

INHIBITOR SELECTION BASED ON NICHOLS PLOT IN CORROSION STUDIES

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Abstract

Inhibition effects have been studied on carbon steel in solutions containing different amines. These compounds were dissolved in some petroleum/water corrosive mixtures containing acetic acid and NaCl. Corrosion inhibition afforded by propylamine (PA), isopropylamine (i-PA), butylamine (BA), tert-butylamine (t-BA), hexylamine (HA), ethylenediamine (EDA), diethanolamine (DEA), 3-amino-1-propanol (3-AP), 2-dimethylethanolamine (2-DEA), cyclohexylamine (CHA), N-methylcyclohexylamine (N-MCA) and dicyclohexylamine (DCHA), have been investigated by electrochemical impedance spectroscopy (EIS) with a carbon steel rotating disc electrode at 25 °C. In the previous works, the corrosion inhibition behavior of aliphatic and cyclic substituents amines has not been compared. The aim of this work is to introduce a simple graphical approach for comparison of corrosion inhibition behavior of the above mentioned amine compounds. The complex plane and Bode plots were used for this study but these graphical methods were not adequate to understand the effect of inhibition behavior due to small structural changes in the amines. Therefore, a logarithm of impedance magnitude versus phase angle (Nichols) plot of EIS data was used for this purpose and the results showed that this graphical method provides a good interpretation of corrosion inhibition behavior. Finally, a guideline to select the best inhibitor for carbon steel protection in petroleum/water system was drawn.

Keywords: electrochemical impedance spectroscopy, corrosion inhibitor, Nichols plot, Bode plot, amines

Introduction

Study of carbon steel corrosion in petroleum/water mixtures is important in the petrochemical industries.¹⁻⁵ The corrosion by the aqueous-organic solvents could be effectively controlled using corrosion inhibitors.⁶⁻¹⁰ In order to select the best inhibitor in this media, a number of methods can be used. Among the rapid methods of detection, electrochemical impedance spectroscopy (EIS) is the most valuable. Generally,

electrical models (equivalent circuits) are used to interpret the electrochemical impedance spectra of inhibitors performance in corrosion studies.¹⁻¹³

The electrical models developed to explain the electrochemical impedance results use a combination of resistor, capacitor or other elements such as constant phase element and so on. In these models, the capacitor and resistor elements have a direct physical connotation: the first one represents a reversible, conservative energy accumulation/recovery in electrode processes and the latter represents the irreversible, dissipative kinetics of these processes.¹⁴⁻¹⁶ On the other hand, although a constant phase element (CPE) is not a capacitor but it exhibits capacitance frequency dispersion.¹⁷ This dispersion is always an indication of energy dissipation in a non-ideal capacitor involving some resistive components.¹⁸ In other words, the constant phase element is a dissipative element.¹⁸⁻²⁰ However, the equivalent circuit method is very useful but in some cases results in ambiguity due to degeneracy of the electrical models,¹⁴⁻¹⁶ or the elements of the electrical models are not easily related to a single elementary step of a complex reaction.¹⁴ Also, another shortcoming was complexity of the stability conditions when formulated in terms of the electrical model. Fortunately, to overcome this problem a pole-zero approach has been suggested.¹⁴ Owing to these shortcomings, in this work, the complex plane, Bode plots and a new graphical method were used instead of equivalent circuit models to study corrosion inhibition performance of the twelve amines. Since, using loop gain in decibels versus loop phase in degrees, which is called Nichols chart,²¹ is common in control systems for design purposes, the logarithm of impedance magnitude versus impedance phase angle plot has been called Nichols plot in this article.

Results and discussion

The spectra in Figure 1 shows the complex plane plots of the resulting impedance data for carbon steel with and without inhibitor in petroleum/water system. As it can be seen from this figure, among the twelve amines examined as possible inhibitors, only *i*-PA, *t*-BA, EDA and DEA show high corrosion resistance in comparison with the other amines. The high frequency EIS response that has been scale-expanded, as represented in the inset of Figure 1, shows the details of the specimens exhibiting the higher corrosion rates.

