

Zinc electrowinning from acidic sulphate solutions

Part II: Effects of triethylbenzylammonium chloride

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The effects of triethylbenzylammonium chloride (TEBACl) on the electrowinning of zinc from acidic sulfate solutions have been studied in the presence and absence of antimony(III). The factors considered included the current efficiency (CE), power consumption, polarisation behaviour, and the crystallographic orientations and surface morphology of the deposits. Compared with the traditional industrial additive, glue, the addition of TEBACl increased CE, reduced power consumption and improved the surface morphology. Maximum CE and minimum power consumption were obtained at 2 mg dm^{-3} TEBACl and 0.01 mg dm^{-3} Sb(III). The exchange current density, Tafel slope and transfer coefficient were determined to elucidate the nature of the electrode reactions involved.

Keywords: Zinc electrowinning, antimony, triethylbenzylammonium chloride, current efficiency, polarization, morphology, power consumption

1. Introduction

The role of impurities [1–4] in the electrolytic solutions used for zinc electrowinning is of considerable industrial importance. The increase in impurity concentrations decreases the induction period [5] associated with zinc electrowinning process resulting in deterioration of zinc deposit quality and decrease in current efficiency. High current efficiencies and high quality Zn deposits are known to be obtained from high purity electrolyte solutions. However, rigorous electrolyte purification is economically nonviable. An alternative way to reduce the harmful effects of impurities is to use suitable organic additives [6–16]. Although additives like glue [17–21] and gum arabic [22] are commonly used for this purpose industrially, there is a need for better additives. Additives like 2-butyl-1,4-diol [9], tetrabutylammonium chloride (TBACl) [10–12], nonylphenoloxethylene [14] and combinations of nonylphenol polyethylene glycol, dinaphthylmethane-4, 4'-disulphonic acid and polyethylene glycol [15, 16] give better results than either glue or gum arabic.

Cruz *et al.* [23] have reported the effects of TBACl on zinc electrodeposition from chloride and perchlorate electrolytes. They observed that, up to a particular concentration of TBACl, the zinc deposition overpotential increases and at higher concentrations the electrode surface is blocked by the additive. However they could not get any definitive

relationship between the degree of surface leveling, additive concentration and change in overpotential. MacKinnon *et al.* [24] studied the effect of various tetraalkylammonium chlorides and found that TBACl was the most effective additive to obtain smooth, compact and dendrite-free zinc deposits. The present authors [25, 26] have studied the effect of 2-picoline, 4-ethylpyridine and 2-cyanopyridine in the presence and absence of antimony(III). These additives reduced current efficiency and increased power consumption, but the presence of very small amounts of antimony(III) reversed these effects. Sodium lauryl sulphate (SLS) also gave better results than glue and the zinc deposit obtained was smooth and compact [27]. A maximum current efficiency of about 97% was observed when SLS was combined with 0.02 mg dm^{-3} of antimony [27].

The influence of triethylbenzylammonium chloride (TEBACl) on the kinetics of zinc deposition and dissolution in acidic sulphate electrolytic solution containing Ni^{2+} ions has been investigated [28]. TEBACl was found to decrease the screening effect of hydrogen bubbles responsible for the formation of local galvanic cells [29, 30]. TEBACl also increases the induction period for the dissolution of galvanostatically deposited zinc in nickel-containing solutions [31].

The present study investigates the effects of TEBACl on the current efficiency, power consumption, polarisation behaviour and deposit morphology during the electrowinning of zinc from acidic sulphate solutions. The results were compared with

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those for glue which is widely used as an industrial additive [17–21].

2. Experimental details

The experimental procedures and the composition of the electrolyte used in this work were similar to those described previously [27]. The TEBACl was of commercial grade (Trizma Chemical Co. Ltd, India.). For the polarisation studies a glass cell of 250 cm³ was used. The working electrode of area 1 cm² was made from high purity (>99.99%) aluminium. A platinum sheet was used as the auxiliary and a saturated calomel as the reference electrodes. Cyclic voltammetry was carried out by initiating scans at -0.7 V and cycling between the limits -0.7 to -1.3 V using a 50 mV s⁻¹ scan rate. Deposit morphology was examined by using a WILD stereo microscope and a SEM (SE 101B).

