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Ionic Liquid [BMPy]Br as an Effective Additive During Zinc Electrodeposition from an Aqueous Sulfate Bath

by

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ABSTRACT

The effects of a new ionic liquid additive 1-butyl-3-methylpyridinium bromide [BMPy]Br on the electrodeposition of zinc on steel substrates from acidic sulfate solution was investigated by employing potentiodynamic polarization and cyclic voltammetry techniques complemented with XRD and SEM measurements. Kinetic parameters such as the Tafel slope, transfer coefficient and exchange current density obtained from Tafel plots, indicated that [BMPy]Br had a pronounced inhibiting effect on Zn⁺² electroreduction and led to more leveled and fine-grained deposits, especially at low concentrations. In addition, [BMPy]Br was found to improve the throwing power as well as the throwing index of the electrolytic solution. Data obtained from x-ray diffraction spectra revealed that the presence of this additive did not change the crystal structure of the electrodeposited zinc but strongly affected the crystallographic orientation of the crystal planes.

Keywords: zinc electrodeposition, zinc sulfate bath, 1-butyl-3-methylpyridinium bromide, ionic liquids

Introduction

Adding organic compounds to an electroplating bath is one of the most effective and most frequently used methods to improve the quality of the deposits, control the surface morphology and improve the throwing power of the baths.¹ However, ionic liquids are a fascinating group of new chemicals with the potential to improve development in chemical technology,^{2,3} stimulating considerable research in the field. Over the past few decades the number of publications concerning ionic liquids has increased substantially.⁴ In recent years, air and water-stable ionic liquids (ILs) have emerged as a powerful alternative to conventional molecular organic solvents due to their particular properties, such as undetectable vapor pressure, wide liquid range, as well as ease of recovery and reuse, making ILs a greener alternative to volatile organic solvents.⁵⁻⁷

Currently, scientists are interested in the applications of ionic liquids as additives. Reports on ionic liquids used as lubricant additives,^{8,9} organic synthesis and catalytic reactions,^{10,11} mobile phase additives in liquid chromatography¹² and corrosion inhibitors.¹³ Many researchers have been used ionic liquids in electrodeposition process.¹⁴⁻¹⁷ However, a few studies have been reported using ionic liquids as additives in electrodeposition processe.¹⁸ Therefore, the present work aims to study the effect of 1-butyl-3-methylpyridinium bromide [BMPy]Br on the electrodeposition of zinc from an aqueous sulfate bath. In addition, the study aims to throw more light on the kinetics and the mechanism of zinc deposition as well as on the throwing power.

Experimental procedure

Microwave-assisted preparation of [BMPy]Br was carried out as follows: a mixture of 3-methylpyridine (10 mmol) and 1bromobutane(10 mmol) in 25 mL of toluene was prepared in a Borosil 50 mL conical flask and exposed to microwave irradiation at power level (200 W) for 10 min. The flask was allowed to cool and extracted with 10 mL x 2 of ethyl acetate. The resulting viscous liquid was obtained at a 91% yield. The synthetic products were characterized by NMR, and the corresponding spectral characteristics were described as follows.

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98 (8), 6-15 (November 2011)

The ¹H NMR spectrum (400 MHz; D₂O) consists of the following peaks: 0.99 (3H, t), 1.40 (2H, m), 2.05 (2H, m), 2.62 (3H, s), 4.64 (2H, t), 7.89 (1H, t), 8.33 (1H, d), 8.64 (1H, d) and 8.69 (1H, s). The ¹³C NMR spectrum (400 MHz; D₂O) consists of the following peaks: 15.41, 20.41, 21.37, 35.21, 64.10, 130.05, 142.45, 143.95, 146.34 and 148.55.



1-butyl-3-methylpyridinium bromide ([BMPy]Br)

For the electrodeposition runs, a steel sheet cathode (0.5 mm) and a zinc sheet anode (0.38 mm, 99.9%, BDH), each of dimensions (2.5 × 3.0 cm) were used. The zinc deposition was carried out from a solution containing 0.15M ZnSO₄ and 0.15M Na₂SO₄. The deposition cell used and the calculation of the cathodic current efficiency have been described elsewhere.^{19,20} All experiments were carried out using unstirred solutions and the duration of plating was 10 min. All of the experiments were carried out at 25°C.

