CORROSION INHIBITION OF CARBON STEEL IN PETROLEUM /WATER MIXTURES BY N-CONTAINING COMPOUNDS

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Abstract

Inhibition effects have been carried out on carbon steel in solutions containing different amines. These compounds were dissolved in some petroleum/ water corrosive mixtures containing of acetic acid and NaCl. Corrosion inhibition afforded by diethanolamine (DEA), 3-aminopropanol(1) (3-AP), 2-dimethylethanolamine (2-DEA), cyclohexylamine (CHA), N-methylcyclohexylamine (N-MCA) and dicyclohexylamine (DCHA) has been studied by cyclic polarization (CP) and electrochemical impedance spectroscopy (EIS) with a carbon steel rotating disk electrode at 25°C. The best corrosion inhibition was obtained for the 4% of DEA, which is able to act as polarizing agent on the carbon steel surface. Thus, analysis of the change of inhibitor structure and its concentration in the solution allowed us to find the optimum parameters for obtaining the best inhibition. The observed difference in behavior of the additives can be attributed to the differing of solubility in various solvents ratio and to the differing of strict hindrance of the compounds to metal surface.

Keywords: Mild steel, Cyclic polarization, EIS, Neutral inhibitors, Petroleum.

Introduction

Studies on the corrosion of metals in organic medium have attracted considerable interest in recent years due to their wide applications.[1-4] It has been reported that the overvoltage for the cathodic reaction on metals in contact with such medium is lower than to the aqueous medium. Hence, it causes accelerated, uniform and localized types of corrosion attack.[5] It has been found earlier that the corrosion caused by the aqueous organic solvents can be effectively controlled by the use of corrosion inhibitors.[3] Use of suitable inhibitors for a system can not only extend the life of the reaction vessels in use but could also enable the use of a less expense.[5]

Therefore, in this investigation, the authors have chosen carbon steel to study corrosion inhibition, in contact with a very important aqueous organic medium, petroleum having acetic acid and NaCl. Amines that are reported[3] as good organic inhibitor for aqueous acid solutions have been used as inhibitor in this study. The aim of our study was to propose a surface protection that will be able both to act in the

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corrosive mediums having petroleum, and to have a tumble rule to chosen a best chemical structure for such mediums.

In previous work[6] the mode of action of some alkyl amines to protect of a carbon steel was studied. It was shown that two intermediates adsorbed on the steel surface. Because these amines are different in attached groups, we chose to investigate the electrochemical corrosion behavior of carbon steel inhibited by amines with different structures.

These organic compounds adsorb on the metal surface and suppress metal dissolution and reduction reactions. In most cases, it appears that adsorption inhibitors affect both the anodic and cathodic process although in many cases the effect is unequal.[7] We will discuss the numerical rule of fine structure in the next article.

Experimental method

Materials

The sample selected for study was a carbon steel and had the following composition in wt% C, 0.15 - 0.2; Si, 0.25; Mn, 0.2- 0.5; S, 0.05; Fe, balance; that classified as 1017 according to SAE-AISI number.[3] For all the experiments, the carbon steel samples were polished with abrasive papers from 100 to 2000 grades, degreased with ethanol, cleaned with water and then dried in warm air. The corrosion medium was an aqueous solution containing NaCl, 2 wt%; acetic acid, 8 wt% and various amounts (0 -16 wt%) of (40 - 60°C bp) petroleum in contact with air, maintained at $25 \pm 1°C$. Corrosion inhibition afforded by 3-aminopropanol(1) (3-AP), diethanolamine (DEA), N-methylcyclohexylamine (N-MCA), 2-dimethylethanolamine (2-DEA), cyclohexylamine (CHA) and dicyclohexylamine (DCHA) that all of these materials were in reagent grade.

