APPLICATION OF BENZOTRIAZOLE AS CORROSION INHIBITOR OF API 5L X65 CARBON STEEL IN SODIUM CHLORIDE SOLUTION

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ABSTRACT

APPLICATION OF BENZOTRIAZOLE AS CORROSION INHIBITOR OF API 5L X65 IN SODIUM CHLORIDE SOLUTION. The inhibition mechanism of API 5L X65 carbon steel corrosion by benzotriazole (BTAH) in 0.5% NaCl solution saturated with CO_2 at temperatures of 25, 45, 65 and 85°C was investigated using electrochemical impedance spectroscopy (EIS). The measurements were done on the steel specimens after they were immersed into the test solutions containing BTAH for 30 hours. The polarization resistance, R_p, of each specimen was then determined with respect to electrical equivalent circuit proposed by Randall for a metal which is actively corroding in its environment. The data were then used to calculate the inhibition efficiency and surface coverage of carbon steel by BTAH. It was found that the BTAH concentration and temperatures of the test solutions affected significantly the inhibition efficiency. The presence of carbonic acid decreases the inhibition efficiency, however by using 8.40 mmol/L BTAH the inhibition efficiency had reached more than 90% at all temperatures. The increase of temperature has reduced the surface coverage and has lead to decrease the inhibition efficiency. The re-increase of inhibition efficiency at 85°C was related to the decrease in $FeCO_3$ and CO_2 solubility. Moreover, it was revealed that the adsorption of BTAH on the steel surface obeyed the Temkin's adsorption isotherm.

Key words : API 5L X65 carbon steel corrosion inhibitor, benzotriazole, electrochemical impedance spectroscopy, inhibition efficiency, surface coverage.

ABSTRAK

PENGGUNAAN BENZOTRIAZOL SEBAGAI INHIBITOR KOROSI BAJA KARBON API 5L X65 DALAM LARUTAN NATRIUM KLORIDA. Mekanisme inhibisi korosi baja karbon API 5L X65 oleh benzotriazole (BTAH) di dalam larutan 0,5 % NaCl yang jenuh dengan CO_2 pada temperatur 25 °C, 45 °C, 65 °C dan 85 °C dikaji menggunakan spektroskopi impedansi elektrokimia (EIS). Pengukuran dilakukan terhadap spesimen-spesimen baja karbon setelah direndam dalam larutan uji yang mengandung BTAH selama 30 jam. Tahanan polarisasi, R_p, dari setiap spesimen ditentukan berkaitan dengan rangkaian listrik ekivalen yang diusulkan oleh Randall untuk logam yang aktif terkorosi di dalam lingkungannya. Kemudian data yang diperoleh digunakan untuk menghitung efisiensi inhibisi dan penutupan permukaan baja karbon oleh BTAH. Ditemukan bahwa konsentrasi BTAH dan temperatur larutan uji mempengaruhi secara signifikan efisiensi inhibisi. Adanya asam karbonat menurunkan efisiensi inhibisi, meskipun demikian dengan menggunakan 8,40 mmol/L BTAH efisiensi inhibisi telah mencapai lebih dari 90 % pada semua suhu pengujian. Kenaikan suhu telah menurunkan penutupan permukaan dan menyebabkan penurunan efisiensi inhibisi. Kenaikan kembali efisiensi inhibisi pada 85 °C berkaitan dengan penurunan kelarutan $FeCO_3$ dan CO_2. Selain itu, dapat dinyatakan bahwa adsorpsi BTAH pada permukaan baja karbon mengikuti isoterm adsorpsi Temkin.

Kata kunci : Inhibitor korosi baja karbon API 5L X65, benzotriazol, spektroskopi impedansi elektrokimia, efisiensi inhibisi, penutupan permukaan.

INTRODUCTION

The use of organic inhibitors is one of the most practical methods for protecting internal surface of steel pipe used to transport oil and gas. The inhibition properties of such organic inhibitors are attributed to their molecular structures. It is well known that heterocyclic compounds containing nitrogen atoms are good corrosion inhibitors for many metals and alloys in various aggressive media [1, 2]. The π and lone pairs of electrons present on heteroatoms are the important structural features that determine the adsorption of these molecules on the metal surface. Obviously the corrosion inhibition efficiency of such these organic compounds is related to their adsorption properties. Quraishi and Sardar [3] have reconfirmed that the presence of π -electrons and heteroatoms induce greater adsorption of such the inhibitor molecules onto the surface of metal. Benzotriazole (BTAH) is one of these organic inhibitors that are being investigated recently by many researchers.

