



# Isotope fractionation in phase-transfer processes under thermodynamic and kinetic control – Implications for diffusive fractionation in aqueous solution



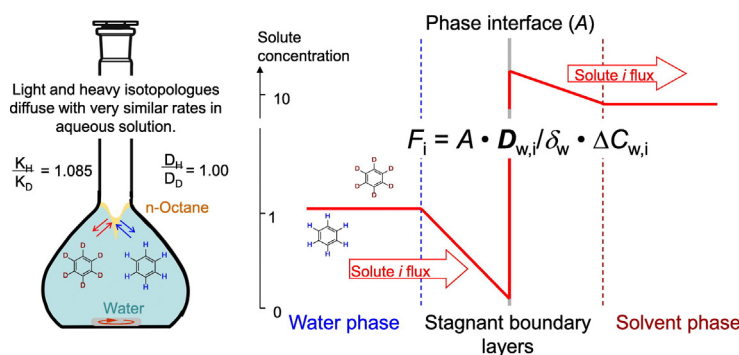
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## HIGHLIGHTS

- Hydrogen isotope fractionation was measured for partitioning of benzene, toluene, cyclohexane between water and n-octane
- Relative aqueous-phase diffusion coefficients of isotopologues were derived under kinetic control.
- Light and heavy isotopologues of all investigated solutes show very similar aqueous-phase diffusion coefficients.
- Thermodynamic control of partitioning produces much stronger isotope fractionation than kinetic control.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Diffusive isotope fractionation of organic compounds in aqueous solution was investigated by means of liquid–liquid and liquid–gas partitioning experiments under kinetic control. The two-film model was used to describe phase-transfer kinetics. It assumes the diffusion of solutes across a stagnant water boundary layer as the rate-controlling step. For all investigated solutes (benzene- $D_0$  and - $D_6$ , toluene- $D_0$ , - $D_5$ , and - $D_8$ , cyclohexane- $D_0$  and - $D_{12}$ ), there was no significant observable fractionation effect between nondeuterated and perdeuterated isotopologues, resulting in a ratio of diffusion coefficients  $D_{\text{light}}/D_{\text{heavy}} = 1.00 \pm 0.01$ . In addition, isotope fractionation due to equilibrium partitioning of solutes between water and n-octane or gas phase was measured. The deuterated compounds are more hydrophilic than their light isotopologues in all cases, giving rise to fractionation coefficients  $\alpha_{H_{\text{part}}} = K_{\text{octane/water,H}}/K_{\text{octane/water,D}} = 1.085$  to 1.15. Thus, thermodynamic fractionation effects are much larger than diffusive fractionation effects. Methodical and environmental implications of these findings are discussed.

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## 1. Introduction

Compound-specific isotope analysis (CSIA) is a powerful tool to trace the fate of organic pollutants in the environment (Elsner, 2010;

Elsner et al., 2012; Hunkeler et al., 2009; Thullner et al., 2012). CSIA is based on the shift in isotope composition of a target compound mainly due to chemical or biochemical reactions. However, isotopic patterns can also be affected – usually to a lower extent – by a number of physical processes, such as volatilization and sorption (Bouchard et al., 2008; Eckert et al., 2012; Imfeld et al., 2014; Jeannotat and Hunkeler, 2012, 2013; Kopinke et al., 2005, 2017; Kuder et al., 2009; van Breukelen and Prommer, 2008; Wanner and Hunkeler, 2015). Elemental steps

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which are involved in most of these processes - chemical or physical - are mass transfer across phase interfaces and molecular diffusion (Hoehener and Yu, 2012; Jeannotat and Hunkeler, 2012, 2013; Jin et al., 2014; LaBolle et al., 2008; Rolle et al., 2010; Rolle and Jin, 2017; Wanner and Hunkeler, 2015; Xu et al., 2016). Focusing on isotope effects in aqueous diffusion, literature data are available (Bourg and Sposito, 2007; Bourg and Sposito, 2008; Bourg et al., 2010; Eggenkamp and Coleman, 2009; Richter et al., 2006; Tyroller et al., 2014; Watkins et al., 2011) but scarce for organic compounds (Jeannotat and Hunkeler, 2012, 2013; Jin et al., 2014; Rolle et al., 2010; Rolle and Jin, 2017; Wanner and Hunkeler, 2015; Xu et al., 2016).

