Isotope fractionation of benzene during partitioning — Revisited

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HIGHLIGHTS

- Hydrogen isotope fractionation was measured for partitioning of benzenes from water.
- 1-Octanol and n-octane yield similar fractionation factors.
- C_6D_6 behaves more hydrophilically than C_6H_6.
- Solvent extraction fractionates slightly stronger than evaporation from water.
- Diffusion may fractionate opposite to thermodynamic control.

GRAPHICAL ABSTRACT
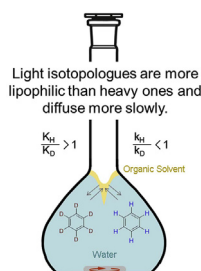
ARTICLE INFO

ABSTRACT

Isotope fractionation between benzene-D_0 and benzene-D_6 caused by multi-step partitioning of the benzenes between water and two organic solvents, n-octane and 1-octanol, as well as between water and the gas phase, was measured. The obtained fractionation factors $\alpha H = K_H/K_D$ are $\alpha H = 1.080 \pm 0.015$ and $\alpha H = 1.074 \pm 0.015$ for extraction into n-octane and 1-octanol, respectively, and $\alpha H = 1.049 \pm 0.010$ for evaporation from aqueous solution. The comparison of solvent- and gas-phase partitioning reveals that about 2/3 of the driving force of fractionation is due to different interactions in the aqueous phase, whereas 1/3 is due to different interactions in the organic phase. The heavy benzene isotopologue behaves more 'hydrophilically' and the light one more 'hydrophobically'. This synergistic alignment gives rise to relatively large fractionation effects in partitioning between water and non-polar organic matter. In contrast to a previous study, there is no indication of strong fractionation by specific interactions between benzene and octanol.

Partitioning under non-equilibrium conditions yields smaller apparent fractionation effects due to opposite trends of thermodynamic and kinetic fractionation parameters, i.e. partition and diffusion coefficients of the isotopologues. This may have consequences which should be taken into account when considering isotope fractionation due to sorption in environmental compartments.

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1. Introduction

Recently, Imfeld et al. (2014) published a study on "Carbon and hydrogen isotope fractionation of benzene and toluene during hydrophobic sorption in multistep batch experiments" in this journal. In their study, partitioning of benzene and toluene between water and a number of organic solvents and sorbents (i.e. 1-octanol, dichloromethane, cyclohexane, hexanoic acid, and Amberlite XAD-2) was investigated by means of multistep partitioning

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experiments. Generally, very small carbon and hydrogen isotope fractionation effects were observed, with the exception of benzene in 1-octanol. This solute-solvent pair gave rise to significant isotope fractionation, expressed as fractionation factors $\alpha C = 1.0030 \pm 0.0005$ and $\alpha H = 1.195 \pm 0.026$ (with α defined as K_{light}/K_{heavy}, i.e. ratio of partition coefficients for light and heavy isotopologue). This surprising finding was tentatively interpreted in terms of specific solute-solvent interactions between π-electrons of benzene with OH-groups of octanol.

However, the experimental approach applied in their study did not completely avoid solute evaporation losses and incomplete equilibration. Although Imfeld et al. attempted to take these effects into account for data evaluation, they may give rise to some uncertainties in the conclusions. This is the reason for our re-inspection of benzene fractionation in solvent/water partitioning by a more detailed study and refined experimental setup using benzene-D_0 and benzene-D_6 as solutes and 1-octanol and n-octane as solvents.

When investigating small fractionation effects, such as were found for benzene partitioning between water and non-polar solvents (e.g. for cyclohexane $\alpha H = 1.006 \pm 0.002$; Imfeld et al., 2014), it may be useful to work with labelled or even multi-labelled solutes in order to amplify the observable fractionation effects. For this reason, benzene-D_6 was used in the present study. The translation of fractionation factors for isotopologues with different numbers of deuterium atoms in a molecule can be carried out by approximations, e.g. $\alpha H_{D1} = (\alpha H_{Dn})^{1/n}$ (Hoehener and Yu, 2012). The state-of-the-art background and environmental relevance of the topic are extensively considered in the previous study (Imfeld et al., 2014) and are, therefore, not reiterated here.