Electrochemical Measurements

The working electrode was a rotating disc consisting of a carbon steel rod of 0.132 cm^2 cross-sectional area. A thermorectactable sheath prevented the cylindrical area from making contact with the solution so that the electrode surface was only the cross-section. All the experiments were carried out with a rotation rate of 720 rev.min^{-1}. The

auxiliary electrode was smooth platinum. A saturated calomel electrode (SCE) was used as reference. Cyclic polarization (CP) measurements were carried out with an Amel 2053 Potentiostat- Galvanostat and Amel 568 Function Generator equipped with Advantech PCL 818L Interface. A Pentium 166 computer processed data. Electrochemical impedance spectroscopy (EIS) were carried out with an AUTOLAB/PGSTAT30 system at range of 10 mHz to 100 kHz with 5 mV perturbation signal at corrosion potential. After polishing and cleaning, the carbon steel electrode was immediately immersed in torbulated petroleum /water mixtures (0, 4, 8, 12 or 16 wt%) containing of (0,1, 2, 4, or 8 wt%) inhibitor. Cyclic polarization studies were carried out when the corrosion potential was nearly re-established. The potential was varied in steps of 20 mV.min^{-1} and steady state current was recorded.

Optical Microanalysis

The surface of the carbon steel electrode was observed and analyzed after each experiment by an Olympus PME3 optical microscope.

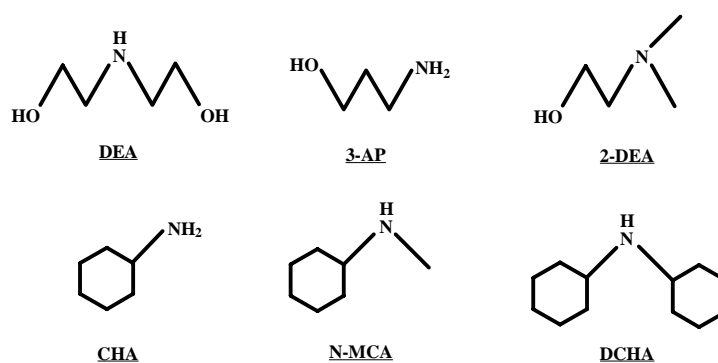## Experimental results and discussion

Fig.1.Structural formula of diethanolamine (DEA), 3-aminopropanol(1) (3-AP),2-dimethylethanolamine (2-DEA), cyclohexylamine (CHA) , N-methylcyclohexylamine (N-MCA) and dicyclohexylamine (DCHA).

The effects of petroleum content of solution on corrosion rates of carbon steel at different amounts of inhibitor are shown in Figure 3. These corrosion rates have been obtained at the corrosion potentials for the same experiments as reported in figure 2.
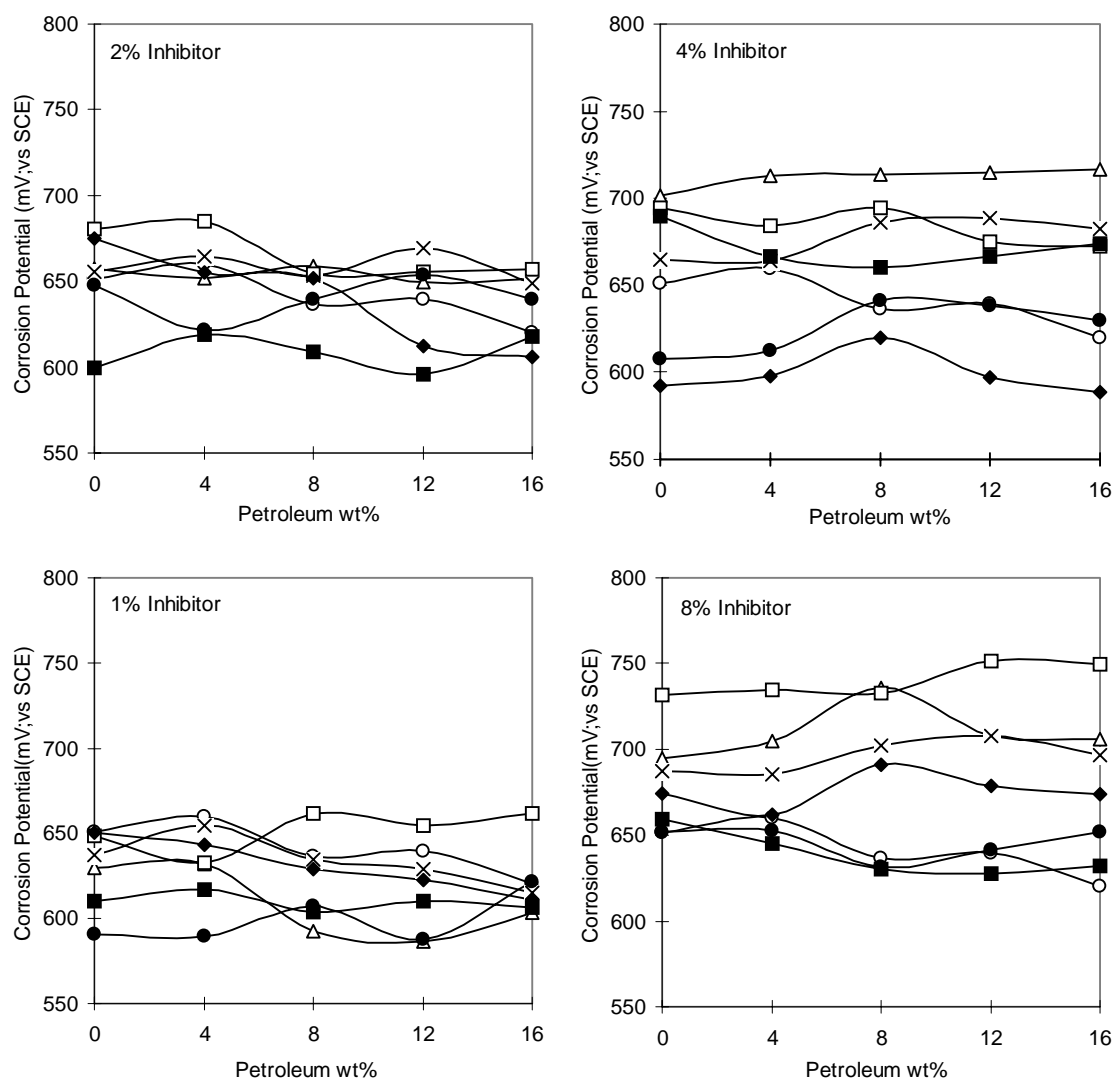

