

Research Journal of Pharmaceutical, Biological and Chemical

Sciences

Quantum chemical calculations, synthesis and corrosion inhibition efficiency of (2R,3R,4S,5S,6S)-N,N-didodecyl-5-ethyl-4-hydroxy-6-(hydroxymethyl)-N-(5hydroxypentyl)-2-(methoxymethyl)-2,3,4,5,6-pentamethyltetrahydro-2Hpyran-3-aminium chloride on X-65 tubing in Acidic Solution.

MA Migahed, SM Elsaeed, AM Al-Sabagh, EA Khamis , EG Zaki*

Egyptian petroleum research institute, Nasr city 11727, Cairo, Egypt.

ABSTRACT

In this work a new quaternized N-alkyl chitosan based on prepared polymeric ionic liquid was synthesised and its chemical structure was confirmed using FTIR spectroscopy. The corrosion inhibitive effect of the prepared polymeric ionic liquid on steel corrosion in 1.0 M HCL was studied using different electrochemical techniques. Potentiodynamic polarization data revealed that the prepared ionic liquid reduces both dissolution and hydrogen evolution corrosion reactions. Impedance technique shows one capacitive loop that indicated the charge-transfer process of the carbon steel corrosion. The quantum chemical calculations were carried out to study the molecular geometry and electronic structure of obtained compound. The energy gap between the highest occupied molecular orbital and lowest unoccupied molecular orbital has been calculated using the theoretical computations to reflect the chemical reactivity and kinetic stability of compounds. Chitosan ionic liquid (CIL) displays good corrosion inhibitation characteristics and it shows appreciable solubility in water.

Keywords: Ionic liquids, synthesis, corrosion, quantum chemical calculations, EIS

*Corresponding author



INTROUDUCTION

In recent years, ionic liquids have experienced considerable attention, since they have attractive physical properties. They are in many cases nonvolatile, nonflammable, less toxic, good solvents for both organics and inorganics and can be used over a wide temperature range. Moreover, some of the ionic liquids have large electrochemical windows of more than five volts, and hence they give access to elements which cannot be electrodeposited from aqueous or organic solutions. Another advantage of ionic liquids is that problems associated with hydrogen ions in conventional aprotic solvents can be eliminated in ionic liquids because ionic liquids are normally aprotic Low vapor pressure also reduces solvent losses in bulk processing and so ILs are the subject of much interest and speculation in respect of green chemistry. Moreover, the ionic liquids are "designable" as it is possible to design ILs with the necessary properties for specific applications by a proper choice of cations and anions. In addition to their extraordinary features, ionic liquids also typically have reasonable conductivities and viscosities contributing to their potential as neoteric solvents for a wide variety of applications including electrodeposition, electrocatalysis, electropolymerization, electrochemical capacitors, sensors, separations, and organic synthesis. The present themed issue demonstrates the potentialities of ionic liquids in electrochemical applications [1]. Therefore, ionic liquids, especially air and water stable ones, are considered to be promising solvents for a wide variety of applications including electrodeposition, batteries, catalysis, separations and organic synthesis. Carbon steel has been widely employed as construction material for pipe work in oil and gas production facilities such as down hole tubular, piping systems and transmission pipelines [2-6]. Carbon steel has remarkable economic attractive properties for engineering applications owing to its low cost, easy availability and high mechanical strength. Corrosion control of metals is an important activity of technical, economical, environmental and aesthetical importance. Thus, the search for new and efficient corrosion inhibitors has become a necessity to protect metallic installations against corrosion to be effective, an inhibitor must displace water from the metal surface, interact with anodic or catholic reaction sites to retard the oxidation and reduction corrosion reaction, prevent transportation of water and corrosion active species on the surface [7]. Inhibition of metal corrosion by organic compounds is a result of adsorption of organic molecules or ions at the metal surface forming a protective layer. This layer reduces or prevents corrosion of the metal. The extent of adsorption depends on the nature of the metal, the metal surface condition, the mode of adsorption, the chemical structure of the inhibitor, and the type of corrosion media [8]. To prevent the attack of the corrosive species on the metallic surface, it is very important to add a corrosion inhibitor to decrease the rate of metal dissolution in such solutions. Thus, many studies concerning the inhibition of carbon steel corrosion using corrosion inhibitors of nonionic surfactants are conducted in the medium [9–13]. Corrosion inhibitors can be divided into three kinds: (i) inorganic inhibitors, (ii) organic inhibitors and (iii) mixed material inhibitors [14]. Most well-known inhibitors are organic compounds containing nitrogen, sulfur and oxygen atoms [15–18].

