

## COMPUTATIONAL INVESTIGATION OF STRUCTURAL, ELECTRONIC AND THERMODYNAMIC PROPERTIES OF NONYLPHENOL ETHOXYLATE SURFACTANTS

Dinesh R. Pandithavidana\* and W. Isuru Madushan Jayalath

Department of Chemistry, Faculty of Science, University of Kelaniya,  
Kelaniya 11600, Sri Lanka

E-mail: dinesh@kln.ac.lk (\*Corresponding Author)

**Abstract:** Nonylphenol ethoxylates (NPEs) are group of non-ionic surfactants commonly known as Tergitol NP surfactants. The hydrophilic-lipophilic-balance (HLB value) is used as the key parameter by surfactant formulators to study the properties of non-ionic surfactants. Even though the HLB values of two surfactants are equal or close enough to each other, the expected properties cannot be obtained by replacing one surfactant with another one. This issue leads to a necessity to carry out many trial and error tests to identify the equivalent surfactants in industrial applications. The strong hydrogen bonding with water, Gibbs free energy change of solvation ( $\Delta G_{\text{solv}}$ ), molecular dipole moment and maximum absorption wavelength ( $\lambda_{\text{max}}$ ) have been developed as key performance indicators of a better surfactant in this research work. Computed results predict that NPEs are well stabilized in the aqueous medium with the extension of ethoxylate chain length, illustrating a linear relationship of  $\Delta G_{\text{solv}}$  with respect to the number of ethylene oxide units. This evidence has been further supported by the decrease in hydrogen bond length, between the NPEs and water molecules with the extension of the ethoxylate chain of the surfactant. Among ortho-, meta-, and para-substituted NPEs, due to the presence of higher dipole moments of meta-substituted NPEs indicated that they form more efficient secondary interactions in aqueous medium. Moreover meta-substituted NPEs demonstrate relatively higher thermodynamic stability (than ortho- and para- substituted NPEs) due to the presence the highest HOMO-LUMO gap.

**Keywords:** Nonylphenol ethoxylates, NP surfactants, thermodynamic properties.

### INTRODUCTION

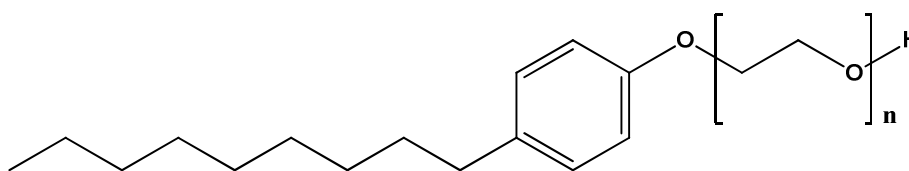
A surfactant (surface active agent) is a chemical agent capable of reducing the surface tension of a liquid in which it is dissolved. The distinct properties of the surfactants in the aqueous medium can be described with the presence of a hydrophilic group and a hydrophobic chain in the molecule [1,2]. Nonylphenolethoxylate surfactants (NPEs) are odorless, pale yellow liquids or waxes which commercially abbreviated as Tergitol NP surfactants [3]. A molecule of Nonylphenolethoxylates contains one lipophilic, nonyl-hydrocarbon chain and one hydrophilic, ethoxylate chain (Figure 1). Most of physical properties such as melting point,

density and water solubility depend on number of ethylene oxide (EO) units attached to the molecule [4,5].

Hydrophilic–lipophilic balance (HLB) is the net effect of size and strength of the hydrophilic and lipophilic moieties of a surfactant molecule [6]. The HLB value for a particular surfactant is calculated by utilizing the ratio of the hydrophobic to the hydrophilic portion of the molecule as shown in the equation-(1).

$$HLB = \frac{MH}{MW} \times 20 \text{ ----- Equation (1)}$$

Where, **MH** is the molecular weight of the hydrophilic portion of the molecule and **MW** is the molecular weight of the whole surfactant molecule. Solving the equation results an arbitrary scale of starts from 0 to 20 [7]. Thus HLB value of a surfactant is related to its solubility; a surfactant is having a low HLB tends to be oil-soluble (lipophilic), and one is having a high HLB tends to be water-soluble (hydrophilic).



