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Investigation of Chemical Warfare Agent Diffusion in Metal-Organic Frameworks in the Presence of Water

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Chemical warfare agents (CWAs) are highly toxic substances that pose severe threats to human health and the environment, often leading to fatal consequences. These hazardous materials have been used in warfare and terrorist attacks, highlighting the urgent need for protective materials capable of capturing and neutralizing them. Over the past few decades, various materials and methods have been explored for this purpose.[1] Research studies demonstrated that metal-organic frameworks (MOFs) are promising candidates for adsorption and degradation of CWAs. Both the equilibrium capacity and kinetics of the adsorption of CWAs are essential in MOFs. One key kinetic parameter is the diffusion coefficient, which has been studied rarely and is mostly unknown for these systems. Given the extreme toxicity of CWAs, experimental studies often rely on simulant compounds with similar chemical and physical properties but significantly lower toxicity.[2] Due to the toxicity of CWAs, molecular simulation techniques such as molecular dynamics (MD) simulations provide a valuable approach to investigate their diffusion behavior.[3] Moreover, the presence of adsorbed water molecules can influence the diffusivity and adsorption characteristics of CWAs and their simulants, making it a critical factor to consider in these studies.

In this study, we investigated the self-diffusion of the CWAs sarin and soman, along with the simulants DMMP, DIMP, and DIFP, within the MOF NU-1000 and DMMP in a series of zirconium-based MOFs with varying connectivities, topologies, and linkers, including MOF-808, UiO-67, and MOF-841. The MOF structures were optimized using density functional theory calculations, and partial charges were assigned based on the Density-Derived Electrostatic and Chemical (DDEC06) approach. All MOFs were modeled as rigid frameworks, and the TIP4P/2005 model was used for water molecules. Various agent loadings were examined for each MOF at three relative humidities: 0%, 20%, and 70%. The initial placements of agents and water molecules within the MOFs were determined using either NVT simulations or grand canonical Monte Carlo simulations in the RASPA code. Subsequently, equilibration was performed through 5 ns NVT MD simulations in LAMMPS at 298 K, followed by 300 ns or longer production runs under NVT conditions to analyze diffusion behavior. Beyond calculating self-diffusivities and identifying the preferred locations of guest molecules, we analyzed the water-water, CWA-water, CWA-framework, and water-framework hydrogen bonding interactions. Our analysis offers valuable physical insights into the behavior and dynamics of these materials in the presence of water molecules in selected MOFs.

References

[1] Y.J. Jang, K. Kim, O.G. Tsay, D.A. Atwood, and D.G. Churchill, Destruction and detection of chemical warfare agents, Chem. Rev. **115** (2015) 5345–5403.

[2] S. Balasubramanian, A.J. Kulandaisamy, K.J. Babu, A. Das, and J.B. Balaguru Rayappan, Metal Organic Framework Functionalized Textiles as Protective Clothing for the Detection and Detoxification of Chemical Warfare Agents - A Review, Ind. Eng. Chem. Res. **60** (2021) 4218–4239.

[3] A. Emelianova, E.A. Basharova, A.L. Kolesnikov, E.V. Arribas, E. V. Ivanova, and G.Y. Gor, Force Fields for Molecular Modeling of Sarin and its Simulants: DMMP and DIMP, J. Phys. Chem. B **125** (2021) 4086–4098.

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