The throwing power (*TP*) of the solution was measured using a Haring-Blum rectangular Perspex cell (3.0 cm wide, 13.0 cm long, with a 2.5 cm solution depth) fitted with one anode between two parallel cathodes where the ratio of the far-to-near distance was 5:1. The percentage throwing power was calculated from Field's formula:²¹

$$TP(\%) = (L - M / L + M - 2) \times 100$$

(1)

where *L* is the current distribution ratio or linear ratio (5:1) and *M* is the metal distribution ratio of the near-to-far distance on the cathodes. The values of *M* were measured as a function of *L* over a wide range of linear ratios varying between 1:1 and 5:1. The throwing index (*TI*) of each bath was considered as the reciprocal of the slope of the *M* versus *L* plot.²²

The potentiodynamic cathodic polarization measurements were performed in the rectangular cell as published earlier.^{23,24} The potentiodynamic polarization measurements were carried out by sweeping the potential from about 0 V_{SCE} to -1.4 V_{SCE}, at a scan rate of 10 mV/sec. The classic three-electrode cell was used for the cyclic voltammetry measurements. The working electrode was a glassy carbon rod (GC)(area = 0.1963 cm²) embedded in a PVC cylinder. The GC electrode was polished before each run with diamond paste (0.25 µm) until a mirror surface was obtained, then washed several times with doubly distilled water. The counter-electrode was a platinum wire. All potentials were recorded with respect to a saturated calomel electrode placed in a Luggin capillary. The cyclic voltammetry was carried out in the potential range of -0.5 V_{SCE} to -1.4 V_{SCE}. The sweep potential was initiated at -0.5 V_{SCE} and swept in the negative direction up to -1.4 V_{SCE}. The scan was then reversed in the anodic direction up to -0.5 V_{SCE}. Some CVs were carried out with different ionic liquid concentrations and others were carried out with different scan rates. A potentiostat/galvanostat controlled by a personal computer was used for all the electrochemical measurements. The zinc deposit morphology was evaluated using scanning electron microscopy. The crystalline structure of zinc deposited on copper was examined by x-ray diffraction using a diffractometer (40 kV, 30 mA) with a Ni filter and Cu k_a radiation.

Results and discussion

Voltammetric behavior

Potentiodynamic polarization curves and Tafel lines

The potentiodynamic cathodic polarization (*i*/*E*) curves for zinc electrodeposition were measured with and without the addition of different concentrations of [BMPy]Br (100-1000 ppm) as shown in Fig. 1. The curves were swept from the rest potential (about 0 V) up to -1.40 V_{SCE} at a scan rate of 10 mV/sec. The data reveal that, in general, the deposition of zinc from these solutions is





98 (8), 6-15 (November 2011)

accompanied by a high polarization. Simultaneous discharge of hydrogen ions was observed during the deposition of the Zn⁺² ions. A great shift in the polarization curves towards more negative potentials is clearly observed during the electrodeposition of zinc in the presence of the ionic liquid [BMPy]Br. To obtain quantitative information about the kinetics of zinc deposition in the presence of the ionic liquid, the Tafel lines (the straight lines in the polarization curves) were used to calculate the electrochemical parameters such as the Tafel slope *b* and the transfer coefficient *a*. The exchange current densities *i*₀ for zinc deposition were obtained by extrapolating the Tafel lines to zero overpotential (Table 1). The data indicate that the Tafel slopes decrease in the presence of the ionic liquid, while the transfer coefficient *a* increases with increasing ionic liquid concentration, implying that the charge transfer reaction is affected by the presence of the ionic liquid. Moreover, the exchange current density, *i*₀, is markedly decreased with increasing the ionic liquid concentration. Generally, the exchange current density *i*₀ is decreased when the electrochemical reaction is inhibited.²³ This means that [BMPy]Br decreases and inhibits the rate of Zn⁺² ion transfer across the electrical double layer. The inhibitory effect of this ionic liquid could be due to its adsorption on the metal surface.



