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Original Research Article

A Thermodynamic Study on Nano-graphene Interaction with the Amino acid Phenylalanine in Acidic and Alkaline conditions at different temperatures

Mahnaz Sadat Zolfaghari*

Department of chemistry, Faculty of chemistry and petroleum sciences, Shahid Beheshti university, General campus evin, Tehran, Iran

*Corresponding author Fax number: Tel.: +98 937 965 9317

*E-mail: Mahnazzolfaghari627@yahoo.com

ABSTRACT

The project is comparing two types of calculation derived graphene. Which one of these carbon graphene linked to the phenylalanine amino acid from the acidic site (-COOH) and another from the base site ($-NH_2$). For this purpose, at first the material contained in the both sides of reaction were geometrically optimized, then the calculation of the thermodynamic parameters performed on all of them. The amount of ΔH, ΔS and ΔG of this reaction at different temperatures in form of sum of parameters discrepancy in the products than reactants are obtained, and finally, the best temperature for the synthesis of derivations of phenylalanine - Graphene according to the obtained thermodynamic parameters were evaluated.

Keywords: phenylalanine amino acid, Graphene, base & acid binding position, density functional theory.

1-Introduction

The oil and gas industry is one of the most significant and productive industries in the country. This industry has been known as the most important supplier of energy in the world and predictions have also shown that, due to the drop in the pressure of Iran oil reservoirs and reach to the half-life of the reservoirs, the need for advanced technologies in order to increase the rate of oil recovery from these sources and the abundant capacities in downstream oil and gas industries for using nanotechnology to improve the process and producing high-efficient products are expected.

Nanotechnology can play a remarkable role in the future. Hence it has been noticeable in fundamental and applied researches drastically. Graphene and its derivatives that are novel-bio-materials are widely used in different fields including tissue engineering, medicines and tumor treatment. The effectiveness of these applications will be changed due to the modifications by polymers and other nanomaterials.

Modification with materials which have two different poles, increases the efficiency of the drug which placed on the surfaces. Bipolar copolymers are so profitable that improve different properties including, increasing mechanical strength and facilitating the entrance into the cellular environment.

In order to design a targeted drug delivery by using nanoparticles, graphene and its derivatives have some advantages rather than other nanoparticles, so the utilizes of graphene and its derivatives are in the priority to enhance the efficiency and effectiveness of the drug (1-8).

For this purpose, in this project at first phenylalanine amino acid via acidic functional group is connected to the graphene carbon surfaces in hexagon and then from glutamine basic functional groups connects to the graphene carbons.

In different aspects of survey, the components were optimized geometrically and then energy calculations were executed to calculate thermochemical parameter at the temperature range of 300-400 kelvin, and then thermal capacity for the formation of the studied states, enthalpy,

entropy and Gibbs free energy in both acidic and basic states and the temperatures that mentioned above, were calculated and compared with each other.

The applying method in this study is the functional density theory and the computational theory method have been analyzed at B3lyp/6-31g in the gas phase.

With a view to study the project easily, two graphene derivates and individually named and abbreviated as AGER and BGER.

A) The first compound which consists of graphene with phenylalanine amino acid is shown in AGER when it has connected via carboxylic acid functional group (-COOH) in acidic state (figure 1).

B) The second compound which consists of graphene with phenylalanine amino acid is illustrated in AGER, BGER when it has connected via basic functional group (-NH2) in basic state (figure 1, 2).

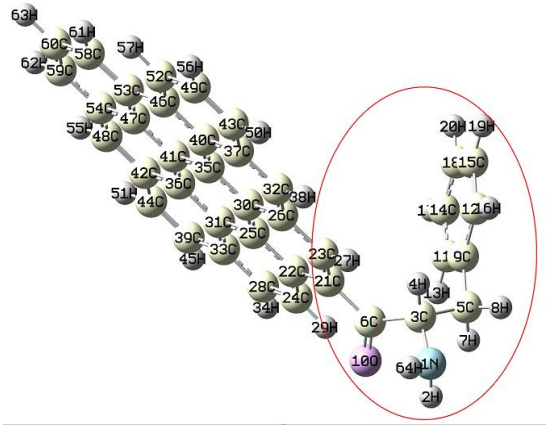

Fig 1. Optimized structure of AGER compound of phenylalanine amino acid connected to graphene from carboxylic acid (-COOH) functional group by DFT method.

