JOURNAL OF APPLIED ELECTROCHEMISTRY **23** (1993) 339–345

Influence of additives on the electrodeposition of nickel from a Watts bath: a cyclic voltammetric study

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Received 16 June 1992; revised 28 July 1992

The electrochemical reactions occurring during the deposition of nickel from a Watts bath have been examined using a voltammetric technique. The important reactions taking place at the anode and cathode have been systematically identified. The influence of the additives on the cathodic and anodic reactions show the importance of careful bath preparation for a quality controlled product. From the surface coverage data, the free energy change (ΔG_a^0) for the adsorption of the brighteners has been calculated and compared with results from methods used earlier.

1. Introduction

It is known that organic additives are added in traces to electroplating baths to modify the structure, morphology and properties of the metal deposits. For nickel plating from the Watts bath (WB), two types of additives, such as aromatic sulphones or sulphonates and compounds containing unsaturated groups such as $>C=O$, $>N-C=S$, $-C=N$ etc. are recognized as brighteners [1]. The influence of the additives as brighteners during electroplating is not yet, clearly understood [2]. In recent years the cyclic voltammetric technique has been extensively used in diagnosing the mechanisms of electrode processes. However, it has been applied only to a limited extent for deposition processes [3, 4]. In the present communication results pertaining to cyclic voltammetric investigations of a Watts bath containing coumarin, substituted coumarin, naphthalene disulphonic acid and *p*-toluene sulphonamide are reported.

2. Experimental details

The solutions were prepared using distilled water and analytical grade chemicals. Additives such as coumarin (C), 6-nitrocoumarin (NC), 7-4-dimethyl coumarin (DMC), naphthalene disulphonic acid (NDS), *p*-toluene sulphonamide (PTS) and *d*-10, camphorsulphonic acid (CSA) were recrystallized before use. Experiments were conducted at 298 ± 0.1 K and pH 4.0 under a nitrogen atmosphere using a Watts bath solution: 0.22 M $NiSO_4 \cdot 7H_2O$, 0.33 M $NiCl_2 \cdot 6H_2O$ and 0.13 M H_3BO_3.

An all glass single compartment cell of 50 ml capacity was used. A working platinum electrode of area 0.5 cm^2 was used along with two platinum counter electrodes. The electrodes were pre-cleaned by the normal procedures [5] before use. Cyclic voltammetric and chronoamperometric studies were carried out using a scanning potentiostat (PAR model 362 USA). The voltammograms were recorded after obtaining reproducible traces on repeated scanning.

3. Results

3.1. *Studies in the potential region −0.70 to +1.65 V*

Figure 1 shows cyclic voltammograms recorded in the Watts bath when the platinum electrode was cycled at different scan rates between −0.70 V and +1.65 V. Three cathodic peaks c_I, c_{II} and c_{III} and an anodic peak a_I appear. In order to understand the nature of the reactions corresponding to these peaks, a systematic study was undertaken. The voltammogram in Fig. 2 obtained at the scan rate of 50 mV s^{-1} in 0.22 M $NiSO_4$ alone shows the disappearance of the current peaks a_I, c_I and c_{III} (curve 1). The cathodic peak c_{II} also disappeared on stirring the solution. The addition of $NiCl_2$ to the $NiSO_4$ solution resulted in the original voltammogram (Fig. 1, curve 2). However, addition of H_3BO_3 to the $NiSO_4$ solution brought back the c_{III} peak only, the current of which increased with increase in the concentration (0.6 M) of H_3BO_3 in the plating bath solution (Fig. 2, curve 2). When the brighteners – (C), (NC), (DMC), (NDS), (PTS) and (CSA) – were added in traces (10^{-4}–10^{-5} M) similar voltammograms to that of Fig. 1, but with the peak currents affected significantly, were obtained (Fig. 3).