**Figure 1.** Common structure of the Nonylphenolethoxylates.

Although, in commercial industries, the HLB classification is used to categorize surfactants, it suffers from a number of limitations. First, HLB method does not take into consideration of major factors like temperature, pressure and pH of the medium or the environment of the surfactant. The HLB value is also not specific to the solvent which the surfactant is dissolved. Therefore two emulsifiers may have the same HLB and yet exhibit quite different solubility characteristics [6]. Thus it is advantageous to quantify properties of surfactants which can correlate to the interactions with water as changing the structure of the surfactant.

Computational chemistry can be used as a versatile tool to get a deeper percept of atomistic and electronic properties of these surface active agents. Among various computational procedures, the DFT calculations allow investigating the solvation energy of dispersants which directly relate to the structure of the molecule and the polarity of the solvent used [8]. So it provides insight to understand the surfactant behavior in both aqueous and non aqueous phases. The DFT method also provides information related to the electronic perturbation caused by substituent effect of functional groups present in the surfactant. Thus properties

revealed from DFT calculations are very versatile to understand the behavior of surface active agents in aqueous media which can be utilized for their industrial applications [9,10].

In this research work, we computationally investigated how solvation Gibbs free energy ( $\Delta G_{\text{solv}}$ ) varies with extension of the length of ethoxylate chain (4 to 16 ethoxylate units) of NPEs in aqueous medium to predict their thermodynamic stabilities. The variation of the hydrogen bond distance between the para-substituted nonylphenoethoxylates and water molecules was studied because it is a key determinant [11, 12] to indicate the interactions between NPEs and water. Then how thermodynamic stability was affected by changing the position of substituents at benzene ring and the branching of the nonyl hydrocarbon chain of NPEs were also interpreted in this study. Moreover UV spectra of some selected NPEs were computationally generated to reveal how their absorption maxima ( $\lambda_{\text{max}}$ ) have been significantly affected by the change in position of substituents.

## **MATERIALS AND METHODS**

All computational simulation work was carried out using well-known hybrid B3LYP level of theory [13] using 6-311G basis set in Linux version of Gaussian 09 (64 bit) computer software package in Linux Mint 16 Cinnamon 64 bit operating system and Gauss view 5.0.8 software package on Wine in Linux.

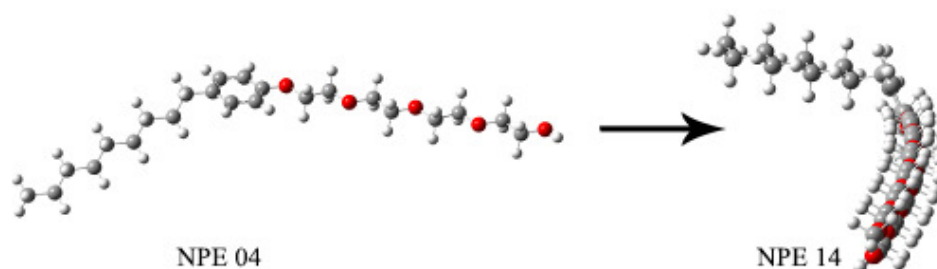
Solvation energies were investigated at the aqueous phase with the conductor-like polarizable continuum model (CPCM) [14]; the energy difference between the aqueous phase and the gas phase of each NPE molecule was used to determine the Gibbs free energy of solvation ( $\Delta G_{\text{solv}}$ ) [15]. Intermolecular hydrogen bond distances (at the gas phase) were investigated by placing two water molecules which were closed to the first and the last “ethoxy-oxygens” of each NPE molecule. The effect of the change in substituted position (ortho, meta and para) on  $\Delta G_{\text{solv}}$  and molecular dipole moment were computed at the same level of theory for selected NPE surfactants [16]. The dipole moments and UV spectra (to investigate  $\lambda_{\text{max}}$ ) of the optimized molecules were obtained from the corresponding simulated files.

