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Zinc electrowinning from acidic sulphate solutions. Part III: Effects of quaternary ammonium bromides

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Abstract

The effects of the organic additives cetyltrimethylammonium bromide (CTABr) and tetrabutyl ammonium bromide (TBABr) on the electrowinning of zinc from acidic sulphate solutions were studied in the presence and absence of trace amounts of antimony(III). The results indicated that CTABr has similar properties to the commonly used industrial additive glue with respect to current efficiency, power consumption, polarization behaviour, and the crystallographic orientation and surface morphology of the zinc deposits. TBABr was generally less useful with respect to all these properties. Voltammetric studies indicate that polarisation for zinc electrodeposition decreased in the order CTABr > glue > TBABr. The nature of the electrode reactions were investigated through measurements of exchange current densities, Tafel slopes and transfer coefficients.

1. Introduction

The role of metallic impurities [1–6] in the acidic sulphate electrolytic solutions used industrially for zinc electrowinning is complex. Such impurities decrease the current efficiency (CE), lower the quality of the zinc deposits and increase the power consumption during zinc electrowinning process. Although high purity zinc can be electrowon with high CE using ultrapure zinc sulphate solutions, this is uneconomical on the industrial scale since it consists of costly purification steps. It is well known that suitable organic additives are used during zinc electrowinning to reduce the harmful effects of metallic impurities present in the cell feed solution. These organic additives [7–18] do so either by increasing the induction period or by forming complex with the harmful metallic impurities.

Among the many organic additives which have been used, glue [19–23] and gum arabic [24] are of industrial importance. Nevertheless, research is being continued for better additives. For example, additives like 2-butyne-1,4-diol [11], nonylphenoloxyethylene [16] and a combination of nonylphenolpolyethyleneglycol, dinaphthylmethane-4,4′-disulphuric acid and polyethylene–glycol [17, 18] have been reported to be superior to glue and gum arabic. The present authors have investigated the use of 2-picoline [25], 4-ethylpyridine and 2-cyanopyridine [26], and sodium laurylsulphate (SLS) [27] as alternatives to gum arabic and glue. Gum arabic, 2-picoline, 4-ethyl pyridine and 2-cyanopyridine showed a reduction in CE at all concentrations [25, 26] but glue and SLS showed an increase in CE at 5 and 1 $\mathrm{mg\,dm^{-3}}$, respectively [27]. However, a reduction in CE was seen at higher concentrations of glue and SLS. When combined with antimony(III) in solution all additives showed an increase in CE except gum arabic where reduction in CE was observed [25–27].

A variety of quaternary ammonium salts have also been investigated as additives for zinc electrowinning. MacKinnon et al. [28] have found that tetrabutylammonium chloride (TBACl) was an effective levelling agent for zinc electrodeposits in chloride media. Cruz et al. [29] reported an increase in overpotential at some concentrations of TBACl in both chloride and perchlorate media. At higher concentrations, blocking of the electrode surface was observed but no definite correlations were found between the degree of surface leveling, additive concentration and change in overpotential. The present authors [30] have investigated triethylbenzylammonium chloride (TEBACl) and showed it to be better than glue as an additive. The influence of TEBACl on the kinetics of zinc deposition and dissolution in acidic sulphate electrolytic solution containing Ni^{2+} ions has also been investigated [31]. TEBACl was found to decrease the screening effect of hydrogen bubbles responsible for the formation of local galvanic cells [32, 33] and to increase the induction period for the dissolution of electrodeposited zinc in nickel-containing solutions. Addition of cetyltrimethylammonium bromide (CTABr) to zinc electrolytic solutions during electrodeposition has been found to show varied effects of hydrogen absorption in acid and alkaline baths [34, 35]. Bressan and Wiart [36] have shown that tetrabutylammonium bromide (TBABr) is effective in inhibiting dendrite formation during zinc deposition from Leclanché cell electrolytes. Diggle and Demjanovic [9] have also found that TBABr acts as a suppressor of dendritic growth and that it can increase the compactness of the zinc deposits in alkaline zincate solutions.

As part of a continuing search for more suitable organic additives for the electrowinning of zinc from acidic sulphate solutions, the present paper reports the effects of CTABr and TBABr on the current efficiency, power consumption, polarisation behaviour and deposit morphology during the electrowinning of zinc from acidic sulphate solutions. The results have been compared with those obtained with the industrial additive glue.

