Asian Journal of Chemistry; Vol. 25, No. 4 (2013), 1871-1874

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13197

Corrosion Inhibition Mechanism of Benzimidazole and Its Derivatives on Mild Steel: Quantitative Structure and Property Relationship Study

GUANGZENG LIU[1,2,3,4*], WENCAI ZHU[2] and HONGFAN MA[3]

[1]State Key Laboratory of Crystal Material, Shandong University, Jinan 250100, P.R. China
[2]Department of Chemistry, Advance Material Institute of Research, Qilu Normal University, Jinan 250013, P.R. China
[3]Department of Materials, Shandong Jianzhu University, Jinan 250101, P.R. China
[4]Key Laboratory of Colloid and Interface Chemistry, Education Ministry, Shandong University, Jinan 250100, P.R. China

*Corresponding author: Fax: +86 531 66778065; Tel: +86 531 66778065; E-mail: gzliusd@gmail.com

(*Received*: 8 December 2011; *Accepted*: 5 October 2012) AJC-12239

A theoretical method named as quantitative structure and property relationship (QSPR) was used to investigate corrosion inhibition efficiency of benzimidazole and its derivatives on mild steel in 1 M hydrochloric acid. Some electronic, spatial and thermodynamic properties were selected as descriptors to build relationships between inhibition efficiency and micro-structure information. These descriptors include frontier molecular orbits (LUMO and HOMO), molecular surface area and molecular volume, molecular flexibility, *etc*. The relationships between descriptors and inhibition efficiency were described by several equations, respectively. Furthermore, an overall equation was built up to describe accurately the relationship between inhibition efficiency and most of the descriptors. These equations were proven to be successful in explaining the corrosion inhibition mechanism of benzimidazole and its derivatives.

Key Words: Benzimidazole, Inhibition mechanism, Inhibition efficiency, Quantitative structure and property relationship.

INTRODUCTION

Corrosion is a real challenge to many chemical industries, as well as a difficult problem to study scientifically[1]. Corrosion can happen in circulating water systems, oil wells, building materials, reaction vessels, pipelines and many other areas where materials such as fuels, lubricants, detergents and metal working fluids are used[2,3]. Corrosion inhibitors have been designed to work in several ways, such as blocking either the cathodic or anodic sites, or scavenging activating ions. These inhibitors must be transported to material surface and adsorbed successfully onto the surface before the inhibition acts effectively. This process involves physisorption and chemisorption. Usually, inhibitors must build up thick layers of coating so that corrosion and oxidation can be prevented. The processes involved are too complicated to model with traditional DFT theory, though DFT methods have been widely used in many areas[4-7].

Quantitative structure and property relationship has been already applied in corrosion research[4,5]. The best way of using molecular modeling to help the design of new and better corrosion inhibitors is to encapsulate knowledge about how existing inhibitors perform into a structure-property relation and use this to predict the behaviour of new structures. Then the structures with the best predicted property can be investigated in the laboratory.

Popova *et al.*[8] investigated the corrosion inhibition of eight diazoles on mild steel in 1 M hydrochloric acid using gravimetric and polarization techniques. They got a good experiment result that inhibition efficiency vary with change of substituents and IE follows as: 5(6)-NO_2-BIM < BIM < 2-CH_3-BI < 5(6)-COOH-BIM < 2-CH_2OH-BIM < 2-NH_2-BIM < 2-CH_2CN-BIM < 2-SH-BIM, but no simple correlations were found between the electronic parameters (induction and mesomeric effects of the substituents, ionization potential values) of diazole molecules and their inhibiting properties, neither between molecular area and inhibiting properties.

The present paper focuses on how to build appropriate relationships between macro properties (such as inhibition efficiency, IE) and micro-structure information of these eight diazole inhibitors reported by Popova *et al.*[6]. To build a good relationship between inhibition efficiency and diazole inhibitors, based on comparing several simple equation, an overall multi-parameter equation was obtained by quantitative structure and property relationship, parameters in this equations were selected from adequate descriptors about micro-structure information (electronic, spatial and thermodynamic properties).

EXPERIMENTAL

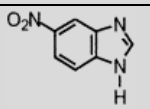
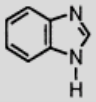
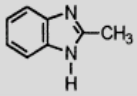
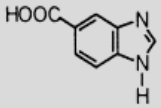
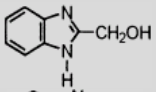
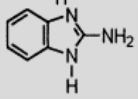
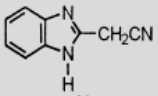
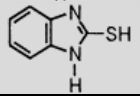
The theoretical foundation of quantitative structure and property relationship is based on the principle of polylinearity.