3.2. *Studies in the potential region −1.40 to +1.35 V*

Voltammograms recorded at a scan rate of 50 mV s^{-1}

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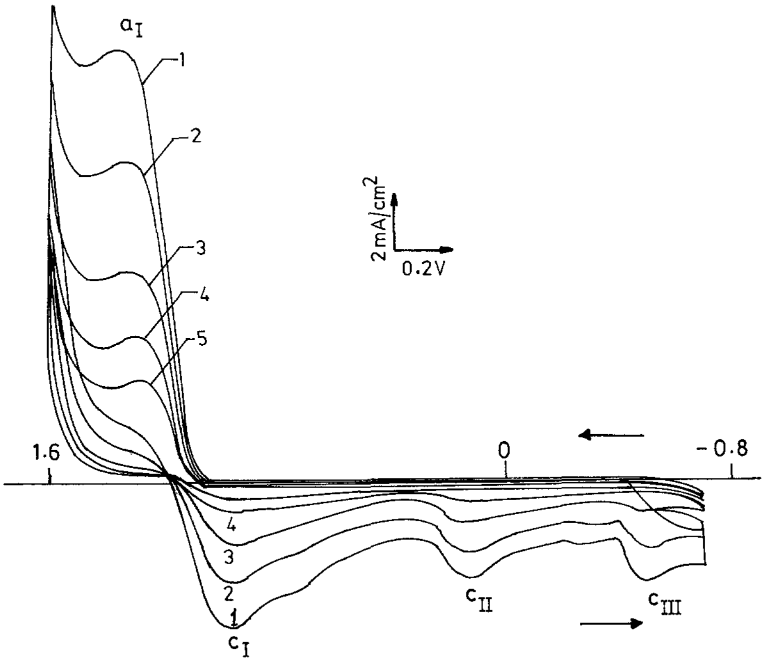

Fig. 1. Cyclic voltammogram obtained on platinum in Watts bath in the potential range of -0.70 to $+1.65$ V as a function of the sweep rate: (1) 100, (2) 50, (3) 20, (4) 10 and (5) 5 mV.

beginning from -1.40 V, with and without additives are shown in Fig. 4. Two anodic, a_{II} and a_{III}, and a cathodic, c_{IV} peaks appear and the cathodic peak current at the extreme negative potential is large. The voltammetric peaks a_{II}, a_{III} and c_{IV} are also influenced by the additives in a similar way to that shown in Fig. 3 of the previous section.

Further potential step measurements were carried out in the region between -0.80 V and -1.40 V. The current-time transients recorded at platinum in a Watts bath with and without coumarin are presented in Fig. 5.

4. Discussion

As the potential range studied is wide (-1.40 to $+1.65$ V) and the plating bath solution contains different ions, several electrode reactions are possible. In order to understand these reactions, cyclic voltammetric results were obtained by cycling the electrode in two segments of the potential range and by altering the composition or condition of the solution when required.

4.1. *Reactions in the potential region -0.70 to $+1.65$ V*

The cyclic voltammogram recorded with the platinum electrode cycled between -0.70 V and $+1.65$ V in the Watts bath (Fig. 1) consists of an anodic current peak, a_I, and three cathodic current peaks, c_I, c_{II} and c_{III}. The influence of scan rate on these current peaks reveal that the majority of the corresponding reactions are irreversible. The disappearance of the current peaks a_I and c_I in the voltammogram recorded in the absence of nickel chloride (Fig. 2, curve 1) indicates that these peaks are associated with the chloride ion. The anodic peak a_I, appearing at about $+1.40$ V, is

