

Interaction between Volatile Organic Compounds and Functional Monomers in Molecularly Imprinted Materials

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ABSTRACT

Molecularly imprinted polymers (MIPs) have been playing an increasingly important role in volatile organic compounds (VOC) sensing for air quality control. The unique feature of these materials is their biomimetic molecular recognition functionality. Theoretical chemistry can advance our ability to design and synthesize new MIPs with specific functions, providing valuable insight into the system at the atomistic level, and therefore are able to explain microscopic behavior.

In this work, we have studied the interaction of pyridine, as a recognition element, with methacrylic acid as the functional monomer, in a pre-polymerization step in the formation of a specific molecularly imprinted polymer. Quantum chemistry calculations were performed at the M052X/6-311++g(d,p) level. The binding characteristics of the imprinted polymer were examined in detail. Ethylene glycol dimethacrylate is proposed as the cross-linker, and chloroform as the solvent. In addition, we investigate adsorption of toluene and benzene in the MIP structure. The aim is to test whether the model is able to recognize pyridine among these similar species and to explore the theoretical sensitivity range of these materials towards pyridine and other VOCs. Another test of the model is its ability to exhibit preferential adsorption of toluene over benzene, as has been observed experimentally in similar systems. The performed quantum chemistry calculations reproduce the preferential adsorption of pyridine over toluene and benzene, as well as the preferential adsorption of toluene over benzene.

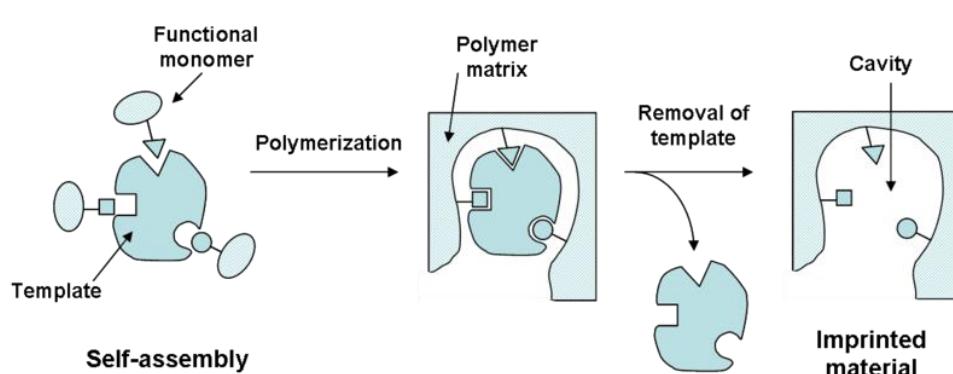
Keywords: Molecularly imprinted polymers (MIP), volatile organic compounds sensing, air quality control, quantum chemistry.

1 INTRODUCTION

Molecularly imprinted polymers (MIPs) are synthetic polymers possessing specific cavities designed for a target molecule. By a mechanism of molecular recognition, the MIPs are used as selective tools for the development of various analytical techniques such as liquid chromatography, capillary electrochromatography, solid-phase extraction (SPE), binding assays and biosensors. The application of MIPs to the determination of environmental pollutants in these different analytical approaches, with a special emphasis on their potential as selective SPE sorbents for the selective extraction of target analytes from complex matrices, has been playing an increasingly important role in volatile organic compound (VOC) sensing for air quality control.

Theoretical chemistry can advance our ability to design and synthesize new MIPs with specific functions, providing valuable insight into the system at the detailed atomistic level, and therefore are able to explain microscopic behavior.

The principles of this technique are schematically shown in Scheme 1. The prepolymerization mixture consists of cross-linker, functional monomer, template, and solvent species. Template molecules form transient associations with the functional monomers, and this stage of the synthesis is usually called the complexation step. This is followed by polymerization, with the cross-linker providing the rigidity and integrity of the structure. Removal of the template and solvent leaves cavities in the structure that possess the shape and interaction patterns complementary to the template molecules. Hence, one obtains a MIP which is able to recognize and rebind the original template species.



