Original Research Article

DFT Calculations of Mesembryanthemum nodiflorum compounds as Corrosion Inhibitors of Aluminum

Abstract

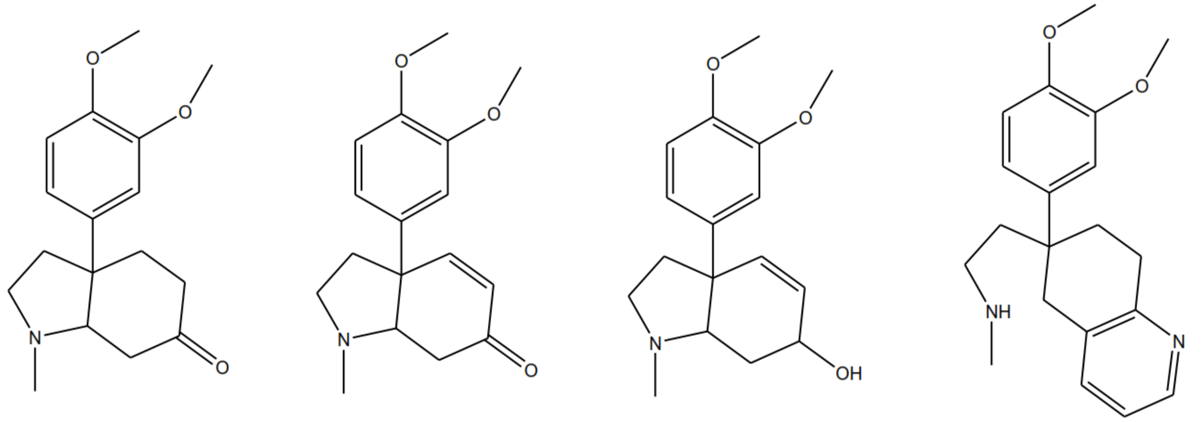
DFT calculations have been performed on Mesembrine, Mesembrenone, Mesembrenol and Tortuosamine, using G03 program with complete optimization of geometries. Quantum parameters and thermodynamic Gibbs function have been used to investigate the efficiency of the corrosion inhibition of each compound. Mesembrenone has been found to have very good corrosion inhibition efficiency as compared to the other compounds. Quantum parameters and frontier orbitals together with calculated thermodynamic function ∆G for adsorption show spontaneous physical adsorption of the Mesembrenone on aluminum.

Keywords: DFT, Aluminum, Inhibitors, Mesembryanthemum nodiflorum, Corrosion

1- Introduction

Extracts of several natural products of plant origin, containing organic compounds with multiple bonds and having the hetero atoms (O, N, S, and P), are useful and widely used as effective corrosion inhibitors [1-6]. Aluminum is one of the most important metals and has been used in a wide range of alloys [7]. It is the second to iron in terms of production and consumption. This is attributed to the following distinguished Aluminum characteristics: low atomic mass, being inexpensive, environmentally friendly, pleasing appearance, and its industrial application [8,9]. This area of research is of much importance due to naturally friendly, plant results are readily available, renewable sources of materials and inexpensive. Plant products are organic in nature and some of the constituents including tannins (organic and amino acids) alkaloids, and pigments are known to exhibit inhibiting action. Therefore, plant extract has become important because it is a rich source of natural products which can be extracted by simple methods at low cost [10]. Recently, leaf extract of Mesembryanthemum nodiflorum has been reported as natural and green inhibitors for aluminum corrosion [11].

The leaf extract of Mesembryanthemum nodiflorum is organic and contains four major chemical constituents, which are classified as indole alkaloids (Figure 1), namely, Mesembrine, Mesembrenone, Mesembrenol and Tortuosamine.



