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Quantum Chemical Calculations of Some Amines Corrosion Inhibitors/ Copper Alloy Interaction in Hydrochloric Acid

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Abstract

The corrosion inhibition of copper alloy was studied experimentally in our previous work. The effect of phenylenediamine (PDA), Tetraethylenepentamine (TEPA), Diethylenetriamine (DETA) and Ethylenediamine (EDA) were used and evaluated. Quantum chemical and theoretical calculations were carried out in present study. Several quantum parameters are obtained via two computer software. Maximum energy band gab was 6.263 eV for PDA, while minimum one was 3.057 eV in the case of EDA, which support the experimental results of inhibitors efficiency. A comparative study was done. Theoretical calculations are a powerful way for estimation inhibitors efficiencies. A good correlation was seen between experimental inhibitor efficiency and theoretical one with high correlation coefficients.

1. Introduction

Organic materials have been used widely as corrosion inhibitors [1 – 3], which some of them adsorbed on the metal surfaces; reduce the cathodic reaction as well as the anodic process of dissolution of the metal [4]. Quantum chemical methods have already confirmed to be valuable in discovery the molecular structure as well as reactivity [5]. Therefore, it has become a common practice to perform quantum chemical calculations in corrosion inhibition researches. The concept of measuring the performance of a corrosion inhibitor with the assistance of computational chemistry is to look for compounds with desired properties using chemical insight and knowledge into a mathematically quantified and computerized form [6]. Once a relationship between the structureand action or property is evaluated, any number of compounds,including those not yet manufactured, can be readily screenedemploying computational procedure [7] and a set of the mathematicalequations which are capable of representing precisely thechemical phenomenon under research [8, 9].

The research of corrosion manners and their control by organic inhibitors is a very significant field of research [10]. Several researchers state that the inhibition effect mainly depends on some physical, chemical and electronic properties of the organic anticorrosion component, which relate to its steric effects, functional groups, electronic density, and orbital character of donating electrons, etc [11, 12]. The protection mechanism is generally clarified by the creation of a physically and/or chemically adsorbed layer on the metal surface [13, 14]. It is well known that organic compounds which work as inhibitors are rich in heteroatoms, such as oxygen, nitrogen, and sulphur [15, 16]. These compounds and their derivatives are excellent corrosion inhibitors in a wide range of environments and are selected basically from empirical knowledge based on their macroscopic physico-chemical properties.

In our previous works the corrosion inhibition of copper in hydrochloric acid by phenylenediamine (PDA) [17]**,** Tetraethylenepentamine (TEPA) [18], Diethylenetriamine (DETA) and Ethylenediamine (EDA) [19]. Weight loss technique and electrochemical technique were used to evaluate the corrosion parameters.

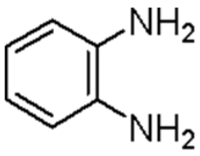
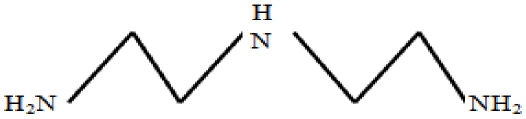
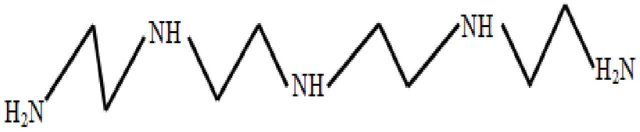
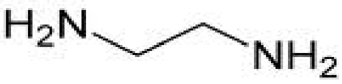
The present work is a step in the direction of application the theoretical and quantum chemical calculations for above four amines in copper alloy – hydrochloric acid system. The comparisons between experimental and theoretical data were estimated.