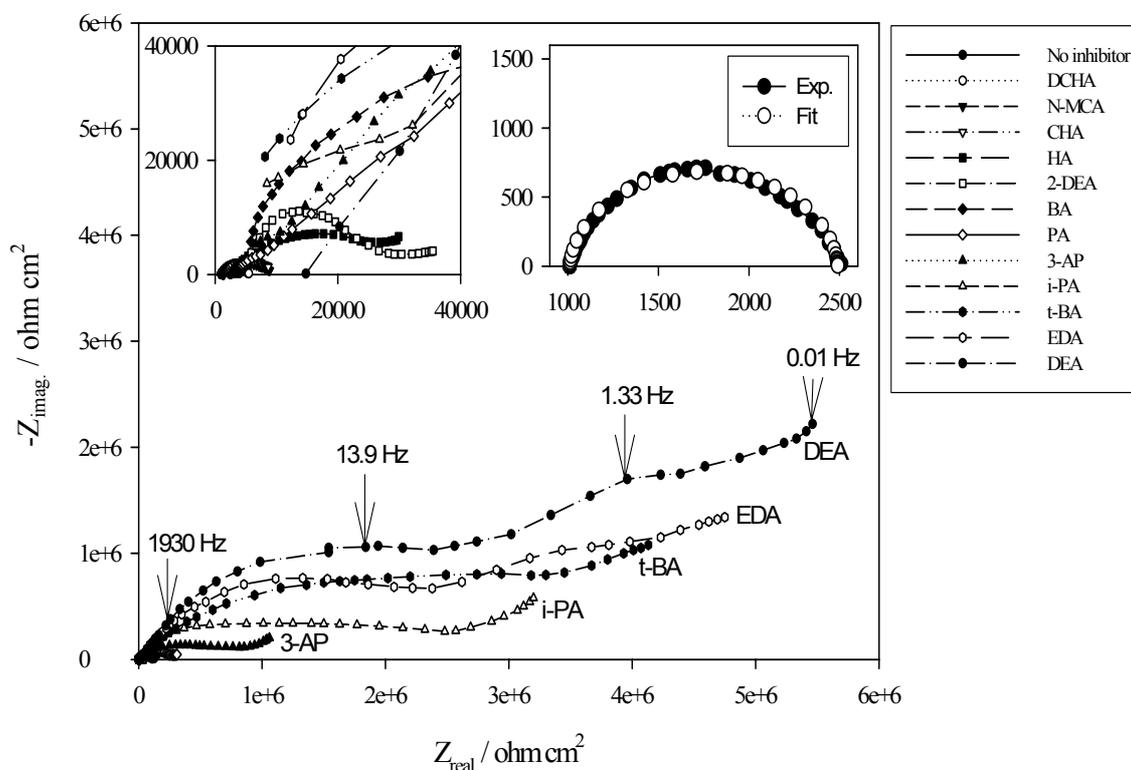


Figure 1. Complex plane plots obtained for carbon steel corrosion with and without inhibitor in petroleum- water system. The high-frequency EIS response has been scale-expanded, as presented in the inset of the figure at the left hand side and the EIS data of carbon steel system without inhibitor with corresponding fitting data at the right hand side.

Figure 2 shows the phase angle versus logarithm of frequency for the carbon steel electrode in petroleum/water solutions containing the twelve amines. For comparison, the behavior of the electrode in the absence of inhibitor is also shown (which is not clear in this figure). It can be seen that the phase angle of the double layer capacitor (or constant phase element) in the presence of i-PA, t-BA, EDA and DEA inhibitors were shifted toward higher degrees. It seems that in the presence of these compounds, constant phase elements were converted to nearly ideal capacitors behavior. This means that, these compounds have significant effects on the frequency dispersion of the double layer capacitance. As it was mentioned previously, energy dissipation took place in CPE type elements. This energy dissipation accompanied by transformation of potential energy into heat,^{18,20} in turn, would cause acceleration of the corrosion processes. Therefore, it seems that energy dissipation is decreased and corrosion rate is reduced in

going from amines with cyclic substituents such as DCHA towards aliphatic amines such as DEA.