Mesembrine Mesembrenone Mesembrenol Tortuosamine

Figure 1: Structure of major chemical constituent's indole alkaloids in the Mesembryanthemum nodiflorum

In this study, the major compounds have not been isolated, instead the whole plant extract has been dealt with. Moreover, the quantum chemical parameters and molecular dynamics simulations have been performed to investigate the effect of Mesembryanthemum nodiflorum indole alkaloids as corrosion inhibitors of aluminum using density functional theory DFT to find their inhibitors activity. Furthermore, these theoretical calculations have been used to investigate the efficiency of each compound as a corrosion inhibitor of Al.

2- Computational

The molecules were optimized using density functional theory DFT/B3LYP using 6-31G (d) main set (Gaussian 03, Revision B.03) [12], the corresponding geometries of all molecules under investigation were optimized without any geometric constraints for full geometric optimizations [13]. No imaginary frequency was found, indicating minimal energy structures. Self- consistent reaction field (SCRF) was used to perform calculations in the presence of a solvent by open up an inhibitor cavity within the solvent reaction field [14a]. To accelerate the calculation process, PM3 semi-empirical method was used in optimizing the molecular structures of the indole compounds. After that, re-optimizations for the structures were repeated by DFT/B3LYP method. This method is a Becke's three-parameter functional (B3) and including mixture of Hartree – Fock (HF) wave function and DFT energy calculation that adds exchange term correlation in DFT terms together with the functional of Lee, Yang, and Parr (LYP) [15-17].

E_{HOMO} and E_{LUMO} (the energy of the frontier molecular orbitals) [18], the energy gap (ΔE), the hardness (η), the softness (σ), the fraction of the electron transferred (ΔN), the electrophililcity index (ω), and the ΔG of adsorption of inhibitors on aluminum have been calculated for these compounds. The absolute electronegativity (X), the absolute hardness (η) of the inhibitor, the softness (σ), and the electrophililcity index (ω) are given as follow [19]:

$$X = (I+A)/2 \qquad \eta = (I-A)/2 \qquad \sigma = 1/\eta \qquad \omega = \mu^2/2\eta$$

where the ionization potential (I) and the electron affinity (A) are calculated by the following relations according to molecular orbital theory [18]:

$$I = -E_{HOMO} \quad \text{and} \quad A = -E_{LUMO}$$

and μ represents the chemical potential and is assumed to be equal to the negative of the X [18a]. ω was proposed by Parr [19] as a measure of the electrophilic power of a molecule.

Herein, electrons flow from lower X (inhibitor) to higher X (metal) until the chemical potentials become equal. ΔN has been calculated from the obtained values of X and η, from the inhibitor to metallic surface as follow [20, 21]:

$$\Delta N = (X_{metal} - X_{inh}) / 2 (\eta_{metal} + \eta_{inh})$$

where X_{metal} and X_{inh} denote the absolute electronegativity and η_{metal} and η_{inh} denote the absolute hardness of metal and the inhibitor, respectively. The difference in electronegativity drives the electron transfer, and the sum of the hardness parameters acts as resistance [19].

3- Results and Discussion

The compounds under investigation are Mesembrine, Mesembrenone, Mesembrenol and Tortuosamine [11]. The calculated results of the energies of frontier molecular orbitals for the inhibitors are shown in Table 1.

Table 1. Calculated HOMO – LUMO energies of the inhibitors by the DFT method

Compound	E_{HOMO} (eV)	E_{LUMO} (eV)
Al	-5.98^a	0.43^a
Mesembrine	-5.54	-0.40
Mesembrenone	-5.41	-1.60
Mesembrenol	-5.16	-0.22
Tortusamine	-5.31	-0.59

a from Ref. [25]

