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Zinc electrowinning from acidic sulfate solutions Part I: Effects of sodium lauryl sulfate

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The effects of sodium lauryl sulphate(SLS) in the presence and absence of antimony(III) on the current efficiency, power consumption and polarization behaviour of zinc were determined. The surface morphologies and deposit crystallographic orientations were also evaluated. The results were compared with glue as the addition agent. The addition of sodium lauryl sulfate to the zinc sulfate solution increased current efficiency, reduced power consumption and improved the surface morphology. Maximum current efficiency and minimum power consumption were achieved on addition of 0.02 mg dm^{-3} Sb with 1 mg dm^{-3} sodium lauryl sulfate.

1. Introduction

Zinc electrowinning from acidic sulfate solutions is sensitive to the presence of certain metallic impurities [1–4]. To counteract the harmful effects of these metallic impurities additives such as glue [5–9], gum arabic [10] etc. are usually added to the electrolytic bath. However, the search for better additives is continuing [11–21]. Piron *et al.* [14] reported improvement in current efficiency (CE) with 2-butyne-1,4-diol. MacKinnon *et al.* [15–17] found that the use of TBACl (tetrabutylammonium chloride) resulted in better surface morphology and higher current efficiency. The use of pure and mixed surfactants has also been investigated [19–21]. The surfactants may be classified into nonionic, anionic and cationic types [22]. In industrial zinc deposition the most commonly used surfactants are the naturally occurring gums or glues which, in acid solution, are cationic. Recently, several synthetic surfactants of the cationic type [14–17, 19–21] have been tested in zinc electrowinning. However, information on the use of anionic surfactants in zinc electrowinning is rather rare. Anionic surfactants usually contain polar and solubilizing groups like carboxylates, sulfonates, sulfates and phosphates. Among these compounds, the alkyl sulfates containing eight or more carbon atoms are often used [23]. The addition of these anionic surfactants reduces the interfacial tension indicating their adsorption on the surface of the substrate [24]. Sodium lauryl sulfate and sodium lauryl ethoxy sulfonates, which belong to this category, have been widely used commercially in the electroplating of nickel [25, 26].

The present study was undertaken to investigate the effect of sodium lauryl sulfate on the current efficiency, power consumption and polarization behaviour of zinc. The results were compared with deposits obtained from solutions containing glue, which is a common additive used in zinc industries.

2. Experimental details

2.1. *Electrolysis*

A stock solution of zinc electrolyte for electrolysis studies was prepared by dissolving AnalaR zinc sulfate ($ZnSO_4 . 7H_2O$, AR, s.d. Fine Chem. Ltd, India) in doubly distilled water. This solution was purified by adding 2 g dm^{-3} zinc dust, heating to boiling point with stirring for about 30 min and then filtering. The purified neutral zinc sulfate solution containing 150 g dm^{-3} Zn had the following impurities in mg dm^{-3} (determined by AAS), Cu (0.06), Co (0.35), Mn (0.27), Ni (0.47), Fe (0.47), Pb (0.72) and Cd (0.06). Test solutions were prepared from appropriate amounts of this solution and AnalaR sulfuric acid (BDH), reagent grade sodium lauryl sulfate (SLS), AR potassium antimonyl tartrate and animal glue of commercial grade available locally.

The electrolysis cell consisted of a 250 cm^3 beaker with a Perspex lid provided with slits to accommodate the electrodes. An aluminium sheet (3 mm thick and 10 cm^2 area) was used as the cathode and a Pb–Ag (Ag, 1%) sheet as the anode. The anode to cathode distance was kept at 3 cm.

All the electrowinning experiments were carried out for 2 h at 400 A m^{-2} and at 40 ± 1 °C. The electrolytic solution contained 55 g dm^{-3} zinc and 150 g dm^{-3} H_2SO_4. After electrolysis, the cathode was removed from the cell and washed thoroughly with water and acetone and finally dried in an oven

(50–60 °C). The current efficiency was calculated by weight.

