Journal of Engineering Research and Applied Science
Available at www.journaleras.com
Volume 13 (2), December 2024, pp 2608-2614
ISSN 2147-3471 © 2024

Synthesis, Characterization, Spectroscopic, DFT and Adsorption of Ca^{+2} Ion Studies of Monoacetin

Ozlem Kuran, Yunus Kaya*

Department of Chemistry, Faculty of Engineering and Natural Sciences, Bursa Technical University, Bursa, Turkey.

Accepted 28 November 2024

Abstract
In this study, theoretical and experimental studies of monoacetin (M-GLA) molecule formed because of the reaction of glycerol and acetic acid were investigated. M-GLA molecule was obtained because of the reaction of acetic acid and glycerin. Characterization of the molecule was performed using IR and UV visible region spectroscopy. M-GLA molecule was optimized and energy and frequency values were calculated using DFT B3LYP method and Gaussian package program using 6-31G(d,p) basis set. In a normal frequency calculation, all frequency values obtained are expected to be positive. All frequency values being positive means that all vibration and rotational movements of the molecule are optimized to a minimum. FT-IR and UV-VIS spectra of M-GLA molecule were compared experimentally and theoretically. In addition, interaction of M-GLA molecule with Ca+2 ion was investigated and binding energy was calculated as -5.42 eV.

Keywords: *Monoacetin, DFT, FTIR, UV Vis.*

1. Introduction

The most widely used building material in the world is concrete [1]. The water/cement ratio is of great importance in cementitious systems. It is known that the use of too much water causes a decrease in the strength of the cement mortar, while the use of too little water reduces the workability of the cement mortar [2]. The most effective way to improve the properties of cementitious materials is through the use of additives [3]. The use of superplasticizing admixtures in concrete production to produce concretes with high strength and performance has been a turning point in the construction industry. Superplasticizers reduce both the water/cement ratio and the amount of cement used [4]. Thus, it has been an important invention in reducing the consumption of both energy and natural resources. Calcium ions are very common and important in cementitious systems. The conformational properties of superplasticizers at the cement interface, the interaction between the negatively charged groups of superplasticizers and calcium (Ca^{+2}) ions are strongly influenced by Ca^{+2} ions [5]. This results in delayed setting time and increased dispersibility due to hydrogen bonds formed by hydroxyl and O^{-2} structures at the cement interface [6].

Deng and others (2024), The effects of the use of alcohol amine modified with water reducing agent (triethanolamine (TEA) and diethanol monoisopropanolamine (DEIPA)) in cementitious system were investigated. As a result, they explained that the addition of alcohol amine modified with water-reducing agent to cementitious materials greatly improved the fluidity of mortar, the modified TEA could reduce the calcium-silicon ratio of hydration products more uniformly, and the modified DEIPA could further improve the hydration process [3].

In this study, the modified additive consisting of glycerol and acetic acid was obtained by esterification polymerization. The esterification polymerization is shown in Figure 1. Optimization and frequency calculations of the resulting product were performed with DFT/B3LYP method, 6.31G (d, p) basis set and absorption energies with Ca^{+2} ion was calculated.

2. Material and Method

2.1. Material

Glycerin ($C_4H_8O_3$, 99%; Aldrich), acetic acid (CH_3COOH, 99%; Aldrich), sulfuric acid (H_2SO_4, 98%; Aldrich).

*Corresponding author: yunus.kaya@btu.edu.tr

2.2. Method

In this study, glycerin (18.27 ml, 0.25 mol), acetic acid (39.03 ml, 0.31 mol) and sulfuric acid (1.33 ml, 0.025 mol) are taken into a 250 ml flask. The reaction takes place at 80 ˚C for 3 hours under a reflux cooler. The reaction scheme is shown in Figure 2.

2.3. Theoretical Study

The synthesized modified dopant was calculated using density functional theory (DFT/B3LYP) and the 6,31 G(d,p) basis set. Frequency calculations of the molecule were also performed and proved to be calculated in the correct geometry. The most probable geometrical structures are shown in Figure. Theoretical frequency and UV-VIS calculations of the molecule were also performed and compared with experimental data. The interaction of Ca^{+2} ion with the dopant was also calculated and the binding energy was calculated. Gaussian 09 program was used in all calculations.