Scheme 1: Molecularly imprinted polymers formation.

A number of MIPs have been proposed over the years for chromatographic separations, artificial immunoassays, drug delivery, and other applications.^{1,2,3} Sensing applications of MIPs have been recently reviewed by Blanco-Lopez et al.⁴ and by McCluskey et al.⁵ For example, Fu and Finklea proposed a series of MIPs for quartz crystal microbalance (QCM) sensors to detect toluene, benzene, and other VOCs.⁶ In their study, the proposed polymers were based on ethylene glycol dimethacrylate (EGDMA) as the cross-linker, methacrylic acid (MAA) as the functional monomer, and either hydroquinone or phenol as the template. Among several interesting results, they successfully demonstrated that a sufficient level of sensitivity can be obtained using the proposed MIPs, with toluene adsorbing stronger than benzene and MIPs exhibiting binding constants several times higher than those for non-imprinted control polymers. In another interesting example, Bunte and co-workers recently proposed several materials based on EGDMA and a range of functional monomers for 2,4,6-trinitrotoluene (TNT) gas phase sensing.⁷ Despite these successes, several challenges exist for the rational design of new MIPs with specific sensing functionalities.

In this work, we have studied the interaction of pyridine, as a recognition element, with methacrylic acid as the functional monomer, in a pre-polymerization step in the formation of a specific molecularly imprinted polymer. Quantum chemistry calculations were performed at the M052X/6-311++g(d,p) level. The binding characteristics of the imprinted polymer were examined in detail. Ethylene glycol dimethacrylate has been proposed as the cross-linker and chloroform as the solvent. In addition, we investigate adsorption of toluene and benzene in the MIP structure. The aim is to test whether the model is able to recognize pyridine among these similar species and to explore the theoretical sensitivity range of these materials toward pyridine and other VOCs. Another test of the model is its ability to exhibit preferential adsorption of toluene over benzene as has been observed experimentally in similar systems.

2 COMPUTATIONAL METHODOLOGY

All electronic calculations were performed with the Gaussian 09 system of programs.⁸ Geometry optimizations and frequency calculations were carried out using the M05-2X functional⁹ in conjunction with the 6-311++G(d,p) basis set. No symmetry constraints were imposed in the geometry optimizations. Thermodynamic corrections at 298 K were included in the calculation of relative energies. All stable structures were further characterized as minima on the potential energy surface (PES) by using analytical second derivatives obtained in frequency calculation. SMD continuum model¹⁰ have been employed, using chloroform and acetonitrile as solvents.

Relative binding energies in the adsorption complex were calculated with respect to the sum of the separated

species, i.e. MAA and VOC. We report both ΔE and ΔG values. Zero-point energies (ZPE) and thermal corrections to the energy (TCE) are included. The complexation energies, ΔE and ΔG are obtained from the following equations:

$$\Delta E = E_{\text{complex}} - (E_{\text{VOC}} + E_{\text{MAA}}) + \Delta(\text{ZPE})$$

$$\Delta G = G_{\text{complex}} - (G_{\text{VOC}} + G_{\text{MAA}})$$

3 RESULTS

We have studied the interaction of pyridine, benzene and toluene with methacrylic acid (MAA) as the functional monomer in a pre-polymerization step in the formation of a specific molecularly imprinted polymer. We have carried out calculations in the gas phase, and chloroform and acetonitrile as solvents.

The fully optimized structures of the methacrylic acid (MAA) and of the VOC species (pyridine, benzene and toluene) are shown in Figure 1. The computational results show that pyridine has only one recognition site to MAA functional monomer.