2. Experimental details

The experimental procedures and the composition of the electrolyte used in this work were similar to those described previously [27]. CTABr and TBABr were obtained from Spectrochem, Bombay, India. A PAR model 362 scanning potentiostat connected to an X–Y recorder was used for the polarisation studies. All the polarisation measurements were performed at ambient temperature. The working electrode of area 1 cm^2 was made from high purity (99.99%) aluminium. A platinum sheet was used as the auxiliary electrode and a saturated calomel (SCE) as the reference electrode. Cyclic voltammetry was carried out by initiating scans at -0.7 V vs SCE and cycling between -0.7 to -1.3 V vs SCE using a 10 mV s^{-1} scan rate. Deposit morphology was examined by using a SEM (SE 101B) and a X-ray diffractometer (PW 1050) was used to determine the preferred crystal orientation of the zinc deposits relative to ASTM standard zinc powder.

3. Results and discussion

3.1. *Current efficiency and power consumption*

The effects of CTABr and TBABr on current efficiency and power consumption were studied over an additive concentration range of 0–40 mg dm^{-3} (Table 1). In the absence of additive, the current efficiency is ~89% . At 0.5 mg dm^{-3} CTABr the CE increases to ~92% and goes through a maximum of 93% at 1 mg dm^{-3} then drops steadily to ~79% at 40 mg dm^{-3}. With TBABr there is a steady increase in CE reaching a maximum (93%) at 10 mg dm^{-3} which drops to 91% at 40 mg dm^{-3}. These trends are similar to that of glue [27] where a CE of ~92% was achieved at 5 mg dm^{-3} which subsequently dropped to 67% at 40 mg dm^{-3}. Decreases in CE with increasing additive concentrations have been ascribed to the blocking of the active nucleation sites of the cathode surface by adsorption of the additive [16, 21, 27, 30, 37, 38], which results in an increase in the interfacial viscosity and slows the zinc deposition rate by decreasing the mass transfer rate.

Among the metallic impurities which commonly occur in acidic zinc sulphate solutions, antimony is regarded as the most harmful for zinc electrodeposition [2, 5, 6, 21]. Nevertheless, traces of antimony(III) in electrowinning solutions in the presence of organic additives have been shown [25–27, 30] to produce high CEs with good deposit morphologies. The presence of 0.01 mg dm^{-3} Sb(III) with 1 mg dm^{-3} CTABr increased the CE to ~94% although it decreased with further increases in either additive or Sb(III) concentrations. On the other hand, Sb(III) had an adverse effect in presence of TBABr at all concentrations studied. For example, addition of 10 mg dm^{-3} TBABr to the zinc electrolyte increased the CE to 93%, but, on addition of 0.01 and 0.04 mg dm^{-3} Sb(III), the CE decreased to ~90% and ~80% respectively.

The effects of CTABr and TBABr, alone or in the presence of Sb(III), on power consumption are also listed in Table 1. With CTABr alone, the maximum reduction

Table 1. The effects of CTABr and TBABr on current efficiency and power consumption

[Additive]/mg dm^{-3}	[Sb(III)]/mg dm^{-3}	CE/%	PC/kWh t^{-1}	Preferred crystal orientation/($h\ k\ l$)
CTABr				
0	0	89.3	2608	(1 0 1) (0 0 2) (1 0 0) (1 0 3)
0.5	0	92.4	2557	
1	0	93.0	2549	(1 0 1) (1 0 2) (1 1 2) (1 0 3)
1	0.01	94.2	2516	(1 0 1) (1 0 2) (1 1 2) (1 0 3)
1	0.04	89.5	2658	(1 0 1) (1 0 2) (1 0 3) (1 1 2)
2	0	92.7	2566	(0 0 2) (1 0 2) (1 0 1) (1 0 3)
5	0	91.4	2611	(0 0 2) (1 0 1) (1 0 2) (1 1 0)
40	0	78.6	3068	(1 0 1) (1 0 2) (2 0 1) (2 0 3)
TBABr				
2	0	89.5	2658	(1 0 1) (1 1 0) (1 1 2) (1 0 3)
5	0	90.7	2641	(1 0 1) (1 0 2) (2 0 1) (1 0 0)
10	0	93.0	2575	(1 0 1) (2 0 1) (1 0 0) (1 0 2)
10	0.01	89.6	2664	
10	0.04	80.1	2970	(1 0 1) (1 0 0) (1 0 2) (0 0 2)
40	0	91.0	2650	(1 0 1) (0 0 2) (1 1 0) (1 1 2)

in power consumption was 60 kWh t^{-1} at an additive concentration of 1 mg dm^{-3}. A further reduction of 30 kWh t^{-1} was achieved with the addition of 0.01 mg dm^{-3} Sb(III). With TBABr alone, the maximum reduction in power consumption was ~30 kWh t^{-1} at an additive concentration of 10 mg dm^{-3} but it increased with Sb(III) in solution even at very low concentration (0.01 mg dm^{-3}).

