ELECTROWINNING OF ZINC FROM ELECTROLYTES CONTAINING ANTI-ACID MIST SURFACTANT

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Key Words: Electrowinning; nonyl phenol oxyethylene; acid mist; zinc CE.

ABSTRACT

A series of experiments were conducted to measure the current efficiency of synthetic zinc electrolytes containing additions of nonyl phenol oxyethylene surfactant. The values of cell voltage were also measured and the specific power consumptions were calculated. The surfactant added in order to prevent acid mist problem. The experiments were carried out for non-sparged and sparged systems with different surfactant concentrations at several operating conditions such as current density and zinc/acid ratio. The zinc current efficiency values varied from 56.10 to 90.02 and specific power consumptions were in the range of 2898 to 5222 K.W.h/ton according to operating conditions, surfactant concentrations and system type.

1. INTRODUCTION

In electrowinning processes acids are usually added to the electrolytes to improve conductivity and enhance energy consumption. The metal deposition reaction is usually accompanied by gas evolution reactions, namely hydrogen at the cathode and oxygen at the anode. The gas bubbles formed on electrode surfaces entrain acid drops as they leave the cell, thus causing a case of acid mist in the surrounding environment. The acid mist formed causes a corrosion to the electrical power connections and equipment in addition to its serious effects on environment. Therefore, surface active agents are usually added to control this problem [1-2]. Zinc electrowinning process is an example of metal deposition process where sulfuric acid is added to zinc sulphate electrolytes. Hydrogen and oxygen gases are evolved on cathodes and anodes respectively, and carry out droplets of sulfuric acid into electrolysis areas. Recent studies show that gas sparging of the electrolytic cells is an efficient method to increase mass transfer, consequently production rates of metal deposition are enhanced [3-5]. The case of gas sparging could intensify the problems arising from acid mist formation in the plant area.

The surfactants usually used in acidic electrolytes must be stable in this medium, have an effective foaming power and do not change the zinc deposition process

significantly. Therefore, there is always a need to investigate the role of effective surfactants on the performance of zinc electrowinning process in both traditional non-sprged zinc electrolytic system and in new sparged system. Nonyl phenol oxyethylene surfactant is considered an effective surfactant for many industrial applications. However, its role in zinc electrowinning process has not been studied before.

The present work aims to study the effect of nonyl phenol oxyethylene concentrations on zinc current efficiencies, cell voltage and specific energy consumptions under different current densities for both non-sparged and sparged systems containing different zinc/acid ratios, such study would assist in assessing the feasibility of using surfactants as anti-acid mist materials.

2. EXPERIMENTALDETAILS

Current efficiency measurements, CE, were carried out using synthetic zinc electrolytes prepared from additions of sulfuric acid AR from BDH to pure zinc sulphate powder from Prolab company. The ratios of zinc/acid concentration per liter were 0.25 (50 gm Zn, 200 gm acid), 0.5 (50 gm Zn, 100 gm acid) and 1.0 (100 gm Zn, 100 gm acid). The nonyl phenol oxyethylene concentrations were

varied from 0.0 to 44.4 mg/l. The measurements of zinc current efficiency (CE) for non-sparged system were carried out using regular electrolysis cell. The CE measurements for sparged system were carried out in glass cell similar to regular electrolysis cell with the necessary modifications required for gas sparging. Figure (1) shows a schematic diagram of the cell used.
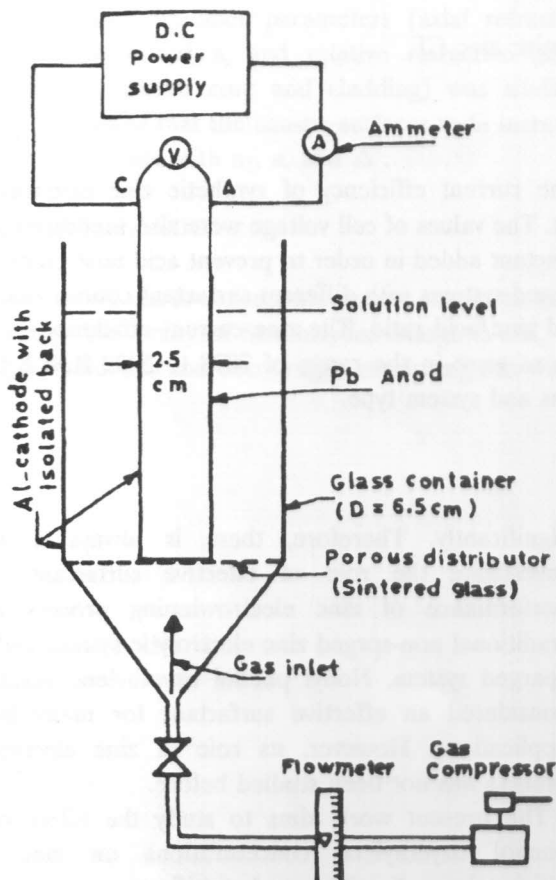
deposition process were carried out at $22\pm1^\circ$C for one hour. The current efficiency was calculated according to Farady's law and the cell voltage was measured by a voltmeter and consequently specific energy, E, was calculated.

