

Corrosion-Protecting Properties of Bis Quaternized Derivates of Some N-Arylnicotinamides

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Abstract

Some N-Arylnicotinamides were obtained by acylation of 2- and 4-aminopyridines, 3-aminoquinoline with nicotinic acid chloride and converted in bis quaternary salts by quaternization with benzyl chloride, allyl chloride and allyl bromide. Corrosion properties of the salts obtained were studied with respect to corrosion of 08 kp steel in 3M HCl at 40-80°C. Quantum chemical calculations using DFT at the B3LYP/6-31G(d) level have been applied in order to explain the different inhibition efficiencies of these compounds act as inhibitors for iron steel in acid media. The theoretical results were found to be consistent with the experimental data reported.

Keywords

N-Arylnicotinamides, Bis Quaternary Salts on the Base of N-Arylnicotinamides, Synthesis, Hydrochloric Acid, 08kp Steel, Anticorrosion Activity

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1. Introduction

The use of inhibitors is one of the most practical methods to protect metals against corrosion, especially, in acid media [1]. The inhibitor molecule should have centers capable of forming bonds with the metal surface via electron transfer. For example, most inhibitors are organic compounds containing quaternary ammonium centers and π -electrons in double bonds. Heteroatoms and oxo group as well as aromatic rings in structure of inhibitors are also the major adsorption centers [2-5]. Many of organic inhibitors promote the formation of the chelates on the metal surface and, consequently, inhibit the corrosion process [3]. The inhibition efficiency depends also on the substituent type, whether an electron-donating or electron-withdrawing group and the concentration of the inhibitor [4]. Among the organic compounds used a corrosion inhibitors amides of organic acids were found to inhibit the corrosion of steel in acid chloride solutions [5]. It is connected with a lone electron pair on the nitrogen atom and with donor-acceptor interaction

between oxo group and corroding metal. Creation of additional adsorption centers in these compounds, such as one or two quaternary ammonium ions will allow obtaining substances, the inhibition action of which can be raised as a result of summation of several effects [6-9]. For example, 3-(N-Arylcarboxamido)-N-benzylpyridinium salts are known as one of the classes of organic compounds, some of which show significant anticorrosion activity [10]. As a prolongation of the last work on the synthesis and studying of anticorrosion properties of such compounds, we have synthesized N-Arylnicotinamides 1-3 and bis quaternary ammonium salts based on them 4-8 and having two adsorption centers – two quaternary ammonium ions, which affects electrode processes due to electrostatic adsorption [1].

To estimate corrosion-protecting properties of synthesized compounds 4-8 we have studied their influence on the corrosion of 08kp steel in 3M hydrochloric acid at 40-80°C, determining inhibition coefficient γ and the degree of protection Z .

Now in order to explain the different inhibition efficiencies

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of the organic compounds quantum chemical calculations have proved for studying [11-13]. The aim of this paper is to investigate the applicability of such calculations to explain the inhibition efficiency of the synthesized salts 4-8. The structure of these compounds have been optimized and the frontier molecular orbital energy (E_{HOMO} , E_{LUMO}), gap energy ΔE , electron affinity (A), ionization potential (I) and global hardness (η) were calculated at the B3LYP/6-31G(d) level using the Firefly (GAMESS) program package [14-17].

2. Experimental

General

$^1\text{H-NMR}$ spectra were recorded on a JEOL spectrometer (90MHz) in DMSO-d_6 or CDCl_3 with TMS as internal reference, chemical shifts were measured in the δ scale. IR spectra of compounds were recorded as potassium bromide pellets on a Specord 75-IR instrument.

General Procedure for Synthesis of N-Arylnicotinamides 1-3.

Chemically-pure grade reagents were used for the experiments.

A mixture 0,011mol of 2- or 4-aminopyridines, 3-aminoquinoline and 0,011 mol nicotinic acid chloride were stirred in CHCl_3 (50ml) by cooling, then the reaction mixture was refluxed for 8h, washed with 10% NaOH. The obtained precipitate was filtered and washed with cool ethanol. The crude products were crystallized from benzene to give compounds 1-3. Their yield based on the starting arenes, analytical data the amides are consistent with their empirical formulas. Physicochemical constants of the synthesized amides corresponded to the published data [18-19].