3. Results and discussion

3.1. Current efficiency and power consumption

The effects of TEBACl and glue on current efficiency (CE) and power consumption (PC) were studied over an additive concentration range of 0–40 mg dm⁻³ (Table 1). As the TEBACl concentration in the electrolytic solution is increased the CE first increases, goes through a maximum at around 2 mg dm⁻³ and then drops steadily. For example, in the absence of TEBACl the current efficiency was ~89% whereas at 2 mg dm⁻³ TEBACl, the CE was ~92.8% and then fell to 89.7% at 40 mg dm⁻³. The observed trend of CE with increasing TEBACl concentration is similar to that reported for glue [27], where a CE of 92% was obtained at 5 mg dm⁻³ but a reduction occurred at higher glue concentrations. However, the rate of decrease in the CE for TEBACl is lower than that for glue, for example, at an additive concentration of 40 mg dm⁻³ the CE in the presence of TEBACl is 89.7% compared to only

67% for glue. Decreases in CE with increasing additive concentrations have been observed frequently and are usually ascribed to blocking of the deposition process by adsorption of the additive on the cathode surface [14, 19, 32, 33]. This also increases the interfacial viscosity, thereby decreasing the rate of mass transfer and hence the zinc deposition rate.

Antimony has long been recognised as one of the most deleterious solution impurities for zinc electrodeposition [2, 21, 34, 35, 36]. Nevertheless, traces of antimony also play a beneficial role when combined with organic additives [25, 26] producing high current efficiencies and good deposit morphologies. Antimony is found to have similar beneficial effects in the presence of TEBACl. Thus, in the presence of 0.01 mg dm⁻³ antimony(III) the addition of TEBACl up to 2 mg dm⁻³ results in an increase in CE up to 95.6%, although the CE again decreases at higher TEBACl concentrations. The CE was found to be ~79.8% in a solution containing 0.08 mg dm⁻³ Sb(III) and 2 mg dm⁻³ TEBACl. As seen in Table 1, the CE values are fairly constant at different TEBACl and antimony ratios. A similar effect is observed for varying glue and antimony ratios. Although the data are not included in Table 1, it is found that at concentrations 10 mg dm⁻³, glue provides higher CEs than TEBACl when Sb(III) is also present in the electrolytic solution.

The effects of TEBACl and glue, alone or in the presence of antimony, on power consumption (PC) are also listed in Table 1. With TEBACl alone, a maximum reduction in PC of ~180 kWh t⁻¹ was obtained at an additive concentration of 2 mg dm⁻³. A further reduction of ~140 kWh t⁻¹ was achieved on the addition of 0.01 mg dm⁻³ of Sb(III). In the case of glue, the decrease in PC was maximal (100 kWh t⁻¹) at 5 mg dm⁻³ of glue and 0.02 mg dm⁻³ Sb(III) which is considerably less than the *in toto* saving of ~320 kWh t⁻¹, achieved with the above TEBACl/Sb(III) combination.

Table 1.

[Additive]/mg dm ⁻³	[Sb(III)]/mg dm ⁻³	CE/%	PC/kWh t ⁻¹	Preferred crystal orientation (h k l)
<i>TEBACl</i>				
0	0	89.3	2608	(101) (002) (100) (103) (112)
1.0	0	90.9	2463	(101) (102) (112) (103)
1.5	0	92.6	2436	(112) (002) (101) (110)
2.0	0	92.8	2430	(112) (101) (002) (110)
2.5	0	92.6	2445	(112) (101) (102) (110)
5.0	0	91.3	2497	(112) (101) (102) (110)
40	0	89.7	2588	(112) (101) (103) (102)
2.0	0.01	95.6	2291	(101) (112) (102) (103)
2.0	0.02	94.1	2336	(110) (112) (101) (103)
5.0	0.01	92.2	2402	(101) (100) (110) (112)
5.0	0.02	90.1	2449	(101) (002) (100) (103)
<i>Glue</i>				
1.0	0	90.8	2566	(101) (112) (100) (110)
2.0	0	91.3	2560	(101) (112) (102) (114)
5.0	0	92.2	2553	(101) (002) (103) (102)
2.0	0.01	91.9	2526	(101) (002) (100) (103)
2.0	0.02	90.9	2545	(101) (100) (110) (112)
5.0	0.02	92.5	2509	(101) (112) (102) (103)