According to the theory, a continuous and singular dependence between a property P, which is experimentally measurable and some intrinsic structural factors of molecule x_i, is assumed to be linear in a certain domain of this factor a_i. Under this assumption, the experimental property P may depend only on one structure factor x_i, so, a regression equation can be found.

$$P = a_0 + \sum_{i=1}^{m} a_i x_i$$

Benzimidazole and its derivatives are selected to carry out the QSPR calculation by using Cerius2 workstation or materials studio (Accelrys Inc., San Diego, CA)[7] and their structures are shown in Table-1.

TABLE-1
STRUCTURAL AND INHIBITION EFFICIENCY OF BENZIMIDAZOLE AND ITS DERIVATIVES

No.	Compound	Structural formulate	Abbreviation	IE (%)[6]
1	5(6)-Nitrobenzimidazole		5(6)-NO_2-BIM	26.0
2	Benzimidazole		BIM	29.5
3	2-Methylbenzimidazole		2-CH_3-BIM	39.0
4	5(6)-Carboxybenzimidazole		5(6)-COOH-BIM	59.0
5	2-Hydroxymethyl benzimidazole		2-CH_2OH-BIM	72.0
6	2-Aminobenzimidazole		2-NH_2-BIM	88.0
7	2-Benzimidazolylacetonitrile		2-CH_2CN-BIM	90.5
8	2-Mercaptobenzimidazole		2-SH-BIM	98.0

Molecular structures of eight inhibitors of benzimidazole and its derivatives are optimized by forcite module and the values of descriptors are acquired by using VAMP module. Forcite module is a collection of molecular mechanics tools that can investigate a wide range of systems. The key approximation is that the potential energy surface is represented by a classical forcefield, which are developed by parameterize data from experiment and high level quantum mechanical calculations. VAMP module is a semiempirical molecular orbital package capable of predicting geometries, heats of formation and a host of molecular properties. The forcefield used in this paper is COMPASS (condensed-phase optimized molecular potentials for atomistic simulation studies)[8], which is the first *ab initio* forcefield that enables accurate and simultaneous prediction of gas-phase properties (structural, conformational, vibrational, *etc*.) and condensed-phase properties (equation of state, cohesive energies, *etc*.) for a broad range of molecules and polymers.

The statistical technique used in our QSPR analysis is genetic function approximation (GFA) approach[9], which takes inspiration from natural genetics and evolution.

RESULTS AND DISCUSSION

Some important descriptors, which are possibly correlative with inhibition efficiency, include frontier molecular orbits (LUMO and HOMO), nitrogen atomic charges and ring's charge, molecular surface area and molecular volume, molecular refractivity, molecular flexibility and so on. Table-2 demonstrates the values of these descriptors, which are used to fit and educe the following equations.

HOMO and LUMO eigen values: The following is a simple two-parameter equation including only HOMO and LUMO eigenvalues:

$$Y_1 = 21.10 \times X_1 + 5.10 \times X_2 + 256.72, \; R^2 = 0.192 \quad (1)$$

where, X_1 and X_2 denote HOMO and LUMO eigen value, respectively, R^2 represents the square value of the correlative coefficient. Predicted values about inhibition efficiency were calculated according to this equation and listed in Table-3 as predicted values 1. By comparing the predicted values with the actual values of inhibition efficiency, it is obvious that the predicted values given by equation (1) have bad accuracy, since only one residual value is less than 5 %.

HOMO and LUMO represent highest occupied molecular orbital and lowest unoccupied molecular orbital respectively, the former is associated with the electron donating ability of the molecules and the latter indicate the ability of the molecules to accept electrons. The higher the HOMO eigenvalue, the higher the inhibition efficiency. Fang and Li[10] found that there are satisfactory correlations between the quantum chemical parameters and the inhibition efficiency of imidazoline derivatives or amides, respectively. Shokry *et al.*[11] got an equation about inhibition efficiency *via* HOMO energy and LUMO energy, found that high value of HOMO energy and lower value of LUMO would improve efficiency. However, Khalil didn't found HOMO and LUMO energy correlate well with inhibition efficiency of the tested thiosemicarbazide and its derivatives[12].