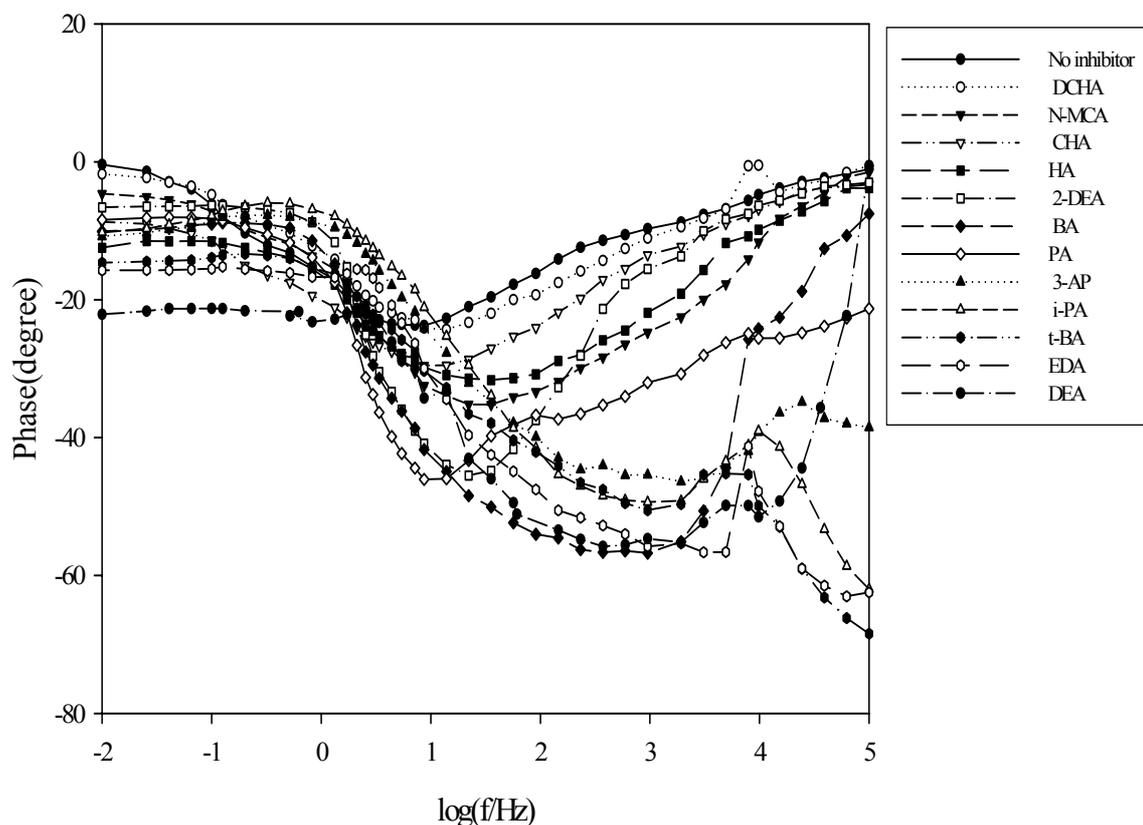


Figure 2. Bode - phase angle plots obtained for carbon steel corrosion with and without inhibitor in petroleum-water system.

Figure 3. shows the logarithm of impedance magnitude versus logarithm of frequency for the carbon steel with and without inhibitor in petroleum/water system. Mansfield and his coworkers^{22,23} have suggested that the sum of series resistances in low frequency region in the Bode-magnitude plot can be used as a criterion for selection of the best inhibitor. Thus, with respect to this suggestion, it is evident that the DEA inhibitor shows the greatest inhibition among the compounds investigated. i-PA, t-BA and EDA also exhibited good inhibition. The inhibitory effect of these compounds was three to four orders of magnitude more than that without inhibitor.