BTAH has been reported as an effective corrosion inhibitor of copper [4,5] and its alloys [6,7] and iron [8, 9]. The corrosion inhibition and adsorption behavior of BTAH on copper and its alloys have been investigated mostly at higher temperatures. Whereas, the studies in using BTAH as corrosion inhibitor for iron base materials were focused only on the effect of BTAH on the anodic and cathodic processes in acid solution at room temperature. To continue the previous works, the corrosion-inhibiting behavior of BTAH was studied on API 5L X65 carbon steel (material used for oil pipeline) in 0.5% NaCl solution saturated with CO_2 at the temperature ranging from 25°C to 85°C. The appropriate adsorption isotherm and the change of standard free energy of adsorption (ΔG^0_{ads}) are determined with respect to the electrochemical impedance spectroscopy (EIS) data obtained.

EXPERIMENTAL METHOD

Specimens were prepared by cutting API 5L X65 carbon steel sample obtained from Total Indonesie. Each sample (Φ 1.0 cm and thickness 1.3 cm) was soldered to a copper wire and then washed in acetone and dried. Each specimen was covered by cold resin in order to have exposed area of 0.78 cm^2. It was then polished to P-1200 grit silicon carbide paper and degreased with acetone and dried before they were immersed into the test solutions which were prepared by dissolving analytical grade reagents from Merck® in aquabidest. The EIS measurements were made using a Radiometer® potentiostat/galvanostat with a VoltaLab 40® software. All measurements were done using a 1200 mL corrosion cell in which a standard electrode (saturated calomel electrode), a counter electrode (Pt electrode) and a working electrode (the carbon steel specimen) were immersed in the test solutions.

All of the EIS measurements were performed at the open circuit corrosion potential at temperatures of 25, 45, 65 and 85°C using 10 mV amplitude alternating current at various frequencies ranging from 100 kHz to 100 mHz. These were conducted on all of the tested specimens after they were immersed for 30 hours. The impedance spectra obtained from the EIS measurements were then plotted as a function of Zi (imaginary impedance) and Zr (real impedance).

RESULTS AND DISCUSSION

Effect of BTAH Concentration

The effect of inhibitor concentrations on the corrosion resistance of API 5L X65 carbon steel in 0.5% NaCl solution saturated with CO_2 containing 1.68, 4.20 and 8.40 mmol/L BTAH has been studied using EIS measurements. Figure 1 shows the Nyquist diagrams obtained from EIS measurements in solutions in the absence and presence of BTAH at 65°C.

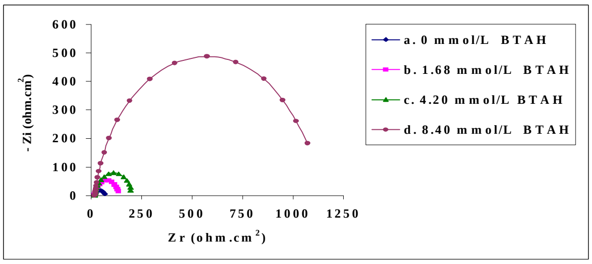

Figure 1. Nyquist diagrams for API 5L X65 carbon steel in 0.5% NaCl saturated with CO_2 containing different concentrations of BTAH at 65°C.

All measurements were done after the specimens were immersed for 30 hours in the test solutions containing BTAH, while the measurement in the test solution free from inhibitor was done just after immersion. The polarization resistance values obtained from the Nyquist diagrams are presented together with calculated surface coverage (θ) and inhibition efficiency (IE) in Table 1.

It is apparent from the diagrams that the impedance response of API 5L X65 carbon steel is altered by the presence of inhibitor in the test solutions saturated with CO_2. The polarization resistance of an inhibited substrate increases with increasing concentration of inhibitor in the solution. It is obvious that the higher the BTAH concentration, the higher is the inhibition efficiency.

Effect of Temperature

The inhibition efficiencies of BTAH obtained from EIS measurements are then plotted as a function of temperature (Figure 2). In general, the inhibition efficiency of insufficient amount of BTAH decreases as

Table 1. The polarization resistance (Rp), surface coverage (θ) and inhibition efficiency (IE) of inhibitor on the steel specimens immersed in the test solutions containing different concentrations of BTAH.