3.2. Polarization behaviour

The effect of TEBACl on the cathodic polarization of zinc was investigated by recording the current–potential curves and determining the nucleation overpotential. The addition of TEBACl ($0\text{--}40\text{ mg dm}^{-3}$) shifted the polarisation curves for zinc electrodeposition to more negative potentials. At very high concentrations (i.e. $\sim 200\text{ mg dm}^{-3}$) of TEBACl a much stronger polarisation was seen. The nucleation overpotential (NOP) value shifted negatively and was highest at 200 mg dm^{-3} (Fig. 1(a)). It was found that the effect of TEBACl was more pronounced during zinc deposition on a zinc substrate *cf.* that on aluminium substrates (Fig. 1(b)). The effect of glue on the cathodic polarisation has been reported earlier [27]. Glue was found to be a stronger polarizer than TEBACl. For example, at 10 mg dm^{-3} TEBACl the NOP increases by $\sim 5\text{ mV}$ only, whereas at 5 mg dm^{-3} of glue the NOP is increased by $\sim 10\text{ mV}$.

The presence of antimony in solution, even at 0.02 mg dm^{-3} , decreases the NOP in a similar manner to that reported earlier for glue and SLS [27].

Figures 2(a) and 2(b) show the effects of 0.02 mg dm^{-3} Sb in the presence of varying amounts of TEBACl on the zinc electrodeposition over aluminium and zinc substrates respectively. An important finding is that even though glue is a stronger polariser than TEBACl, it is not as effective as TEBACl in smoothing the zinc deposits. (Time dependence has not been investigated.)

From the cathodic polarisation curves for zinc deposition Tafel slopes were determined and transfer coefficients were calculated using the following equations:

$$\eta = a + b \log I \quad (1)$$

$$b = RT/\alpha nF \quad (2)$$

where η is the overpotential (V), b is the Tafel slope (V decade^{-1}), α is the transfer coefficient and I the current density (mA cm^{-2}).

Exchange current densities, I_0 , for zinc deposition were found by extrapolating the Tafel lines to zero overpotential. The values of b , α and I_0 are given in Table 2 as functions of additive concentrations. Small changes in the Tafel slopes indicate that the

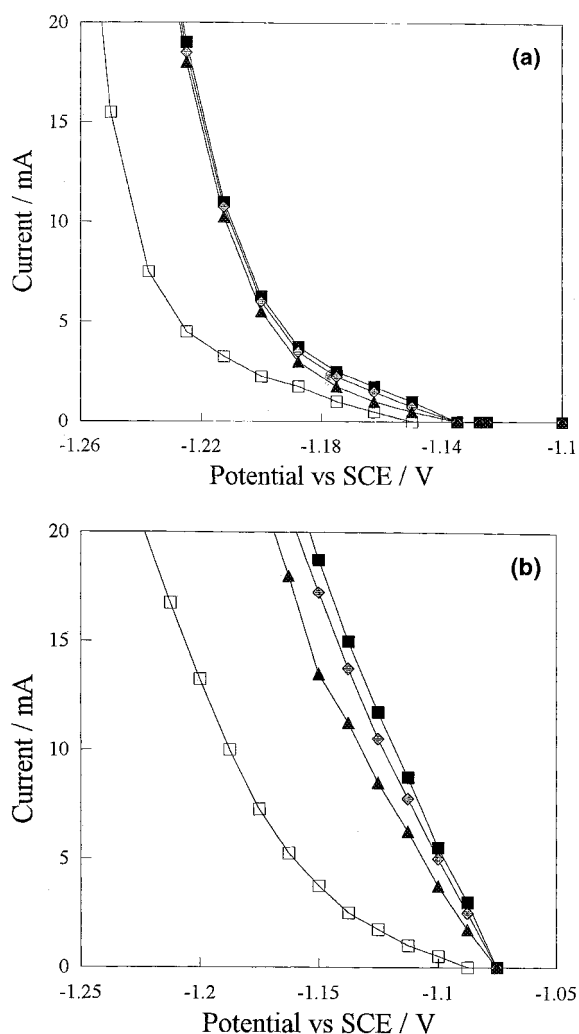


Fig. 1. Effects of TEBACl on the cathodic polarization during zinc deposition on (a) aluminium and (b) zinc, from solutions containing 55 g dm^{-3} Zn and 150 g dm^{-3} H_2SO_4 . TEBACl concentrations: (■) blank, (◆) 10, (▲) and (□) 200 mg dm^{-3} .

