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UNTANGLING THE INHIBITION EFFECTS OF ALIPHATIC AMINES ON SILVER CORROSION: A COMPUTATIONAL STUDY

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Abstract. The topic of corrosion inhibition of different metals by organic compounds has been the focus of intense scrutiny for decades. The enormity of the problem is reflected in the need to understand the underlying inhibition mechanisms of such compounds, one of which is the class of aliphatic amines. Electrochemical measurements represent protective effect of these compounds at ever-increasing levels of detail but these methods lack the resolution to represent inhibition efficiency-molecular structure relations adequately. In this study, the dependence of the inhibition effect of four aliphatic amines (methylamine, ethylamine, *n*-propylamine, and *n*-butylamine), on their molecular and electronic structure is analysed using quantum chemical calculations. The obtained results of these calculations were found to be consistent with the experimental findings.

Keywords: corrosion inhibitor, silver, aliphatic amines, density functional theory.

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Introduction

Silver is used extensively for industrial purposes due to its unique properties, such as high electrical and thermal conductivity, malleability, ductility, and its resistance to corrosion. However, the resistance of silver to oxidising acids is generally lower than that of the other noble metals, while in halogen acids it forms a protective film of insoluble halide. Oxidising acids, e.g. nitric acid, hot sulphuric acid at concentrations exceeding 80% and reducing acids containing oxidising agents, are corrosive to silver [1].

Corrosion protection of silver by inhibiting additives is of considerable practical importance and is the subject of significant research activities [2,3]. A number of formulations of corrosion inhibitors have been reported in the literature for silver [4]. The aliphatic amines in this regard are an interesting group of nitrogen-containing organic compounds which act as inhibitors in the dissolution of various metals, including silver, in

aggressive media [5-8]. The consensus is that organic compounds inhibit corrosion of silver by adsorbing at the metal / solution interface.

The most pertinent study of silver inhibition in acidic media is that of Abd El Wanees, S. *et al.* [8], who recently performed an experimental study on the efficiencies of four aliphatic amines, namely, methylamine, ethylamine, *n*-propylamine, and *n*-butylamine (Figure 1) in 0.01 M HNO₃ using galvanostatic polarization technique. They concluded that the inhibitory activity of such compounds was due to simple blocking of the electrode surface through adsorption. Although current understanding of the factors contributing to aliphatic amine inhibition for the corrosion of silver is incomplete, there is rising evidence that quantum chemical calculations can play a significant role in providing insights regarding how structure and substituents modulate the inhibition properties of different classes of corrosion inhibitors [9-17].

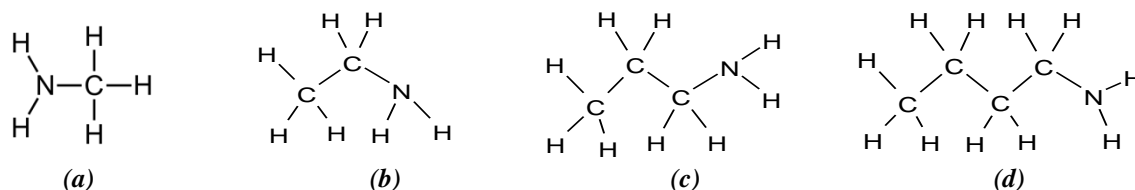


Figure 1. Molecular structure of (a) methylamine, (b) ethylamine, (c) *n*-propylamine and (d) *n*-butylamine.

Taken together, such studies do provide a strong basis for determining whether proposed inhibition mechanisms might be valid or not. It is the purpose of the present study to show how growth of chain length affects the molecular electronic structure of these aliphatic amines with possible implications toward inhibition of corrosion by means of the density functional theory (DFT) calculations, as it is the case for most corrosion inhibitors.