The chemical reactivity is a function of the interaction between the HOMO and LUMO levels of the reacting species [22] based on the frontier molecular orbital (FMO) theory. The energy of the highest occupied molecular orbital E_{HOMO} shows the electron donating ability of the molecule. High value of E_{HOMO} indicates a tendency of the molecule to donate electrons to the appropriate acceptor molecule of low empty molecular orbital energy [23]. On the other hand, E_{LUMO} represents the energy of the lowest unoccupied molecular orbital and indicates the ability of the molecule to accept electron [24]. Consequently, the lower the value of E_{LUMO}, the more the molecule accepts electrons. Therefore, when increasing HOMO and decreasing LUMO the binding ability of the inhibitor to the metal surface increases. The values of the energies of HOMO and LUMO for metal- Al [25] have been compared to the calculated values calculated for Mesembryanthemum nodiflorum major compounds to determine the type of the interaction. LUMO - HOMO gaps for the interaction aluminum-inhibitors (given in Table 2), show that aluminum will act as a Lewis base while the inhibitor Mesembrenone act as a Lewis acid. So, aluminum utilizes the HOMO orbital to initiate the reaction with LUMO orbital of Mesembrenone. The interaction has a certain amount of ionic character because the values of $LUMO_{inh} - HOMO_{Al}$ gap approximately fall between 4 to 5 eV. Strong covalent bond can be expected only if the $LUMO_{inh} - HOMO_{Al}$ gap is approximately zero [26].

The inhibitors Mesembrine, Mesembrenol and Tortuosamine act as a Lewis base and aluminum acts as Lewis acid (Table 2). In this case Mesembrenone act as cathodic inhibitors while the other inhibitors act as anodic inhibitors.

Table 2. HOMO – LUMO gap interaction of Al- inhibitor by the DFT method

Inhibitors	$LUMO_{inh} - HOMO_{Al}$ (eV)	$LUMO_{Al} - HOMO_{inh}$ (eV)
Mesembrine	5.58	5.11
Mesembrenone	4.38	4.98
Mesembrenol	5.75	4.73
Tortusamine	5.39	4.88

In Table 3, the energy separation, $\Delta E_{gap} = (E_{LUMO} - E_{HOMO})$, is an important parameter and it is a function of the reactivity of the inhibitor molecule towards the adsorption on metallic surface. As ΔE_{gap} decreases, the reactivity of the molecule increases leading to an increase of the inhibitor efficiency [27]. The effectiveness of Mesembryanthemum nodiflorum compounds under investigation as inhibitors has been further addressed by evaluating the global reactivity parameters. The electronegativity, X, the global chemical hardness, η, the global softness, σ, the fraction of electrons transferred, ΔN, and the electrophililcity, ω, are shown in Table 3.

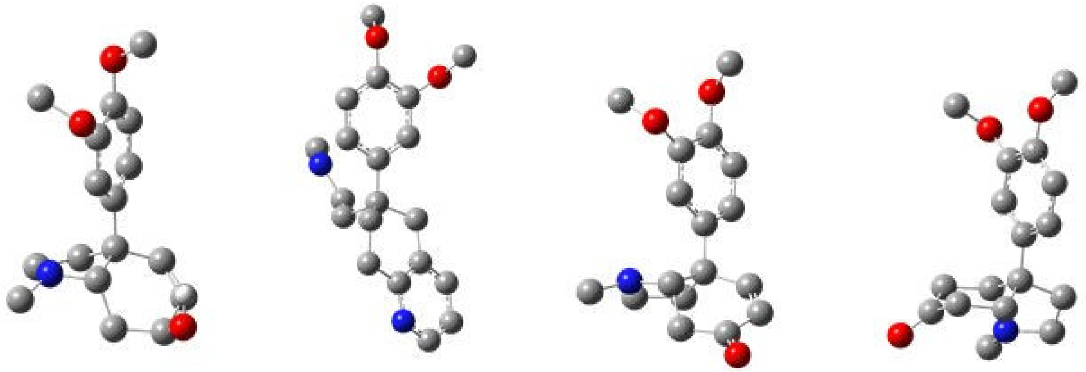
Table 3. Calculated quantum chemical parameters for the inhibitors