2.2. *Cyclic voltammetry*

All cyclic voltametric experiments were carried out at 25 °C using a rotating disc apparatus and pyrex cell as described in the literature [27]. A high purity aluminium disc of 3 mm dia. mounted on a Teflon shaft was used as the working electrode. Before each experiment the aluminium disc electrode was wet polished with 800 grit silicon carbide paper and washed with acetone followed by distilled water. A platinum wire was used as counter and a saturated calomel (SCE) as the reference electrode. Experiments were conducted by taking $100\,\mathrm{cm}^3$ of zinc solution containing $55\,\mathrm{g\,dm}^{-3}$ zinc and $150\,\mathrm{g\,dm}^{-3}$ H_2SO_4 prepared from zinc sulfate under nitrogen atmosphere. The cathodic potentials were cycled between −0.7 V and −1.2 V vs SCE at 2000 rpm and a potential sweep rate of $2\,\mathrm{mV\,s}^{-1}$ using a PAR175 universal programmer and a PAR173 potentiostat.

2.3. *Deposit examination*

A Philips PW 1050 X-ray diffractometer was used to examine zinc deposits to determine their preferred crystal orientations relative to ASTM standard zinc powder. The surface morphology of the deposits was examined by scanning electron microscopy (SEM) using a Philips SE 101B microscope.

3. Results and discussion

3.1. *Current efficiency*

The effects of SLS and glue on current efficiency and power consumption were studied in the range $0–40\,\mathrm{mg\,dm}^{-3}$. Table 1 and Fig. 1 show the effect of increasing concentration of additives on current efficiency. In both cases the initial addition of the additive improves the current efficiency but at higher concentrations the efficiency drops. For SLS the maximum in CE (93.3%) occurs at around $1\,\mathrm{mg\,dm}^{-3}$, whereas for glue the maximum (92%) occurs at around $5\,\mathrm{mg\,dm}^{-3}$. It can be seen from Fig. 1 that glue is less effective than SLS in improving CE. Further, CE drops off much more rapidly at higher concentrations of glue than SLS, for example, at $40\,\mathrm{mg\,dm}^{-3}$ of the additive the CE is only 67% for glue as compared to 87% for SLS. Such decreases in current efficiencies on increasing additive concentrations have also been observed by other workers [7, 19, 22, 28] and are generally attributed to the surface coverage of the cathode by a strongly adsorbed additive layer. Such a layer increases the interfacial viscosity and thereby decreases the mass transfer and zinc deposition rates.

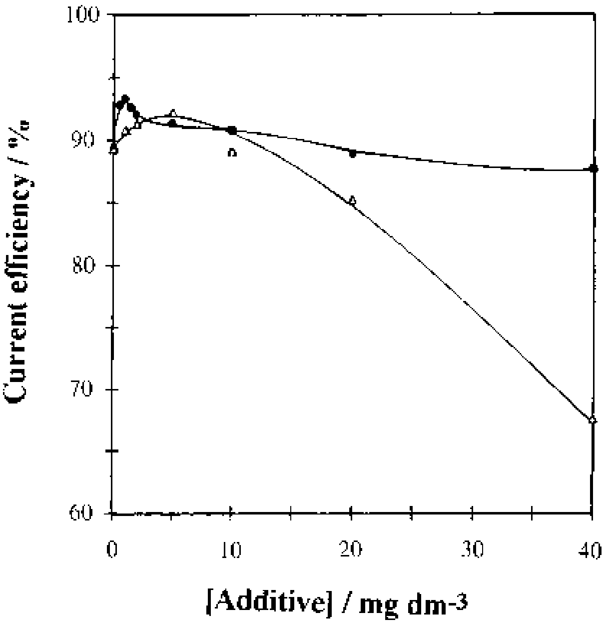

Fig. 1. Effect of additives on current efficiency during zinc electrowinning. Key: (●) SLS and (△) glue.