3.2. *Polarization behaviour*

The effects of CTABr and TBABr on the cathodic polarisation of zinc electrodeposition were investigated by linear sweep and cyclic voltammetry. Addition of CTABr and TBABr (0–40 mg dm^{-3}) shifted the polarisation curves for zinc electrodeposition to more negative potentials (Figures 1 and 2). But at very high concentration (i.e., at 200 mg dm^{-3}) very strong polarization was observed. For both the additives the nucleation overpotential (NOP) values increase with increase in additive concentrations (Figures 3(a) and 4(a)). However, the effect of CTABr, which is similar to that of glue [27, 30], is greater than that of TBABr. For addition free solution the NOP value is 116 mV [27]. But in presence of 2 mg dm^{-3} CTABr it becomes 130 mV. At 5 mg dm^{-3} TBABr the NOP value becomes 122 mV, which is less than that of glue (126 mV at 5 mg dm^{-3}) [27, 30]. Thus the overall polarizing effect of these additives is: CTABr > glue > TBABr.

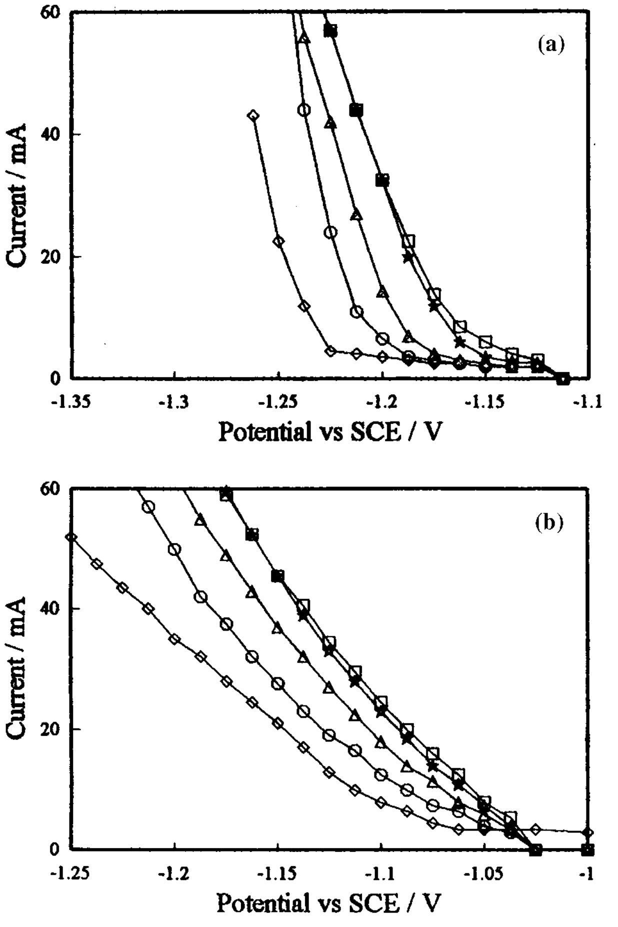

Fig. 1. Effect of CTABr on the cathodic polarization during zinc deposition on (a) aluminium (b) zinc, from solution containing 55 g dm^{-3} Zn and 150 g dm^{-3} H_2SO_4. CTABr concentrations; (–□–) blank, (–▲–) 2, (–△–) 10, (–○–) 40, (–◇–) 200 mg dm^{-3}.

