LABORATOIRE DE CHIMIE ENS DE LYON

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Porous Liquids for Separations Processes in Sustainable Chemistry

Liquides Poreux pour des Procédés de Séparation en Chimie Durable

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Porous liquids are novel materials combining fluidity with permanent porosity of molecular size. They were created in 2015 [2] and can be made in different types [1,3] using molecular cages or nanoparticles of porous solids in a solvent whose molecules are too large to enter the pores. This thesis is focused on suspensions of a nanoporous solid, namely a metal-organic framework (MOF), in an ionic liquid (IL) [4]. These porous ILs offer enormous potential for separations, capture and delivery of small molecules and gases (adding just 10% of MOF to an IL almost doubles the solubility of CO_2 [5]). Because of their fluidity they are easier and safer to handle in chemical processes than finely-divided solids, and their stability and absence of volatility allow absorbent recycling. The ionic nature of the solvent imparts a configurability to the porous IL, reinforced by the wide choice of MOF materials, providing means to tune solubility and selectivity. Giv en their novelty, porous ILs are far from being well understood, and achieving their rational design faces numerous knowledge gaps. The aim of this thesis is to enhance our fundamental understanding of porous ILs and to design them for challenging applications in the capture and separation of gases of major importance, including CO_2, SO_2, N_2, CH_4, or fluorinated refrigerants.

This thesis will be in computational physical chemistry, using state-of-the-art molecular dynamics (MD) simulations, both with classical, polarizable force fields and density functional theory (ab initio MD) to study interactions, local structure and dynamics in porous ILs. There will be close interactions with experimentalists in the Theoretical Chemistry and Molecular Thermodynamics group at ENS de Lton that study the same systems, providing a rich scientific environment.

The main knowledge gaps about porous ILs addressed with this thesis will be:

Suspension stability of porous ILs. Some porous ILs are stable suspensions over timescales of many months, but the origins of this stability are not understood. Although the IL forms a dense interfacial layer around MOF particles [5], these are not truly decorated by the ions in a long-lasting manner. Besides, Coulomb interactions are screened, precluding electrical double-layer forces beyond a few ionic layers. Using molecular dynamics (MD) with the latest polarizable force fields developed in the group, we will obtain free energy profiles between MOF particles in the IL medium, to relate stability with the structure of the interfacial layers. These results will be combined with dynamic light scattering, TEM and SAXS to characterize the structure of the porous ILs [5].

Combining physical and chemical sorption. Designing reversible sorption systems relies on a compromise between (strong) chemical sorption, leading to high loads but also energetic costs for sorbent regeneration; or (weak) physical sorption, leading to low solubility and possibly selectivity, but facilitating regeneration. We will combine physical sorption, through Coulomb and van der Waals interactions of the gases with the IL, and also through the pore aperture size and free volume in the MOF, with moderate chemical driving forces, which can take place both in the IL and in the MOF, namely in its metal centres. MD simulations using non-reactive force fields provide information on the structure of local environments and the main interaction sites, indicating clearly where chemistry will take place. These non-reactive simulations will be complemented with quantum chemical DFT studies of the reactivity, giving access to thermochemical quantities and reaction mechanisms. The computational studies will be accompanied by gas sorption and NMR experiments under pressure.

Grand challenge applications. Separating CO_2 from atmospheric gases or light hydrocarbons is capital for carbon capture and biogas purification, and sorbent design is the main challenge. Biogas is a renewable energy source obtained from agricultural waste, sewage or food waste, mainly composed of CH_4 (35-65%) and CO_2 (15-50%) with smaller levels of toxic sulphur and ammonia contaminants. Biogas must be purified Biogas must be purified to reach 95–99% CH_4 and 1–5% CO_2 with little or no trace of sulphur. Conversion of N_2 to ammonia using renewable energies is a major challenge to replace the energy-intensive Haber-Bosch process and to produce hydrogen without emitting CO_2. We aim to design porous ILs to capture weakly-interacting gases such as CH_4 and N_2.

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