

Synthesis and application of urethane as corrosion inhibitor for ZA-27 in 0.5M NaCl

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ABSTRACT

Urethane was prepared from Naphtho[2,1]furan -2-carboxyazide and chloramphenicol. The inhibition of the corrosion of ZA-27 in 0.5 M NaCl by urethane has been investigated using weight loss, potentiodynamic polarization. The results obtained in weight loss studies, show that these investigated compounds are good inhibitors and their inhibition efficiencies (IE %) increase with the increase of inhibitor concentration, whereas decreases with increase in immersion time and temperature. Potentiodynamic polarization studies demonstrate the inhibitors under investigation act as mixed type inhibitors and inhibitors changes the mechanism of hydrogen evolution. Effect of temperature is studied between 303 and 333 K differing by 10K and determination of activation parameters is also discussed. The mechanism of adsorption had been explained on the basis of chemical structure of the investigated inhibitors. It was found that there is a good agreement between the different tested techniques. Scanning electron microscopic (SEM) was used to evaluate the surface morphology and surface coverage inhibited and uninhibited samples of ZA-27 alloy. The effect of corrosion on the surface morphology of the ZA-27 alloy sample was analyzed by recording the SEM images of the alloy samples.

KEYWORDS: Corrosion inhibition, urethane, ZA-27 alloy, NaCl, Potentiodynamic polarisation, Tafel extrapolation, Scanning electron microscopy.

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I. INTRODUCTION:

Zinc and its alloys have been extensively used under different conditions in the chemical and allied industries for handling alkalis, acids and salt solutions and in power generating units, heat exchangers and cooling towers. Zinc is a metal which is mainly used for the corrosion protection of steel [1]. Therefore, zinc and its alloys are considered as industrially important materials. To address the increasing demand for high performance quality die casting, a family of hypereutectic Zn-Al alloys have been developed and are generically identified as ZA-8, ZA-12, ZA-27, where the numerical components designate the appropriate aluminum content. Zn-Al alloys can be used for manufacturing fittings exposed to steam or seawater, gears, bushings and other components subject to friction.

ZA-27 is ultra high performance material having the highest strength and elongation [2]. It has a whole range of applications. The high tensile properties of the alloy, coupled with its cast ability, enable the engineer to use it but at the same time reduce the overall material content of competitive materials. ZA-27 has good bearing properties and is very suitable for wear resistant applications. Therefore, zinc and its alloys are considered as industrially important materials. However, they are corroded by many agents, of which aqueous acids are the most dangerous [3].

The dissolution behavior of zinc and its alloys in acidic and nearly neutral media is known to be inhibited by nitrogen and sulphur containing organic compounds. Such compounds contain electron donating groups that decrease the corrosion rate by increasing the hydrogen overvoltage on the corroding metal [4]. Looking at its increasing use, the study of corrosion inhibition is of paramount importance. Most organic inhibitors are substances with at least one functional group that considered being a reaction centre for the adsorption of the compound on the corroding surface. Efficiency of compounds containing oxygen and nitrogen as inhibitors of corrosion for different metals in different corrosive environments has been studied by several workers [5-7] and their inhibition efficiency is due to the formation of a protective layer or film on the metallic surface.

Corrosion inhibitors for zinc alloys:

A number of substances ranging from inorganic to organic compounds investigated as corrosion inhibitors for zinc and its alloys in various corrosive media have been reported. Development of selective and environmentally acceptable corrosion inhibitors as alternatives of chromates [8-9], which are toxic and carcinogenic, is desirable for inhibition of zinc and galvanized steel corrosion in a neutral chloride solution [10]. Various organic inhibitors have been studied for inhibition of zinc and galvanized steel corrosion in neutral, weak acid and alkaline solutions. They are 2-quinoline carboxylic acid [11], 8-quinolinol [12], salicyl alcohol [13], mercaptobenzothiazole [14], mercaptobenzoxazole [15], benzotriazole [16], 3-amino-5-heptyl-1,2,4-triazole[16], polythioglycolates[17-18] and 2-hydrazone-3-bromo- methylenedithiol [19].

