Int. J. Electrochem. Sci., 8 **(2013)** 12613 - 12627

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Influence of Polyethylene Glycols on the Corrosion Inhibition of Carbon Steel in Butyric Acid Solution: Weight Loss, EIS and Theoretical Studies

M.A.Deyab[1,*], *S.S. Abd El-Rehim*[2]

[1]Egyptian Petroleum Research Institute (EPRI), Nasr City, Cairo, Egypt.
[2]Chemistry Department, Faculty of Science, Ain Shams University, Egypt.
[*]E-mail: hamadadeiab@yahoo.com

Received: 11 September 2013 / *Accepted:* 5 October 2013 / *Published:* 20 October 2013

The effect of polyethylene glycols (PEG) of various average molecular weights (MW =1200, 4000 and 6000) as inhibitors for the corrosion of carbon steel in 1.0 M butyric acid was investigated using weight loss and electrochemical impedance spectroscopy (EIS) methods. Quantum chemical parameters were calculated and discussed for theoretical study. The corrosion rate of carbon steel in butyric acid decreased with increasing PEG concentration and molecular weight and increased with increasing temperature. PEG inhibits the corrosion of carbon steel by an adsorption mechanism, which follows Temkin adsorption isotherm. Phenomenon of physical adsorption is proposed from the values of E_a and ΔG^0_{ads} obtained.

Keywords: Polymers; chemical techniques; electrochemical techniques; corrosion inhibition; butyric acid

1. INTRODUCTION

Carbon steel is the most common structural material in refineries due primarily to a combination of strength, availability, relatively low cost, and a resistance to fire [1]. For refining operations, the acidity of the crude oil is an important consideration for carbon steel corrosion [2-4]. A number of organic low molecular fatty acids such as formic, acetic, propionic, and butyric acids are released from crude and cause the corrosion of carbon steel [5]. Most research on corrosion inhibition of carbon steel has been done in mineral acids [6-9]. Despite the importance of organic acids in industry, few corrosion studies involving these acids [10-13] have been made. However, at high temperatures, these acids can dissociate, forming more aggressive ions that can cause faster corrosion than might otherwise be expected. The inhibiting action of organic compounds on the corrosion of metals in acid media is usually related to their adsorption on the metal surface [14-17]. Adsorption results in an effective blocking of the active sites of metal dissolution and/or hydrogen evolution, thus diminishing the overall corrosion rate. The relationship between the adsorption of organic inhibitors and their molecular structure has attracted the attention of many investigators [18-19]. The presence of functional groups and the electron density distribution in the molecules of the organic substances are factors that strongly influence their adsorption behavior. The present study was undertaken to investigate the inhibition mechanism of polyethylene glycols as additive polymers (different in molecular weights equal 1200, 4000 and 6000) for carbon steel in butyric acid solution. Polyethylene glycols were chosen because they are more environmentally benign, have low toxicity and are more cost effective than petroleum based products. Their properties were investigated by weight loss and electrochemical impedance spectroscopy (EIS) techniques as well as by quantum chemical studies.

2. EXPERIMENTAL

For the weight loss measurements, samples of carbon steel sheet of the following chemical composition (wt. %), 0.06 C; 0.06 Si; 0.7 Mn; 0.005 P; 0.001 S; 0.012 Ni; 0.015 Cr; 0.004 Mo; 0.002 V; 0.02 Cu and 99.12 Fe, were used. The surface area of each sample was about 2 cm^2. The samples were abraded with 600, 800, 1000 and 1200 grit emery paper, followed by washing with double distilled water and finally degreased with acetone and dried at room temperature.

The weight loss expressed in mg cm^{-2} was determined by weighing the cleaned sheets before and after immersion in the tested medium for 24 h at 298 K using an analytical balance (GM1502-Sartorius). The solution temperature was stabilized at 298, 308, 318, 328 and 338 K, with the help of an air thermostat.

Table 1. The chemical structures and abbreviation of the three selected polymers.

Chemical Name	Chemical Structure	Abbreviation
Polyethylene glycol (1200)	[$HOCH_2(CH_2OCH_2)_{35}CH_2OH$] Molecular weight = 1200	PEG(A)
Polyethylene glycol (4000)	[$HOCH_2(CH_2OCH_2)_{89}CH_2OH$] Molecular weight = 4000	PEG(B)
Polyethylene glycol(6000)	[$HOCH_2(CH_2OCH_2)_{135}CH_2OH$] Molecular weight = 6000	PEG(C)

For electrochemical impedance spectroscopy measurements, the specimen was machined into cylindrical form electrode of 0.384 cm^2 cross-sectional area. The electrode was sealed with epoxy resin so that only the cross-section area exposed to electrolyte. The cell used was a conventional three-electrode Pyrex glass cell with a platinum wire counter electrode, saturated calomel reference electrode (all potentials referred to the SCE) and the given sample as a working electrode. Impedance measurements were performed at open circuit potential with voltage amplitude 10 mV in the frequency range of 1.0 mHz to 30 kHz. M 398 impedance software from EG & G Princeton Applied Research was used for the EIS measurement. The chemical structures and abbreviation of the three selected polymers are summarized in Table 1. All solutions were prepared from analytical grade chemical reagents using doubly distilled water. Standard solutions of butyric acid solutions were prepared by diluting analar grade 98% n- butyric acid by using double distilled water.

Theoretical calculations were carried out using density functional theory (DFT) at the level of B3LYP/6-31G (d,p) basis set for all atoms with Gaussian 03W program.