3. Result and Discussion

Monoacetin (M-GLA) was obtained by the reaction of acetic acid and glycerol catalyzed by sulfuric acid at 80 °C for 3 hours under a reflux cooler. The obtained molecule was elucidated by FTIR and UV-VIS spectroscopic techniques.

3.1 Optimized Molecular Structure

The M-GLA was modeled and calculated using the DFT/B3LYP method and the 6-31(d,p) basis set. Frequency calculations were also performed using the same method and basis set. The optimized structure is given in Figure 3.

After optimizing the synthesized M-GLA molecule, bond length, bond angle and dihedral angles were calculated theoretically (Table 1).

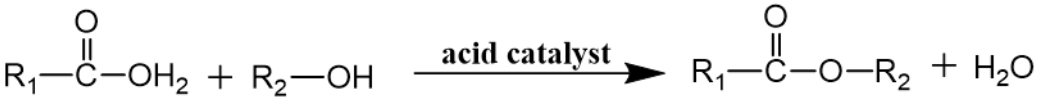

Figure 1. Esterification reaction

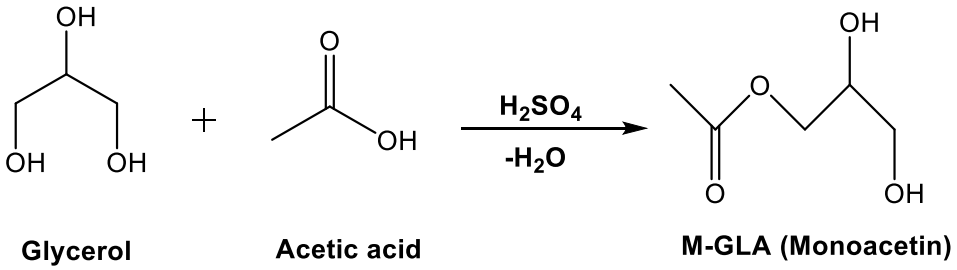

Figure 2. Reaction scheme

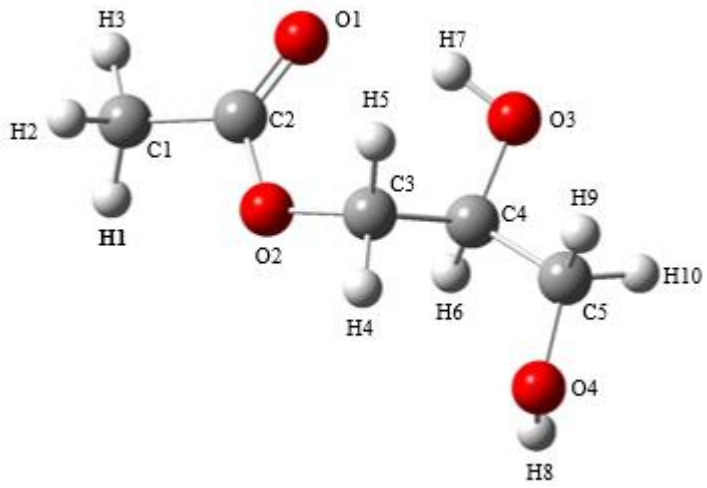

Figure 3. Optimized structure of M-GLA

Table 1. Calculated bond length, bond angles and dihedral angles of the M-GLA molecule.

Bond Length (Å)	**6-31G(d,p)**	**Bond Angle (°)**	**6-31G(d,p)**
C1-C2	1.50774	C1-C2-O1	124.3
C2-O1	1.21920	C1-C2-O2	111.3
C2-O2	1.34219	O1-C2-O2	124.4
O2-C3	1.45563	C2-O2-C3	118.5
C3-C4	1.53028	O2-C3-C4	114.7
C4-O3	1.41082	C3-C4-O3	113.9
C4-C5	1.53629	C3-C4-C5	109.7
C5-O4	1.42109	C4-C5-O4	113.0
O3-C4-C5	106.1		
Dihedral Angle (°)			
C1-C2-O1-O2	179.2		
O1-C2-O2-C3	7.10		
O2-C3-C4-O3	88.0		
O2-C3-C4-C5	-153.3		
C3-C4-C5-O4			61.92
O3-C4-C5-O4	-174.7		