2. Methodology

2.1 Experimental data

Detailed study for the corrosion inhibition of copper alloy in hydrochloric acid was carried out [19]. The effect of phenylenediamine (PDA), Tetraethylenepentamine (TEPA), Diethylenetriamine (DETA) and Ethylenediamine (EDA) were estimated at different concentrations and different temperatures [19]. Many kinetics and thermodynamics parameters were evaluated experimentally. The data of different inhibitors at 1, 5, 10, 15 g/l, 35 ^{o}C and 5% HCl [19] were selected and will be compared with theoretical quantum chemical calculations. Table 1 shows the chemical structure and formula of inhibitors.

Table 1 Chemical structure and formula of inhibitors

Inhibitor	Formula	C (g/l)	IE%	Structure
PDA	$C_6H_4(NH_2)_2$	1	1.6	
		5	7	
		10	8.5	
		15	10	
DETA	$C_4H_{13}N_3$	1	4	
		5	8	
		10	10.9	
		15	15	
TEPA	$C_8H_{23}N_5$	1	13.6	
		5	25	
		10	36	
		15	48	
EDA	$C_2H_8N_2$	1	17.5	
		5	37.3	
		10	57.8	
		15	75	

IE% is inhibitor efficiency at temperature of 35 ^{o}C [19].

3. Results and discussion

3.1 Quantum chemical simulations

Quantum-chemical calculations have been widely used to study reaction mechanism. It is also proved to be a very significant tool for studying corrosion control mechanism [22]. Through the method of quantum chemical calculations, the structural parameters, such as the frontier molecular orbital (MO), HOMO (highest occupied molecular orbital), LUMO (lowest unoccupied molecular orbital), dipole moment (μ) and ΔN were calculated. The structure of inhibitor was optimized by ArgusLab 4.0.1 package. The quantum chemical parameters were estimated by PM3 and AM1 method. The optimized minimum energy geometrical configurations of test compounds aregiven in Fig. 1. For the HOMO of the studied compounds, it can be observed that the benzene ring, –C,N– and the substituent on the amines (NH_2) have a large electron density. The LUMO were mainly on the benzene ring and the nitrogen of the amines groups. The computed quantum chemical parameterslike energy of highest occupied molecular orbital (E_{HOMO}), energyof lowest unoccupied molecular orbital (E_{LUMO}), HOMO–LUMO energy gap and dipole moment are summarizedin Table 2.