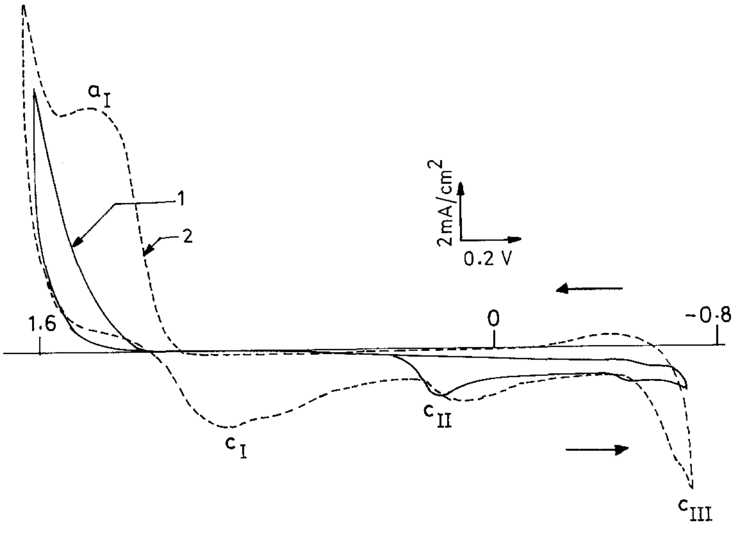

Fig. 2. Cyclic voltammograms obtained on platinum in the absence of $NiCl_2$ (curve 1) and in the presence of excess H_3BO_3 (curve 2) from Watts bath in the potential range of -0.70 to $+1.65$ V at a scan rate of 50 mV s^{-1}.

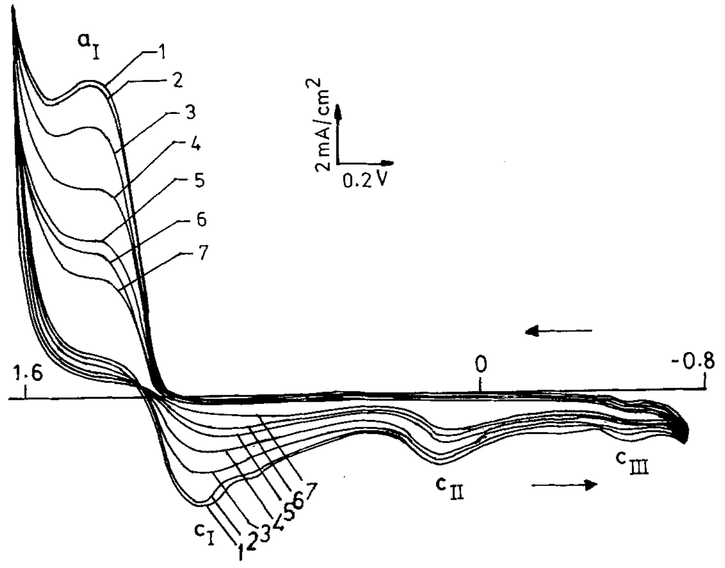

Fig. 3. The effect of additives on the cyclic voltammograms obtained on platinum in Watts bath from -0.70 to $+1.65$ V at a scan rate of 50 mV s^{-1}. Key: (1) CSA, (2) WB, (3) DMC, (4) NDS, (5) PTS, (6) C and (7) NC.

therefore due to the oxidation of the chloride ion.

$$2Cl^- \longrightarrow Cl_2 + 2e^- \qquad (1)$$

The increasing current thereafter is due to the commencement of oxygen evolution.

$$2H_2O \longrightarrow O_2 + 4H^+ + 4e^- \qquad (2)$$

The potential sweep was reversed at $+1.65$ V before vigorous evolution of oxygen took place. Consequently, the pre-electrode layer of the quiescent electrolyte is likely to be concentrated with chlorine molecules formed by Reaction 1. During the reverse scan, reduction of chlorine (reverse of Reaction 1) takes place. The hump on the peak c_I indicates that this reaction probably proceeds in two separate steps [6].

$$Cl_2 + e^- \longrightarrow Cl_{ad} + Cl^- \qquad (3)$$

$$Cl_{ad} + e^- \longrightarrow Cl^- \qquad (4)$$

The evolved or adsorbed oxygen species by Reaction 2 is reduced in the cathodic scan resulting in