So that, the present work aims to synthesis of CIL as corrosion inhibitor for X-65 tubing, study the quantum chemical calculations and electrochemical measurements.

EXPERIMENTAL

Materials

Chemical composition of Carbon Steel

X-65 type carbon steel specimens used in this investigation were cut from unused petroleum pipeline. The chemical composition of carbon steel alloy is listed in **Table (1)**.

Element	С	Si	Mn	Р	S	Ni	Cr	Мо	V	Cu	AI	Fe
Content wt%	0.009	0.22	1.52	0.01	0.05	0.04	0.02	0.004	0.002	0.02	0.04	reset

Table 1: Chemical composition of X-65 type carbon steel alloy



Chitosan of (MW~7.8×105, degree of deacetylation (DD)was 89%) was extracted from crab shell and Glutaraldehyde were purchased from Sigma-Aldrich, All solvents were analytical grade and purchased from Aldrich Chemicals Co. and used without further purification ethanol, ether, acetone, acetic acid (AcOH), chloro dodecane ($C_{12}H_{25}CI$), N-methyl pyrrolidone (NMP), methyl iodide (CH₃I), sodium iodide (NaI) and sod borate (NaBH₄) were purchased from Shanghai Chemical Co. Hydrochloric acid solution (1M HCl) used for the study is of analytical grade.

Synthesis of Ionic Liquid Chitosan (CIL)

Quaternized chitosan derivatives were prepared as illustrated in **Scheme 1** that shows a schematic representation of the preparation of quaternized chitosan derivatives. The chitosan solutions were prepared by dissolving 7 g of chitosan into 1% AcOH with stirring for 2h, and then 10 ml glutraldehyde was added to the chitosan solution. To this solution, 10% NaBH₄ solution (1.5-fold excess to added aldehyde) was added, and the solution stirred for 1.5 h. The precipitant of N-Alkyl chitosan was obtained by adjusting the PH of the solution to 10. These precipitants were washed with the distilled water to neutrality and the unreacted aldehyde and the inorganic products were soxhlet-extracted with EtOH and ether for 2 days. N-Alkyl chitosan (5g) was dispersed in 250 mL of NMP for 12h then 1 mol/L NaOH and $C_{12}H_{25}Cl$ (fivefold excess to amine of chitosan) were added to dispersed alkyl chitosan. Nal was added to adjust the concentration in the reaction medium to 0.2 mol/l. The reaction was carried out with stirring for 12 h at 50 °C. The solution was collected by precipitation with acetone, which was dried to obtain the (CIL).





Confirmation structure of prepared (CIL)

The Chitozan and prepared Ionic liquid chitosan were investigated by FTIR-spectroscopy using FTIR-spectrophotometer (Mattson-infinity series bench Tab 961, Perkin Elmer Spectrum GX-USA). All samples were ground and mixed with KBr and then pressed to form pellets.

July-August

2016

RJPBCS 7(4)

Page No. 1671



Computational Model and Methods:

Theoretical calculations have become a powerful tool for clarifying the mechanism of selective capture and transportation of metal ions by ligands. All the geometries including the chitosan and CIL chitosan of the reaction are fully optimized using the PM3 semi-empirical method ever used for organic inhibitor's calculation at an Unrestricted Hartree Fock (UHF) level which are implemented in Hyperchem 8.0.