## **RESULTS AND DISCUSSION**

### **Investigation of thermodynamic stability and dipole moments of para substituted Nonylphenoethoxylates in the aqueous medium:**

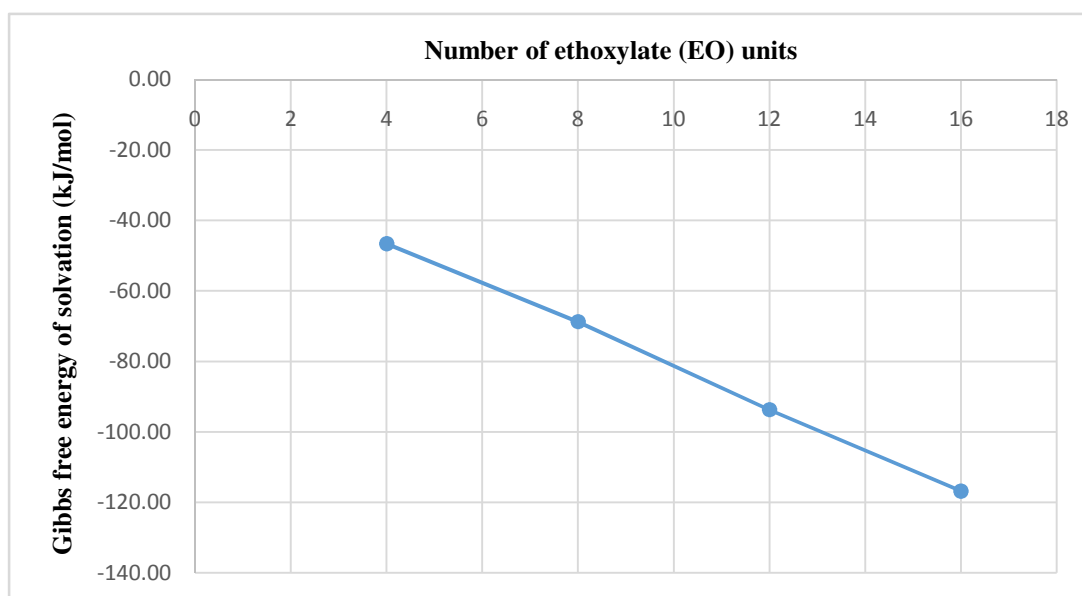
The change in solvation Gibbs free energy ( $\Delta G_{\text{solv}}$ ) and the dipole moment of the para-substituted NPEs were computed with extension of the ethoxylate chain by increasing ethoxylate units (EO) of the hydrophilic part of the molecule. The extension of the ethoxylate chain of NPE molecules caused the deviation of the linearity (curving) of the hydrophilic

region of the molecule at the aqueous medium due to the presence of secondary interactions (such as Hydrogen bonding) with the water molecules (Figure 2).



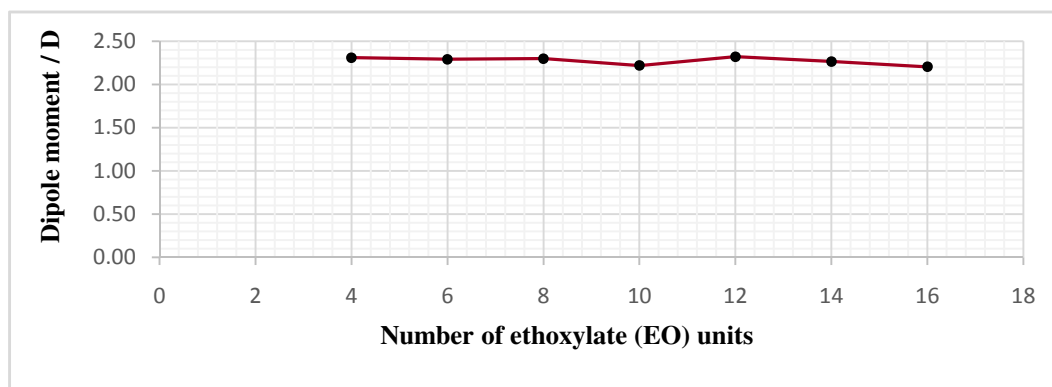
**Figure 2.** Extension of the ethoxylate chain of NPE