3. RESULTS AND DISCOUSSIONS

The relation between zinc CE and surfactant concentrations at 50 mA/cm^2 c.d are shown in Figures (2) and (3) for non-sparged and sparged systems, respectively.
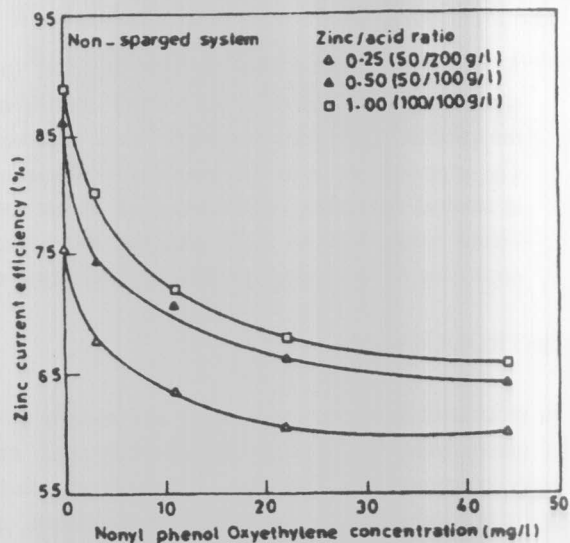

Figure 1. Schematic digram for eletrolsis cell used in gas sparged system.

The experimental set up used for this study was the most effective set ups tested to give reproducible results during gas sparging process. The gas enters the zinc electrolyte through a porous distributor with superficial air velocity equals 0.13 cm/sec. This velocity provides uniform gas bubbles distribution inside the cell. The electrodes used in CE measurements were rectangular sheets of lead ,anode, and aluminum ,cathode, of 99.9% purity. The cathodes were polished by SiC paper (350), cleaned with soapy solution, tap water then rinsed by distilled water and dried. The cathode was 1.5 cm wide and 5.5 cm high and separated from equal size anode by 2.5 cm. The current density values were varied from 30 to 130 mA/cm^2. The

Figure 2. The effect of surfactant conc. on zinc CE for non-sparged system, at 50 mA/cm^2 CD.
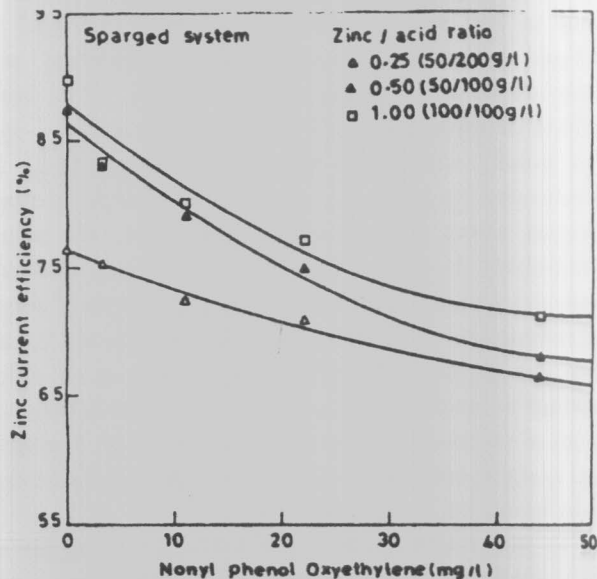

Figure 3. The effect of surfactant conc. on zinc CE for sparged system, at 50 mA/cm^2.