Electrochemical measurements

All electrochemical experiments were carried out by Volta lab80 (Tacussel-radiometer PGZ402) controlled by Tacussel corrosion analysis software model (Volta master 4) attached to traditional three-electrode cell. The working electrode (WE) was a rod of API X65 steel pipeline embedded in PVC holder using epoxy resin so that the flat surface of the electrode (1.0 cm^2) was the only exposed area to the corrosive media the electrode was abraded with emery paper (grade 320–400–600–800–1000–1200) on the test face, rinsed with distilled water, degreased with acetone and dried.

A platinum wire electrode with (0.63 cm² surface area) and a saturated calomel electrode (SCE) were used as auxiliary and reference electrode, respectively. All potential data reported were referred to SCE reference electrode. Before starting the experiments, the working electrode was immersed in test solution for 30 min at open circuit potential (OCP). All electrochemical techniques were carried out at 298 K as follow:

Open circuit potential measurements

All measurements were carried out until the steady state potentials are attained. The steady state represents an equilibrium state at which oxidation current density (I_{ox}) equal to reduction current density (I_{red}) . It is clear that the potential of the carbon steel electrode immersed in formation water (blank curve) tends toward more negative potential firstly, giving rise to short step .Addition of inhibitor molecules to the aggressive medium produces a slightly positive shift in the potential. This shift can be attributed to the formation of a protective film on the carbon steel surface.

Potentiodynamic polarization measurements

Polarization curves were recorded at a constant sweep rate of 2 mVs⁻¹. The values of corrosion current densities were calculated using Tafel extrapolation method by taking the extrapolation interval of 250 mV with respect to E_{corr}.

Electrochemical impedance spectroscopy (EIS)

Impedance spectra were obtained in the frequency range between 100 kHz and 50 mHz using 10 steps per frequency decade at open circuit potential after 3h of immersion time. AC signal with 10 mV amplitude peak to peak was used to perturb the system. EIS diagrams are given in Nyquist and Bode representations

RESULTS AND DISCUSSION

Synthesis of CIL

The synthesis of modified quaternary chitosan as described in **scheme 1**, Schiff's base intermediates were produced by free amino groups of aminoglucose units of deacetyl chitozan with glutraldehyde, sodium hydroxide was added to avoid the protonation of the NHCH₂R groups and fix the chlorohydric acid liberated. In the absence of base, a low degree of quaternization was achieved despite the use of a large excess of $C_{12}H_{25}Cl$. The present work aims to change the solubility of chitosan in water by quaternization 60% of chitozan amine group.

Figures (1&2) show the FTIR spectra of chitosan and CIL. There are two characteristic peaks of chitosan at 3455 and 1093 cm⁻¹ of –OH and 1ry, 2ry alcohol respectively did not change in two spectra and the



peak of amine -NH vibration deformation appeared at 1571 cm^{-1} for chitosan, this peak of -NH disappears in CIL that proved formation of quaternary ammonium salt in the chitosan.



Figure 1: FTIR of chitosan

Figure 2: FTIR of quaternary chitosan





Figure 3: Potential-time curves for carbon steel immersed in acidic solution in the absence and presence of various concentrations of QAS.



Potentiodynamic polarization measurements

Open circuit potential

The potential of carbon steel electrodes immersed in acidic solution was recorded as a function of immersion time in the absence and presence of synthesized CIL. It is clear that the potential of carbon steel immersed in acid (blank curve) tends towards more negative potential firstly as shown in **Figure (3)**, giving rise to short step [19].

Potentiodynamic polarization measurements

Figure (4) shows the cathodic and anodic polarization curves of carbon steel immersed in acid solution in the absence and presence of different concentrations of compound CIL as a representative sample. Electrochemical parameters such as corrosion potential (E_{corr} .), corrosion current density (i_{corr} .), cathodic and anodic Tafel slopes (b_c and b_a) were calculated. From the obtained polarization curves, it is clear that the corrosion current densities (i_{corr} .) were decreased with increasing concentration of compound CIL with respect to the blank (inhibitor free solution). These results greatly agree and confirm the formation of a good protective layer on the surface of carbon steel. The degree of surface coverage (θ) and the percentage inhibition efficiency (η %) were calculated using the following equations [20]:

$$\theta = 1 - \frac{i}{i_0}$$
 (1)
 $\eta \% = (1 - \frac{i}{i_0}) \times 100$ (2)

Where, i₀ and i are the corrosion current densities in the absence and presence of the inhibitor, respectively.

