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A theoretical investigation of the effect of some compounds on the corrosion of Aluminium

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ABSTRACT

In the aviation industry, corrosion is a very important form of damage. Aluminium alloys are a good choice for aircraft wings and various construction materials due to their higher damage tolerance and longer durability. In this study, the effects of Na_2CrO_4, $CeCl_3$, $SrCrO_4$, $C_7H_5NaO_2$ compounds were examined theoretically by density functional theory (DFT) method as inhibitors of aluminium corrosion in 0.1 M NaCl environment. Several quantum chemical parameters such as E_{HOMO}, E_{LUMO}, ΔE, dipole moment (μ), electronegativity (χ), global hardness (η), and electrophilicity index (ω) were calculated. The comparison of theoretical data and experimental results showed that there is no direct correlation between the inhibition properties and the electronic structure parameters for the compounds. However, computational findings obtained in the presence of a NaCl compound revealed that Na_2CrO_4 is the best inhibitor among the others which is also consistent with the experimental findings.

1. INTRODUCTION

Aluminium is remarkably resistant to corrosion considering its low electrode potential. This is mainly due to an oxide layer on its surface in the pH range of 4 to around 9, which strongly influences its electrochemical behaviour. The oxide spontaneously forms in oxidising media; however, it is unstable in many acidic and alkaline solutions, especially chloride-containing ones (Szklarska-Smialowska, 1999). Accordingly, the corrosion of aluminium is primary concern and a widespread phenomenon in aerospace materials and vehicles (Wanhill and Windisch,2018). Therefore, corrosion protection for aluminium is required, typically achieved by using several types of corrosion inhibitors (Xhanari and Finšgar, 2019; Zor and Özkazanç, 2010; Su et al., 2020).

Kabasakaloglu et al. (1997) evaluated the inhibition activity of Na_2CrO_4, $CeCl_3$, $SrCrO_4$, and $C_7H_5NaO_2$ for the corrosion of A1(2024) alloy in 0.1M NaCl solution via electrochemical measurements. It is well-known that chromate-based inhibitors (Na_2CrO_4 and $SrCrO_4$) pose significant risks due to the high toxicity and persistence of hexavalent chromium in the environment. $CeCl_3$ is explored as a less harmful alternative but still exhibits toxicity to aquatic life. On the other hand, $C_7H_5NaO_2$ is generally less toxic but its widespread use could affect microbial ecosystems. All these inhibitors are historically known for their high effectiveness in preventing corrosion across various metals and in diverse conditions (Bahadur, 1992). In comparison to some other organic inhibitors, like amines or

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phosphates, the effectiveness of these four compounds can vary greatly depending on the specific application and conditions (Ma et al., 2022). They achieve this by forming a robust, self-healing passive layer on the metal surface. The experimental results of Kabasakaloglu et al. (1997) also confirmed that these compounds effectively inhibit both cathodic and anodic processes and act as mixed-type inhibitors. Although much has been learned from this experimental study, certain aspects of the inhibition behavior of such compounds are not directly accessible through such electrochemical analyses.

There is increasing use of density functional theory (DFT) calculations on model systems designed to shed light on many aspects of the inhibition efficiency of corrosion inhibitors (Abdallah et al., 2021; Abdellattif et al., 2021; Gece, 2008; Zhang et al., 2021). To connect molecular behavior to experimental observations, this study attempted to address the identified knowledge gap by presenting molecular-level insights into the corrosion inhibition of these compounds using a quantum chemical approach

2. MATERIALS AND METHODS

All quantum chemical calculations for Na_2CrO_4, $CeCl_3$, $SrCrO_4$, $C_7H_5NaO_2$ were performed using Gaussian09W software (Frisch et al.,2009) by DFT with hybrid function of Becke three-parameters Lee, Yang and Parr (B3LYP), that is DFT-B3LYP method, and Stuttgart/Dresden effective core potential (SDD) basis set. The calculations were carried out in both gas and aqueous media in the absence and presence of a NaCl molecule, and the water solvent has been selected based on the polarizable continuum model (PCM) using the integral equation formalism variant (IEFPCM) (Mennucci et al., 2002).

