Calculation of Quantum Chemical Values of Corrosion Inhibitors Molecules by Heterocyclic Compounds

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Abstract. Theoretical concepts of inhibition mechanism in metal corrosion and forecasting of protective properties of substances are connected with experimental (electrochemical, adsorption, mechano-chemical) research. Inhibition mechanism may be fully demonstrated by comparing experimental research data with results of calculating quantum-chemical values of the proposed corrosion inhibitors molecules. The latter therewith enable to detect those physico-chemical characteristics that directly demonstrate protective properties of the inhibitor. Molecular moment, number of atoms in molecule and number of electrons in outer molecular orbitals are found to have maximum affect on the protection level. Application of petrochemical products including semi-finished products and petrochemical wastes for making new highly efficient and relatively inexpensive corrosion inhibitors is shown to be promising. Calculation results of quantum chemical values of corrosion inhibitors molecules by heterocyclic compounds may be used in learning corrosion inhibition mechanism by the compounds studied.

1. Introduction

Nowadays there are several ways in metal corrosion prevention. The most efficient and economical means of protection are corrosion inhibitors [1, 2, 3].

Protection of metals against corrosion by inhibitors is based on properties of certain chemical compounds or compositions being added to corrosion medium in small quantities either to reduce rate of attack or absolutely inhibit the corrosion process [4]. Corrosion inhibitors are used in numerous facilities both in water supply systems and actually any energy installations, and protection of microelectronics and the newest military hardware. Inhibitors are changing the surface to be protected by absorption or formation of poorly-soluble compounds together with metal cations [5].

Ufa State Petroleum Technological University together with Research Institute of fine chemicals and agents (NIIRReaktive) headed by D.L. Rakhmankulov for more than 25 years has been engaged in research of ways for getting, analyzing reactivity and practical application of 1,3-diheterocycloalkanes, in particular 1,3-dioxanes, 1,3-tetrahydrooxazines, etc. Monographs and a great number of reviews, over 1000 scientific papers both in Russian journals and abroad have been published and over 1000 author’s certificates and patents have been obtained under results thereof. One of the ways for practical application of such compounds is using thereof as metal corrosion inhibitors [3, 6, 7, 8, 9].
2. Materials and methods
Some data to be obtained by corrosion and electrochemical and adsorption analyses are required for evaluation of corrosion inhibitors action [10-13]. Further researching has been made by using separate compounds being main components of complex inhibiting compositions proposed by us, or the ones that modeling properties thereof [3].

The research has been done with samples made from St 3 construction steel, 20 quality carbon steel and 17G1S construction low-alloy steel. NACE (US National Association of Corrosion Engineers) blank medium saturated with hydrogen sulfide has been used as the working solution [11, 13]. Generally accepted corrosion testing procedure was used [1, 13]. Adsorption of organic inhibiting compositions has been studied by method for measuring double-electric layer capacity appearing in “metal-electrolyte” interface (measurements were made using AC bridge) [7, 15].

Polarization measurements have been made on stationary electrode in potentiostatic mode using potentiostat. Specially made electrochemical cell has been used for making electrochemical measurements [1, 3, 7].

3. Research
Analysis of inhibition mechanism of various compounds and making of new inhibitors thereunder enables us to expand inhibiting compositions range and to find the most efficient and technologically advanced ones among them [6]. Application of petrochemicals, including intermediate products and petrochemical wastes is promising for making new highly efficient and quite cheap corrosion inhibitors nowadays [3, 7].

4. Theoretical
Principal opportunity for applying organic compounds as highly efficient inhibitors against mechanismal steel corrosion [16] has been demonstrated by us earlier [3, 6, 13]. Inhibition mechanism may be fully demonstrated by comparing results of electrochemical, adsorption, corrosion and mechanical and quantum-chemical researching [17, 18]. The latter ones therewith enable to detect those physico-chemical characteristics that directly demonstrate protective properties of the inhibitor (called by Prof. D.L. Rakhmankulov as protective ability indices - PAI [8]). Values of atomic charges, molecule ionization potentials, energies of the lowest unoccupied molecular orbitals, dipole moments of molecules, number of atoms and number of valence shell electrons and total charges in substituents have been used as assumed PAIs. Acetal PAIs and analogs thereof have been calculated by modified neglecting of diatomic overlap method [19], while major PAIs have been found by group method of data handling (GMDH) [20] based on self-organizing math model theory. Program for multirow selection of arguments with supporting function as polynom has been used for calculations [21, 22]. Standard criteria for regularity and unbiasedness as well as mixed criteria have been applied. The models have been constructed by ten points. The remaining four points have been used for calculating external criterion value. The results of calculations are given in Table 1.