Table 1. Effect of additives on current efficiency and power consumption during zinc electrowinning

[Additive] / $\mathrm{mg\,dm}^{-3}$	*CE** / %	*Power consumption** / $\mathrm{kWh\,t}^{-1}$
SLS		
0	89.3 (89.1)	2608 (2596)
1	93.3 (97.6)	2391 (2244)
2	92.0 (89.0)	2434 (2424)
5	91.3 (88.7)	2462 (2460)
10	90.8 (87.9)	2484 (2491)
Glue		
1	90.8 (91.7)	2566 (2522)
2	91.3 (90.9)	2560 (2545)
5	92.2 (92.5)	2553 (2509)
10	89.1 (91.2)	2651 (2554)

* The values in parentheses are obtained when $0.02\,\mathrm{mg\,dm}^{-3}$ of Sb is also present in the solution.

The effect of antimony on zinc electrowinning has been studied extensively [2, 5, 9, 29–34]. Although antimony has been recognized as one of the most deleterious and toxic solution impurities, it also plays a beneficial role when combined with organic additives like glue producing optimum current efficiencies and acceptable surface morphologies. Our results on the effects of Sb variation at different SLS and glue concentrations are given in Table 1 and Figs 2 and 3. As can be seen from Fig. 2, the addition of Sb has a beneficial effect on current efficiency in the presence of SLS. The advantage is most pronounced at lower concentrations of SLS particularly at around $1\,\mathrm{mg\,dm}^{-3}$ of SLS where the CE first increases with increasing Sb concentration. The maximum (~97%) occurs at around $0.02\,\mathrm{mg\,dm}^{-3}$ Sb and then gradually decreased. With no additive, the CE drops rapidly as Sb concentration is increased. In the presence of glue ($1–10\,\mathrm{mg\,dm}^{-3}$) the CE values remained almost constant up to $0.02\,\mathrm{mg\,dm}^{-3}$ of Sb beyond which it decreased (Fig. 3). However, the decrease in current

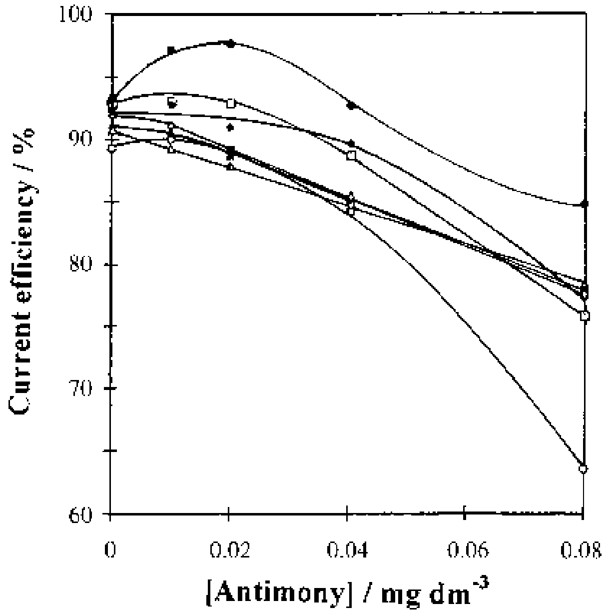

Fig. 2. Effect of antimony on current efficiency during zinc electrowinning in presence of: (○) blank, (□) 0.05, (●) 1.0, (◆) 1.5, (◇) 2.0, (▲) 5 and (△) 10 mg dm^{-3} SLS.

efficiency due to Sb was found to be insignificant when the concentration of glue in the electrolyte was 10 mg dm^{-3}.

The effect of the SLS and glue alone or in combination with 0.02 mg dm^{-3} Sb on power consumption can be seen from Table 1. Although, experimentally the masses of zinc deposits were measured in grams, the power consumptions are expressed in kWh t^{-1} in Table 1 for consistency with the units commonly used in the zinc industry. On the one hand, addition of 1 mg dm^{-3} of SLS resulted in the highest reduction (217 kWh t^{-1}) in power and further reduction (147 kWh t^{-1}) is obtained if 0.02 mg dm^{-3} Sb is also present in this solution. On the other hand, glue alone, or in combination with Sb, does not reduce the power consumption to any significant extent.