The structural geometry of each of the studied compounds was firstly optimized, followed by the vibrational frequency analysis, prior to other quantum chemical calculations whose outputs were used to estimate some useful derived parameters such as the energy of highest occupied molecular orbital (EHOMO), the lowest unoccupied molecular orbital (ELUMO), and the energy gap (ΔELUMO-HOMO), electron affinity (EA), ionization potential (IP), global hardness (η), electronegativity (χ), global electrophilicity index (ω) using Eqs. (1)–(5) below.

$$\mathrm{EA} = -E_{\mathrm{LUMO}} \tag{1}$$

$$\mathrm{IP} = -E_{\mathrm{HOMO}} \tag{2}$$

$$\eta = (\mathrm{IP}-\mathrm{EA}) / 2 \tag{3}$$

$$\chi = (\mathrm{IP}+\mathrm{EA}) / 2 \tag{4}$$

$$\omega = \mu^2 / 2\eta \tag{5}$$

3. RESULTS AND DISCUSSIONS

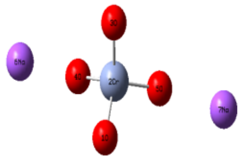
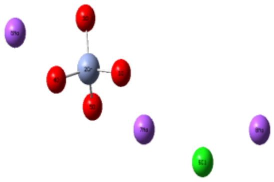
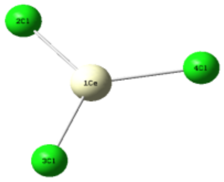
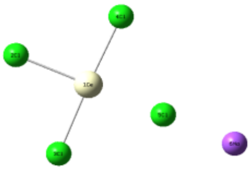
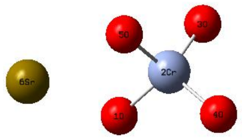
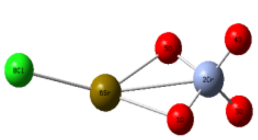
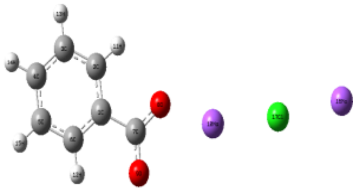
The molecular structures of the inhibitors are presented in Figure 1 which shows the composition and numbering of atoms in the compounds, and also the structures obtained in the presence of a NaCl molecule.

In these optimized structures, the partial charges of each atom are associated with areas that are likely to adhere to the metal surface. Although there are many different methods in the calculation of partial charges, Mulliken population analysis, one of the most common methods, was preferred in this study.

In Figure 2, the calculated Mulliken charges in the gas and aqueous phases on the atoms of the optimized structures of the compounds were compared with those of including a NaCl molecule.

From the examination of the neutral forms of the inhibitors in Figure 2, it is understood that the highest negative charges of Na_2CrO_4 molecule are located on oxygen atoms (-0.640 and -0.641), respectively. On the other hand, as expected, the highest positive charges belong to Sr, Ce, and Na ions (1.733, 1.457, and 0.952) which are the cations of all compounds, respectively. In general, it is seen that the calculated charges in the aqueous phase are higher than those in the gas phase.

The contour plots of frontier molecular orbitals, HOMO and LUMO, obtained for neutral forms of the compounds in aqueous phase and in the presence of a NaCl molecule are presented in Figure 3.As exemplified in this figure, the HOMO orbitals of both inhibitors are mainly distributed around the horizontal part, which consists of Cr, Ce and O atoms, whereas the LUMO orbitals are located on O and Sr atoms and benzene ring. Due to their inherent

