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Heterocyclic compounds as corrosion inhibitors for mild steel in hydrochloric acid medium — correlation between electronic structure and inhibition efficiency

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Abstract

Relationships between electronic parameters of aromatic corrosion inhibitors and inhibition efficiency have been investigated. Our earlier results obtained for corrosion inhibitors of mild-steel demonstrated that correlation exists between inhibition efficiency and the energy band gap (ΔE) between the energy of the highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}). It was found that efficiency (related to 0.001 M inhibitor concentration) is optimal at $\Delta E \cong 1.3$ beta. These investigations have been extended to include new classes of molecules, namely oxadiazole, thiadiazole, and triazole derivatives. The new results have modified the conclusions drawn from earlier investigations: efficiency depends, besides ΔE, on the conformation of the molecules, *viz.* planar (unsaturated) molecules are more efficient than partially saturated (and therefore twisted) derivatives.

Keywords: Structure-activity relationships; Quantum chemistry; Heterocyclic compounds; Inhibition corrosion

1. Introduction

The term "quantitative structure-activity relationships" (QSAR) was first used in pharmacology in 1964, when Hansch and his co-workers [1] discovered that variation of pharmacological efficiency of (closely related) drugs might be explained in terms of simple variables, the substituent constants. In pharmacology research on QSAR has produced thousands of papers, and there is even a scientific journal (besides others devoted to QSAR) bearing this abbreviation. The aim of these theoretical studies is to reduce the cost of research, since in many cases based on the results of an OSAR analysis, many prospective derivatives can be safely excluded from further screening, even without the necessity to synthesise and test them. In this paper the term QSAR will denote any relationship between quantitative measures of efficiency and indices related to the molecular structure. The relationship between efficiency and the structure of corrosion inhibitors became, soon after Hansch's discovery, the topics of electrochemical research [2]. Nevertheless the number of papers published so far on QSAR is much less in corrosion research than in pharmacology. A brief review may be found in ref. [3].

The results obtained for corrosion inhibitors of mild-steel by Lukovits et al. demonstrated that correlation exists between inhibition efficiency and the band gap (ΔE); the difference between the energy of the highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}) ($\Delta E = E_{\mathrm{HOMO}} - E_{\mathrm{LUMO}}$) [4]. It was found that efficiency (related to 0.001 M inhibitor concentration in acidic media) is optimal at $\Delta E \cong 1.3$ beta. The rule is valid in series of pyrimidines, amino-acids and benzothiazoles. The aim of this paper was to extend these investigations in order to test, whether it remains valid for other series of corrosion inhibitors, too. Derivatives of oxadiazole, thiadiazole, and triazole have been investigated. It has been found that the value of optimal ΔE was rather close to ΔE_{opt} determined earlier (ΔE_{opt} = 0.9 beta), but the interpretation of the correlation had to be changed. Inhibition efficiency depends, besides ΔE, on the conformation of the molecules; planar unsaturated molecules are more efficient than partially saturated (and therefore non-planar) derivatives.

2. Experimental

Materials—Results concerning 2,5-bis(4-dimethyl aminophenyl)–1,3,4-oxadiazole (DAPO), 2,5-bis(4-dimethylamino phenyl)–1,3,4–thiadiazole (DAPT), 2,5–bis(4-nitrophenyl)–1,3,4–oxadiazole (PNOX), and 2,5–bis(4-aminophenyl)–1,3,4–oxadiazole (PAOX) were published earlier [5,6]. Inhibitor efficiencies of 3,5–diphenyl–4H–1,2,4–triazole (DHT), 3,5–di(4-chloro phenyl)–4H–1,2,4–triazole (CHT), 3,5–di(4-pyridyl)–4H–1,2,4–triazole (PHT), and 3,5–di(4-methylthio phenyl)–4H–1,2,4–triazole (4-MTHT) were measured in this work.

The organic compounds (4H-triazoles (CHT, PHT, DHT, 4-MTHT), oxadiazoles (DAPO, PNOX, PAOX) and thiadiazole (DAPT) tested as corrosion inhibitors, were prepared in the laboratory according to a previously described procedures, respectively [7-9]. The molecular formulas of these inhibitors are shown in Figure 1. Mild steel strips composed of (wt%): 0.09% P, 0.38% Si, 0.01% Al, 0.05% Mn, 0.21% C, 0.05% S, and balance Fe were pre-treated prior to the experiments by grinding with emery paper SiC (grades 600 and 1200), then cleaned in ultrasonic bath with ethanol, rinsed with doubly distilled water and finally dried at room temperature. The agressive solutions (1 M HCl) were prepared by dilution of an analytical reagent grade 37% HCl with doubly distilled water. The concentration of organic compounds employed was 1×10^{-4} M.

