Quantum Chemistry Study on Scale and Corrosion Inhibition Performance of Polyaspartic Acid

Yushan Cheng, Min Chen, Ju Xiao, Naihao Xing and Changshan Huang*

Energy research institute limited company, Henan academy of sciences, Zhengzhou, Henan, 450008, China

smwang@haue.edu.cn

*Corresponding author’s e-mail: hnsnys163@163.com

Abstract. The corrosion and scale inhibitions performance of polyaspartic acid (PASP) was investigated based on the quantum chemistry calculation method of semi-empirical method by using the software of GaussView 6 and Gaussian 16. The calculation results show that, for scale inhibition, as the nitrogen atoms of PASP molecules and the oxygen atoms in carboxyl group were electronegative, which caused the electrostatic interaction to happen easily between the oxygen ions of carboxyl and the calcium ions on the calcite surface, in addition, the space between the two nitrogen, oxygen ions in PASP molecule was exactly matched the space between the calcium ions on the calcite surface, the adsorption effect of the scale inhibitor to the calcite surface was obviously improved, thereby, the aim that inhibiting CaCO$_3$ scale was achieved, the calculation results were in accordance with the test results. For corrosion inhibition performance, the HOMO energy, the LUMO energy and the difference of the two values was gotten through the calculation. The results were coincident with the mechanism description, and the calculation results were consistent with the test results.

1. Introduction

The research on the theory and application of scale and corrosion inhibitors is always one of the important subjects in the field of water treatment and corrosion science. The molecular structure of organic scale inhibitor has a decisive influence on its performance, so it is of great significance to study the relationship between them. In recent decades, the relationship between molecular properties and structures has been widely studied and achieved some success [1], such as linear free energy relationship (LFER) or hemmet equation; free wilsin and Hansch relationship and theory of hard and soft acids and bases (HSAB). In 1971, the quantum chemical method (QM) to study the correlation between the performance of inhibitors and the quantitative parameters was first used by Vosta and Eliasek. So far, the quantum chemical method (QM) has achieved great success in the study of molecular structure, performance and reactivity [2].

The molecular formula of polyaspartic acid (PASP) is C$_4$H$_6$NO$_3$ (C$_4$H$_5$NO$_3$) C$_4$H$_6$NO$_4$, with a relative molecular weight of 1000-5000. The structural formula is shown in Figure 1. It is a typical green water treatment agent, with dual functions of scale and corrosion inhibition. Gaussian 16 and GaussView 6 were employed to Quantum chemical calculation, the microcosmic electronic performance is compared with the macroscopic scale and corrosion inhibition performance to further understand the microcosmic mechanism of scale and corrosion inhibition, so as to provide a reliable theoretical basis for the design of PASP high-efficiency compound water treatment agent in the future.
2. Overview of scale and corrosion inhibition mechanism of PASP

2.1. Study on scale inhibition performance

In recent years, the research and development of scale and corrosion inhibitors have entered the level of "molecular design"; such as quantum chemical interpretation of obvious scale inhibition effect on barite. Some researchers have begun to study the scale inhibition and corrosion inhibition mechanism at the molecular level. According to the domestic and foreign literature [3], the mechanism of scale inhibitor is mainly explained by the crystallization process of precipitate. Up to now, there are several hypotheses about the mechanism of scale inhibitors: chelating solubilization, lattice distortion theory and dispersion. For PASP, there are four mature scale inhibition mechanisms: complexation mechanism, lattice mechanism, Demembrane mechanism and dispersion mechanism.

Therefore, the quantum chemical calculation method was used to obtain the spatial configuration of PASP. After optimization, the relevant parameters were obtained, including the net charge, bond length, spatial distance between atoms, dihedral angle and so on. In this way, the influence of adsorption process of PASP molecule on the scale inhibition performance of calcite (thermodynamic stable form of calcium carbonate scale) crystal surface was analyzed, and the static scale inhibition test of calcium carbonate by national standard method was adopted to verify.