July-August 2016 RJPBCS 7(4) Page No. 1674



A careful inspection of the polarization curves indicated that corrosion current values corresponding to anodic and cathodic Tafel lines are shifted to less current values with respect to the blank curve. This means that the selected compound acts as mixed type inhibitor, i.e., promoting retardation of both anodic and cathodic discharge reactions. Complete data obtained from polarization measurements are summarized and listed in Table (2).

Inhibitor	Conc.,	I _{corr,}	-E _{corr} , (vs.SCE)	b _{c,} (mV dec ⁻¹)	b _a ,	θ	ղ %
	(ppm)	(mA cm⁻²)	(mV)		(mV dec ⁻¹)		
Blank	0	0.374	651	248	178.9		
CIL	100	0.113	693	260	191	0.697	69
	200	0.0979	704	248	197	0.7382	73
	300	0.088	669	245	199	0.7647	76
	400	0.086	700	252	206.9	0.770	77
	500	0.092	698	240	190	0.7540	75

 Table 2: data obtained from potentiodynamic polarization measurements of carbon steel in acidic solution in the absence and presence of various concentrations of compound CIL

The anodic Tafel slope (ba) and cathodic Tafel slope (bc) of quaternary compound were slightly changed with inhibitor concentrations; this indicates that this inhibitor affected both the anodic and cathodic reactions [21]. The slight change of anodic and cathodic Tafel lines indicates that the prepared compound don't change the corrosion mechanism [22]. The adsorption of inhibitor can affect the corrosion rate in two ways: (i) by decreasing the available reaction area, the so-called geometric blocking effect, and (ii) by modifying the activation energy of the cathodic and/or anodic reactions occurring in the inhibitor-free metal in the course of the inhibited corrosion process. Theoretically, no shifts in E_{corr} should be observed after addition of the corrosion inhibitor if the geometric blocking effect is stronger than the energy effect [23]. The change observed in E_{corr} values upon addition of surfactant molecules indicates that the energy effect is stronger than geometric blocking effect [24]. The addition of inhibitors shifts the E_{corr} values towards the positive since the largest displacement does not exceed 80 mV at 298 K as shown in Table (2); it may be concluded that theses inhibitors reduce the anodic dissolution of carbon steel and also retards the cathodic reaction but the effect on the anodic dissolution reactions is more pronounced than on the cathodic reaction.

Figure 4: Potentiodynamic polarization curves (E – log I relationship) of carbon steel in acidic solution in the absence and presence of different concentrations of compound QAS.





Figure 5: Nyquist plots for carbon steel in acidic solution in the absence and presence of various concentrations of compound QAS

Chitosan

QAS Chitosan



Electrochemical impedance spectroscopy (EIS)

The corrosion behaviour of carbon steel in deep acidic solution in the absence and presence of various concentrations of compound CIL was investigated by EIS technique. Nyquist plot of compound CIL is shown in **Figure (5)**. It is clear from the plots that the impedance response of carbon steel in formation water was significantly changed after the addition of the inhibitor molecules. Also as the inhibitor concentration increased, the charge transfer resistance (R_t) increased and the double layer capacitance (C_{dl}) tended to decrease due to a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer suggesting that the inhibitor molecules acted by adsorption at the metal/solution interface. Addition of synthesized inhibitors provided lower C_{dl} values probably as a consequence of replacement of water molecules by inhibitor molecule at the electrode surface.

Various parameters such as the charge transfer resistance R_t , double layer capacitance C_{dl} and percentage inhibition efficiency were calculated from equivalent circuit model and listed in **Table (3)**. Inhibition efficiency η % was calculated according to the following equation [25]:

$$\eta\% = \left[1 - \frac{R_t}{R_t(inh)}\right] \times 100 \tag{3}$$

Where, R_t and $R_{t(\text{inh.})}$ are the charge transfer resistance values in the absence and presence of inhibitor, respectively.