Fig.2. Effect of inhibitor concentration (1-8 wt%) on corrosion potential of carbon steel: DEA (×), N-MCA ( ), CHA (■), 3-AP (Δ), 2-DEA (●), DCHA (◆) and No Inhibitor (○).

The data from electrochemical measurements have shown that for carbon steel, the aggressivity of the medium seems to be related significantly to the petroleum content of the solution: in absence of inhibitor, the corrosion rate shows a minimum at petroleum content between 8-12 wt%. Figure 3 also shows that corrosion rate decreased with increase in inhibitor concentration. The best inhibition was obtained at 4% inhibitors for

DEA, 3-AP, 2-DEA, CHA, N-MCA and DCHA respectively. The slope of curve for DEA shows that inhibition effect is greater at higher content of petroleum.
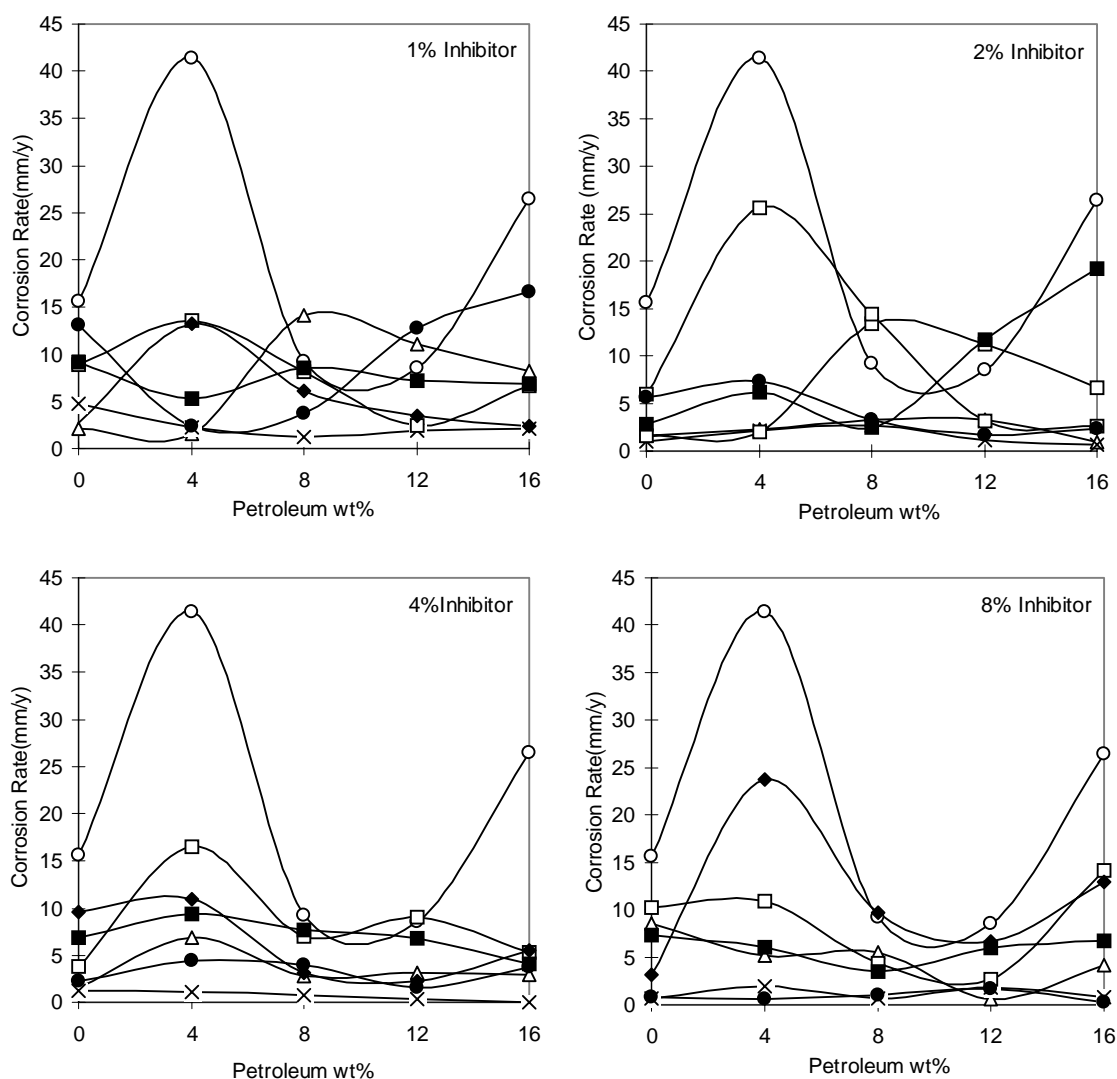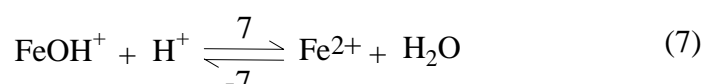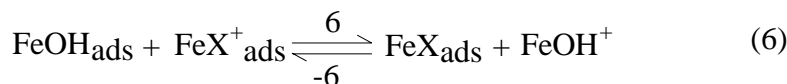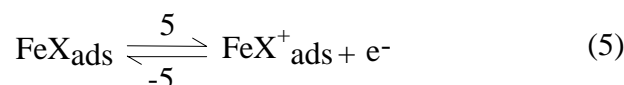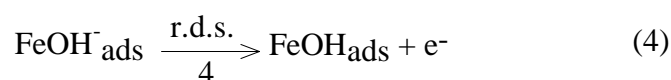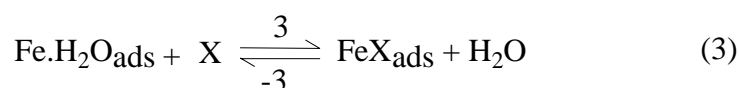

Fig.3.Effect of inhibitor concentration on corrosion rate of carbon steel; compositions and symbols as in Fig. 2.

The variation in corrosion rate values is ascribed to the different solubility of the six additives in the two solvents.[7] In fact, because of alkyl branch length effect, for example, solubility of DEA is greater in water than petroleum, and of DCHA is vice-versa. This agrees with the fact that increasing effective concentration of inhibitor on the metal surface facilitates its polarizing action. This behavior can be explained by considering the mechanism of iron oxidation in acidic solution proceeding via one

adsorbed intermediate, while in the presence of inhibitor a different mechanism has to be developed, involving to adsorbed intermediates. It is commonly accepted that the kinetics of iron anodic oxidation in acid depends on the adsorbed intermediate $FeOH_{ads}$.[8-9] An iron anodic oxidation mechanism, which is valid in the presence of inhibitor, could be one similar to that discussed by McCafferty et Hackerman,[10-11] and also Sternberg et Brânzoi.[12]

$$Fe + H_2O \underset{-1}{\overset{1}{\rightleftharpoons}} Fe.H_2O_{ads} \qquad (1)$$