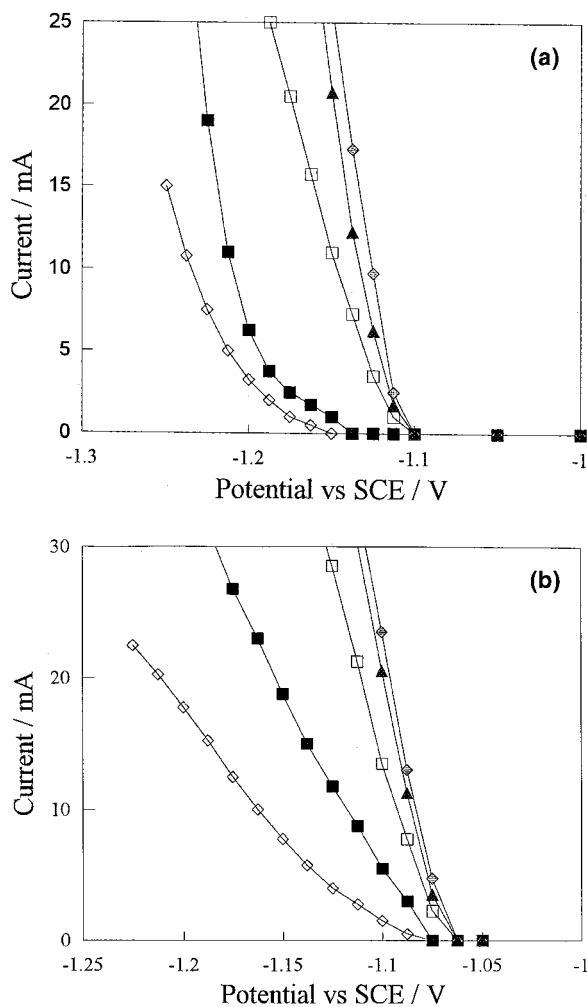


Fig. 2. Effects of TEBACl on the cathodic polarization during zinc deposition on (a) aluminium and (b) zinc, from solutions containing 55 g dm^{-3} Zn and 150 g dm^{-3} H_2SO_4 and 0.02 mg dm^{-3} Sb(III). TEBACl concentrations: (■) blank, (◆) blank + Sb, (▲) 10 + Sb, (□) 40 + Sb and (◇) 200 mg dm^{-3} + Sb.

Table 2.

[Additive] /mg dm ⁻³	Tafel slope, b/mV		Transfer coefficient, α		Exchange current density, log I_0 /mA cm ⁻²	
	TEBACl*	Glue*	TEBACl*	Glue*	TEBACl*	Glue*
0	-123.0 (-63.4)	-123.0 (-63.4)	0.48 (0.93)	0.48 (0.93)	6.2 (9.0)	6.2 (9.0)
5	-	-120.0 (-75.0)	-	0.49 (0.78)	-	3.37 (4.58)
10	-130.0 (-56.7)	-	0.45 (1.0)	-	4.4 (4.9)	-
40	-124.0 (-70.0)	-110.8 (-101.0)	0.47 (0.84)	0.53 (0.58)	3.6 (4.6)	2.18 (4.15)
200	-131.0 (-175.0)	-100.5 (-132.4)	0.45 (0.34)	0.59 (0.44)	1.5 (3.25)	0.66 (1.92)

*Values in parentheses were obtained when 0.02 mg dm⁻³ of Sb(III) was also present in the solution.

charge transfer reaction is not controlled by the concentration of glue or TEBACl, whereas the marked decrease in the Tafel slopes on addition of Sb(III) indicates that the charge transfer reaction was affected strongly by the presence of Sb(III) in the solution, which is probably due to hydrogen evolution reaction along with zinc deposition. The transfer coefficient remains essentially unaffected by the presence of the additives at almost all concentrations, but increases significantly when 0.02 mg dm⁻³ Sb(III) is in solution.

