

## **Carbon and Hydrogen isotope fractionation during aqueous diffusion of benzene**

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Aquifer monitoring of benzene using compound-specific isotope analysis presumably allows for the evaluation of its natural attenuation. However, molecular diffusion also has the potential to induce isotope fractionation during kinetic mass transfer of trace compounds. Although gas-phase diffusive isotope fractionation can be predicted using the kinetic theory, no theoretical framework can describe diffusive isotope fractionation in liquids. Here, we investigate isotope fractionation due to the diffusion of benzene in water under aquifer conditions ( $T=310\text{K}$ ,  $P=70\text{ bars}$ ). We use external field – non-equilibrium molecular dynamics (EF-NEMD) to infer benzene diffusion coefficients in water and their relationship with molecular mass [1]. For this, we measured diffusion coefficients of simulated benzene isotopologues with fictive masses (up to  $>1000\text{ amu}$ ) in order to amplify the isotope effect. Similar to previous work on ionic species, noble gases and other molecules, we find that aqueous-phase diffusion coefficients vary with  $M^{-\beta}$ . However, different mass substitution configurations revealed some potential influence of mass distribution within the benzene molecule on diffusivity, questioning the use of some model perdeuterated molecules in laboratory experiments.  $\beta$ -exponents determined for benzene isotopologues (0.02 – 0.04) suggest only minor diffusive isotope fractionation, which can be safely neglected in aquifer monitoring programs.

[1] Enrico, Le Hécho, Galliero, Carrier, Petit & Vermorel (2024), *Geochimica et Cosmochimica Acta* 391, 96-105.