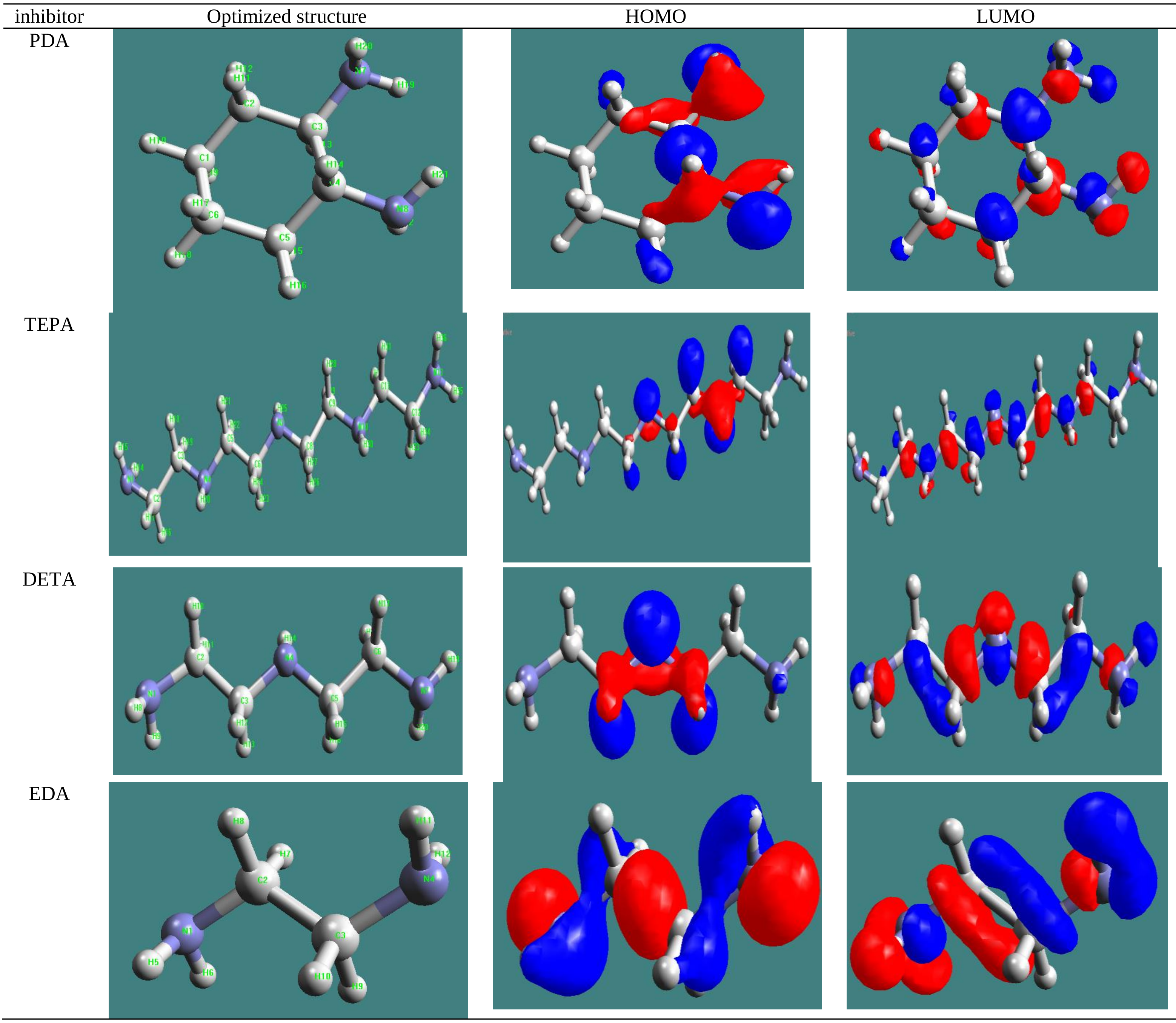


Figure 1: Optimized structure, HOMO and LUMO energies using AM1 method.

3.2 Molecular orbital energies

Highest occupied molecular orbital energy and lowest unoccupied molecular orbital energy are very common quantum chemical parameters. It is also called the frontier orbitals; determine the way the molecule interacts with other molecule. It has been well documented in literature that[23] higher the value of E_{HOMO} of the inhibitor, the greater is the easeof inhibitor to offer electrons to the unoccupied d orbital of metal atomsand higher is the inhibition efficiency of the inhibitor. Further lowerthe E_{LUMO}, easier is the acceptance of electrons from metal atom toform feedback bonds. The gap between HOMO–LUMO energy levelsof molecules were another important parameter that needs to beconsidered. Smaller the value of ΔE of an inhibitor, higher isthe inhibition efficiency of that inhibitor [24]. According to to the work of Issa*et al*. [24], a low ΔE facilitates adsorption of the molecule and thus will cause higher inhibition efficiency. The order of band gap energy was PDA>DETA>TEPA>EDA which agree with order of inhibitor efficiency EDA>TEPA>DETA>PDA (Table 1).

Table 2 Quantum chemical parameters

Method	Inhibitor	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	Dipole moment, μ (debye)	ΔN	E_{total} (kcal/mol)	$E_{formation}$ (kcal/mol)
PM3	PDA	-9.611	-3.348	6.263	4.323	0.104	-18004.78	-10.667
	DETA	-9.396	-2.031	7.365	4.111	0.169	-26788.44	-5.8175
	TEPA	-9.942	-6.601	3.341	3.367	1.134	-28879.77	-19.4359
	EDA	-9.386	-6.329	3.057	2.345	1.105	-48764.97	-8.0219
AM1	PDA	-9.541	-3.323	6.218	5.261	0.107	-18004.78	-10.667
	DETA	-9.669	-2.682	6.987	4.779	0.179	-30269.62	-6.6417
	TEPA	-10.512	-6.551	3.961	3.631	1.023	-31737.19	-26.028
	EDA	-9.534	-5.911	3.623	2.557	0.895	-54803.06	-2.3401