The solvation Gibbs free energy ( $\Delta G_{\text{solv}}$ ) of NPEs plays an important role to understand the behavior of NPEs in aqueous phase [17]. Solvation Gibbs free energy ( $\Delta G_{\text{solv}}$ ) values obtained for optimized structures of NPEs in aqueous medium (Figure 3) illustrated that the extension of the length of ethoxylate chain has decreased the  $\Delta G_{\text{solv}}$  of molecules in aqueous media. The more negative values (-46.62 to -116.88 kJ/mol) of  $\Delta G_{\text{solv}}$  indicated the stability of the NPEs in aqueous medium increased with the extension of the length of ethoxylate chain (4 to 16 ethoxylate units).



**Figure 3.** Change in  $\Delta G_{\text{solv}}$  of para substituted NPEs with the extension of ethoxylate units.

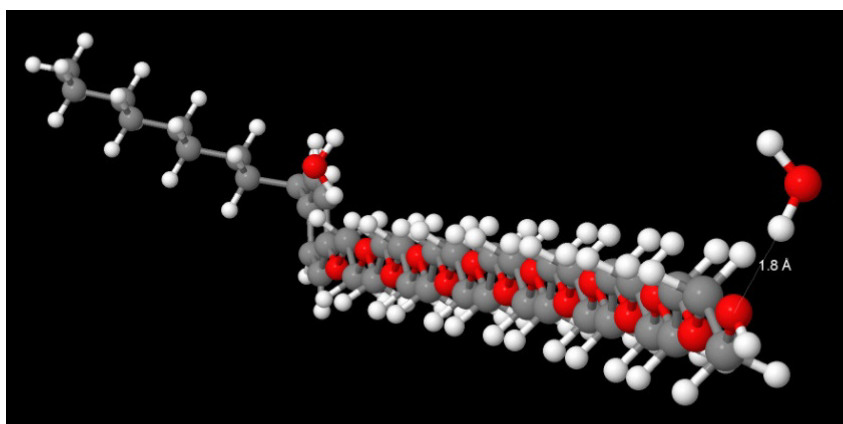
It was pointing out a linear relationship between  $\Delta G_{\text{solv}}$  versus ethoxylate units (EO) as shown in Figure 3. Computed dipole moments of para-substituted NPEs did not fluctuate significantly with the extension of the ethoxylate chain length (Figure 4); thus all values stood between 2.2D – 2.3 D.



**Figure 4.** The change in the dipole moment with the extension the ethoxylate chain.

**The study of how extension of the ethoxylate chain of NPEs affects on the hydrogen bond length between water molecules and surfactants:**

Intermolecular hydrogen bonding plays a key role in estimating the stability of the NPEs in the aqueous medium when it forms emulsions [18]. Therefore it was considered as a key determinant to compute the interactions between NPEs and water. Intermolecular hydrogen bond distances (in gas phase) were investigated as placing two water molecules which were closed to the first and the last “ethoxy-oxygens” of NPEs (Figure 5).