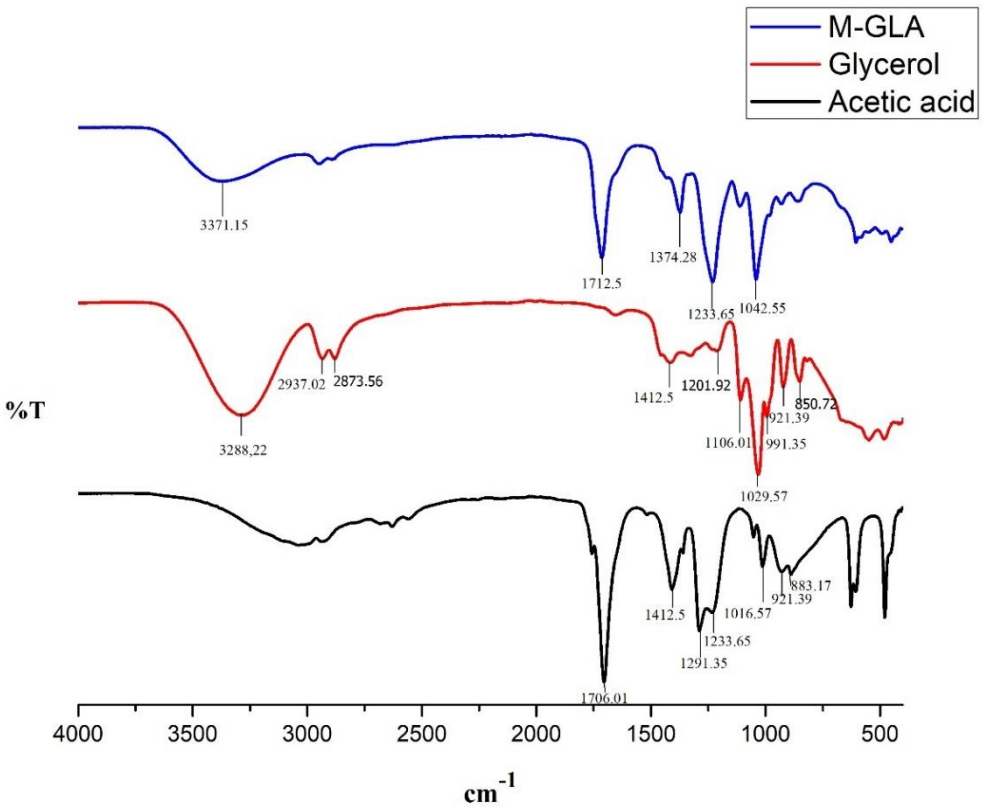

Figure 4. Experimental FT-IR spectra

3.2 Infrared spectroscopy

3.2.1 Study of the infrared spectroscopy of the precursors

The M-GLA additive obtained as a result of esterification polymerization was illuminated by FT-IR (Figure 4) and UV-VIS spectroscopy. When the spectrum of the reacted glycerol was examined, it showed the flat -OH stretching at 3288.22 cm^{-1}, -CH stretching at 2937.02 cm^{-1}- 2873.56 cm^{-1}, -COH bending at 1412.5 cm^{-1}, C-O stretching at 1106.01 cm^{-1}, C-C vibration bands at 991.35 cm^{-1}-921.39 cm^{-1}-850.72 cm^{-1} [7]. When the spectrum of acetic acid is examined, it corresponds to the C=O stretching at 1706.01 cm^{-1}, -CH3 asymmetric stretching at 1412.5 cm^{-1}, -CH3 symmetric stretching at 1233.65 cm^{-1} and -COH bending bands [8]. When the spectrum of M-GLA is examined, it is seen that the flat -OH stretching at 3371.15 cm^{-1} as a result of glycerol losing its hydroxyl group during the reaction and forming water, the C=O stretching of the ester molecules at 1712.5 cm^{-1}, and the band at 1233.65 cm^{-1} shows the C-C(O)-C stretching of the acetate group ester [9].

