

“Inhibiting Action of Quaternary Ammonium Salts on the Corrosion Behaviour of Za-27 Alloy in 1m Na₂SO₄”

Lokesh H. B¹, Sanaula Pathapalya Fakrudeen, Bheema Raju V. B³

¹Department of Engineering Chemistry, Vivekanand Institute of Technology, Kumbalagodu, Bangalore-560074, Karnataka, India.

²Department of Engineering Chemistry, HKBK College of Engineering, Nagawara, Bangalore -560045, Karnataka, India.

³Department of Engineering Chemistry, Dr. Ambedkar Institute of Technology, Mallathalli, Bangalore -560056, Karnataka, India.

Abstract: The inhibition of the corrosion of ZA-27 in 1M Na₂SO₄ by Quaternary ammonium salts Benzyl tri methyl ammonium chloride (BTMAC) and Benzyl tri ethyl ammonium chloride (BTEAC) has been investigated using weight loss, potentiodynamic polarization. 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. 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.

Keywords: Corrosion inhibition, Quaternary ammonium salts, ZA-27 alloy, Na₂SO₄ Potentiodynamic polarisation, Tafel extrapolation, EIS techniques.

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 inhibitors quaternary ammonium salts 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 1M Na₂SO₄ 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:

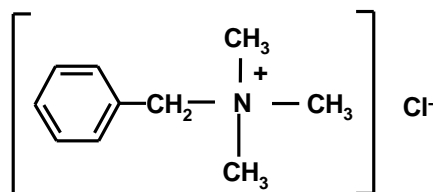
Cylindrical alloy rods were cut into 24 mm dia x 2mm height circular disc specimens using an abrasive cutting wheel and a 2 mm mounting hole at the centre of the specimen was drilled for weight loss experiments. Before each experiment, the electrodes were abraded with a series of emery papers of different 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.

2.3. Specimen preparation for electro chemical measurements:

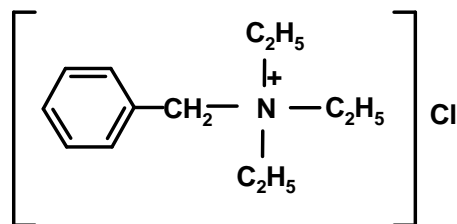
The cylindrical test specimens were moulded in cold setting acrylic resin, thus a surface area of 1.0 cm² of alloy was exposed to corrosive medium in electrochemical measurements. Before each experiment, the electrodes were abraded with a series of emery papers of different grades (600, 800, and 1200), 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.

III. Inhibitors:

3.1 In the present study, quaternary ammonium compounds Benzyl tri methyl ammonium chloride(BTMAC) and Benzyl tri ethyl ammonium chloride(BTEAC) have been selected for the study and their structures are as follows.



Benzyl tri methyl ammonium chloride(BTMAC)



Benzyl tri ethyl ammonium chloride(BTEAC)

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, 1M Na₂SO₄ 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 all the inhibitors 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 (8.76x 10⁴)

W = Weight loss in grams

D = Density in g/cm³

A= Surface area of test specimen in cm² and

T = Time of exposure in hours.

Calculation of corrosion efficiency:

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

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

$$(3) \quad \theta = \frac{W_o - W_i}{W_o}$$

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. 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 $1 \text{ M Na}_2\text{SO}_4$ as corrosive media without and with inhibitors using CHI Electrochemical workstation model 660C series from Sinsil International.

Tafel plots were obtained by polarizing the electrode automatically from -250 to $+250 \text{ mV}$ 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 ($\mu\%$) was evaluated from the I_{corr} values using the following relationship(4) .

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

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 1 shows the effect of increasing concentrations of compounds BTMAC and BTEAC on the corrosion of ZA-27 alloy in Na_2SO_4 at 303 K . The calculated values of the percentage inhibition efficiency ($\mu_{\text{WL}}\%$) are listed in Table 1. Inspection of Table 1 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. All the quaternary ammonium compounds investigated show a decrease in inhibition efficiency with increase in immersion time from 2 to 8 hours as shown in fig 2. The calculated values of the percentage inhibition efficiency ($\mu_{\text{WL}}\%$) at different time of exposure are listed in Table 2. 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 for the two inhibitors BTMAC and BTEAC decreases with increase in temperature from 303 to $333 \pm 1 \text{ K}$ as shown in fig 3. The decrease in inhibition efficiency with rise in temperature were tabulated in table 3. 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 inhibitors are also shown in fig 4. The calculated values of corrosion rates and surface coverage are tabulated in table 4. It is observed that the surface coverage and % of inhibition efficiency is more in BTEAC than that of BTMAC.