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

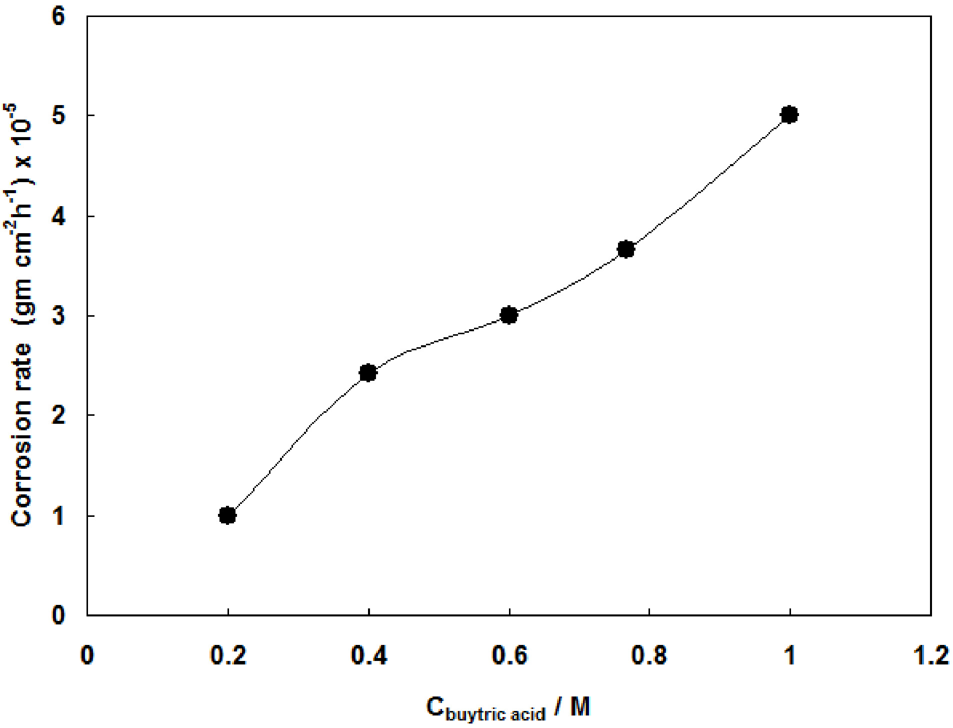

Figure 1. Variation of corrosion rate of carbon steel with butyric acid concentration at 298K.

The corrosion rates of carbon steel in different concentrations of butyric acid solutions (from 0.2 M to 1.0 M) were determined chemically by weight loss measurements at 298 K. They can be expressed as variation in the weight loss per unit surface area per unit time. This expression is valid as we refer to generalized and uniform corrosion processes. Fig.1 gives the variation of corrosion rate of carbon steel with butyric acid concentration at 298 K. It is obvious that, the corrosion rates of carbon steel increase with increasing the concentration of butyric acid. This increase in corrosion rates can be attributed to increased aggressiveness of solutions with increase in acid concentration. For the corrosion of carbon steel in butyric acid the anodic (metal dissolution) and cathodic (hydrogen evolution) half reactions are:

$$Fe \rightarrow Fe^{+2} + 2e^{-} \quad (1)$$

$$2H^{+} + 2e^{-} \rightarrow H_2 \quad (2)$$

Fig.2 shows the variation of corrosion rate of carbon steel in 1.0 M butyric acid solution in the presence of various concentrations of polyethylene glycols. It is obvious that in all cases studied, the corrosion rates decrease with increasing the concentration of the polymers. The degree of inhibition depends upon the nature and the concentration of the polymers. The inhibition efficiency of the polyethylene glycols in butyric acid solution was obtained from weight loss measurements at 298 K. The percentage inhibition efficiency (η_w %) of each concentration were calculated using the following equations:

$$\eta_w\% = [1 - C_R/ C_{R0}] \text{ x } 100 \quad (3)$$

where C_{R0} and C_R are respectively the corrosion rate of carbon steel without and with polymers. Plot of the inhibition efficiency η_w% vs. log ($C_{polymer}$) [where $C_{polymer}$ is the polymers concentration] in 1.0 M butyric acid solution at 298 K is shown in Fig.3.

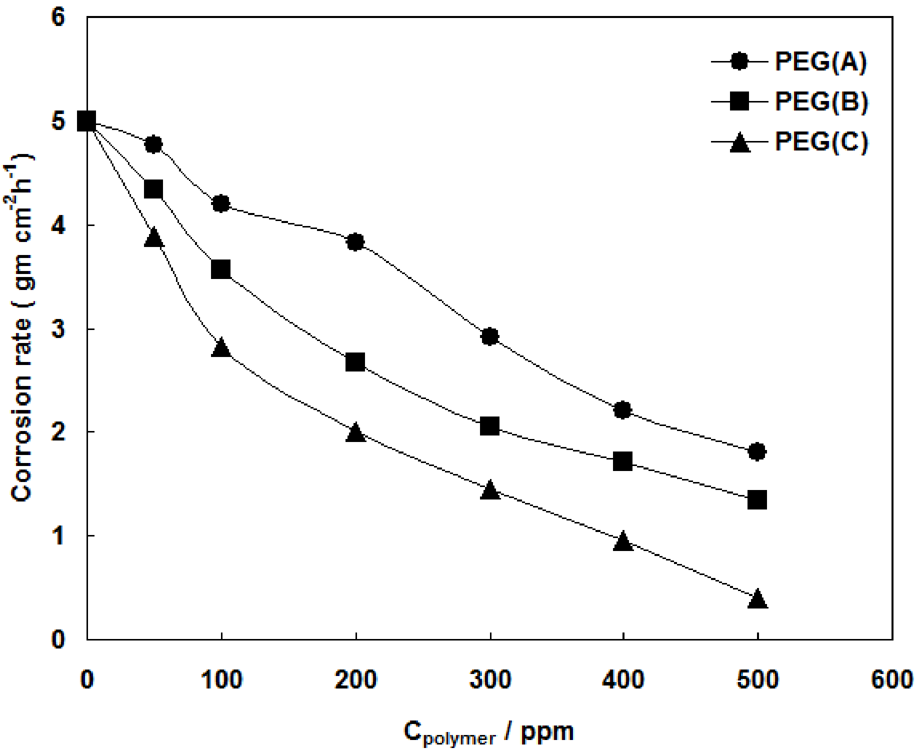

Figure 2. Variation of corrosion rate of carbon steel with polymers concentration in 1.0 M butyric acid solution at 298K.