$$Fe.H_2O_{ads} + X \underset{-2}{\overset{2}{\rightleftharpoons}} FeOH^-_{ads} + H^+ + X \qquad (2)$$

$$Fe.H_2O_{ads} + X \underset{-3}{\overset{3}{\rightleftharpoons}} FeX_{ads} + H_2O \qquad (3)$$

$$FeOH^-_{ads} \xrightarrow[4]{r.d.s.} FeOH_{ads} + e^- \qquad (4)$$

$$FeX_{ads} \underset{-5}{\overset{5}{\rightleftharpoons}} FeX^+_{ads} + e^- \qquad (5)$$

$$FeOH_{ads} + FeX^+_{ads} \underset{-6}{\overset{6}{\rightleftharpoons}} FeX_{ads} + FeOH^+ \qquad (6)$$

$$FeOH^+ + H^+ \underset{-7}{\overset{7}{\rightleftharpoons}} Fe^{2+} + H_2O \qquad (7)$$
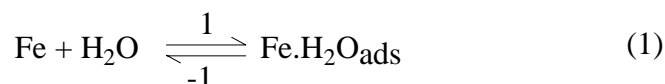
where the species X are the inhibitor molecule, in our case. This mechanism shows that the anodic reaction kinetics is affected by two intermediates: one involving adsorbed hydroxyl ($FeOH^-_{ads}$) and the other involving the adsorbed inhibitor molecule (FeX_{ads}). The main effect of the petroleum content on the value of corrosion rate may account for the high effect exerted by the organic inhibitor molecule on the anodic reaction. The rate of anodic dissolution (step 4) depends to the product of step 2, but the two competitive steps 2 and 3 are based on the FeH_2O_{ads}. Displacements of the adsorbed water molecule by the species X, can affects on the step 4. Every condition, such as molecular shape or localized partial charges or by another view, strict hindrance of X molecule to the metal surface, can variegate the above competition. The influence of two solvents on each inhibitor molecule causes dispersion of inhibition ability. This dispersion

