Chapter 4

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Abstract

In this study, molecular simulations of polyvinylpyrrolidone (PVP) were obtained using PM3 and AM1 methods containing. PVP was characterized by FTIR, electrostatic potential, molecular orbitals, respectively. The results of the computer simulation indicated that a Gibbs free energy is very similar between two methods.

Keywords: PVP, Simulation, PM3, AM1

4.1 Introduction

The chemistry of acetylene, developed at BASF in the 1920s byWalter Reppe, opened up numerous application possibilities, especially in the young field of plastics. In 1938, the year Nylon and Perlon were discovered, BASF succeeded in using acetylene chemistry to develop a highly interesting derivative: by reacting acetylene with pyrrolidone, vinylpyrrolidone was obtained, which in turn was used to form polyvinylpyrrolidone (PVP). The process patent was granted on January 1, 1939. It soon became apparent that PVP was an all-

around talent. It is readily soluble in water, physiologically compatible, non-toxic, essentially chemically inert, temperature-resistant, pH-stable, non-ionic, and colorless. This remarkable combination of properties predestined its use in numerous applications in medicine, pharmaceutical technology, cosmetics, and in the technical industry. Even as early as 1939, PVP was used as a plasma expander and was widely used in this form during World War II. During the 1950s, PVP replaced the schellac hitherto used in hair sprays [1].

4.2 Synthesis and Structure

PVP is soluble in water and other polar solvents. When dry it is a light flaky powder, which readily absorbs up to 40% of its weight in atmospheric water. In solution, it has excellent wetting properties and readily forms films. This makes it good as a coating or an additive to coatings. PVP is a branched polymer, meaning its structure is more complicated than linear polymer, though it too lies in a two-dimensional plane. In general, compositions of polymers are made up of many simple molecules that are repeating structural units called monomers.

A single polymer molecule may consist of hundreds to a million monomers and may have a linear, branched, or network structure. Covalent bonds hold the atoms in the polymer molecules together and secondary bonds then hold groups of polymer chains together to form the polymeric material. Copolymers are polymers composed of two or more different types of monomers [2]. PVP is synthesized via a free radical polymerization reaction starting from the vinylpyrrolidone (VP) monomer, using a free radical initiator such as Azobisisobutyronitrile (AIBN) (see Figure 4.1) [3].

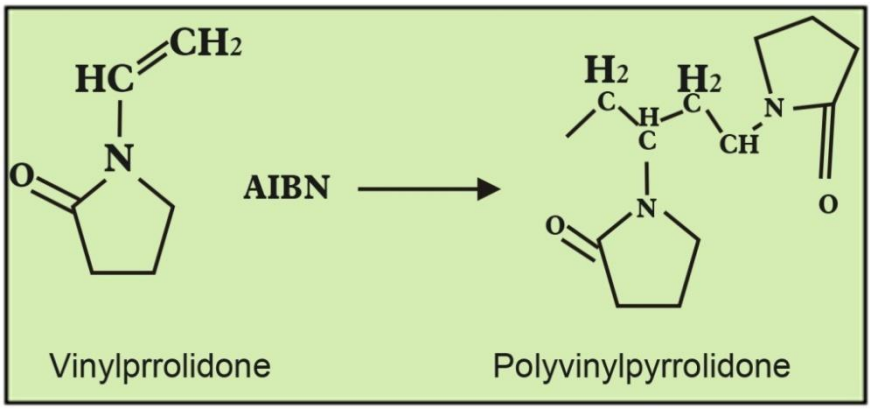

Figure 4.1 *Reaction for the synthesis of polyvinylpyrrolidone.*

4.3 Applications

The polymer PVP was used as a blood plasma expander for trauma victims after the 1950s. It is used as a binder in many pharmaceutical tablets; it simply passes through the body when taken orally. However, autopsies have found that crospovidone does contribute to pulmonary vascular injury in substance abusers who have injected pharmaceutical tablets intended for oral consumption. The long-term effects of crospovidone within the lung are unknown. PVP added to iodine forms a complex called povidone-iodine that possesses disinfectant properties. This complex is used in various products like solutions, ointment, pessaries, liquid soaps and surgical scrubs. It is known under the trade name Betadine and Pyodine. It is used in pleurodesis (fusion of the pleura because of incessant pleural effusions). For this purpose, povidone iodine is equally effective and safe as talc, and may be preferred because of easy availability and low cost [4-6].

4.4 Results and Discussion of Simulations Analyses

4.4.1 Optimization Energy

Table 4.1 shows the Gibbs energy free for PVP structure using different methods, in where the negative values of ΔG by means different methods shows that the electrostatic binding is energetically favorable. The difference in the energy values are attributed to the formula of the method applied [7]. Attractive interaction between π systems is the interaction between two or more molecules leading to self-organization by formation of a complex structure which has lower conformation equilibrium than of the separate components and shows different geometrical arrangement with the AM1 and PM3 method (Figure 4.2).