Amide 1: Yield 70,6%; mp 212°C; IR(cm^{-1}): 730, 740(2-subst.Py, δCH), 790(3-subst.Py, δCH), 1430-1600(C-C, C-N, νPy), 1680(C=O), 3200(NH). $^1\text{H-NMR}(\text{CDCl}_3)$: 7.04 (1H,dd, $^3\text{J}=6.5\text{Hz}$, $^3\text{J}=4\text{Hz}$), 7.31(1H,d, $^3\text{J}=6.5\text{Hz}$), 7.42(1H, dd, $^3\text{J}=6.5\text{Hz}$, $^3\text{J}=4.5\text{Hz}$), 7.74(1H, td, $^3\text{J}=6.5\text{Hz}$, $^4\text{J}=1.5\text{Hz}$), 8-12-8.40(2H, m), 8.75 (1H, dd, $^3\text{J}=4.5\text{Hz}$, $^4\text{J}=1.5\text{Hz}$), 9.14(1H, $^4\text{J}=1.5\text{Hz}$), 9.36(1H,s, NH).

Amide 2: Yield 67,5%; mp 189°C. IR(cm^{-1}): 730,740(2-subst. Py, δCH), 810(4-subst. Py, δCH), 1410-1550(C-C,C-N, νPy), 1685(C=O), 3220(NH); $^1\text{H-NMR}(\text{CDCl}_3)$: 7.32(1H,d, $^3\text{J}=6.5\text{Hz}$), 7.40(1H,dd, $^3\text{J}=6,5\text{Hz}$, $^3\text{J}=4.5\text{Hz}$), 8.25(1H, dd, $^3\text{J}=6.5\text{Hz}$, $^4\text{J}=1.5\text{Hz}$), 8.77(1H, dd, $^3\text{J}=4.5\text{Hz}$, $^4\text{J}=1.5\text{Hz}$), 8.93(2H, dd, $^3\text{J}=6.5\text{Hz}$, $^4\text{J}=1.5\text{Hz}$), 9.10(1H, d, $^4\text{J}=1.5\text{Hz}$), 9.41(1H,s, NH).

Amide 3: Yield 62%; mp 152°C; IR(cm^{-1}): 1640(C=O), 3050-3330. $^1\text{H-NMR}(\text{CDCl}_3)$: 7,94-7,41(m, 7H), 8.34(1H,d, $\text{j}=6.0\text{Hz}$), 8.92(1H,s, CH), 9.13(1H,s, CH), 9.87(1H, s, NH).

General Procedure for Synthesis of bis quaternary salts 4-8.

A mixture of the corresponding amides 1-3 (0.012mol) and benzyl chloride (0.024mol) were refluxed in benzene (50ml) for 8h. The mixture was cooled to room temperature and the obtained precipitate was filtered and washed with benzene to give salts 4-5,8, their elemental analyses corresponded to their empirical formulas.Their yield based on the starting amides.

Salt 4: Yield 65,4%; mp 300°C. IR(cm^{-1}): 1630(C=O), 3250(NH). $^1\text{H-NMR}(\text{DMSO-d}_6)$: 5.91(2H,s, CH_2) 7.03(3H,m, Ph), 7.38(3H, m, Ph,Py), 7.74(2H,m, Py), 8.22(5H, m, Ph), 8,76(2H, m,Py), 9.18(3H, m, Py), 9.44(3H, s,NH, CH_2).

Salt 5: Yield 67,5%, mp >300°C. IR(cm^{-1}): 1650(C=O), 3210(NH). $^1\text{H-NMR}(\text{DMSO-d}_6)$:4.75(2H,s, CH_2), 5.31(2H, s, CH_2), 6.95(3H, m, Ph), 7.02(3H, m, Ph), 7.30(2H, m, Ph), 7.75(2H, m, Ph), 8.31(4H, m, Py), 9.09(4H, m, Py), 9.41(1H, NH).

