



Dependence of Anti-Corrosion Properties on the Energy Characteristics of Benzylated N-Arylnicotinamides

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Abstract The dependence of the anticorrosion properties of benzylated N-arylnicotinamides upon corrosion of O8kp steel in 3M HCl at 80 ° C on their energy characteristics was investigated. For cations of these structures, the optimized geometries and quantum-chemical parameters of E_{NOMO} , E_{LUMO} , and $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$ were calculated and the dependences of the reduced corrosion inhibition coefficient $[\gamma]$ on ΔE and $e^{\Delta E}$ with correlation coefficients of 0.96 and 0.99, respectively, are presented. The structure of inhibitors significantly affects the corrosion rate, which is observed when comparing their calculated optimized geometries.

Keywords Benzylated N-arylnicotinamides, corrosion, reduced corrosion inhibition coefficient, energy characteristics, optimized geometries

Introduction

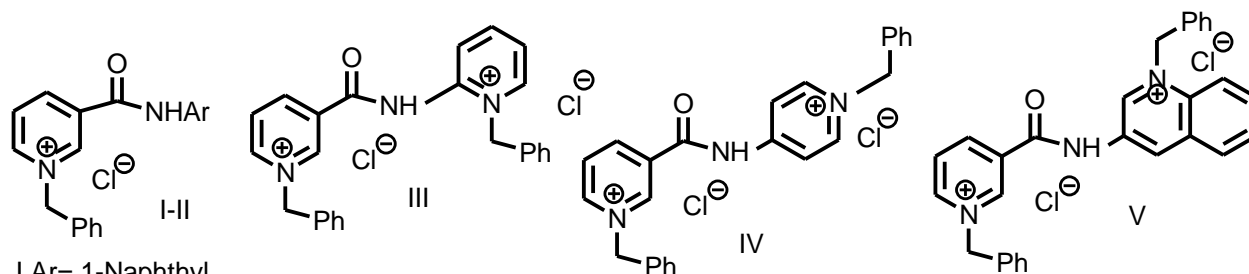
It is known [1] that acid corrosion inhibitors are used to protect microelectronics and electrical equipment. For this aim, organic inhibitors with internal “synergism” are most widely used, containing in their structure, in addition to ion-type adsorption centers, functional groups that differ in magnitude and sign of charge [2]. Previously, the selection of inhibitors of this type was mainly carried out experimentally based on the results of their effect on corrosion in various environments, but recently in the literature [3-8] data are given on studying the correlation of inhibitory effects and such characteristics of organic compounds as molecular geometry and energy parameters: E_{HOMO} , E_{LUMO} , $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$. Such information allows the selection of organic compounds as promising corrosion inhibitors.

The aim of this work is to study the dependence of anticorrosion properties on structure and energy characteristics of a number of benzylated N-arylnicotinamides.

Materials and Methods

The benzylated N-arylnicotinamides (IV) required for research were obtained by known methods [7, 9] in two stages: in the first stage, N-arylnicotinamides were synthesized by acylation of 1- and 2-naphthylamines, quinoline and 1- and 4-aminopyridines with nicotinic acid chloride, in the second stage, the quaternization of the obtained N-arylnicotinamides was carried out with benzyl chloride. The individuality and structure of salts I-V were confirmed using IR and PMR spectrometry:





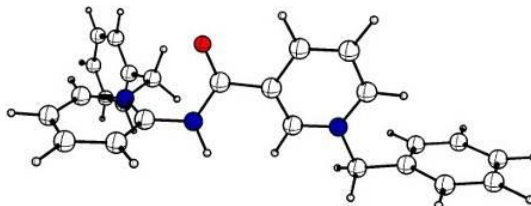
I Ar= 1-Naphthyl
II Ar= 2-Naphthyl

Corrosion tests were carried out by massometric method in 3M HCl at 80 ° C, using 08 kp steel samples with a working surface of $7.2 \cdot 10^{-4} \text{ m}^2$. For inhibition $0.01 \text{ mol} \cdot \text{L}^{-1}$ of synthesized compounds were used, the test period was 0.25 h. Corrosion inhibition coefficient γ was determined from the results of the experiments. The reduced corrosion inhibitory coefficient $[\gamma]$, taking into account the molar mass of organic inhibitors, was calculated by the formula $[\gamma] = \gamma / M$, where M is the molar mass of the inhibitor.

For quantum chemical calculations, the Firefly software package [10] was used, partially based on the GAMESS (US) source code [11], according to the B3LYP method with the basic set 6-31G (d) [12-13], which allows one to find the conformation with the minimum energy, determine the energies of the HOMO and LUMO, the charges of the adsorbed centers of cations of structures I-V.