The results show that zinc CE decreases with increasing surfactant concentrations in both systems, e.g., the percentage zinc CE's values at 0.5 zinc/acid ratio for non-sprged system are 86.2, 74.3 and 64.08 for 0.0, 3.3 and 44.4 mg/l surfactant concentrations, respectively and for the same surfactant concentrations the values of zinc CE for sparged system are 87.5, 82.83 and 68.05% respectively. Similar trend is also observed for other zinc / acid ratios such as 0.25 and 1.0.
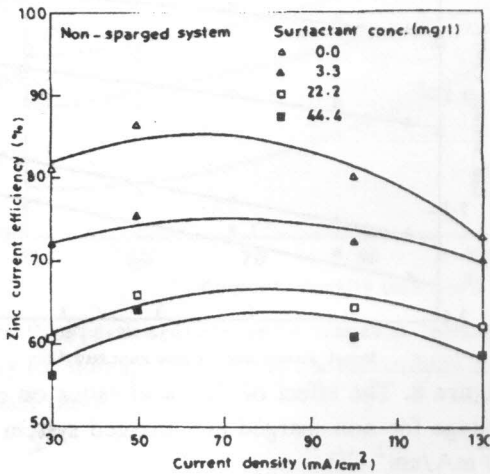

Figure 4. The effect of current density on zinc CE for non-sparged system for electrolytes contain 0.5 zinc/acid ration.
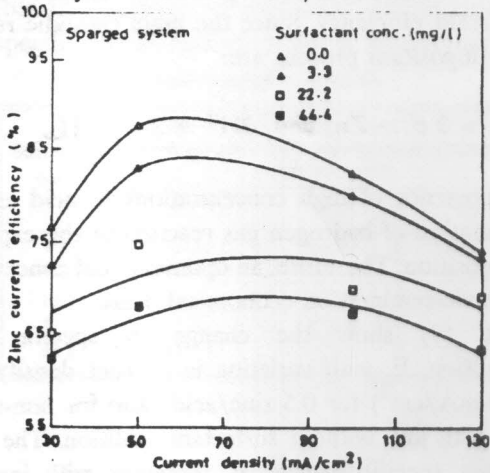

Figure 5. The effect of current density on zinc CE for sparged system for electrolytes contain 0.5 zinc/acid ratio.

Figures (4) and (5) show the change in zinc CE values with current density at 0.5 zinc/acid ratio for non-sparged and sparged systems, respectively. The addition of surfactant concentrations decrease the zinc CE for all current density values examined for both non-sparged and sparged systems. For example, in non-sparged system the

zinc CE at 100 mA/cm^2 drops from 80.3 to 61% as the surfactant concentration increases from 0.0 to 44.4 mg/l. Similar drop is obtained for sparged system, e.g., at 100 mA/cm^2 the percentage zinc CE decrease from 82.5 to 67.38 as surfactant concentration increases from 0.0 to 44.4 mg/l, respectively. The decrease in zinc CE is due to the decrease in the zinc deposition reaction rate. This is probably due to the adsorption of surfactant material on the whole electrode surface area with a consequent increase in the interfacial viscosity. This leads to decreasing the effective diffusivity of Zn^{++}, accordingly, the rate of mass transfer and the rate of Zn deposition decreases. This explanation is consistent with previous studies which indicated that mass transfer rates decrease in presence of surfactants [6].
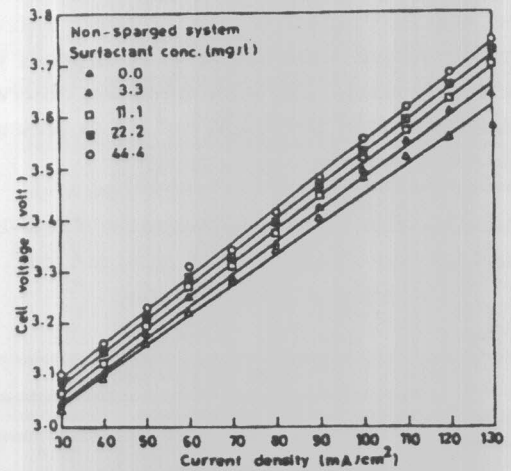

Figure 6. Cell voltage versus current density for non-sparged system for electrolytes contain 0.5 zinc/acid ratio.
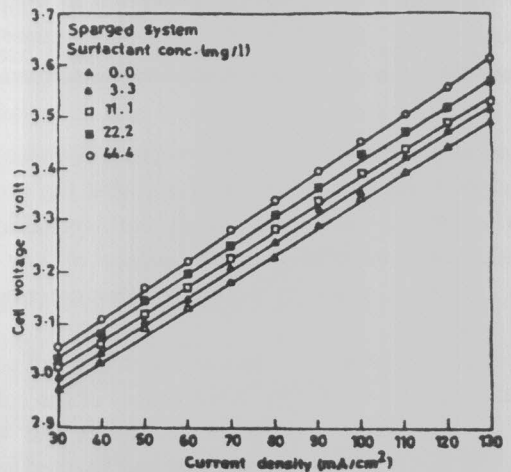

Figure 7. Cell voltage versus current density for sparged system for electrolytes contain 0.5 zinc/acid ratio.