3.2.2 Theoretical IR Calculations

The optimized structure of the compound for theoretical FT-IR spectra was obtained using the DFT B3LYP method and the Gaussian package program with the 6-31G(d,p) basis set. The same method and basis set were also used to calculate vibrational wave numbers. The vibrational values obtained as a result of frequency calculations were scaled by a factor of 0.958 [10] for the 4000-1700 cm^{-1} range and by a factor of 0.978 [11] for the 1700-400 cm^{-1} range. When the theoretical and experimental IR spectra of the M-GLA molecule (Figure 5) are examined, it is observed that the broad -OH stretching is observed at 3371.15 cm^{-1} in the experimental spectrum, while the sharp -OH stretching is observed at 3518.27 cm^{-1} in the theoretical spectrum, aliphatic -CH stretching is observed at 2956.49 cm-1- 2880.05 cm^{-1} in the experimental spectrum, aliphatic -CH stretching is observed at 2943.5 cm^{-1}- 2803.6 cm^{-1} in the theoretical spectrum, C=O stretching is observed at 1712.5 cm^{-1} in the experimental spectrum, C=O stretching is observed at 1719 cm^{-1} in the theoretical spectrum, the band at 1233.65 cm^{-1} in the experimental spectrum shows the C-C(O)-C stretching of the acetate group ester, and the C-C(O)-C stretching of the acetate group ester is observed at 1271.88 cm^{-1} in the theoretical spectrum. The vibration types and regions found in the experimental and theoretical FT-IR spectra of M-GLA are listed in Table 2.

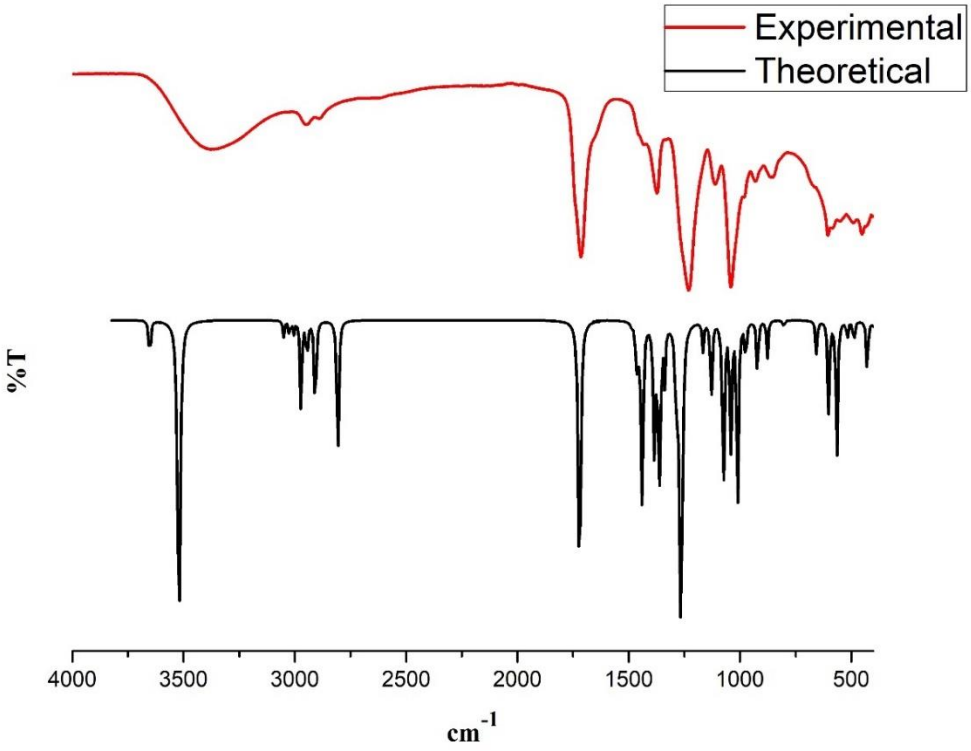

Figure 5. Theoretical and experimental FT-IR spectra of M-GLA

Table 2. Experimental and theoretical vibrational frequencies of M-GLA

Vibration Mode	Group	Experimental	Without Scale	Scale	Intensity
11	γCH, γOH		438	428	18,37
14	γOH		577	564	59,29
15	γCH		615	601	35,49
16	γCO, γCH		671	656	11,87
18	γCO, γCH		897	877	12,51
19	γCO, δCH	921	942	921	20,47
20	γCO, δCH		996	974	15,41
21	γCO, δCH, γOH	1043	1033	1010	89,87
22	δCH		1064	1041	45,37
23	γCH		1068	1045	10,69
24	vCC		1097	1073	68,07
25	γCH	1106	1105	1081	14,57
26	vC-O, vCC	1234	1154	1129	33,62
28	δC=O, δCH, vCO	1272	1294	1266	306,35
30	δCH, δOH		1315	1286	39,83
31	δCH	1374	1369	1339	19,93
32	δCH, δOH		1390	1359	57,27
33	δCH, δOH		1396	1365	40,03
34	δCH		1414	1383	60,71
36	δOH		1471	1439	88,59
37	δCH		1482	1449	10,82
39	δCH		1499	1466	18,57
41	vCO	1719	1796	1721	211,23
42	vCH	2880	2931	2808	66,54
43	vCH	2956	3036	2908	43,06
45	vCH		3075	2946	14,05
46	vCH		3102	2972	32,8
50	vOH	3371	3675	3521	299,58