Quantum parameters	**Mesembrine**	**Mesembrenone**	**Mesembrenol**	**Tortusamine**
E_{HOMO} (eV)	-5.54	-5.41	-5.16	-5.31
E_{LUMO} (eV)	-0.40	-1.60	-0.22	-0.59
ΔEgap	5.14	3.81	4.94	4.72
I (eV)	5.54	5.41	5.16	5.31
A (eV)	0.40	1.60	0.22	0.59
X (eV)	2.97	3.50	2.69	2.95
η (eV)	2.57	1.90	2.47	2.36
σ	0.38	0.52	0.40	0.42
ΔN	0.02	0.03	0.04	0.02
ω	1.72	3.22	1.47	1.84

$X_{Al} = 3.20$, $\eta_{Al} = 2.77$

Hard-Soft-Acid–Base (HSAB) terms have been used to discuss the bonding tendencies of the inhibitors towards the metal atom and the frontier-controlled interaction concepts [28, 29]. The principle of HSAB says that hard acids prefer to co-ordinate to hard bases and soft acids prefer to co- ordinate to soft bases. Metal atoms are known as soft acids [30]. Therefore, hard molecules have a high HOMO–LUMO gap and soft molecules have a small HOMO–LUMO gap [31], and thus soft bases inhibitors are the most effective ones for metals [27]. So, Mesembrenone which has the lowest energy gap and the highest softness, is expected to have the largest inhibition efficiency as compared to Mesembrine, Mesembrenol and Tortuosamine. This could also be confirmed by calculating another quantum chemical parameter, σ, which measures the softness of the molecule and so its reactivity. In Table 3, it is shown that Mesembrenone has the larger σ values than the others. Table 3 also presents the hardness values, η, obtained for the inhibitors. Herein, the Mesembrine, Mesembrenol, and Tortuosamine have the larger hardness values than Mesembrenone. This tendency is the reverse with the results of softness. Therefore, the inhibitor with the smallest value of global hardness (hence the highest value of global softness) is the best. This is because a soft molecule is more reactive than a hard molecule [32].

The fraction of transferred electrons (ΔN) is also calculated and tabulated in Table 3. The values of ΔN of Mesembrenone and Mesembrenol are greater than of Mesembrine and Mesembrenone. The electrophilicity index, ω, shows the ability of the inhibitor molecules to accept electrons from aluminum (Table 3). Mesembrenone exhibits the highest electrophilicity value as compared to the electrophilicity values of Tortuosamine, Mesembrine and Mesembrenol; consequently, this observation confirms its high capacity to accept electrons. The observed electrophilicity value for Mesembrenone is attributed to the low E_{LUMO} of Mesembrenone (E_{LUMO}= -1.60 eV) compared to other compounds. That is, aluminum acts as Lewis base while Mesembrenone act as Lewis acids (cathodic inhibitor). Also, the Al atoms can accept electrons from inhibitor molecule to form a coordinated bond (anodic inhibitor). The inhibitor molecule can accept electrons from aluminum atom to form back-donating bonds depending on the orientation of optimized structure of the inhibitor on the spatial (Figure 2). These donation and back-donation processes strengthen the adsorption of Mesembrenone onto the aluminum surface and increase the inhibition efficiency.



Mesembrenol Tortuosamine Mesembrenone Mesembrine

Figure 2: Optimized structure of major chemical constituent's indole alkaloids in the Mesembryanthemum nodiflorum plant without H-atom (for clarity)

The ΔG values for adsorption of the investigated inhibitors on aluminum surface are calculated and given in Table 4.

Table 4. Calculated Δ G (kJ mol^{-1}) values of the investigated inhibitors

Inhibitors	Cathodic Inhibitors	Anodic Inhibitors	Dipole Moment (Debye)
Mesembrine		22.4	2.7
Mesembrenone	-28.8		2.2
Mesembrenol		49.5	1.2
Tortuosamine		24.4	2.9

All compounds show positive ΔG values except Mesembrenone. The difference between physical adsorption and chemical adsorption depends on the magnitude of Gibbs free energy changes [33-35]. For physical adsorption, ΔG value is in the range of 0 to -40 $kJ.mol^{-1}$, whereas for chemical adsorption, ΔG value is in the range of -80 to -400 $kJ.mol^{-1}$. The suggested mechanism for Mesembrenone is physical adsorption because ΔG value is -28.8 $kJ.mol^{-1}$, whereas the other compounds show non-spontaneous process. The measured ΔG value for nodiflorum extract at temperature 298K is -11.5 $KJ.mol^{-1}$, which suggests a physical adsorption [11]. It is difficult to make comparison between the nodiflorum extract [11] and the present theoretical results because performing individual calculations for each compounds.