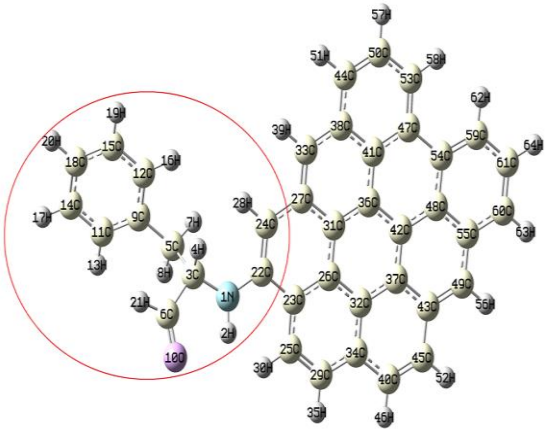

Fig2. Optimized structure of BGER compound, connected from (-NH2) functional group in basic state by DFT method.

2- Results and discussion

2-1- Analysis the values of enthalpy changes (**ΔH) :**

By using Gussian 98, the enthalpy values for graphene, phenylalanine amino acid and each of the above compounds were calculated.

- **First group of enthalpy results:**

With regard to the following equation, enthalpy changes in the reactions of A+B→AB is calculated.

Equation (1):

$\Delta H = H_2 - H_1$

Now with considering to the reaction, Geraphene +phen-ala →AGER+ H2 and enthalpy values for AGER(the connection of graphene to phenyl alanine is from acidic site) by using Gussian software, for instance to AGER compound:

Equation (2):

$\mathbf{\Delta H_{AGER}} = [H_{AGera} + H_{H2}] - [H_{Ger} + H_{Phen\text{-}ala}]$

The value of ΔH_{AGER} indicates that the process of adsorption of the amino acid phenylalanine on the graphene at the acidic state is an exothermic reaction (table 1, figure 4).

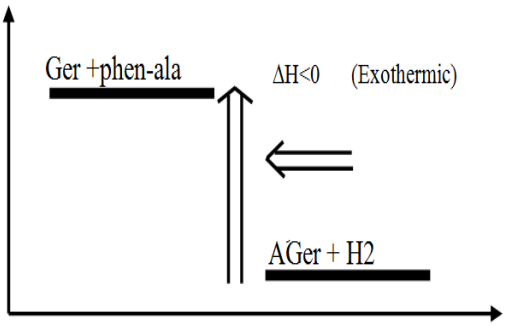

Fig3. Enthalpy changes diagram for AGER compound

Table 1. ΔH_{AGER} values for the adsorption process phenylalanine amino acid on graphene from acidic site.

Temperature(K)	ΔH_{AGER} (kJ/mol)
300.00 K	-27.4339
310.00 K	-27.3082
320.00 K	-27.187
330.00 K	-27.0673
340.00 K	-26.9499
350.00 K	-26.8605
360.00 K	-26.7473
370.00 K	-26.6137
380.00 K	-26.4955

390.00 K	-26.3774
400.00 K	-26.2729

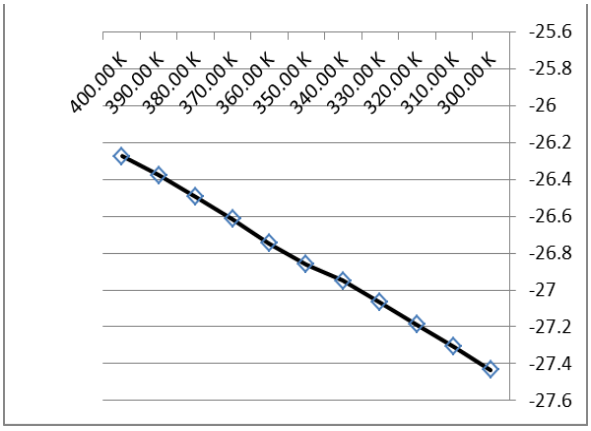

Fig 4. Enthalpy changes chart for formation of AGER compound at 300-400 kelvin.

- **Second group of enthalpy results**

Geraphone + phen-ala → BGer + H2

And also for BGER compound:

Equation (3):

$\Delta H_{BGer} = [H_{BGer} + H_{H2}] - [H_{Ger} + H_{Phen\text{-}ala}]$

The ΔH_{BGER} demonstrates that the process of adsorption of amino acid phenylalanine on the graphene at basic state is an exothermic reaction (table 1, figure 4).