2.2. Study on corrosion inhibition performance

Since the 1970s, the Homo value of the highest orbital energy occupied by organic compounds has been considered as a physical index reflecting the molecular activity. It is often used to compare the advantages and disadvantages of the corrosion inhibition performance of organic compounds with similar main chain and structure. Some researchers have made quantitative structure activity correlation analysis between HOMO value and inhibition efficiency of organic compounds, and drawn semi empirical linear regression curve, which is used as an important basis for the synthesis and screening of organic inhibitors [4,5]. In recent years, the internal relationship between electronic properties of organic compounds and their macro corrosion inhibition properties has been discussed by quantum chemical calculation at home and abroad [6]. The orbital energy difference is a very important stability index, the greater the value, the better the stability and the better the reactivity in chemical reactions [7]. It can be concluded that the higher the HOMO energy of organic molecules, the easier it is to provide electrons to the unoccupied d orbital of metals, and the higher the corrosion inhibition rate; the lower the LUMO energy, the easier it is to accept the d orbital electrons of metals, and the higher the corrosion inhibition rate.

Therefore, the highest occupied orbital energy (HOMO) and the lowest orbital energy (LUMO) of PASP molecule were calculated by quantum chemistry, and the nucleophilic reaction strength was judged. According to the orbital energy difference, the stability of PASP was studied. At the same time, the traditional test method was used to study the corrosion inhibition performance of PASP, and compared with the results of quantum chemistry calculation.
3. Study on scale inhibition performance of PASP

3.1. Quantum chemical calculation method
First, the initial configuration of PASP molecule was obtained by GaussView 6, and at the Restricted Hartree Fock (RHF) level, the semi-empirical method was used to pre-optimize the molecular configuration (including bond length, bond angle and dihedral angle). Then, the pre-optimized molecule was fully optimized in geometry, calculation in frequency and calculation in orbit. The convergence accuracy was taken as the internal fixed value of the program, and the structures were all the minimum points (no virtual frequency) on the potential energy surface, and the semi-empirical method was used to scan the molecular potential energy surface [8, 9], the molecular space structure was shown in Figure 2.

![Figure 2. The molecular space structure of PASP](image)

3.2. Bond length of some atoms
The bond length of PASP partial atoms calculated by Gaussian16 Single Computer for Linux was shown in Table 1.

| Atomic bond | C1-N2 | C1-C5 | C1-C10 | C5-O6 | C5-O7 | C10-C13 |
|-------------|-------|-------|--------|-------|-------|---------|
| Bond length/Å| 1.47366 | 1.53573 | 1.54744 | 1.21027 | 1.35618 | 1.51520 |
| Atomic bond | C13-O14 | C13-N16 | N16-C15 | C15-C18 | C18-O19 | C18-O20 |
| Bond length/Å| 1.21389 | 1.40993 | 1.47056 | 1.54265 | 1.20800 | 1.35746 |
| Atomic bond | C15-C23 | C23-C26 | C26-O27 | C26-N29 | N29-C28 | C28-C31 |
| Bond length/Å| 1.53627 | 1.51508 | 1.22335 | 1.39453 | 1.47712 | 1.55906 |
| Atomic bond | C31-N40 | N40-C39 | C42-O44 | C39-C47 | C47-C50 | C50-O54 |
| Bond length/Å| 1.39618 | 1.47684 | 1.36096 | 1.53136 | 1.49500 | 1.37319 |

3.3. Net charge on PASP atom
The atomic charge distribution of PASP (see Table 2) and the net charge data of main functional groups (see Table 3) were calculated by GaussView 6 software.

| PASP (m=1;n=1) | C1  | N2  | C5  | O6  | O7  | C10 | C13 | N16  |
|----------------|-----|-----|-----|-----|-----|-----|-----|------|
|                | -0.016 | -0.508 | 0.614 | -0.528 | -0.505 | -0.494 | 0.628 | -0.537 |
|                | C15 | C18 | O19 | O20 | C23 | C26 | O27 | N29 |

Table 2. The atomic charges of PASP (Unit:e)
It can be seen from Table 2 that PASP molecules, which are generally electrically neutral, contain carboxyl and imino functional groups. The most negatively charged are the oxygen atom on the carboxyl group and the nitrogen atom on the imino group. The net charge is shown in Table 3.