The decrease in I_0 with increasing additive concentrations is consistent with increased additive adsorption on the cathode. The increase in I_0 in the presence of 0.02 mg dm⁻³ Sb(III) may be due to hydrogen evolution. This increase is more prominent when Sb(III) is present in the solution without additive. This indicates the influence of Sb(III) on the H₂ evolution reaction. Changes in kinetic parameters are also reflected in current efficiency, deposit morphology, crystallographic orientation and NOP value. Thus the organic additives have a leveling effect on the deleterious effect resulting from enhanced hydrogen evolution on the metal electrodeposition.

3.3. Deposit morphology and crystal orientation

The zinc deposited from additive-free solution is bright but not smooth [27]. At low concentrations, glue produces bright and smooth deposits. However, at higher glue concentrations (≥ 20 mg dm⁻³) dull and even nodular deposits are obtained [27]. For TEBACl, bright and smooth deposits are obtained at all

concentrations studied and in the presence of Sb(III). The stereo micrographs of zinc deposits obtained from acidic sulphate solutions containing 2 mg dm⁻³ TEBACl alone and with 0.02 mg dm⁻³ Sb are shown in Fig. 3. The effects of TEBACl and Sb(III) on the zinc deposit morphology are compared with those of glue in the SEM micrographs shown in Fig. 4.

With regard to crystallographic orientations, the addition of 1 mg dm⁻³ TEBACl changed the orientations from (101) (002) (100) (103) (102) to (101) (102) (112) (103) with an increase in platelet size. There is a change in crystal orientation to (112) (101) (002) (110) at 2 mg dm⁻³ TEBACl, where basal and diagonal planes are developed (Fig. 4(a)). At 5 mg dm⁻³ TEBACl the crystal orientations changed to (112) (101) (102) (110) and remained almost the same, even at 40 mg dm⁻³ of TEBACl, where a cluster-type deposit was seen. A reduction in platelet size was observed with increasing TEBACl concentrations.

Addition of 0.02 mg dm⁻³ Sb(III) to the solution containing 2 mg dm⁻³ TEBACl, changed the crystal orientation to (101) (112) (102) (103) and reduced the platelet size (Fig. 4(c)) producing a smooth and compact deposit. From Fig. 4(c) it appears that very small crystallites were formed on the bigger crystal platelets. At higher concentrations of Sb(III) the deposits obtained were not smooth and pits developed in the microstructure. The optimum leveling effect was achieved with low TEBACl concentrations, particularly with 2 mg dm⁻³ TEBACl and 0.02 mg dm⁻³ Sb(III). The deposit morphology of zinc obtained at different concentrations of glue have been discussed previously [27]. With 2 mg dm⁻³ glue

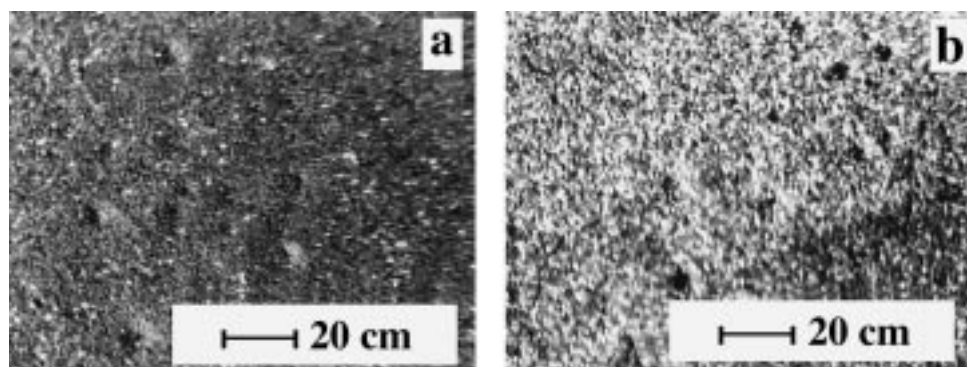


Fig. 3. Stereomicroscopic photographs of zinc deposits. (a) TEBACl, 2 mg dm⁻³; (b) TEBACl, 2 mg dm⁻³ and Sb(III), 0.02 mg dm⁻³.

