Diffusive isotope fractionation of benzene in water

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Benzene (C_6H_6) is an organic molecule present in trace concentrations in natural gas. Its fate during gas storage in aquifers is of general concern due to its solubility in water and its toxicity. Once dissolved in aquifers, benzene might migrate by advection and diffusion/dispersion, and can be degraded by micro-organisms. Compound-specific isotope analysis on groundwater samples has emerged as a powerful tool to assess the biodegradation of benzene in aquifers. It however relies on the assumption that biodegradation is the single significant process affecting isotope ratios and thus ignores the potential effect of diffusion. We aim at verifying this hypothesis by evaluating the fractionation factor of carbon and hydrogen isotopes during the diffusion of benzene in water. For this purpose, we developed a method based on non-equilibrium molecular dynamics (NEMD) simulations. It relies on an external force (F_{ext}) which is continuously applied to a benzene molecule in a simulation box containing 1500 water molecules. This External-Field – NEMD (EF-NEMD) method allows the determination of diffusivity (ð) from the linear relation between the velocity of the particle, F_{ext} and Đ in Maxwell-Stefan formalism, the latter quantity being equal to the Fickian diffusion in such diluted conditions. We successfully used EF-NEMD to determine $Đ_{benzene}$ in water (310K, P=70 bar), with results matching experimental data. We further evaluate the effect of mass and mass distribution on $Đ_{benzene}$ in order to derive fractionation factors. We find that the general kinetic fractionation law predicting a dependence between the square root of the reduced mass and diffusion coefficients does not apply to benzene isotopologues. Results from the most likely scenarios, involving the substitution of one single Carbon or Hydrogen isotope, suggest relatively small fractionation factors, ε_{diffu}, on the order of -0.6 and -0.7 ‰ for Carbon and Hydrogen isotopes, respectively. These are lower than fractionation factors determined for biodegradation, especially for Hydrogen (ε_{biodeg} = -49 to -79 ‰), while diffusion might slightly interfere in biodegradation evaluation using Carbon isotopes (ε_{biodeg} = -1.6 to -3.6 ‰).