3.3 Mulliken charge distributions and adsorption behavior

The Mulliken charge distributions of the inhibitors are presented in Table 3. It can be readily detected that nitrogen atoms and some carbon atoms have higher charge densities. The areas of highest electron density are generally the potential sites for the electrophiles attacked [25, 26]. The use of Mulliken population analysis to probe adsorption center of inhibitors has earlier been reported [27]. Based on the calculations, the highest electron densities were located on N and C atoms implied that the N and C atoms were the active centers, which have the strongest ability of bonding to the metal surface. On the other hand, HOMO (Fig. 1) was mainly distributed on the area containing carbon and nitrogen atoms and this area is probably the primary site of the bonding. It was found that these amines inhibitors apart from existing in the cationic form can also interact with metal surface through the electrostatic attraction. This interaction with the metal surface with several numbers of active centers is forming a protective layer on the mild copper surface. The number of transferred electrons (ΔN) was also calculated according to Eq. 1 [6, 28]

$$\Delta N = \frac{X_{Cu} - X_{inh}}{2(\eta_{Cu} + \eta_{inh})} \tag{1}$$

where X_{Cu} and X_{inh} denote the absolute electronegativity of copper and the inhibitor molecule, respectively; η_{Cu} and η_{inh} denote the absolute hardness of copper and the inhibitor molecule, respectively. These quantities are related to electron affinity (A) and ionization potential (I)

$$X = \frac{I + A}{2}$$

$$\eta = \frac{I - A}{2}$$

I and A are related in turn to E_{HOMO} and E_{LUMO}

$$I = -E_{HOMO}$$

$$A = -E_{LUMO}$$

Values of X and η were calculated by using the values of I and A obtained from quantum chemical calculation. The theoretical value of X_{Cu} is 4.48 according to Pearsons electronegativity scale and η_{Cu} 0 eV/mol, respectively [29]. The fraction of electrons transferred from inhibitor to the copper surface (ΔN) was calculated and listed in Table 2. According to other reports [6, 28], value of ΔN showed inhibition effect resulted from electrons donation. According to Lukovits [30], if $\Delta N < 3.6$, the inhibition efficiency increased with increasing electron donating ability at the metal surface. In this study, EDA, TEPA, DETA and PDA was the donor of electrons, and the metal surface was the acceptor. This result supports the assertion that the adsorption of inhibitor on the metal surface can occur on the bases of donor- acceptor interactions between the Л electrons of the compound and the vacant d-orbitals of the metal surface [31].

3.4 Dipole moment

The quantity to describe the polarity is the dipole moment of the molecule [32]. Dipole moment is the measure of polarity of a polar covalent bond. It is defined as the product of charge on the atoms and the distance between the two bonded atoms. The total dipole moment, however, reflects only the global polarity of a molecule. For a complete molecule the total molecular dipole moment may be approximated as the vector sum of individual bond dipole moments [6]. The dipole momentis another parameter to obtain data on the electronic distribution in a molecule and is one of the properties used traditionally to discuss and rationalize the structure and reactivity of many chemical systems [33]. It is confirmed in the literature that, in general, lower dipole moment is associated with high inhibition efficiency [33]. According to the quantum chemical calculations, the dipole moment of PDA, DETA, TEPA and EDA are listed Table 2. The lower value calculated for EDA agrees with the experimentally measured larger inhibitor efficiency of EDA. While larger value of dipole moment is computed for low inhibitor efficiency (PDA).