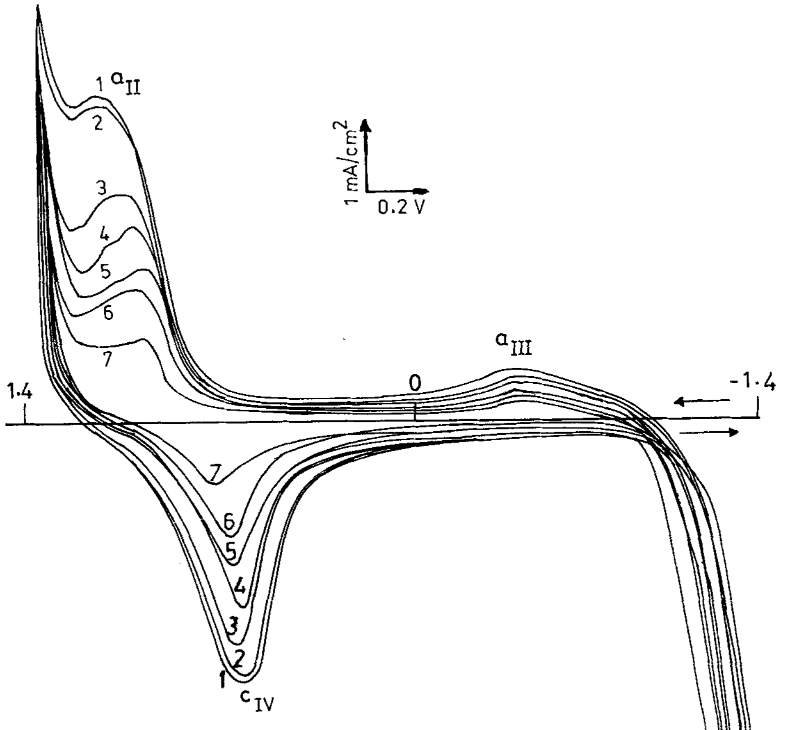

Fig. 4. Cyclic voltammograms obtained on platinum with and without additives in the Watts bath at a sweep rate of 50 mV s^{-1} in the potential range of -1.40 to $+1.35$ V. Key: (1) CSA, (2) WB, (3) DMC, (4) NDS, (5) PTS, (6) C and (7) NC.

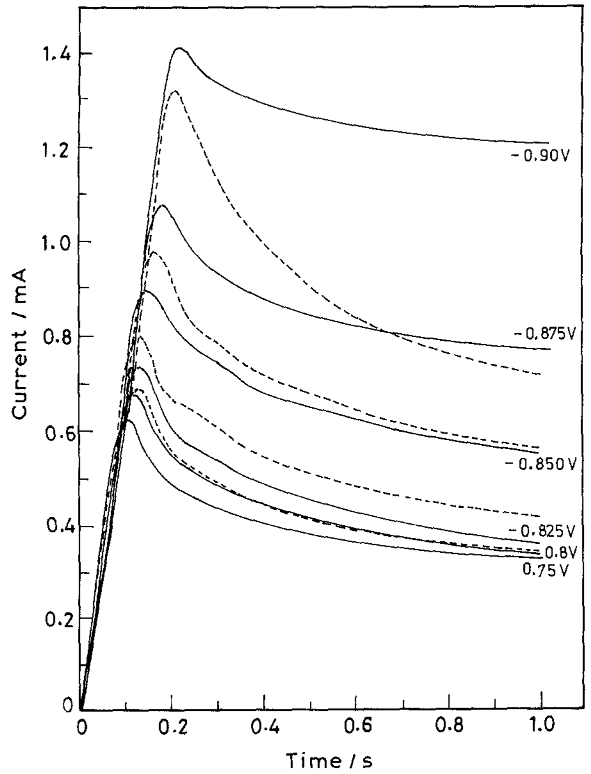

Fig. 5. The effect of coumarin on the potentiostatic current time transients for the deposition of nickel on platinum from Watts bath. (——) WB, (– – –) C.

peak c_{II} similar to that observed at platinum in dilute acidic solution [7]. It is known that the hydrogen reduction reaction occurs reversibly on the platinum surface and at low pH.

$$2H_2O + 2e^- \longrightarrow H_2 \qquad (5)$$

The peak c_{III} is associated with hydrogen evolution and its subsequent reduction in the anodic scan. It was further observed that this peak current increased with boric acid concentration (0.6 M, Fig. 2, curve 2). Thus, it is likely that the reduction of boric acid to diborane occurs at this potential [8].

$$2H_3BO_3 + 12H^+ + 12e^- \longrightarrow B_2H_6 + 6H_2O \qquad (6)$$

The diborane enriched solution becomes readily hydrogen saturated through the hydrolysis reaction [9] and the anodic

$$B_2H_6 + H_2O \longrightarrow H_3BO_3 + H_2 \qquad (7)$$

oxidation of the borohydride ion is known to ionize the evolved hydrogen [10].