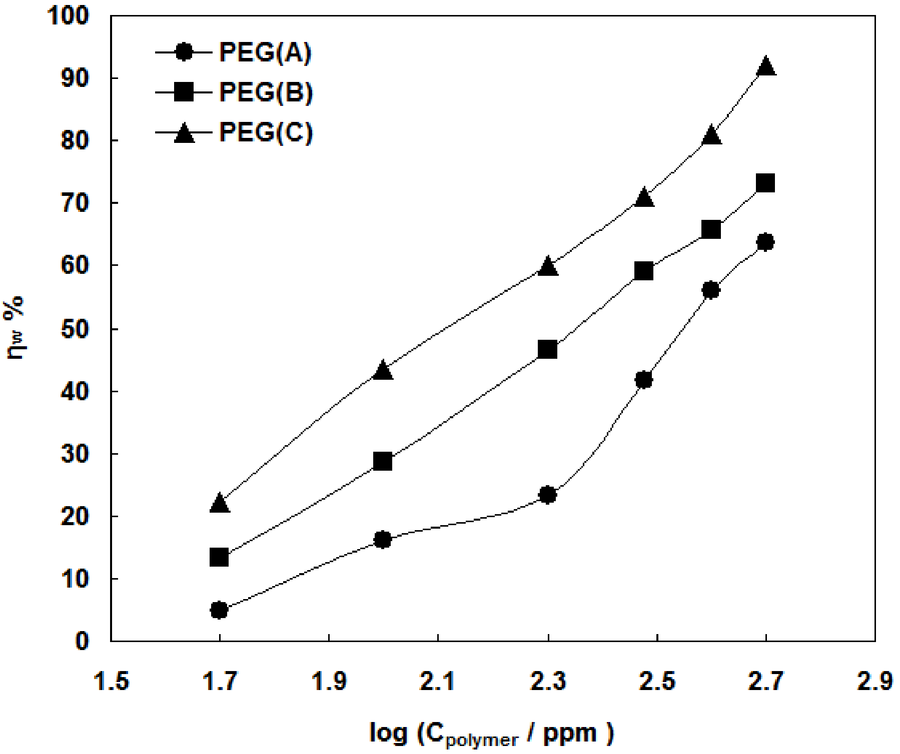

Figure 3. Variation of η_w % with logarithmic polymers concentration in 1.0 M butyric acid solution at 298 K.

The data reveal that. The inhibition efficiency for all the compounds increases with increase in concentration. The inhibition efficiency η_w% of these compounds increases in the order: PEG(A) < PEG(B) < PEG(C). It is clear that these compounds are good corrosion inhibitors for carbon steel in butyric acid solution. These polymers inhibit the acid dissolution of carbon steel by adsorption at the Fe/acid solution interface. The adsorption process takes place via ion pair and ion exchange mechanism by their ethylene oxide groups [20]. Inhibition of the polyethylene glycol can be explained by a substitution adsorption of the polymers according to equation (4).

$$\text{Polymer}_{(aq)} + xH_2O_{(ads)} \rightleftarrows \text{Polymer}_{(ads)} + xH_2O_{(aq)} \qquad (4)$$

The data imply that the PEG(C) has higher corrosion inhibition than PEG(B) and PEG(A), indicating that the corrosion inhibition of these polymer increases with the increasing their molecule weights. This due to the increase in the number of ethylene oxide group [$(-CH_2OCH_2-)_n$] with increasing the molecular weight of polymer. This causes an increase in the bulkiness of the groups attached to the adsorption center [20] and hence reduces the rate of corrosion.

The influence of temperature at maximum concentration (i.e., 500 ppm) of the polyethylene glycol compounds on η_w% is shown in Fig.4.

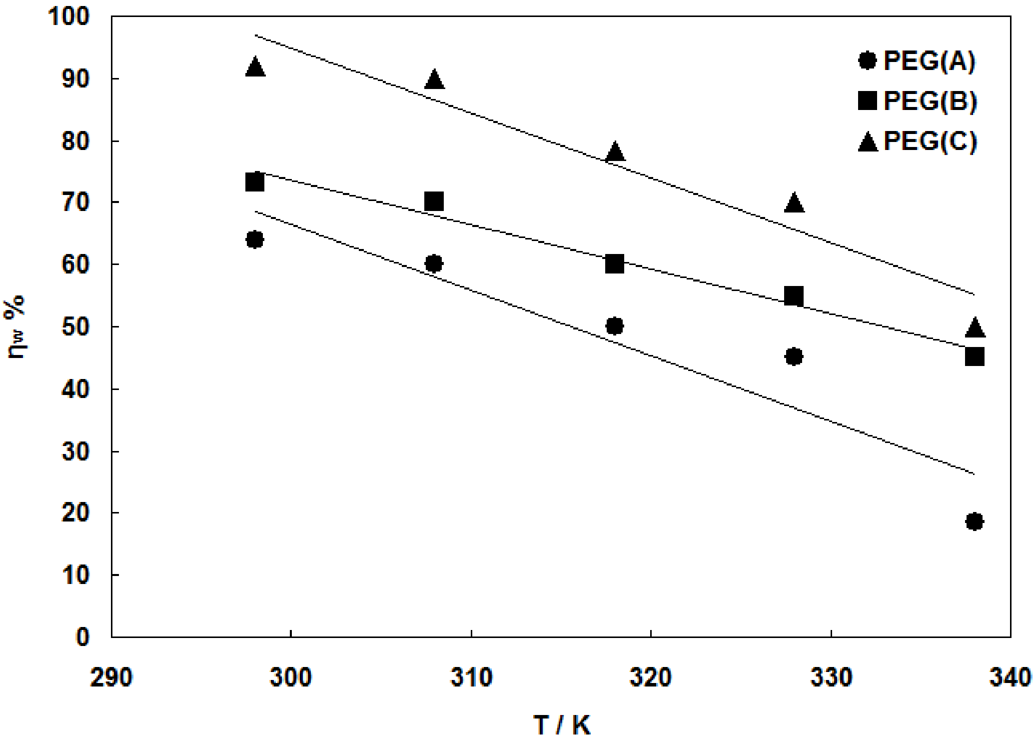

Figure 4. Variation of inhibition efficiency η_w % with solution temperature in butyric acid solution in the presence of 500 ppm polymers.