Nitrogen-containing compounds are commonly applied as corrosion inhibitors .The dissolution behavior of zinc in acidic and nearly neutral media is known to be inhibited by nitrogen and sulfur-containing organic compounds. Studies of the effect of organic additives on the corrosion rate of zinc had been the subject of many investigators [20-25]. Hence, the study on corrosion of zinc based alloys and its control is an active area of research. The present investigation is confined to the study of inhibiting action of non toxic and non carcinogenic biologically active inhibitor urethane on the corrosion behavior of zinc based alloy ZA-27. In this context, an extensive investigation on the corrosion inhibition of above said alloys in 0.5M NaCl has been done. The detailed investigation includes the effect of concentration of the inhibitors, temperature and also the immersion time on the corrosion rate of ZA-27 alloy.

II. MATERIALS AND METHODS

2.1. Procurement and moulding of zinc alloys:

ZA-27 alloys in the form of ingots were procured from M/S. Fenfee Metals, Bangalore, manufacturers of various kinds of quality metal alloys. The typical chemical composition in weight percentage of ZA-27 selected for the investigation is shown in Table 1.

Table.1 Typical Chemical Composition of ZA-27

Alloy	Al wt%	Cu wt%	Mg wt%	Fe wt%	Pb wt%	Cd wt%	Sn wt%	Zn wt%
ZA 27	26.0-28.0	2.0-2.5	0.01-0.02	Max. 0.075	Max. 0.006	Max. 0.006	Max. 0.003	Remaining

The alloy was melted by using electrical furnace. The melt was thoroughly stirred using a mechanical stainless steel stirrer coated with alumina to prevent migration of ferrous ions from the stirrer material to the zinc alloy and subsequently degasified by the addition of degassifier. Castings were produced in permanent moulds in the form of cylindrical rods of dimensions 26 mm dia and 170 mm length by Gravity Die casting Method.

2.2. Specimen preparation for weight loss studies:

Cylindrical alloy rods were cut into 24 mm dia x 2mm height circular disc specimens using an abrasive cutting wheel and a 2 mm mounting hole at the centre of the specimen (Fig1) was drilled for weight loss experiments. Before each experiment, the electrodes were abraded with a series of emery papers of different grades (600, 800, and 1200), washed with double distilled water, rinsed with acetone and dried at 353 K for 30 min in a thermostated electric oven and stored in a desiccator prior to use.



(Fig1)

2.3. Specimen preparation for electro chemical measurements:

The cylindrical test specimens were moulded in cold setting acrylic resin (Fig 2), thus a surface area of 1.0 cm² of alloy was exposed to corrosive medium in electrochemical measurements. Before each experiment, the electrodes were abraded with a series of emery papers of different grades (600, 800, and 1200), washed with double distilled water, rinsed with acetone and dried at 353 K for 30 min in a thermostat electric oven and stored in desiccator prior to use.