4.2. *Reactions in the potential region − 1.40 to + 1.35 V*

When the platinum electrode was cycled between − 1.40 V and + 1.35 V in the Watts bath, the voltammograms recorded during the initial few cycles were not

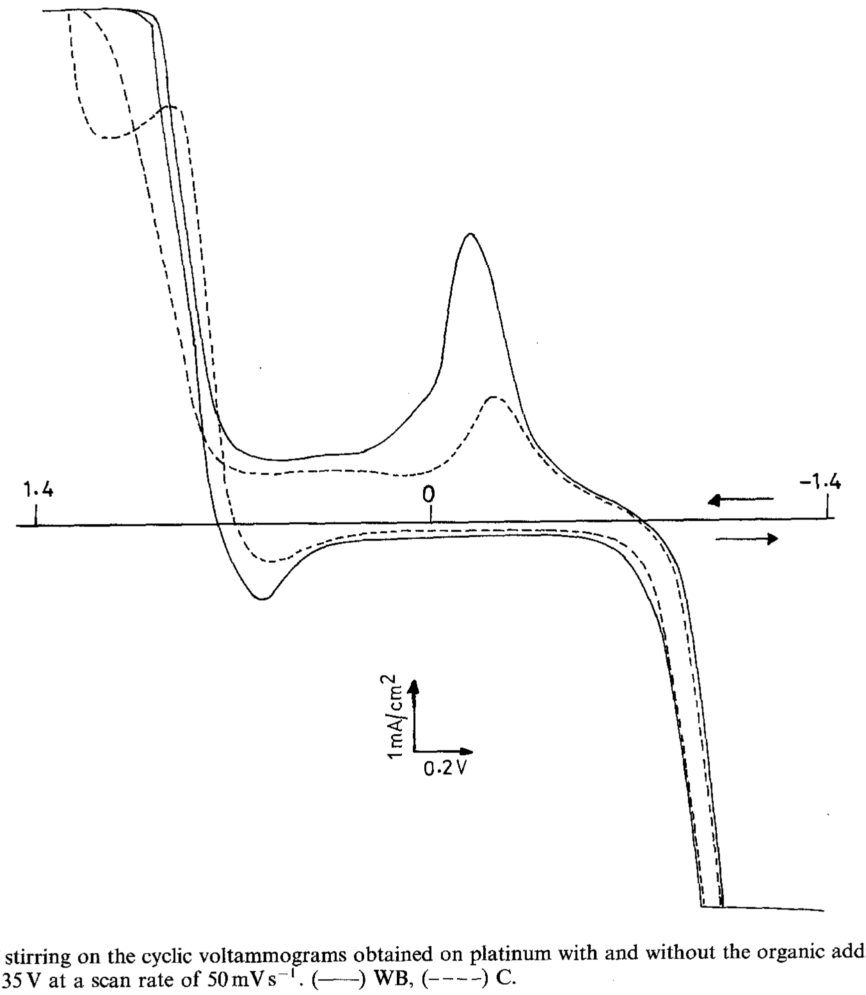

Fig. 6. The effect of stirring on the cyclic voltammograms obtained on platinum with and without the organic additive in the Watts bath from − 1.40 to + 1.35 V at a scan rate of 50 mV s^{-1}. (——) WB, (----) C.