The plot shows that the inhibition efficiency decreases with increase in temperature from 298 to 338 K, which may be attributed to desorption of the polymers molecules from the carbon steel surface at higher temperature, leading to a greater area of metal being exposed to the acid [21]. The activation parameters such as apparent activation energy (E_a), the enthalpy change of activation (ΔH^*), and the entropy change of activation (ΔS^*), are obtained from an Arrhenius-type (Equation 5) and Eyring transition-state (Equation 6):

$$\ln (C_R) = (-E_a / RT) + A \quad (5)$$

$$\ln (C_R/T) = - (\Delta H^* / RT) + \ln (R / Nh) + (\Delta S^* / R) \quad (6)$$

where C_R is the corrosion rate in the absence and presence of polymers, R is the universal gas constant, A is the frequency factor, N is Avogadro’s number and h is Planck’s constant. Plots of ln C_R against 1/T (as shown in Fig.5) and In (C_R/T) against 1/T (as shown in Fig.6) give straight lines with slops of ($-E_a/R$) and - (ΔH^*/ R), respectively. The intercepts are A and ln (R/Nh) + (ΔS^*/R) for Arrhenius and Eyring transition-state equations, respectively.

The calculated values of E_a, ΔH^* and ΔS^* obtained from these plots are tabulated in Table 2. It is observed that the addition of polymers to blank acid solution increases the apparent activation energy. The value of E_a depends on the structure of the polymers used. The apparent activation energy E_a values increases with increasing the molecular weigh of polyethylene glycol i.e., E_a decreases in order: PEG(C) > PEG(B) > PEG(A). The increase in apparent activation energy E_a may be interpreted as physical adsorption [22].

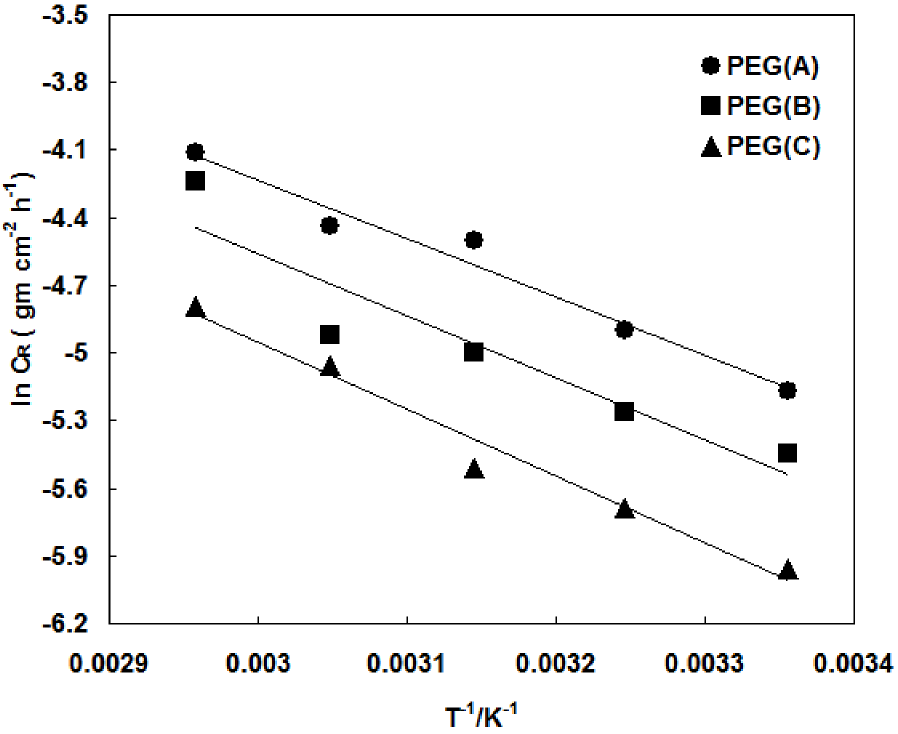

Figure 5. Arrhenius plot for carbon steel corrosion in 1.0 M butyric acid solution in the presence polymers.

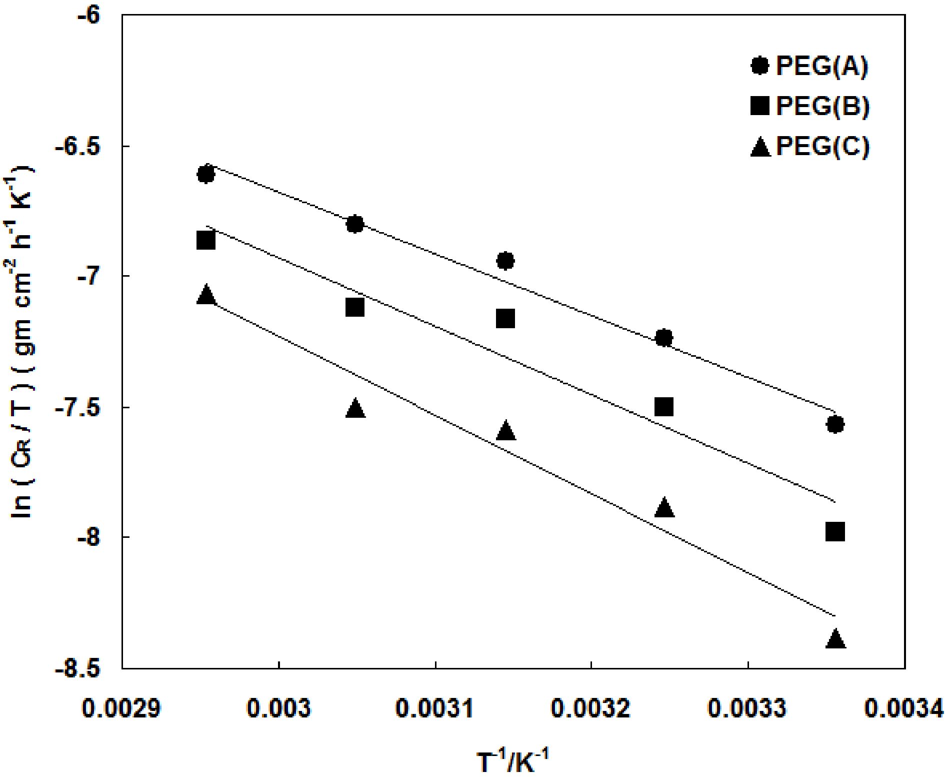

Figure 6. Eyring plot for carbon steel corrosion in 1.0 M butyric acid solution in the presence polymers.