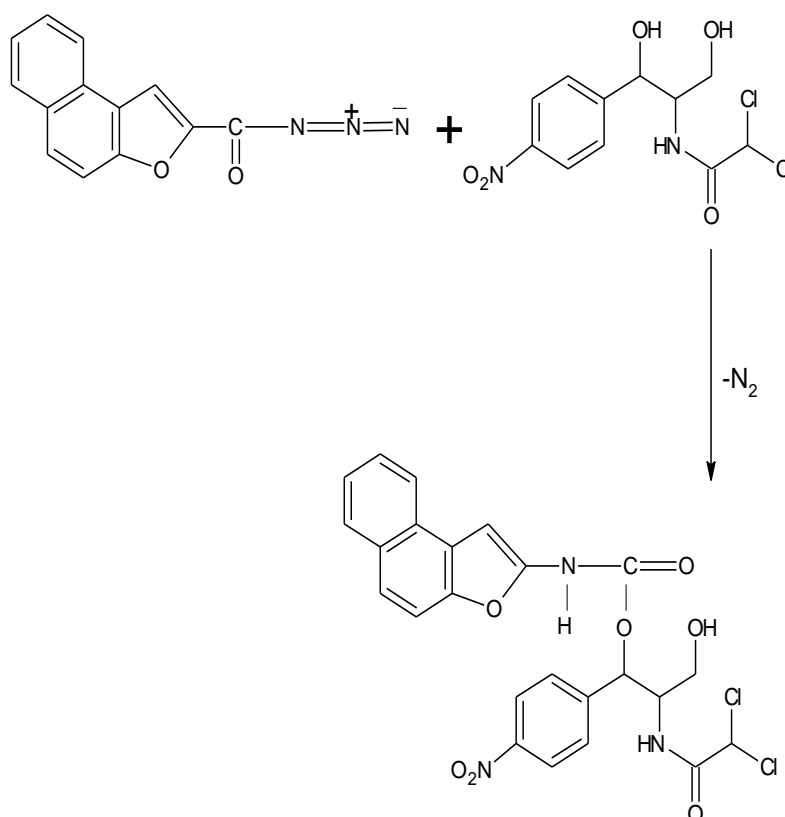


(Fig2)

III. INHIBITORS

3.1 Synthesis of inhibitor

Urethane was prepared from Naphtho[2,1]furan -2-carboxyazide and chloramphenicol. Curtius reaction took place resulting in the formation of urethane. Melting point of synthesized urethane is found to be 144⁰c



3.2. Preparation of inhibitor solution:

All the solutions for the experiment were prepared using AR grade chemicals in double distilled water. The inhibitor concentrations such as 100,200,300 and 400 ppm were used and the temperatures being 303, 313, 323 and 333±1 K. using thermostat water bath in all the experimental work. Fresh solutions were used for each experiment.

3.3 .Preparation of corrosion medium:

In the present work, 0.5M NaCl was used as the corrosive media which contained the desired quantity of the inhibitor (100ppm to 400ppm).The corrosive media selected for this study were prepared from analytical grade Merck chemicals in double distilled water.

IV. EXPERIMENTAL METHODS:

As metallic corrosion is highly diverse in its occurrence, no universal testing procedure is found satisfactory to cover all aspects of corrosion. But for reproducible and informative evaluation, it is very essential to select a relevant method to correlate laboratory tests with actual service conditions. Detailed information regarding the suitable method to be adopted in corrosion testing is available in literature [26-31]. Though absolute reproducibility is rather impossible to achieve due to several factors, reproducibility within a reasonable degree of accuracy is of considerable importance. According to Evans [32] and Champion [27], this is possible by taking precautionary measures regarding the size and shape of the specimen, design of the set up, time of exposure and a careful control of experimental conditions such as temperature and stirring of the corroding medium. It is also desirable to perform the tests at least in duplicate or triplicate to minimize the error. The surface treatment of the test specimen prior to corrosion tests is another important factor. The exposed surface should be free from oxides, grease etc., for unambiguous results. In the present work, a systematic and comprehensive approach to the understanding of the corrosion process during corrosion of ZA-27 alloys has been made as under.

4.1. Weight loss measurements:

Weight loss measurements were performed on test specimens as per ASTM Method [33].The specimens were immersed in 100ml solution of corrosive medium in absence and presence of different concentrations of the inhibitor at different temperatures and in thermostat water bath. The difference in weight for an exposed period of 2, 4, 6 and 8 hours was taken as the total weight loss. The weight loss experiments were carried out in triplicate and average values were recorded.

Calculation of corrosion rate

The corrosion rate (CR) was evaluated as per ASTM Method using equation (1).

$$CR = \frac{K \times W}{DAT} \quad (1)$$

Where, CR= Corrosion rate in mmpy,

K = a constant (8.76×10^4)

W = Weight loss in grams

D = Density in g/cm^3

A= Surface area of test specimen in cm^2 and

T = Time of exposure in hours.

Calculation of corrosion efficiency:

The percentage of inhibition efficiency ($\mu_{\text{WL}\%}$) and the degree of surface coverage (θ) were calculated using the following equations(2) and (3).

$$\mu_{\text{WL}\%} = \frac{W_o - W_i}{W_o - W_i} \times 100 \quad (2)$$

(3)

$$\theta = \frac{W_o - W_i}{W_o - W_i}$$

Where W_o and W_i are the weight loss values of specimen in the absence and presence of the inhibitor and θ is the degree of surface coverage of the inhibitor.