Results and Discussion

From the literature [14] it is known that the protective properties of corrosion inhibitors depend on the structure of their molecules.. We carried out calculations of optimized geometries of cations of structures IV, which showed that the conformations of I-II cations containing naphthyl fragments are the closest to planar ones, which makes it possible to cover a large surface area of the metal, while the conformations of III-V diquaternized structures do not allow two adsorption centers equally fix on the metal surface and act simultaneously, which is especially noticeable for the salt III cation, the optimized geometry of which is given below:



The charges on the nitrogen atoms for all cations are almost the same and, on average, for the nitrogen of the pyridine ring of the nicotinic acid fragment are -0.926, for the amide nitrogen atom -1.069, for the nitrogen atoms of the aryl fragments of the biquaternized structures -0.977. It follows from the above that the amide fragment is also an adsorption center and can take part in fixing the inhibitor molecules on the metal surface.

The adsorption of the inhibitor on the metal surface can occur on the basis of donor-acceptor interactions between the π -electrons of the heterocycle compound and the vacant *d*-orbitals of the metal surface atoms. The authors of [3–8] found that increasing values of E_{HOMO} such compounds facilitate adsorption and therefore increase the inhibition efficiency by influencing the transport process through the adsorbed layer. The energy of lowest unoccupied molecular orbital indicates the ability of the molecule to accept electrons. The lower the value of E_{LUMO} , the more probable it is the molecule would accept electrons. Consequently, concerning the value of the energy of the gap $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$, larger values of the energy difference will provide low reactivity to a chemical species. Lower values of the energy difference will render good inhibition efficiency, because the energy to remove an electron from the last occupied orbital will be low.

We carried out calculations of these parameters for the cations of the studied structures I-V and their results, as well as the given corrosion inhibition coefficients, are presented in the table, from which the conclusions on the dependence of inhibitory effects on the energy characteristics set forth in the indicated works follow:



Table 1: Inhibitory effect and quantum chemical parameters cations of structures I-V

Structure	γ	$[\gamma]$	E_{HOMO} , eV	E_{LUMO} , eV	ΔE , eV	$e^{\Delta E}$
I	766	2.05	-10.13	-2.49	7.64	2078
II	733	1.96	-9.89	-2.50	7.39	1618
III	65	0.14	-14.19	-4.84	9.35	11487
IV	229	0.50	-13.96	-4.77	9.19	9787
V	326	0.65	-14.33	-5.17	9.16	9500

As can be seen from the table, the dependence of the anticorrosion properties on the E_{HOMO} value of the following order II > I > IV > III > V is observed for the compounds studied, and the decrease in ΔE occurs in the series III > IV > V > I > II, which correlates with the values of γ and $[\gamma]$. According to the table, a graph of the linear dependence $[\gamma] = f(\Delta E)$ was constructed and an approximation was performed ($R = 0.96$).

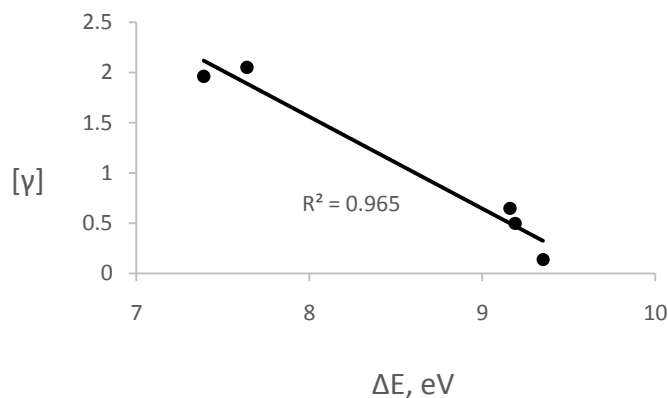


Figure 1: Correlation between the reduced corrosion inhibition coefficient $[\gamma]$ and ΔE during steel corrosion 0.8 kp in 3M HCl at 80 °C

With the introduction ΔE to the power, the dependence graph $[\gamma] = f(e^{\Delta E})$ was constructed and the equation $[\gamma] = k \cdot e^{\Delta E} + C$ was derived, where $k = -2.03 \cdot 10^{-5}$; $C = 2.6$.

