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Theoretical study of the solvent effects on the thermodynamic functions of ALanine and Valine Amino Acids

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ABSTRACT

Using Gaussian 03, software the thermodynamic functions such as Gibbs free energy, G°, Enthalpy, H°, and Entropy, S°, of Alanine and Valine amino acids were theoretically studied at different solvents. First, the Density Functional Theory (B3LYP) level with 3-21G, 6-31G and 6-31+G basis sets were employed to optimization of isolated Alanine and Valine amino acids in the gas phase. Moreover, Vibrational frequencies were calculated in gas phase on the optimized geometries at the same level of theory to obtain the thermodynamic functions such as Gibbs free energy, G°, Enthalpy, H°, and Entropy, S°,. Then, the calculation about the solvent effects on the thermodynamic functions of Alanine and Valine amino acids were performed for the various solvents (Water, Methanol and Ethanol) by using self consistent Reaction-Field (SCRF=PCM) model at B3LYP/6-31+G. Thermodynamically analysis shows the relative Gibbs free energy changes, ΔG°, Enthalpy changes, ΔH°, are negative values but the Entropy changes, ΔS°, are positive values for Alanine and Valine amino acids. Also, the results shows, with increasing of dielectric constant of solvents the stability of considered amino acids increases.

Keywords: Alanine; Valine; Solvent effects; PCM model; Thermodynamic functions

INTRODUCTION

Amino acids are important function is to serve as the building blocks of proteins, which are linear chains of amino acids. Due to their central role in biochemistry, amino acids are important in nutrition and are commonly used in food technology and industry. In industry, applications include the production of biodegradable plastics, medicines, and chiral catalysts. Amino acids can be linked together in varying sequences to form a vast variety of proteins. Twenty amino acids are naturally incorporated into polypeptides and are called standard amino acids. Alanine (Ala) is a nonessential amino acid meaning it can be manufactured by the human body, Alanine is found in a wide variety of foods, but is particularly concentrated in meats. Alanine can be manufactured in the body from pyruvate and branch chain amino acids such as valine, leucine, and isoleucine. Alanine is most commonly produced by reductive amination of pyruvate. Valine, is an essential amino acid

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*Corresponding author: f-rezaei@iau-arak.ac.ir it cannot be produced by the human body and must be obtained through food or supplements. Valine is important for the muscle tissue as well as for the regulation of the immune system. This particular amino acid is not processed by the liver, but is taken up by muscles. We can obtain it through kidney beans, leafy vegetables, poultry and milk [1-3].

In this study, the structural optimization of the amino acids Alanine and Valine were investigated. The optimization results of the isolated Alanine and Valine molecules in the gas phase, at the Density Functional Theory (B3LYP) level with 3-21G, 6-31G and 6-31+G basis sets have also been carried out. Moreover Vibrational frequencies were calculated in gas phase on the optimized geometries at the same level of theory to obtain the Gibbs free energy, G°, Enthalpy, H°, and Entropy, S°. The calculations about the solvent effects on the thermodynamic functions such as Gibbs free energy, G°, Enthalpy, H°, and Entropy, S°, of Alanine and Valine were performed for the three solvents (Water, Methanol and Ethanol**)** using PCM model and vibrational frequencies method at B3LYP/6-31+G and then the dielectric effects of solvents in surrounding Alanine and Valine amino acids were analyzed.

COMPUTATIONAL METHODS

Geometries

All calculations for the optimization, vibrational frequencies and solvent effects of the Alanine and Valine amino acids were done with the Gaussian 03 [21], Ab initio packages at the Density Functional Theory (B3LYP) level of theory. Three basis sets were used including 3-21G, 6-31G and 6-31+G. At first, the geometries of Alanine and Valine were full optimized at the B3LYP/ 3-21G, 6-31G and 6-31+G levels of theory in the gas phase. Moreover, Vibrational frequencies were calculated in gas phase on the optimized geometries at the same level of theory to obtain the thermodynamic functions such as Gibbs free energy, G°, Enthalpy, H°, and Entropy, S°.