4.2. Potentiodynamic Polarization studies (Tafel Extrapolation)

The electrochemical experiments were carried out in a conventional three electrode cell(Fig3). The specimen samples were welded with copper wire and embedded in teflon holder using epoxy resin with an exposed area of 1 cm^2 as working electrode, a platinum foil of 1 cm^2 was used as counter electrode and the reference electrode was a saturated calomel electrode (SCE) with a Luggin capillary, which can be at close proximity to the working electrode to minimize ohmic drop. All potentials are measured with respect to the SCE. The polarization studies were carried in 0.5M NaCl as corrosive media without and with inhibitors using CHI Electrochemical workstation model 660C series from Sinsil International.



(Fig 3)

Tafel plots were obtained by polarizing the electrode automatically from -250 to $+250$ mV with respect to open circuit potential (OCP) at a scan rate 10 mV s^{-1} . The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential (E_{corr}) to obtain corrosion current densities (I_{corr}). Using Potentiodynamic Polarization parameters Corrosion Current (I_{corr}), Corrosion Potential (E_{corr}), Anodic and Cathodic Slopes (b_a and b_c) and Corrosion Rate (C.R.) were Evaluated.

The inhibition efficiency ($\mu_p\%$) was evaluated from the I_{corr} values using the following relationship(4) .

$$(4) \quad \mu_p\% = \frac{I_{\text{corr}}^0 - I_{\text{corr}}}{I_{\text{corr}}^0} \times 100$$

Where, I_{corr}^0 and I_{corr} are values of corrosion current densities in absence and presence of inhibitor respectively.

V. RESULTS AND DISCUSSION

5.1 Weight loss measurements

Fig 4 shows the effect of increasing concentrations of compound urethane on the corrosion of ZA-27 alloy in 0.5M NaCl at 303K. The calculated values of the percentage inhibition efficiency ($\mu_{\text{WL}\%}$) are listed in Table 2. Inspection of Table 2 reveals that inhibition efficiency increased with increase in the concentration of inhibitor. Increase in inhibition efficiency at higher concentration of inhibitor may be attributed to larger coverage of metal surface with inhibitor molecules. The linearity obtained indicates that insoluble surface film formed during corrosion and that the inhibitors were first adsorbed onto the metal surface and therefore, impede the corrosion process [34]. The maximum inhibition efficiency was achieved at 400 ppm and a further increase in inhibitor concentration caused no appreciable change in performance. The compound investigated shows a decrease in inhibition efficiency with increase in immersion time from 2 to 8 hours as shown in fig 5. The calculated values of the percentage inhibition efficiency ($\mu_{\text{WL}\%}$) at different time of exposure are listed in Table 3. This indicates desorption of the inhibitor molecules over a longer test period and may be attributed to various other factors such as formation of less persistent film on the metal surface, and increase in cathodic reaction. The inhibition efficiency of the inhibitor decreases with increase in temperature from 303 to 333 ± 1 K as shown in fig 6. The decrease in inhibition efficiency with rise in temperature were tabulated in table 4. The decrease in inhibition efficiency with rise in temperature may be attributed to desorption of the inhibitor molecules from metal surface at higher temperatures and higher dissolution rates of zinc alloy at elevated temperatures. The variation of corrosion rate and surface coverage as a function of concentration of inhibitor is also shown in fig 7. The calculated values of corrosion rate and surface coverage are tabulated in table 5. It is observed that the surface coverage and % of inhibition efficiency increases with increase in the concentration of the inhibitor.

Table 2: Weight loss parameters for ZA-27 in 0.5M NaCl in the absence and presence of various concentrations of inhibitor at 2 hours of exposure time

Inhibitor	Concentration (ppm)	CR (mils/year)	θ	$\mu_{WL}\%$
Urethane	Blank	126.98 x10 ²	---	---
	100	86.79 x10 ²	0.31	31.65
	200	45.34 x10 ²	0.64	64.29
	300	28.47 x10 ²	0.77	77.79
	400	14.56 x10 ²	0.88	88.53