Table 1: Weight loss parameters for ZA-27 in 1M Na₂SO₄ in the absence and presence of various Concentrations of inhibitors at 2 hours of exposure time

Inhibitor	Concentration (ppm)	CR (mils/year)	θ	$\mu_{wt}\%$
BTMAC	Blank	26.1×10^2	---	---
	100	24.4×10^2	0.06	6.13
	200	14.14×10^2	0.46	46.97
	300	10.16×10^2	0.61	61.07
	400	3.36×10^2	0.87	87.12
BTEAC	Blank	24.4×10^2	---	---
	100	18.9×10^2	0.22	22.5
	200	12.52×10^2	0.49	49.50
	300	9.39×10^2	0.61	61.5
	400	2.90×10^2	0.88	88.11

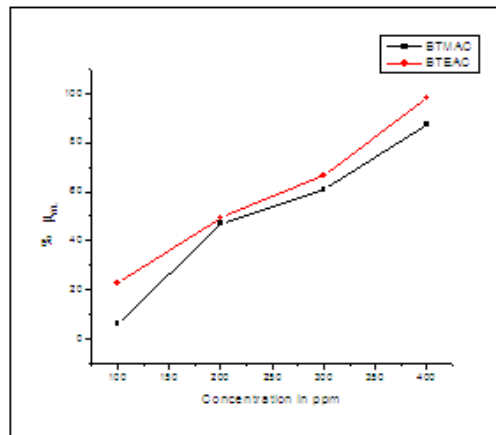


Fig: 1 Variation of inhibition efficiency with concentration of inhibitors BTMAC & BTEAC

Table: 2 Inhibition efficiency of inhibitors With Exposure time

Inhibitor	Time in Hrs	$\mu_{wt}\%$
BTMAC	2	74
	4	65
	6	58
	8	46
BTEAC	2	80
	4	69
	6	60
	8	52

Table: 3 Inhibition efficiency of inhibitors with Temperature

Inhibitor	Temperature in K	$\mu_{wt}\%$
BTMAC	303	74
	313	67
	323	60
	313	56
BTEAC	303	80
	313	75
	323	67
	313	60

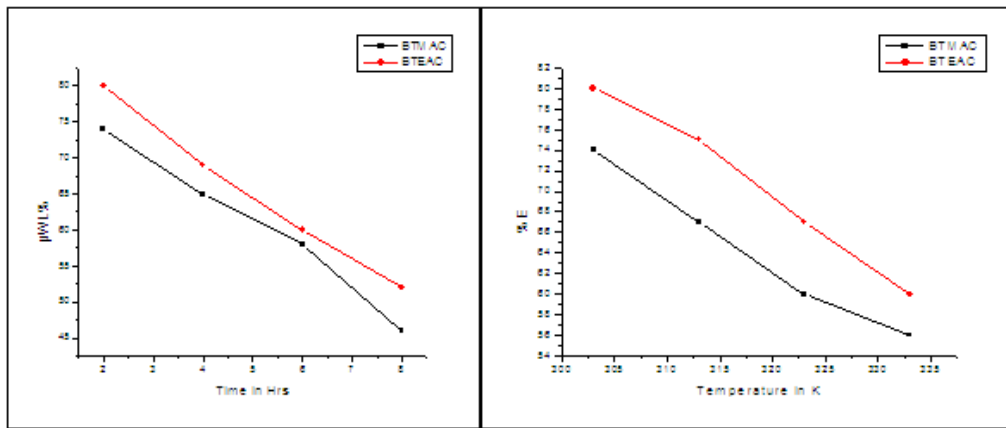


Fig: 3 Variation of inhibition efficiency
With Time of Exposure

Fig: 4 Variation of inhibition efficiency
with Temperature

Table: 4 Corrosion rate and Surface coverage in the presence and absence of inhibitors

