Research Article

Using Solvation Free Energy as an Additional Parameter for Corrosion Inhibition Inspection of Organic Compounds in Acid Media: An Evaluation Study

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The energies of frontiers molecular orbitals and derived electronic parameters are widely used to explain experimentally obtained inhibition effectiveness of several organic inhibitors against metallic corrosion. In this context, the present study aims to reevaluate the use of solvation free energy (ΔG_{Solv}) as an additional parameter for the corrosion inhibition inspection. Three organic molecules set previously reported as corrosion inhibitors in acidic solutions were selected to conduct this *in silico* study. The solvation free energy in the aqueous phase of chosen inhibitors was determined using DFT-based calculations in combination with integral equation formalism-polarizable continuum solvation model. The acquired data show that ΔG_{Solv} can be used together with other known parameters to inspect the inhibition performance of organic inhibitors in acidic media.

1. Introduction

The contact of many metals and alloys with acid media during their use (e.g., acid pickling and cleaning) involves corrosion of these materials, which implies a great economic and potential lives loss [1, 2]. To overcome this undesirable phenomenon, the introduction of corrosion inhibitor compounds into corrosive solutions is known as a practical and attractive method [3, 4]. Many oxygen, nitrogen, and sulfur-containing organic compounds have been reported to act as good corrosion inhibitors for various metallic materials in acid media [5]. Among reported compounds, there are 1,5-benzodiazepin-2-one derivatives [6], 1,2,4-triazole-based compounds [7], and several simple α -amino acids [8].

Nowadays, the application of computational modeling approach in the inhibition of corrosion search has been widely reported in the literature [9–11]. Such an approach is applied to understand and to explain observed inhibiting activity at a molecular and atomic scale [12]. In this context, various electronic structure parameters characterizing the inhibitor molecule (indicators of reactivity), e.g., LUMO,

HOMO and gap energies, were calculated using density functional theory-based methods, after that they are correlated through simple linear, multilinear, or nonlinear models with the obtained inhibition efficiencies [13–16].

On the other hand, as almost inhibition processes occur in the aqueous solutions, the solvation process of the inhibitor molecule is of interest, which can be estimated via its free energy of solvation (ΔG_{Solv}) [17]. This thermodynamic parameter has been used to evaluate the impact of solvent on the property of molecules in many scientific disciplines, such as pharmaceutical, biological, and chemical sciences [18]. In this regard, the present work aims to evaluate the use of this parameter in the field of corrosion inhibition, i.e., expect the inhibition ability of organic inhibitors largely employed in acid media. This subject has been not sufficiently studied in the literature and is still lacking. From the computational point of view, there are two different theoretical manners to predict ΔG_{Solv} , namely, implicit and explicit considering solvent molecules. It is well known that continuum solvation models (i.e., implicit approach), such as integral equation formalism-polarizable continuum model (IEF-PCM), are

TABLE 1: Chosen organic inhibitors data set and corresponding experimental data.

Inhibitor (abbreviation)	Solution	Metal	[Inh.] (mM)	IE (%)	Ref.
1,2,4-Triazole (TR)	1M H ₂ SO ₄	Copper	1	66	[6]
3-Amino-1,2,4-triazole (ATR)				71	
3,5-Diamino-1,2,4-triazole (DATR)				73	
4,7-Dimethyl-1,5-benzodiazepin-2-one (DMBD)				88	
3-Phenyl-1,5-benzodiazepin-2-one (PBD)	1M HCl	Iron	10	90	[7]
4-Methyl-7-phenyl-1,5-benzodiazepin-2-one (MPBD)				96	
Asparagine (Asn)	1M HNO ₃	Copper	1	45	[8]
Glutamine (Gln)				40	
Alanine (Ala)				25	
Acide glutamique (Glu)				38	
Acide aspartique (Asp)				28	
Leucine (Leu)				34	
Threonine (Thr)				50	

computationally fast than those with the explicit introduction of solvent molecules [19–21].

2. Computational Details

2.1. Data Set. Three classes of organic inhibitor molecules are selected randomly to perform this study, namely, 1,2,4-triazole (3 inhibitors), 1,5-benzodiazepin-2-one (3 inhibitors), and α -amino acid (7 inhibitors) set. All these compounds have been experimentally tested and reported as corrosion inhibitors in acid media for iron and copper metals [6–8]. To avoid possible differences in the obtained inhibition efficiencies of considered classes, which can be due to how the experimentations were done, the same authors have evaluated each of the above-listed classes of inhibitors. Obtained inhibition effectiveness (IE), as well as prior adopted operating conditions, are summarized in Table 1. The molecular structure of these organic inhibitors is depicted in Figure 1.

2.2. Solvation Free Energy Calculations. The calculation of solvation free energy (ΔG_{Solv}) of chosen organic inhibitors was conducted using DFT/B3LYP method at 6-311++G (*d*, *p*) basis set [22, 23] in combination with the IEF-PCM solvation model by setting water as a solvent [24–27]. As the acidic environment was used in the experimental studies, its effect on the protonation state of inhibitor molecules cannot overlook, for this, the protonated forms of these inhibitors are considered throughout the calculations using Gaussian 09 software. The full optimization of studied molecules was checked by the absence of possible imaginary frequencies [28]. Figure 1 displays the optimized molecular structure of selected organic inhibitors.