4- Conclusion

It can be concluded that theoretical calculations gave a good picture about the Mesembryanthemum nodiflorum leaf extract by suggesting that Mesembrenone shows the most inhibition efficiency as compared to the other compounds, because it has low E_{LUMO} that can form a strong interaction with aluminum to act as cathodic inhibitor. Also, the highest electrophilicity of Mesembrenone as compared to the other compounds which represents a measure of the electrophilicity power of the molecule. Also, the energy gap is smallest as compared to the other three compounds indicates the most reactive compound. On addition Mesembrenone has negative Gibbs free energy while other compounds show non-spontaneous Gibbs free energy. The leaf extract shows spontaneous energy which may suggests that is corrosion inhibition mainly from Mesembrenone.

References

[1] Oquzic, E. E., *Mater. Chem. Phys.*, 2006, 99 (2-3), 441.
Uma, K., Rekha, S., *J. Chem. and Pharma. Res.*, 2015, 7 (4),165.
[2] Oquzi, E. E., *Corros. Sci.*, 2007, 4, 1579.
[3] Aror, P., Kuma, S, Sharma, M. K., Muthur, S. P., E., *J. Chem.*, 2007, 4, 450.
[4] Quraishi, M. A., Rafique, M. Z. A., Khan, S., Saxn, N., *J. Appl. Electrochem*, 2007, 37, 1153.

[5] Abio, O. K., Ofork, N. C., Ebens, E. E., Nwinuka, N. M., *Anti-Corros. Methods Mater.*, 2007, 4, 219.

[6] Oguzi, E.E., Onuoha, G. N., Ejik, E. N., *Pigment and Resin Technol.*, 2007, 30, 44.

[7] Rajendran, S., Manivanna, M., Sahayaraj, J. W., Selvi J. A., *J. SAEST.*, 2006, 41, 63.

[8] Oguzi, E. E., Okolu, B. N., Ogukwe, C. E., Unaegb, C., *Mater Lett.*,2006, 60, 3376.

[9] Beulah, J. R., Thavamani, E. R., Jeyaraj, T., *J. Chem. and Pharma. Res.*, 2012, 4 (7), 3541-3549.

[10] Lakshmi, P. K, Shameela, R., Subramaniya, A., *J. Chem. and pharma. Res.*, 2012, 4 (1), 337 – 347.

[11] Al Shboul, T., Jazzazi, T., Tareq T. Bataineh, T., Al-Qudah, M., Alrawashdeh, A. *Jord. J. Chem.*,2014, 9 (3), 149-158.

[12] Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Montgomery, J. A., Vreven, Jr., T., Kudin, K. N., Burant, J. C., Millam, J. M., Iyengar, S. S Tomasi, J., Barone, V., Mennucci, B., Cossi, M., Scalmani, G., Rega, N., Petersson, G. A., Nakatsuji, H., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Klene, M., Li, X., Knox, J. E., Hratchian, H. P., Cross, J. B., Adamo, C., Jaramillo, J., Gomperts, R., Stratmann, R. E., Yazyev, O., Austin, A. J., Cammi, R., Pomelli, C., Ochterski, J. W., Ayala, P.Y., Morokuma, K., Voth, G. A., Salvador, P., Dannenberg, J. J., Zakrzewski, V. G., Dapprich, S., Daniels, A. D., Strain, M. C., Farkas, O., Malick, D. K., Rabuck, A. D., Raghavachari, K. , Foresman, J. B., Ortiz, J. V., Cui, Q., Baboul, A.G., Clifford, S., Cioslowski, J., Stefanov, B. B., Liu, G., Liashenko, A., Piskorz, P., Komaromi, I., Martin, R. L., Fox, D. J., Keith, T., Al-Laham, M. A., Peng, C. Y., Nanayakkara, A., Challacombe, M., Gill, P. M. W., Johnson, B., Chen, W., Wong, M. W., Gonzalez, C., and Pople, J. A., *Gaussian*, Inc., Pittsburgh PA, 2003.