may accelerate from the adsorption of the inhibitor molecule onto the different metal surface sites having different activation energies for chemisorption (lattice planes, edges, kinks, dislocations, inhomogeneities, etc.).[8] Figure 4 shows electrochemical impedance (Nyquist) diagrams plotted for the carbon steel electrode in 4% of different inhibitors and 16% petroleum :
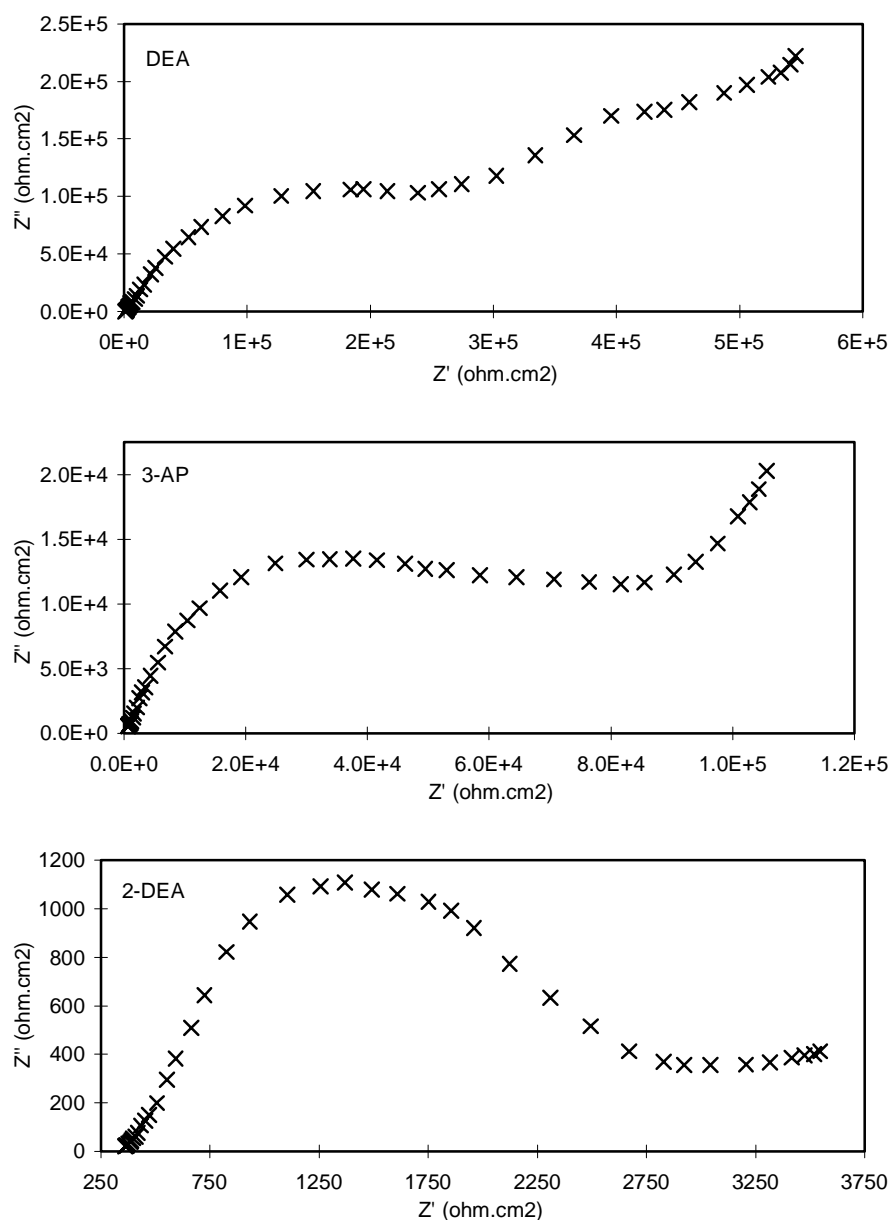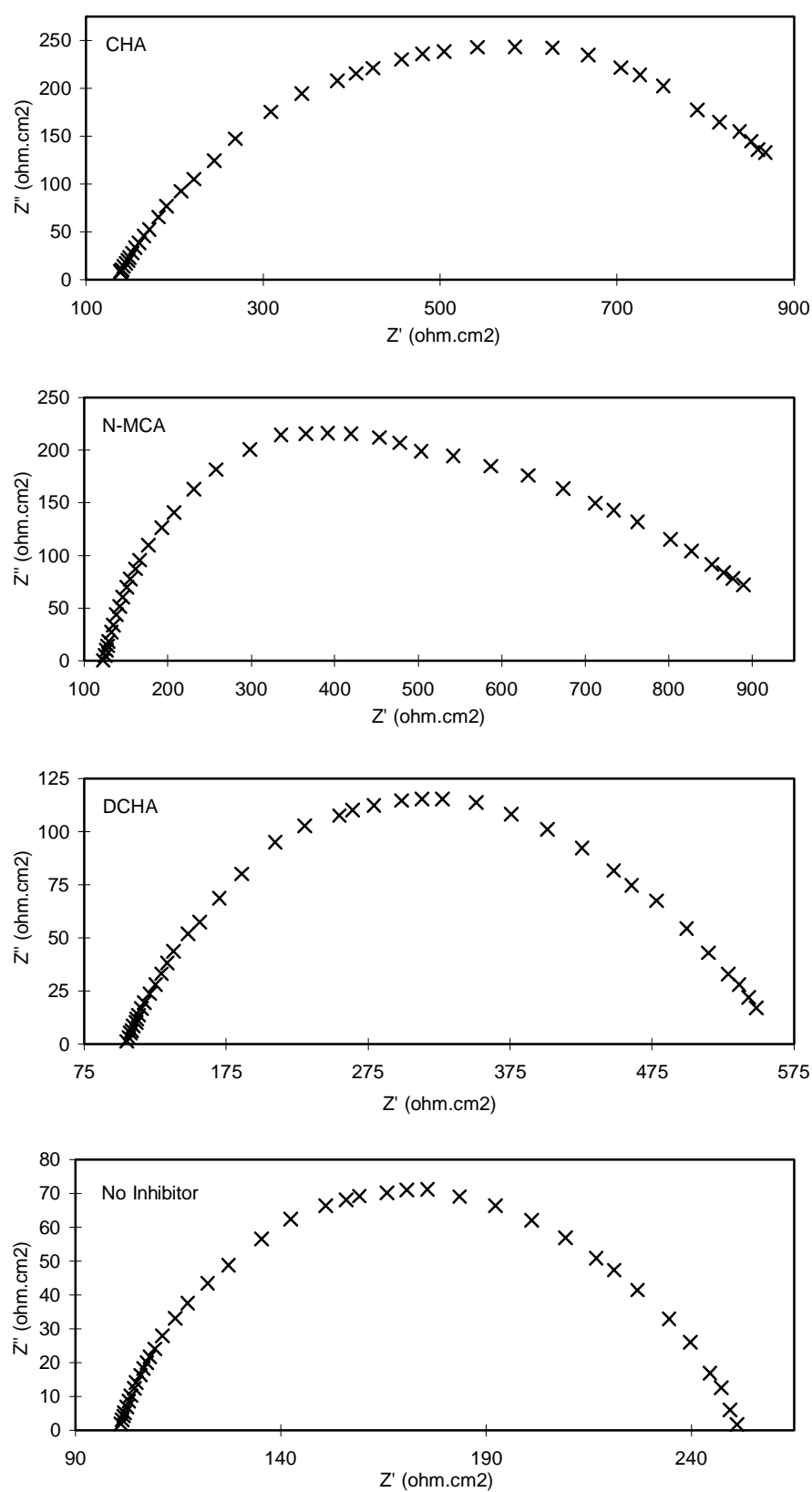
Fig.4. Electrochemical impedance (Nyquist) diagrams plotted for the carbon steel electrode in 4% of different inhibitors and 16% petroleum : a)DEA b)3 -AP c)2-DEA d)CHA e)N-MCA f)DCHA g)No Inhibitor.