2. Material and methods

2.1. Equilibrium partitioning − thermodynamic control

1 L of deionized water was spiked with 500 mg each of benzene-D_0 and benzene-D_6 (from Merck, Germany) into a 1 L volumetric flask and shaken vigorously until the benzene was completely dissolved and homogeneously distributed. Then 10 mL of a solvent, either n-octane or 1-octanol, containing 10 mg/L of n-nonane as internal standard, was added. The flask was shaken again, firstly 10 min manually and then 20 min on an automatic shaker, such that the solvent phase was finely distributed in the water phase. After stopping the benzene extraction, the flask was allowed to stand vertically for 10 min for separation of the solvent phase in the upper narrow neck of the flask. The solvent was completely withdrawn by means of a pipette and replaced by another 10 mL of fresh solvent. This extraction procedure was repeated many times until the benzenes were largely depleted (>99%) from the water phase.

The extraction procedure was designed in such a way that: (i) partition equilibration was largely complete (>98%, no change in benzene-nonane peak ratios upon elongation of extraction time), and (ii) evaporation of benzenes was minimized (<1%).

The organic phases were analyzed by means of GC-MS (QP2010, Shimadzu) in the selected ion monitoring (SIM) mode. The two benzene isotopologues were quantified on the basis of their molecular ion peaks (m/z = 78 and 84). The benzene peak areas were kept in an optimal range by sample dilution and variation of the GC conditions (injector split ratio) in order to avoid any peak discrimination. It was verified that the measured ratio of peak areas (A_{84}/A_{78}) was constant ($SD_{single\ value} \leq \pm 1\%$) over a range of 5 orders of magnitude in the original benzene sample concentration.

After removal of the equilibrated solvent phases, 1 mL of the aqueous phase was withdrawn and extracted exhaustively with 1 mL of the applied solvent, octane or octanol (also containing the internal standard n-nonane), in a 4 mL vial. These extracts were also analyzed by means of GC-MS under identical conditions. This procedure ensures a perfect comparability between the isotope analyses of benzenes in the solvent and the water phase.

2.2. Non-equilibrium partitioning − kinetic control

Most of the partitioning experiments were conducted under shaking of the water-solvent mixture as described above. In experiments aiming at a kinetic control, partitioning was conducted by magnetic stirring rather than by shaking in order to allow more defined mixing conditions. For this procedure, 10 mL of the 1 L aqueous phase were removed, such that the interface area between the two phases was increased (interface in the broader range of the volumetric flask). The stirring rate was controlled in such a way that a deep waterspout was formed but the two phases were not dispersed into each other (no visual droplet formation). This procedure results in internally mixed phases with a diffusion-controlled mass transfer between the two phases (diffusion through the two stagnant boundary layers) as the rate-limiting process. For the kinetic experiments, 100 μL of the solvent phase was withdrawn after defined stirring periods (e.g. after 15 min, 30 min etc. up to 20 h) and analyzed by means of GC-MS.

The described procedures provide access to the benzene concentrations and isotope compositions in the two involved phases. Due to the mass balance in a closed system, it is sufficient to analyse only one of the phases in order to trace the isotope fractionation. For equilibrium partitioning experiments we preferred the solvent phases, whereas for kinetic experiments we analyzed both phases in order to verify the results.

2.3. Water-gas phase partitioning

In addition to the above, experiments on partitioning of benzene between water and the gas phase were conducted according to the following procedure: 50 mL of deionized water was filled into a 245 mL glass bottle equipped with a Mininert™-valve, purged with He and then spiked with 10 mg each of benzene-D_0 and -D_6 (volume ratio headspace/water: $V_{headspace}/V_w = 3.92$, $T = (25 \pm 1)°C$). The bottle was shaken for 1 min manually and for 5 min on a horizontal shaker, after which the headspace (25 μL samples each) was analyzed several times by means of GC-MS. The headspace was then purged with about 1 L of fresh He over about 20 min by means of a steel cannula inserted through the valve and placed in the gas phase without any agitation of the water phase. This ensured that only the gaseous benzene fraction was removed by the purging step. After closing the valve, water and headspace phase were equilibrated again by shaking as described above. This equilibration-purging procedure was repeated 11 times until the benzene concentrations were decreased by about three orders of magnitude.

3. Data evaluation

The GC-MS analyses yield ratios of peak areas of the two benzene isotopologues and the internal standard n-nonane. This allows the calculation of not only the benzene extraction extents per step but also the isotope composition shift in the extracts over the extraction sequence. We use the following terminology and formulas:

$$\alpha H_i = K_{i,benzene-D0} / K_{i,benzene-D6} \tag{1}$$

with αH_i as the fractionation coefficient of benzene-D_0 vs. benzene-D_6 for partitioning between a solvent i and water. For