Inhibitor	Concentration, (ppm)	coefficient	R t, (Ω cm ⁻²)	C _{dl} (mF cm ⁻²)	ղ %
CIL	Blank	0.97	18.65	0.477	
	100	0.98	23.13	2.079	21
	200	0.99	28.56	0.480	35
	300	0.98	37.21	0.850	51
	400	0.96	53.22	5.46	64
	500	0.97	82.97	6.06	77

Table 3: Data obtained from electrochemical impedance spectroscopy (EIS) measurements of carbon steel acidic solution in absence and presence of various concentrations of the inhibitor CIL

Increasing the value of charge transfer resistance (R_t) and decreasing the value of double layer capacitance (C_{dl}) by increasing the inhibitor concentration indicate that the surfactant molecules inhibit corrosion rate of carbon steel in acidic solution by adsorption mechanism [26]. For analysis of the obtained

July-August

2016



impedance spectra, the equivalent circuit (EC) as shown in <u>Fig 6</u> was obtained using EIS analyzer program, where R_s is the solution resistance, R_t is the charge transfer resistance , C_{dl} is the electrochemical double layer capacitance [27,29].

Inhibitor	Е _{номо} (eV)	E _{LUMO} (eV)	ΔE(eV)	μ(debye)	Log P	Polarizabilit y (Å3)	Hydration energy, E _{hydr} , (k cal mol ⁻¹)	Total energy, E _T , (eV)	ΔN(eV)
Chitosan	-8.71	2.134	10.844	4.5	0.16	25.28	-5.08	-69359	0.342
CIL	-3.68	1.955	5.635	2.38	2.7 8	56.85	-5.60	-134852	1.089

Table 4: Quantum Chemical Parameters of the Investigated Inhibitor

Quantum chemical calculations

Quantum structure–activity relationships have been used to study the effect of molecular structure on inhibition efficiency of the investigated inhibitor. **Table (4)** shows certain quantum-chemical parameters related to the molecular electronic structure, which were obtained by means of the application semi-empirical methods (MENDO3), such as (EHOMO, ELUMO) and the energy band gap ($\Delta E = ELUMO - EHOMO$), dipole moment (μ) and Log P. These parameters were calculated in liquid phase. The HOMO (highest occupied molecular orbital) and LUMO (lowest unoccupied molecular orbital) of inhibitors used are shown in **Figure (6)**. The HOMO energy (E_{HOMO}) is often associated with the electron donating ability of the 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_{HUMO} facilitate adsorption (and therefore inhibition) by influencing the transport process through the adsorbed layer [30]. E_{LUMO} indicates the ability of the molecules to accept electrons. The lower values of the E_{LUMO} , the more probable it is that the molecule would accept electrons [31, 32]. Low absolute values of the energy band gap ($\Delta E = E_{LUMO} - E_{HOMO}$) will provide good inhibition efficiencies, because the energy to remove an electron from the last occupied orbital will be low [33].

As shown in Tables 3, in the case of the compound chitosan, the energy of highest occupied molecular orbital (E_{HOMO}) is -8.71 eV, and the energy of the lowest unoccupied molecular orbital (E_{LUMO}) is 2.13 eV. Then, the frontier orbital gap in the compound chitosan is about 10.84 eV. For the compound CIL, the energy of HOMO orbital (E_{HOMO}) is -3.68 eV, and the energy of the LUMO orbital (ELUMO) is 1.955 eV. Thus, the frontier orbital gap in the compound CIL is about 5.635 eV. As a result, the compound CIL has more kinetic stability and less chemical reactivity than others, whereas the compound chitosan has less kinetic stability and more chemical reactivity than others.