Figure 1 - Potentiodynamic cathodic polarization curves during zinc electrodeposition in the absence (blank) and presence of different concentrations of [BMPy]Br.

Concentration of [BMPy]Br (ppm)	Tafel slope b (mV/decade)	Exchange current density, log i₀ (A/cm²)	Transfer Coefficient a
0	-256.4	1.40 × 10⁻⁵	0.05
200	-197.2	2.53 × 10-6	0.07
300	-151.9	2.47 × 10 ⁻⁷	0.08
500	-115.7	1.09 × 10 ⁻⁸	0.11
700	-112.0	9.09 × 10 ⁻⁹	0.12
1000	-71.5	4.75 × 10 ⁻¹²	0.18

Table 1 - The electrochemical parameters deduced from the polarization curve	Table 1 - The electrochemical	parameters deduced from	the polarization curves
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Cyclic voltammetry

The cyclic voltammetry study was carried out at a glassy carbon (GC) electrode over a potential range of -0.5 to -1.40 V_{SCE} with a scan rate of 100 mV/sec in the presence and absence of [BMPy]Br as shown in Fig. 2. During the forward scan in the negative





98 (8), 6-15 (November 2011)

direction, the cathodic current increased sharply once zinc deposition began at Point B, corresponding to the reduction of Zn⁺² ions. The current then increases sharply to Point C, where it was reversed. This resulted in a decrease in current which subsequently reached zero at the crossover potential A. The current then became anodic, corresponding to the dissolution of the cathodically-deposited zinc. The appearance of such a hysteresis loop is a characteristic feature of metal deposition occurring by nucleation and growth processes. In such cases, overpotential is required to form the first nuclei on the substrate surface.



Figure 2 - Cyclic voltammetric curves recorded at GC electrode in the absence (blank) and presence of different concentrations of [BMPy]Br (scan rate = 100 mV/sec).

The potential difference between the reduction potential of zinc ions at "B" and the crossover potential at "A" is a measure of the nucleation overpotential (NOP) for zinc deposition at the steel substrate. It is obvious that the addition of [BMPy]Br increased the NOP value (Table 2), in addition to the reduction in the cathodic area, indicating an inhibition of the electrodeposition process. This is attributed to the surface coverage of the cathode by a strongly adsorbed ionic liquid layer, which blocks the active sites.

[BMPy]Br, ppm	NOP, mV	TP %	TI
0	86.9	-14.8	0.74
150	107.7		
200		2.8	1.10
300	172.3	18.2	1.52
500	204.5		

Table 2 - The nucleation overpotential (NOP) and the throwing power (*TP*%) as well as the throwing index (*TI*) as a function of ionic liquid concentrations.

Figure 3 shows the cyclic voltammograms of the zinc plating solutions in the presence of 300 ppm [BMPy]Br, recorded at the glassy carbon (GC) electrode with different scan rates (10 to 150 mV/sec). The results of the study of the variation of the current density of the cathodic peak (i_{cp}) as a function of the scan potential rate (v) are shown in the inset of Fig. 3. The linear relation observed between i_{cp} and $v^{1/2}$ indicates diffusion control. The rate of growth is controlled by mass transfer of zinc ions to the growing center.²⁵ On the other hand, the negative value of the cathodic peak current density i_{cp} at $v^{1/2} = 0$, is consistent with a deposition process involving a nucleation mechanism controlled by mass transfer.²⁶





98 (8), 6-15 (November 2011)



Figure 3 - Cyclic voltammetric curves recorded at GC electrode in the absence and presence of 300 ppm of [BMPy]Br at different scan rates. The insert shows the relation between the cathodic peak (*i*_{cp}) as a function of the scan rate (*v*).