[13] Khalil, S. M., *Z. Naturforsch.*, 2008, 63a, 42.

[14] a) Wong, M. W., Frisch, M. J., Wiberg, K. B., *J. Am. Chem. Soc.*, 1991, 113, 4776.
b) Khalil, S. M., Ali-Shattle, E. E., Nozha, M. A., Z. Naturforsch., 2013, 68a, 581.

[15] Stephens, P.J., Devlin, F.J., Chabalowski, C.F., Frisch, M.J., *J. Phys. Chem.*, 1994, 98, 11623‑11627.

[16] Becke, A.D., *J. Chem. Phys.*, 1993, 98, 5648‑5652.

[17] Lee, C., Yang, W., Parr, R.G., *Phys. Rev. B*,1988, 37,785.

[18] Fukui, K., *Angew. Chem. Int. Ed. Engl.*, 1982, 21, 801.

[19] Lesar, I. Miosev, *Chem. Phys.*, 2009, 483, 198.
Parr, R. G., Szentpaly, L. V., Liu, S., *J. Am. Chem. Soc.*, 1999, 121, 1922, R. G. Parr, R.

[20] Donnelly, A., Levy, M., Palke, W. E., *J. Chem. Phys.*, 1978, 68, 3081.

[21] Li, X., Deng, S., Fu, H., Li, T., *Electrochem. Acta.*, 2009, 54, 4089.

[22] Musa, A. Y., Kadhum, A. H., Mohamad, A. B., Rohoma, A. B., Mesmari, H., *J. Mol. Struct.*, 2010, 969, 233.

[23] Gece, G., Bilgic, S., *Corros. Sci.*, 2009, 51, 1876.

[24] Ahamd, I., Prasad, R., Quraishi, M. A., *Corros. Sci.*, 2010, 52, 1472.
[25] Lide, D. R., *CRC Handbook of Chemistry and Physics*, 88th ed., 2007-2008.
[26] Klopman, G., *J. Am. Chem. Soc.*, 1968, 90, 233.
Jensen, W. B., *Chem. Rev.*, 1978, 78, 1.
[27] Awad, M. K., Mustafa, M. R., Abo Elnga, M. M., *J. Mol. Struct.*, (Theorem), 2010, 959, 66.
[28] Pearson, R. G., *Inorg. Chem.*, 1988, 27, 734.
[29] Koch, E., *Propellants Explos. Pyrotech.*, 2005, 30, 5.
[30] Obi-Egbedi, N.O., Obot, I. B., El-Khaiary, M.I., *J. Mol. Struct.*, 2011, 1002, 86.
Mutombo, P., Hackerman, N., *Anti-Corros. Meth. and Mat.*, 1998, 45, 413.
[31] Li, X., Deng, S., Fu, H., Li, T., *Electrochem. Acta.*, 2009, 54, 4089.
[32] Arslan, T., Kandemirli, F., Ebenso, E. E., Love, I., Alemu, H., *Corros. Sci.*, 2009, 51(35).
[33] Singh, K. P., Malik, A., Sinha, S., Ojha, P., *J. Hazard Mat.*,2008, 150, 626.
[34] Srihan, V., Das, A., *Desalination*, 2008, 225, 220.
[35] Humpola, P. D., Odetti, H. S., Fertitta, A. F., Vicente, J. L., *J. Chil. Chem. Soc.*, 2013,58, 1541.