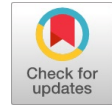


# Density Functional Theory Analysis of Poly Glycolic Acid with Metal Ions (Na<sup>+</sup>, K<sup>+</sup>) Interaction

Mahendiraprabu Ganesan, Selvarengan Paranthaman



**Abstract--** The complexation between Poly glycolic acid (PGA) and alkali metal ions (Na<sup>+</sup>, K<sup>+</sup>) have been studied using B3LYP/6-311++G\*\* method. The binding site of metal ion interaction on PGA is carbonyl oxygen. Both metal ions form bidentate complexation with PGA. Further, it can be noted that the PGA with K<sup>+</sup> complex is more stable than the PGA with Na<sup>+</sup> complex. The binding affinities ( $\Delta H$ ), basicity ( $\Delta G$ ) and the complexation entropies ( $\Delta S$ ) of all the studied systems are calculated. The interaction energy is maximum in PGA-Na<sup>+</sup> than the PGA-K<sup>+</sup> complex. This is due to more charge transfer taking place between PGA and Na. The stability of the complex is studied by the chemical hardness value. The condensed Fukui functions are calculated and are used to predict the favourable reactive site.

**Keywords:** Polyglycolic acid, chemical hardness, condensed Fukui functions, density functional theory calculations, metal ions.

## I. INTRODUCTION

In the past few years, biologically important natural and synthetic polymers, such as collagen [1], chitin [2], chitosan [3] proteins [4], polyhydroxybutyrate(PHB) [5], polylactic acid (PLA) [6], polyglycolic acid (PGA) [7] and polypropylene (PP) [8] have been used extensively in biological as well as medicinal applications. Among these polymers, polyglycolic acid (PGA) is got attention in the last several decades [9] because of its importance in medicinal industry. In general, the biodegradation of these polymers are due to excessive heat [10], photolysis, hydrolysis, and oxidation. However it is not a big problem when PGA is exposed to physiological conditions. In PGA there are two functional group (-OH and -COOH) were present in the same polymer, therefore the PGA act as a versatile ligand in coordination chemistry [11].

An interaction of metal cation with neutral molecule is an important intermediate step or process in gas-phase chemistry [12, 13]. Because of this, many efforts have been taken to the investigation of the formation, and reactivity of organometallic complexes of biochemical importance [14-17].  $\alpha$ -Hydroxycarboxylic acid is simplest ligand which is presented in many biochemical reactions. Previously,

Lic'inia et al have performed DFT study of oxoperoxo vanadium(V) complexes. They have studied two glycolic acid metal ion complexes. They have reported the structural modifications far from the metal nucleus and which does not significantly affect the metal chemical shift [18]. Recently, Ersen Gökürk found new approach to synthesize polyglycolic acid (PGA). They have obtained PGA using cationic alternating copolymerization of formaldehyde (from trioxane) and carbon monoxide (CO)[19]. Apart from these studies, there are soA many experimental [20-22] and theoretical [23-28] studies have been carried on the interaction of glycolic acid and its derivatives with metal ions. To the best of our knowledge, no systematic DFT study performed on PGA metal complexes. The present study aims at investigating structure, intermolecular interaction, thermochemical properties and vibrations of PGA when interacting with metal ion (Na<sup>+</sup>, K<sup>+</sup>) using DFT. The stability of the PGA metal ion interactions also calculated. Condensed Fukui functions are calculated to find the favorable reactive sites of a neutral PGA. The vibrational frequency analysis is also carried out to find out the stretching vibrations of the PGA metal ion complexes.

## II. COMPUTATIONAL DETAILS

In this study, the DFT calculations are performed to determine the molecular structure, energetics, vibrational frequency and thermochemical properties. Becke's three-parameter hybrid functional [29] combined with the gradient-corrected correlation functional of Lee, Yang, and Parr (LYP) [30] with 6-311++G\*\* basis set is used for geometry optimization. The basis set superposition error (BSSE) corrected interaction energy between metal cation and PGA is calculated. [31]. The standard thermodynamical calculations [32] are used to obtain the affinities ( $\Delta H_{298}$ ) and basicity ( $\Delta G_{298}$ ) at 298.15 K and complexation entropies ( $\Delta S$ ). The DFT reactivity parameter, chemical hardness ( $\eta$ ) [33] is calculated using the B3LYP/6-311++G\*\* level of theory, using the relation:

$$\eta = \frac{I - A}{2}$$

Where I is the ionization potential, and A is electron affinity of the studied system. I and A can be calculated using Koopman's theorem. Condensed Fukui functions are calculated using the mulliken charges which can be obtained from Mulliken population analysis:

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# Density Functional Theory Analysis of Poly Glycolic Acid with Metal Ions (Na<sup>+</sup>, K<sup>+</sup>) Interaction

$$f^+_{\text{K}} = q_{\text{K}}(N + 1) - q_{\text{K}}(N)$$

$$f^-_{\text{K}} = q_{\text{K}}(N) - q_{\text{K}}(N - 1)$$

$$f^0_{\text{K}} = \frac{1}{2} [q_{\text{K}}(N + 1) - q_{\text{K}}(N - 1)]$$

where  $f^+_{\text{K}}$ ,  $f^-_{\text{K}}$  and  $f^0_{\text{K}}$  are the nucleophilic, electrophilic, and radical attacks, respectively. All the above mentioned calculations are done using Gaussian 09W program. [34]

## III. RESULTS AND DISCUSSION

PGA, PGA with metal ions complexes are optimized using B3LYP/6-311++G\*\*. The optimized structures of PGA, PGA-Na<sup>+</sup> and PGA-K<sup>+</sup> in gas phase are shown in Fig. 1. The total energies, van der Waals bond length, interaction energies, dipole moments, chemical hardness, affinities, basicity and complexation entropies for the above complexes are calculated using B3LYP / 6-311++G\*\* and are shown in Table 1. The molecular orbital diagram for the PGA metal ion complexes are shown in Fig. 2. The condensed Fukui functions for the PGA structure are shown in Table 2. The vibrational frequency of PGA metal ion complexes are calculated and plotted in Fig. 3.

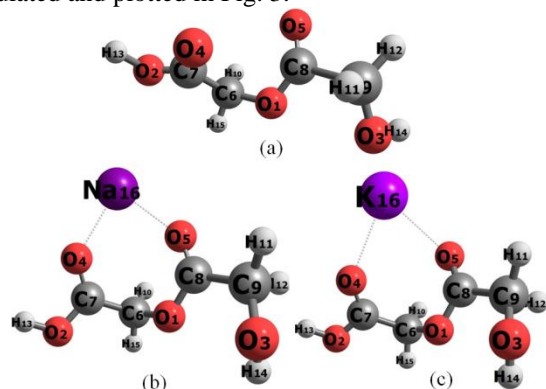


Fig. 1. Optimized structures of (a) PGA, (b) PGA-Na and (c) PGA-K using B3LYP/6-311++G\*\* level of theory.

Table- I: Total Energy (E, in hartree), van der Waals bond length (R<sub>v</sub>, in Å), interaction energy (E<sub>int</sub>, in kcal / mol), dipole moment (μ<sub>M</sub>, in Debye), chemical hardness (η, in eV), affinity (ΔH<sub>298</sub>, kcal mol<sup>-1</sup>), basicity (ΔG<sub>298</sub>, kcal mol<sup>-1</sup>) and complexation entropies (ΔS, cal mol<sup>-1</sup> K<sup>-1</sup>) calculated using B3LYP / 6-311++G\*\* for PGA metal complexes.

	PGA	PGA-Na <sup>+</sup>	PGA-K <sup>+</sup>
E	-531.98136	-694.48807	-1132.14273
R <sub>v</sub>	C7=O4	2.223	2.610
	C8=O5	2.257	2.642
E <sub>int</sub>		269.83	31.38
μ <sub>M</sub>	4.24	6.70	6.85
η	0.74	3.00	3.14
ΔH <sub>298</sub>		-261.213425	-249.566846
ΔG <sub>298</sub>		-252.804796	-241.729251
ΔS		-28.218	-26.291