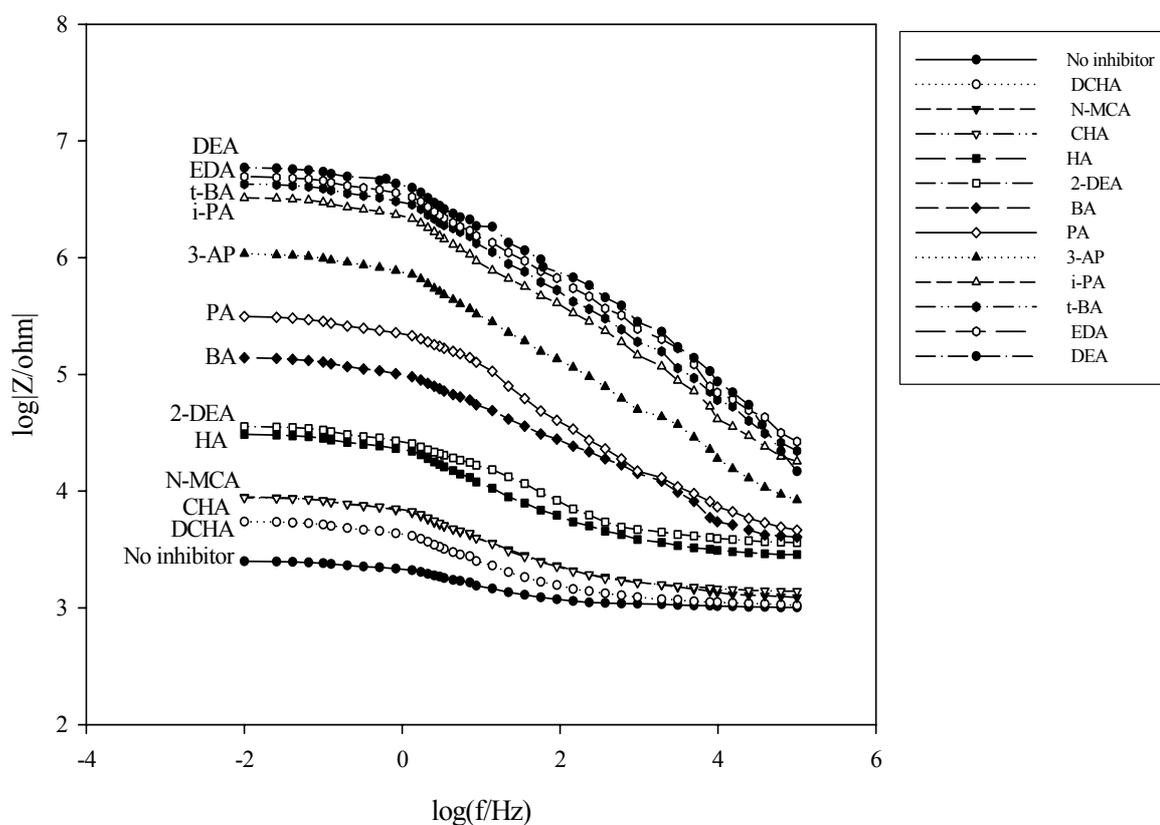


Figure 3. Bode-magnitude plots obtained for carbon steel corrosion with and without inhibitor in petroleum/water system.

Figure 4 shows the Nichols plots for carbon steel corrosion in petroleum/water system in the presence and absence of amines. In spite of apparent complexity of this figure, the Nichols plot has advantages to the other conventional impedance plots as follows:

At first, it is known that the complex plan plot emphasize series circuit elements, if high and low impedance networks are in series, you will probably not see the low impedance circuit, because of the larger impedance controls plot scaling. Since, in Nichols plot the vertical axis is in logarithmic scale and horizontal axis is in degrees, this shortcoming is solved. For instance, in Figure 1, the electrochemical impedance spectra of CHA or DCHA have been buried under the 3-AP or DEA spectra. While in Figure 4, this limitation is not observed. Secondly, Figure 4 shows both Figure 2 and Figure 3, simultaneously.