v: stress, δ: in-plane, γ: out-of-plane bending,

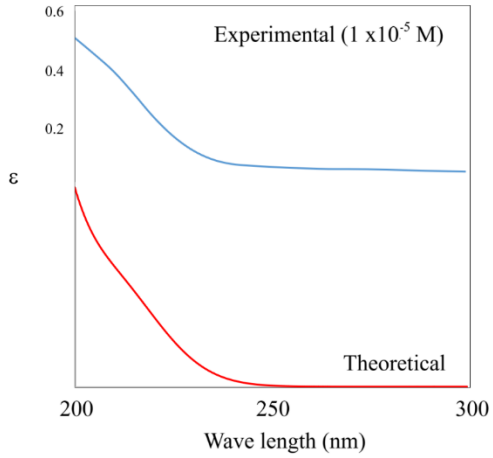

Figure 6. Theoretical and experimental UV-Vis. spectra of M-GLA

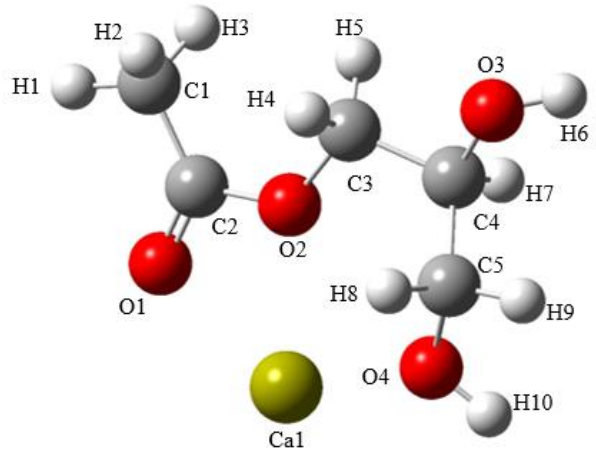

Figure 7. M-GLA and its interaction with Ca+2 ion

3.3 UV Vis. Spectra

The calculated absorptions of the M-GLA molecule associated with their oscillator strengths, the main configurations, and their assignments as well as the experimental results as seen in Figure 6. The absorption bands of the title complex appear at around 215 and 203 nm. The high energy absorption at 215 nm is contributed by the electron excitation from HOMO to LUMO with oscillator strength of 0.21. The absorption at 203 nm is contributed by electron excitation from HOMO-2 to LUMO. The HOMO, HOMO-2 and LUMO are dominantly localized on the carbonyl group. Therefore, the absorption may be assigned mainly to π-π transitions.

3.4 Interaction of M-GLA with Ca^{+2} ion

To investigate the binding of M-GLA additive with Ca^{+2} ion, calculations were performed using the DFT/B3LYP method and the 6-31(d,p) basis set. It is shown in Figure 7. The binding energy of the M-GLA molecule is -5.42 eV. Negative energy binding indicates the self-association of the molecule with calcium ions.

4. Conclusions

In this study, theoretical and experimental infrared vibration and UV-VIS analyses of M-GLA molecule were carried out. In order to examine the optimization and vibrational spectra of the molecule, all calculations were successfully performed using DFT/6-31G(d,p) level. The calculated frequency values and experimental spectrum are compatible with the measured values. All calculations were calculated with Gaussian 09 program. The calculated theoretical FT-IR and UV-VIS spectra of M-GLA molecule were calculated and compared with the experimental spectra. The calculated theoretical spectra are compatible with the experimental spectra. At the same time, the interaction of M-GLA molecule with Ca^{+2} ion was calculated and the binding energy value was calculated as -5.42 eV. As a result of this study, it is aimed to be used as a water reducing additive for cementitious systems.

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