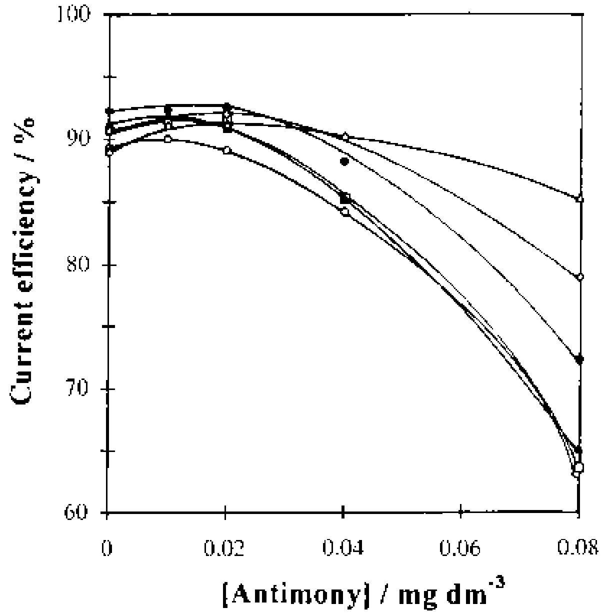

Fig. 3. Effect of antimony on current efficiency during zinc electrowinning in presence of: (○) blank, (□) 1, (▲) 2, (●) 5, (◇) 7.5 and (△) 10 mg dm^{-3} glue.

3.2. *Polarization behaviour*

The effect of various additives alone and in combination with Sb on electroreduction of Zn^{2+} ion on a rotating aluminium disc electrode was investigated cyclic voltammetrically (Figs 4 and 5). The cycle started at −0.7 V vs SCE (point ‘A’, Fig. 4) and the scan swept in the cathodic direction. The current increased sharply at ‘B’ up to ‘C’ (−1.2 V vs SCE) where it was reversed. This resulted in a decrease in current which subsequently reached zero at the crossover potential, ‘D’ and the current then became anodic corresponding to the dissolution of the deposited zinc. The potential difference between the decomposition potential at ‘B’ and the crossover potential at ‘D’ is a measure of nucleation overpotential (NOP) for zinc deposition on an aluminium substrate. The addition of SLS increased the ‘NOP’ value substantially in comparison to glue for example: addition of 1 mg dm^{-3} of SLS increased the NOP from 116 to 132 mV. Co-addition of 0.04 mg dm^{-3} Sb decreased the NOP to 72 mV. Glue alone increased the NOP slightly lower than SLS. At 5 mg dm^{-3} glue the NOP was 126 mV but dropped very significantly to 65 mV when combined with 0.04 mg dm^{-3} Sb (Fig. 5). It should, however, be noted that, in the absence of SLS or glue, the presence of Sb causes a relatively larger decrease in NOP (from 116 to 54 mV at 0.04 mg dm^{-3} Sb). Generally the combination of Sb with the additives decreases the ‘NOP’ and increases the cathodic

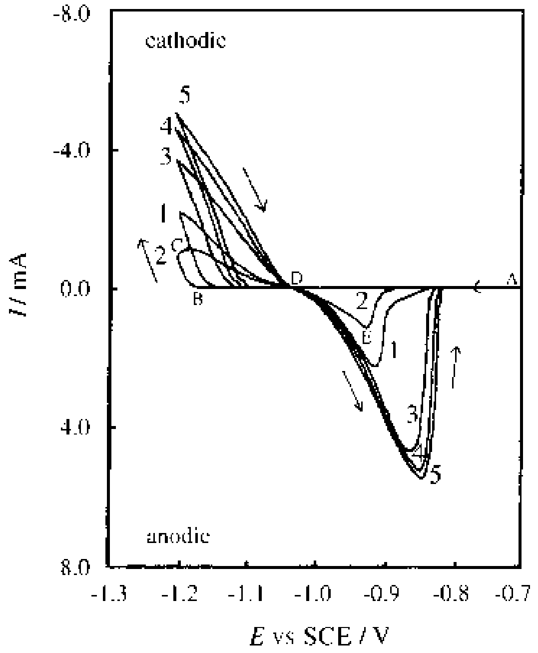

Fig. 4. Cyclic voltammograms for zinc solution in presence of SLS and antimony. Key: (1) addition-free; (2) SLS 1 mg dm^{-3}; (3) [2] + Sb 0.02 mg dm^{-3}; (4) [2] + Sb 0.04 mg dm^{-3}; (5) [1] + Sb 0.04 mg dm^{-3}.

