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Quantum chemical density functional theory studies on the molecular structure and vibrational spectra of Gallic acid imprinted polymers

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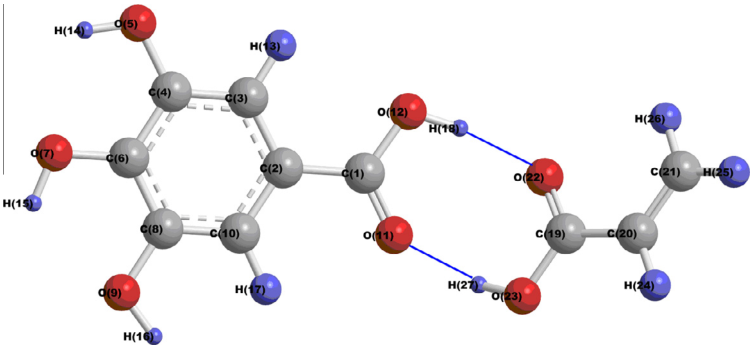
HIGHLIGHTS

- Density functional theory based computational studies for the Gallic acid based MIP.
- Vibrational wavenumbers calculations based on DFT employing B3LYP/6-31+G(2d,2p) level.
- Optimal mole ratio of 1:4 with formation of intermolecular hydrogen bond between GA and AA.

GRAPHICAL ABSTRACT



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ABSTRACT

Gallic acid (GA) is known by its antioxidant, anticarcinogenic properties and scavenger activity against several types of harmful free radicals. Molecularly imprinted polymers (MIPs) are used in separation of a pure compound from complex matrices. A stable template–monomer complex generates the MIPs with the highest affinity and selectivity for the template. The quantum chemical computations based on density functional theory (DFT) was used on the template Gallic acid (GA), monomer acrylic acid (AA) and GA–AA complex to study the nature of interactions involved in the GA–AA complex. B3LYP/6-31+G(2d,2p) model chemistry was used to optimize their structures and frequency calculations. The effect of porogen acetonitrile (ACN) on complex formation was included by using polarizable continuum model (PCM). The results demonstrated the formation of a stable GA–AA complex through the intermolecular hydrogen bonding between carboxylic acid groups of GA and AA. The Mulliken atomic charge analysis and simulated vibrational spectra also supported the stable hydrogen bonding interaction between the carboxylic acid groups of GA and AA with minimal interference of porogen ACN. Further, simulations on GA–AA mole ratio revealed that 1:4 GA–AA was optimum for synthesis of MIP for GA.

Introduction

Molecularly imprinted polymers (MIPs) are the macromolecular materials with the tailor-made binding sites for the template molecule. MIPs are used in wide range of applications including sensors [1], drug delivery [2] and chromatographic separations [3,4] as it offers easy and economical synthesis, robust mechanical properties and selectivity.

The synthesis of MIPs is initiated by the complexation of a template with a functional monomer through either covalent or non-covalent interaction, in a solvent which serves as a porogen. The polymerization with an excess of cross-linker results in the formation of highly cross-linked polymer matrix. On removal of the

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template molecule from the polymer matrix, specific recognition sites/cavities are exposed which are complementary to the template in terms of size, shape, and functionality [5–7]. A stable template–monomer complex generates MIPs with template-specific cavities and increases the recognition capabilities [8]. Thus, the optimization of the factors which enhance the strength of interaction between the template and monomer is crucial.

Computational techniques are the robust predictive tools used to investigate molecular level events occurring in the template–monomer pre-polymerization complex. Computer-aided design of MIPs is considered as a rational, fast and economic method to find the optimal imprinting conditions in order to improve the properties of MIPs [9]. Quantum chemical computational methods such as Density functional theory (DFT) allow rational MIPs design by predicting the interaction energy between the template and monomer. DFT describes the nature of interactions present in the template–monomer pre-polymerization complex and offers a unique perspective on the molecular level understanding of various thermodynamic and spectroscopic properties of a system.

GA is an important antioxidant which exhibits anticancer and antimutagenic activity and it is an important precursor for many important synthetic compounds [10]. GA has attracted considerable interests as a biologically and clinically significant compound [11]. GA is generally extracted from the natural matrix by conventional chromatographic methods which consume a large quantity of solvents [12]. Thus, development of a simple extraction procedure for GA from the complex matrices of natural resources is important.