Recently, Kopinke et al. (2017) investigated isotope fractionation of benzene isotopologues (molecular species of a compound that differ only in their isotopic composition, e.g. C<sub>6</sub>H<sub>6</sub> and C<sub>6</sub>D<sub>6</sub>) during partitioning between water and organic solvents. They found a significant fractionation effect, expressed as fractionation factor  $\alpha_{H_{part}} = K_{C_6H_6} / K_{C_6D_6} = 1.080 \pm 0.015$  for n-octane (with  $K_{benzene} = C_{benzene\ in\ octane} / C_{benzene\ in\ water}$ ), i.e. the deuterated benzene is more hydrophilic than its nondeuterated isotopologue. The authors also discussed fractionation effects for incomplete equilibration, i.e. under partial kinetic control. This raises the question about the extent and direction of isotope fractionation in diffusion-controlled systems, which can be described by a diffusion fractionation coefficient:

$$\alpha_{H_{diff}} = D_{light} / D_{heavy} \quad (1)$$

with  $D_{light}$  and  $D_{heavy}$  as diffusion coefficients of the light and heavy isotopologues, respectively. The present study explicitly aims on quantifying diffusion isotope fractionation coefficients.

In order to interpret diffusion fractionation it is useful to understand which molecular properties control diffusivities. Diffusion coefficients in condensed media can be calculated with two different approaches (Bhattacharyya and Bagchi, 2000; Cussler, 2009; Schwarzenbach et al., 2003; Tyrell and Harris, 1984): (i) From the hydrodynamic framework based on the Stokes-Einstein relation it follows  $D_{solute} \sim r_{solute}^{-1}$  with  $r_{solute}$  as the hydrodynamic radius of the solute molecule. (ii) Alternatively, in the framework of the kinetic theory, based on the Enskog relation it follows  $D_{solute} \sim \mu_{solute/solvent}^{-1/2}$  with  $\mu_{solute/solvent} = m_{solute} \cdot m_{solvent} / (m_{solute} + m_{solvent})$  as the reduced mass of the solute-solvent pair with  $m_i$  as molecular masses. More recent molecular dynamics simulations (MDS) of diffusion isotope effects make use of the generalized equation  $D_1/D_2 = (m_1 / m_2)^{-\beta}$  where  $\beta$  is a dimensionless exponent  $\leq 0.5$ , frequently in the range of 0 to 0.2, i.e. significantly smaller than the classical value of the kinetic theory (Bhattacharyya and Bagchi, 2000; Bourg and Sposito, 2007; Bourg and Sposito, 2008; Bourg et al., 2010; Richter et al., 2006). A plausible physical notation of the variable extent of mass dependence of self-diffusion coefficients in solution is the interplay of two different modes of motion: The strongly mass dependent short-term kinetic like mode (collision between hard spheres) and the mass independent long-term hydrodynamic mode of motion (sliding through a viscous continuum).

When applying the two basic approaches on the solute pair benzene-D<sub>0</sub> vs. benzene-D<sub>6</sub> in aqueous solution they predict different diffusion fractionation effects. Using the apparent molar volumes of the two benzene isotopologues in the dissolved state,  $V_{C_6H_6} = 88.76$  mL/mol and  $V_{C_6D_6} = 87.92$  mL/mol (at 20 °C) (Dutta-Choudhry et al., 1982; Eltayar et al., 1984; Wade, 1999), and the approximation of Hayduk and Laudie (Hayduk and Laudie, 1974; Schwarzenbach et al., 2003) ( $D_1/D_2 = (V_1/V_2)^{-0.589}$ ) which is an empirical extension of the Stokes-Einstein relation, Eq. (2) results:

$$\alpha_{H_{diff}} = D_{C_6H_6} / D_{C_6D_6} = (V_{C_6H_6} / V_{C_6D_6})^{-0.589} = 1.0096^{-0.589} = 0.9944 \quad (2)$$

The kinetic theory predicts

$$\alpha_{H_{diff}} = D_{C_6H_6} / D_{C_6D_6} = (\mu_{C_6H_6} / \mu_{C_6D_6})^{-1/2} = ((78 \cdot 18 / (78 + 18)) / (84 \cdot 18 / (84 + 18)))^{-1/2} = 1.0068 \quad (3)$$