A clear difference is observed between these diagrams. Without inhibitor, the impedance diagram is characterized by a single capacitive loop. The value of the polarization resistance, R_P, is about 164 $\Omega.cm^2$. With addition of inhibitor, the diagrams present two capacitive loops: the first loop characterized by a relatively small flattened loop added to second. The impedance plots are very similar to those obtained for a porous electrode.[14] especially for DEA. The first capacitive loop is well defined in the high frequency (HF) range. Conversely, the low frequency (LF) part of the diagram is not clearly defined. The HF part represents the intact part of the adsorbed film whereas the LF data points are associated with the faradaic process occurring on the bare metal through defects and pores in the adsorbed inhibitor layer. From these two loops, two values of resistance and capacitance are obtained (Table 1). This model can confirm that in this medium, the corrosion mechanism involves two adsorbed intermediates.

Inhibitor	R_{LF} ($\Omega.cm^2$)	C_{LF} ($F.cm^{-2}$)	R_{HF} ($\Omega.cm^2$)	C_{HF} ($F.cm^{-2}$)
DEA	6.835e5	3.36e-10	3.21e4	4.28e-10
3-AP	8.52e4	1.68e-11	2.01e3	1.01e-8
2-DEA	1.64e3	4.22e-5	2.16e3	4.23e-9
CHA	836	3.34e-6	230	3.84e-7
N-MCA	540	1.877e-5	715	2.38e-7
DCHA	455	2.37e-6	708	3.33e-7

Table 1. Values of high frequency (HF) and low frequency (LF) resistance and capacitance for inhibitors obtained from Fig. 4.