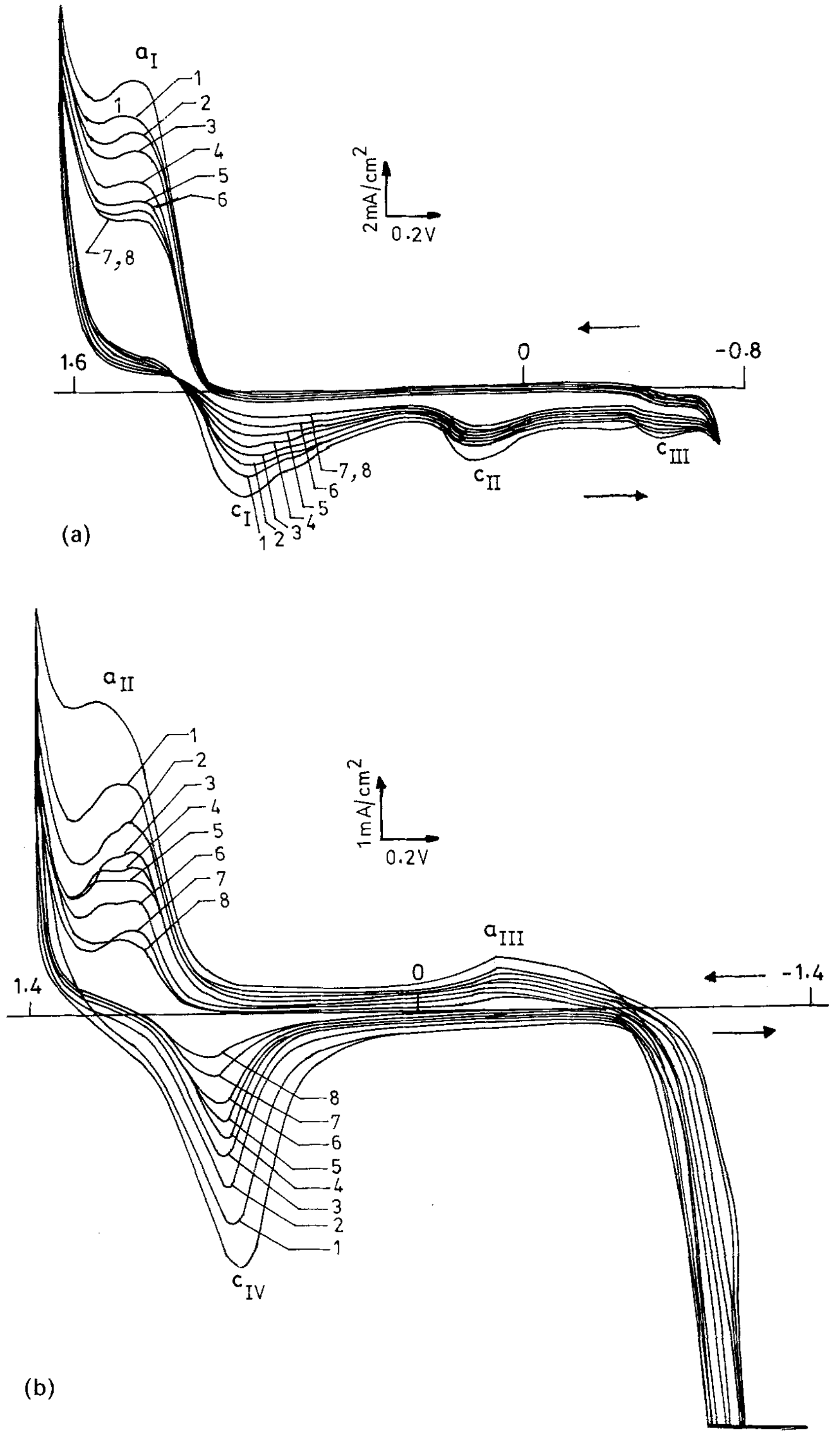

Fig. 7. Cyclic voltammograms obtained on platinum with varying concentrations of coumarin (from curve 1, 0.01×10^{-4} M to curve 8, 5×10^{-4} M) in the Watts bath at a scan rate of $50\,\mathrm{mV\,s^{-1}}$ in the potential range (a) -0.70 to $+1.65$ V and (b) -1.40 to $+1.35$ V.

reproducible in the potential region 0.80–1.35 V. However, reproducible voltammograms (Fig. 4) obtained after repeated scanning, showed the presence of anodic peaks a_{II} and a_{III} and a cathodic peak c_{IV} at $+0.75$ V (which are absent when the cathodic limit is -0.70 V). The appearance of a_{II}, a_{III} and c_{IV} and the disappearance of a_I, c_I, c_{II} and c_{III} in the range from -1.40 to $+1.35$ V can be attributed to the electrode processes taking place at potentials below -0.70 V.