**Figure 5.** Illustration of intermolecular hydrogen bonding between NPE and H<sub>2</sub>O.

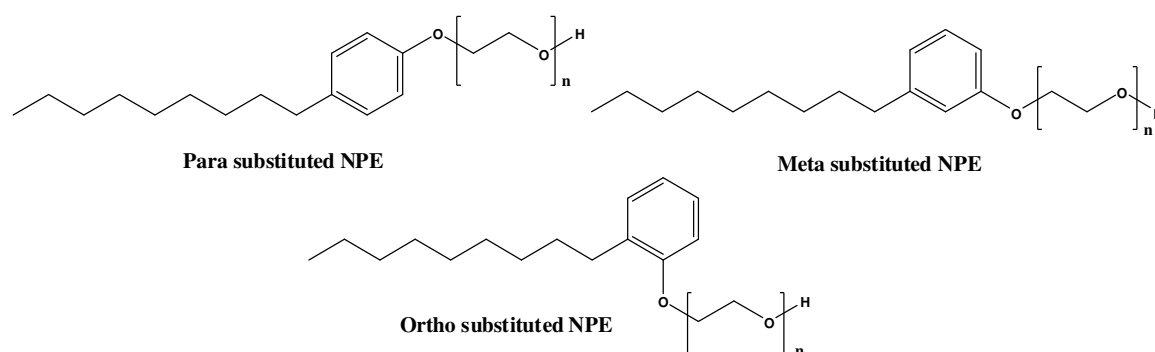
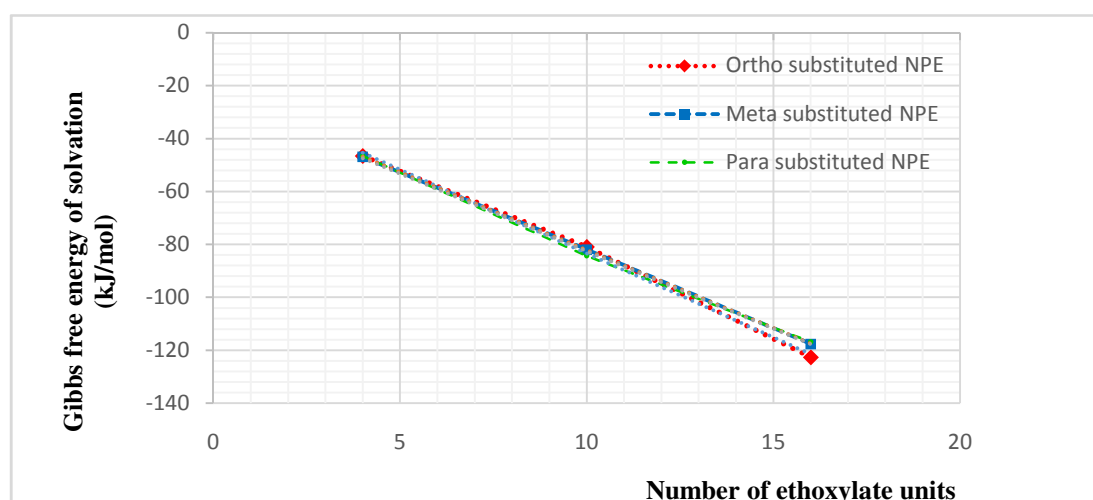
It was evident that the hydrogen bond length between the NPEs and water molecules decreased with the extension of the ethoxylate chain of the surfactants (Table 1). Although this variation was non-linear, the trend was uni-directional.

**Table 1.** Variation of hydrogen bond length between para substituted NPEs and water molecules with the extension of ethoxylate chain.

Number of ethoxylate units	Hydrogen bond length (Å )
4	1.79635
6	1.79582
8	1.79560
13	1.79555
18	1.79550
20	1.79509

**The effect of changing the position of substituents of NPE molecules on their  $\Delta G_{\text{solv}}$ :**

The next task was to compute the effect of the change in position (from ortho- to meta-to para-) of substituted NPEs on their Solvation Gibbs free energy (Figure 6). Computed results (in Figure 7) revealed that the altering the position of the substituents did not significantly affect the  $\Delta G_{\text{solv}}$  of the NPEs in the aqueous medium.