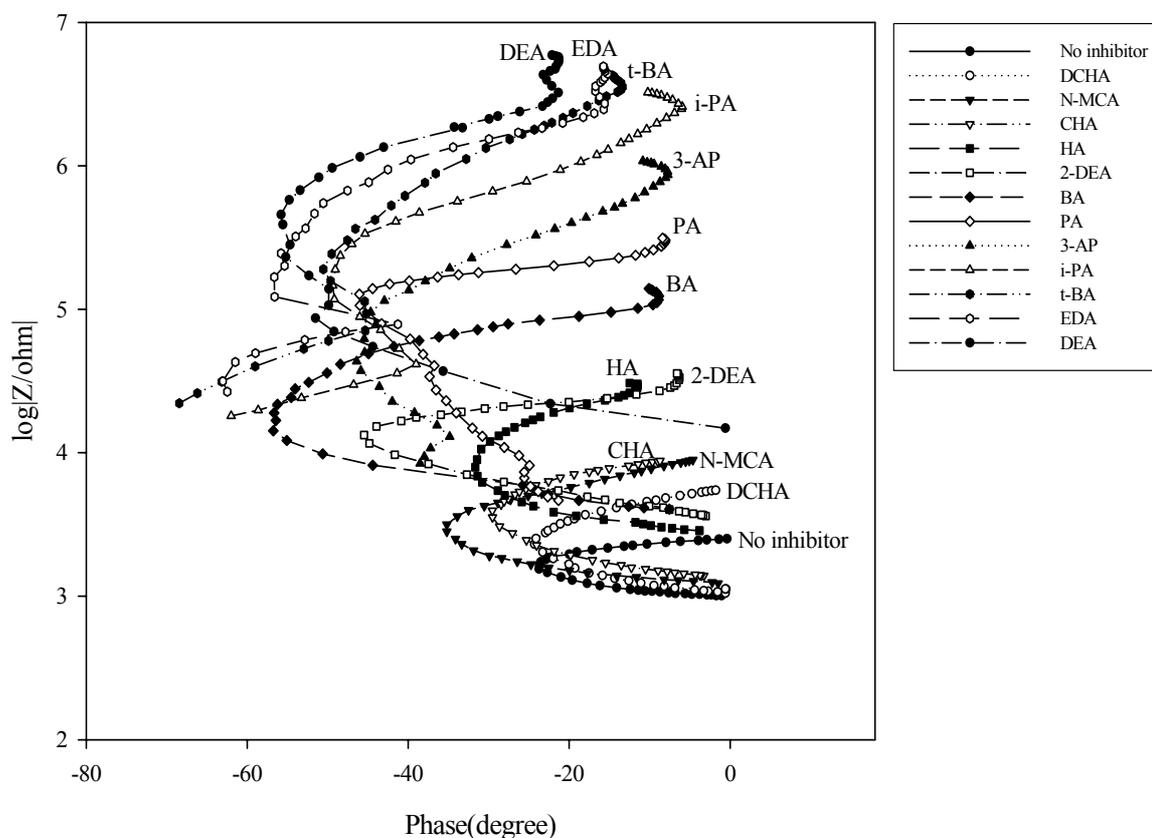


Figure 4. Nichols plots obtained for carbon steel corrosion with and without inhibitor in petroleum-water system.

Equivalent circuit

In this section, in order to have a quantitative comparison, we attempted to introduce a proper equivalent circuit for the experimental EIS data. In this connection, all the impedance spectra obtained with and without inhibitors were interpreted according to the equivalent circuit shown in Figure 5. In this equivalent circuit R_s is uncompensated solution resistance and R_{Ad} and C_{Ad} are adsorbed inhibitor layer resistance and capacitance, respectively. R_{dl} and C_{dl} are also double layer resistance and capacitance, respectively. The resulting parameters, which have been evaluated from the EIS spectra using the complex non-linear least square method, are tabulated in Table 1. It should be mentioned that the very low frequency region has been neglected in this equivalent circuit. The comparison of experimental determined values from impedance measurements and obtained values on the basis of this equivalent circuit presented as inset of Figure 1.

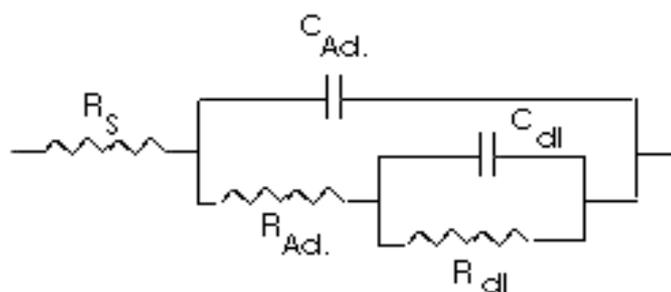


Figure 5. Equivalent circuit evaluated from the EIS spectra recorded with and without inhibitors.

Table 1. Parameters of the equivalent circuit of Figure 5 evaluated from the EIS spectra recorded with and without inhibitors.