The increasing current at about -0.80 V is due to the deposition of nickel on platinum (Reaction 8) and the evolution of hydrogen (Reaction 5) which take place at potentials [11] close to each other. As a result of these two reactions,

$$Ni^{2+} + 2e^- \longrightarrow Ni \qquad (8)$$

the platinum electrode in the unstirred solution is now deposited with nickel and the solution around it is more alkaline. Consequently, nickel present in this solution region precipitates as $Ni(OH)_2$ and deposits on the electrode. During the anodic potential sweep $Ni(OH)_2$ undergoes oxidation (Reaction 9) resulting in

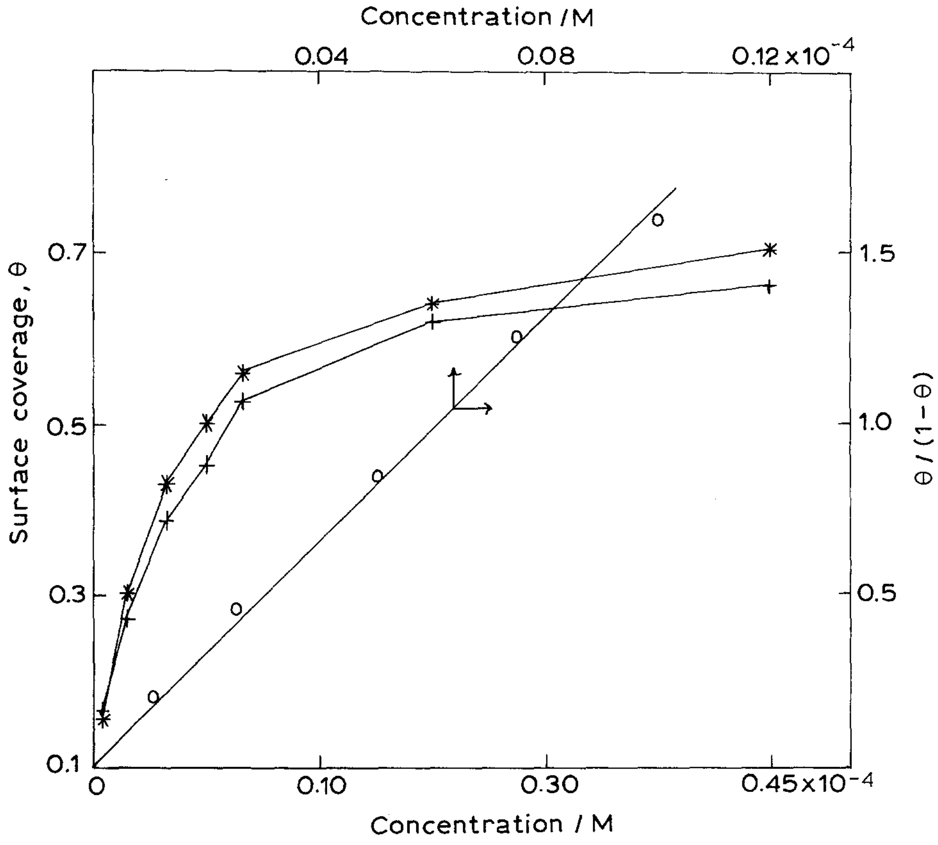

Fig. 8. Plot of surface coverage (θ) against the concentration C of coumarin showing Langmuir type of adsorption (∗) βNiOOH reduction, (+) chlorine reduction; and $\theta/(1-\theta)$ against concentration to evaluate ΔG_a^0 (o).

the current peak a_{II}.

$$\mathrm{Ni(OH)_2 + OH^- \rightleftharpoons \beta\ NiOOH + H_2O + e^-} \tag{9}$$

This is known to proceed reversibly [12] and, thus, the current peak c_{IV} is due to the cathodic Reaction 9. Above +1.30 V the evolution of oxygen occurs. The appearance of a_{II} and c_{IV} after repeated scanning only, may be attributed to the presence of the chloride ion, which depassivates the anode and, thus, its oxidation process (Reaction 1) which competes with the oxide formation (Reaction 9) makes the voltammograms less reproducible.