**Figure 6.** Ortho-, meta- and para-substituted NPEs.**Figure 7.** The effect of changing the position of substituents of NPEs on their  $\Delta G_{\text{solv}}$

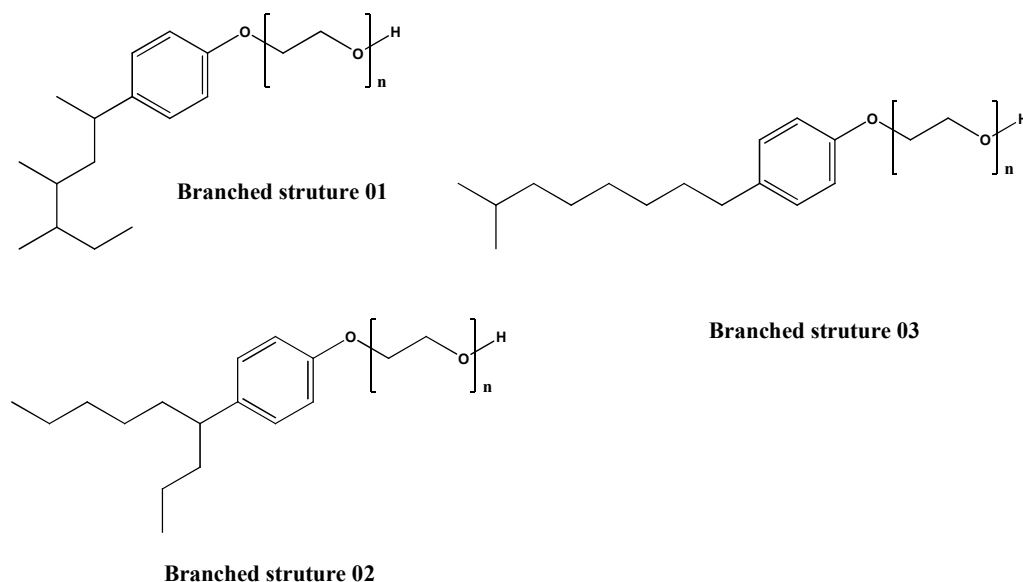
Although the dipole moment of NPE molecules did not fluctuate drastically with the extension of ethoxylate chain, a noticeable change was observed when the substituent-position was altered as ortho, meta and para. Computed results (in Table 2) disclosed that meta-substituted NPEs possess relatively higher values for the dipole moment. This evidenced that meta-substituted NPEs could form more efficient secondary interactions with water in aqueous media with compared to ortho- and para-substituted NPEs.

**Table 2.** Dipole moments of ortho-, meta- and para-substituted NPEs.

Number of Ethoxylate units	Dipole moment (D)		
	Ortho	Meta	Para
4	1.99	2.77	2.31
10	1.97	2.78	2.22
16	2.01	2.66	2.20

### The effect of branching of the nonyl hydrocarbon chain of NPE molecules on their $\Delta G_{\text{solv}}$ :

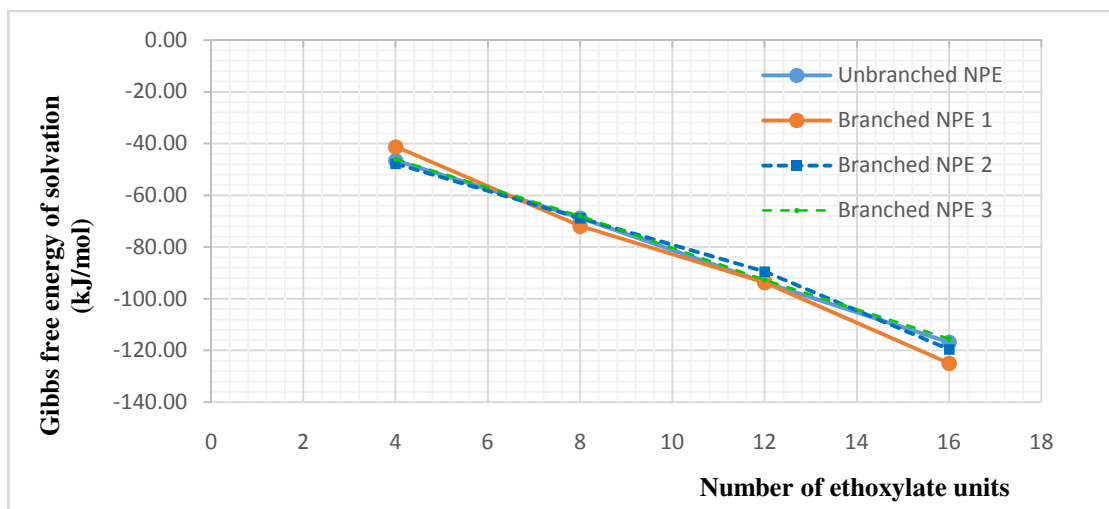
The nonylhydrocarbon chain of the para substituted NPEs was branched randomly (as shown in Figure 8) to obtain different structural isomers.  $\Delta G_{\text{solv}}$  of optimized geometries were computed with the extension of the ethoxylate (EO) chain. These results were compared with the unbranched para substituted NPEs.