Computational

All calculations have been performed using standard gradient techniques and default convergence criteria with the Gaussian 09 package [18]. The calculated geometries showed no imaginary frequencies and consequently proved to be minima on the potential hyper surface. Molecular properties such as ionisation potential, electronegativity, chemical potential, chemical hardness and softness have been deduced from HOMO–LUMO analysis in the gas and aqueous phases employing B3LYP functional and a triple-zeta basis set augmented with polarization and diffuse functions, 6-311++G(d,p) basis set as well as within the integral equation formalism - polarizable continuum model (IEF-PCM) with water as solvent [19,20].

Results and discussion

Amines are hydrocarbon derivatives of ammonia, and according to the nature of the N-substituent and bonding patterns, they are sub-classified as aliphatic, cycloaliphatic, aromatic or heterocyclic. Aliphatic amines have simple hydrocarbon substituents (alkyl groups), and the origin behind the remarkable inhibition efficiency in acidic solutions could be indubitably attributed to the presence of strong intermolecular H-bonding-assisted favourable interactions between the amine moieties and the metal surface [21]. The basicity of amino group as well as the number of nitrogen atoms have influence over the corrosion suppression efficiency [22,23]. There is herein a particular need to clarify the exact condition of these compounds in strong acid solution, since the experimental data used in this study relies heavily on the results of electrochemical measurements in 0.01 M HNO₃ solution. It is well known that aliphatic amines as strong bases are subject to protonation with decreasing pH. This is due to the presence of nitrogen atoms with lone pairs of electrons that form bonds with hydrogen ions [24]. Thus, extension of calculations is required towards structures which include the protonated forms of

these inhibitors explicitly. The fully optimized structures of neutral and protonated forms of four aliphatic amines at the B3LYP/6-311++G(d,p) level of theory are illustrated in Figure 2.

To corroborate the data on the optimized geometries of the compounds, some selected parameters compared to those obtained either by experimental (*i.e.*, electron diffraction and microwave spectroscopies) or theoretical methods [25-31] are listed in Table 1. This comparison may serve as a satisfactory starting observation for the eligibility of the theoretical approach used here. The C-N bond lengths are very uniform with an average value of 1.473 Å which is consistent with reference data. As expected, these bonds are affected more noticeably upon protonation, and all of them elongated within the range of 1.502–1.571 Å. The fit of the calculated bond angles for neutral forms is also congruous with the differences being less than 3°. The changes in the bond length and angle in protonated amines are comparable with those in neutral forms, suggesting that the determined structural parameters are probably as accurate as can be obtained by experimental methods, and can be a mainstay of calculating other parameters, such as the energies of the frontier molecular orbitals.

Paraphrasing Fukui, those orbitals will interact most which overlap best and are closest in energy [32]. If the two orbitals contain two or three electrons, the interaction will result in stabilization, or a net lowering of electronic energy, while if four electrons are present, destabilization or closed-shell repulsion results. Of the stabilizing terms, those arising from the interaction of the HOMO(highest occupied molecular orbital) of one molecule with the LUMO(lowest unoccupied molecular orbital) of the second, and vice versa, will dominate energy changes, since these orbitals are closest in energy [33]. A small HOMO-LUMO gap implies low kinetic stability, because it is energetically favourable to add electrons to a high-lying LUMO, and/or to extract electrons from a low-lying HOMO, and so to form the activated complex of any potential reaction. This frontier orbital approximation is a thriving attempt in rationalizing reactivity and is a theoretical basis for a close relationship found between the HOMO-LUMO energies and the adsorption of the inhibitor molecules which can occur either by chemical or by physical bonding on the metal surfaces [9]. The HOMO density is closely related to the charge transfer, whereas for an acceptor compound, the LUMO density is important.