The peak current a_{III} due to the hydrogen oxidation (discussed in Section 4.1) is very distinct, although the corresponding cathodic peak c_{III} associated with hydrogen evolution and boric acid reduction is less distinguishable. This is because both the hydrogen evolution and boric acid reduction reactions shift towards more negative potential and merge with the nickel deposition region.

The above arguments are further confirmed by recording the voltammograms under stirred conditions (Fig. 6, curve 1) where the system is more homogeneous. The formation of the oxide is not seen due to the lower pH of the solution and new anodic peaks of hydrogen oxidation, followed by nickel dissolution, are observed, as reported by Hoare [13]. The current due to the evolution of chlorine and oxygen beyond +0.70 V is large, although the reduction current is less because of the effect of stirring.

4.3. *Adsorption of organic additives*

Of the various organic compounds added to the solution, it is observed in Figs 3 and 4 that all the compounds except (CSA) decrease the peak currents of the reactions discussed earlier. The decrease in peak currents by these additives indicate that they undergo adsorption [14] at the platinum/electrolyte interface. It is interesting to note that the effect of adsorption is present over the wide potential range scanned both in the stirred (Fig. 6, curve 2) and unstirred conditions. In order to closely examine the adsorption effect on the nickel deposition process (Reaction 5) chronamperometric transients for the nucleation and growth of nickel on platinum was studied in the potential region −0.80 to −1.40 V. It is found that the additive (coumarin) added to the plating solution affects the nickel deposition process by reducing the peak and growth currents (Fig. 5).

Further the results of the effect of the concentration of coumarin (Fig. 7a and b) reveal that the voltammetric pattern is unchanged, the peak currents decrease with increase in the concentration of coumarin, both at the platinum and nickel surfaces. The organic brighteners used in the plating baths are known to be adsorbed at the metal solution interface [15]. Thus the surface coverage (θ) of coumarin is calculated by measuring the peak currents of the voltammograms obtained with (i_p^*) and without (i_p) coumarin in the solution using the equation:

$$\theta = 1 - i_p^*/i_p \tag{I}$$

The surface coverage calculated from the peaks corresponding to the cathodic reductions of chlorine and βNiOOH is plotted as a function of the concentration of coumarin (Fig. 8). The maximum coverage (θ_{max}) exhibited by coumarin is in the range 0.6–0.8. An examination of the above data confirms that the adsorption of coumarin on platinum during nickel deposition follows a Langmuir type adsorption given by:

$$\theta/(1 - \theta) = KC \qquad \text{(II)}$$

From the adsorption isotherm shown in Fig. 8 the adsorption constant K was evaluated to be $14 \times 10^4 M^{-1}$. The standard free energy change (ΔG_a^0) for adsorption was estimated using the quation:

$$\Delta G_a^0 = -RT \ln (55.5K) \qquad \text{(III)}$$

in a similar way as reported for organic molecules [16]. The large value of free energy change of -39 kJ mol^{-1} confirms the earlier findings that coumarin undergoes reduction followed by chemisorption at the metal solution interface [17]. Further, it has been observed that the evaluation of the adsorption parameters of the additives by the cyclic voltammetric technique is in close agreement with those calculated by the cathodic polarization or the exchange current density method as reported earlier [18]. Thus this method can also be used to study the thermodynamic and kinetic aspects of the adsorption processes.

5. Conclusions

The present cyclic voltammetry study throws light on the various electrochemical reactions taking place during the deposition of nickel from a Watts bath. From these observations it may be concluded that, during direct current deposition, the main reactions taking place at the cathode are: the reduction of (i) nickel ions, (ii) boric acid, and (iii) hydrogen ions, while that at the anode are (i) oxygen evolution, (ii) chloride oxidation, and (iii) hydroxide formation (in the unstirred bath). The effect of stirring on the overall electrochemical reactions shows the significance of bath agitation in controlling the plating process to obtain deposits of desired quality. The influence of the adsorbants at the cathode is observed at the anode. Of the important reactions, the suppression of the reduction of nickel ions at the cathode and the oxidation of chloride at the anode are significant. The participation of boric acid in the electrochemical reactions gives further insight into the understanding of its catalytic, buffering or complexing action.

Acknowledgements

One of the authors (TM) thanks CSIR, New Delhi for a Senior Research Fellowship.

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