Nitrogen atomic charges and ring's total charges: Total charges of six-atom ring and five-atom ring also have great effect on inhibition efficiency of benzimidazole and its derivatives. The relationship between inhibition efficiency and total charges of atoms in the ring is described as the following equation:

$$Y_2 = -123.26 \times X_3 + 123.30 \times X_4 + 50.02, \; R^2 = 0.337 \quad (2)$$

where, X_3 and X_4 denote total charges of six-atom ring and five-atom ring, respectively. Predicted values given by equation (2) were listed in Table-3 as predicted values 2. The eqn. (2) indicated that the total charges of six-atom ring and five-atom ring had different effects on inhibition efficiency. Increase of the total charges of six-atom ring would decrease inhibition efficiency, for five-atom ring the situation is opposite.

The effect of charges of two nitrogen atoms in five-atom ring on inhibition efficiency was studied by eqn. (3) as the following:

TABLE-2
VALUES OF DESCRIPTORS CALCULATED BY QSPR

Structures	Inhibition efficiency[8]	AlogP	Molecular refractivity	Molecular flexibility	Total molecular mass	Atom count	Element count	HOMO	LUMO
5(6)-NO_2-BIM	26.0	1.2433	43.3501	1.2981	163.136	17	7	-9.9117	-1.9160
BIM	29.5	1.2897	36.0254	0.8026	118.139	15	7	-8.9792	0.1345
2-CH_3-BIM	39.0	2.0357	38.1169	1.0051	132.166	18	8	-8.8961	0.1346
5(6)-COOH-BIM	59.0	0.9881	42.7838	1.4121	162.148	18	8	-9.5906	-0.4722
2-CH_2OH-BIM	72.0	1.4801	39.8191	1.3650	148.165	19	8	-8.8857	0.1044
2-NH_2-BIM	88.0	1.0096	40.6398	0.9168	133.154	17	7	-8.5262	0.3338
2-CH_2CN-BIM	90.5	2.2326	43.4403	1.5247	157.176	19	9	-9.1201	-0.1391
2-SH-BIM	98.0	1.7492	44.0473	1.1081	150.199	16	7	-9.1170	-0.2738

Structures	Molecular area (vdW area)	Molecular volume (vdW volume)	Total dipole	Mean polarizability	N(H) : Mülliken charge	N(ring) : Mülliken charge	Ring (6)	Ring (5)	HOMO-LUMO
5(6)-NO_2-BIM	164.2838	131.3672	8.649	16.3344	-0.3822	-0.1710	-0.5089	-0.6617	-7.9957
BIM	136.3086	107.5056	3.091	14.0764	-0.3884	-0.1916	-0.7765	-0.7141	-9.1137
2-CH_3-BIM	157.9927	124.1978	3.129	15.9956	-0.3760	-0.1882	-0.7714	-0.5888	-9.0307
5(6)-COOH-BIM	166.4388	134.0946	7.629	16.6132	-0.3844	-0.1778	-0.6910	-0.6853	-9.1184
2-CH_2OH-BIM	166.9200	132.5315	2.370	16.5738	-0.3567	-0.1912	-0.7651	-0.5737	-8.9901
2-NH_2-BIM	151.2504	118.3593	3.300	15.4143	-0.3973	-0.2506	-0.7594	-0.4804	-8.8600
2-CH_2CN-BIM	176.2351	141.3032	0.555	17.8315	-0.3684	-0.1777	-0.7567	-0.5768	-8.9810
2-SH-BIM	158.9427	125.4962	3.095	17.1711	-0.3497	-0.1349	-0.7651	-0.6855	-8.8432

(Ring (5) and Ring (6) represent the five-atom ring and the six-atom ring, respectively. N(H) and N(ring) is -NH- and –N= in the five-atom ring, respectively)

TABLE-3
ALL DATA ABOUT ACTUAL VALUES, PREDICTED VALUES AND RESIDUAL VALUES FOR IE (%)

Actual values for IE[8]	Predicted values 1	Residual values 1	Predicted values 2	Residual values 2	Predicted values 3	Residual values3
26.0	37.784387	-11.784387	31.160917	-5.160917	43.652245	-17.652245
29.5	67.916569	-38.416569	57.683370	-28.183370	45.536888	-16.036888
39.0	69.671529	-30.671529	72.503950	-33.503950	63.387993	-24.387993
59.0	51.920477	7.079523	50.695971	8.304029	44.029470	14.970530
72.0	69.737115	2.262885	73.589231	-1.589231	95.915097	-23.915097
88.0	78.493405	9.506595	84.390336	3.609664	65.074728	22.925272
90.5	63.548761	26.951239	72.171660	18.32834	69.515236	20.984764
98.0	62.927756	35.072244	59.804564	38.195436	74.888343	23.111657
Actual values of IE[8]	Predicted values 4	Residual values 4	Predicted values 5	Residual values 5	Predicted values 6	Residual values 6
26.0	74.898203	-48.898203	58.892619	-32.892600	26.038000	-0.038000
29.5	38.725718	-9.225718	28.689012	0.810988	29.967000	-0.467000
39.0	47.964354	-8.964354	75.082538	-36.082500	39.000000	0.000000
59.0	69.378538	-10.378538	49.885618	9.114382	58.546000	0.454000
72.0	51.992549	20.007451	75.557410	-3.557410	71.143000	0.857000
88.0	65.054483	22.945517	68.920253	19.079750	87.920000	0.080000
90.5	71.401346	19.098654	75.083875	15.416130	91.648000	-1.148000
98.0	82.584809	15.415191	69.888675	28.111330	97.738000	0.262000

