

Assessment of Performance of Sodium Benzoate Corrosion Inhibitor Performance on AA6063 in Sea water

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Corrosion is a fundamental process which plays an important role in economics and safety. Apparently, corrosion cannot be avoided, but its severity can be reduced. Inhibitors have always been considered to be the first line of defense against corrosion. Several corrosion inhibitors are available today. The objective of this study was to evaluate the effectiveness of sodium benzoate as an inhibitor to slow down or prevent corrosion. This project involves the use of gravimetric measurements, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) to evaluate inhibitive action of sodium benzoate on corrosion behavior of AA6063 aluminium alloy in seawater. The electrochemical measurements showed that the presence of sodium benzoate as an inhibitor significantly decrease the weight loss, corrosion current densities (i_{corr}), corrosion rates and double layer capacitance (C_d), whilst increasing the polarization resistance (R_p).

Key words: Aluminium Alloy, Weight loss, Polarization, EIS, Adsorption.

Aluminium alloys are important materials with wide ranges of industrial applications and commonly used in marine applications as well. The most popular aluminium alloys for use in corrosive environments such as seawater are the 5xxx and 6xxx series alloys, which demonstrate adequate strength and excellent corrosion resistance. These series are highly suitable in various structural, building, marine, machinery, and process-equipment applications. Alloy 6063 is a heat treatable aluminium-magnesium-silicon alloy. It provides good combination extrudability and

mechanical properties. It responds well to polishing chemical brightening, anodizing and dyeing.

Corrosion inhibitors seem to be attractive because of their low cost and easy handling, compared to other preventive methods. Normally inhibitors are chemicals that interact with a metallic surface, or the environment this surface is exposed, giving the surface a certain level of protection. Inhibitors often work by adsorbing themselves on the metallic surface by forming a film and reducing corrosion by:

Increasing the anodic or cathodic polarization behavior (Tafel slopes).

Reducing the movement or diffusion of ions to the metallic surface.

Increasing the electrical resistance to the metallic surface.

Several techniques and methods have been developed to combat corrosion efficiency are continually being sought after, as a result of

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exorbitant amount spent on corrosion annually (Abd El Rahim *et al.*, 2003, Bethencourt *et al.*, 1997). Among the several methods of corrosion control and prevention, the use of corrosion inhibitor is very popular. Benzoate compounds offer interesting possibilities for corrosion inhibition and are of particular interest because of their safe use and high solubility in water (Rosliza *et al.*, 2008a).

Sodium benzoate converts to benzoic acid when used in acidic mixtures. Benzoic acid has good anti-microbial features, but does not dissolve well in water, whereas sodium benzoate dissolves very well in water. It is also used as a corrosion inhibitor in automotive anti-freeze products. In this study gravimetric measurements, potentiodynamic polarization and EIS are applied to evaluate the inhibitive action of sodium benzoate on corrosion behavior of AA6063 aluminium alloys in seawater.

Methodology

Materials

The material employed for this study was AA6063 (25 × 25 × 1.5 mm coupons) with following chemical composition (wt); Si (0.20%), Fe (0.35%), Cu (0.10%), Mn (0.10%), Mg (0.45%), Cr (0.10%), Zn (0.10%), Ti (0.10%) and Al (remainder). The test solution used for the investigation was seawater collected from Pantai Teluk Kalong, Kemaman, Terengganu (port area) and the inhibitor used was sodium benzoate, NaBz (1g/dm³ concentration).

Several studies have been done on corrosion inhibitor, many of them concluded that corrosion was uniform with sodium benzoate. Sodium benzoate, also called benzoate of soda, has chemical formula C₆H₅COONa. Benzoic acid and its sodium salt (sodium benzoate) are the most common, safe, food preservatives and antimicrobial agents. Benzoic acid and sodium benzoate are classified in the United States as Generally Recognized as Safe (GRAS) and their use in food is permitted up to a maximum level of 0.1%. Commercial availability and low cost of benzoic acid and sodium benzoate make them attractive candidates to be incorporated into coatings as environmentally benign alternatives (Al-Juhni and Newby, 2006). The schematic structure of sodium benzoate is illustrated in Fig 1.