Temperature (°C)	BTAH concentration (mmol/L)	R_p (ohm.cm^2)	Surface coverage (θ)	IE (%)
25°C	0	112.6	-	-
	1.68	1460.0	0.923	92.3
	4.20	2598.0	0.957	95.7
	8.40	5096.0	0.978	97.8
45°C	0	67.6	-	-
	1.68	179.7	0.624	62.4
	4.20	813.0	0.917	91.7
	8.40	1728.0	0.961	96.1
65°C	0	49.8	-	-
	1.68	123.5	0.598	59.8
	4.20	200.3	0.751	75.1
	8.40	1110.0	0.955	95.5
85°C	0	47.6	-	-
	1.68	300.6	0.842	84.2
	4.20	459.8	0.896	89.6
	8.40	856.4	0.944	94.4

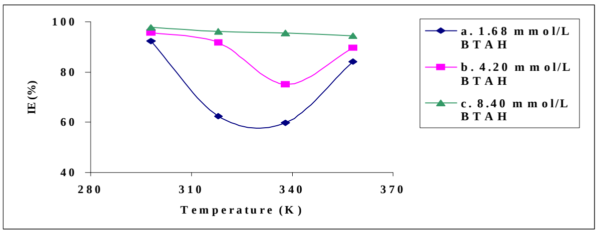

Figure 2. Effect of temperature on the inhibition efficiency of BTAH on API 5L X65 carbon steel immersed in 0.5% NaCl solution saturated with CO_2.

the temperature increases up to approximately 65 °C, except the excess quantity of inhibitor is used. The higher the temperature the lower is the inhibition efficiency. However, the inhibition efficiency at 85 °C after immersion time of 30 hours is higher than that at 65 °C after the same immersion time.

At low temperatures (below 60 - 70 °C) the corrosion rate increases (the inhibition efficiency decreases) as the temperature increases. Whereas at higher temperatures (i.e. at 85 °C) the corrosion rate of the test specimen decreases due to the formation of a protective scale as a result of the decrease in both $FeCO_3$ and CO_2 solubility. This has reconfirmed to that reported by Gunaltun who was believed that the corrosion rate in the solution saturated with CO_2 decreases with increasing temperature higher than 80 °C [10]. The requirement of the inhibitor is likely to be proportional to the corrosion rate of the steel. Increasing temperature will increase the corrosion rate due to the increase in mass transfer and its charge transfer rates. This will decrease the inhibition efficiency for the solution containing insufficient inhibitor.

Adsorption Isotherm

Basic information on the interaction between the inhibitor and API 5L X65 carbon steel surface can be provided by the adsorption isotherm. In order to obtain the adsorption isotherm, the fractional coverage value, θ, as a function of inhibitor concentration must be determined. It is well known that the surface coverage, can be obtained from the EIS measurement via the Equation (1) as follow:

$$\text{Inhibition efficiency (IE)} = \frac{R_p - R_{p(0)}}{R_p} \text{ x } 100\ \% \quad ...... \quad (1)$$

Where $R_{p(0)}$ and R_p are the polarization resistance in the absence and presence of BTAH respectively. The change of standard free energy of adsorption (ΔG^0_{ads}) at different temperatures was then calculated using the following equation:

$$\Delta G^0_{ads} = -RT\ln(55.5K) \quad .... \quad (2)$$

where 55.5 is the concentration of water in the solution in mol/L and K (equilibrium constant) is given by:

$$K = \frac{\theta}{C(1-\theta)} \quad .... \quad (3)$$

where θ is the degree of coverage on the metal surface and C is the concentration of the inhibitor in mol/L. The value of K and for ΔG^0_{ads} corrosion of the carbon steel in 0.5 % NaCl solution saturated with CO_2 containing different concentrations of BTAH at 25, 45, 65 and 85 °C after immersion time of 30 hours are given in Table 2.

Table 2. The equilibrium constant (K) and the change of standard free energy of adsorption (ΔG^0_{ads}) of inhibitor in the steel surface in 0.5% NaCl solution saturated with CO_2 at 25, 45, 65 and 85°C.

BTAH Concentration (mmol/L)	25°C		45°C		65°C		85°C	
	K (L/mol)	$-\Delta G^0_{ads}$ (kJ/mol)	K (L/mol)	$-\Delta G^0_{ads}$ (kJ/mol)	K (L/mol)	$-\Delta G^0_{ads}$ (kJ/mol)	K (L/mol)	$-\Delta G^0_{ads}$ (kJ/mol)
1.68	7135.13	31.24	987.84	28.22	885.45	29.70	3172.09	35.17
4.20	5299.00	30.52	2630.52	30.76	718.11	29.12	2051.28	33.90
8.40	5292.21	30.52	2933.46	31.04	2526.46	32.58	2006.80	33.84

The negative values of ΔG^0_{ads} have indicated spontaneous adsorption of ΔG^0_{ads} the BTAH on the surface of API 5L X65 carbon steel in 0.5% NaCl solution saturated with CO_2. The significant negative values of ΔG^0_{ads} have also suggested a strong interaction of the BTAH molecules with the iron atoms from the carbon steel surface. The average values of - slightly decrease with temperature in the range of 25 °C to 45 °C and then re-increase up in the range of 65 °C to 85 °C (Figure 3).