The linkage between the molecular structures of compounds with its respective biological activities is central to the QSAR paradigm [34]. Molecular descriptors play a crucial role in providing numerical description of the physicochemical properties of molecules. In order to properly account for these structural features, it is essential that suitable descriptors be chosen for QSAR investigation. The dipole moment (μ) is an index that can also be used for the prediction of the direction of a corrosion inhibition process [35]. Low values of the dipole moment will favour the accumulation of inhibitor molecules on the metallic surface.

It can be seen that compounds with the highest dipole moment were compounds CIL > chitosan with values respectively. It was observed that CIL bearing alkyl and more methylene group. Such high value is associated with the asymmetric distribution of electrons as afforded by the strong electron withdrawing nature of nitrogen, oxygen atoms.

A LogP provides a measure of a molecule's lipophilicity where high A LogP value indicates high lipophilicity while low value suggests low lipophilicity [36]. The results indicated that compounds having the highest lipophilicity were CIL > chitosan.

July-August 2016 RJPBCS 7(4) Page No. 1677





Figure 6: The frontier molecule orbital density distributions of compounds chitosan and quaternary chitosan.

Figure 7: Molecular electrostatic potential map of the chitosan and quaternary chitosan.

Compounds











Molecular Electrostatic Potential (MEP)

Molecular electrostatic potential is related to the electronic density and is a very useful descriptor in understanding sites for electrophilic attack and nucleophilic reactions as well as hydrogen bonding interactions. **Figure (7)** shows the Molecular electrostatic potential map of the investigated compound CIL. The

July-August

2016

RJPBCS 7(4)

Page No. 1679



negative (red color) regions of MEP were related to electrophilic reactivity and the positive (green color) ones to nucleophilic reactivity shown in **Figure (6)**. As can be seen in from the Figure, that oxygen of hydroxide group, nitrogen atoms were thought to be the effective part of this compound.

The number of transferred electrons (ΔN):

The number of transferred electrons (ΔN) was also calculated according to Eq. (8) [37].

$$\Delta N = (X_{\rm Fe} - X_{\rm inh}) / [(2(\eta_{\rm Fe} - \eta_{\rm inh})] \tag{4}$$

Where X_{Fe} and X_{inh} denote the absolute electro negativity of iron and the inhibitor molecule, respectively; η_{Fe} and η_{inh} denote the absolute hardness of iron and the inhibitor molecule, respectively. These quantities are related to electron affinity (A) and ionization potential

$$X = (I+A)/2$$

$$\eta = (I-A)/2$$
(5)

I and A are related in turn to $E_{HOMO}\,and\,E_{LUMO}$

$$I = -E_{\rm HOMO}$$
$$A = -E_{\rm LUMO} \tag{6}$$

Values of X and η were calculated by using the values of I and A obtained from quantum chemical calculation. The theoretical values of X_{Fe} and η_{Fe} are 7 and 0 eV/mol, respectively [38]. The fraction of electrons transferred from inhibitor to the iron molecule (ΔN) was calculated. According to other reports [39], value of ΔN showed inhibition effect resulted from electrons donation.

According to Lukovits's study, if the value of $\Delta N < 3.6$, the inhibition efficiency increased with increasing electron donating ability of inhibitor at the metal surface [40]. The values of (ΔN) presented in Table (3) represents the number of electronic charges that will be exchanged between the surface and the adsorbed species. It is observed from Table (2) that, the inhibition efficiency increased with the increase in the values of ΔN .

Mechanism of adsorption and inhibition

Results obtained from all the experimental techniques reveal that addition of Quaternary chitosan derivatives to the acid corrosive medium retarded the corrosion of carbon steel. The corrosion inhibition process no doubt occurs by virtue of adsorption mechanism where the oxygen and nitrogen hetero atoms present in Quaternary chitosan structure serves as adsorption centres to contain excessive negative charges. In acidic medium, the anodic dissolution of iron is accompanied by the cathodic hydrogen evolution reaction as follows:

$$Fe \longrightarrow Fe^{+2} + 2e^{-}$$

$$2H^{+} + 2e^{-} \longrightarrow H_{2}$$
(8)