The nitrogen atom on the imino group and the double bond oxygen atom on the carboxyl group in PASP molecule are easy to form strong electrostatic interaction with the calcium ion on the surface of calcium carbonate, and the interaction strength is related to the spatial matching density [10]. If the distance between the double bond oxygen atom on the carboxyl group and the calcium ion on the surface of calcium carbonate is close, PASP will be adsorbed on the crystal surface of calcium carbonate under the action of static electricity, occupy the active growth point, induce crystal lattice distortion, thus showing a strong performance of inhibiting the growth of the crystal surface of calcium carbonate, namely scale inhibition performance. It can be seen that imino group and carboxyl group are scale inhibition groups. The introduction of imino group and carboxyl group into organic molecules can improve the scale inhibition performance of the molecules.

### 3.4. Spatial scale analysis of PASP

GaussView 6 was employed to calculate the space distance between atoms of PASP and the results were shown in Table 4.

Table 5 shows the spatial distance between the nearest calcium ions on three typical low Miller index crystal planes of calcite [11].

As can be seen from Table 4 and 5, there are six sets of data on the PASP molecule match well with the distance between the nearest calcium ions on the calcite crystal plane, including N40-O38 (4.091 Å), O6-O14(4.095 Å), O7-O14(4.021 Å), O14-O19(4.939 Å), O43-O52(4.936 Å) and O43-O54(4.912 Å). From an energy perspective, these negatively charged atoms are easy to become...
the adsorption sites of scale inhibitor molecules and crystal surfaces, which can effectively prevent the continuous growth of these crystal surfaces, or make the crystal lattice distorted, resulting in the scale body soft and easy to be washed away by water. It can be seen that PASP molecule has good scale inhibition effect on calcium carbonate.

3.5. Experimental study on scale inhibition performance of PASP

The scale inhibition performance was evaluated by the static scale inhibition test method of calcium carbonate. The test conditions of scale inhibition performance were as follows: the Ca²⁺ concentration is 600mg / L (calculated by CaCO₃), HCO₃⁻ concentration is 600mg / L (calculated by CaCO₃), pH8.0, water temperature is 55℃, and the test time is 10h.

The test results were shown in Figure 3.

![Figure 3: The relationship between PASP dosage and scale inhibition rate](image)

It can be seen from Figure 3 that PASP has significant scale inhibition effect on calcium carbonate scale. PASP is a flexible molecule, which can prevent the growth of many kinds of scale crystals through the change of its dominant configuration. Meanwhile, PASP also has good scale inhibition performance for barium sulfate and strontium sulfate [12].

4. Study on corrosion inhibition of PASP

4.1. Dipole moment and frontline orbital energy of PASP

Table 6 lists the frontier orbital energy and energy gap of PASP molecule, in which $E_{\text{HOMO}}$ represents the highest occupied orbital energy and $E_{\text{LUMO}}$ is the lowest orbit energy. The negative value of $E_{\text{HOMO}}$ is approximately equal to the first ionization energy, and the negative value of $E_{\text{LUMO}}$ is electron nucleophilic. Therefore, the lower the $E_{\text{HOMO}}$, the more difficult it is to lose electrons; the higher the $E_{\text{LUMO}}$, the more difficult it is to get electrons. $\Delta E$ is the absolute value of the difference between $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$, indicating the relative stability of the compound. $\Delta E$ is large, the stability is good; on the contrary, the stability is poor.

| PASP | Dipole moment | $E_{\text{LUMO}}$/eV | $E_{\text{HOMO}}$/eV | $\Delta E$/eV |
|------|---------------|-----------------------|----------------------|--------------|
| PASP | 5.2367        | -0.38092              | -0.01215             | 0.36877      |

Figure 3. The relationship between PASP dosage and scale inhibition rate

It can be seen from Figure 3 that PASP has significant scale inhibition effect on calcium carbonate scale. PASP is a flexible molecule, which can prevent the growth of many kinds of scale crystals through the change of its dominant configuration. Meanwhile, PASP also has good scale inhibition performance for barium sulfate and strontium sulfate [12].