Adsorption isotherms

The additive molecules of [BMPy]Br are thought to adsorb on the cathode surface. This phenomenon increases the deposition overpotential by decreasing the sites available for discharge of Zn^{+2} ions. Therefore, the surface coverage by the additive can be estimated from equation (2):

$$\theta = (1 - i_{add}/i) \tag{2}$$

where *i* and i_{add} are the current density without and with the ionic liquid, respectively, at a constant potential value (-1.30 V_{SCE}). The data are fitted by a Langmuir adsorption isotherm, Equation (3):

$$\theta / (1 - \theta) = K[C]$$

(3)

where *K* is the equilibrium constant of the adsorption reaction and [*C*] is the ionic liquid concentration in the bulk of the solution. Figure 4 gives the results of the Langmuir plots for the adsorption data of the ionic liquid [BMPy]Br. From the adsorption isotherm shown in Fig. 4, the equilibrium constant *K* was evaluated to be 151.7 M⁻¹, suggesting a chemisorption.²⁷ A large value of *K* means higher adsorption of a given compound, *i.e.*, stronger electrical interactions between the double layer existing at the phase boundary and the adsorbing molecules. The standard free energy change (ΔG°_a) for adsorption was estimated using Equation (4):

$$\Delta G_{a}^{\circ} = -RT \ln (55.5 \text{ K}) \tag{4}$$

in a similar way as reported for organic molecules,²⁸ where *R* is the universal gas constant, *T* is the absolute temperature and 55.5 is the molarity of water. The high value of free energy change of -22.4 kJ/mol for [BMPy]Br confirms the extent of the chemisorption at the metal-solution interface.²⁹





98 (8), 6-15 (November 2011)



Figure 4 - Plot of $[\theta/(1 - \theta)]$ versus concentration [C] to evaluate ΔG_{\circ_a} .

Cathodic current efficiency

The effect of applied current density on the cathodic current efficiency, F%, during zinc electrodeposition in the absence and presence of [BMPy]Br, was studied and the results are shown in Fig. 5. Inspection of the data shows that the efficiency is strongly dependent on the current density and the F% in the absence of additives is high (about 98%) at low current densities (up to 1.3 A/dm²), then falls to 37% at 2.0 A/dm² as a result of simultaneous hydrogen evolution.³⁰ Generally speaking, most additives have no significant effect on the F% of metal deposition.³¹ However, they did affect the surface morphology and crystallographic orientation.



Figure 5 - Cathodic current efficiency versus current density for zinc electrodeposition in the presence and absence of [BMPy]Br.





98 (8), 6-15 (November 2011)

Throwing power and throwing index

The throwing power of the acidic sulfate baths was measured using a Haring-Blum cell in the presence and absence of the ionic liquid [BMPy]Br. According to the cell geometry, the total cell current *i* is divided into two partial currents, i_n and i_t , corresponding to the respective cathodes. In the absence of polarization, the primary current ratio (i_n/i_t) depends on the electrical resistance of the electrolyte between the anode and the respective cathodes, *i.e.*, it is inversely proportional to the ratio of their distances from the anode. Thus the primary current ratio should be equal to the distance ratio, *L*. Once the current passes, polarization takes place and it is assumed that it will be higher at the nearer cathode than at the far one. Because polarization resistance may be considered as being in series with the ohmic resistance, the current at the nearer cathode is decreased, giving rise to a more uniform secondary current distribution ratio. More equalization of the current ratio could be achieved by increasing the conductivity of the bath.



Figure 6 - Metal distribution ratio *M* versus the linear ratio *L* in the presence and absence of [BMPy]Br.