Solvent Model

Polarized Continuum Model (PCM) was used for three solvents including (Water**,** Methanol and Ethanol) in these calculations. First, molecular geometries were obtained by B3LYP/6-31+G level of optimization for Alanine and Valine in the gas phase. Then, Alanine and Valine molecules were separately placed in each of three solvents and then by using vibrational frequencies calculations Gibbs free energy, G°, Enthalpy, H°, and Entropy, S°, were obtained and the results were compared with each other and gaseous phase.

RESULTS AND DISCUSSION

The geometries optimizations of Alanine and Valine molecules were chosen as the starting step in the gas phase. The Alanine and Valine were found to be stable in the optimized gas phase at B3LYP/ 3-21G, 6-31G and 6-31+G level. The result is summarized in Table1.

In accordance with the obtained results, the minimum energies were related to the basis set of 6-31+G level. Therefore, here the basis set 6-31+G was selected for the other calculations. Then, vibrational frequencies calculations were applied in the gas phase on the basis set 6-31+G level to obtain the thermodynamic functions Such as Gibbs free energy, G°, Enthalpy, H°, and Entropy, S°. The result is shown in Table2.

A Self Consistent Reaction-Field (SCRF=PCM) model were used for obtain an estimation of the solvent effects on the optimized geometries gaseous phase in various solvents such as (Water, Methanol and Ethanol) Then, calculations about vibrational frequencies for determining thermodynamic functions such as Gibbs free energy, G°, Enthalpy, H°, and Entropy, S°, were applied of considered solvents. The Gibbs free energy changes are identified by: $\Delta G^{\circ}=G^{\circ}_{solute}- G^{\circ}_{gas\ phase}$, the Enthalpy changes are identified by: $\Delta H^{\circ}=H^{\circ}_{solut} -H^{\circ}_{gas\ phase}$ and entropy changes are identified by: $\Delta S^{\circ}=S^{\circ}_{solut}-S^{\circ}_{gas\ phase}$. The thermodynamic functions such as, Gibbs free energy changes, ΔG°, Enthalpy changes, ΔH°, and Entropy changes, ΔS°, (in kcal mol^{-1}) for Alanine and Valine as a function of dielectric constant,ε, of considered solvents are indicated in Table3. These values were obtained by using B3LYP/6-31+G method, and were performed at STAP condition [T=298.150(k), P=1(atm)]. The results show the stability of Alanine and Valine reduces by decreasing the polarisability of the solvents. The most stability is observed for Water with ε=78.39 and the lowest one for Ethanol with ε=24.55.

Regular alterations were observed concerning thermodynamic function *versus* dielectric constant. With increasing dielectric constant of solvents the Gibbs free energy changes, ΔG°, and Enthalpy changes, ΔH°, were decreased and Entropy changes, ΔS°, were increase (Fig.1a-c). Fig.1a shows the plot of the Gibbs free energy changes, ΔG°, (in kcal mol^{-1}) of Alanine and Valine versus the dielectric constant,ε, of the three solvents. Obviously, the magnitude of ΔG° is decreased by increasing the dielectric constant,ε, of the solvents. Fig.1b shows the plot of the Enthalpy changes, ΔH°, (in Kcal mol^{-1}) of Alanine and Valine versus the dielectric constant, ε, of the three solvents. As can be seen from Fig.1b, with increasing dielectric constant,ε, of solvents, the Enthalpy changes, ΔH°, is decreases. Fig.1c shows the plot of the Entropy changes, ΔS° (in Kcal mol^{-1}) of Alanine and Valine versus the dielectric constant,ε, of the three solvents. As shown in Fig.1c, with increasing dielectric constant,ε, of solvents, the Entropy changes, ΔS°, is increases.