Table 2. Activation thermodynamic parameters of the corrosion process in the absence and presence of polyethylene glycols

Solution	E_a kJ mol^{-1}	ΔH* kJ mol^{-1}	Δ S* J $K^{-1}mol^{-1}$
1.0 M butyric acid	11.96	9.87	-122.31
1.0 M butyric acid+500 ppm PEG(A)	21.60	19.44	-82.36
1.0 M butyric acid+500 ppm PEG(B)	24.89	22.01	-75.42
1.0 M butyric acid +500ppm PEG(C)	28.77	25.47	-13.26

The increase in activation energy can be attributed to an appreciable decrease in the adsorption of the polymers on the carbon mild steel surface with increase in temperature and a corresponding increase in corrosion rates occurs due to the fact that greater area of metal is exposed to the acid environment. Inspection of data of Table 2 reveals also that the activation enthalpy ΔH* in the blank solution is equal to 9.87 kJ mol^{-1} and for the inhibited solution, the ΔH* values are higher. The positive signs of enthalpies ΔH* reflect the endothermic nature of dissolution process [22].

The values of entropy of activation ΔS* in tested solutions are large and negative. The table illustrates that values of ΔS* move towards less negatives values with increasing polymer molecular weight. However many authors have discussed this phenomenon [23]. As in the free acid solutions, the transition state of the rate determining recombination step represents a more orderly arrangement relative to the initial state. Hence, a large negative value for the entropy of activation is obtained. In the presence of the inhibitors, the rate-determining step is the discharge of hydrogen ions to form adsorbed hydrogen atoms. The discharge of hydrogen ions at the metal surface will be retarded by adsorption of inhibitor molecules on the surface metal. This causes the system passes from a more orderly to a less orderly arrangement, and hence the less negatives values of activation entropy is observed.

3.2. Adsorption isotherm

The mechanism of corrosion inhibition may be explained on the basis of adsorption behavior. The degrees of surface coverage (θ) for different inhibitor concentrations were evaluated by the weight-loss method using the following equations:

$$\theta = (C_{R0} - C_R / C_{R0}) \qquad (7)$$

Attempts were made to fit these θ values to Temkin adsorption isotherm, which has the form [24]:

$$\exp(-2a\theta) = K_{ads}C_{polymer} \qquad (8)$$

where ‘a’ is molecules interaction parameter and K_{ads} is equilibrium constant of adsorption process. The plot of surface coverage θ as a function of logarithms of polymers concentration is shown in Fig.7. The correlation coefficient (R^2) was used to choose the isotherm that best fit the experimental data. From the plot, straight lines were obtained with $R^2 > 0.9$ for all polymers used, indicating that the experimental data fit well into the Temkin adsorption isotherm. The adsorption parameters from Temkin adsorption isotherm are estimated and listed in Tables 3. The calculated values of molecular interaction parameter ‘a’ are positive for all polymers showing that attraction forces exist in the adsorption layer [25]. It is evident that the values of K_{ads} increase with increasing the polymer molecular weight (i.e. PEG(C)>PEG(B)> PEG(A)). This clearly indicates that the strength of electrical interactions between adsorbing molecules and the surface increases in the same order as mentioned previously [26], thus increasing the inhibition efficiency.

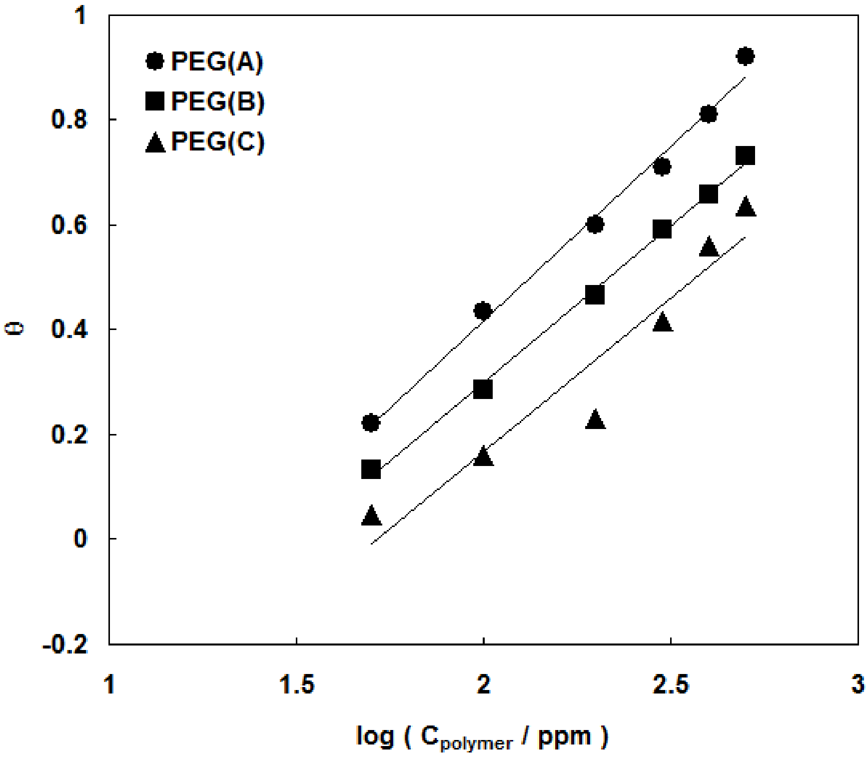

Figure 7. Curve fitting of the corrosion data of carbon steel in 1.0 M butyric acid solution in the presence of polymers at 298 K to Temkin isotherm.