3. Results and Discussion

There is a large agreement in the literature that the ability of an organic inhibitor to prevent metallic corrosion is a consequence of its adsorption on the metal surface [29, 30]. However, the adsorption of the inhibitor molecule can occur after its prior release from its solvation shell in the aqueous solution. Consequently, the stronger hydration (i.e., lower ΔG_{Solv} values) of an inhibitor molecule can decrease its capacity to adsorb on the

metallic surface, which leads to lower protection of metal against corrosion, i.e., lesser inhibition efficiency is obtained [31].

Beginning by the smaller inhibitor set containing three inhibitors per each set, namely, 1,2,4-triazole and 1,5-benzodiazepin-2-one ones, the calculated solvation free energies (ΔG_{Solv}) using IEF-PCM solvation model for the protonated form of 1,2,4-triazole and 1,5-benzodiazepin-2-one inhibitors set are listed in Table 2. As can be noted in this table, all calculated values indicate that the hydration process of selected organic inhibitors is an exothermic process. The obtained solvation free energy values are ordered as $\text{TR} < \text{ATR} < \text{DATR}$ and $\text{DMBD} < \text{PDB} < \text{MPBD}$ for 1,2,4-triazole and 1,5-benzodiazepin-2-one inhibitors set, respectively. It is clear that the latter ranking is coherent with the experimentally recorded inhibition effectiveness for both inhibitors classes, in which less ΔG_{Solv} value is associated with higher inhibition efficiency. Meaning that the adsorption affinities of DATR and MPBD inhibitors are great than other ones in the same inhibitor set. Hence, better inhibition efficiencies are obtained for DATR and MPBD inhibitors. Furthermore, the computed correlation coefficients (*R*) between solvation free energy and inhibition efficiency are 0.96 and 0.86 for 1,2,4-triazole and 1,5-benzodiazepin-2-one inhibitor set, respectively, indicating a remarkable proportional ΔG_{Solv} /IE relationship. This finding outlines the possibility to employ the ΔG_{Solv} energy as a useful parameter to shed more light on the observed inhibition efficiency of these organic inhibitors in acid media.

Evaluating now the ΔG_{Solv} /IE relationship on the third inhibitors set, i.e., α -amino acid molecules, this larger set includes eight inhibitors, in which their molecular structures are more diverse (see Figure 1). Figure 2 presents the linear correlation curve between calculated ΔG_{Solv} and experimentally obtained inhibition efficiency of α -amino acids set. As can be noted in this figure, the ΔG_{Solv} /IE relationship is acceptable because the calculated correlation coefficient is 0.70. This means that ΔG_{Solv} can explain over 50% of the obtained experimental inhibition efficiency of this set, which is an interesting achievement. Moreover, it is evident from Figure 2 that the slope of the plotted line (red line in the figure) is positive, which means an increase of the inhibition efficiency of evaluated α -amino acid inhibitors by increasing

FIGURE 1: Optimized molecular structure of selected organic inhibitors in this study using DFT/B3LYP method with 6-311++G (*d, p*) basis set in the aqueous phase.

TABLE 2: Calculated solvation free energy (ΔG_{Solv}) and experimentally obtained inhibition efficiency (IE) of 1,2,4-triazole and 1,5-benzodiazepin-2-one inhibitors set.

Inhibitor	1,2,4-Triazole				1,5-Benzodiazepin-2-one	
	TR	ATR	DATR	DMBD	PDB	MPBD
ΔG_{Solv} (Kcal mol ⁻¹)	-73.97	-70.98	-70.97	-61.77	-57.91	-56.47
IE (%)	66	71	73	88	90	96

FIGURE 2: Linear correlation curve of ΔG_{Solv} with IE of chosen α -amino acids in protonated form.

their ΔG_{Solv} . The obtained data reveal that the solvation free energy can be also served to expect the inhibition effect of a large organic inhibitor set with diversity in their molecular structures.

It is important to underline that the inhibition of corrosion is a complex phenomenon that implies the extrinsic (i.e., experimental conditions, e.g., metal nature, corrosive

solution, and temperature) and intrinsic (i.e., inhibitor property) factors to be understood [32]. Under given operational conditions, as presumed to conduct the current study, in addition to the solubility (solvation) of the inhibitors, this phenomenon involves also the electronic/molecular aspects of the inhibitor molecules and their interfacial interactions with the metallic surface as well. In other words, we can implement the ΔG_{Solv} parameter within the known theoretical approach to understand more the noted inhibition trend in acidic media. On the other hand, the energies of frontiers molecular orbitals and derived electronic parameters are commonly used to explain experimentally obtained inhibition effectiveness of several organic inhibitors against metallic corrosion [33]. However, in some cases, it has reported the noncoherence between those parameters and the observed inhibition behaviors, which is due to the complexity of the studied inhibition systems [34–37]. In this context, the use of ΔG_{Solv} can also show some exceptional cases in this regard [38].

4. Conclusion

The present evaluation study repoints out the possibility to employ the solvation free energy (ΔG_{Solv}) as an intrinsic property of the inhibitor molecule to inspect its inhibition ability against metallic corrosion in acid media. Such a parameter can be implemented within the widely adopted

theoretical demarche in the literature to understand the observed inhibition trend for a given inhibitor set under fixed extrinsic conditions.

Data Availability

No additional data were used to support this study.

Conflicts of Interest

The author declares that he has no conflicts of interest.

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