**Figure 8.** Some selected branching patterns of NPEs.

In Figure 9, it could be shown that the trends of change in solvation Gibbs free energies ( $\Delta G_{\text{solv}}$ ) of three branched and one unbranched structural isomers of NPEs (with increase of

ethoxylate units as 4, 8, 12 and 16) were superimposable with each other irrespective of the branching pattern.

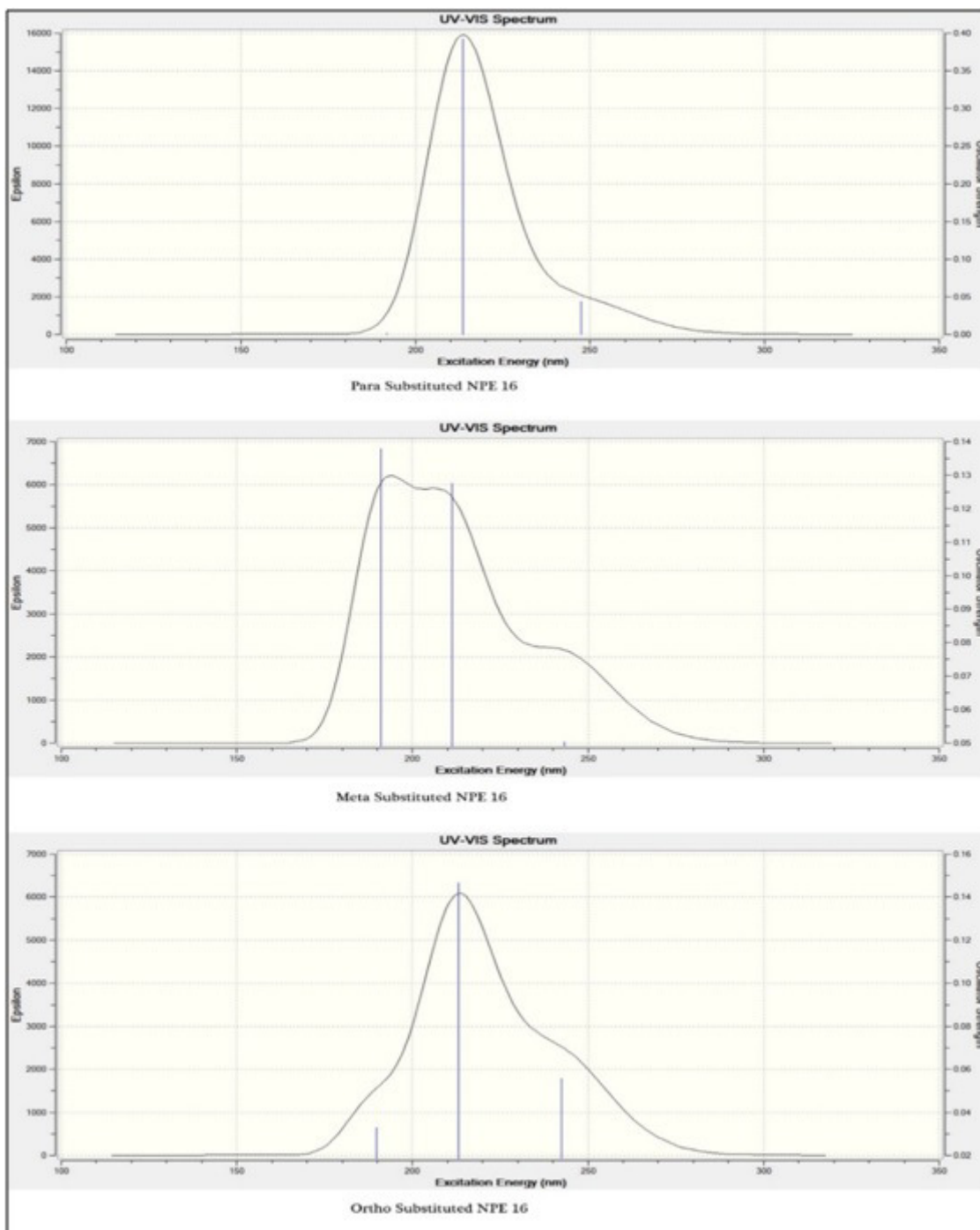


**Figure 9.** The effect of branching of the nonyl hydrocarbon chain of NPE molecules on their  $\Delta G_{\text{solv}}$ .

### The comparison of relative thermodynamic stabilities of ortho-, meta- and para-substituted NPEs by means of their computed UV spectral data:

Since NPEs possess UV sensitive chromophores, their maximum absorption ( $\lambda_{\text{max}}$ ) were computationally investigated expending their optimized geometries. The  $\lambda_{\text{max}} = 213$  nm was the most common absorption band which was unique for para-substituted NPEs, irrespective of their number of ethoxylate-units. These theoretical results well matched with the experimental data, reported by M. Ihos et. al. [19]. Thus the UV spectra showed a significant difference when the substituent position was altered (from ortho to meta to para). The  $\lambda_{\text{max}}$  has been shifted to high frequency region in meta-substituted NPEs compared to the para-substituted NPEs.





**Figure 10.** The comparison UV spectra of para-, meta- and ortho-substituted NPEs. Both ortho- and para-substituted NPEs showed a narrow absorption maxima ( $\lambda_{\text{max}}$ ) which is centered at 213 nm while meta-substituted NPEs possessed broad absorption maxima at 190 nm to 213 nm (Figure 10). In meta-substituted NPEs, the  $\lambda_{\text{max}}$  has shifted from 213 nm to 190 nm (high frequency