Methods

Sophisticated corrosion inhibitor test methods, typically designed to reproduce the most extreme conditions in a system, have been employed to improve inhibitor capabilities. Research of uniform corrosion is the most widespread application of electrochemical measurements both in the laboratory and industry. The widespread use of these electrochemical methods comes with limitation. The limitation in performing polarization measurements are (Al-Juhni and Newby, 2006, Yagan *et al.*, 2006):

Effect of solution resistance where the distance between the lugging capillarity of the salt bridge to the reference electrode and the working electrode is purposely reduced to minimum in most measurements to limit the effect of the solution resistance which can be problematic in highly resistivity solution.

Changing surface conditions where the surface is changed, due to processing conditions, active corrosion or other reasons leads to change in potential which has impaction the polarization curves.

Determination of pitting potential in analysis of polarization curves where the appearance of a hysteresis loop between the forward and reverse scans is often thought to denote the presence of localized corrosion. Effect of scan rate where the rate at which the potential is scanned may have a significant effect on the amount of current produced at the rate at which the potential is changed. Error in choosing the scan rate during experiment can cause a misinterpretation of the data.

Electrochemical impedance spectroscopy (EIS)

Circuit model or circuit description code and initial circuit parameters were assumed and input by the operator based on the shape of the EIS spectrum. The program then fits the best frequency response of the given EIS spectrum, to obtain fitting parameters. The quality of the fitting was judged by how well the fitting curve overlaps the original spectrum. The fitted EIS data was used to obtain a set of parameters which can be correlated with the coating condition and the corrosion of the steel substrate.

Electrochemical analysis process

The preparation of working electrode before measurements is the same as described before (Rosliza *et al.*, 2008). Electrochemical potentiodynamic reactivation (EPR) is probably the most commonly used polarization testing method for measuring corrosion resistance and is used for a wide variety of functions. Potentiodynamic polarization is a technique where the potential of the electrode is varied at a selected rate by application of a current through the electrolyte. This technique uses a potentiodynamic scan over a range of potentials from passive to active (called

reactivation) to measure the degree of sensitization of stainless steels

All electrochemical measurements were accomplished with Autolab frequency response analyzer (FRA) coupled to an Autolab potentiostat connected to a computer. The potentiodynamic current-potential curves were recorded by changing the electrode potential automatically from -250 mV to +250 mV with the scanning rate of 5 mVs⁻¹. Impedance measurements were conducted over a frequency range of 10⁴ Hz to 10⁻¹ Hz. The data were presented as Nyquist plots.

Table 1. The electrochemical parameters: E_{corr} , i_{corr} , b_a , b_c and R_p of AA6063 in seawater

Condition	NaBz	Days	Potentiodynamic polarization		Linear polarization
			E_{corr} (mV)	i_{corr} (mA cm ⁻²)	R_p (kΩ cm cm ²)
Static	Absence	30	-658	0.04	206.3
		60	-669	0.17	112.3
		90	-659	0.49	46.6
		120	-669	0.79	18.2
		150	-668	1.54	9.2
		180	-656	2.18	1.1
	Presence	30	-708	0.01	650.9
		60	-664	0.06	296.0
		90	-624	0.23	98.0
		120	-670	0.33	43.8
		150	-687	0.53	26.3
		180	-689	0.66	3.7
		180	-629	1.86	1.0

Table 2. R_{ct} and C_{dl} of AA6063 in seawater obtained using impedance method

Days	NaBz	Static	
		R_{ct} (kW cm ²)	C_{dl} (mF cm ⁻²)
30	Absence	212.00	5.45
60		118.00	9.03
90		47.00	10.99
120		19.10	11.35
150		9.70	23.67
180		1.33	28.90
30	Presence	680.00	0.12
60		324.00	0.23
90		103.00	0.26
120		44.50	0.37
150		26.30	0.42
180		3.93	0.47