Table 3. The adsorption parameters for adsorption of polyethylene glycols on carbon steel surface in butyric acid, obtained by applying Temkin adsorption isotherm

Polymer type	R^2	K_{ads} (ppm^{-1})	a	ΔG^0_{ads} kJ/mol
PEG(A)	0.935	0.0194	0.855	-11.05
PEG(B)	0.922	0.0316	0.823	-12.33
PEG(C)	0.955	0.0425	0.751	-12.45

The free energy of inhibitor adsorption ΔG^0_{ads} on carbon steel surface can be evaluated using the following equation:

$K_{ads} = 1 / 55.5 \exp [-\Delta G^0_{ads} / RT]$ (9)

where the value 55.5 is the concentration of water in solution in M, R is the universal gas constant and T is absolute temperature. ΔG^0_{ads} values are listed in Table 3. Negative values of ΔG^0_{ads} are the characteristic feature of strong spontaneous adsorption for the studied polymer, which also reflect the high values of inhibition.

The negative ΔG^0_{ads} values are consistent with the spontaneity of the adsorption process and the stability of the adsorbed layer on the carbon steel surface [27]. In general, the standard free energy values of -20 kJ mol^{-1} or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface, resulting in physisorption and those of -40 kJ mol^{-1} or more negative involve charge sharing or transfer from the inhibitor molecules to the metal surface to form a coordinate covalent bond, resulting in chemisorption [27]. The ΔG^0_{ads} values obtained for the studied polymers on the metal surface are less than -20 kJ mol^{-1}, indicating physical adsorptions.

3.3. Impedance measurements

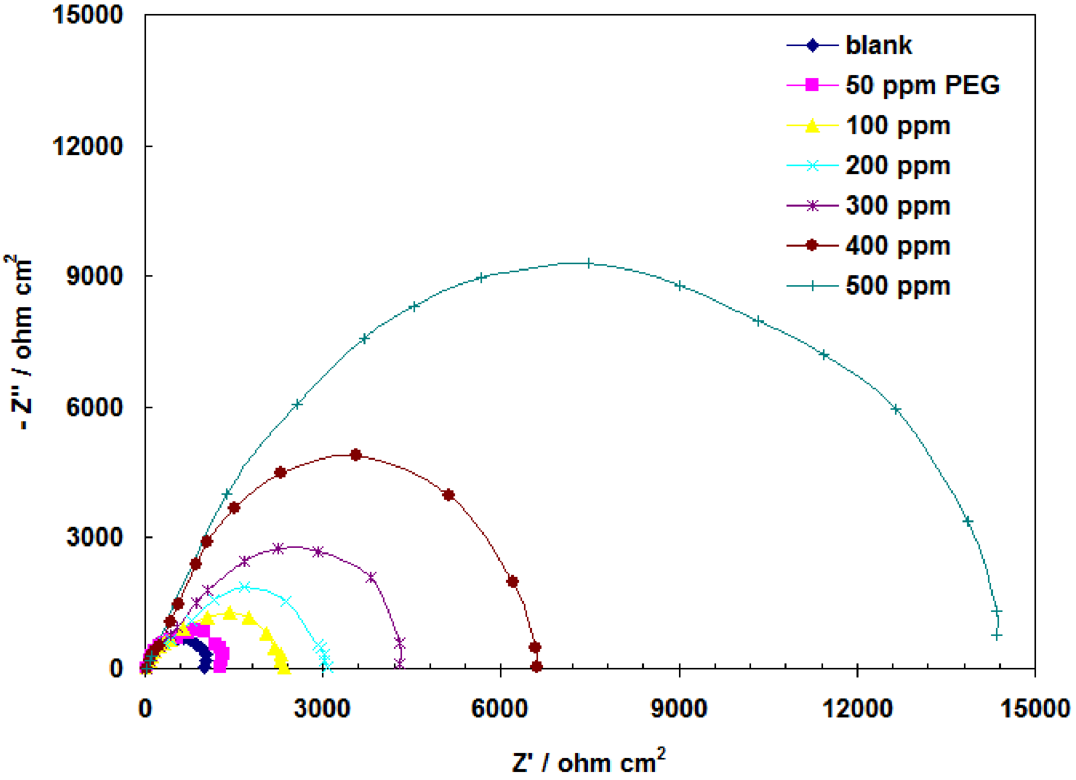

Figure 8. Nyquist diagram of carbon steel in 1.0 M butyric acid solution in the absence and presence different concentrations of PEG(C) at 298 K.

Impedance spectra for carbon steel in 1.0 M butyric acid solution in absence and presence of different concentrations of PEG(C) (as an example) at 298 K are shown in the form of Nyquist plots (Fig. 8). In all cases, the Nyquist plots are not perfect semicircles. Deviations of this kind are often referred to as the frequency dispersion of interfacial impedance. This anomalous phenomenon can be attributed to the inhomogeneity of the electrode surface arising from surface roughness or interfacial phenomena [28]. The equivalent circuit containing solution resistance (R_s) in series with charge transfer resistance (R_{ct}) and double layer capacitance (C_{dl}) was used to model the experimental data as shown in Fig.9. The charge transfer resistance values R_{ct} were calculated from the difference in impedance at the lower and higher frequencies, as suggested by Haruyama and Tsuru [29].

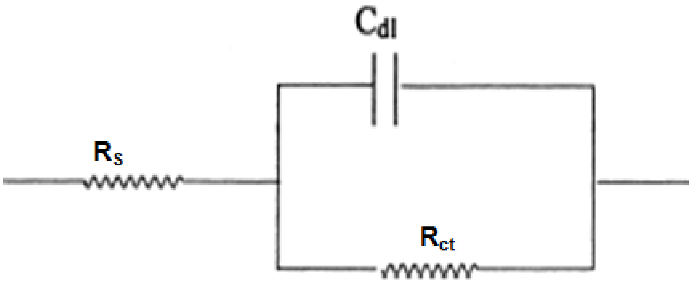

Figure 9. Equivalent circuit used for modeling the impedance results.