Among the more number of samples that we have studied, the optical micrographs of corrosion behavior of samples in medium containing 4% inhibitor and 16% petroleum have been shown in figure 5.
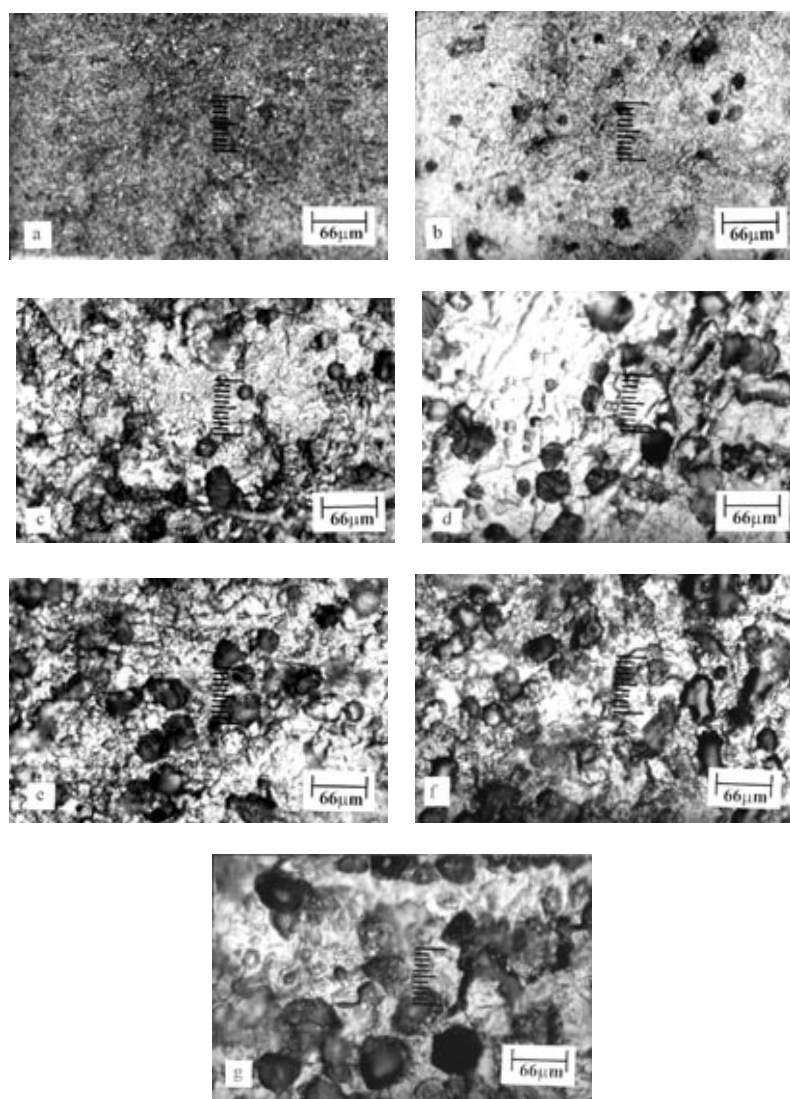
Fig.5. Optical micrographs showing pitting of carbon steel surface in 4% of different inhibitors and 16% petroleum (250×): a)EDA b)t-BA c)i-PA d)PA e)BA f)HA g)No Inhibitor.

The micrographs reveal that both the pit sizes and the pitting propensity are found to be dependent on the molecule structure. It seems that without inhibitor (Fig. 5g) pitting intentionally developed on the carbon steel surface, the pits have 50~60 micrometer dimensions, explaining the high aggressivity of medium. By addition of inhibitor to the solution, the corrosion is observed on the surface, but the size and distribution of pits affected by additive's structure (Fig.5a-f). In the case of DEA, the pits obviously eliminated and only uniform corrosion at low rate observed (Fig. 5a).

Conclusion

The protection of carbon steel by DEA, N-MCA, CHA, 3-AP, 2-DEA and DCHA was investigated by cyclic polarization (CP), electrochemical impedance spectroscopy (EIS) measurements and micrograghic technique. It can be concluded that the corrosion inhibition of these compounds are due to formation of adsorbed $FeOH^-_{ads}$ and FeX_{ads} on lowering of the anodic reaction kinetics. The optimum of inhibition was obtained at 4% of inhibitor and at higher content of petroleum, the inhibition effects of inhibitor will be high enough. Among the six compounds studied, it has been found that DEA is a good inhibitor.

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Povzetek

Raziskovan je bil inhibitorski vpliv raztopin različnih aminov na ogljikovem jeklu. Te spojine so bile raztopljene v korozivnih mešanicah nafta/voda z dodatkom ocetne kisline in NaCl. Preprečevanje korozije z dodatki dietanolamina (DEA), 3‑aminopropanola (3-AP), 2-dimetiletanolamina (2-DEA), cikloheksilamina (CHA), *N*-metilcikloheksilamina (N-MCA) in dicikloheksilamina (DCHA), je bilo raziskovano s ciklično polarizacijo (CP) in elektrokemično impedančno spektroskopijo (EIS) na vrtljivi elektrodi v obliki diska pri 25 °C. Najboljše preprečevanje korozije je bilo doseženo s 4% DEA, ki je sposoben delovati na površini ogljikovega jekla kot polarizator. S spreminjanjem sestave inhibitorja in njegove koncentracije je možno ugotoviti optimalne parametre za inhibicijo. Razlike v učinkovitosti dodatkov pri preprečevanju korozije lahko pripišemo različni topnosti in različnem zadrževanju teh spojin na poti h kovinski površini.