Using the generalized inverse power-law function from MDS with an estimated value of  $\beta = 0.1$  (Bhattacharyya and Bagchi, 2000)  $\alpha_{H_{diff}} = (78 / 84)^{-0.1} = 1.0074$  results. Obviously, molecular mass and volume related methods predict different fractionation directions. It is common to all these estimations that the predicted fractionation effects are smaller than 1%. A compilation of relevant properties of benzene, toluene and cyclohexane, including their perdeuterated isotopologues, is given in the Supplementary material (SM) part (Table S-1) to this article.

Mills (1976) has directly measured diffusion coefficients of two tritiated benzenes (C<sub>6</sub>H<sub>5</sub>T and C<sub>6</sub>D<sub>5</sub>T) in benzene and cyclohexane as solvents at 25 °C. The fractionation coefficient  $\alpha_{H_{diff}}$  was in the range of 0.998 to 0.995.

In two recent studies by Jin et al. (2014) and Rolle and Jin (2017) the diffusive fractionation of three benzenes (benzene, toluene, ethylbenzene as non- and perdeuterated isotopologues) and two chlorinated ethenes (trichloroethene and *cis* dichloroethene) in aqueous solution has been measured using the method of gel diffusion tubes. The authors found large fractionation effects for the benzenes ( $\alpha_{H_{diff}} = 0.98$  to 1.04), whereas for the chlorinated ethenes these effects were a factor of 10 to 20 smaller, e.g.  $\alpha_{Cl_{diff}} = D_{C_2H_3Cl_3} / D_{C_2H_4Cl_2} = 1.0019 \pm 0.0004$ , even though the relative increase in molecular masses for the heavy isotopologues is similar for the two compound classes. It is remarkable that the direction of fractionation is contrarian for the benzene ( $D_{C_6H_6} / D_{C_6D_6} = 0.98$ ) and the alkylbenzenes ( $D_{C_7H_8} / D_{C_7D_8} = 1.040$ ). In terms of  $\beta$  in the inverse power law, the experimental fractionation data result in  $\beta = -0.27$  for benzene,  $\beta = +0.455$  for alkylbenzenes and  $\beta = +0.043$  to 0.088 for the chlorinated ethenes. Obviously, the mass dependency of relative diffusion coefficients is not uniform even within one compound class.

In another recent study Tyroller et al., 2014 measured diffusive fractionation in water between Ne and Ar isotopes. The resulting fractionation factors  $D_{20Ne} / D_{22Ne} = 1.010 \pm 0.003$  and  $D_{36Ar} / D_{40Ar} = 1.055 \pm 0.004$  are quite different again, although the mass ratios of the isotopes are identical. The authors conclude that none of the existing theories including MDS calculations are capable of giving a general explanation of the isotope fractionation due to aqueous diffusion.

The article of Jin et al. (2014) as well as others (Hoehener and Yu, 2012; Rolle et al., 2010; Tyrell and Harris, 1984; Wanner and Hunkeler, 2015; Xu et al., 2016) provide an up-to-date survey on the state of knowledge concerning data and theories of diffusion in aqueous media, including the environmental significance of the diffusive fractionation in subsurface environments (Jeannotat and Hunkeler, 2012, 2013; Wanner and Hunkeler, 2015). Most of these studies come to the conclusion that an improved understanding of diffusive isotope fractionation of organic compounds is of critical importance for the correct interpretation of isotopic data in groundwater systems, due to the role of diffusion as a major transport mechanism in saturated porous media.

Summing up the presently available data, it is not clear to what extent and in what direction deuterium substitution affects diffusion rates of simple organic solutes in aqueous solution. Motivated by this lack in database and basic understanding, we measured relative aqueous phase diffusivities of isotopologues (nonlabeled and deuterated) of benzene, toluene and cyclohexane by means of a two-phase partitioning approach under selected mixing conditions. In order to rely on diffusion data derived from mass-transfer kinetics, it has to be verified that the latter is actually controlled by molecular diffusion rather than by large scale mixing effects. We devoted special attention to this issue (see Sections 5.1 and S-11 in the SM part). The observed fractionation effects are quite different for the 'forward' and the 'reverse'

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