Table 4.1 *Gibbs energy free for PVP structure.*

Method	ΔG (Kcal/mol)
AM1	-1494
PM3	-1626

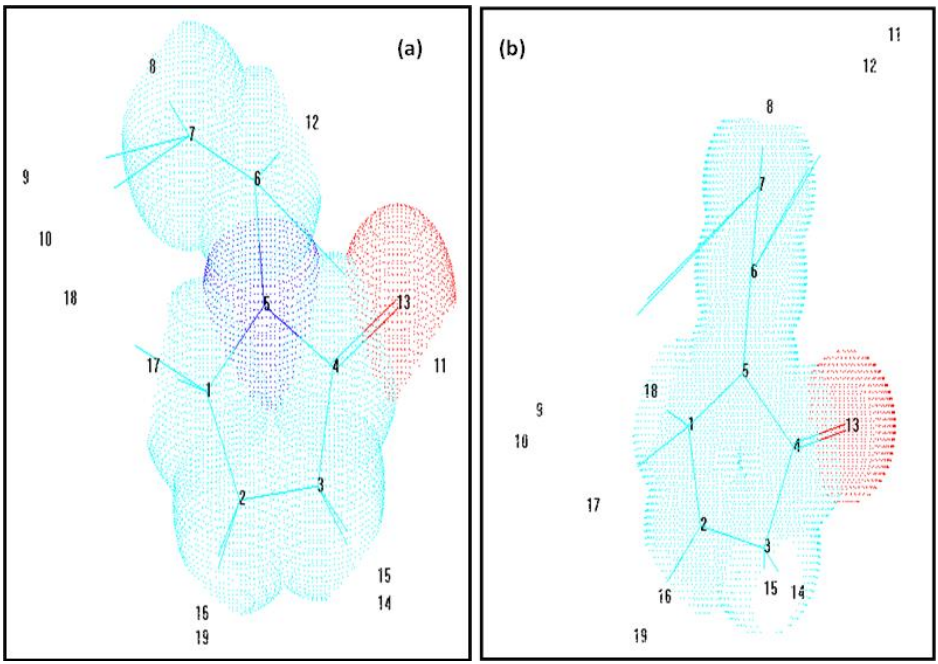

Figure 4.2 *Molecular geometry of PVP, in where (a) PM3 and (b) AM1, respectively.*

4.4.2 Structural Parameters

From the structural data given in Table 4.2, it is observed that the various bond lengths and angles are found to be very same at PM3 and AM1 methods. For the title molecule, the PVP is planar, and also CH_3-CH_2 (6-11 atoms) attached to nitrogen element (atom #5) as evident from the bond lengths and angles. According to their observations, deformations of the PVP structure depend of CH bond of the PVP ring [8].

Table 4.2 *Structural parameters calculated for PVP employing PM3 and AM1 methods.*

Bond length (Å)	PM3	AM1
1-2	1.37	1.37
2-3	1.41	1.41
3-4	1.38	1.38
4-5	1.42	1.42
5-1	1.42	1.42
5-6	1.42	1.42
6-7	1.32	1.32
6-11	3.85	3.81
6-12	1.10	1.01
7-8	1.06	1.06
7-9	3.05	3.03
7-10	2.99	2.97
4-13	1.36	1.36
3-14	1.65	1.65
3-15	1.65	1.65
2-16	1.66	1.66
2-19	1.68	1.67
1-17	1.09	1.10
1-18	2.76	2.76

Bond angle (°)	PM3	AM1
1-2-3	109.8	109.7
2-3-4	107.75	107.8
3-4-5	107.74	107.7
4-5-1	107.77	107.8
5-1-2	106.9	106.8
1-17-18	6.970	7.52
2-16-19	25.29	25.32
3-14-15	25.58	25.57
3-4-13	133.0	133
4-5-13	119.24	119.23
5-6-11	51.04	51.6
6-11-12	65.3	66
6-7-8	157.24	156.91
6-7-10	130.39	130
7-8-9	57.26	57.6
7-9-10	15.09	15.19

4.4.3 FTIR Analyses

The resulting vibrational frequencies for the optimized geometries and the proposed vibrational assignments as well as FTIR also given in Table 4.3 in where, the results are very similar between AM1 and PM3 method. From 4328 to 4279 corresponds to CH_2 symmetric stretching, from 3329 at 2976 cm^{-1} were attributed at CH stretching, at 2263 was assigned to CH (CH_3-CH_2), at 1420-1500 cm^{-1} of the CH_3 scissoring, at 1651 cm^{-1} the C–N stretching reveal the characteristic absorbance peak of PVP [9-12]. The peak between 2194 at 2121cm^{-1} is assigned to the stretching vibration of the C=O in the PVP amide unit [12-13]. The C=O groups of pure PVP show a prominent peak at 1663 cm^{-1} in FTIR spectrum. This characteristic peak can be investigated to explore about the interaction between PVP and metal species [14-15].