5. Practical research results
The best result was achieved when using regularity criterion. Average error in checking sequence was 6% and remained invariant with respect to breaking the data table into training and checking sequence.

Functional dependence of protection level of compounds analyzed on PAI is as follows:

\[ Z = 24.01 + 0.67 X_{10}^2 + 0.15 \cdot 10^{-4} X_{10}^2 X_{15}^2 ; \]
\[ X_{10}^2 = 109.90 - 0.64 X_6^1 + 0.36 \cdot 10^{-2} X_6^1 X_{10}^1 ; \]
\[ X_{15}^2 = 82.70 - 0.10 \cdot 10^{-3} X_6 X_{14}^1 ; \]
\[ X_6^1 = 349.15 - 4.18 X_4 + 0.43 X_6 ; \]
\[ X^1_{10} = -36.21 + 9.68 X_5 - 92.63 X_7 - 1.82 X_5 X_7; \]
\[ X^1_{14} = -11 \cdot 743.30 - 14.78 X_6^0 + 13974 X_9^0 - 58.62 X_6^0 X_9^0, \]
where, superscripts of variables mean number of selection row, while subscripts mean number of a variable.

Substituting successively expressions for variables in (1) and neglecting second-order terms, we get resultant expression:

\[ Z = 33.03 + 0.17 X_6 - 0.02 X_4 X_6 + 13.40 X_5 - 129.30 X_7 - 2.50 X_5 X_7; \]  

Its analysis enable to conclude that dipole molecular moment, amount of atoms in a molecule and amount of electron in outer molecular orbitals make maximum effect upon the protection level. Therefore, it is these values that may be accepted as PAI of the analyzed substances.

**Table 1.** Quantum chemical values of acetal molecules and analogs thereof.

|                        | 1  | 2  | 3  | 4  | 5  | 6  | 7  | 8  | 9  | 10 |
|------------------------|----|----|----|----|----|----|----|----|----|----|
| Oxygen atomic charge (X_1) | -0.3612 | -0.3612 | -0.3612 | -0.3612 | -0.3612 | -0.3612 | -0.3612 | -0.3612 | -0.3612 | -0.3612 |
| Ionization potential, eV (X_2) | 10.8463 | 10.8469 | 10.8473 | 10.8477 | 9.1318 | 9.0624 | 9.5298 | 10.9400 | 10.8900 | 10.8458 |
| Energy of the lowest unoccupied molec. orbitals, eV (X_3) | 2.6582 | 2.6559 | 2.6546 | 2.6539 | 0.1677 | 0.1716 | 0.2028 | 0.7400 | 2.3500 | 2.6610 |
| Amount of atoms (X_4) | 33  | 39  | 42  | 45  | 25  | 28  | 23  | 56  | 30  |
| Amount of electrons (X_5) | 78  | 90  | 96  | 102 | 70  | 76  | 76  | 64  | 112 | 72  |
| Dipole moment, D (X_6) | 1.5634 | 1.5540 | 1.5490 | 1.5371 | 1.0202 | 1.0400 | 1.3573 | 1.4262 | 1.3857 | 1.5683 |
| Max charge (X_7) | 0.1852 | 0.1853 | 0.1853 | 0.1853 | 0.1488 | 0.1510 | 0.2373 | 0.3595 | 0.1860 | 0.1852 |
| Protection level, % experimental | 63.7  | 84.5  | 91.7  | 97.2  | 82.7  | 85.1  | 86.2  | 59.5  | 92.1  | 46.4  |
| Protection level, % calculated | 61.66 | 81.35 | 88.40 | 93.66 | 81.03 | 89.69 | 85.24 | 54.53 | 97.33 | 49.00 |

6. Results
Petrochemical heteroorganic compounds are found to be efficient metal corrosion inhibitors with acetals and analogs thereof taken as an example. Calculation results of quantum chemical values of the analyzed compounds may be used to know corrosion inhibition mechanism.

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