

4P118 Quantum chemical study of the interaction of short-chain poly(oxyethylene)s with water in the solution

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Since poly(oxyethylene) (abbreviated as POE) $(-\text{OCH}_2\text{CH}_2-)_m$ is soluble in water at moderate temperatures, it has been experimentally studied as a good simplest model of biological polymers. Experimentally, it is well-known that the solubility of POE is strongly correlated to its chemical structure and conformation and the hydration of poly(oxyethylene) is one of the important factors that are responsible for the high solubility of POE. In the present study, we focused on the hydration to the $(-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-)$ unit and studied the role of a water molecule on the stabilization of the POE by the quantum chemical method. We used $\text{Me}(-\text{OCH}_2\text{CH}_2-)_m\text{OMe}$ ($\text{C}_1\text{E}_m\text{C}_1$) as a model of POE and carbon tetrachloride (CCl_4) as a solvent.

Quantum chemical calculations were performed using the GAUSSIAN 03 program. Energy calculations as well as geometry optimizations were carried out at the second-order Møller-Plesset perturbation (MP2) method using the 6-311G** basis set for all the atoms. The Gibbs free energies were calculated at the temperature of 298.15 K for the calculated vibrational frequencies. The effect of the solvent, carbon tetrachloride, was analyzed by the polarized continuum model (PCM) approximation method with the dielectric constant $\epsilon = 2.228$.

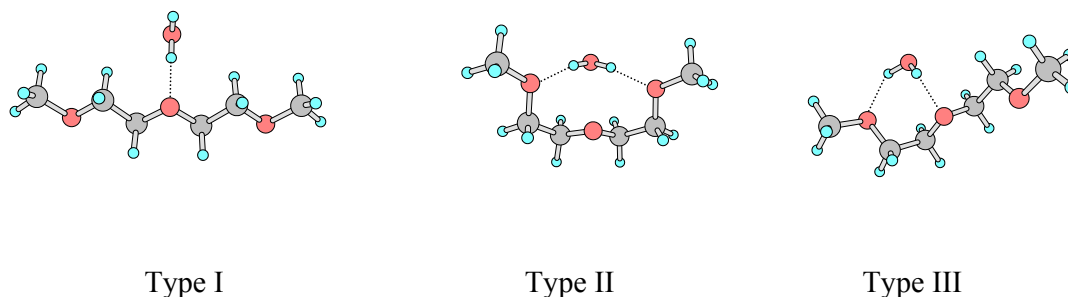


Fig.1. Three types of hydration modes of a water molecule on the POE chain with the conformation of $\text{C}_1\text{E}_2\text{C}_1$. Type I (TTTTTT): monodentate, Type II (TGTTG'T): bidentate, Type III (TGTTGT): bidentate.

Table 1. Relative potential energy (ΔE), enthalpy (ΔH), entropy ($T\Delta S$) and Gibbs free energy (ΔG) in kcal/mol of $C_1E_2C_1$ with and without a water molecule in the gas phase and the CCl_4 solution.

	Conformer	Type of H-bonding	With a water molecule				Without a water molecule
			ΔE	ΔH	$T\Delta S$	ΔG	ΔG
Gas phase	TTTTTT	Type I	0.000	0.000	0.000	0.000	0.000
	TGTTGT	Type III	-2.537	-2.640	-1.718	-0.922	0.831
		Type II	-5.405	-5.336	-2.027	-3.309	
TGTTG'T	Type II	-5.322	-5.182	-2.658	-2.524	1.210	
CCl_4 solution	TTTTTT	Type I	0.000	0.000	0.000	0.000	0.000
	TGTTGT	Type III	-2.144	-1.642	-0.016	-1.625	0.439
		Type II	-4.984	-4.264	-0.044	-4.219	
TGTTG'T	Type II	-5.155	-4.336	-0.922	-3.414	1.002	

$$\Delta G = \Delta H - T\Delta S \text{ at } 298.15\text{K.}$$

We have calculated three essentially important conformations of $C_1E_2C_1$, i.e., TTTTT, TGTTGT and TGTTG'T. The optimized structures of $C_1E_2C_1$ with a water molecule are presented in Figure 1. A water molecule forms the H-bonding with $C_1E_2C_1$ with three modes, type I, type II and type III. Without a water molecule, TTTTT was more stable in energy than TGTTGT and TGTTG'T as shown in Table 1. However, this tendency was reversed with a water molecule, because both conformations, TGTTGT and TGTTG'T, are significantly stabilized by the H-bonding with a water molecule. As presented in Figure 1, a water molecule interacts with the bidentate mode in both TGTTGT and TGTTG'T conformations. The dihedral angle $O-C-C-O$ is reduced due to the strong H-bonding. In contrast, a water molecule interacts with the monodentate mode in the TTTTT conformation. We found that the H-bonding with the bidentate mode is further strengthened in the CCl_4 solution. Table 1 shows that the H-bonding with the type II obviously more stabilizes the conformers compared to that with the type III. These computational results are in good agreement with the experimentally observed results.¹

Reference

1. H. Matsuura, Md. R. Matin, and K. Okura, *Chem. Lett.*, **32**, 122–123 (2003).