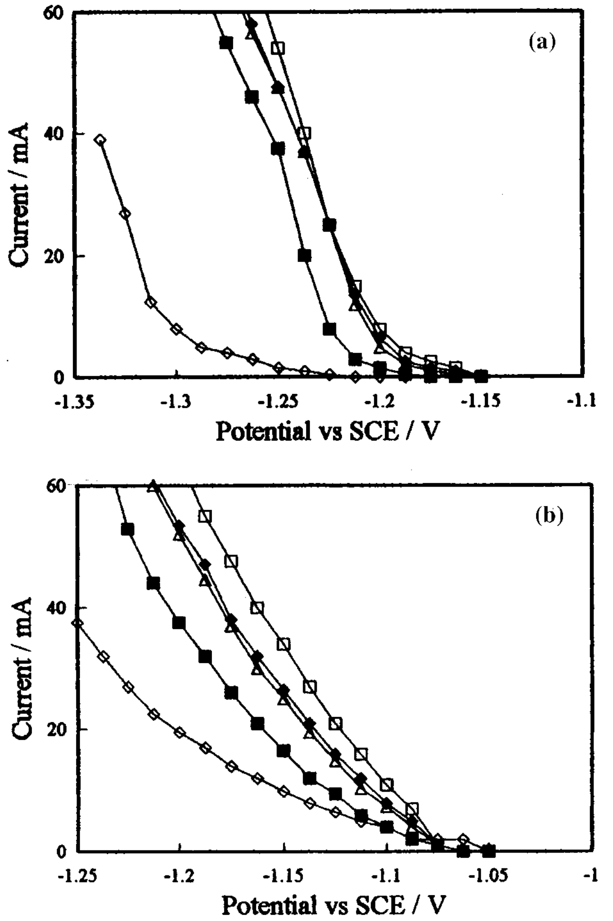

Fig. 2. Effect of TBABr on the cathodic polarization during zinc deposition on (a) aluminium (b) zinc, from solution containing 55 g dm^{-3} Zn and 150 g dm^{-3} H_2SO_4. TBABr concentrations; (–□–) blank, (–◆–) 5, (–△–) 10, (–■–) 40, (–◇–) 200 mg dm^{-3}.

The presence of Sb(III) in solution even at a concentration of 0.02 mg dm^{-3} with CTABr or TBABr shifted the deposition potential to less negative potentials (Figures 5 and 6). Decrease of NOP was observed to be similar to that for glue, SLS and TEBACl [27, 30]. Figures 3(b) and 4(b) show the effects of different concentrations of these two additives on NOP in the presence of 0.02 mg dm^{-3} Sb(III) in solution.

From the cathodic polarisation curves for zinc deposition in the presence of either CTABr or TBABr with Sb(III) in solution (Figures 1, 2, 5 and 6), Tafel slopes (*b*), transfer coefficients (α), and exchange current densities (I_0), were determined (Table 2). Small changes in Tafel slopes in the presence of additives with and without Sb(III) in solution indicates that the charge transfer reaction is not controlled by the concentrations of CTABr or TBABr alike glue and TEBACl [30]. The transfer coefficient remains essentially unaffected by the

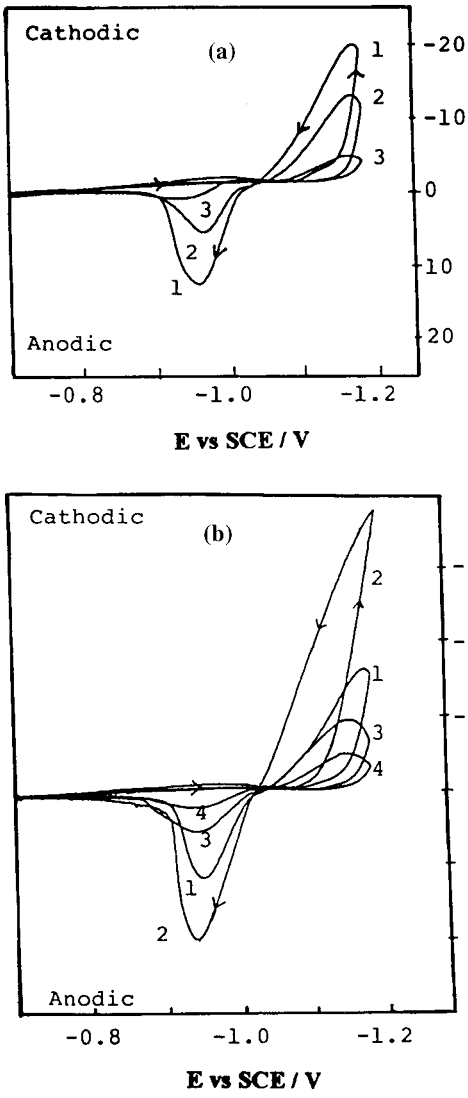

Fig. 3. Cyclic voltammograms of zinc solution in presence and absence of CTABr and 0.02 mg dm^{-3} antimony. (a) (1) Blank, (2) CTABr–2 mg dm^{-3}, (3) CTABr–10 mg dm^{-3}. (b) (1) Blank, (2) Blank + antimony, (3) CTABr–10 mg dm^{-3} + antimony, (4) CTABr–40 mg dm^{-3} + antimony.