Inhibitor	Neutral	NaCl-added
Na_2CrO_4		
$CeCl_3$		
$SrCrO_4$		
$C_7H_5NaO_2$		

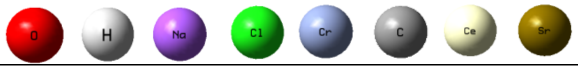
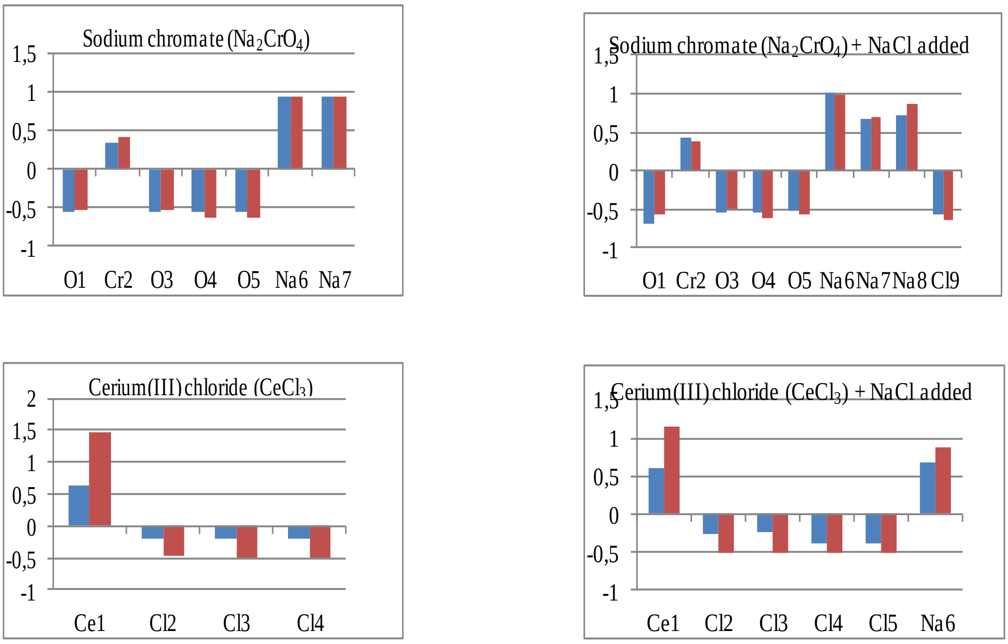


Figure 1. Optimized structures of the compounds in their neutral form and with the addition of NaCl in the aqueous phase



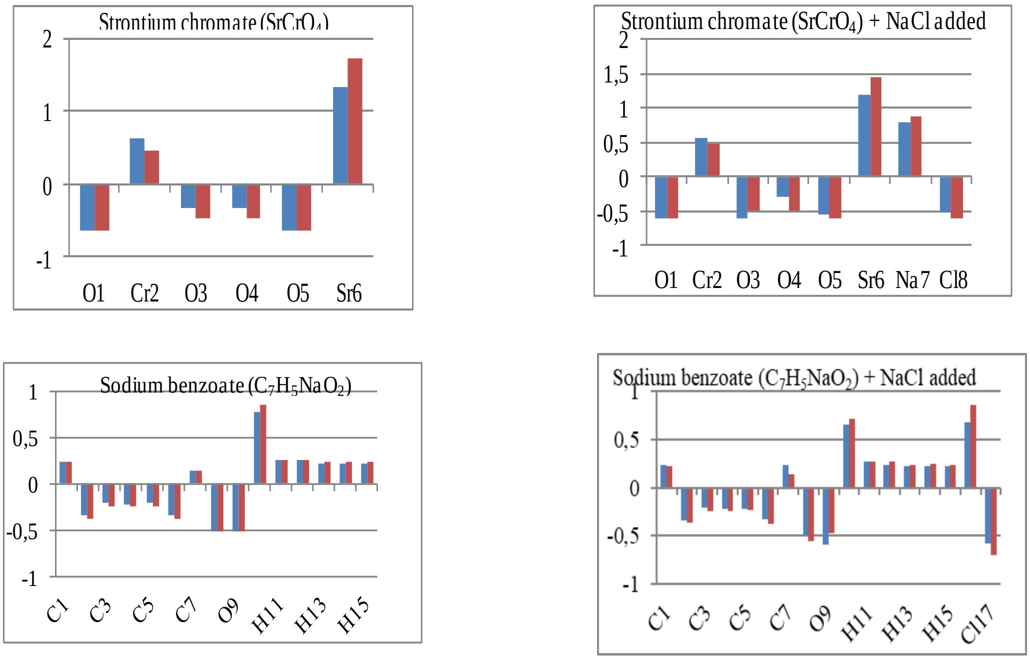


Figure 2. Net Mulliken charges on each atom of the compounds in gas and aqueous phases

reactivity, these sites exhibit the strongest affinity for the metal surface and are therefore the most likely adsorption sites.