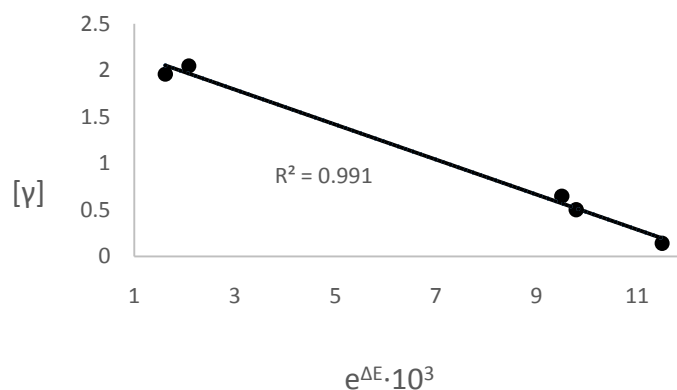


Figure 2: The correlation between the reduced inhibition corrosion coefficient $[\gamma]$ and $e^{\Delta E}$ during steel corrosion 0.8 kp in 3M HCl at 80 °C.

For such dependence, the correlation coefficient R is 0.99, which is significantly higher than for the dependence $[\gamma] = f(\Delta E)$, which was previously used in the works [3-4]. When applying the principle of LCMS to the processes of metal dissolution and corrosion inhibition, the studied compounds I-V can be attributed to “hard” molecules because of the ΔE values found for them and possessing the ability to create strong bonds with the metal surface.



Conclusion

It was established that the reduced coefficient of inhibition of corrosion $[\gamma] = \gamma / M$, where M is the molecular weight of the inhibitor, when studying corrosion of 08 kp steel in 3M HCl at 80 ° C in the presence of inhibitors, benzylated N-arylnicotinamides, correlates with such energy characteristics of the latter as E_{HOMO} and $\Delta E = E_{\text{LUMO}} - E_{\text{HOMO}}$, and a higher correlation coefficient is achieved for the dependence $[\gamma] = f(e^{\Delta E})$. The structure of inhibitors has a significant effect on the corrosion rate, which is observed when comparing their calculated optimized geometries.

References

- [1]. Kunze E. *Korrosion und Korrosionsschutz*. (2001). Willy, VCH.
- [2]. Kuznetsov Yu. I., Kazanskii L.P. (2008) Fiziko-chimicheskii aspekti zaschiti metallov inhibitorami korozii klasa azolov. *Uspehi himii*. 77, № 3, 227-241. (in Russ.)
- [3]. Sastri V.S., Perumareddi J.R. (1997) Molecular Orbital Theoretical Studies of Some Organic Corrosion Inhibitors. *Corrosion*. 53, (8), 617-622.
- [4]. Wang He., Wang X., Wang Ha., Wang Li., Liu Ai. (2007) DFT study of new bipyrazole derivatives and their potential activity as corrosion inhibitors. *J. Mol. Model.*, 13, 147-153.
- [5]. Lukovits I., Shaban A., Kalman E. (2003) Corrosion inhibitors: quantitative structure-activity relationships. *Russ. J. Electrochem.*, 39, 177-181.
- [6]. Pisanenko D.A., Gaidai A.V., Klimko Yu.I., Avilov V.O. 2-N-Polibenzylopirazoliichloridi kak sostavl'yayushchie inhibitorov kislotnoi korozii. (2015) *Ukr. Him.URN*. 81, №3, 52-54. (in Russ.)
- [7]. Pisanenko D.A., Klimko Yu.I., Gaidai A.V. Corrosion-Protecting properties of bis quaternized derivatives of some N-arylnicotinamides. (2016) *Intern. J. Mater. Chem. Phys.*, 2, (2), 45-49.
- [8]. Kurmakova J.M., Bondar O.S., Vorobyova V.J., Chygyrynets O.E. (2018) The inhibitory effect of imidazo[1,2-A]azepinium bromides on corrosion of carbon steel in hydrochloric medium. *Voprosy khim. i khim. tekhnologii.*, N1, 31-36.
- [9]. Pisanenko D.A., Klimko Yu. E., Lihmitskii K.V. (2011) Sintez i antikoroziionnie svoistva N-Arylnicotinamidov i ih proizvodnyh- 3-(N-Arilarboxamido)- N-benzylpiridiihloridov. *Zurn. prikl. himii*, 84, №8, 1384-1386. (in Russ.)
- [10]. Granovsky A.A. Firefly version 8. <http://classic.chem.msk.su//gran/firefly.index.html>.
- [11]. Schmidt M.W., Baldrige K.K., Boatz J.A. (1993). Computational methods for large systems. *J. Comput. Chem.*, 14, 1347-1363.
- [12]. Parr R.G., Donnelly R.A., Levy M., Palke W.E. (1978) Theoretical aspects of chemical reactivity. *J. Chem. Phys.*, 68, 3801-3807.
- [13]. Parr R.G., Pearson R.G. (1983). Absolute hardness: companion parameter to absolute. *J. Am. Chem. Soc.*, 105, 7512-7516.
- [14]. Ivanov E.S. *Inhibitori korrozii metallov v kislih sredah* (1986). Metallurgija, Moskva. (in Russ.)