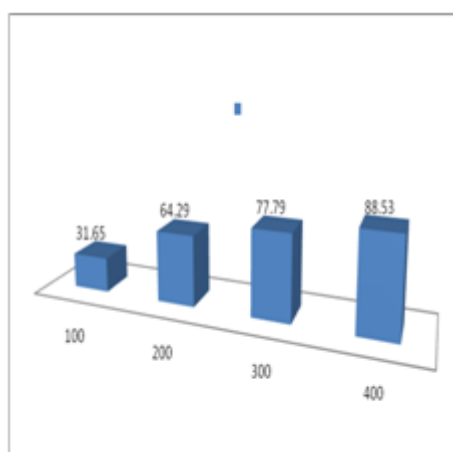


Fig:4 Variation of inhibition efficiency with concentration of inhibitor urethane

Table: 3 Inhibition efficiency of inhibitor with Exposure time with Temperature

Inhibitor	Time in Hrs	$\mu_{WL}\%$
Urethane	2	79.53
	4	66.42
	6	54.68
	8	31.06

Inhibitor	Temperature in K	$\mu_{WL}\%$
Urethane	303	79.53
	313	67.12
	323	54.60
	333	39.44

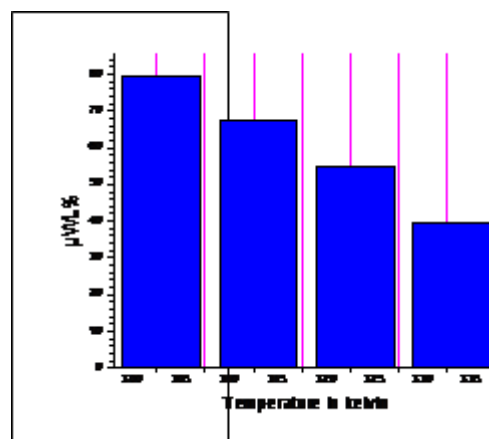
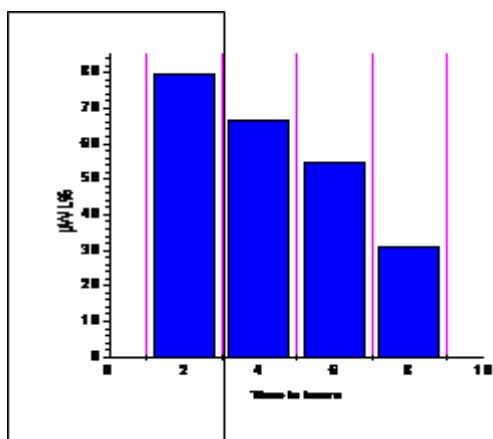


Fig: 5 Variation of inhibition efficiency With Time of Exposure

Fig: 6 Variation of inhibition efficiency with Temperature

Table: 5 Corrosion rate and Surface coverage in the presence and absence of inhibitor

Inhibitor	Concentration (ppm)	CR (mils/year)	θ
Urethae	Blank	84.64 x10 ²	---
	100	68.98 x10 ²	0.18
	200	43.09 x10 ²	0.49
	300	26.83 x10 ²	0.68
	400	17.32 x10 ²	0.79

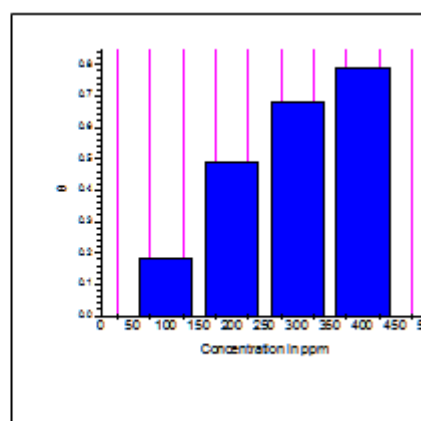
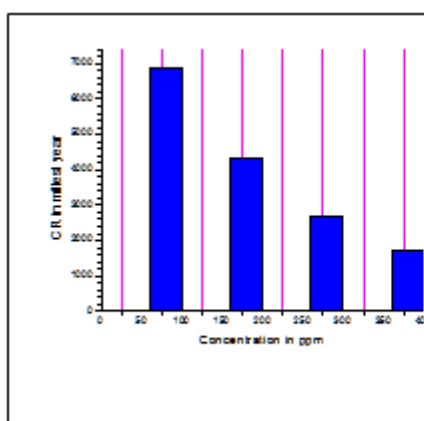