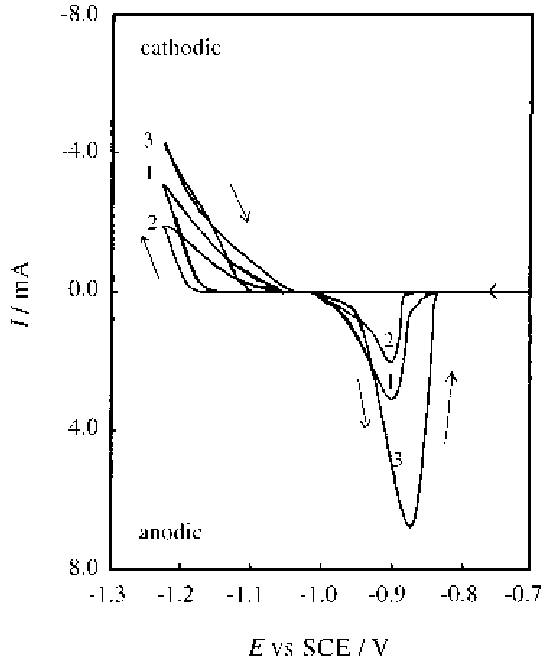

Fig. 5. Cyclic voltammograms for zinc solution in presence of glue and antimony. Key: (1) addition-free; (2) glue 5 mg dm^{-3}; (3) [2] + Sb 0.04 mg dm^{-3}.

current. This may be due to the catalytic production of hydrogen [35]. Because of the reduced 'NOP' the rate of zinc deposition and hydrogen evolution both increase but at higher Sb concentrations the hydrogen evolution reaction becomes dominant, so that the CE of zinc deposition decreases. The important thing here is that there is a specific combination of Sb with the additive where CE is actually maximum. The specific combination of SLS is 1 mg dm^{-3} SLS + 0.02 mg dm^{-3} Sb and for glue is 5 mg dm^{-3} glue + 0.02 mg dm^{-3} Sb. This effect was also reflected in the current efficiency. The catalytic effect of Sb was the highest in the addition-free solution as can be seen from curve 5, Fig. 4. This is also supported by the low CE value obtained (~83%, Fig. 2).

3.3. *Deposit morphology and orientation*

The zinc deposit obtained from addition free solution was bright but not very smooth. At lower concentrations of SLS and glue smooth and bright deposits are obtained. At higher concentrations of SLS bright and smooth deposits are obtained except at $\geq$ 20 mg dm^{-3} where a dull bright, but smooth, deposit was seen. In the case of glue bright and smooth deposits are obtained up to 10 mg dm^{-3} but thereafter a dull bright and even nodular deposit is obtained. SLS at lower concentration (< 5 mg dm^{-3}) is found to counteract the deleterious effect of relatively high concentrations of Sb ($\leq$ 0.08 mg dm^{-3}) on zinc deposit quality. In this context SLS is a better additive than glue which produces porous and dull deposits when Sb exceeds 0.02 mg dm^{-3}. Even very high concentration of glue ($\geq$ 5 mg dm^{-3}) are ineffective in counteracting the deleterious effect when Sb concentration exceeds 0.04 mg dm^{-3}.