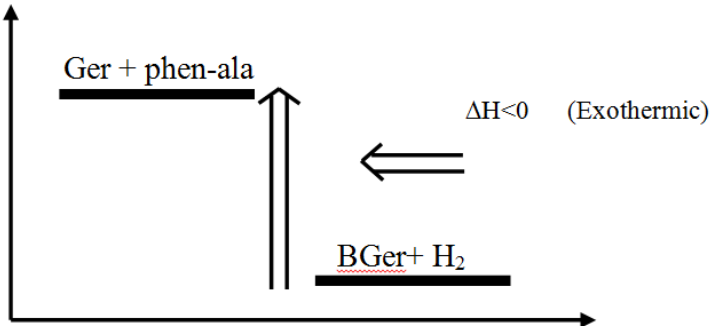

Fig 5. . Enthalpy changes diagram for BGER compound

Table 2. . ΔH_{BGER} values for the adsorption process phenylalanine amino acid on graphene from basic site.

Temperature(K)	ΔH_{BGER} (kJ/mol)
300.00 K	-29.6487
310.00 K	-29.5366
320.00 K	-29.4428
330.00 K	-29.3713
340.00 K	-29.3109
350.00 K	-29.2469
360.00 K	-29.1544
370.00 K	-29.0443
380.00 K	-28.9248
390.00 K	-28.7761
400.00 K	-28.6576

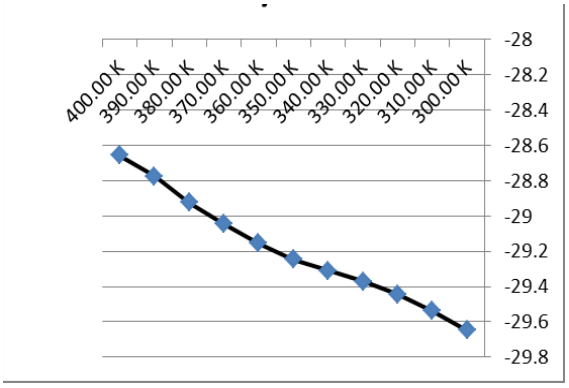

Fig 6. Enthalpy changes chart for formation of BGER compound at 300-400 kelvin.

According to the values of ΔH_{BGER} and comparing them together, it is clear that the adsorption of phenylalanine amino acid or graphene carbon at basic state has a different states of enthalpy changes. In fact at basic phase reaction is more exothermic and more negative (table 2, figure 5).

ΔH values for both compounds of AGER, BGER have been shown below.

Table 3. ΔH values for two compounds of AGER and BGER.

دما(کلوین)	آنتالپی واکنش اتصال اسیدی kJ/mol	آنتالپی واکنش اتصال بازی kJ/mol
300.00 K	-27.4339	-29.6487
310.00 K	-27.3082	-29.5366
320.00 K	-27.187	-29.4428

330.00 K	-27.0673	-29.3713
340.00 K	-26.9499	-29.3109
350.00 K	-26.8605	-29.2469
360.00 K	-26.7473	-29.1544
370.00 K	-26.6137	-29.0443
380.00 K	-26.4955	-28.9248
390.00 K	-26.3774	-28.7761
400.00 K	-26.2729	-28.6576

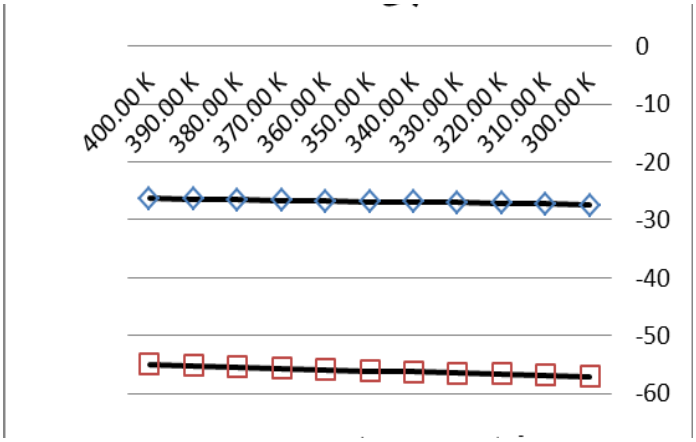

Fig 7. ΔH diagram for compounds AGER and BGER.

3-1- Analysis the enthalpy changes (Δs):

The value of Δ**s** for two compounds AGER, BGER according to the following reactions :

Geraphene +phen-ala →AGER+ H2

Geraphene +phen-ala → BGER + H2

For AGER(graphene connection to phenylalanine from acidic site) and BGER graphene with phenylalanine amino acid at the connection via basic functional group (-NH_2) in basic state, by using Gussian software at B3LYP/6-31G* computational level is obtained.