Carbon steel with and without inhibitor	R_s $\Omega \cdot \text{cm}^{-2}$	C_{Ad} $\text{F} \cdot \text{cm}^{-2}$	R_{Ad} $\Omega \cdot \text{cm}^{-2}$	C_{dl} $\text{F} \cdot \text{cm}^{-2}$	R_{dl} $\Omega \cdot \text{cm}^{-2}$
No inhibitor	101	—	—	3.90E-4	164
DCHA	106	3.33E-7	708	2.37E-6	455
N-MCA	123	2.38E-7	715	1.87E-5	540
CHA	139	3.84E-7	230	3.34E-6	836
HA	286	9.29E-8	2.78E+2	8.101E-8	2.45E+3
2-DEA	362	4.23E-9	2.16E+3	4.22E-5	1.64E+3
BA	401	1.40E-8	3.75E+2	1.93E-7	2.53E+2
PA	433	1.11E-10	2.47E+2	3.39E-7	8.53E+2
3-AP	658	1.01E-8	2.01E+3	1.68E-11	8.52E+4
i-PA	846	3.48E-9	8.99E+2	1.29E-10	1.54E+3
t-BA	814	2.89E-9	5.63E+2	8.85E-11	2.37E+3
EDA	1230	1.14E-8	5.84E+3	1.87E-10	2.52E+5
DEA	1480	4.28E-10	3.21E+4	3.36E-10	6.83E+5

From these quantitative results and with respect to figures 3 and 4, the following results were obtained:

CHA, N-MCA and DCHA have no significant influence on the solution Ohmic resistance, but slightly increase the electron transfer resistance. The resistance against corrosion has been decreased for the amines containing cyclic substituents, which can probably be related to the steric hindrance imposed by such substituents.

In primary aliphatic amines with one functional group, the corrosion inhibition was increased by reducing the chain length (e.g. PA and BA). For homologous compounds such as PA and i-PA or BA and t-BA, by increasing the symmetry of the

molecules the corrosion inhibition is increased. Also, t-BA with higher molecular symmetry compared to i-PA and t-BA shows a better corrosion inhibition.

Substitution of the terminal methyl group in PA with another amine group (EDA) increased the corrosion inhibition. In the same manner, substitution of OH in the terminal methyl group of butylamine (3-AP) has improved the corrosion inhibition in comparison with BA, but the corrosion inhibition of 3-AP has decreased in comparison with EDA. These behaviors can be interpreted according to Pearson's hard and soft acid-base principle.²⁴ Iron as a hard acid and oxygen of the hydroxyl groups as hard bases are expected to have a strong interaction compared to the amine group substitutions.

Amines with two OH substitutions, such as DEA, showed a very high corrosion inhibition in comparison with those containing two hexyl group substitutions, such as DCHA. Comparison of the simple aliphatic amines with those having cyclic substituents reveals that the steric hindrance factor is dominant to the molecular symmetry factor in obtaining higher resistance against corrosion.

The above findings can be used for a better understanding of the Nichols plot and also for the design of suitable corrosion inhibitors by considering the following points in relation to Figure 6.

- A number of inhibitors such as BA and DEA shift up the Nichols plot along the vertical axis, i.e., parallel with the magnitude axis. Thus, it seems that these inhibitors increase the resistance of the solution, resulting in decreased corrosion.
- A number of inhibitors such as BA, PA, t-BA and N-MCA shift the Nichols plot along the horizontal axis, i.e., parallel with the phase angle axis. This behavior is due to double layer structural changes, which is shown by the potential energy dissipation. By increasing the phase angle, energy dissipation and corrosion rate have been decreased.
- A number of inhibitors such as DCA and DEA widen the orifice of the Nichols plot (C in Figure 6). This kind of behavior shows the electron transfer resistance between the electrical double layer and the adsorbed layer. By increasing the orifice of the Nichols plot, the rate of corrosion has been decreased.