Table 3 ZDO and Mulliken atomic charges using PM3 method.

inhibitor	Atom number	atoms	ZDO Atomic Charges	Mulliken Atomic Charges
PDA	1	C	-0.0978	-0.2363
	2	C	-0.0921	-0.2324
	3	C	-0.1159	-0.1898
	4	C	-0.1160	-0.1899
	5	C	-0.0921	-0.2324
	6	C	-0.0978	-0.2363
	7	N	-0.0377	-0.1108
	8	N	-0.0377	-0.1109
	9	H	0.0517	0.1199
	10	H	0.0507	0.1212
	11	H	0.0514	0.1180
	12	H	0.0635	0.1378
	13	H	0.0748	0.1429
	14	H	0.0748	0.1429
	15	H	0.0514	0.1180
	16	H	0.0635	0.1378
	17	H	0.0517	0.1199
	18	H	0.0507	0.1212
	19	H	0.0232	0.0618
	20	H	0.0282	0.0678
	21	H	0.0232	0.0618
	22	H	0.0282	0.0678
TEPA	1	N	-0.0319	-0.1055
	2	C	-0.1128	-0.2548
	3	C	-0.1182	-0.2528
	4	N	-0.0628	-0.1134
	5	C	-0.0916	-0.2260
	6	C	-0.0907	-0.2251
	7	N	-0.0712	-0.1221
	8	C	-0.0907	-0.2252
	9	C	-0.0907	-0.2249
	10	N	-0.0682	-0.1232
	11	C	-0.0897	-0.2249
	12	C	-0.1039	-0.2252
	13	N	-0.0340	-0.2249
	14	H	0.0247	-0.1087
	15	H	0.0221	0.0646
	16	H	0.0722	0.1449

	17	H	0.0582	0.1256
	18	H	0.0322	0.0955
	19	H	0.0546	0.1244
	20	H	0.0494	0.0987
	21	H	0.0448	0.1128
	22	H	0.0554	0.1224
	23	H	0.0476	0.1215
	24	H	0.0548	0.0987
	25	H	0.0494	0.1146
	26	H	0.0478	0.1207
	27	H	0.0541	0.1119
	28	H	0.0440	0.1119
	29	H	0.0572	0.1243
	30	H	0.0455	0.0944
	31	H	0.0311	0.0937
	32	H	0.0696	0.1418
	33	H	0.0675	0.1390
	34	H	0.0254	0.0870
	35	H	0.0261	0.0671
	36	H	0.0210	0.0600
DETA	1	N	-0.0321	-0.1057
	2	C	-0.1131	-0.2552
	3	C	-0.1182	-0.2528
	4	N	-0.0609	-0.1113
	5	C	-0.0911	-0.2252
	6	C	-0.1040	-0.2424
	7	N	-0.0335	-0.1082
	8	H	0.0253	0.0652
	9	H	0.0218	0.0611
	10	H	0.0728	0.1455
	11	H	0.0571	0.1244
	12	H	0.0581	0.1263
	13	H	0.0310	0.0941
	14	H	0.0464	0.0954
	15	H	0.0695	0.1420
	16	H	0.0298	0.0921
	17	H	0.0686	0.1404
	18	H	0.0253	0.0870
	19	H	0.0264	0.0675
	20		0.0209	0.0599
EDA	1	N	-0.3286	-0.4397
	2	C	-0.1304	-0.2246
	3	C	-0.1304	-0.2246
	4	N	-0.3286	-0.4397
	5	H	0.1318	0.1875
	6	H	0.1318	0.1875
	7	H	0.0914	0.1447
	8	H	0.0914	0.1447
	9	H	0.0914	0.1447
	10	H	0.0914	0.1447
	11	H	0.1381	0.1875
	12	H	0.1381	0.1875