$Y_3 = 1596.44 \times X_5 - 571.97 \times X_6 + 556.01$ $R^2 = 0.400$ (3)

where, X_5 and X_6 denote the Mülliken charges of N(H) and N(ring), respectively. Predicted values were listed in Table-3 as predicted values 3. The coefficient of X_5 was three times bigger than that of X_6, X_5 had a positive effect on the inhibition efficiency, but X_6 had a negative effect.

Only two of absolute values of the residual values given by eqn. (2) were less than 5 % and no absolute value of the residual values given by eqn. (3) was less than 5 %, so, neither eqn. (2) nor eqn. (3) has good accuracy.

It is concluded from the eqns. (2) and (3) that nitrogen atomic charges and ring's charges have an important effect on inhibition efficiency, which is according to Shokry *et al.*[11] *i.e.*, good inhibitors not only could be synthesized conveniently, but also contain electron cloud on the aromatic ring or the electronegative atoms such as nitrogen and oxygen.

Molecular refractivity and flexibility: The effect of molecular refractivity and flexibility on inhibition efficiency was described by the following equation:

$Y_4 = 6.15 \times X_7 - 17.89 \times X_8 - 168.42$ $R^2 = 0.273$ (4)

where, X_7 and X_8 denote molecular refractivity and molecular flexibility, respectively. Predicted values were listed in Table-3 as predicted values 4. The coefficient of X_8 was three times more than that of X_7, X_8 had a positive effect on inhibition efficiency, while had a negative effect. Only two of absolute values of the residual values given by eqn. (4) were less than 10 % and no one was less 5 %.

Molecular area and volume: The effect of molecular area and volume was described by the following equation:

$Y_5 = 11.95 \times X_9 - 12.74 \times X_{10} - 230.123$, $R^2 = 0.329$ (5)

where, X_9 and X_{10} denote molecular area (vdW area) and molecular volume (vdW volume), respectively. The molecular

surface area and volume determines the extent to which a molecule exposes itself to the external environment. These two descriptors are related to binding, transportation and solubility. Increasing molecular area can help to get greater inhibition efficiency. Only three of absolute values of residual values given by eqn. (5) were less than 10 % and two were less than 5 %.

A certain tendency of IE increase with molecular area increase can be followed according to eqn. (5), but the effects of molecular area and volume are slightly pronounced[6,13].

Total impact and a multi-parameter equation: It was necessary to make an overall multi-parameter equation, because these simple equations without good accuracy can only explain how single or a few descriptors affect simply the inhibition efficiency. The multi-parameter equation with six-variables was shown as the following:

$$Y = 10.80 \times X_1 + 43.03 \times X_2 + 103.84 + X_3 - 4.73 \times X_4 - 225.43 \times X_5 - 240.54 \times X_6 + 324.28, R^2 = 0.999 \quad (6)$$

where, X_1, X_2, X_3, X_4, X_5 and X_6 denote molecular refractivity, molecular flexibility, HOMO eigenvalue, LUMO eigen value, Mülliken charge of N(ring) and ring(5) charge, respectively. Predicted values were listed in Table-3 as predicted values 6. R^2, the square value of the correlative coefficient of equ. (6), was as high as 0.999. The absolute values of all the residual values were less than 2 %, obviously this overall equation has a very high accuracy. Using the data from the first and last two columns in Table-3, Figs. 1 and 2 were drawn to investigate how good the accuracy is. It is clear that the difference between actual values and predicted values given by eqn. (6) is quite small, their curves are perfectly overlapped.