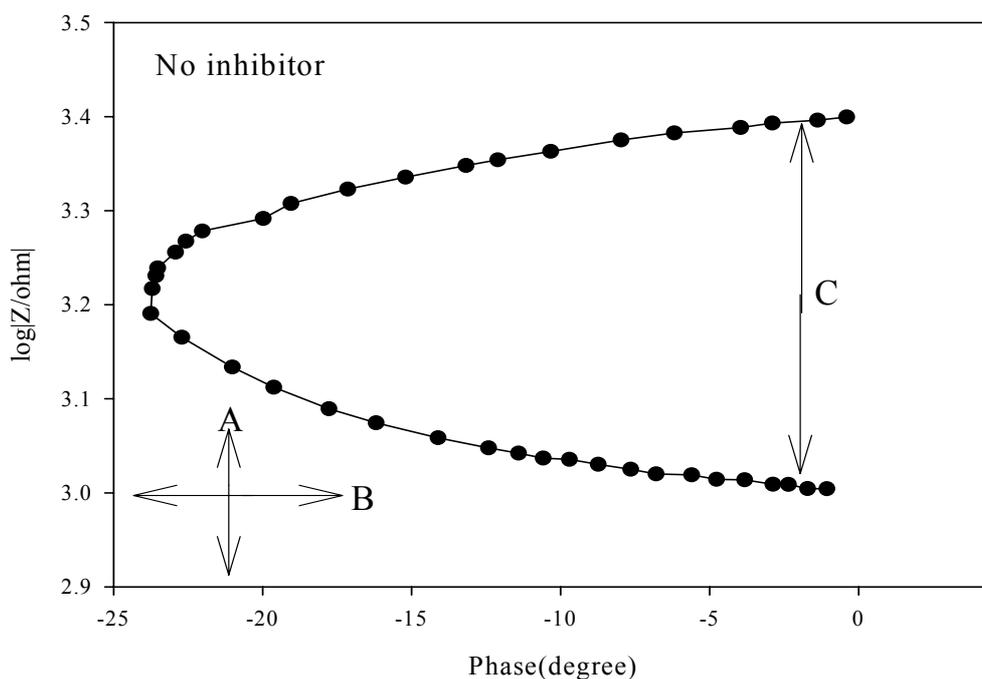


Figure 6. Nichols plot obtained for carbon steel corrosion without inhibitor in petroleum-water system.

As an application of the above mentioned behaviors, we consider the inhibition performance of two amines N-MCA and CHA. Nichols plot shows a better resolution between inhibition performances of these compounds with a close structure. This resolution is shown in Figure 7, which can be compared with the unresolved ones in Figure 1 and Figure 3. The difference in the performance of N-MCA and CHA is not clear in Figure 3, while Figure 7 shows a significant difference between these inhibitors. As it can be seen from Figure 7, the charge transfer resistance of N-MCA is clearly greater than that of CHA and impedance phase angle of N-MCA is also greater than that of CHA. Therefore, we can conclude that N-MCA is a better inhibitor than CHA.

Conclusions

From the results obtained in this work the following conclusions could be made regarding the inhibition resistance of the twelve amine compounds for carbon steel in petroleum/water media:

- For corrosion inhibition design purposes, in addition to the complex plane and Bode plots, the Nichols plot is also necessary.

- Three structural and molecular factors should be considered for selection of an inhibitor: symmetry, steric hindrance and number of functional groups. The best inhibitor is the one with greatest number of functional groups, higher symmetry and lower steric hindrance.