E_{HOMO} value is an indicator of the ability of the compound to give electrons. This energy is often considered as a measure of the electron donating ability of a molecule to an appropriate acceptor molecule of vacant, low-energy electron orbital. Thus, high values of E_{HOMO} are related to easier adsorption on the metal surface and better inhibition efficiency. Conversely, the LUMO energy is related to the molecule's propensity to accept electrons from the metal surface. The lower the energy of this molecular orbital, the more readily the molecule will accept electrons (Abdallah et al., 2021; Abdellattif et al., 2021; Gece, 2008; Zhang et al., 2021).

A diminished energy gap (ΔE) between the frontier molecular orbitals is indicative of enhanced chemical reactivity and, consequently, superior inhibition performance.Such frontier molecular orbital interactions result in high adsorption of theinhibitors onto the metal surface. Table 1 summarizes the values obtained for derived quantum chemical descriptors.

When the data for neutral forms of the compounds is examined in the Table 1, no direct correlation between the calculated quantum chemical parameters and experimental corrosion rates and polarization resistances could be found in the gas and aqueous phases. According to experimental results, Na_2CrO_4 stands out as the best corrosion inhibitor, followed by $SrCrO_4$, $CeCl_3$ and $C_7H_5NaO_2$, respectively. For this reason, the highest E_{HOMO} value and the lowest E_{LUMO} and ΔE values are expected to belong to Na_2CrO_4 compound. However, according to the results in the gas phase, the lowest E_{LUMO} (-3.060 eV) and ΔE (3.764 eV) values belong to $SrCrO_4$ and the highest E_{HOMO} value (-6.062 eV) belong to Na_2CrO_4. In other words, experimental and theoretical findings are compatible only for the gas phase in terms of the E_{HOMO} parameter.

A comparable pattern emerges when examining the dipole moment values.The compound with the lowest (0.003 D) dipole moment is Na_2CrO_4, whereas $SrCrO_4$ has the highest (14.934 D). On the other hand, according to the data related to the aqueous phase, the highest E_{HOMO} value (-6.367 eV) was found for Na_2CrO_4, and the lowest E_{LUMO} (-2.028 eV) and ΔE (4.822 eV) values were found for $SrCrO_4$ and $CeCl_3$, respectively. Again, the dipole moment is the highest (25.523 D) for $SrCrO_4$. Therefore, experimental and theoretical data are accordant only with the E_{HOMO} parameter in the aqueous phase.