Table 1. Absolute calculated results of the conformational energy (E(in kcal mol^{-1})) of Alanine and Valine obtained by geometry optimization at basis set 6-31+G, 6-31G and 3-21G levels

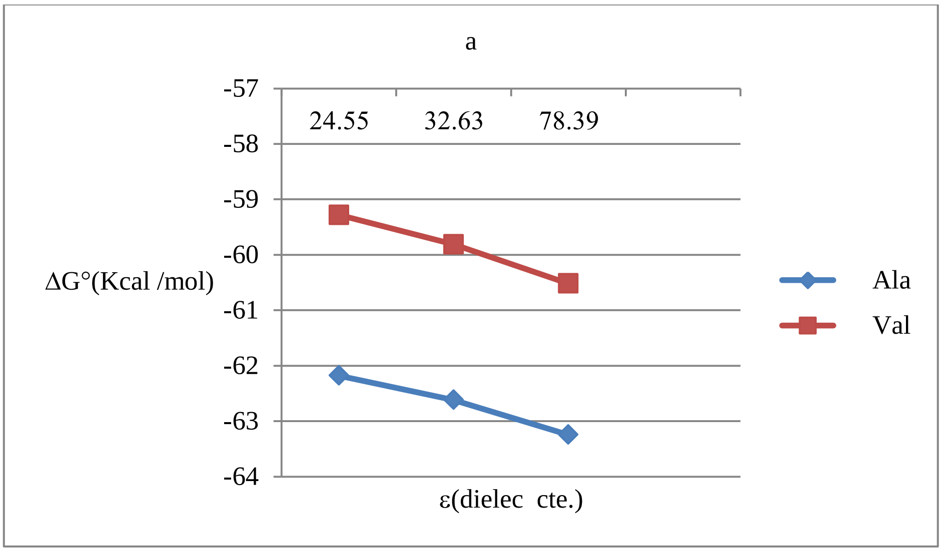
	E(Kcal mol^{-1})	
Basis set	Ala	Val
3-21G	-203051.829	-250839.124
6-31G	-203086.583	-250862.219
6-31+G	-203092.347	-250868.017

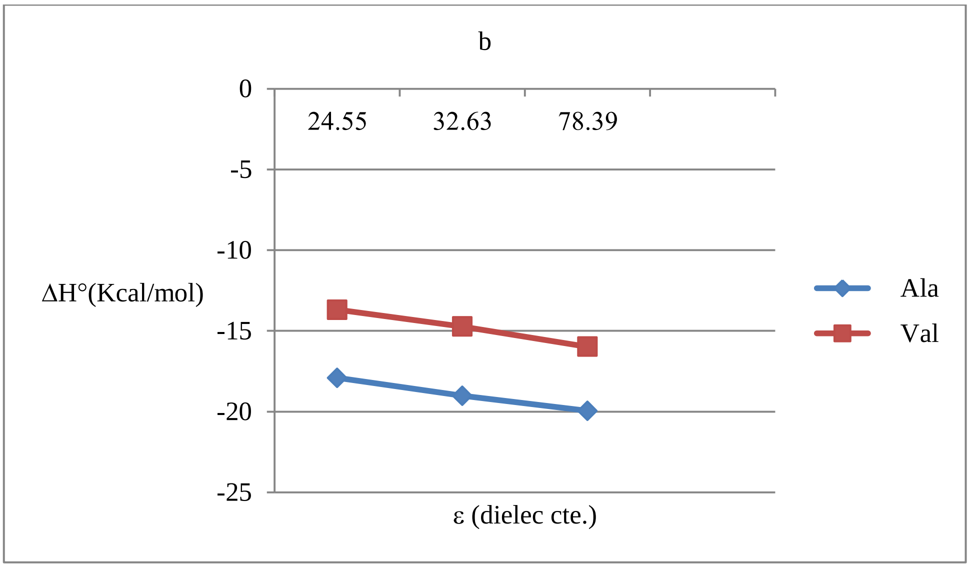
Table 2. The results relative thermodynamic functions of Alanine and Valine by using vibrational frequencies calculations on the basis set 6-31+G level in the gas phase