Fig:7 Variation of corrosion rate and surface coverage with concentration of inhibitor urethane

5.2 Potentiodynamic polarization (PDP) measurements: The polarization measurements of ZA-27 specimens were carried out in 0.5M NaCl in the absence and presence of different concentrations (100 - 400 ppm) of urethane at 303±1K in order to study the anodic and cathodic reactions. The Potentiodynamic polarisation curves (Tafel plots) of ZA-27 alloy in 0.5M NaCl in the absence and presence of various concentrations urethane at 303±1K were analysed. The electrochemical parameters i.e. corrosion potential (E_{corr}), corrosion current density (I_{corr}), cathodic and anodic Tafel slopes (b_a and b_c) associated with the polarization measurements are recorded in table 6 . Potentiodynamic polarization curves (Tafel plots) of ZA-27 alloy in 0.5M NaCl in absence and presence of various concentrations of inhibitor at 303±1 K are depicted in fig 8 . The corrosion current densities were determined from the intersection by extrapolating the cathodic and anodic Tafel lines. The inhibition efficiency (μ_p %) of inhibitors (at different concentrations) was calculated from the equation (4). It is observed from the PDP results, that the corrosion potential shifts to positive potential with respect to the blank but the displacement in corrosion potential is less than 35 mv for all inhibitors. According to Ferreria [35] and Li [36] if the displacement in corrosion potential is more than 85mV with

respect to the corrosion potential of the blank, the inhibitor can be seen either as a cathodic or anodic type. The maximum displacement was less than 35 mV which indicates that the quaternary ammonium compounds acts as mixed type inhibitors [36]. It is also observed from the data that both anodic and cathodic slopes increases thereby suggesting that the inhibitor acts as mixed type inhibitors. It can be seen from polarization results, the corrosion current density decreases with increase in inhibitor concentration and inhibition efficiency increases with increase in concentration.

Table: 6 Potentiodynamic polarization parameters of ZA-27 alloy in 0.5M NaCl in the absence and presence of various concentrations of inhibitor urethane at 303±1K.

Tafel data						
Inhibitor	Concentration(ppm)	$-E_{corr}$ (mV vs. SCE)	I_{corr} (mA cm ⁻²)	b_c (mV dec ⁻¹)	b_a (mV dec ⁻¹)	$\mu_p\%$
Urethane	Blank	1140	12.89	130.37	36.73	---
	100	1122	8.54	136.64	49.52	33.74
	200	1080	3.98	140.6	52.36	0.69
	300	1050	1.56	142.3	54.85	87.88
	400	1032	1.26	148.4	65.61	90.22

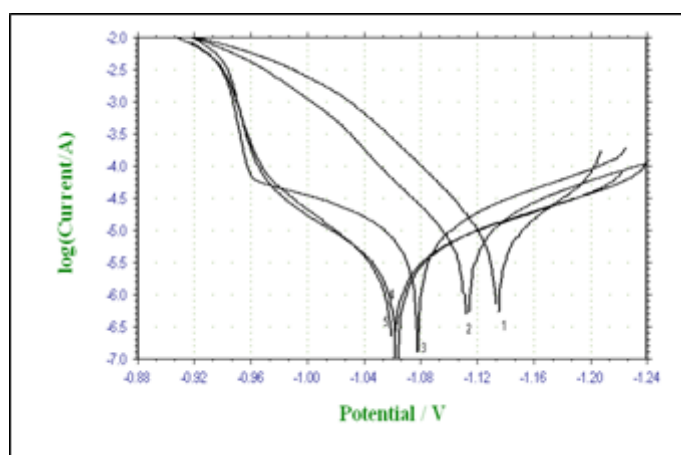


Fig: 8 Potentiodynamic polarization curves (Tafel plots) of ZA-27 alloy in 0.5M NaCl in the absence and presence of various concentrations of urethane at 303±1 K.

Table 8: Comparison of inhibition efficiency & surface coverage by different techniques.

