Thermodynamic Properties for the Sorption of Perfluorooctanoic Acid and Perfluorooctanesulfonic Acid in Microplastics: A Molecular Simulation Study

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***Abstract*: The interaction between per- and polyfluoroalkyl substances (PFAS) and microplastics (MPs) is emerging as a critical environmental concern due to their persistence, mobility, and combined toxicity. MPs possess large surface areas and hydrophobic properties, making them ideal vectors for PFAS sorption. PFAS-contaminated MPs can transport pollutants across ecosystems, including long-range movement through water systems, even reaching remote regions. The sorption of PFAS is influenced by the type of MP as well as its physicochemical properties at different environmental conditions. The present study investigates sorption thermodynamic parameters such as Gibbs free energy, entropy, and enthalpy change to understand the uptake mechanism of perfluorooctanoic acid (PFOA) and perfluorooctanesulfonic acid (PFOS) on polyethylene (PE) and polypropylene (PP). Molecular simulations were conducted using the extended-Flory Huggins approach in Material Studio over a temperature range of 325 K to 825 K, with varying degrees of polymerization (100, 500, and 1000). The findings reveal that PFOA uptake on PP and PE is non-spontaneous below 625 K, becoming spontaneous at 625 K for PP and 725 K for PE. PFOS uptake remained non-spontaneous on both MPs. Both PFOA and PFOS uptake processes showed positive enthalpy and entropy change values, indicating endothermic behaviour and increased affinity with temperature. The degree of polymerization had no significant effect. The study concludes that PP and PE have low affinity for PFOS, reducing MPs' potential as transport vectors and posing health risks in aquatic environments.**

***Keywords*— Microplastics, Gibbs Energy, Standard Enthalpy, Standard Entropy**

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