Table 3. Values of IE (%) for AA6063 samples in seawater

Condition	Days	IE (%)		
		Weight loss	PP	EIS
Static	30	66.1	72.0	68.82
	60	59.3	63.8	63.58
	90	51.0	53.1	54.37
	120	57.8	58.9	57.08
	150	64.7	65.5	63.12
	180	68.4	69.7	66.16
	180	40.9	50.1	49.11

RESULTS

Fig. 2 illustrates the weight loss of AA6063 alloys in seawater with static condition with and without NaBz as inhibitors. Fig. 3 presents the corrosion rate versus the immersion time of the aluminium alloy samples in seawater

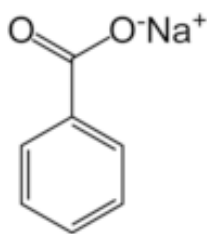


Fig. 1. Schematic structure of sodium benzoate

with and without inhibitor. Fig. 4 represents the potentiodynamic polarization curves of AA6063 in seawater in the absence and the presence of NaBz.

The values for the corrosion potentials and corrosion current densities were estimated from the intersection of the anodic and cathodic Tafel lines. The corresponding corrosion potentials (E_{corr}), corrosion current density (i_{corr}), anodic Tafel slopes (b_a) and cathodic Tafel slopes (b_c) are listed in Table 1. Fig. 5 demonstrates the impedance spectra obtained from AA6063 after varied immersion period.

The values of R_{ct} and C_{dl} of AA6063 in seawater obtained using impedance method are shown in Table 2 meanwhile Table 3 displays the results of the values of the IE (%) from the weight