Potentiodynamic polarization results indicate that Quaternary chitosan follow mixed inhibition mechanism. It could be assumed that the cationic form of Quaternary chitosan may be adsorb on the cathodic sites of carbon steel and inhibits the cathodic hydrogen evolution reaction. On the other hand, OH groups have lone pairs of electrons and can be adsorbed on the anodic sites of the metal surface via interaction with the vacant d-orbital of iron. It inhibits the anodic metal dissolution reaction. These processes effectively help in isolating the metal surface from the aggressive ions present in the acid medium and thereby inhibiting corrosion. It is also known that in the acid corrosive medium, the inhibitor Quaternary chitosan may be

2016



protonated and exists as polycation. However, the specific adsorption of chlorides ions (Cl⁻) and replacing hydroxyl groups on the metal surface would render the metal surface negatively charged [41–44]. Hence Quaternary chitosan in the form of polycation will be adsorbed on negatively charged metal surface and inhibit corrosion. When iron is immersed in the Quaternary chitosan solution, the protective film is formed through the hydroxyl group of the chitosan adsorbed on the iron surface. But the film is not compact because there are some defects in it.

CONCLUSIONS

- CIL from chitosan backbone was easefully prepared using Borch reduction process, as was characterized by FTIR.
- Various electrochemical techniques were employed to evaluate the potential of CIL as an inhibitor for carbon steel corrosion in acidic medium. Results obtained show that CIL act as good inhibitor for acid-induced corrosion of carbon steel.
- Electrochemical data showed that CIL have good corrosion protection performance for acid-induced corrosion of steel.
- Impedance spectra show a single capacitive loop and its diameter increases with increasing the CIL concentrations.
- The calculated values of IE from EIS method follow the same trend as those obtained from the polarization results.

ACKNOWLEDGMENTS

This work has been supported by Egyptian Petroleum Research Institute (EPRI). The authors are greatly thanked to EPRI support.

REFERENCES

- [1] M.A. Migahed , M.M. Attya, S.M. Rashwan, M. Abd El-Raouf, A.M. Al-Sabagh . Egyptian Journal of Petroleum ,2013; 22: 149–160.
- [2] M.A Migahed, H.M Mohamed, A.M Al-Sabagh. Materials Chemistry and Physics. 2003: 80 :169–175.
- [3] W. Li, Q. He, C. Pei, B. Hou.Electrochem. Acta 2007;52: 6386-6394.
- [4] R. Solmaz, G. Kardas, B. Yazıcı, M. Erbil, Prot. Met. 2005;41: 581-585.
- [5] G. Kardas.Mater. Sci. 2005;41: 337-334.
- [6] F. Endres and S. Zein El Abedin. Phys. Chem. Chem. Phys. 2006; 8: 2101 -2116.
- [7] I.B. Obot, S.A. Umoren, N.O. Obi-Egbedi. J. Mater. Environ.Sci. ,2011;2:49-60.
- [8] A.A. Mazhar, W.A. Badaway, M.M. Abou-Romia. Surf. Coat.Techo. ,1986;29: 335-345.
- [9] M. Stern, A.I.J. Geary. J. Electrochem. Soc. 1957;104: 56-63.
- [10] A.K. Maayta, N.A.F. Al-Rawashdeh.Corros. Sci. 2004;46:1129-1140.
- [11] E.E. Ebenso, P.C. Okafor, U.J. Ekpe, Anti-Corros. Method M 2003;50: 414-421.
- [12] G. Bereket, A. Pinarbasi, C. Ogretir, Anti-Corros. Method M , 2004;51:282-293.
- [13] A.S. Fouda, M.N. Moussa, F.I. Taha, A.I. Elneanaa. Corros.Sci. 1986;26: 719-726.
- [14] E.E. Ebenso, H. Alemu, S.A. Umoren, I.B. Obot. Int. J.Electrochem. Sci.2008;3: 1325-1339.
- [15] F. Bentiss, M. Lagrenee, M. Traisnel, Corrosion 56 (07) (2000)733.
- [16] B. Obat, N.O. Obi-Egbedi.Corros. Sci. 2010;52: 198-204.
- [17] L. Wang,. Corros. Sci.2006;48: 608-618.
- [18] M. Bouklah, B. Hammouti, M. Lagrenee, F. Bentiss. Corros. Sci. 2006;48:2831-2842.
- [19] M.A. Migahed, A.M. Abdul-Raheim, A.M. Atta, W. Brostow. Materials Chemistry and Physics 2010;121: 208–214 .
- [20] S. Liu, N. Xu, J. Duan, Z. Zeng, Z. Feng, R. Xiao. Corros. Sci.2009; 51:1356–1363.
- [21] K.C. Emregul, M. Hayvali. Corros. Sci. 2006;38:797–812.
- [22] Q.B. Zhang, Y.X. Hua. Electrochim. Acta 2009;54 :1881-1887.
- [23] F.G. Liu, M. Du, J. Zhang, M. Qiu. Corros. Sci., 2009; 51 : 102–109.
- [24] Xianghong Li, Shuduan Deng, Hui Fu. Corros. Sci.2012;55 : 280–288.
- [25] F.S. de Souza.Corros. Sci.2009;51 : 642–649.