Inhibitor	Concentration (ppm)	CR (mils/year)	θ
BTMAC	Blank	26.1×10^2	---
	100	24.4×10^2	0.06
	200	14.14×10^2	0.46
	300	10.16×10^2	0.61
	400	3.36×10^2	0.87
BTEAC	Blank	24.4×10^2	---
	100	18.9×10^2	0.22
	200	12.32×10^2	0.49
	300	9.39×10^2	0.61
	400	2.90×10^2	0.88

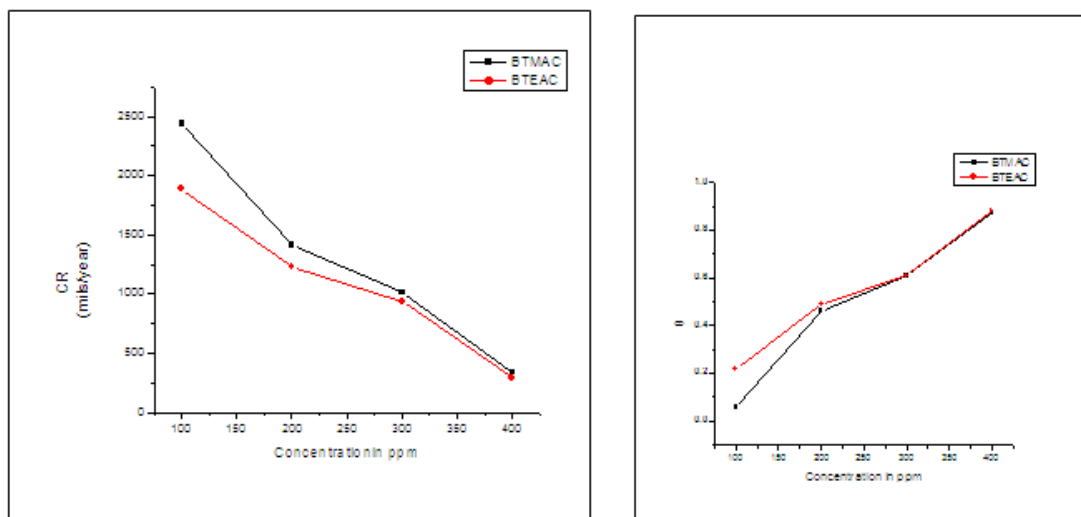


Fig: 4 Variation of corrosion rate and surface coverage with concentration of inhibitors BTMAC & BTEAC

5.2 Potentiodynamic polarization (PDP) measurements:

The polarization measurements of ZA-27 specimens were carried out in 1M Na₂SO₄ in the absence and presence of different concentrations (100 - 400 ppm) of BTMAC and BTEAC at 303±1K in order to study the anodic and cathodic reactions. The Potentiodynamic polarisation curves (Tafel plots) of ZA-27 alloy in 1 M Na₂SO₄ in the absence and presence of various concentrations of BTMAC and BTEAC 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 5 and 6. Potentiodynamic polarization curves (Tafel plots) of ZA-27 alloy in 1M Na₂SO₄ in absence and presence of various concentrations of BTMAC and BTEAC at 303±1 K are depicted in fig 5 and 6 respectively. 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 for BTMAC and BTEAC inhibitors and inhibition efficiency increases with increase in concentration. From the polarization studies the order of inhibitor efficiency for zinc alloys was found to be BTEAC I > BTMAC.

Table: 5 Potentiodynamic polarization parameters of ZA-27 alloy in 1M Na₂SO₄ in the absence and Presence of various concentrations of inhibitor BTMAC 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)	μ _p %
BTMAC	Blank	850	2.64	148.30	164.55	---
	100	817	2.4	208.98	194.55	9.09
	200	809	1.47	225.78	198.41	44.31
	300	799	1.01	255.42	204.91	61.74
	400	783	0.27	276.70	216.21	89.77