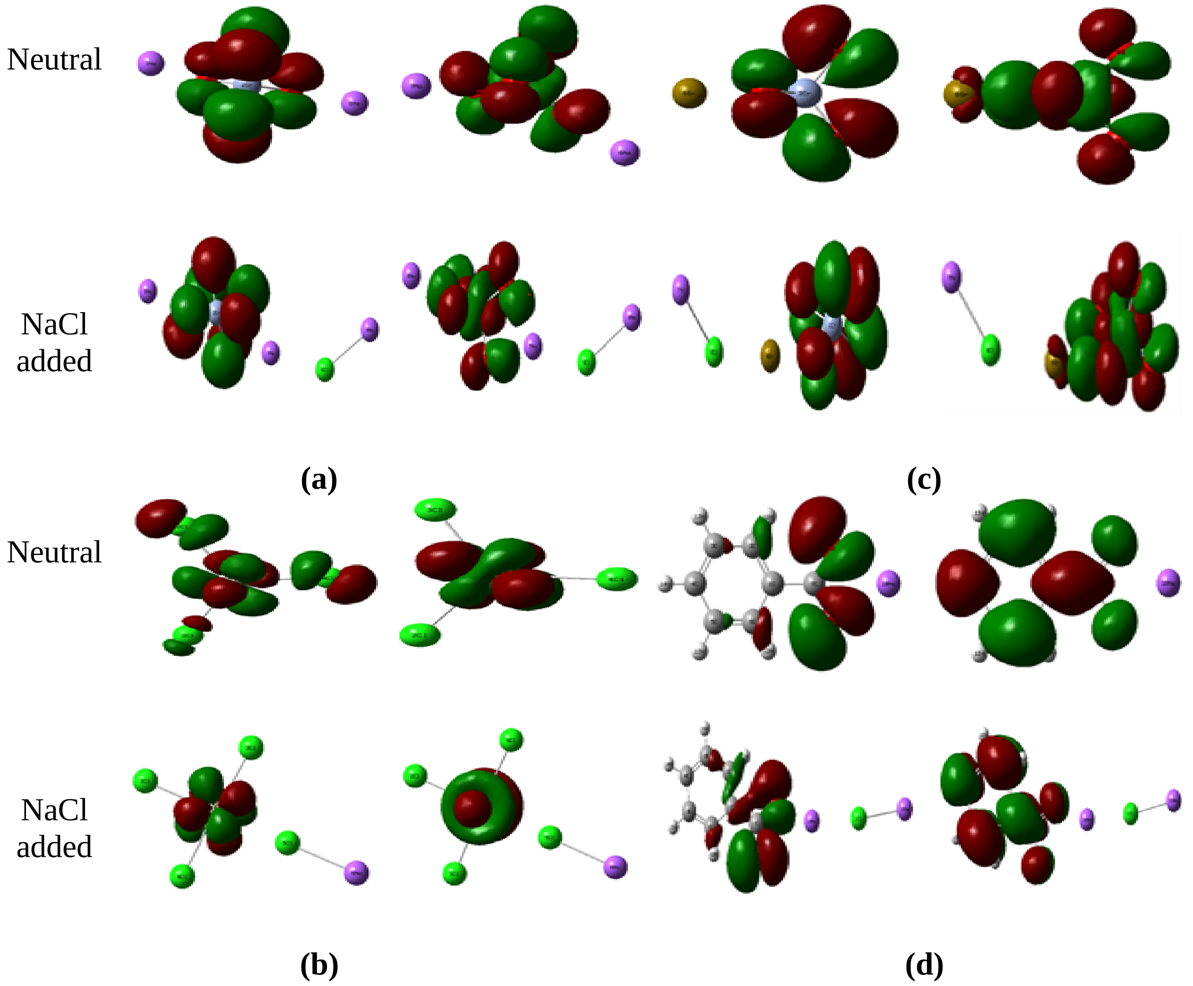


Figure 3. HOMO-LUMO contour plots of (a) Na_2CrO_4, (b) $CeCl_3$, (c) $SrCrO_4$ and (d) $C_7H_5NaO_2$ in aqueous phase (Left: HOMO, right: LUMO)

Table 1. Quantum chemical parameters calculated for the studied compounds in neutral form and in the presence of a NaCl molecule.

		Neutral				NaCl added			
Parameter	Phase*	Na_2CrO_4	$CeCl_3$	$SrCrO_4$	$C_7H_5NaO_2$	Na_2CrO_4	$CeCl_3$	$SrCrO_4$	$C_7H_5NaO_2$
E_{HOMO} (eV)	G	-6.062	-7.727	-6.824	-6.300	-6.606	-6.901	-7.122	-6.775
	A	-6.367	-6.860	-6.768	-6.549	-6.522	-6.473	-6.800	-6.285
E_{LUMO} (eV)	G	-1.628	-3.033	-3.060	-1.571	-2.040	-2.289	-2.474	-1.224
	A	-1.479	-1.946	-2.028	-1.117	-1.632	-1.519	-1.952	-0.979
ΔE (E_L-E_H) (eV)	G	4.434	4.694	3.764	4.729	4.566	4.612	4.648	5.551
	A	4.888	4.822	4.832	5.432	4.890	4.954	4.848	5.306
μ (D)	G	0.003	0.108	14.934	5.595	9.220	9.655	8.036	3.610
	A	15.039	0.261	25.523	7.051	9.761	24.279	34.338	22.828
χ (eV)	G	3.845	5.380	4.942	3.935	4.323	4.595	4.798	3.998
	A	3.923	4.357	4.444	3.833	4.077	3.996	4.376	3.632
η (eV)	G	2.217	2.347	1.882	2.364	2.283	2.306	2.324	2.775
	A	2.444	2.411	2.416	5.432	2.445	2.477	2.424	2.653
ω (eV)	G	3.334	6.166	6.488	3.275	4.092	4.578	4.952	2.880
	A	3.148	3.936	4.087	2.704	3.399	3.223	3.949	2.486
Corrosion rate (mdg)		1.6	2.3	1.7	3.0				