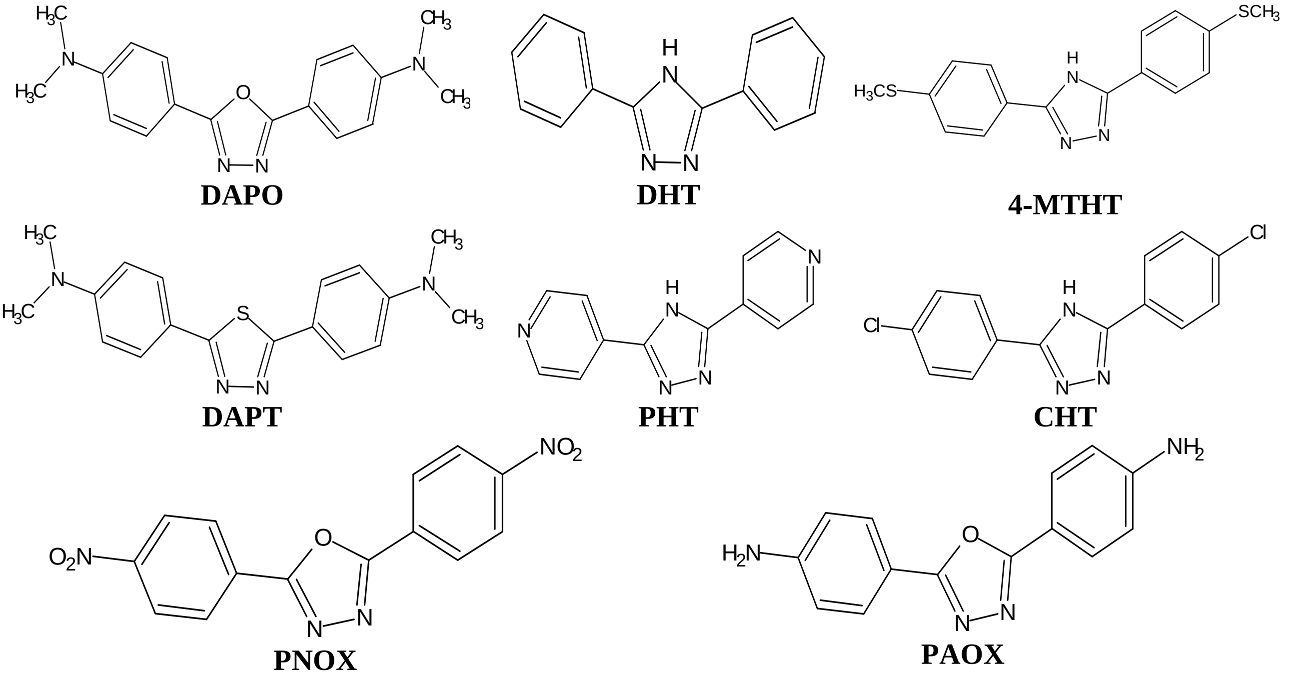

Fig. 1. Chemical structures of the investigated compounds.

Electrochemical Studies — Electrochemical impedance spectroscopy (EIS) — experiments were conducted using impedance equipment (Tacussel-Radiometer PGZ 3O1) and controlled with Tacussel corrosion analysis software model Voltamaster 4. EIS measurements were carried-out in a polymethyl methacrylate (PMMA) cell with a capacity of 1000 ml in the frequency range of 100 kHz to 10 mHz, with ten points per decade, at the rest potential, after 24 h of immersion, by applying 10 mV a.c. voltage peak-to-peak. All tests have been performed at 30 ± 1°C in non-de-aerated solutions under unstirred conditions. Square sheets of mild steel of size (5 cm by 5 cm by 0.06 cm), which exposed a 7.55 cm^2 surface to the agressive solution, were used as the working electrode. A platinum foil counter electrode (3 cm × 3 cm) was used for measurements. Nyquist plots were made from these experiments. The best semicircle can be fit through the data points in the Nyquist plot using a non-linear least square fit so as to give the intersections with the x-axis [10]. The charge-transfer resistance (R_{ct}) values were calculated from Nyquist plots as described elsewhere [11].