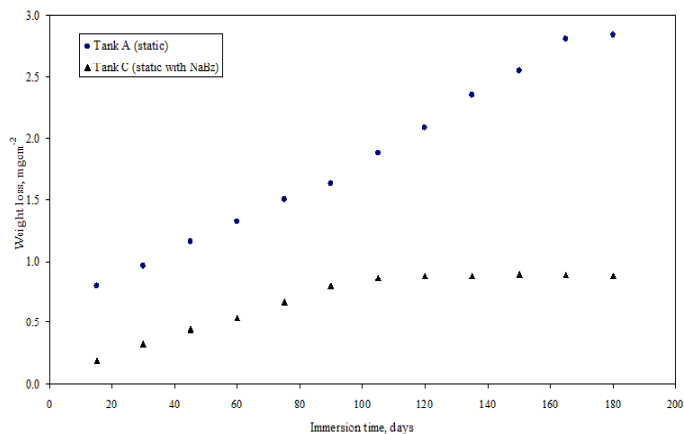


Fig. 2. Weight losses versus immersion time of AA6063

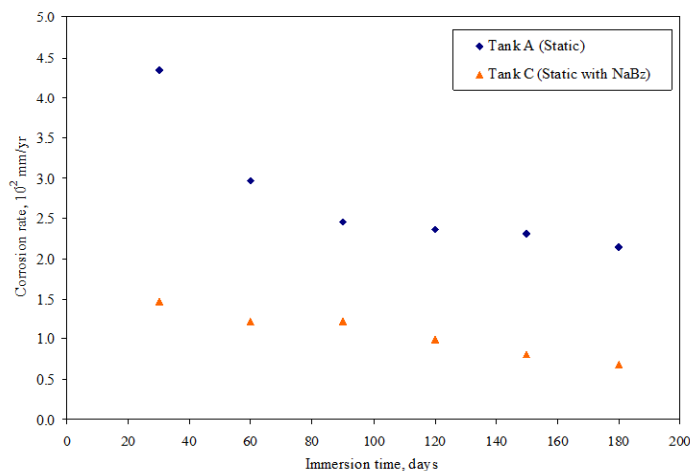


Fig. 3. Corrosion rate versus immersion time of AA6063

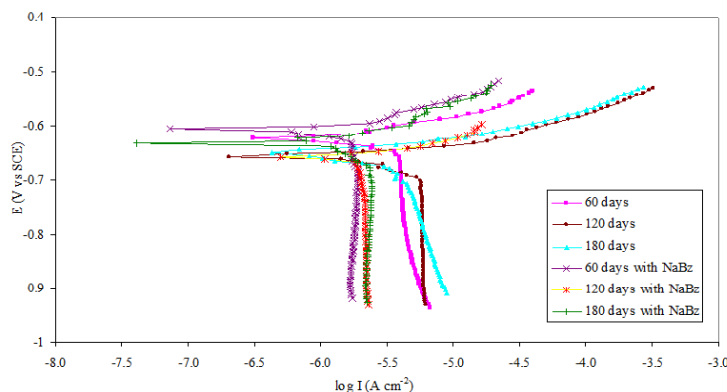


Fig. 4. Potentiodynamic polarization curves for AA6063

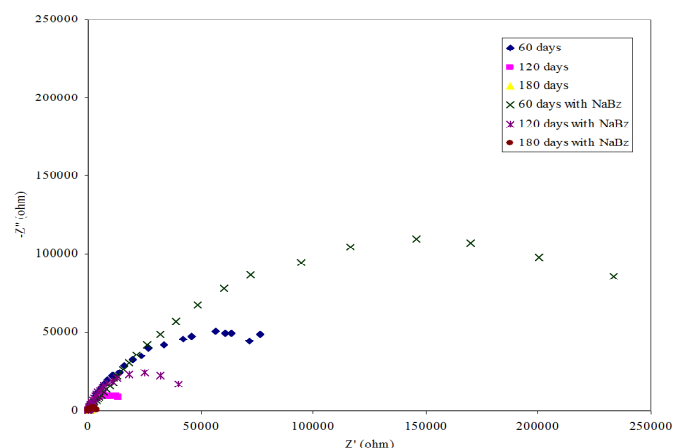


Fig. 5. Nyquist plot for AA6063 in seawater

loss and electrochemical tests.

DISCUSSION

Weight loss measurements

Results from Fig. 2 show that the weight losses of AA6063 for all samples increase with the immersion time. The corrosion rate tends to be increased by decreasing temperature, pH, and flow velocity and by increasing dissolved oxygen (Hollingsworth and Hunsicker, 1987). Values of salinity and pH measured during the immersion test are stable (in the range of nature seawater). Baorong *et al.* (2001) reported that there was no obvious effect when the seawater salinity was varied from 30‰ to 10‰.

Clear differences can be noted between the samples exposed to seawater containing NaBz

as compared to that immersed in the absence of the inhibitor. The test without inhibitor addition had the higher weight loss. There was a reduction in weight loss; hence reduced the corrosion rate with the introduction of NaBz as an inhibitor into the seawater for both cases in static condition.

The obtained results from Figure 3 demonstrate that the test without inhibitor addition in static condition had the higher corrosion rate. The results indicated that introduction of NaBz obviously minimize the rate of corrosion and abridged aluminium dissolution in seawater. Therefore this inhibitor can be considered as efficient inhibitor for AA6063 in seawater.

Potentiodynamic polarization studies

The changes observed in the polarization curves after addition of the inhibitor are usually used as criteria to classify inhibitors as cathodic,

anodic or mixed (Bethencourt *et al.*, 1997). From the Figure 4, it can be seen that the anodic and cathodic current densities obtained in the presence of inhibitor are lower than as compared to that of in the absence of inhibitor. The corrosion potential (E_{corr}) values in the presence of inhibitor are shifted to negative direction and leftward displacement in the cathodic branch of the curves. According to Trabanelli *et al.* (2005), these are the typical features of cathodic inhibitors, this being in agreement with the results obtained for other aluminium alloys.

EIS research has proved that EIS is a powerful and accurate method for measuring corrosion rates. In order to access the charge transfer resistance and polarization resistance that is proportional to the corrosion rate at the monitored interface, EIS results is interpreted by model of the interface. Advantage of EIS techniques is the possibility of using very small amplitude signals without disturbing the properties being measured. In EIS measurement, a small amplitude signal, usually a voltage between 5 to 50 mV is applied to a specimen over frequency range of 0.001 Hz to 100,000 Hz.