G°(Kcal mol^{-1})	H°(Kcal mol^{-1})	S°(Kcal mol^{-1})
	Ala	
-203046.284	-203021.6375	0.082664
	Val	
-250463.129	-250438.470	0.082706

Table3. The result relative thermodynamic functions changes (Kcal mol^{-1}) of Alanine and Valine by using solvent effect calculations with the B3LYP/6-31+G method

Solvents	ΔG° (Kcal mol^{-1})	ΔH° (Kcal mol^{-1})	ΔS° (Kcal mol^{-1})
		Ala	
Water	-63.246	-19.150	0.1479
Methanol	-62.618	-19.028	0.1467
Ethanol	-62.180	-17.909	0.1458
		Val	
Water	-60.517	-15.978	0.1524
Methanol	-59.812	-14.732	0.1512
Ethanol	-59.283	-13.690	0.1499





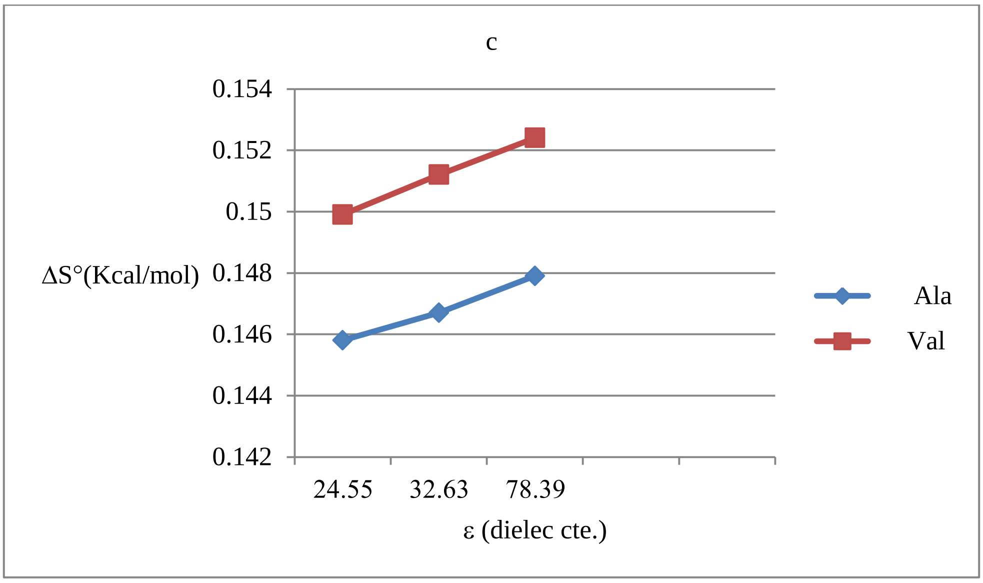


Fig. 1. The plots of the Gibbs free energy changes ΔG°(in kcal mol^{-1}) versus the dielectric constant, ε, (a), Enthalpy changes, ΔH°(in Kcal mol^{-1}) versus the dielectric constant, ε, (b) and Entropy changes, ΔS°(in Kcal mol^{-1}) versus dielectric constant, ε, (c) of Alanine and Valine in various solvents.

CONCLUSIONS

The thermodynamically analysis shows with increasing dielectric constant from gas phase to water, the Gibbs free energy changes ΔG° (Kcal mol^{-1}) and Enthalpy changes ΔH° (Kcal mol^{-1}) of Alanine and Valine decreases and Entropy changes ΔS° (Kcal mol^{-1}) of Alanine and Valine increases. This means, with increasing of dielectric constant, the stability of Alanine and Valine increases. We have proposed an empirical communication between effects of solvent and length of hydrocarbon chains in two amino acids.

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