Table 4. Δs values for compounds AGER and BGER.

دما(کلوین)	آنتروپی واکنش اتصال اسیدی J/mol.K	آنتروپی واکنش اتصال بازی J/mol.K
300.00 K	-116.6832	-118.0051
310.00 K	-116.6013	-118.2248
320.00 K	-116.7092	-118.4579
330.00 K	-116.9461	-118.6857
340.00 K	-117.1595	-118.7498
350.00 K	-117.3057	-118.9128
360.00 K	-117.3533	-119.0275
370.00 K	-117.4639	-119.0828
380.00 K	-117.6129	-119.2901
390.00 K	-117.7633	-119.5276
400.00 K	-117.9155	-119.9239

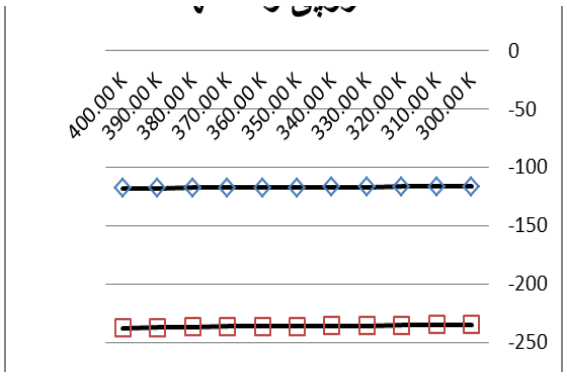

Fig 8. Δs diagram for compounds AGER and BGER.

4-1- Study of the values of Gibbs free energy changes (ΔG) at 300 K

The value of ΔG for two compounds AGER, BGER according to following reactions:

Geraphene +phen-ala →AGER+ H2

Geraphene +phen-ala → BGER + H2

For AGER (graphene connection to phenylalanine from the acidic site) and BGER graphene with phenylalanine amino acid that has connected via basic functional group (-NH2) at basic phase, by using Gussian software at the computational level B3LYP/6-31G* is obtained.

Table 5. ΔG values for compounds AGER and BGER

Temperature	ΔG acidic kJ/mol.K	ΔG alkaline kJ/mol.K
300.00 K	**7.5709**	**5.7527**
310.00 K	**8.8382**	**7.1131**
320.00 K	**10.160**	**8.4639**
330.00 K	**11.5248**	**9.7949**
340.00 K	**12.8844**	**11.0641**
350.00 K	**14.1965**	**12.3726**
360.00 K	**15.500**	**13.6956**
370.00 K	**16.848**	**15.0164**
380.00 K	**18.1974**	**16.4054**
390.00 K	**19.5503**	**17.8397**
400.00 K	**20.8937**	**19.3124**

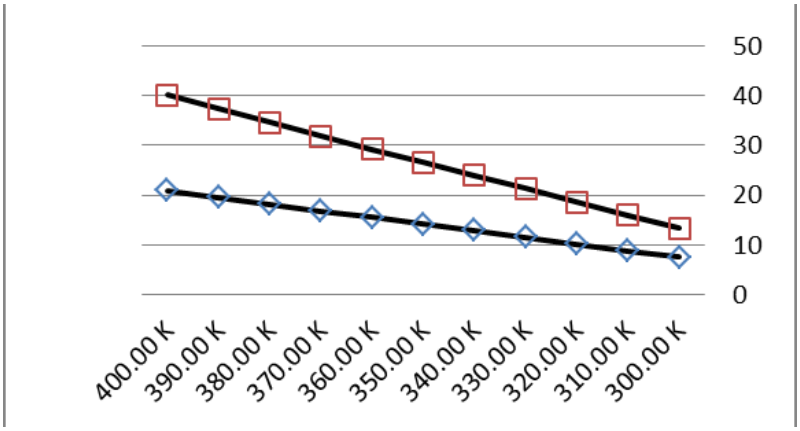

Fig 9. ΔG diagram for the formation reactions of compounds AGER and BGER.

Conclusion

Comparison of the values related to the thermodynamic parameters in the adsorption of the phenylalanine amino acid on the graphene nanoparticle in both acidic and basic positions shows that these reactions are exothermic and, on the other hand, it is investigated that in the range of 300 to 400 degrees Kelvin in this study, the reaction is spontaneous. The Gibbs free energy for the various cases studied shows that it is more probable to reach the AGER state, and it is more difficult to achieve BGER state. Therefore, adsorption in the acid bonding state when the graphene composite is formed with phenylalanine shows better adsorption.

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