Transport mechanism of guest methane in water-filled nano-pores

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Understanding the transport behavior of molecules confined inside narrow pores is crucial in various industrial processes and technological applications e.g. gas separation, hydraulic fracturing and enhanced gas recovery. Generally, the properties of confined geo-fluids are purely understood compared to those of bulk fluids. To improve upon the state of the art, we computed the transport of methane through 1 nm wide slit-shaped pores carved out of selected solid substrates using classical molecular dynamics simulations. The transport mechanism was elucidated via the implementation of the well-tempered metadynamics algorithm, which allowed for the quantification and visualization of the free energy landscape sampled by the guest molecule. Models for silica, magnesium oxide, alumina, muscovite and calcite were used as solid substrates. Slit-shaped pores of width 1 nm were carved out of these materials, and filled with liquid water. Methane was then inserted at low concentration. The results show that the diffusion of methane through the hydrated pores is strongly dependent on the solid substrate. While methane molecules diffuse isotropically along the direction parallel to the pore surfaces in most of the pores considered, anisotropic diffusion was observed in the hydrated calcite pore. The differences observed in the various pores are due to local molecular properties of confined water, including molecular structure and solvation free energy. The transport mechanism and the diffusion coefficients are dependent on the free energy barriers encountered by one methane molecule as it migrates from one preferential adsorption site to a neighbouring one. It was found that heterogeneous water distributions in different hydration layers and the low free energy pathways in the plane parallel to the pore surfaces yield the anisotropic diffusion of methane molecules in the hydrated calcite pore. Our observations contribute to an on-going debate on the relation between local free energy profiles and diffusion coefficients, and could have important practical consequences in various applications, ranging from the design of selective membranes for gas separations to the sustainable deployment of shale gas.