Salt 8: Yield 87%; mp >300°C. IR(cm^{-1}): 1710(C=O), 3370(NH). $^1\text{H-NMR}(\text{DMSO-d}_6)$: 6.05(2H,s, CH_2), 7.42 -8.10(m, 20H), 9.44(2H,s, CH_2), 10.19(1H, s, NH).

For the synthesis of 6 salt dissolved 0.025 mol of amide 2 in 30 ml of allyl chloride was refluxed for 5 hours, and then allyl chloride was distilled off and the residue was crystallized from methanol. Quaternization by allyl bromide was performed by refluxing 0.025 mole of the same amide with 0.05 mol of allyl bromide in benzene for 9 hours. The precipitated salt was filtered off and crystallized from methanol. The elemental analyses of salts 6-7 corresponded also to their empirical formulas.Their yield based on the starting amide.

Salt 6: Yield 60,8%; mp 248°C. IR(cm^{-1}): 1680(C=O), 3340(NH). $^1\text{H-NMR}(\text{DMSO-d}_6)$: 4.85(4H,s, 2 CH_2), 5.20(2H,m, CH_2), 5.53(2H,m, CH_2), 6.30(2H,m, CH) 8.48(2H,d, $\text{J}=6\text{Hz}$, CH, Py), 8,61(2H,d, $\text{J}=6\text{Hz}$, CH, Py), 9.25(2H,d, $\text{J}=6\text{Hz}$, CH, Py), 8.34-9.05(2H,m, CH, Py), 9.75(1H,s, NH).

Salt 7: Yield 71,3%; mp 256°C. IR(cm^{-1}): 1690(C=O), 3360(NH). $^1\text{H-NMR}(\text{DMSO-d}_6)$: 4.77(4H,s, 2 CH_2), 5.12(2H,m, CH_2), 5.48(2H,m, CH_2), 6.25(2H,m, CH) 8.48(2H,d, $\text{J}=6\text{Hz}$, CH, Py), 8,52(2H,d, $\text{J}=6\text{Hz}$, CH, Py), 9.17(2H,d, $\text{J}=6\text{Hz}$, CH, Py), 8.34-9.05(2H,m, CH, Py), 9.75(1H,s, NH).

Anticorrosion activity

Corrosion tests in 3M hydrochloric acid were carried out by gravimetric method, using 08kp steel samples with working surface area of $7.2 \times 10^{-4} \text{ m}^2$. Samples of 3g l^{-1} of the synthesized salts were used for the inhibition tests. Test periods were 2h at 40°C, 1h at 60°C and 0.25h at 80°C. The results of the tests are presented in Table 1.

Table 1. Effects of the salts 4-8 on corrosion of 08kp steel in 3M HCl.

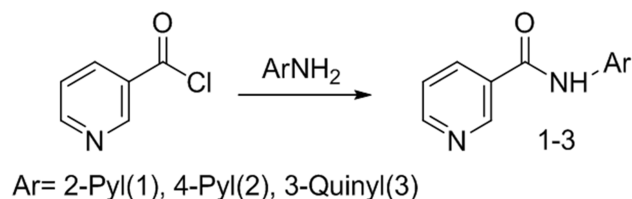
Salt No.	40°C		60°C		80°C	
	γ	Z, %	γ	Z, %	γ	Z, %
4	44,0	97,7	56,3	98,2	65,2	98,4
5	133,5	99,3	197,5	99,5	228,9	99,6
6	10,7	90,7	18,2	94,5	27,3	96,3
7	8,7	88,5	16,3	93,3	26,3	96,2
8	113,9	99,1	206,7	99,5	326,2	99,7