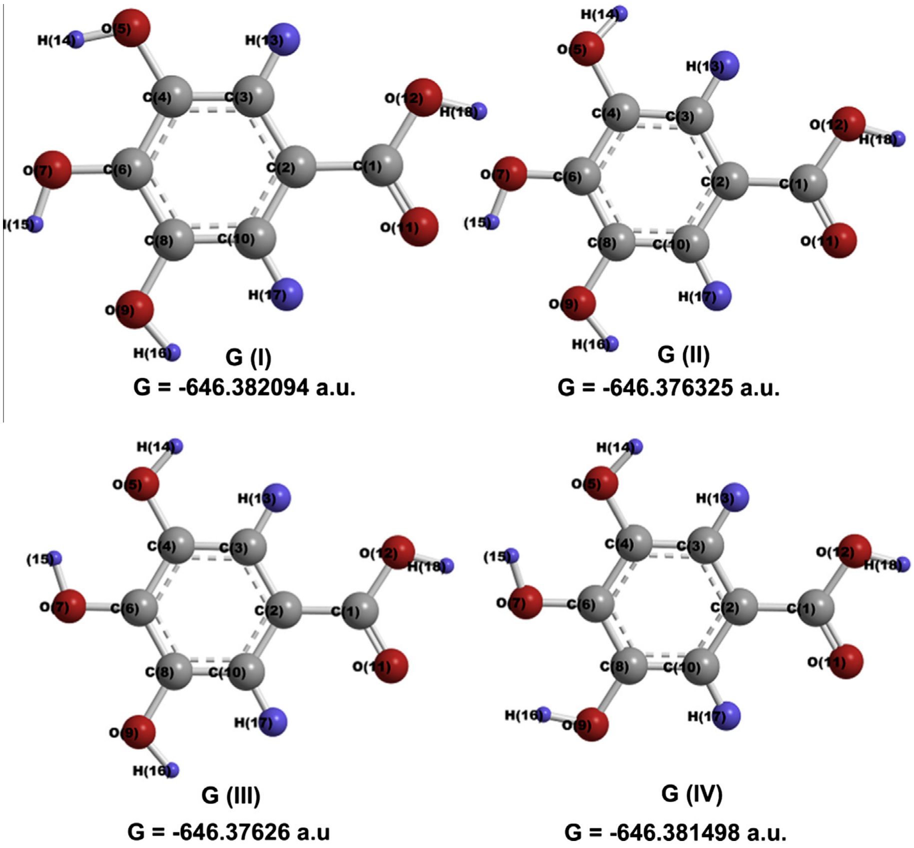
In our previous research, DFT calculations were performed on a virtual library of eighteen functional monomers. Acrylic acid (AA) was selected as it formed a template–monomer complex with the highest binding energy [13]. In the present work, a comprehensive investigation on template GA, monomer AA and their complexes is carried out in order to study the nature of interaction involved between the GA and AA in the porogen acetonitrile (ACN). Additionally, data on structural arrangement of GA–AA template–monomer complex, interaction energy and charge transfer analysis is examined. A detailed theoretical vibrational frequency analyses is performed in vacuum and the porogen. The simulated IR spectra are compared with the experimental FT-IR spectra. To the best of our knowledge, this is first report presenting quantum chemical calculations on the structural and vibrational properties of GA–AA template–monomer complex in presence of porogen for GA based MIPs.

Computational methods

All theoretical computations presented in this study were performed using Gaussian 03 program package [14] installed on a workstation with the Linux operating system.

Molecular geometry optimization

The 3-D ground state molecular structure of GA, AA and their subsequent complex were optimized using the B3LYP (Becke-Style three-Parameter-Lee–Yang–Parr correlation function) with 6-31+G(2d,2p) basis set. The optimizations were performed to obtain the stable structures with minimum energy in vacuum. Subsequently, the presence of the porogen ACN was included in the GA, AA and GA–AA complex using the self consistent reaction field-polarizable continuum model (PCM) implicitly, developed by Tomasi and coworkers [15]. A continuum model considers the solvent as a uniform polarizable medium with a dielectric constant (ε) of the solvent, while the solute is placed in a suitably shaped cavity in the medium.



G (I)
G = -646.382094 a.u.

G (II)
G = -646.376325 a.u.

G (III)
G = -646.37626 a.u

G (IV)
G = -646.381498 a.u.

Fig. 1. Optimized structures of various conformers of GA with their Gibbs free energy value (a.u.).