Table 4.3 *The calculated frequencies using PM3 and AM1 methods, respectively.*

ASSIGNMENT	PM3 (FREQUENCIES CM^{-1})	AM1 (FREQUENCIES CM^{-1})
CH (CH_2) symmetric stretching	---	4328
CH (CH_2) symmetric stretching	---	4279
CH stretching	---	3329
CH stretching	3179	3182
CH stretching	3058	3061
CH stretching	2976	2976
CH (CH_2) symmetric stretching	---	2839
CH (CH_3-CH_2) stretching	---	2263
C=O stretching	2194	2121
C-N	---	1651
CH deformation of cycli CH_2 groups	1489	1492
C-C (PVP ring)	1386	1382
C-C (PVP ring)	---	1321
Amide or CH_2 rock	730	733
CH deformations	618	618
C-N, C-C	658	---

4.4.4 Electrostatic Potential

Figure 4.3 shows the electrostatic potential of the PVP using PM3 and AM1 method, where Figure 4.3(a) shows that the CH_3-CH_2 bond presents a neutral electrostatic potential, while in the area of green color of CH bond of the PVP ring is attributed to positive values of the potencal, in fact, reppresenta electron-poor regions, while ring like C-N bond presented the negative regions, i.e., where the majority of electrons are, while Figure 4.3(b) shows that, C-C and C-N ring bonds shown positive potentials and the CH_3-CH_2 bond characteristic potential is negative, these differences are due to the method used to determine the values maximum and minimum of the electrostatic potential of the PVP.

4.4.5 Molecular Orbitals

The excitation band is attributed to the electronic transitions in PVP molecular orbitals. Alternatively, the blue emission band of PVP at 394 nm is attributed to the radiative relaxation of electrons from the lowest energy unoccupied molecular orbital (LUMO) to the highest energy occupied

molecular orbital (HOMO) levels in PVP [16].

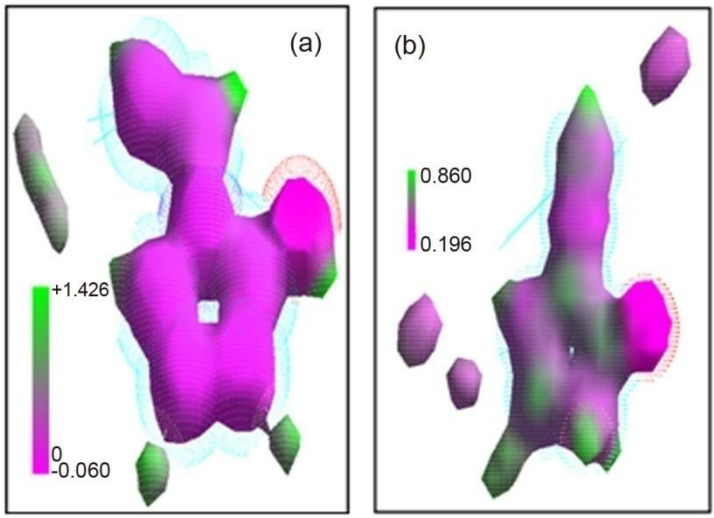

Figure 4.3 *Electrostatic potential of PVP, in where (a) PM3 and (b) AM1, respectively.*

Table 4.4 *HOMO and LUMO orbitals for PVP using PM3 method.*

ORBITAL	HOMO		LUMO	
	ENERGY (eV)	SYMMETRY (Å)	ENERGY (eV)	SYMMETRY (Å)
50	-14.25	16	1.86	27
20	-39.51	1	6.62	42
10	-16.38	11	4.03	32
5	-14.25	16	1.86	27
-5	1.731	26	-13.20	17
-10	3.563	31	-15.88	12
-20	6.134	41	-36.68	2
-50	1.730	26	-13.20	17

Table 4.5 *HOMO and LUMO orbitals for PVP using AM1 method.*

ORBITAL	HOMO		LUMO	
	ENERGY (eV)	SYMMETRY (Å)	ENERGY (eV)	SYMMETRY (Å)
50	-18.08	16	-2.59	27
20	-45.76	1	1.76	42
10	-20.51	11	-1.40	32
5	-18.08	16	-2.59	27
-5	-3.59	26	-17.94	17
-10	-1.56	31	-20.13	12
-20	1.37	41	-42.58	2
-50	-3.59	26	-17.94	17

4.4.6 Conclusions

As a consequence of the development of theory, computers and computer software, molecular orbital model calculations are important tools in all branches of chemistry. The quantum mechanical models help us to explain, and to better understand, the physical cause of isotope substitution effect using different techniques of analysis. In this work, the PVP was analyzed using PM3 and AM1 method, in where both results confirm all the typical adsorption bands of PVP. These methods can be used quite satisfactorily in predicting the chemical reactivity of the molecules and the effect of substitution of either donor electron or acceptor electron.

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