Computational Chemistry — Quantum chemical calculations were done by using the well-known Hückel method by using the parameter set proposed by Wahl [12]. All other quantum theoretical calculations were performed with SPARTAN PRO V. 1.05 software package for PC (Irvine Inc.) using semi-empirical AM1 method at RHF (Restricted Hartree Fock) level [13], starting without any geometry constraints for full geometry optimisations.

3. Results and discussion

The corrosion behaviour of mild steel in 1 M HCl solution in the absence and presence of heterocyclic derivatives was investigated by the electrochemical impedance spectroscopy (EIS) at 30 °C after 24 h of immersion. The inhibition efficiency $E(\%)$ is calculated by R_{ct} using Eq. 1, where R^{0}_{ct} and R_{ct} are the charge-transfer resistance values without and with inhibitor, respectively :

$$E(\%) = \frac{1/R^{0}_{ct} - 1/R_{ct}}{1/R^{0}_{ct}} \times 100 \qquad (1)$$

The R_{ct} and inhibition efficiency values are given in Table 1. From these experimental data it can be seen, that with the exception of PNOX and CHT, all derivatives are highly efficient, in fact efficiency could not be improved much by increasing the concentrations to 10^{-3} M. PNOX slightly increased the corrosion rate, while CHT was (nearly) inefficient.

All members of the subset of pyrimidines consisting of 2–mercapto-3,4–dihydro-pyrimidine, 2–mercapto-3,4–dihydro-6-methylpyrimidine, 3,4-dihydropyrimidine, 2–mercapto–4–amino-1,6-dihydro-pyrimidine, 2,5,6–triamino-3,4-dihydropyrimidine, and 2–mercapto-4-amino–5–nitro-1,6–dihydropyrimidine are nearly inefective or even slight corrosion activators [4]. All other pyrimidines (and also the benzothiazole derivatives and amino-acids) with values of ΔE > 1.3 may be efficient, but efficiency decreases with increasing values of ΔE.

Table 1. Resistance charge transfer (R_{ct}), inhibition efficiencies values (related to 10^{-4} M concentration) and the calculated quantum chemical (AM1) indices of different organic compounds studied.

Inhibitor	R_{ct} (Ω cm^2)	E (%)	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	ΔE (Hückel) (beta units)
Blank	20.0	—	—	—	—	—
DAPO	196.1	89.8	-7.15	2.84	-9.99	0.758
DAPT	327.9	93.9	-7.05	2.41	-9.46	0.796
PNOX	21.6	7.4	-10.06	-2.275	-7.785	0.344
PAOX	952.3	97.9	-8.19	-0.67	-7.52	0.975
DHT	266.7	92.5	-8.773	-0.593	-9.366	1.049
CHT	22.4	10.6	-9.22	1.66	-10.88	1.045
PHT	416.7	95.2	-7.92	2.41	-10.33	1.027
4-MTHT	2222.2	99.1	-7.74	2.31	-10.05	0.979

The calculated quantum chemical indices, E_{HOMO}, E_{LUMO}, and ΔE of different heterocyclic compounds are calculated and shown in Table 1. The correlation between values of ΔE and $E(\%)$ is shown in Fig. 2.

When data related to PNOX, PAOX, DAPO, and DAPT were added to the set of pyrimidines, amino-acids and benzothiazoles, the value of the optimal ΔE was unaffected ($\Delta E_{opt} \cong 1.3$ beta and 1 beta $\cong -134$ kJ/mole). On the left hand side of Fig. 2 there are *two* curves, instead the case with the original compounds, where only a single curve can be observed. This discrepancy is due to the fact that pyrimidines with values of beta less than 1.0 are partially saturated [4], and therefore can not be planar. Non-planar molecules can not cover the surface as efficiently as planar derivatives. This is the reason why partially saturated pyrimidine derivatives are less efficient than oxadiazole and thiadiazole derivatives.

The result is supported by inspection of the triazole derivatives. DHT, PHT and 4-MTHT fit into the line obtained by using the oxadiazole/thiadiazole derivatives. The only exception is CHT (the chlorophenyl triazole derivative), which contrary to our expectations, did not have significant efficiency and is similar to partially saturated pyrimidine derivatives [4]. The reason for this phenomenon is not yet clear, however it may be that CHT is also non-planar. This point has to be still investigated in detail although the values of ΔE obtained by using AM1 and the Hückel approaches indicate that CHT should be efficient.