presence of additives at almost all concentrations with or without antimony. The decrease in I_0 with increasing additive concentrations is consistent with increased additive adsorption on the cathode surface. The decrease in I_0 is more pronounced in the case of CTABr indicating comparatively atronger adsorption than TBABr. It would be expected that because of larger cationic size and hence the much more hydrophobic CTA$^+$ would adsorb more strongly onto the cathode surface [39] than TBA$^+$. The presence of 0.02 mg dm^{-3} Sb(III), however, increased the I_0 value in both the cases, which may be accounted for in terms of hydrogen evolution. The increase in I_0 is more prominent when Sb(III) is present in the solution with no additive. The results indicate that both the additives have levelling effects and CTABr is better than TBABr at lower concentrations and is comparable to glue as an additive.

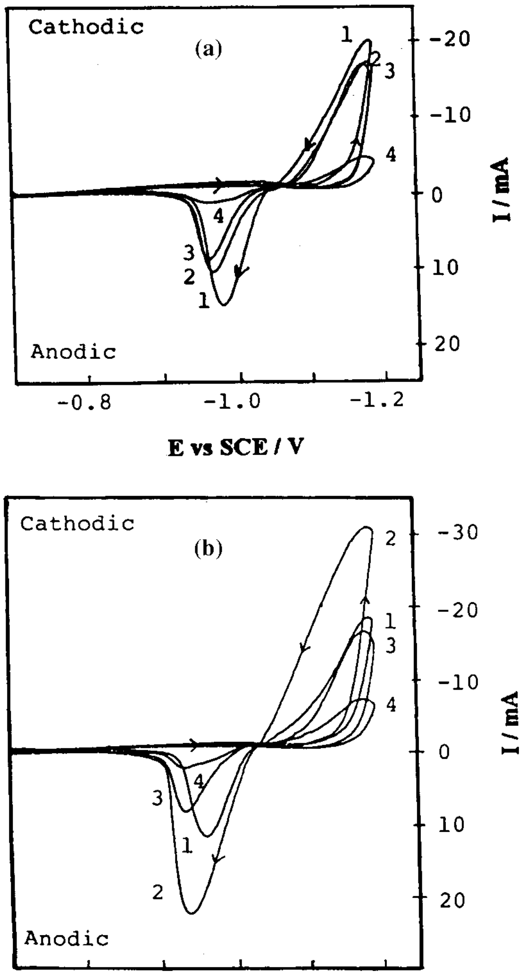

Fig. 4. Cyclic voltammograms of zinc solution in presence and absence of TBABr and 0.02 mg dm^{-3} antimony. (a) (1) Blank, (2) TBABr–5 mg dm^{-3}, (3) TBABr–10 mg dm^{-3}, (4) TBABr– 40 mg dm^{-3}. (b) (1) Blank, (2) Blank + antimony, (3) TBABr–20 mg dm^{-3} + antimony, (4) TBABr–40 mg dm^{-3} + antimony.

Changes in the kinetic parameters are also reflected in current efficiencies, deposit morphologies, crystallographic orientations and NOP values and there exists a correlation among them.

3.3. *Deposit morphology and crystal orientation*

The zinc deposit obtained from addition-free solution is bright and moderately smooth [27]. The addition of CTABr produced bright and smooth deposits at almost all concentrations. On the other hand the presence of TBABr produces smooth and comparatively dull deposits at almost all concentrations but the deposits are brittle at higher concentrations (>20 mg dm^{-3}). When Sb(III) is present in the solution (<0.02 mg dm^{-3}), bright and smooth deposits are obtained at almost all concentrations of CTABr and TBABr. At higher concentrations of Sb(III), nonuniform deposits are obtained. The SEM micrographs (Figure 7) show the effects of CTABr and TBABr on the morphology of zinc deposits with and without Sb(III) in solution.