3. Results and Discussion

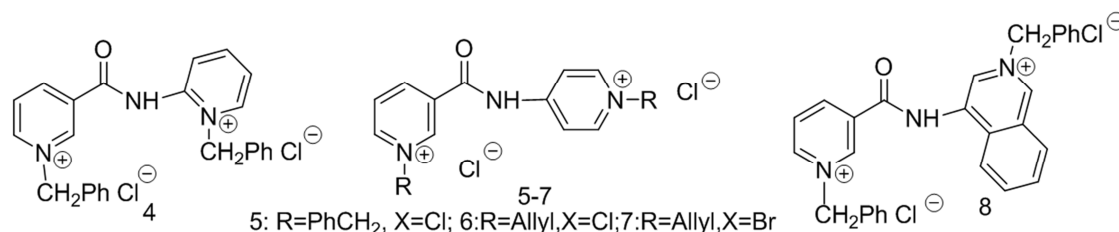
Salts 4-8 were prepared in two steps according to the reported procedure [6].

In the first step 2- and 4-aminopyridines, 3-aminoquinoline

were refluxed with nicotinic acid chloride in CHCl_3 to obtain the corresponding amides 1-3 (Fig. 1):

**Figure 1.** Synthesis of N-Arylnicotinamides.

In the last step the final compounds 4-8 were obtained by quaternization of amides 1-3 with benzyl chloride in benzene, with allylchloride and allylbromide under reflux:

**Figure 2.** Bis quaternary salts on the base of N-Arylnicotinamides.

The structures of the compounds 4-8 were determined by the elemental analyses and by spectral analyses. The IR spectra showed intense absorption band within $3210\text{-}3370\text{ cm}^{-1}$ range and $1630\text{-}1710\text{ cm}^{-1}$ range that were attributed to NH and C=O function vibrations respectively. Singlets of NH-group proton at 9.41-10.19 ppm and of the benzyl radical methylene protons at 4.75-6.05 ppm and at 9.44 ppm (4-5, 8) are presented in $^1\text{H-NMR}$ spectra of these compounds. Probably off-set signals methylene protons for salts 4 and 8 in the region of weak fields are due to the influence of the amide group and of the ammonium nitrogen atom. Fully all the absorption bands in the infrared spectra of salts 4-8 and the signals of all the protons of these salts in the PMR spectra are shown earlier in the experimental part of the work.

Taking into account data on the dependence of the protecting properties of quaternary ammonium salts on their structures we examined this dependence for salts 4-8 in 3M HCl. As seen from the Table 1, salts 6-7, containing in its structure allyl radicals exhibit weaker protective properties than the salt 5 with benzyl radicals derived from the same N-Arylnicotinamide and having the same adsorption centers of electrostatic interaction with the metal surface. This can be explained by greater donor- acceptor interaction of the electron density of the benzene ring with corrosion metal surface than the double bond of the allyl radical and an increasing in the surface of the lock due to the size of the radical [5]. In the transition from the salt 4 to the salt 5 corrosion-protecting properties are significantly increased,

which is probably associated with a planar structure of the salt 5, while conformational arrangement of adsorption centers of the salt 4 does not allow them to equally react with the metal surface. It was expected that the size and less free rotation around the C-N-bond part of 3-aminoquinoline may contribute, as noted for N-(1-naphthyl)nicotinamide [10], the formation of a tight complex chemisorbed on the metal surface. However, this does not happen and there is a slight decreasing of corrosion rate inhibition only at 80°C (Table 1).

The dependence of the effect of salts 4-5, 8 on acid corrosion can be investigated using quantum chemical calculations of structural and electronic parameters of these salts. The calculations of these parameters were performed by using packet Firefly [14], based in part on the source code of GAMESS (US) [15] at the B3LYP/6-31G(d) level [16-17].

It follows from the calculations that the negative charges on the nitrogen atoms are almost the same, and make for the N-atom of the pyridine ring -0.926, for the N-atom of the amide group -1.069, for the N-atom of the quinoline cycle -0.977. Therefore amido group is adsorption center and promotes adsorption on the metal surface, showing intramolecular synergy [20]. When comparing the calculated optimized geometries of salts it has been found that the salt 5 has a flat configuration between the two ammonium N-atoms, whereas these salts atoms in 4 and 8 are located in two mutually perpendicular planes, and only the size of salt 8 may facilitate locking surface of the corroding metal.