In order to understand the mechanism of corrosion inhibition the adsorption behavior of the

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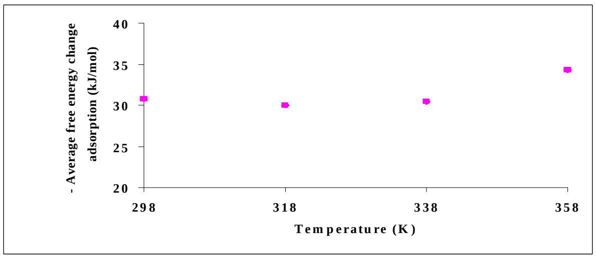

Figure 3. Effect of temperature on the average value of - ΔG^0_{ads} for BTAH on the corrosion of API 5L X65 carbon steel in 0.5% NaCl solution saturated with CO_2 after immersion time of 30 hours.

organic adsorbates on the metal surface must be known (as mentioned previously the surface coverage (θ) were evaluated using polarization resistance (R_p) values obtained from the electrochemical impedance measurements. The θ values for different concentrations of BTAH from the NaCl solution saturated with CO_2 were tested graphically by curve fitting to various isotherms. The plot of θ versus log C gave a straight line exhibited by the API 5L X65 carbon steel immersed at 25, 45, 65 and 85 °C in 0.5% NaCl saturated with CO_2 containing 1.68, 4.20 and 8.40 mmol/L BTAH (Figure 4). All of the measurements were conducted after the specimens were immersed for 30 hours. The adsorption of BTAH on the API 5L X65 carbon steel in the test solutions obeyed Temkin's adsorption isotherm. The strong correlation (coefficient correlation r = 0.998, 0.948, 0.987 and 0.999) of the Temkin's adsorption isotherm at 25 °C, 45 °C, 65 °C and 85 °C respectively, confirmed the validity of this approach. The applicability of Temkin's adsorption isotherm verifies the assumption of monolayer adsorption on a uniform, homogenous metal surface with an interaction in the adsorption layer [11]. This also supports the hypothesis that the corrosion inhibition by this BTAH results from adsorption on the API 5L X65 carbon steel surface.

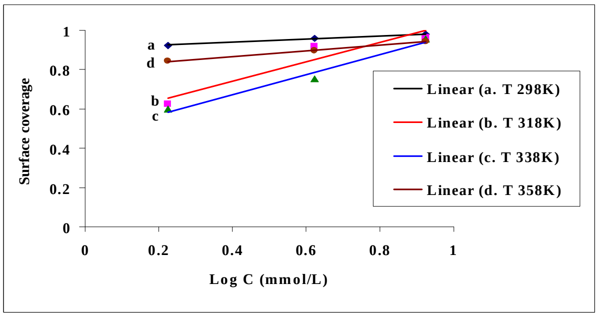

Figure 4. The plot of surface coverage (θ) versus log C for the API 5L X65 carbon steel immersed at 25 °C, 45 °C, 65 °C and 85 °C in 0.5% NaCl solution saturated with CO_2 containing 1.68, 4.20 and 8.40 mmol/L BTAH.

In agreement with Singh [12] and Bentiss, *et.al* [13], inhibition of the corrosion of API 5L X65 carbon steel in 0.5 % NaCl solution saturated with CO_2 by BTAH can be explained on the basis of molecular adsorption. The increase in the inhibition efficiency was explained on the basis of adsorption theory assuming that the inhibitor gave a monolayer adsorption resulted in a decrease in the surface area available for cathodic and anodic reactions. The triazole compounds possess an abundance of π-electrons and unshaped electron pairs on the nitrogen atoms, which can interact with d orbitals of iron to provide a protective film. It is apparent from the molecular structure that the BTAH can be adsorbed on the API 5L X65 carbon steel surface through π-electrons and lone pairs of electrons present on the nitrogen (N) on the triazole ring. BTAH is also one of the triazole compounds possessing an abundance of π-electrons and unshaped electron pairs on the nitrogen atoms, which interact with d orbitals of iron to provide a protective film on the surface of the API 5L X65 carbon steel.

CONCLUSIONS

This study has shown that inhibition efficiency of BTAH on the corrosion of API 5L X65 carbon steel in 0.5 % NaCl solution saturated with CO_2 was dependent on concentration of the inhibitor and temperature. For this test solution the sufficient amount of the inhibitor is 1 g/L.

The inhibition efficiency is likely to be influenced by the concentration of the carbonate ions (CO_3^{2-}). The re-increase of the inhibition efficiency at temperature higher than 65 °C is due to the decrease in both $FeCO_3$ and CO_2 solubility.

The adsorption of BTAH on the API 5L X65 carbon steel surface from the 0.5 % NaCl solution saturated with CO_2 obeyed Temkin's adsorption isotherm.

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