July-August

2016

RJPBCS 7(4)

Page No. 1681



- [26] Y. Ahmed, Musa, H. Abdul Amir, Kadhum, Abu Bakar Mohamad, Mohd Sobri Takriff, Abdul Razak Daud, Siti Kartom Kamarudin. Corros. Sci.2010; 52 :526–533.
- [27] A.P. Yadav, A. Nishikata, T. Tsuru. Corros. Sci. ,2004;46: 169–181.
- [28] M.A. Migahed, A.M. Al-Sabagh, E.A. Khamis, E.G. Zaki. Journal of Molecular Liquids 2015;212:360– 371.
- [29] M.A.Migahed, A.M. Al-Sabagh, E.G. Zaki, H.A. Mostafa, A.S. Fouda. Int. J. Electrochem.Sci. 2014;9: 7693–7711.
- [30] M. Ozcan, I. Dehri, M. Erbil. Appl. Surf. Sci.2004;236: 155-164.
- [31] H. Ashassi-Sorkhabi, B. Shaabani, D. Seifzadeh.Electrochim. Acta ,2005;50:3446-3452.
- [32] H. Ashassi-Sorkhabi, B. Shaabani, D. Seifzadeh. Appl. Surf. Sci. 2005;239:154-164.
- [33] G. Moretti, F. Guidi, G. Grion. Corros. Sci. 2004;46: 387-403.
- [34] V.S. Sastri, J.R. Perumareddi. Corros. Sci. ,1997,53,617-622.
- [35] L.R. Ana, Silva, Victor M.F. Morais, Maria D.M.C. Ribeiro da Silva. J. Mol. Struct. 2014;1078: 197–206.
- [36] E. Scrocco, J. Tomasi. Adv. Quantum Chem. 1978;11: 115–121.
- [37] N. Okulik, A.H. Jubert. Internet electron, J. Mol. Des. 2005;4: 17–30.
- [38] H. Ju, Z. Kai, Y. Li. Corros. Sci. 2008;50: 865-871.
- [39] I. Lukovits, E. Kalman, F. Zucchi. Corros. (NACE) 2001;57: 3-8.
- [40] E.E. Ebenso, T. Arslan, K. Kandem, I. Love, C. Retlr, M.S. Lu, S.A. Umoren.Int. J.Quantum Chem. 2010;110: 2614–2636.
- [41] Samy M. Shaban, I. Aiad, H.Y.Moustafa, Ahmed Hamed. J. Mol. Liq. 2015;212: 907–914.
- [42] E.A. Badr. J. Ind. Eng. Chem. 2014;20:3361–3366.
- [43] S. Ghareba, S. Omanovic.Corros. Sci. 2010;52: 2104-2113.
- [44] S.M. Shaban, I. Aiad, M.M. El-Sukkary, E.A. Soliman, M.Y. El-Awady.J. Mol. Liq., .doi.org/10.1007/s11164-015-2076-4.