4. Study on corrosion inhibition of PASP

4.1. Dipole moment and frontline orbital energy of PASP

Table 6 lists the frontier orbital energy and energy gap of PASP molecule, in which $E_{\text{HOMO}}$ represents the highest occupied orbital energy and $E_{\text{LUMO}}$ is the lowest orbit energy. The negative value of $E_{\text{HOMO}}$ is approximately equal to the first ionization energy, and the negative value of $E_{\text{LUMO}}$ is electron nucleophilic. Therefore, the lower the $E_{\text{HOMO}}$, the more difficult it is to lose electrons; the higher the $E_{\text{LUMO}}$, the more difficult it is to get electrons. $\Delta E$ is the absolute value of the difference between $E_{\text{HOMO}}$ and $E_{\text{LUMO}}$, indicating the relative stability of the compound. $\Delta E$ is large, the stability is good; on the contrary, the stability is poor.

| PASP | Dipole moment | $E_{\text{LUMO}}$/eV | $E_{\text{HOMO}}$/eV | $\Delta E$/eV |
|------|---------------|-----------------------|----------------------|--------------|
| PASP | 5.2367        | -0.38092              | -0.01215             | 0.36877      |
The value of $E_{HOMO}$ of PASP molecule is -0.01215 eV, which indicates that its first ionization ability is relatively strong. Therefore, the water solubility of PASP molecule is relatively excellent and it is easy to participate in nucleophilic reaction. In this way, it is easy to form a coordination bond with the empty d orbit on the metal surface, which enhances the stability of the chemisorption film on the metal surface. At the same time, the value of $\Delta E$ of PASP molecule is relatively large, indicating that the stability is relatively good, so it can be inferred that PASP molecule has outstanding corrosion inhibition performance, which belongs to the electronic cathode inhibitor.

4.2. Corrosion inhibition test of PASP

4.2.1. SEM morphology analysis.
JSM-6510 scanning electron microscopy (SEM) was employed to study the corrosion behavior of A3 carbon steel specimen. The carbon steel specimen was pasted on the sample stage with conductive adhesive, and then it was observed at 15 kV accelerating voltage and $\times$1000 magnification.

Two carbon steel specimens were put into blank solution and PASP solution respectively for rotary hanging-piece experiment, and then analyzed with SEM and the results were shown in Figure 4 (a and b).

![Figure 4. SEM analysis of A3 carbon steel specimen after testing](image)

Figure 4 (a) shows that the carbon steel test piece in blank solution was corroded seriously, with pitting and gap on its surface, uneven and unsmooth; while Figure 4 (b) shows that the surface of carbon steel test piece in PASP solution was smooth, basically without corrosion. Obviously, PASP can protect carbon steel samples from corrosion and has excellent corrosion inhibition performance.

4.2.2. Electrochemical experiment.
The measurement of polarization curve is based on the classic three electrode system at room temperature, including auxiliary electrode, reference electrode and working electrode, which are platinum electrode, saturated calomel electrode and A3 carbon steel (total surface area is 1.0 cm$^2$). The polarization scanning range is $E_{corr} = \pm 0.3$V, the scanning speed is 0.5mV/s, and the test water is tap water. Before the test, the working electrode is polished by 800 ~ 1200 mesh sandpaper, cleaned by distilled water, anhydrous ethanol and acetone, dried naturally, and soaked in the electrolyte for 0.5 h.

The polarization curves of carbon steel test piece in blank solution and PASP solution were obtained by electrochemical workstation. The results were shown in Figure 5.
In the solution without PASP, the self-corrosion potential and current were $E_0 = -0.34 \, \text{V}$, $I_0 = 1.91 \times 10^{-8} \, \text{amp cm}^{-2}$, respectively. In the solution with PASP, the self-corrosion potential and current were $E_0 = -0.31 \, \text{V}$, $I_0 = 1.22 \times 10^{-8} \, \text{amp cm}^{-2}$, respectively. When PASP was added, the polarization curve of carbon steel changed obviously with the increase of self-corrosion potential. In addition, the slope of cathode polarization curve decreased obviously, while the slope of anode polarization curve increased slightly. It is clear from the discussion above that PASP is a kind of cathodic polarization-based inhibitor.

5. Conclusions
The structure-activity relationship between molecule structure of polyaspartic acid (PASP) and its scale corrosion inhibition performance was studied by quantum chemical calculation method. The conclusions are as follows.