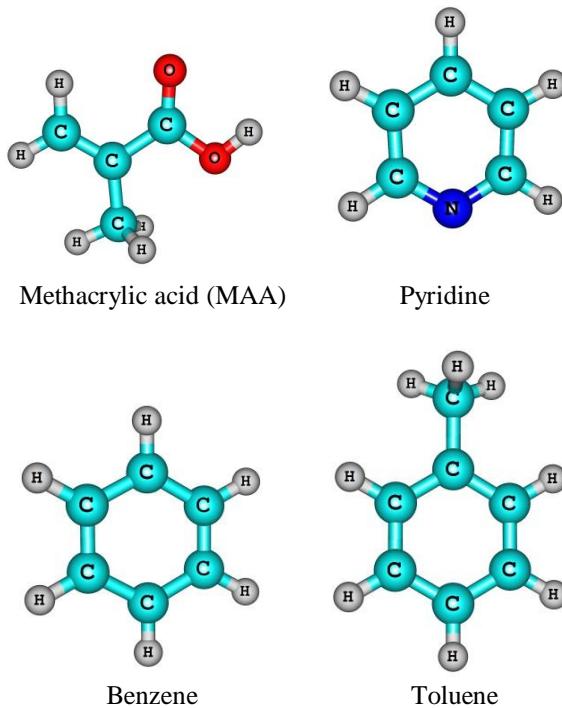


Figure 1: Optimized structures of methacrylic acid (MAA) and VOC species (pyridine, benzene and toluene).

Molecular recognition emerges as a result of shape complementarity between the molecule and the binding site. During the equilibration process, complexes between VOC's and MAA are formed (Figure 2). However, this process is significantly disturbed by the propensity of MAA to form dimers. (These dimers were also observed in experimental studies of MAA in bulk solutions¹¹.) On the

other hand, pyridine exhibits only one functional group, and hence it forms a complex with only one MAA molecule. For this reason the complex is relatively weak, as suggested in previous experimental studies.¹²

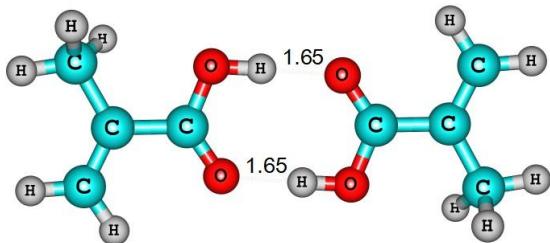


Figure 2: Optimized structures of the MAA dimer.

The fully optimized structures of the adsorption complexes between MAA and VOCs are presented in Figure 3. Relative energies are calculated with respect to the sum of the separated molecules at 0 K, and they are reported in Table 1.

Complex	gas phase	chloroform
MAA dimer	-17.56	-12.00
Pyridine-MAA	-12.56	-9.98
Benzene-MAA	-2.61	-1.00
Toluene-MAA	-3.46	-1.98

Table 1: Relative Electronic Energies (including ZPE), in kcal/mol, in the VOC-MAA interactions.

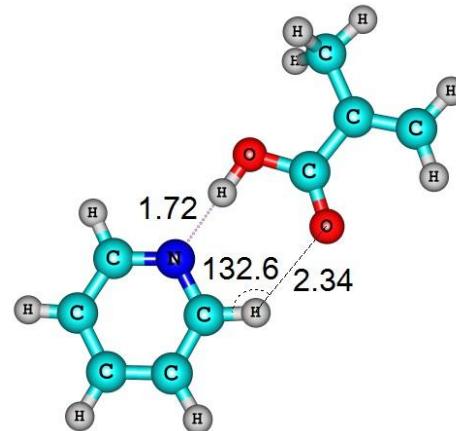
Complex	gas phase	chloroform
MAA dimer	-6.64	-0.73
Pyridine-MAA	-2.67	-0.53
Benzene-MAA	5.67	6.96
Toluene-MAA	5.36	6.19

Table 1: Relative Gibbs free Energies (including TCE), in kcal/mol, in the VOC-MAA interactions.