3.5 Quantitative structure-activity relationship (QSAR)

A number of correlations between the inhibition efficiency of inhibitors and selected quantum chemical parameters have been studied [34–40]. An attempt to correlate some quantum chemical parameters with experimental inhibition efficiencies shows that there is no simple relation or direct trend relationship can be derived with the inhibition performance of this type of anticorrosion materials. The difficulty in obtaining a direct relation between quantum chemical parameters and corrosion inhibition efficiency provides confirmation to the complex nature of interactions that are involved in the corrosion inhibition process.The linear model approximates inhibitor efficiency (E_i) as in Eq.(2) [41]:

$$E_i = A x_j C_i + B \qquad 2$$

Where A and B are the regression coefficients determined by regression analysis; x_j a quantum chemical index characteristic for the molecule j;Ci denotes the experiment's concentration. A non-linear equation was used to correlate all quantum chemical parameters (E_{HOMO}, E_{LUMO}, ΔN andμ) and inhibitor concentration (C_i) with experimental inhibition efficiencies. The non-linear model proposed by Lukovits et al. [36] for the interaction of corrosion inhibitors with metal surface in acidic solutions has been used:

$$E_{theor}\% = \frac{(A x_i + B) C_i}{1 + (A x_i + B) C_i} \times 100 \qquad 3$$

The nonlinear estimation regression of equation 3 yields the equations for PDA, DETA, TEPA, and EDA with average correlation coefficients of R^2=0.946. Fig. 2 shows bar diagram for experimental inhibitor efficiency against the theoretical one which predicted via QSRD. A good agreement can be obtained. Inhibition efficiency at different concentration of the amines can be attributed to the presence of nitrogen atom of amino group (-NH_2). Nitrogen atom in amines acts as the reaction centre, because of its higher electron density.

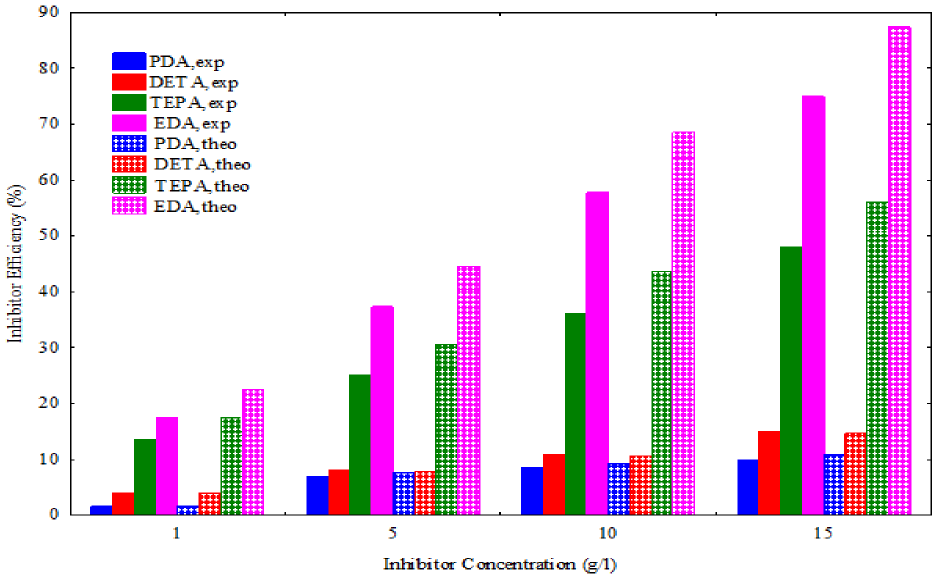


Fig. 2 Experimental inhibitor efficiency against the theoretical one using PM3 method.

Conclusion

The following points can be concluded from current paper:

- PDA, DETA, TEPA, and EDA were a weak corrosion inhibitor with low inhibitor efficiencies. Therefore, they cannot be recommended for copper alloy in hydrochloric acid.
- Theoretical and quantum chemical calculation are a powerful way for estimation inhibitors efficiencies.
- A good agreement was seen between experimental inhibitor efficiency and theoretical one.
- The two semi-empirical calculation methods (AM1 and PM3) gave similar and very good correlation with the experimental inhibition efficiency.
- Maximum energy band gab was 6.263 eV for PDA, while minimum one was 3.057 eV in the case of EDA, which support the experimental results of inhibitors efficiency.

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