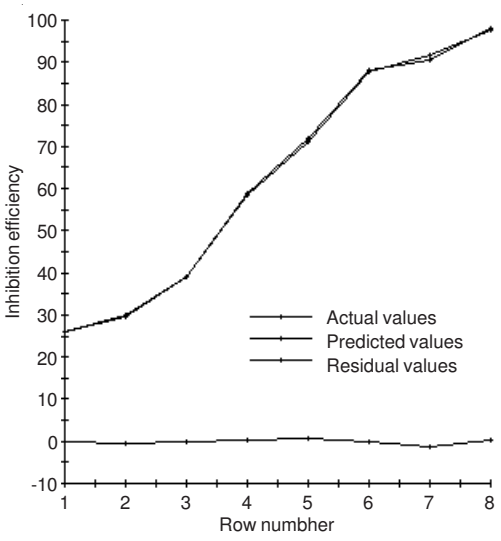


Fig. 1. GFA plot of actual values, predicted values and residual values

Both molecular refractivity and molecular flexibility have opposite effects on inhibition efficiency. The values of N(ring) and ring (5) had similar effects. The HOMO eigen value and LUMO eigen value also have opposite effects and the effect of the former was much higher than that of the latter.

Conclusion

Quantitative structure and property relationship was used to investigate corrosion inhibition mechanism of benzimidazole and its derivatives on mild steel in 1 M hydrochloric acid. Some electronic, spatial and thermodynamic properties were selected as descriptors to build a relationship between the macro-property (such as IE) and the micro-structure. Several simple equations and a multi-parameter equation were obtained, the former could explain how single or a few descriptors affect simply the inhibition efficiency and the latter have good accuracy and could explain how all of the descriptors affect inhibition efficiency.

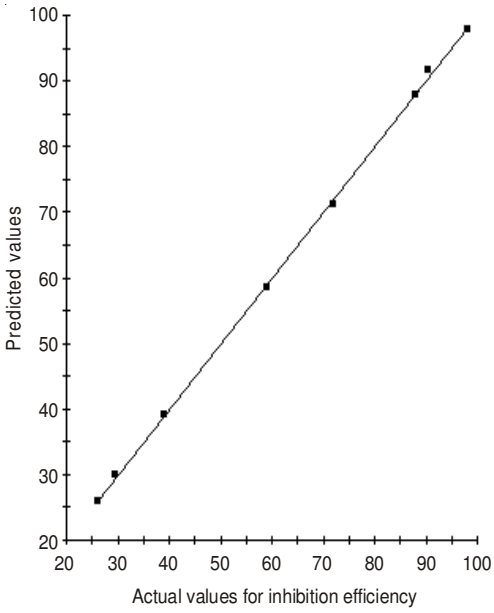


Fig. 2. Disperse pot of actual values and predicted values

ACKNOWLEDGEMENTS

This work is supported by the Outstanding Middle-Aged Scientists Foundation of Shandong Province of China (No. 2008BS04031).

REFERENCES

1. Y. Bao, C.X. Zhang, W.B. Yang, J.T. Hu and X.M. Sun, *Sci. Total Environ.*, **419**, 144 (2012).
2. W.N. Yu, J.T. Hu, F. Xu, X.Y. Sun, R. Gao, Q.Z. Zhang and W.X. Wang, *Environ. Sci. Technol.*, **45**, 1917 (2011).
3. F. Xu, W.N. Yu, Q. Zhou, R. Gao, X.Y. Sun, Q.Z. Zhang and W.X. Wang, *Environ. Sci. Technol.*, **45**, 643 (2011).
4. C.X. Zhang, T.L. Sun and X.M. Sun, *Environ. Sci. Technol.*, **45**, 4756 (2011).
5. K.F. Khaled, K. Babic-Samardzija and N. Hackerman, *Electrochim. Acta,* **50**, 2515 (2005).
6. A. Popova, M. Christov, S. Raicheva and E. Sokolova, *Corros. Sci*., **46**, 1333 (2004).
7. CERIUS2, version 4.6; Molecular Simulations Inc.: San Diego, CA, (2002).
8. H. Sun, *J. Phys. Chem. B,* **102**, 7338 (1998).
9. D. Rogers and A.J. Hopfinger, *J. Chem. Inf. Comput. Sci*., **34**, 854 (1994).
10. J. Fang and J. Li, *J. Mol. Struct. (Theochem.)*, **593**, 179 (2002).
11. H. Shokry, M. Yuasa, I. Sekine, R.M. Isaa, H.Y. El-Baradie and G.K. Gomma, *Corros. Sci.*, **40**, 2173 (1998).
12. N. Khalil, *Electrochim. Acta,* **48**, 2635 (2003).
13. A. Popova, M. Christov and T. Deligeorgiev, *Corrosion*, **59**, 756 (2003).