Semi-Empirical Simulations of Interactions between Edge-Functionalized Graphene Oxides and Bisphenol A

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Abstract

This study reports for the first time an analysis of the interactions between edge-functionalized graphene oxide (GO) sheets and bisphenol A (BPA) examined by semi-empirical simulations. Bisphenol A (BPA), $(CH_3)_2C(C_6H_4OH)_2$, used in synthesis of a variety of polymers, is one of the chemicals produced in very high quantities worldwide, with more than 450 metric tons released annually into the environment. Due to its ability to mimic estrogen and it being an endocrine disruptor, it is a pollutant of serious concern. Graphene oxides have been studied extensively as electrochemical sensor materials for analytes, wherein the sensor performance (e.g., sensitivity) depends on the nature and amount of oxygen-containing functional groups present. This work considers a lattice containing 59 hexagonal cells ($C_{150}H_{34}$), with one edge modified by carbonyl/carboxyl groups, is used to examine interactions with BPA. Simulations are carried out at the semi-empirical PM6 level using MOPAC and the DH2 modification is employed to calculate interaction energies. It is seen that the hydrogen/oxygen atoms of the phenolic group(s) of BPA interact primarily with the oxygen atoms of the carbonyl/carboxyl group or the hydrogen atoms of the carboxyl groups/graphene edges. These interactions are predominantly polar and non-covalent in nature, e.g., hydrogen bonds, in addition to dispersion. The heat of formation of the GO-BPA complex decreases with increasing number of functional groups in GO and becomes exothermic. However, the strength of the GO-BPA interaction goes through a maximum at 4 carboxyl groups (for an edge with 7 carbon atoms). Beyond this, the carboxyl groups start interacting significantly amongst each other, weakening the GO-BPA interaction. Optimized structures, charges and the corresponding interaction energies are presented for eight different GO structures (2 containing carbonyl groups and 6 containing carboxyl groups).