From Fig. 1. It can be seen that in the optimized structures of PGA-Na<sup>+</sup> and PGA-K<sup>+</sup>, the two alkali metals Na<sup>+</sup> and K<sup>+</sup> form bidentate complexation with PGA. That is with the

carbonyl oxygen group of PGA. Further, from the energy values it can be understood that the PGA-K<sup>+</sup> complex is energetically more stable than the PGA-Na<sup>+</sup> (Table 1). But in the case of van der Waals bond length, the bond length of the PGA-Na<sup>+</sup> complex is forming very strong interaction with PGA compared with PGA-K<sup>+</sup> complex. This is due to the low molecular weight of Sodium ion. Earlier Selvarengan et al have discussed the relative energy of the glycine conformers with alkali metal ion complexes. [35]. The dipole moment value for PGA, PGA-Na<sup>+</sup> and PGA-K<sup>+</sup> are 4.24, 6.70 and 6.85 D respectively. The dipole moment value increases as the size of the metal ion increases. In this same way the chemical hardness values also increased while metal ions interact with the pure PGA. The chemical hardness value of PGA, PGA-Na<sup>+</sup> and PGA-K<sup>+</sup> are 0.74, 3.00 and 3.14 eV. From the above hardness value PGA-K<sup>+</sup> is more stable than the PGA-Na<sup>+</sup> interaction. In summary, K<sup>+</sup> interaction with PGA increases the stability of the system. This can be confirmed from chemical hardness values also.

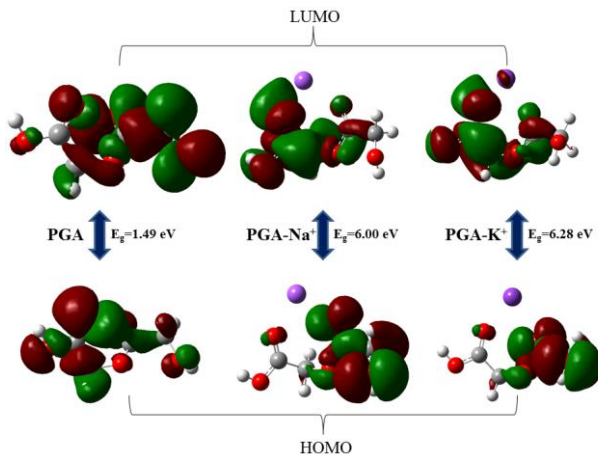
Thermochemical properties such as ΔH<sub>298</sub>, ΔG<sub>298</sub>, and ΔS are calculated using B3LYP / 6-311++G\*\*. The ΔH<sub>298</sub> for PGA-Na<sup>+</sup> and PGA-K<sup>+</sup> are -261.213425 and -249.566846 kcal mol<sup>-1</sup> respectively. The ΔG<sub>298</sub> for PGA-Na<sup>+</sup> and PGA-K<sup>+</sup> are -252.804796 and -241.729251 kcal mol<sup>-1</sup>. This indicates that as the size of the metal ions increases, the thermochemical values decreases. Further, this coincides very well with the interaction energy values. The interaction energy is maximum in sodium binding with PGA than potassium binding.[35]. This is due to more charge transfer taking place between PGA and Na than PGA and K.

Table- II: Calculated Fukui functions for PGA at B3LYP level of theory using 6-311++G\*\* basis set.

PGA	f <sup>+</sup>	f <sup>0</sup>	f <sup>-</sup>
O1	0.033	0.045	0.057
O2	0.026	0.022	0.018
O3	0.198	0.086	-0.026
O4	<b>0.039</b>	<b>0.018</b>	<b>-0.003</b>
O5	<b>0.284</b>	<b>0.158</b>	<b>0.033</b>
C6	-0.028	-0.844	-1.660
C7	0.015	0.091	0.166
C8	0.065	0.195	0.324
C9	0.002	-0.514	-1.030
H10	0.038	0.221	0.404
H11	0.100	0.079	0.058
H12	0.081	0.206	0.331
H13	0.028	0.604	1.180
H14	0.062	0.332	0.603
H15	0.056	0.301	0.546