The throwing power values of the zinc sulfate plating baths calculated by Field's empirical formula at a distance ratio of 1:5 in the absence and presence of the ionic liquid [BMPy]Br are shown in Table 2. Inspection of the table shows that the percentage throwing power, TP%, of the zinc bath in absence of the ionic liquid is very low (TP% = -14.8). Addition of the ionic liquid [BMPy]Br, greatly enhances the throwing power. Its value reached 2.8% and 18.2% at 200 and 300 ppm [BMPy]Br, respectively. This means that the throwing power increases more than two times in comparison with the [BMPy]Br-free bath. This improvement in throwing power is only dependent on the concentration of the additives added. The increase in throwing power could be attributed to the preferential adsorption of the ionic liquid on the cathode surface on particularly active sites. Growth at these locations is then blocked for the reduction of Zn+2 ions.32 These results could be confirmed by the shift of polarization curves in a negative direction with increasing concentration of the additive (see Fig. 1). Jelinek and David²² reported that some of the ambiguities associated with the use of the concept of throwing power can be resolved by the use of "throwing index," which is obtained by plotting the metal distribution ratio M versus the linear current distribution ratio L on arithmetic co-ordinates. The reciprocal of the slope of the line obtained is the throwing index and represents a direct estimate of the bath throwing power. It should be noted that a solution with ideal throwing characteristics would produce a horizontal line at M = 1, whereas a bath with a poor throwing power would exhibit a very steep line in this plot. Some representative linear plots between the metal distribution ratio M, and the linear ratio L (1:1 - 1:5) are given in Fig. 6. The values of throwing power and throwing index given in Table 2 reveal that the calculated values of TI change in a parallel manner to those calculated for TP. Expressing the results in the form of throwing index rather than throwing power is advantageous because five experimental points are taken during the





98 (8), 6-15 (November 2011)

measurements of the throwing index and this minimizes errors in measurement of any one point. In addition, a single number which is characteristic of a range of linear ratios is obtained.

X-ray diffraction analysis and surface morphology of the zinc deposits

The surface morphology of the as-deposited zinc on steel was examined by scanning electron microscopy. The zinc deposited on steel from the bath without the ionic liquid is compact, non-porous and composed of hexagonal zinc crystals, oriented parallel to the substrate as shown in Fig. 7(a). However, the addition of a small concentration of [BMPy]Br (100 ppm) to the zinc bath led to a dramatic change in zinc crystallite morphology. It changed to crystal platelets oriented perpendicular to the cathode surface (Fig. 7(b)). However, increasing the concentration of the ionic liquid additive to 300 ppm led to the formation of agglomerates. Each agglomerate consists of small zinc crystallites (Fig. 7(c)). The zinc crystallites became smaller in size and could lead to the formation of nano-sized zinc deposition. This will be tested in future work to produce nano-grained zinc by electrodeposition.



Figure 7 - Photomicrographs of zinc deposited in the absence and presence of different concentrations of [BMPy]Br: (a) 0 ppm, (b) 100 ppm and (c) 300 ppm.

The microstructure of the as-deposited zinc obtained in presence and absence of [BMPy]Br was examined by x-ray diffraction. The results indicate that the zinc deposited from the [BMPy]Br-free solutions exhibited a hexagonal structure, with strong (101) and (002) diffraction peaks (preferred growth orientation) in addition to (110), (102), (100) and (004) peaks with relatively very low intensities, as shown in Fig. 8(a). This means that most of the zinc crystallites were oriented parallel to (101) and (002) planes. The intensity of the (101) peak increased in the presence of [BMPy]Br (Fig. 8(b)). It is worthwhile to mention here that a further increase in [BMPy]Br concentration had no significant effect on the XRD pattern.





98 (8), 6-15 (November 2011)



Figure 8 - X-ray diffraction analysis of zinc electrodeposited in (a) the absence and (b) the presence of [BMPy]Br.

Conclusions

Analysis of the results led to the following conclusions:

- 1. Addition of [BMPy]Br to the zinc plating solution led to the formation of a fine-grained deposit, especially at low concentrations.
- 2. A great shift in the polarization curves towards more negative potentials values is observed during the electrodeposition of zinc in the presence of the ionic liquid.
- 3. Cyclic voltammetric measurements showed that the addition of the ionic liquid increased the nucleation overpotential, indicating an inhibition of the electrodeposition process.
- 4. The adsorption of the ionic liquid on the cathode surface during zinc electrodeposition obeys the Langmuir adsorption isotherm.
- 5. The throwing power more than doubled in comparison with the [BMPy]Br-free bath.
- 6. X-ray diffraction spectra revealed that the ionic liquid did not change the crystal structure of the electrodeposited zinc, but strongly affected the crystallographic orientation of the crystal planes.

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98 (8), 6-15 (November 2011)

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