Table 4. EIS data of carbon steel in 1.0 M butyric acid in the absence and presence of different concentrations of polyethylene glycols at 298 K

Polymer type	concentration ppm	R_{ct} ohm cm^2	C_{dl} $\mu F\ cm^{-2}$	η_R %
PEG(A)	0	990	3.21	-
	50	1064	2.99	6.9
	100	1237	2.57	19.9
	200	1434	2.22	30.9
	300	1800	1.79	45.0
	400	2414	1.31	58.9
	500	3083	1.03	67.8
PEG(B)	0	990	3.21	-
	50	1154	2.75	14.2
	100	1472	2.16	32.7
	200	2052	1.55	51.7
	300	2655	1.19	62.7
	400	3310	0.96	70.0
	500	3930	0.81	74.8
PEG(C)	0	990	3.21	-
	50	1279	2.49	28.2
	100	2357	1.35	57.9
	200	3193	0.99	68.9
	300	4309	0.73	77.02
	400	6600	0.48	85.00
	500	14142	0.22	92.9

To obtain the double layer capacitance C_{dl}, the frequency at which the imaginary component of the impedance is maximum (f_{max}) was found and C_{dl} values were obtained from the equation:

$C_{dl} = 1 / 2\pi f_{max} R_{ct}$ (10)

The inhibition efficiency (η_R %) in different concentrations of polymers were calculated from the charge transfer resistance according the following equation:

$\eta_R \% = [(R_{ct} - R_{cto}) / R_{ct}] \times 100$ (11)

where R_{ct} and R_{cto} are the charge transfer resistance with and without inhibitor, respectively. Various impedance parameters (R_{ct} and C_{dl}) and η_R % are given in Table 4.

The data of Table 4 reveal that the values of R_{ct} increase with increase in polyethylene glycols concentration and this in turn leads to an increase in the inhibition efficiency. The addition of polyethylene glycols to 1.0 M butyric acid lowers the C_{dl} values, suggesting that the inhibition can be attributed to surface adsorption of the inhibitor. Decrease in C_{dl}, which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that the polyethylene glycols function by adsorption at the metal-solution interface [30]. The data indicate also that the inhibition efficiency of the inhibitors increases in the order: PEG(C) > PEG(B) > PEG(A). It is clear that there is a good agreement between weight loss and EIS measurements, where the two different techniques gave the same trend of inhibition of the polyethylene glycols.

3.4. Theoretical study

In order to correlate experimental data obtained from the two techniques (Weight loss and EIS techniques) for polyethylene glycols and its structural and electronic properties, quantum chemical properties such as energy of highest occupied molecular orbital (E_{HOMO}), energy of lowest unoccupied molecular orbital (E_{LUMO}), energy gap ΔE (E_{LUMO} - E_{HOMO}), dipole moment (μ) and number of transferred electrons (ΔN) has been computed. These computed parameters are listed in Table 5.

Table 5. Quantum chemical parameters for polyethylene glycols

E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	Dipole moment (Debye)	ΔN
–5.28	–1.67	-3.61	3.6	0.97

E_{HOMO} is often associated with the electron donating ability of a molecule. High E_{HOMO} values indicate that the molecule has a tendency to donate electrons to appropriate acceptor molecules with low energy empty molecular orbital. Increasing values of the E_{HOMO} facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer [31]. E_{LUMO} indicates the ability of the molecules to accept electrons. The lower value of E_{LUMO}, the more probable it is that the molecule would accept electrons [31]. Low absolute values of the energy band gap (ΔE) gives good inhibition efficiencies, because the energy to remove an electron from the last occupied orbital will be low [32]. The dipole moment μ is another way to obtain data on the electronic distribution in a molecule and is one of the properties more used traditionally to discuss and rationalize the structure and reactivity of many chemical systems [32].

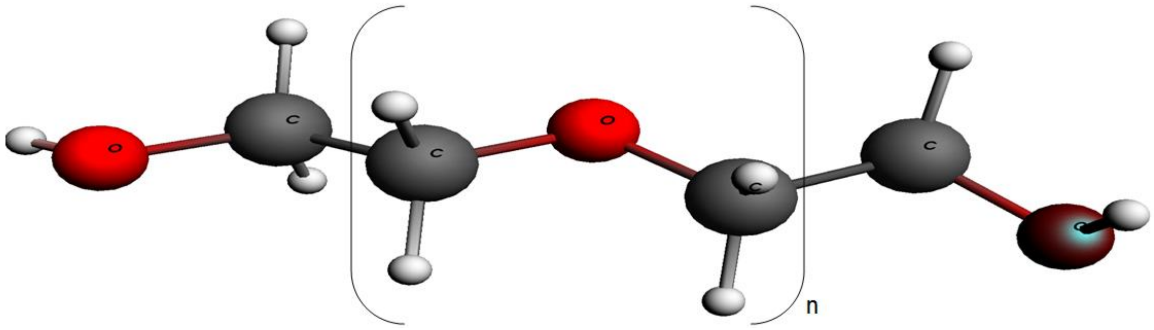

Figure 10. Optimized structure of polyethylene glycols.

The optimized structure of polyethylene glycols is shown in Fig.10. In Table 5, the negative sign of the E_{HOMO} value obtained indicated that the data obtained support physical adsorption mechanism [33]. The results show that the polyethylene glycols have the low energy gap ΔE; this agrees with the experimental results that polyethylene glycols could have better performance as a corrosion inhibitor (see Table 5). Similarly, low value of the dipole moment μ will favor the accumulation of inhibitor molecules on the metallic surface [34]. In addition the number of transferred electrons ΔN was also calculated depending on the quantum chemical method [34]:

$$\Delta N = (\chi_{Fe} - \chi_{inh}) / 2 (\lambda_{Fe} + \lambda_{inh}) \qquad (12)$$

where χ_{Fe} and χ_{inh} denote the absolute electronegativity of iron and the inhibitor molecule, respectively; λ_{Fe} and λ_{inh} denote the absolute hardness of iron and the inhibitor molecule, respectively. These quantities are related to electron affinity (A) and ionization potential (I) as follows:

$$\chi = (I+A) / 2; \lambda = (I-A) / 2 \qquad (13)$$

I and A are related in turn to E_{HOMO} and E_{LUMO} as follows:

$$I = - E_{HOMO}; A = - E_{LUMO} \qquad (14)$$

For iron atom, a theoretical χ value of 7 eV mol^{-1} and λ value of 0 eV mol^{-1} were used to calculate the number of electrons transferred ΔN from inhibitor to the iron atom. Using Eq. 12, the value of electron-donating ability ΔN was calculated and its value is given in Table 5. According to Lukovits [35], if $\Delta N < 3.6$, the inhibition efficiency increased with increasing electron donating ability at the metal surface. In this study, polyethylene glycols were the donor of electrons, and carbon steel surface was the acceptor. This result supports the assertion that the adsorption of inhibitor on the metal surface can occur on the bases of donor- acceptor interactions between inhibitor molecules and the metal surface. Polyethylene glycols were bound to the carbon steel surface, and thus formed inhibition adsorption barrier layer against corrosion at metal/ acid solution interface.