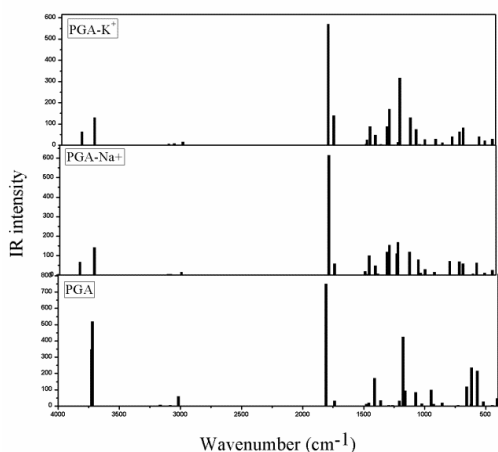
The condensed Fukui functions of PGA and PGA metal ion complexes are calculated and are given in Table 2. Fukui functions are used to predict the favourable reactive site for the particular molecule or ligand. From the above table the reactive binding site for PGA is the carbonyl oxygen namely =O4 and =O5 respectively.

The result shows that all the carbonyl oxygen sites are positively charged and it would be an electrophilic attack. So that it is easy to understand, the carbonyl oxygen group is ready to accept the pair of electrons to form a covalent bond. Earlier, Senthikumar et al. studied the Fukui function for the Halomethane molecule. They have successfully predicted the better results by using Fukui function [36]. Also Selvarangan et al. studied the condensed Fukui functions for the glycine molecule. They have also successfully predicted the reactive binding site for the particular glycine conformer.



**Fig. 2. HOMO to LUMO energy level diagrams of PGA with metal ion complexes.**

The frontier molecular orbitals (HOMO and LUMO) were explained by the electronic absorption properties [37]. The energy gap between HOMO and LUMO is a critical parameter property for quantum chemistry [38]. The calculated HOMO to LUMO energy level diagrams for PGA metal ion interactions are shown in Fig. 2. The energy gap between HOMO to LUMO for PGA, PGA-Na<sup>+</sup> and PGA-K<sup>+</sup> are 1.49, 6.00 and 6.28 eV respectively. This indicates that PGA-K<sup>+</sup> complexes are more stable than PGA-Na<sup>+</sup> complex. This is consistent with the chemical hardness values.



**Fig. 3. Calculated vibrational frequency of PGA, PGA-Na<sup>+</sup> and PGA-K<sup>+</sup> using B3LYP/6-311++G\*\* level of theory**

The vibrational frequency of the PGA and PGA metal ion complexes are calculated using B3LYP/6-311++G\*\* level of theory and plotted in Fig. 3. From the above figure we can clearly understand that, there is some peaks that disappear

and some peaks appear while metal ions were interacted with the PGA. This is due to the presence of metal ion interaction. Earlier, Kister et al. have studied the morphology of PGA using IR and Raman spectroscopy by experimental study. They also reported the FTIR and FT-Raman spectrum for the PGA crystal. For our cases the vibration stretching mode of carbonyl oxygen  $\nu(\text{C}=\text{O})$  group is very important to study the alkali metal ion interaction, because of the alkali metal particularly interact with these carbonyl oxygen only. Theoretically, vibration frequency of  $\nu(\text{C}=\text{O})$  stretching for PGA, PGA-Na<sup>+</sup> and PGA-K<sup>+</sup> are 1809, 1778 and 1788 cm<sup>-1</sup> respectively. Experimentally Kister et al. result for  $\nu(\text{C}=\text{O})$  stretching is 1760 cm<sup>-1</sup> with very strong vibration. Our theoretical results are exactly matching with the available experimental data [20].

#### IV. CONCLUSION

The DFT method is used to study the Polyglycolic acid complexation with alkali metal ions. From the calculated van der Waals bond length, it can be understood that PGA and Na<sup>+</sup> complex is stronger than the PGA-K<sup>+</sup> complex. From the calculated dipole moment, chemical hardness, affinities, basicity and complexation entropies of PGA metal complexes, PGA with potassium ion (PGA-K<sup>+</sup>) is the most stable than the PGA-Na<sup>+</sup> complex. The interaction energy is maximum in PGA-Na<sup>+</sup> than the PGA-K<sup>+</sup> complex. This is due to more charge transfer taking place between PGA and Na. From the condensed Fukui functions, it can be concluded that the carbonyl oxygen is the reactive binding site of PGA. These sites are more favorable for electrophilic attack. The carbonyl oxygen stretching frequency coincides well with the experimental data.

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