*G, gas phase (ε = 1.0); A, aqueous phase (ε = 78.5)

When the hardness (η) values are examined, the best results in the gas phase are obtained with the $SrCrO_4$ compound, since low hardness provides high inhibition efficiency. It was observed that $CeCl_3$ and Na_2CrO_4 compounds gave good results in the aqueous phase. The electrophilicity index (ω) quantifies the degree to which a molecular system stabilizes upon accepting an electron from its surroundings. A higher ω value signifies a stronger propensity for electron acceptance, thereby characterizing a compound as a potent electrophile.A corrosion inhibitor is expected to be a good nucleophile rather than being an electrophile. Best values were obtained for $SrCrO_4$ in the aqueous phase. In accordance with Sanderson's principle of electronegativity equalization (Szentpály, 1991),compounds characterized by lower initial electronegativities exhibit a diminished propensity for rapid electronegativity equilibration. This kinetic hindrance translates to heightened chemical reactivity, thereby conferring superior inhibition efficiency. Similar results were obtained with no correlation in electronegativity (χ) values.

In the examination of these compounds in the presence of NaCl in Table 1, interesting correlations are observed between the quantum chemical parameters calculated in the gas and aqueous phases and the experimental data. As expected, the highest E_{HOMO} value (-6.606 eV) was found for the gas phase Na_2CrO_4. The lowest E_{LUMO} values were found for the SrCrO4 in both gas and aqueous phase (-2.474 eV and -1.952 eV) respectively, while the lowest ΔE values were found for Na_2CrO_4 in the gas phase (4.566 eV) and $SrCrO_4$ in the aqueous phase (4.848 eV). Therefore, for the gas phase calculations in the presence of NaCl, it was concluded that the E_{HOMO} and ΔE parameters for the Na_2CrO_4 are in agreement with the experimental data. In terms of dipole moments, no such correlation was found for either gas or aqueous phase. On the other hand, the theoretical results of the aqueous phase calculations in the presence of NaCl indicate that the best inhibitor should be the $SrCrO_4$. This is not surprising because it has been shown in other studies that the theoretical approach at the core of DFT calculations somewhat miscalculates the frontier molecular orbital energies of strontium containing compounds, especially energy gap values (Errandonea et al., 2015). Consequently, it has been confirmed by the theoretical methods used in this study that the compounds containing chromate are more effective as inhibitors than the others.

4. CONCLUSION

A theoretical study using density functional theory calculations was carried out in order to better understand the properties of Na_2CrO_4, $CeCl_3$, $SrCrO_4$, $C_7H_5NaO_2$ compounds which prevent the corrosion of aluminium in NaCl environment. It was found that there was no direct correlation between the inhibition properties for the neutral forms of the compounds and the electronic structure parameters. However, in the presence of a NaCl compound, EHOMO and ΔE parameters were found to be associated with its efficiency for Na_2CrO_4, being the best inhibitor according to experimental results. In general, the theoretically calculated parameters revealed that the compounds containing chromate in their structure are more effective in protecting the metal from corrosion. The results of the aqueous phase which predict that the $SrCrO_4$ compound would be more effective in preventing corrosion, suggested that such compounds should be investigated with different theoretical methods, i.e., multireference DFT methods, which represent a class of electronic structure approaches that aim to combine the strengths of traditional DFT with multireference wave function theory methods. Although such methods are computationally more demanding, degeneracy or near-degeneracy problems in standard DFT approximations make it necessary to overcome the difficulties in accurately describing the electronic structure and properties of the studied compounds.

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