In order to establish a correlation between the inhibitory

properties of salts 4-5, 8 and electronic parameters we have calculated the energies of the frontier orbitals E_{HOMO} , E_{LUMO} , $\Delta E = E_{\text{HOMO}} - E_{\text{LUMO}}$, the ionization potential $I = -E_{\text{HOMO}}$, the electron affinity $A = -E_{\text{LUMO}}$, global hardness (η) using

known methods [11]. In Table 2 quantum chemical parameters related to the electronic structure of corresponding salts 4-5, 8 and inhibition coefficient γ are presented.

Table 2. Inhibition coefficient γ and quantum-chemical descriptors for molecules 4-5,8.

Molecule	γ at 80°C	HOMO(eV)	LUMO(eV)	ΔE	I	A	η
4	65.3	-14.19	-4.84	9.35	14.19	4.84	4.68
5	228.9	-13.96	-4.77	9.19	13.96	4.77	4.60
8	326.2	-14.33	-5.17	9.16	14.33	5.17	4.58

It is known that corrosion is slowed in the inhibition by heterocycles having a low value E_{LUMO} and low value $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ [11]. Therefore, the lower the value of E_{LUMO} is the more probable the molecule to accept electrons. In our study the salt 8 having low value of $E_{\text{LUMO}} - 5.17$ could have better performance as corrosion inhibitor. This is in good agreement with the experiment where the salt 8 is more efficient than the salts 4-5.

Energy gap is an important parameter as a function of reactivity of the inhibitor molecule toward the adsorption on the metallic surface. As ΔE decreases, the reactivity of the molecule increases leading to increase in coefficient γ . A molecule with a low energy gap is more polarization and is generally associated with the high chemical activity. In our study, the trend for the (ΔE) values follows the order $4 > 5 > 8$, which suggests that the salt 8 ($\Delta E = 9.16$) has the highest reactivity in comparison to the other salts and would therefore likely interact strongly with the metal surface. The results as indicated in Table 2 show that the salt 8 has lowest ΔE , this means that the molecule could have better performance as corrosion inhibitor.

Absolute hardness and softness are important properties to measure study, the molecular stability and reactivity. The inhibitor with the least value of global hardness is expected to have the highest inhibition efficiency [21]. In the present study, the salt 8 with low hardness value 4.58 compared with the other salts have a low energy gap and the highest inhibition activity as seen from the Table 2.

4. Conclusions

In summary we have described the synthesis of N-Arylnicotinamides by acylation of 2- and 4-aminopyridines, 3-aminoquinoline with nicotinic acid chloride. N-Arylnicotinamides were converted in bis quaternary salts by quaternization with benzyl chloride, allyl chloride and allyl bromide. To estimate anticorrosion properties of these salts we have studied their influence on the corrosion of 08kp steel in 3M HCl at 40-80°C. Quantum chemical calculations using DFT have been applied to synthesized salts act as inhibitors for iron steel in acid media.

The structural parameters, such as E_{HOMO} , E_{LUMO} , $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$, the ionization potential $I = -E_{\text{HOMO}}$, the electron affinity $A = -E_{\text{LUMO}}$, global hardness (η) were calculated and correlated with experimental inhibition coefficient γ . Both experimental data and quantum theoretical calculations are in agreement. From the results and findings of the study, it can be concluded that salts 5 and 8 are good inhibitors for the corrosion of mild steel in HCl solution. The inhibitory potentials of the synthesized salts 4-5, 8 are due to the transfer of electron from the salts to Fe in mild steel. From experimental and theoretical data, the trend for the variation of the inhibition efficiencies of the salts is $8 > 5 > 4$. We emphasized also that benzyl radicals, the two ammonium N-centers and amido group are the possible active adsorption sites. Therefore, the use of quantum chemical parameters is appropriate in modeling the inhibitory of the studied salts molecules.

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