142am Effects of Template-Monomer Complex Formation on the Synthesis of Molecularly Imprinted Polymers in Aqueous Medium

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This research envisions the understanding of the physico-chemical interactions that occur during the synthesis of molecularly imprinted polymers (MIP) by the employment Nuclear Magnetic Resonance (NMR) and Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) Spectroscopy. As a result, a rational design will be applied for the development of a non-invasive biosensor based on hydrogel polymeric networks for biological markers by utilizing MIP. To enhance the MIP performance for biomolecules, better insights is needed by observing the role of the functional monomer-template complex stabilization on the synthesis of molecular imprinted polymer and understand its influence on MIP-ligand binding. A copolymerization of methacrylic acid (MAA) as the functional monomer was performed with ethylene glycol dimethacrylate (EGDMA) as the cross linking agent. It was monitored by *in situ* free radical polymerization employing ATR-FTIR spectroscopy. Hydrocortisone was used as the template molecule. The non-covalent approach was employed for the self assembly template-monomer complex formation. The monomer/crosslinker molar ratio was varied 1/1, and 4/1. Solvent effect was compared by utilizing dimethyl sulfoxide-d_6 (DMSO), and a 50% w/w mixture of ethanol-d_6, and water-d_2 as solvents. ATR-FTIR studies identified the formation of hydrogen bonds and electrostatic complexes. It was found a reduction on the initial conversion during MIP polymerization. The conversion reduction was expected recognizing MIP synthesis has a lower initial propagation rate compared to non-MIP. It was understood the segmental mobility of MAA have been decreased by the formation of functional monomer-template complex. It was also observed the formation of carbonyl salt during the MIP synthesis. Electrostatic interaction within carbonyl salts and template molecule were expected to contribute on the MIP recognition process. NMR titration studies were employed to identify interaction sites. Samples were prepared by mixing hydrocortisone with an 18mM concentration on dimethyl sulfoxide-d_6. Acetic acid-d_4 was titrated on samples with a concentration range of 0 to 1.6M. The chemical shifts ($\Delta\delta$) were monitored by ^{1}H-NMR experiments. The chemical shifts were promoted by the interaction of the analog monomer, acetic acid-d_4, with the template molecule. Preliminary studies identified the presence of three interaction sites that were associated to the formation of adducts within the hydroxyl groups of template molecule and functional monomer. Further studies with Job's method of continuous variation will allow the determination of the stoichiometry of the solution complexes between the template molecule and acetic acid.