Figures (6) and (7) show the relationship between cell voltage measurements and current density for non-sparged and sparged systems, respectively. The systems contain 0.5 zinc/acid ratio with several surfactant concentrations for non-sparged and sparged systems, respectively. The results indicated that cell voltage increases with increasing current density and surfactantconcentrations. For example, for non-sparged system without surfactant additions, the cell voltage values are 3.03, 3.16, and 3.58 volt for c.d values of 30, 50 and 130 mA/cm^2, respectively. The cell voltage values at fixed c.d of 50 mA/cm^2 increases from 3.16 to 3.23 volt as surfactant concentration increases from 0.0 to 44.4 mg/l. The same behaviour was found for sparged system, e.g., cell voltage values are 2.97, 3.09 and 3.49 for current densities 30, 50 and 130 mA/cm^2. The surfactant additions also increase cell voltage for sprged system by a value which ranged from 2.3 to 4.7% depends on the current density values. The same trend was observed for other zinc/acid ratios at 50 mA/cm^2 c.d as presented in Table I.

Table I. The effect of surfactant concentrations on cell voltage for non-sparged systems at 50 mA/cm^2, for different zinc/acid ratios.

Surfactant Conc. (mg/l)	CELL VOLTAGE (volt)					
	zinc/acid ratios					
	0.25		0.5		1.0	
	No sparging	sparging	No sparging	sparging	No sparging	sparging
0.0	3.07	3.02	3.16	3.09	3.25	3.17
3.3	3.08	3.04	3.18	3.10	3.26	3.18
11.1	3.09	3.06	3.20	3.12	3.27	3.19
22.2	3.11	3.08	3.21	3.15	3.28	3.20
44.4	3.14	3.10	3.23	3.17	3.29	3.22

In general, the results are in agreement with those found in literature [6-8], where they indicated that the presence of surfactant in solutions leads to formation of non-coalescence bubbles of rigid surface of low rising velocity [7,8]. Consequently, conductivity decreases and cell voltage increases.

An additional important parameter which affects the conductivity of the electrolyte is the acidity of the solution. Figure (8) and Table I show the change in cell voltage values at 50 mA/cm^2 for non-sparged and sparged systems containing zinc electrolytes of zinc/acid ratios (0.25-1.0) and surfactant concentrations varied from 0.0 to 44.4 mg/l. The results indicate that the increasing of zinc acid ratio

decreases cell voltage, e.g., the values measured for non-sparged system without surfactant are 3.07, 3.16 and 3.25 volts for ratios of 0.25, 0.5 and 1.0, respectively. The same behaviour is also noticed for sparged system.
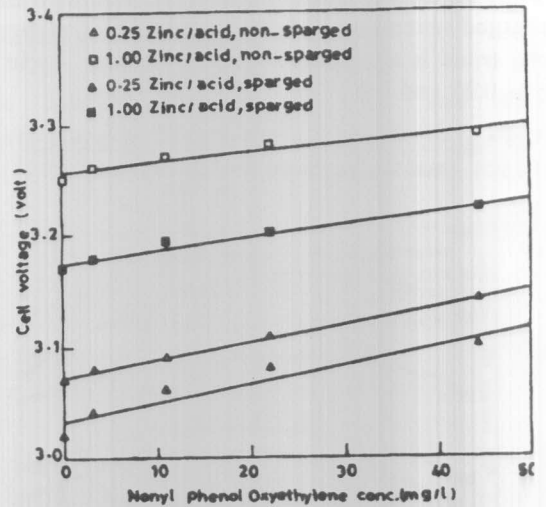

Figure 8. The effect of zinc/acid ratios on cell voltage for non-sparged and sparged system at 50 mA/cm^2 CD.

Although the cell voltage decreases with increasing acid concentrations, this is accompanied by a decrease in the zinc current efficiency. Since the main cathodic reactions in zinc deposition process are:

$$Zn^{+2} + 2\,e^- \rightarrow Zn \quad \text{and} \quad 2H^+ + 2\,e^- \rightarrow H_2,$$

The presence of high concentrations of acid enhances the formation of hydrogen gas reaction at the expense of zinc deposition. Therefore, an optimum acid concentration must be determined on economical basis.