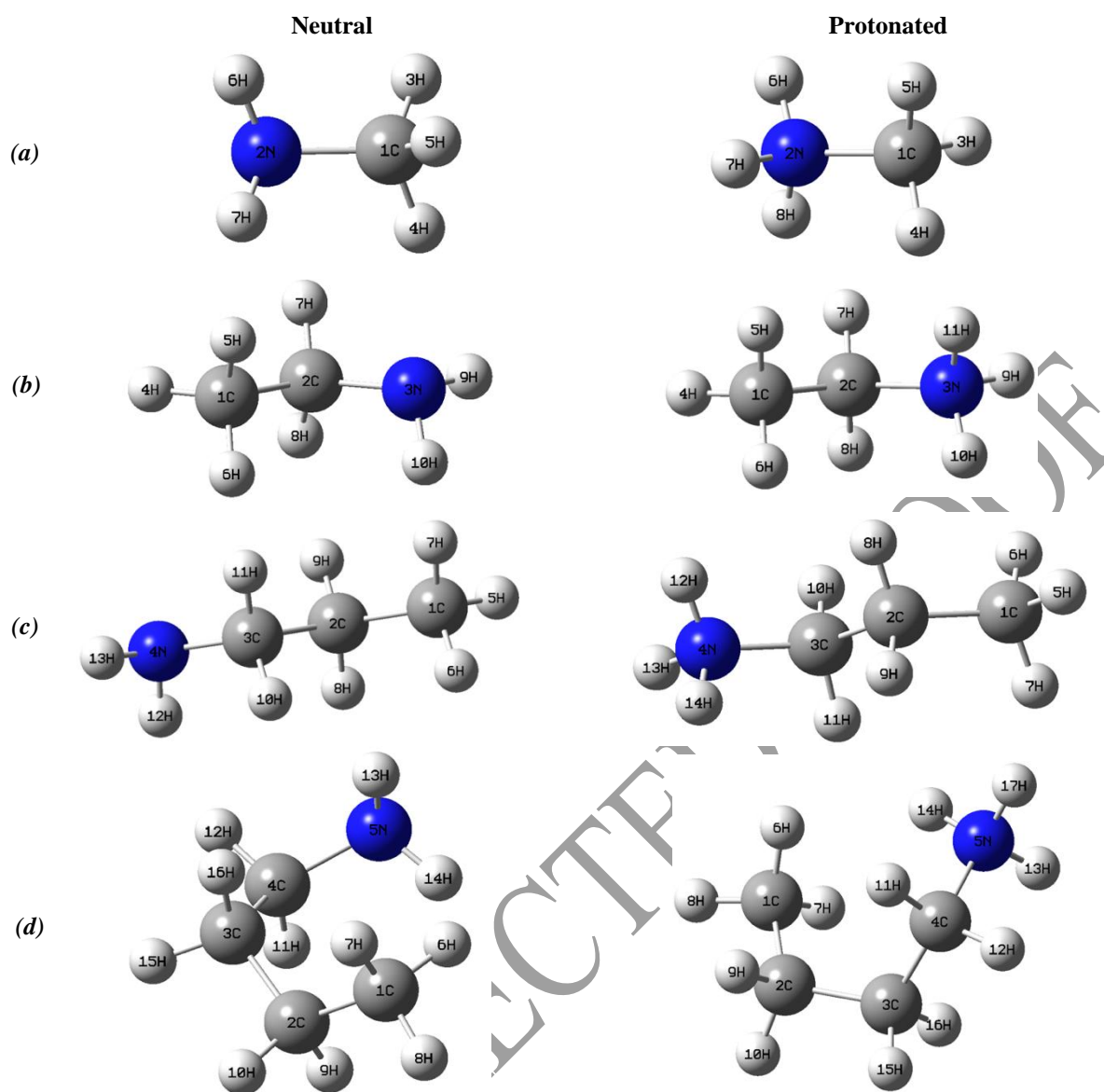


Figure 2. Optimized structures at the B3LYP/6-311++G(d,p) level for the neutral and protonated forms of (a) methylamine, (b) ethylamine, (c) *n*-propylamine and (d) *n*-butylamine in the aqueous phase.

