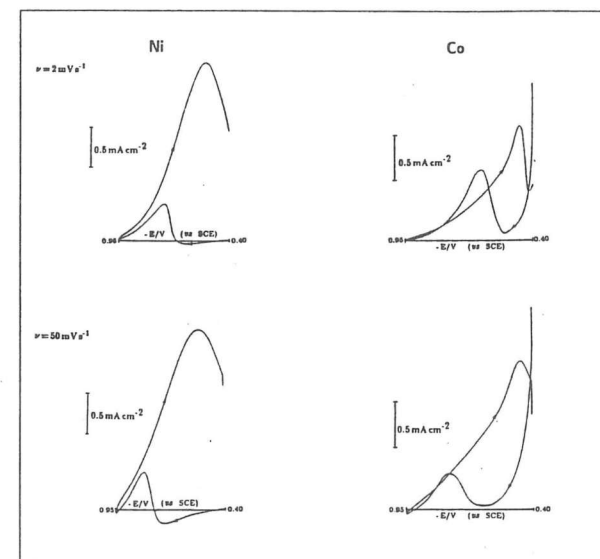


Fig. 2 : Potentiodynamic curves of Ni and Co in NaCH₃COO 0.50 M + DMAB 0.20 M (pH = 8.7 ; T = 25 °C)

With the aim of adjusting the rate of electroless metal deposition, certain organic compounds are often included in the plating solution composition [4].

To evaluate how the above described mechanism is affected, N-methylthiourea was added to the electrolyte. As shown in figure 3, there is no significant difference which can be attributed to reactions 1 and 2. However, the extent of second radical formation and its oxidation is reduced as well as the amount of BH₃OH⁻ in the interface.

For a smaller molecule, thiourea, the induction period is strongly affected (figure 4a). Although under a controlled applied potential reaction 2 seems to be unaffected (figure 4b) the interaction substrate/BH₂(OH)₂⁻ is substantially hindered and a noticeable decrease in the current during anodic sweep is observed (figure 4c).

The results presented here show the importance of reactions 4 and 6 for the overall process. A more detailed analysis of competitive adsorption, when sulphur containing organic additives are present in the solution must consider both its rate of diffusion to the electrode and the reductant and additive concentrations ratio.

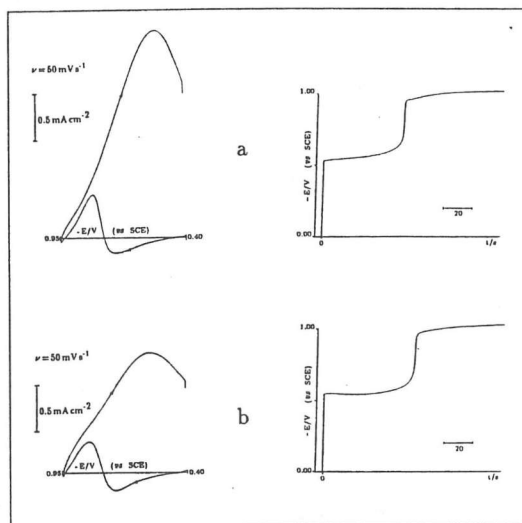


Fig. 3 : Comparison of potentiodynamic responses and open circuit potentials of Ni in electrolyte additive free (a) and containing N-methylthiourea (b).

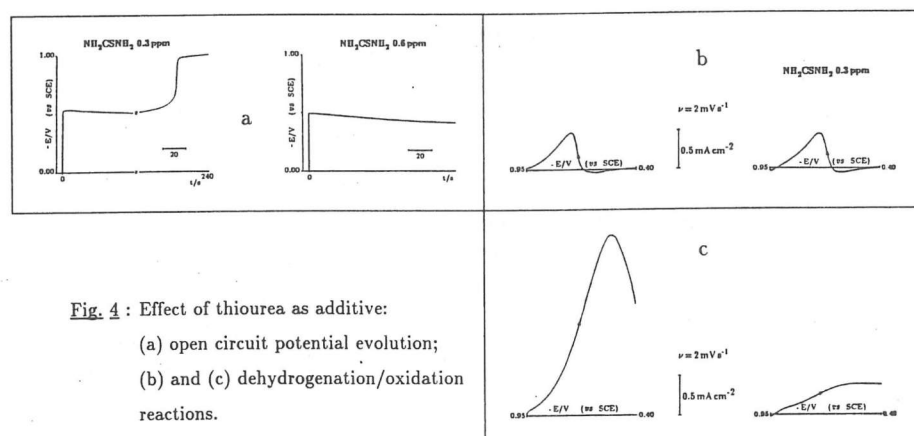


Fig. 4 : Effect of thiourea as additive:
(a) open circuit potential evolution;
(b) and (c) dehydrogenation/oxidation reactions.

(NaCH_3COO 0.50 M + DMAB 0.20 M + thiourea as indicated)

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Oxime-imine reduction in the liquid-gas interface in Fast Atom Bombardment Mass Spectrometry: an electrochemical analogy

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Introduction

The advent of the so-called "soft" ionization methods in Mass Spectrometry, such as Fast Atom Bombardment (FAB) and Liquid Secondary Ion Mass Spectrometry (LSIMS), where the samples under analysis are dissolved or suspended in liquid matrices, enlarged the field of the aforementioned technique from purely gas-phase chemistry to condensed-phase chemistry. Different types of reactions were shown to occur under FAB conditions in the liquid-gas interface: acid-base, substitution and addition, oxidation-reduction and others. Despite the large amount of data obtained since the discovery (1), or as some claim the rediscovery (2), of FAB, the first attempt to establish a systematic correlation between the formation of some ionic species in FAB and LSIMS and the half-wave potential of their neutral counterparts was not made until a later date (3).

As the oxime-imine reduction in the liquid-gas interface in FAB Mass Spectrometry has been found to be relevant in the elucidation of the mechanism of FAB ionization (4), the study of its relation with the electrochemical behaviour in solution of the same system was undertaken.

Results and discussion

FAB Mass Spectrometry was used in positive and in negative mode for aromatic oximes, I, and hydroxyoximes, II. The mass spectra of the two types of compounds show peaks at m/z values corresponding to $[M+H]^+$ and $[(M+H)-O]^+$ ions, (M being the neutral oxime). We observed that the relative abundances of $[M+H]^+$ ions decrease whereas the relative abundances of the $[(M+H)-O]^+$ ions increase with increasing time.