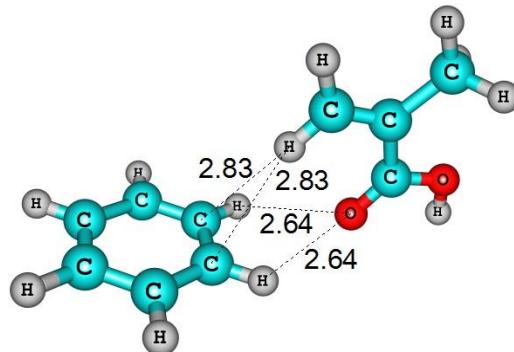
Preferential adsorption of pyridine over toluene is associated with a stronger interaction of pyridine with available carboxyl groups due to the presence of the amino group. Compared to benzene, interaction of toluene with a MIP has an additional Lennard-Jones contribution from the methyl group. Although this contribution is not as strong as the hydrogen bond interaction between methacrylic acid and pyridine, it leads to preferential adsorption of toluene over benzene. This is in qualitative agreement with the recent experimental studies on similar MIPs (where phenol was employed as the template).¹³

The enhancement of adsorption in the imprinted materials over the non-imprinted counterparts for toluene and benzene is comparable with that observed in experiments.¹³ Interestingly, in our study, this enhancement has very similar values for all three adsorbates. It seems that the primary role of pyridine as template is to enhance

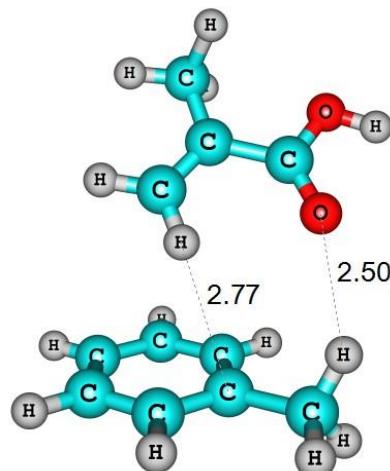
porosity of the imprinted materials compared to the non-imprinted ones. As the sizes of all three adsorbates are similar, the effects of higher porosity are also similar.



Pyridine-MAA interaction.



Benzene-MAA interaction.



Toluene-MAA interaction.

Figure 3: Fully optimized structures of the adsorption complexes between MAA and VOCs.

Computational detailed models of MIPs will not be able to reproduce the recognition process in its full complexity. Therefore, atomistic simulations are invariably limited to microporous features of MIPs.

Even with all these limitations, theoretical models nevertheless open a range of very important opportunities. They provide a detailed description of the binding site, adsorption and recognition processes. The models make it possible to investigate the effect of the solvent and swelling on molecular recognition functionality. The present study focuses on a very simple template (pyridine) with only one functional group, and therefore, the imprinting effects are small. Molecular recognition properties of the model are yet to be investigated (strictly speaking, the preferential adsorption of pyridine over toluene cannot be viewed as molecular recognition).

4 CONCLUSIONS

The present study focuses on a very simple template (pyridine) with only one functional group, and therefore, the imprinting effects are small. Molecular recognition properties of the model are yet to be investigated. However, the current quantum-chemical calculations represent an effective evaluation method to elucidate the type and stability of molecular interactions between a VOC template and a functional monomer during pre-polymerization step in the formation of molecularly imprinted polymers. Stabilization energies, ΔE , lead to the recognition of molecular complexes and of the atoms involved in the interaction between the template molecule and the functional monomer. Binding energies, ΔE and ΔG , obtained for pyridine with MAA, are lower than for toluene, which indicates that pyridine interacts more strongly with MAA than benzene and toluene. Therefore, a MIP synthesized with MAA is expected to be selective to pyridine.

The solvent plays an important role during the polymer synthesis. Theoretical results that include solvent effects show that chloroform has less affinity with all the template molecules with the monomer. These results show that quantum-chemical calculations, based on DFT methods, can be used to characterize functional monomers for a specified imprinted molecule.

In conclusion, this preliminary study indicates that these models will play a key role in the systematic design of new MIPs with tailored functionalities. In future work, we will extend this approach to more complex systems, where molecular recognition effects are expected to emerge.

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