A possible explanation of the ”$\Delta E \cong 0.9$ beta rule” is that if molecules can be excited easily (i.e. those with a low value of ΔE), then they will interact with other molecules and therefore are not able to inhibit the corrosion process. With increasing values of ΔE the binding to the metal surface might become more and more difficult.

4. Conclusion

The observed rule, namely that efficiency of aromatic corrosion inhibitors (in acidic media) is optimal if $\Delta E \approx 0.9$ (beta) is independent of the structure of the aromatic compounds, seems to be general. This rule simplifies the design of new corrosion inhibitors, since all derivatives possessing a non-optimal value of ΔE, are most probably inefficient. Note that the reverse rule, namely if $\Delta E \approx 0.9$ is fulfilled, then the derivative must be efficient, is not true, since obviously there are other (yet unknown) parameters which also may account for inhibition efficiency.

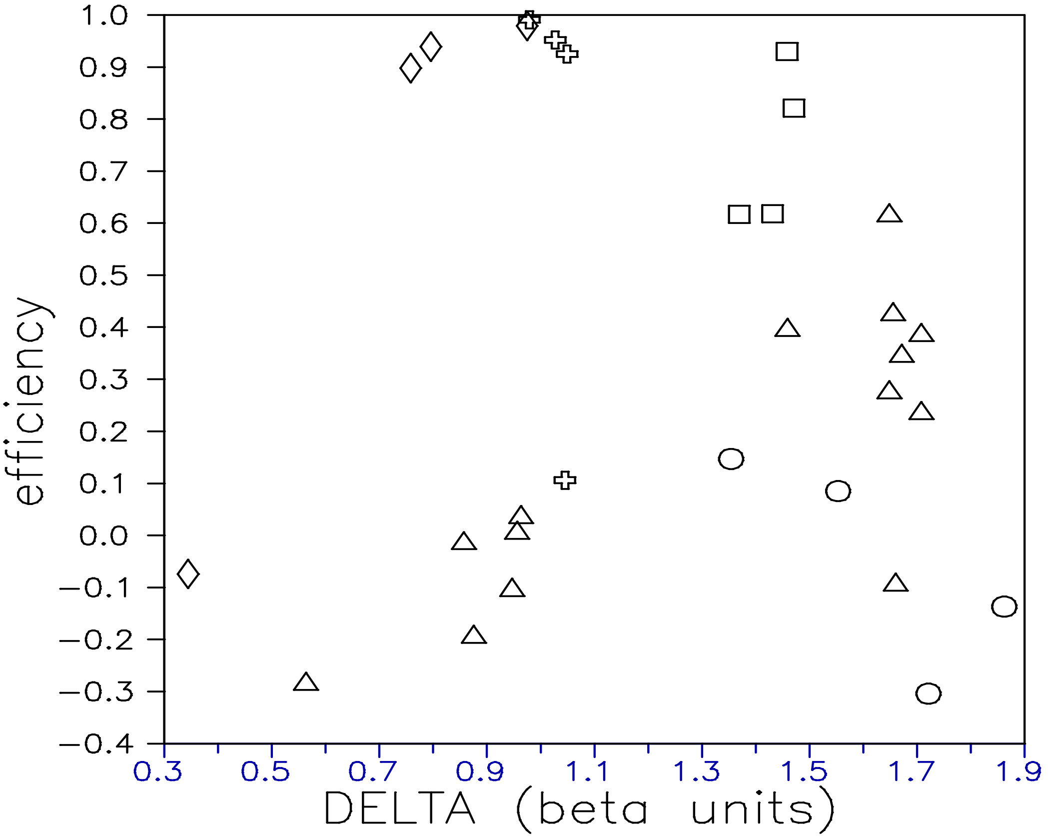

Fig. 2. Correlation between electronic excitation energies ΔE (in beta units) and corrosion inhibition efficiencies on carbon steel of various classes of compounds: pyrimidines (Δ), amino acids (○), benzothiazoles ( ) in 0.001 M concentration and DAPO, DAPT, PNOX and PAOX (◊), and triazoles (╬) in 0.0001M concentration.

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