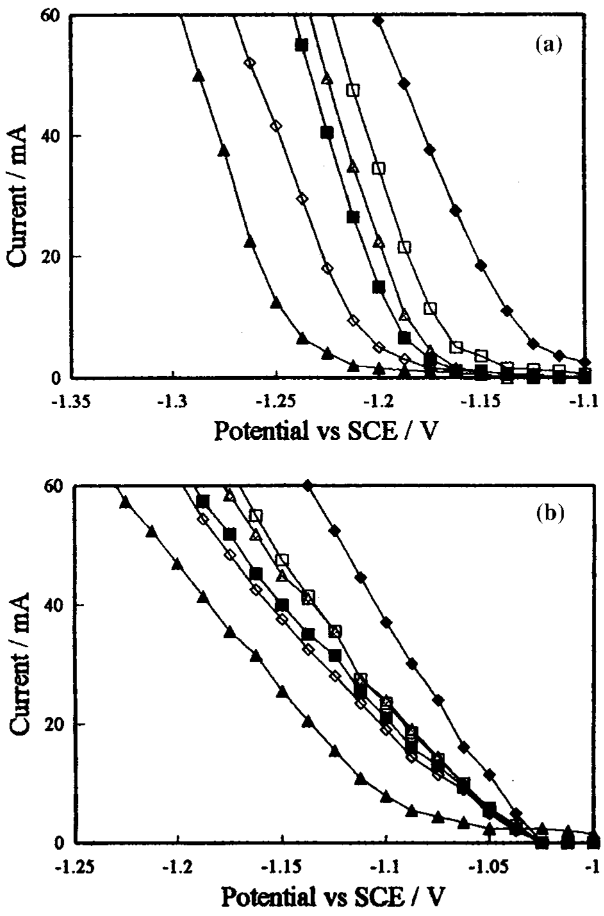

Fig. 5. Effect of CTABr on the cathodic polarization during zinc deposition on (a) aluminium (b) zinc, from solution containing 55 g dm^{-3} Zn and 150 g dm^{-3} H_2SO_4 and 0.02 mg dm^{-3} Sb. CTABr concentrations: (-□-) blank, (-◆-) blank + Sb, (-△-) 5 + Sb, (-■-) 10 + Sb, (-◇-) 40 + Sb, (-▲-) 200 mg dm^{-3} + Sb.

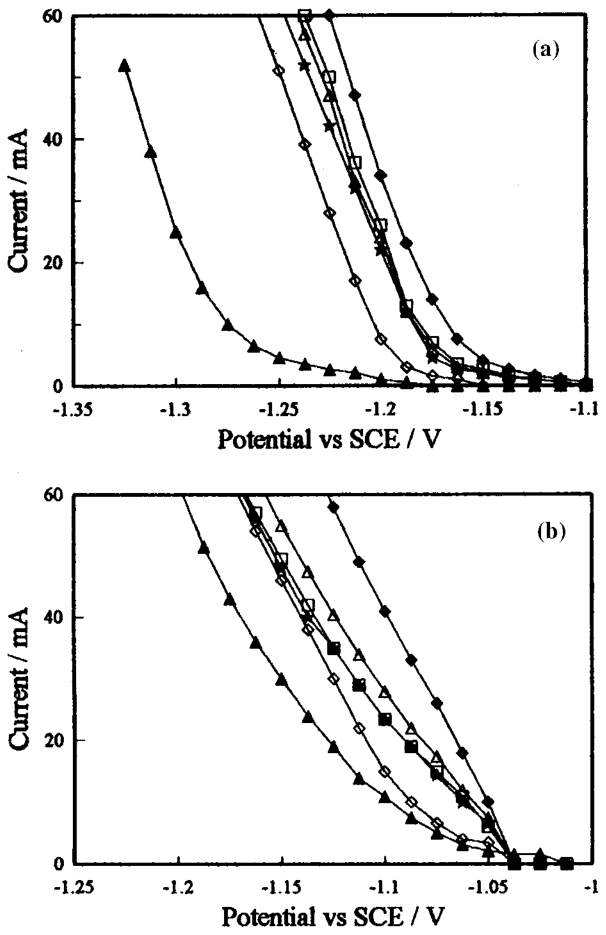

Fig. 6. Effect of TBABr on the cathodic polarization during zinc deposition on (a) aluminium (b) zinc, from solution containing 55 g dm^{-3} Zn and 150 g dm^{-3} H_2SO_4 and 0.02 mg dm^{-3} Sb. TBABr concentrations: (-□-) blank, (-◆-) blank + Sb, (-△-) 5 + Sb, (-★-) 10 + Sb, (-◇-) 40 + Sb, (-▲-) 200 mg dm^{-3} + Sb.