Table 1

Selected geometric parameters for neutral and protonated forms of four aliphatic amines.					
Inhibitor	Bond lengths (Å) ^a		Bond angles (°) ^b		
	DFT	Lit. data	DFT	Lit. data	
neutral	Methylamine	1.471	1.471(3) [25]	110.07	112.1(1) [29]
	Ethylamine	1.474	1.470(10) [26]	110.91	115.0(3) [26]
	<i>n</i> -Propylamine	1.474	1.469(13) [27]	111.21	109.8 [30]
	<i>n</i> -Butylamine	1.472	1.493(6) [28]	118.07	120.10 [31]
protonated	Methylamine	1.502		111.58	
	Ethylamine	1.514		111.12	
	<i>n</i> -Propylamine	1.512		111.14	
	<i>n</i> -Butylamine	1.517		112.66	

^a Carbon-nitrogen bond lengths.

^b Bond angle refers to carbon-nitrogen-hydrogen angle in methylamine, and carbon-carbon-nitrogen angle in other amines.

A high value of the HOMO energy corresponds to copious donation of electrons to congruent molecules with low-energy, empty molecular orbitals. Increasing values of E_{HOMO} lead to an increment in adsorption and exalt the efficiency of inhibition. The energy of the LUMO indicates the ability of the molecule to accept electrons. The lower is the value of E_{LUMO} , the more probable it is that the molecule would accept electrons [9-17].

According to Koopmans' theorem [34], the negative of the HOMO energy ($-E_{HOMO}$) and the LUMO energy ($-E_{LUMO}$) corresponds to ionization potential and electron affinity, respectively (*i.e.* $I = -E_{HOMO}$ and $A = -E_{LUMO}$). The chemical hardness (η), electronegativity (χ), and chemical potential (μ) are thereby defined as $\mu = 1/2 (E_{HOMO} + E_{LUMO})$, $\eta = (E_{LUMO} - E_{HOMO})/2$ and $\chi = -(E_{LUMO} + E_{HOMO})/2$. That is, the energy gap between the HOMO and LUMO is equal to 2η , and χ is halfway between the HOMO and LUMO. The HOMO and LUMO iso-surfaces are plotted in Figure 3. In all cases, HOMOs are delocalized

over the almost entire molecule with a slightly more localization on amino groups. The LUMOs also show delocalization over the entire inhibitor molecules, whereas the electronic cloud is particularly localized on the nitrogen and hydrogen atoms of nitro groups of *n*-propylamine which have a significant contribution to the LUMO state. The comparison of these plots reveals that the localization centre of orbitals determines the overlapping conditions, and accordingly, adsorption capabilities of the compounds are determined by the overlap of frontier molecular orbitals. According to the data given in Table 2, the highest E_{HOMO} and the lowest E_{LUMO} and ΔE values are found for the neutral form of *n*-butylamine molecule in both gas and aqueous phases. It is interesting to note that the protonated form of *n*-propylamine molecule in both gas and aqueous phases has the highest E_{HOMO} values when compared with the data for the neutral molecules.