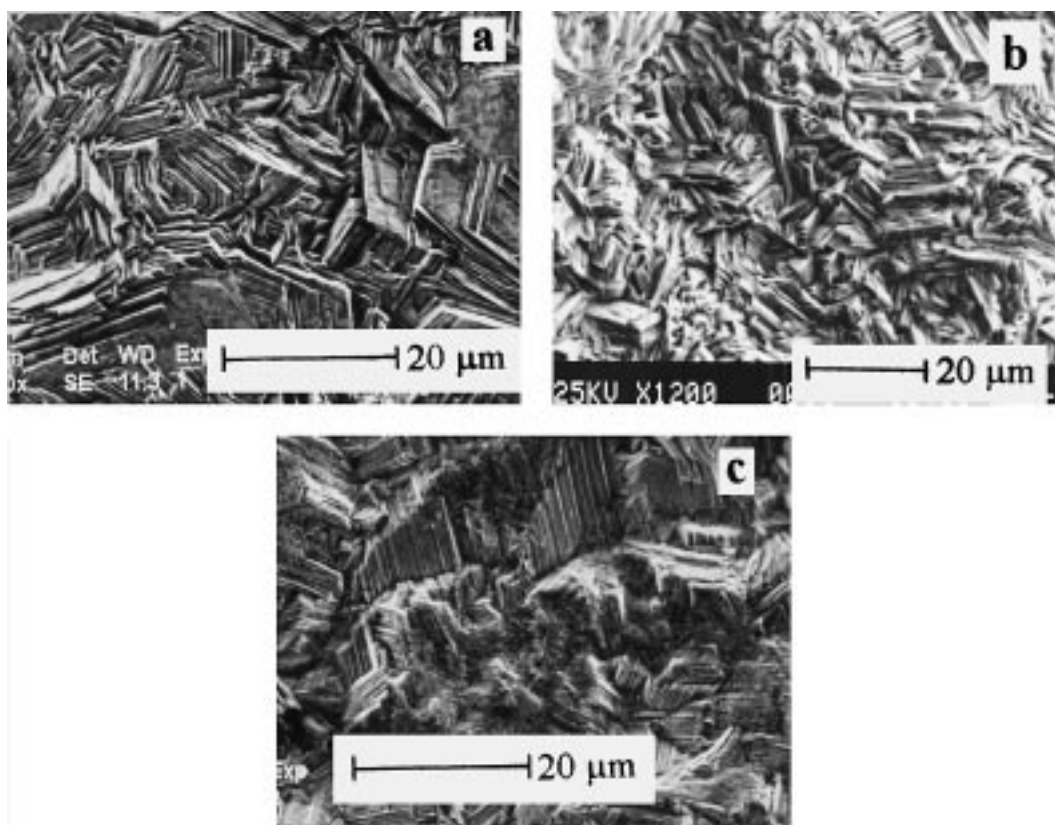


Fig. 4. Scanning electron micrographs of zinc deposits. (a) TEBACl, 2 mg dm^{-3} ; (b) glue, 2 mg dm^{-3} ; (c) TEBACl, 2 mg dm^{-3} and Sb(III) , 0.02 mg dm^{-3} .

(Fig. 4(b)), the deposit was smooth and the crystal orientations changed from (101) (002) (100) (103) (102) in additive-free electrolyte to (101) (112) (102) (114). Addition of 0.02 mg dm^{-3} Sb(III) further changed the crystal orientations to (101) (100) (110) (112) and resulted in a nonsmooth deposit.

4. Conclusions

On the basis of the present study the following conclusions may be drawn:

- (i) TEBACl addition to acidic zinc sulphate solutions increases current efficiency, reduces power consumption and produces smooth and compact zinc deposits.
- (ii) Although glue is a stronger polariser than TEBACl, it is not as effective as TEBACl in smoothing the deposits.
- (iii) The optimum leveling effect was achieved with low TEBACl concentrations, particularly with 2 mg dm^{-3} TEBACl and 0.02 mg dm^{-3} Sb(III) .

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