The crystallographic orientations obtained from XRD analysis of the zinc deposits are given in Table 1. Addition of 1 mg dm^{-3} of CTABr changed the orientations from (1 0 1) (0 0 2) (1 0 0) (1 0 3) to (1 0 1) (1 0 2) (1 0 3) (1 1 2) with an increase in platelet size (Figure 7(a)). Increase in CTABr concentration to 2 mg dm^{-3} changed the crystallographic orientations to (0 0 2) (1 0 2) (1 0 1) (1 0 3) with a further increase in the size of the platelets. At 40 mg dm^{-3} of the additive, the preferred orientation is (1 0 1) (1 0 2) (2 0 1) (2 0 3), showing cluster-type pyramidal deposits (Figure 7(c)). Addition of 0.04 mg dm^{-3} Sb(III) to the electrolytic solution containing 1 mg dm^{-3} CTABr did not change the crystal orientation but reduced the size of the platelets (Figure 7(b)).

Addition of 2 mg dm^{-3} TBABr changed the crystal orientation from (1 0 1) (0 0 2) (1 0 0) (1 0 3) to (1 0 1) (1 1 0) (1 1 2) (1 0 3) where growth of diagonal planes replaces the basal (0 0 2) planes. At 5 mg dm^{-3} the crystal orientation changed to (1 0 1) (1 0 2) (2 0 1) (1 0 0). Increase of TBABr concentration to 10 mg dm^{-3} resulted in a crystal orientation pattern of the type

Table 2. The effects of CTABr and TBABr on Tafel slopes, transfer coefficients and exchange current densities

[Additive]/mg dm^{-3}	Tafel slope (b)/mV (decade)$^{-1}$		Transfer coefficient (α)		Exchange current density (log I_0)/mA cm^{-2}	
	CTABr	TBABr	CTABr	TBABr	CTABr	TBABr
0	−123 (−63.4)	−123 (−63.4)	0.48 (0.93)	0.48 (0.93)	6.2 (9.0)	6.2 (9.0)
2	−108 (−106)	–	0.54 (0.55)	–	4.5 (4.8)	–
5	–	−114 (−129)	–	0.52 (0.45)	–	5.4 (6.4)
10	−121 (−106)	−113 (−128)	0.48 (0.55)	0.52 (0.46)	3.87 (4.33)	5.1 (5.25)
40	−138 (−114)	−126 (−89)	0.43 (0.52)	0.47 (0.66)	3.37 (4.33)	3.75 (4.45)
200	−144 (−134)	−164 (−113)	0.41 (0.44)	0.36 (0.52)	2.45 (3.12)	3.25 (4.45)