To understand the effect of the various additives on the electrodeposited zinc morphology, a detailed study on the crystallographic orientations and examination of zinc deposits using scanning electron microscope were carried out. Typical SEM photomicrographs are shown in Fig. 6(a)–(g). The zinc deposit obtained from addition-free solution consisted of hexagonal platelets of moderate size with (1 0 1) (0 0 2) (1 0 0) (1 0 3) (1 1 2) crystal orientations (Fig. 6(a)). Addition of 1 mg dm^{-3} of SLS markedly reduced the growth of basal (0 0 2) planes and to some extent the pyramidal (1 0 3) plane but increase the platelet size (Fig. 6(b)). 2 mg dm^{-3} of SLS produced random orientations with preferred crystal planes (1 0 1) (1 0 2) (1 0 3) (1 1 4) (1 1 2). By increasing the SLS concentration to 5 mg dm^{-3}, a reduction in platelet size is seen along with the growth of basal (0 0 2) planes (Fig. 6(c)). The results in Table 2 shows that no clear trend relating crystal orientations and additive concentrations is observed. The copresence of Sb with SLS has a marked effect on crystal orientations. For example addition of 0.02 mg dm^{-3} Sb to the solution containing 1 mg dm^{-3} SLS changed the orientations from those described earlier for the Sb-free solution by developing (1 1 0) and (1 1 2) planes along with (1 0 1) (1 0 2) and (1 0 3) showing a peculiar deposit morphology where very close packed smaller platelets were grown around the bigger ones (Fig. 6(d)). Glue affects the growth quite differently from SLS. At 1 mg dm^{-3} glue, the growth of (1 0 0) and (1 1 0) planes is seen. Increasing the glue concentration to 5 mg dm^{-3} enhances the growth of basal (0 0 2) and prismatic (1 0 0) planes and reduced the platelet size (Fig. 6(e)). Further increase in the glue concentration (> 20 mg dm^{-3}) enhanced the growth of all the crystal planes discussed above.

The addition of Sb in the presence of glue also has a marked effect. For example, as shown in Fig. 6(f), a combination of 0.04 mg dm^{-3} Sb with 5 mg dm^{-3} glue produced random orientation (1 0 1) (1 1 2) (1 0 2) (1 0 3) (1 1 4) with reduction in platelet size. The results for other concentrations are listed in Table 2. No clear correlation between concentration and crystal orientation is also observed in this case.

4. Conclusions

The effects of SLS on the electrowinning of zinc from acidic sulfate solution were investigated and the results were compared with glue as the addition agent. The results may be summarized as follows:

(i) SLS addition increased current efficiency, reduced power consumption and produced smooth zinc deposits.
(ii) SLS and glue affected the cathodic polarization of zinc similarly.
(iii) Combining 1 mg dm^{-3} SLS with Sb resulted in a smooth surface, higher CE than that of glue and reduced power consumption.