4. CONCLUSION

The main conclusions are:

1) Polyethylene glycols show good inhibition efficiency for carbon steel in butyric acid solution.

2) The inhibition efficiency of the polyethylene glycols increased with increase in concentration and molecular weight of polyethylene glycols and decreased with increase in temperature.

3) The inhibition action of polyethylene glycols is performed via adsorption of the polymer molecules on carbon steel surface. The adsorption is spontaneous and follows Temkin adsorption isotherm.

4) Thermodynamic values obtained indicate that the presence of polyethylene glycols increases the activation energy

5) The data obtained by weight loss and EIS measurements are in good agreement.

6) Quantum chemical calculations show that the adsorption of polyethylene glycols on the metal surface can occur on the bases of donor- acceptor interactions.

References

1. L. Garverick, Corrosion in the petrochemical industry, ASM International, 1994.
2. R. L. Piehl, *Mater. Perform.* 27 (1988) 37-43.
3. E. Slavcheva, B. Shone, A. Turnbull, *Br. Corr. J.* 34 (1999) 125-13.
4. R. D. Kane, M. S. Cayard, *Mater. Perform.* 7 (1999) 48-54.
5. R. A. White, Materials Selection for Petroleum Refineries and Gathering Facilities, NACE, 1998.
6. L. B. Tang, G. N. Mu, G. H. Liu, *Corros. Sci.* 45 (2003) 2251-2262.
7. M. A. Quaraishi, D. D. Jamal, *Corrosion* 56 (2000)156-160.
8. F. Zucchi, G. Trabanelli, G. Brunoro, *Corros. Sci.* 55 (2012) 407-415.
9. S. Deng, X. Li, *Corros. Sci.* 55 (2012) 407-415.
10. E. Heitz, Corrosion of Metals in Organic Solvents, Plenum Press, New York, 1974.
11. M.A. Deyab, *Int. J. Hydrogen Energy* 38 (2013) 13511-13519.
12. M.A. Veloz, I. González, *Electrochim. Acta* 48 (2002) 135-144.
13. M.A. Deyab, *J. Power Sources* 242 (2013) 86-90.
14. M.J. Bahrami, S.M.A. Hosseini, P. Pilvar, *Corros. Sci.* 52 (2010) 2793-2803.
15. G. Moretti, G. Quartarone, A. Tassan, A. Zlngale, *Electrochim. Acta* 41 (1996) 1971-1980.
16. P. Morales-Gil, G. Negrón-Silva, M. Romero-Romo, C. Ángeles-Chávez, M. Palomar-Pardavé, *Electrochim. Acta* 49 (2004), pp. 4733-4741.
17. R. Solmaz, G. Kardaş, M. Çulha, B. Yazıcı, M. Erbil, *Electrochim. Acta* 53 (2008) 5941-5952.
18. E. Lazarova, G. Petkova, R. Raicheff and G. Neykov, *J. Appl. Electrochem.* 32 (2002) 1355-1361.
19. M.A. Deyab, S.S. Abd El-Rehim, *Corros. Sci.* 65 (2012) 309–316.
20. M.A. Deyab, H.A. Abo Dief, E.A. Eissa, A.R. Taman, *Electrochim. Acta* 52 (2007) 8105–8110.
21. E.E. Food El-Sherbini, S.M. Abd El-Wahab, M.A. Deyab, *J. Mater. Chem. Phys.* 89 (2005) 183–191.
22. E. E. Ebenso, H. Alemu, S. A. Umoren and I.B. Obot, *Int. J. Electrochem. Sci.* 3 (2008) 1325 – 1339.
23. S. K. Shukla, E. E. Ebenso, *Int. J. Electrochem. Sci.* 6 (2011) 3277 - 3291.
24. M. I. Temkin, *Zh. Fiz. Khim* 15 (1941) 296-332.
25. A.A. El-Shafei, M.N.H. Moussa, A.A. El-Far., *Mater. Chem. Phys.* 70 (2001) 175-180.
26. M.A. Quraishi and F.A. Ansari, *J. Appl. Electrochem.* 33 (2003) 233-238.
27. M. Ehteshamzadeh, T. Shahrabi, M. Hosseini, *Anti. Corros. Methods Mater.* 53 (2006) 296-302.
28. M.A. Deyab, S.T. Keera, S.M. El Sabagh, *Corros. Sci.* 53 (2011) 2592–2597.
29. S. Tamil Selvi, V. Raman and N. Rajendran, *J. Appl. Electrochem.* 33 (2003) 1175-1182.
30. E. Mccafferty, *Corros. Sci.* 39 (1997) 243-254.

31. H. Ashassi-Sorkhabi, B. Shaabani, D. Seifzadeh, *Appl. Surf. Sci*., 239 (2005) 154-164.
32. P. Udhayakala , T. V. Rajendiran, S. Gunasekaran, *J. Adv. Scient. Res*., 3 (2012) 37-44.
33. A. Rauk, Orbital interaction Theory of OrganicbChemistry, 2nd Edn John Wiley & Sons, Newyork, 2001.
34. P. Udhayakala, T. V. Rajendiran, S. Gunasekaran, *J. Adv. Sci. Res*., 3 (2012) 67-74.
35. I. Lukovits, E. Kalman, F. Zucchi, *Corrosion*, 57 (2001) 3-8.