* Values in parentheses are for those when 0.02 mg dm −3 Sb is also present

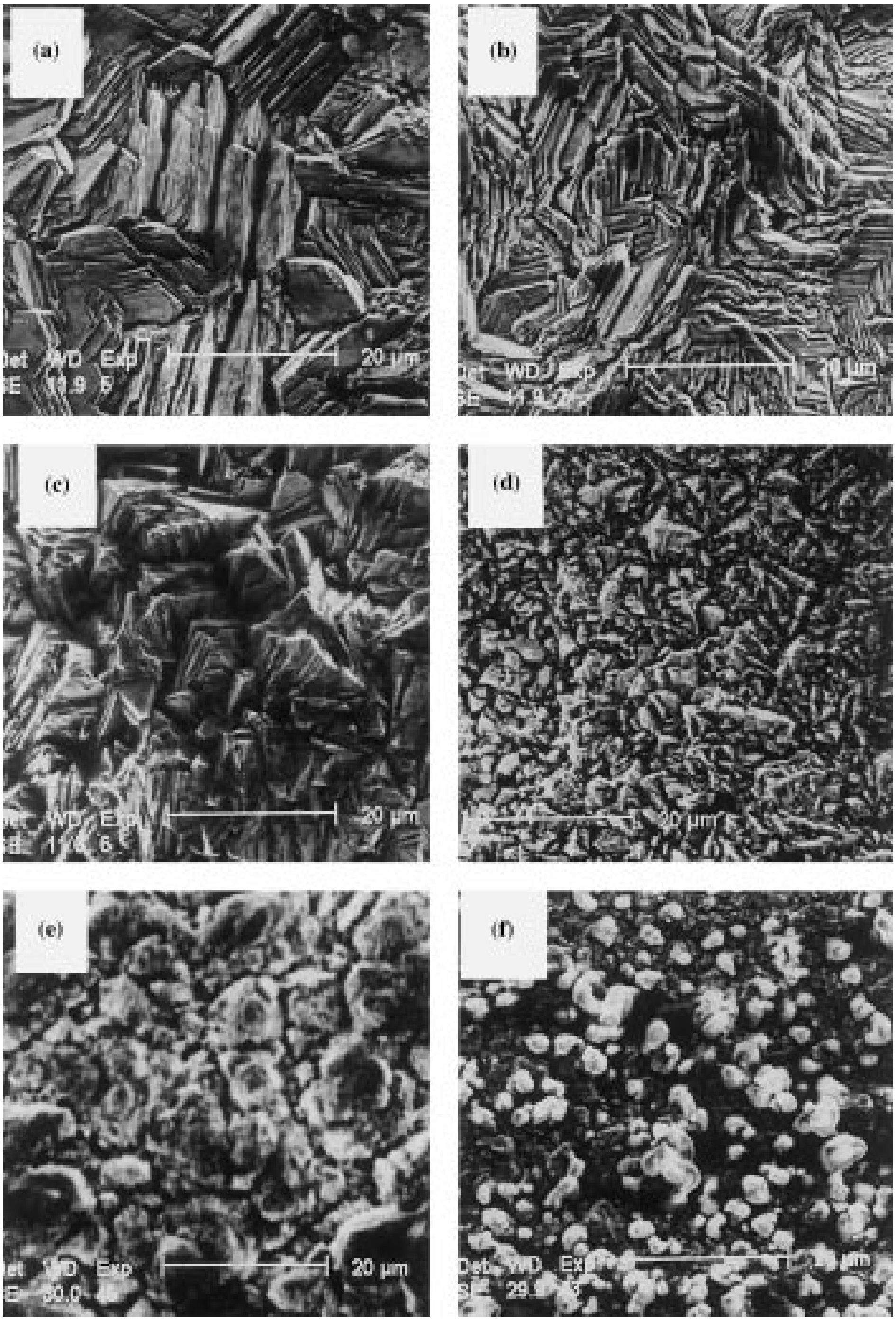

Fig. 7. Scanning electron micrographs (1200×) of zinc deposits. (a) CTABr–1 mg dm^{-3}, (b) CTABr–1 mg dm^{-3} + Sb–0.04 mg dm^{-3}, (c) CTABr–40 mg dm^{-3}, (d) TBABr–10 mg dm^{-3}, (e) TBABr–10 mg dm^{-3} + Sb–0.02 mg dm^{-3}, (f) TBABr-40 mg dm^{-3}.

(1 0 1) (2 0 1) (1 0 0) (1 0 2) containing pyramidal (1 0 1) planes parallel to the aluminium substrate and prismatic (1 0 0) planes, corresponding to the highest CE of about 93%, with smaller platelet sizes (Figure 7(d)). A further increase in TBABr concentration to 40 mg dm^{-3}, developed nodular growth on the surface of the zinc deposits (Figure 7(f)) corresponding to the preferred orientation (1 0 1) (0 0 2) (1 1 0) (1 0 2). Addition of 0.04 mg dm^{-3} Sb(III) to the zinc electrolytic solution containing 10 mg dm^{-3} TBABr changed the crystal orientation pattern to (1 0 1) (1 0 2) (1 0 0) (0 0 2) producing a corroded zinc deposit (Figure 7(e)). This indicates that CTABr can control the negative affect of antimony better than TBABr.

4. Conclusions

It may be concluded that, overall, CTABr behaves similarly to glue and is a better levelling agent than TBABr. Thus the addition of CTABr to acidic zinc sulphate electrowinning solutions increases current efficiency and produces smooth and compact deposits and a reduction in power consumption similar to that achieved with glue. TBABr addition increases CE slightly more than glue but increases the power consumption and produces comparatively dull deposits. The polarization for the zinc electrodeposition decreases in the order: CTABr > glue > TBABr and the optimum levelling effect with CTABr is achieved at much lower concentrations than TBABr.

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