1. After calculation by semi-empirical quantum chemistry method, it is found that the net charge of atom nitrogen and oxygen on PASP are between -0.537 to -0.508 e, which proved that the nitrogen atom on the imine group and the oxygen atom on the carboxyl group has strong electronegativity ability. The strong electronegativity ability makes the oxygen atom on the carboxyl group very easy to interact with calcium ion on the crystal surface. Furthermore, the relative distance between the two nitrogen and oxygen ions in the PASP molecule is very close to the calcium ion spacing on the calcite crystal surface, the excellent matching can significantly enhance the adsorption force between PASP molecule and specific crystal face. Therefore, PASP has obvious scale inhibition performance.

2. The highest occupied molecular orbital energy level, lowest unoccupied molecular orbital energy level, and the energy gaps of them have been calculated are -0.01215 eV, -0.38092 eV and 0.36877 eV, respectively. The value of $E_{\text{HOMO}}$ of PASP molecule is -0.01215 eV, which indicates that its first ionization ability is relatively strong. In addition, the value of $\Delta E$ of PASP molecule is relatively large, indicating that the stability is relatively good. Therefore, PASP has outstanding corrosion inhibition performance.

3. The scale and corrosion inhibition performance of PASP was studied by using the traditional experimental methods of static scale inhibition test, SEM analysis and electrochemical experiment, and the experimental results are completely consistent with the calculated results. Obviously, PASP is a kind of excellent water treatment agent with both scale and corrosion inhibition.

Acknowledgements
This work was supported by the Special project for scientific research and development of Henan Academy of Sciences (200606064 and 200606050).
References
[1] J. Vosta, J. Eliasek. Study on corrosion inhibition from aspect of quantum chemistry [J]. Corros. Sci., 1971, 11(4):223-229.
[2] R.G. Parr, Wu Yang. Density functional theory of atoms and molecules [M]. Oxford: Oxford University Press, 1991.
[3] A. B. Richard, Honghui Lan. Quantum chemical approaches: semi-empirical molecular orbital and hybrid quantum mechanical/molecular mechanical techniques [J]. Curr. Pharm. Design, 2014, 20:4881-4902.
[4] B. Thomas, J. Karl. Theory and range of modern semiempirical molecular orbital methods [J]. Theor. Chem. Acc., 2005, 99:610-625.
[5] A. Zarrouk, B. Hammouti, T. Lakhlifi, et al. New 1H-pyrrole-2,5-dione derivatives as efficient organic inhibitors of carbon steel corrosion in hydrochloric acid medium: electrochemical, XPS and DFT studies [J]. Corros. Sci., 2015, 90:572-584.
[6] I. Belfilali, A. Chetouani, B. Hammouti, et al. Quantum chemical study of inhibition of the corrosion of mild steel in 1 M hydrochloric acid solution by newly synthesized benzamide derivatives [J]. Res. Chem. Intermed, 2014, 40:1069-1088.
[7] Lijun Fu, Yuzeng Zhao, Honghua Ge, et al. Study on scale inhibition performance of polyaspartic acid derivatives with dihydroxyl group on CaCO3 [J]. Adv. Mater. Res., 2012, 361-363:1982-1986.
[8] A. Zarrouk, B. Hammouti, A. Dafali, et al. Inhibition of copper corrosion in acid solution by N-1-naphthylethlenediamine dihydrochloridemonomethanolate: experimental and theoretical study: part-1 [J]. Res. Chem. Intermed, 2012, 38:1079-1089.
[9] Xiwei Zheng, Shao tong Zhang, Mao Gong, et al. Experimental and theoretical study on the corrosion inhibition of mild steel by 1-octyl-3-methylimidazolium L-prolinate in sulfuric acid solution [J]. Ind. Eng. Chem. Res., 2014, 53:16349-16358.
[10] V. V. Torres, V. A. Rayol, M. Magalhaes, et al. Study of thioureas derivatives synthesized from a green route as corrosion inhibitors for mild steel in HCl solution [J]. Corros. Sci., 2014, 79:108-118.
[11] Yuhua Gao, Zhenfa Liu, Lihui Zhang, et al. Study on scale inhibition performance of modified polyaspartic acid [J]. Adv. Mater. Res., 2014, 893:7-10.
[12] Yushan Ceng, Yincong Sun, Xinguang Shi, et al. Study on corrosion and scale resistance of environment-friendly water treatment agent [J]. Henan Sci., 2018, 36(11):1715-1722.