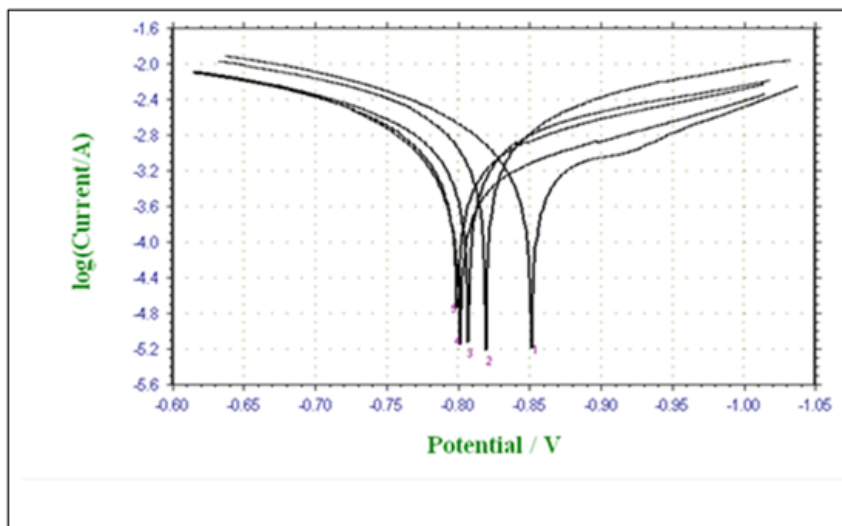


Fig: 5 Potentiodynamic polarization curves (Tafel plots) of ZA-27 alloy in 1M Na₂SO₄ in the Absence and presence of various concentrations of BTMAC at 303±1 K.

Table: 6 Potentiodynamic polarization parameters of ZA-27 alloy in 1M Na₂SO₄ in the absence and Presence of various concentrations of inhibitor BTEAC 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)	μ _p %
BTEAC	Blank	851	2.44	148.30	125.12	---
	100	831	1.62	180.50	148.80	33.60
	200	810	1.15	231.21	164.55	52.86
	300	801	0.89	304.50	175.62	63.52
	400	794	0.20	327.43	184.44	91.80

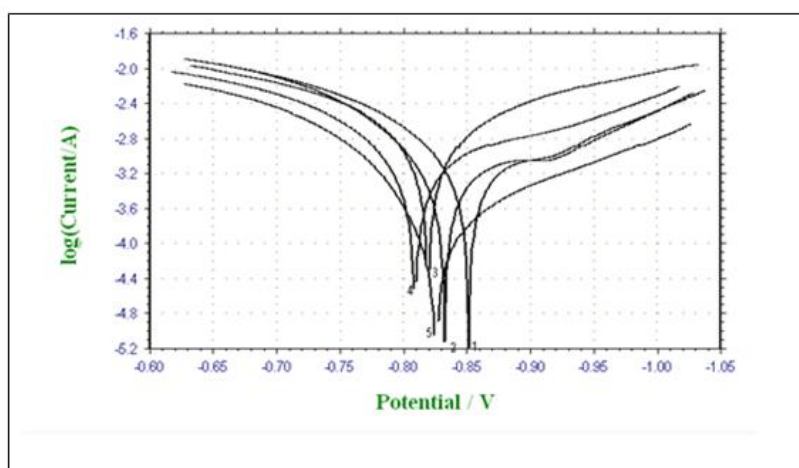


Fig: 6 Potentiodynamic polarization curves (Tafel plots) of ZA-27 alloy in 1M Na₂SO₄ in the Absence and presence of various concentrations of BTMAC at 303±1 K.

VI. Conclusions

The used quaternary ammonium compounds BTMAC and BTEAC as corrosion inhibitors for ZA-27 in 1 M NaNO₃ 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. The data obtained from all different techniques namely weight loss, potentiodynamic polarization are in good agreement. The inhibition efficiency of the investigated compounds decreases in the following order BTEAC > BTMAC. The % inhibition of BTEAC is found to be higher than that of BTMAC. This is attributed to the stronger adsorption of BTEAC on alloy surface owing to its long chain and high molecular mass when compared to that of BTMAC.