Inhibitor	Concentration(ppm)	$\mu_{WL}\%$	$\mu_p\%$	θ_{WL}	θ_{μ_p}
Urethane	Blank	---	---	---	---
	100	31.65	33.74	0.31	0.33
	200	64.29	69.63	0.64	0.69
	300	77.79	87.88	0.77	0.77
	400	88.53	90.22	0.88	0.90

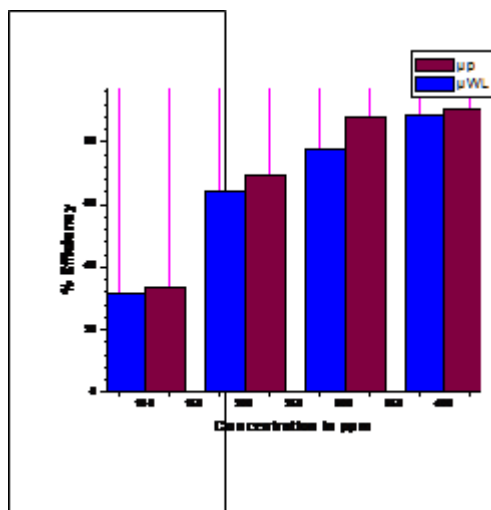
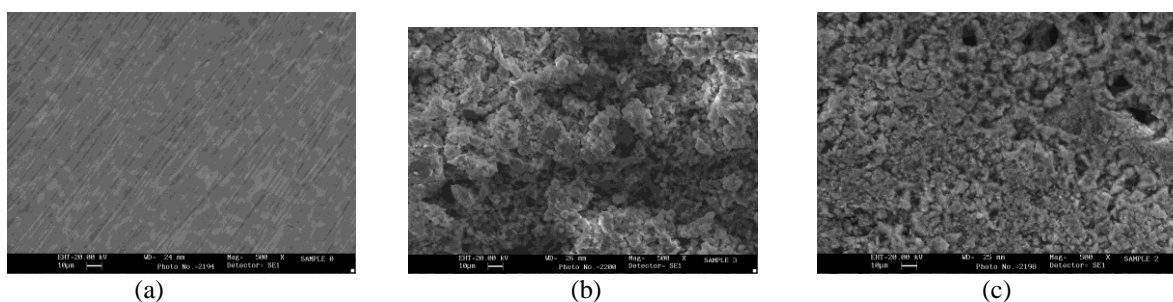


Fig:10 Variation of inhibition efficiency of urethane on ZA-27 alloy in 0.5M NaCl by different techniques

VI. SCANNING ELECTRON MICRO SCOPY

Scanning electron microcopy is a powerful technique to investigate the surface morphology of metals and alloys. Scanning electron microscopy (SEM) was used to evaluate the surface morphology and surface coverage of inhibited and uninhibited samples of ZA-27 alloy. The effect of corrosion on the surface morphology of the ZA-27 alloy sample was analyzed by recording the SEM images of the alloy samples.

The scanning electron micrographs of the cleaned surface of zinc alloy after 2hrs exposure to 0.5M NaCl without and with (400ppm + 0.5M Na₂SO₄) inhibitors was taken using Scanning electron microscope model Hitachi SU-1500. The working potential was 15 kV and the magnification range was 1000 to 5000. The SEM images of bare ZA-27 alloy (a), in 0.5M NaCl (b) in the presence of 400ppm concentration of urethane in 0.5M NaCl (c) are as follows.



It is observed from the sem images, that the the alloy surface is less damaged in presence of urethane compared to ZA-27 alloy surface dipped in 0.5M NaCl solution without inhibitor. Thus it can be concluded that urethane inhibits the ZA-27 alloy effectively by forming a uniform film on the surface of alloy.

VII. CONCLUSIONS

The used urethane compound as corrosion inhibitor for ZA-27 in 0.5M NaCl act as an efficient inhibitors. The inhibition efficiency increases with the increase of inhibitor concentration and decreases with rising of temperature and with increase in time of exposure. Potentiodynamic polarization studies demonstrate the inhibitors under investigation act as mixed type. The data obtained from all different techniques namely weight loss, potentiodynamic polarization are in good agreement.

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