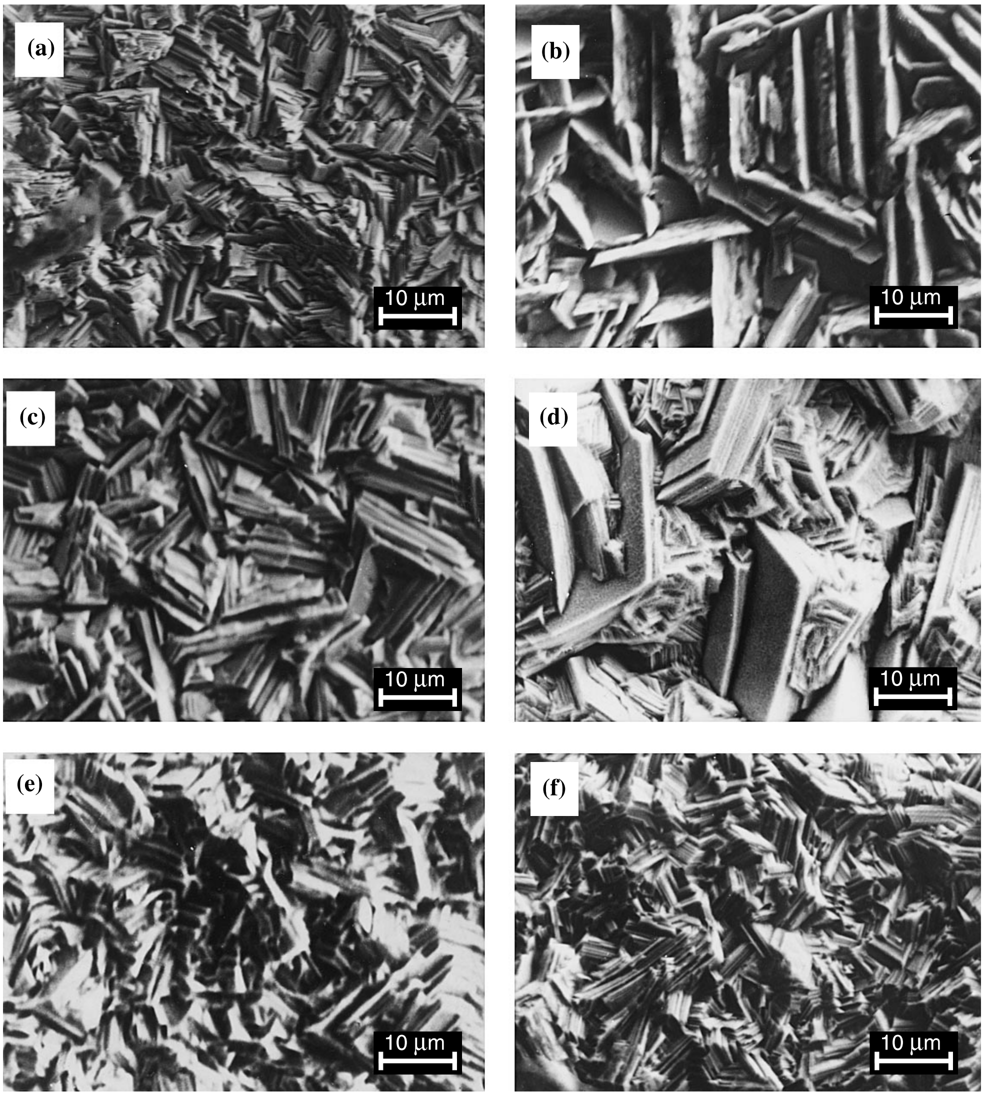

Fig. 6. SEM photomicrographs (1200 ×) of zinc deposits: (a) addition-free; (b) SLS 1 mg dm^{-3}; (c) SLS 5 mg dm^{-3}; (d) SLS 1 mg dm^{-3} + Sb 0.02 mg dm^{-3}; (e) glue 5 mg dm^{-3}; (f) glue 5 mg dm^{-3} + Sb 0.04 mg dm^{-3}.

Table 2. Crystallographic orientations of zinc deposits at different concentrations of SLS, glue and antimony

[*Additive*] / mg dm^{-3}	[*Sb*] / mg dm^{-3}	*Crystallographic orientations* (*h k l*) *Peak intensity ratio* ($I/I_{\max}$)/%							
		(*101*)	(*102*)	(*103*)	(*002*)	(*100*)	(*112*)	(*110*)	(*114*)
0	–	100	21	23	37	29	21	21	10
SLS									
1	–	100	23	15	8	24	13	7	13
1	0.02	63	29	44	7	8	45	100	8
1	0.08	100	18	22	22	22	20	21	10
2	–	100	45	28	3	2	5	–	11
5	–	100	23	28	41	25	–	20	–
10	–	100	17	19	29	25	22	21	9
20	–	100	32	25	4	3	15	15	8
40	–	100	25	15	4	3	6	–	8
Glue									
1	–	100	8	4	1	19	20	15	5
2	–	100	26	21	13	9	37	13	26
5	–	100	18	23	48	25	10	10	10
5	0.02	100	16	13	4	5	38	12	5
5	0.04	100	27	22	10	7	32	8	15
10	–	100	20	24	57	25	18	17	10
20	–	100	40	32	10	11	21	19	9
30	–	100	24	28	20	13	24	13	11

(iv) SLS is more effective than glue in counteracting the deleterious effects of Sb on electrowinning of zinc from acidic sulfate solution.

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