region) which indicated the energy gap between the Frontier molecular orbitals (HOMO-LUMO gap) was higher in the meta-substituted NPEs with compared to ortho- and para-substituted species. Molecules have relatively high HOMO-LUMO gap said

to be thermodynamically stable [20]. Therefore meta- substituted NPEs can be predicted as more stable ones than ortho- and para- substituted NPEs.

## CONCLUSION

Nonylphenol ethoxylates were well stabilized in the aqueous medium with the extension of ethoxylate chain length, illustrating a linear relationship of  $\Delta G_{\text{solv}}$  with respect to the number of EO units. It was apparent that the hydrogen bond length between the NPEs and water molecules decreased with the extension of the ethoxylate chain of the surfactant and it was a non-linear, uni-directional trend. Although it was observed a negligible effect of the change in position (from ortho- to meta-to para-) of substituted NPEs on their solvation Gibbs free energies, a noticeable change was observed in their dipole moments and UV spectra ( $\lambda_{\text{max}}$ ). The relatively high dipole moments of meta-substituted NPEs indicated that they could form more efficient secondary interactions in aqueous media with compared to ortho- and para-substituted NPEs. The meta-substituted NPEs demonstrated relatively higher thermodynamic stability (than ortho- and para- substituted NPEs) due to the presence the lowest  $\lambda_{\text{max}}$  (the highest HOMO-LUMO gap). As a bottom-line these structural, electronic and thermodynamic properties computed from DFT calculations are very versatile to comprehend the behavior of surface active agents in aqueous media which can be utilized for their industrial applications.

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