The EIS instrument records the real resistance and imaginary capacitance components of the impedance response of the system. Equivalent circuits that describe electrochemical of a freely corroding interface at kinetic equilibrium are (Al-Juhni and Newby, 2006, Yagan *et al.*, 2006):

Relaxation time constant with extended diffusion.

Impedance of pitting processes.

RC representation of an electrochemical interface.

The results display in Table 1 show that the values of corrosion current density (i_{corr}) for all samples increase with the immersion time. The change in E_{corr} is assumed to be related to the growth of a passive layer at the surface of electrode (Rosalbino *et al.*, 2006). The rate of cathodic reaction controls the rate of the corrosion process (as the cathodic over voltage is much greater than the anodic one). The corrosion current decreases obviously after sodium benzoate is added in test solution. It is clear that the presence of inhibitor causes markedly decrease in the corrosion rate. The corrosion resistance of the investigated material is remarkably higher in the benzoate containing than

benzoate free solution.

Electrochemical impedance spectroscopy

The shape of the obtained Nyquist plots in Fig. 5 shows single capacitive semicircles, showing that the corrosion process was mainly charge-transfer controlled (El-Etre, 2003 and Trabanelli *et al.*, 2005). The general shape of the curves is very similar for all the samples and this is maintained throughout the whole test period, indicating that almost no change in the corrosion mechanism occurred either due to the immersion time or to the inhibitor addition (Reis *et al.*, 2006). Inspection of the data reveals that the impedance spectra consists of a large capacitive loop at high frequencies corresponding to the relaxation processes in the oxide film covering the electrode surface (Abd El Rahim *et al.*, 2003). In all cases, single capacitive loops are observed which sizes decrease with the exposure time.

The equivalent circuit fitting for these experimental data was a Randles circuit. The Randles equivalent circuit is one of the simplest and most common circuit models of electrochemical impedance. It includes a solution resistance, R_s , in series to a parallel combination of resistor, R_{ct} , representing the charge transfer (corrosion) resistance and a double layer capacitor, C_{dl} , representing the electrode capacitance (Badawy *et al.*, 1999).

After 180 days immersion time, the charge transfer resistance, R_{ct} for the aluminium alloy decreased to the likely formation (or thickening) of a corrosion product layer on the electrode. The R_{ct} values were higher for AA6063 after addition of inhibitor at all the immersion time, indicating that NaBz is inhibiting the corrosion rate. It can be concluded that NaBz is an effective inhibitor for the aluminium alloy.

The results from Table 2 display the R_{ct} values to decrease with increasing immersion time. There are increasing R_{ct} values with addition of inhibitor as compared to that of without inhibitor. It should be noted that whilst R_{ct} values increase with addition of inhibitor, the capacitance, C_{dl} values decrease indicating the formation of a surface film. Effective corrosion resistance is associated with high R_{ct} and low C_{dl} values (Yagan *et al.*, 2006).

Inhibition efficiency and adsorption isotherm

The inhibitor such as benzoate group adsorbs on aluminium alloy. As a result a thin

film is formed on the aluminium alloy to retard the corrosion. Thus, in this case, sodium benzoate worked as filming inhibitor to control the corrosion rate. Instead of reacting with or removing an active corrosive species, filming inhibitors function by strong adsorption and decrease the attack by creating a barrier between the metal and their environment (Al-Juhni and Newby, 2006).

The values of the IE (%) from the weight loss and electrochemical tests were calculated using the same equations as previously report (Rosliza *et al.*, 2008b). The values of IE (%) for the samples at different immersion time are given in Table 3 and the trends were similar for all three different types of measurements.

CONCLUSIONS

The corrosion studies of AA6063 aluminium alloy have been carried out at room temperature using seawater. The results obtained lead to the conclusion that NaBz is an effective corrosion inhibitor of AA6063 in seawater. The potentiodynamic polarization curves suggested a cathodic character for the inhibition process in seawater. EIS measurements clarified that the corrosion process was mainly charge-transfer controlled and no change in the corrosion mechanism occurred either due to the immersion time or the inhibitor addition to seawater.

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