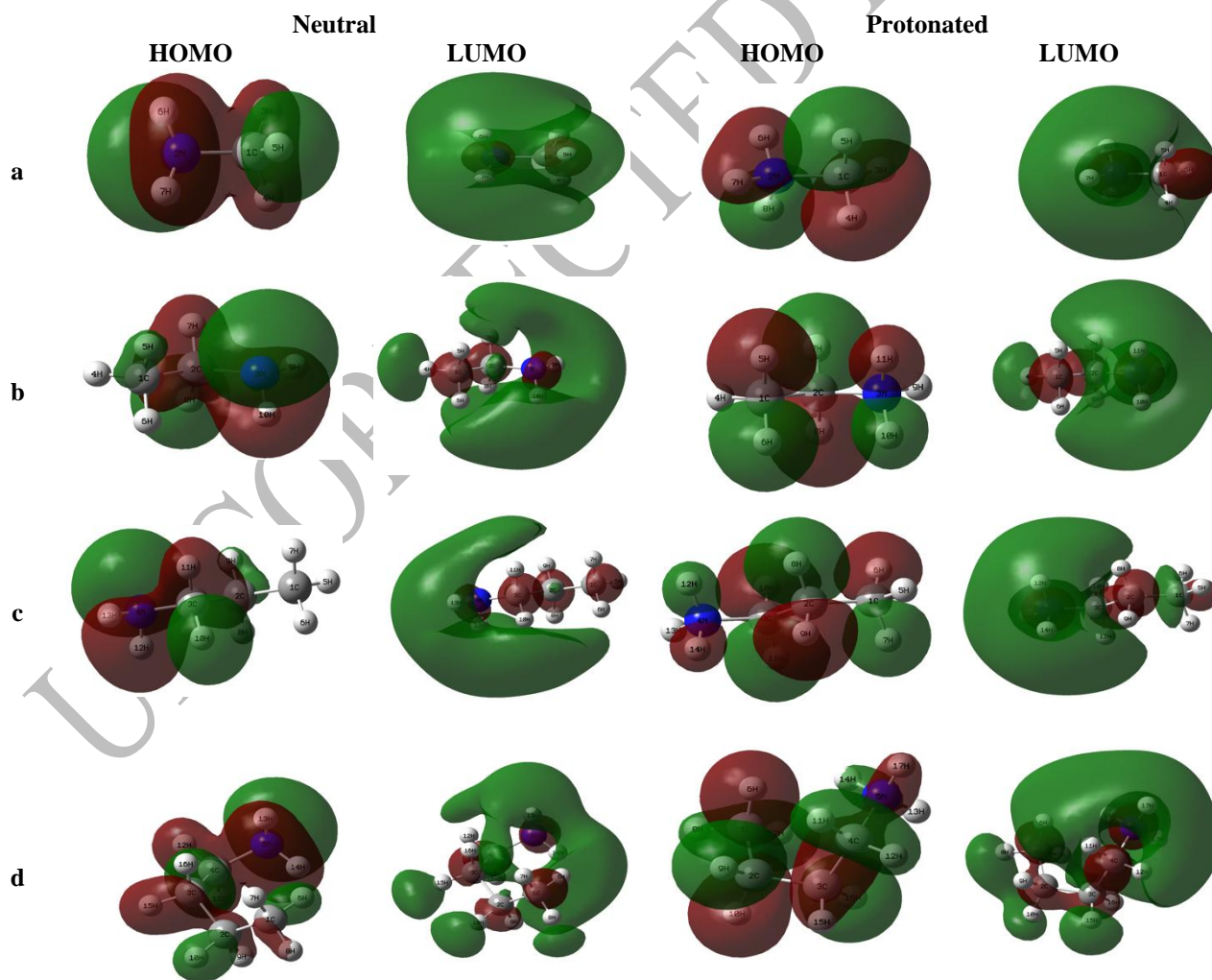


Figure 3. Plots of the HOMO and LUMO orbital distribution for (a) methylamine, (b) ethylamine, (c) *n*-propylamine and (d) *n*-butylamine.

On the other hand, the lowest E_{LUMO} and ΔE values have been found once again for the protonated form of *n*-butylamine in both phases. This suggests that the dominant form responsible for the inhibition efficiency of *n*-butylamine is its protonated form in acidic medium. These are accordant with experimental results [8].

Dipole moment (μ) of the compound is another parameter which predicts the polarized nature of the molecule although its relation to inhibition efficiency is controversial. It has been generally asserted that the efficiency of the inhibitor increases with the growth in the total dipole moment of the compound [9]. The theoretical study has shown that neutral and protonated forms of *n*-butylamine in aqueous phase, albeit deprived of any regularity, have higher values of dipole moment. Taking into account that the estimated errors for the calculated data [34] are around the 10%, we can conclude that both results, experimental and calculated dipole moments, are compatible (Table 2). Apart from dipole moment, atomic charges and charge transfer are potent concepts in chemical reasoning about molecular behaviour and reactivity of corrosion inhibitors [9,36]. It has been documented that the higher magnitude and the number of negatively charged heteroatoms present in an inhibitor molecule, the higher is its ability to be adsorbed on the metal surface via a donor-acceptor type reaction [9]. Mulliken atomic