References:

- [1]. Manov S., Lamazouere A. M. and Aries L. (1999). J. Appl. Electrochem. 29, 995.
- [2]. C. H. Dale, “Zinc and Zinc Alloys” in Castings: Metals Hand- book, ASM International, Metals Park, Ohio, USA, 1988.
- [3]. Gaur J.N. and Jain B.L. (1978). J. Electrochem. Soc. India, 27, 117.
- [4]. Gad Allah A.G., Hefny M.M., Salih S.A. and El-Basiouny M.S. (1989). Corrosion, 45, 574.
- [5]. 5.Aksut A.A, and Onal A.N. (1995). Bull. Electrochem. 11, 513.
- [6]. Selim I.Z. (1998). Bull. Electrochem. 13, 385.
- [7]. Salghi R. , Hamouti B. , Aounti A., Berrabah M., and Kertit S. (2000). J. Electrochem. Soc. India, 49 (1), 40.
- [8]. N.I. Sax, R.J. Lewis Sr., Dangerous Properties of Industrial Materials, seventh ed., vol. III, Van Nostrand Reinhold, New York, 1989, p. 3056.
- [9]. S.A. Katz, H. Salem, J. Appl. Toxicol. 13 (1993) 217.
- [10]. S.M. Powell, H.H. McMurray, D.A. Worsley, Corrosion 55 (1999) 1040.
- [11]. U.F. Ushenina, N.G. Klyuchikov, Zhur. Prikl. Khim. 44 (1971) 191.
- [12]. S. Kawai, H. Kato, Y. Hayakawa, Denki Kagaku 39 (1971) 288.
- [13]. B. Muller, I. Foster, Corrosion 52 (1996) 786.u
- [14]. B. Muller, G. Imblo, Corros. Sci. 38 (1996) 293.u
- [15]. R.L. LeRoy, Corrosion 34 (1978) 98.
- [16]. K. Wippermann, J.W. Schultze, R. Kessel, J. Penninger, Corros. Sci. 32 (1991) 205.
- [17]. R.L. LeRoy, Corrosion 34 (1978) 113.

- [18]. R.L. LeRoy, Mater. Perform. 19 (8) (1980) 54.
- [19]. S. Manov, A.M. Lamazou_re, L. Ari_s, Corros. Sci. 42 (2000) 1235.ee
- [20]. . Abdel Aal M. S., Radwan S., and El-Saied A. (1983). Br. Corros. J, 18, 102
- [21]. Rajappa S.K., Arthoba Naik Y., and Venkatesha T.V. (2001). Bull. Electrochem., 17, 489.
- [22]. Ravindran, Visalakshi and Muralidharan V.S. (1993). Anti-Corros. Methods and Materials, 42, 10.
- [23]. Huang C. , Zhang W. , and Cao X. (1997). J. App. Electrochem., 27, 695.
- [24]. Venckatesh , Syed Shabudeen P.S. and Gopal S. (2007). Eur.J. Chem., 4(1), 137.
- [25]. Ein-Eli Y. ,Auinat M. ,Starosvetsky D. (2003). J. Power Sources, 114,330.
- [26]. W. H. Ailor, "Engine Coolant Testing: State of the Art", ASTM International, 1980, 134.
- [27]. F.A. Champion , (1964) corrosion testing procedures, John Wiley and Sons N.Y.
- [28]. ASTM, (1950) Special Technical publications, pp. 93.
- [29]. H.H Uhling, (1998)The corrosion Handbook , JohnWiley N.Y.
- [30]. E.L. Laque and H.R. Copson, (1963)Corrosion Resistance of metals and alloys , Reinhold publication corporation, N.Y.pp. 107
- [31]. L.L. Shreir , (1963) Corrosion, John Wiley and Sons , N.Y. Vol. 2, pp.20.
- [32]. d Evans (1964) U. R. Evans, "Metallic Corrosion, Passivity and Protection", Edward Arnold and Co., London, 1948, pp 535-540
- [33]. ASTM- Standard Practice for Laboratory Immersion Corrosion testing of Metal-G31-72- 2004.
- [34]. Abdallah, M. (2004). Corros.Sci. 46, 1981.
- [35]. Ferreira E.S., Giacomelli C., Giacomelli F.C. andSpinelli A., Mater. Chem. Phys., Vol 83, 2004, pp 129-134.
- [36]. W. H. Li, Q. He, S. T. Zhang, C. L. Pei, and B. R. Hou, Journal of Applied Electrochemistry, Vol 38-3, 2008, pp 289–295