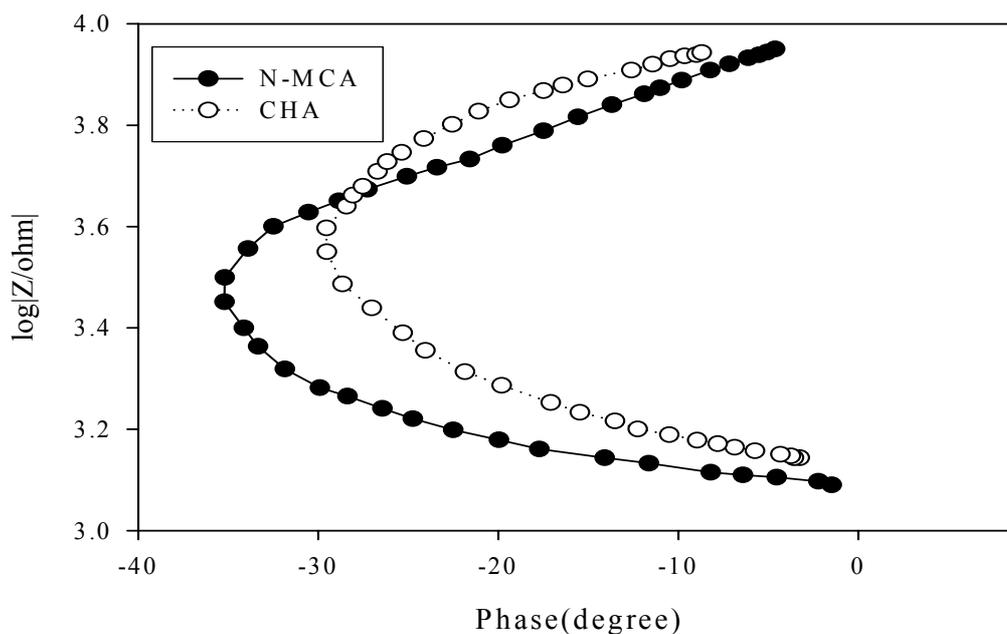


Figure 7. Nichols plots obtained for carbon steel corrosion with N-MCA and CHA inhibitors in petroleum-water system.

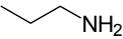
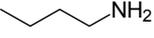
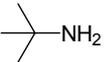
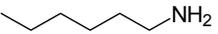
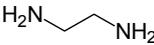
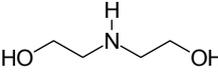
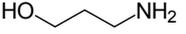
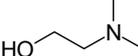
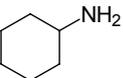
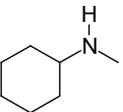
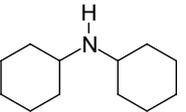
Experimental

Materials

The sample for study was a carbon steel with following composition in wt.%: C, 0.15-0.2; Si, 0.25; Mn, 0.2-0.5; S, 0.05; Fe, to balance.^{9,10} For all experiments, the carbon steel samples were polished with abrasive paper of 100 to 2000 grades.

Polished samples were degreased with EtOH, cleaned with water and then dried with warm air. The corrosion medium was an aqueous solution containing NaCl, 2 wt.%; AcOH, 8 wt.% and various amounts (0-16 wt.%) of (40-60 °C b.p.) petroleum ether in contact with air, maintained at 25±1 °C. Inhibitor materials, all reagent grade from Merck, are listed in Table 2.

Table 2. Chemical structure of the additive used as corrosion inhibitors in petroleum/water mixture.

Number	Inhibitor	Abbreviation	Structural formula
1	Propylamine	PA	
2	iso- Propylamine	i-PA	
3	Butylamine	BA	
4	Tert-Butylamine	t-BA	
5	Hexylamine	HA	
6	Ethylenediamine	EDA	
7	Diethanolamine	DEA	
8	3-Amino-1-propanol	3-AP	
9	2-Dimethylethanolamine	2-DEA	
10	Cyclohexylamine	CHA	
11	N-Methylcyclohexylamine	N-MCA	
12	Dicyclohexylamine	DCHA	

Apparatus and electrochemical measurements

The working electrode was a rotating disc consisting of a carbon steel of $1.32 \times 10^{-5} \text{ m}^2$ cross-sectional area. A thermo-reactable sheet prevented the cylindrical area from making contact with the solution so that the electrode surface was the only the cross-section available to the solution. All the experiments were carried out with a rotation rate of 720 rpm. The auxiliary electrode was smooth platinum. A saturated calomel electrode (SCE) was used as reference. Electrochemical measurements were carried out with an Amel 2053 Potentiostat-Galvanostat and an Amel 568 Function Generator equipped with an Advantech PCL 818L interface and a Pentium 166

computer for data processing. Electrochemical impedance spectroscopy (EIS) was carried out with an Autolab/PGSTAT30 system at frequency range of 10 mHz - 100 kHz with a 5 mV perturbation signal at the corrosion potential. After polishing and cleaning, the carbon steel electrode was immediately immersed in stirring petroleum/water mixtures (0, 4, 8, 12 or 16 wt.% petroleum) each containing 0, 1, 2, 4 or 8 wt.% inhibitor. The immersion time of the electrode before measurements was 12h.

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Povzetek

Namen teh raziskav je bil uvesti preprosto grafično metodo za določanje inhibitorskih vplivov nekaterih aminov v mešanici nafta-vodna raztopina očetne kisline in kuhinjske soli na korozijo ogljikovega jekla. Raziskave so potekale na osnovi elektrokemijske impedančne spektroskopije. Rezultate vplivov inhibicije lahko dobro razložimo s pomočjo diagrama impedančne jakosti v odvisnosti od faznega kota. Na osnovi rezultatov so podana izhodišča za izbiro najboljšega inhibitorja korozije ogljikovega jekla v obravnavanem sistemu.