charges were calculated for neutral and protonated forms of all amines (see *Supplementary Material*). The carbon and nitrogen atoms exhibit a substantial negative charge, whereas hydrogen atoms exhibit a positive charge, which is an indication of their roles as donor atoms and acceptor atoms, respectively. This approach agrees in yielding substantial electronic charge depletion on the hydrogen atoms and substantial charge accumulations on the carbon atoms and on the nitrogen atom, as shown by the calculated fraction of electrons (ΔN) transferred from inhibitors to silver. This fraction is given by: $\Delta N = (\chi_{Ag} - \chi_{inh}) / 2(\eta_{Ag} - \eta_{inh})$ and the corresponding values are also presented in Table 2 for the neutral and protonated forms in both the gas and aqueous phases. To calculate this fraction, a theoretical value for the electronegativity of bulk silver, $\chi_{Ag} = 4.44$ eV/mol [37], and a global hardness of $\eta_{Ag} = 0$ eV/mol were used based on the assumption that for a bulk metal $I = A$ because they are softer than the neutral metallic atoms. If $\Delta N < 3.6$, the inhibition efficiency enhances with increasing electron-donating ability to the metal surface as in Lukovits' work [38]. Since the amines are more electronegative than the densely-packed silver surface, the charge would flow to amines from silver surface ($\Delta N < 0$), which has been verified by the explicitly calculated charge transfer.

Table 2

The calculated quantum chemical descriptors for the neutral and protonated forms of four amines in gas and aqueous phases.

	Compound	Phase*	E_{HOMO} (eV)	E_{LUMO} (eV)	ΔE (eV)	μ (D)	μ (D) [35]	χ	η	ΔN	IE(%) [8]
neutral	Methylamine	G	-6.588	-0.310	6.278	1.411	1.31	3.449	3.139	0.157	43
		A	-6.818	-0.195	6.623	1.869		3.506	3.312	0.140	
	Ethylamine	G	-6.595	-0.307	6.288	1.348	1.22	3.451	3.144	0.157	51
		A	-6.809	-0.198	6.611	1.875		3.504	3.306	0.141	
	<i>n</i> -Propylamine	G	-6.587	-0.271	6.316	1.277	1.17	3.429	3.158	0.160	58
		A	-6.804	-0.159	6.645	1.808		3.482	3.323	0.144	
<i>n</i> -Butylamine	G	-6.472	-0.318	6.154	1.495	1.44	3.395	3.077	0.169	67	
	A	-6.685	-0.205	6.480	1.972		3.445	3.240	0.153		
protonated	Methylamine	G	-13.151	-2.341	10.810	2.223		7.746	5.405	-0.305	
		A	-13.157	-2.324	10.833	2.658		7.741	5.417	-0.304	
	Ethylamine	G	-12.321	-2.324	9.997	3.881		7.323	4.999	-0.288	
		A	-12.319	-2.317	10.002	4.729		7.318	5.001	-0.287	
	<i>n</i> -Propylamine	G	-12.018	-2.365	9.653	6.352		7.192	4.827	-0.285	
		A	-12.020	-2.352	9.668	7.648		7.186	4.834	-0.284	
<i>n</i> -Butylamine	G	-12.062	-2.439	9.623	5.721		7.251	4.812	-0.292		
	A	-12.072	-2.445	9.627	7.408		7.259	4.814	-0.292		

*G – gas phase ($\epsilon = 1.0$), A – aqueous phase ($\epsilon = 78.5$).

Conclusions

In this paper, we presented the first theoretical study on sound evidence for a better understanding of the inhibition mechanism of four aliphatic amines on silver corrosion, which was previously tested by electrochemical measurements. There are two main proposals for superior inhibition efficiency of *n*-butylamine: protonation at low pH and increase in chain length. In spite of the limitations of the calculations, our computational results have allowed to gain insight into greater adsorption capability of inhibitors in protonated form rather than in neutral form through the comparison of several quantum chemical parameters, and showed a plausible coherence with the experimental data.

Supplementary information

Supplementary data are available free of charge at <http://cjm.asm.md> as PDF file.

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