Figure (9) show the change in specific energy consumption, E, with variation in current density values (30-130 mA/cm^2) for 0.5 zinc/acid ratio for non-sparged system with and without surfactant addition. The results show that specific energy, E, increases with increasing surfactant concentrations and current density. For example, E values at 50 mA/cm^2 are 3021, 3473.9, 3733.1 and 4157.5 k.W.h/ton for 0.0, 3.3, 11.1 and 44.4 mg/l surfactant concentration, respectively. In addition, the E values calculated for non-sparged system without surfactant increases from 3211 to 3881 K.W.h/ton as c.d values increases from 30 to 130 mA/cm^2. Similar trend is also observed for other zinc / acid ratios of 0.25 and 1.0 as listed in Table II.
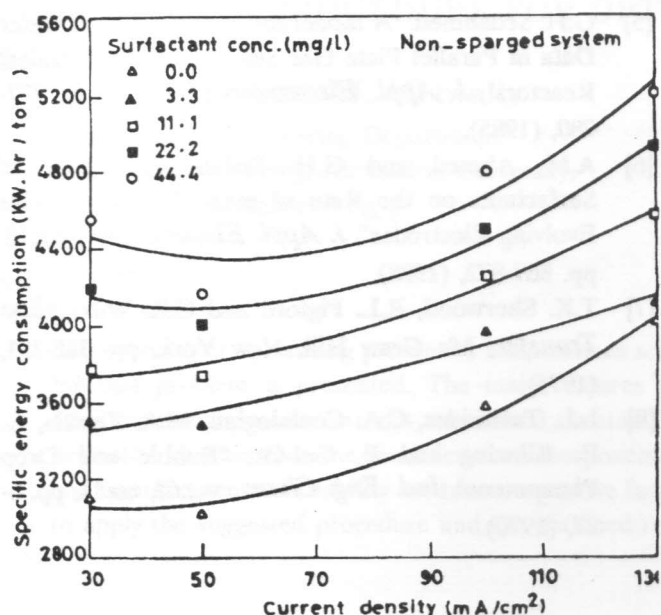
Figure 9. Specific energy consumption versus current density for non-sparged system for electrolytes contain 0.5 zinc/acd ratios.

Table II. The effect of surfactant concentrations on specific energy consumptions at 50 mA/cm^2 for non-sparged system.

Surfactant conc. (mg/l)	Specific energy comsumption (K.W.h/ton)		
	zinc/acid ratios		
	0.25	0.5	1.0
0.0	3316.7	3021.0	3011.9
3.3	3764.5	3473.9	3361.0
11.1	4026.5	3733.1	3740.0
22.2	4273.5	3999.4	3978.4
44.4	4322.9	4157.5	4111.5

The specific energy consumption values for sparged system are listed in Tables III and IV. The addition of surfactant also increases specific energy consumption for sparged system. For example, the E values, at 50 mA/cm^2, are 3211, 3418.5, 3833 and 4048.9 K.W.h/ton for 0.0, 3.3, 22.2 ,44.4 mg/l. The specific energy also increases with increasing current density, e.g., at 0.5 zinc/acid ratio without surfactant additions, the E values are 3211, 3335

and 3881 K.W.h/ton for c.d values 30, 100 and 130 mA/cm^2, respectively.

Table III. The effect of surfactant concentrations on specific energy consumptions at 0.5 zinc/acid ratio for sparged system.

Current density (mA/cm^2)	Specific energy comsumption (K.W.h/ton)				
	Surfactant conc. (mg/l)				
	0.0	3.3	11.1	22.2	44.4
30	3211.2	3418.5	3506.5	3833.0	4048.9
50	2910.1	3086.6	3265.7	3472.0	3842.1
100	3335.4	3419.6	3645.4	4041.5	4223.1
130	3881.3	3932.9	4032.6	4255.1	4695.3

Table IV. The effect of surfactant concentrations on specific energy consumptions at 50 mA/cm^2 for sparged system.

Surfactant conc. (mg/l)	Specific energy comsumption (K.W.h/ton)		
	zinc/acid ratios		
	0.25	0.5	1.0
0.0	3256.0	2910.0	2898.0
3.3	3333.2	3086.9	3154.7
11.1	3491.8	3265.7	3283.5
22.2	3578.0	3472.0	3420.0
44.4	3852.4	3842.1	3748.0

In conclusion, the present study shows that although the addition of surfactant to zinc electrolytes minimize the acid mist problems [1] it increases the specific energy consumption. Therefore, the future applications of such surfactant in zinc electrowinning process should be based on economical consideration.

CONCLUSIONS

Addition of nonyl phenol oxyethylene surfactant to zinc electrowinning solutions was found to decrease zinc current efficiency and increase both cell voltage and specific energy consumptions for non-sparged and sparged systems at different zinc/acid ratios of zinc electrolytes. Additional research studies are needed to investigate the effect of other surfactant materials on the electrowinning of zinc.

5. REFERENCES

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