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Isotopic Fractionation of Potassium by Diffusion in Methanol

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Abstract

We present the results of experiments involving the isotopic fractionation by diffusion of K^+ cations in methanol at 298 K along with supporting molecular dynamic simulations. The experiments, using glass Rayleigh fractionators filled with a methanol solution of KCl, constrain the ratio of the individual diffusivities of ^{41}K and ^{39}K ($D_{^{41}K}/D_{^{39}K}$) in methanol, and so the isotopic fractionation of K^+ due to diffusion in methanol, to 0.9995 ± 0.0001. This isotopic fractionation is 25% of the fractionation resulting from K^+ diffusion in water. This is consistent with published molecular dynamics simulations indicating greater hydrodynamic coupling between K^+ ions and solvating methanol molecules compared to K^+ ions and solvating water molecules.
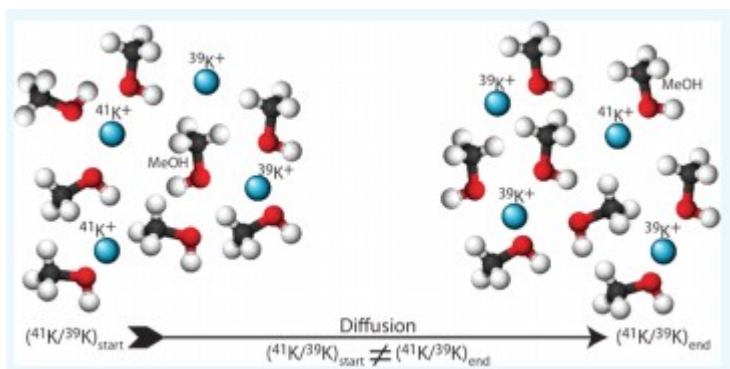
Introduction

The phenomenon of chemical diffusion through a medium, for example, gas or liquid, is commonly observed to produce an isotopic mass fractionation of the diffusing element. In the special case of diffusion involving ideal gases, kinetic theory results in a relationship given by eq 1

$$\alpha = D_x/D_y = (m_y/m_x)^\beta \quad (1)$$

where α is the fractionation factor between isotope x and isotope y of an element or the ratio of the diffusivities of isotope x and isotope y, m is mass of isotopes x and y, and the exponent β is equal to 0.5 (in which case eq 1 becomes Graham's law of effusion/diffusion), and is a good approximation in certain situations such as the isotopic separation of gaseous uranium hexafluoride species.(1) However, in the case of solute atoms diffusing in a fluid such as water, there is no available theory, but it has been experimentally determined that β is typically less than 0.5.(2−5) Molecular dynamics

simulations (MDS) of solute diffusion in water confirm that the mass dependence of solute diffusivity (D) has an inverse power-law form as indicated by eq 1, but where β is less than 0.25 and varies with diffusing species.(6,7) In addition, experiments have shown that for isotopic fractionation of cations by diffusion in molten silicates, β's are also less than 0.25 depending on the cation and the melt composition.(8−12)

Here, we use Rayleigh fractionation apparatus (bulbs) developed by Richter et al.(2) to measure the relative diffusivities of different isotopes of dissolved ionic species in water to instead measure the relative diffusivities of [39]K and [41]K in methanol. This method was inspired by the mid-19th century experiments conducted by the Scottish physical chemist Thomas Graham which would lead to his eponymous law of effusion where the ratio of the rates of effusion of two gas species is equal to the square root of the inverse ratio of their molar masses(13,14) and by his subsequent experiments regarding diffusion in aqueous solutions.(15)

Our experiments were run for lengths of time during which the volume outside the bulb would act in effect as an infinite sink for K. The Rayleigh fractionator system allows direct comparison of the diffusivities of the different isotopes of a dissolved species.(2) In the case of the reported experiments, we are comparing the relative diffusivities of the stable isotopes [41]K and [39]K, the two most common isotopes of potassium. In which case, in eq 1 x stands for [41]K and y stands for [39]K.

Previous work has focused mainly on diffusion in water (e.g. refs(2−5)), and provides a baseline for evaluating the controls on isotopic fractionation during diffusion in fluids. Our purpose is to provide a measurement of isotopic fractionation of K by diffusion in a different solvent, methanol, to provide insights into how solute–solvent molecular interactions affect isotopic fractionation. We also wish to demonstrate the feasibility of the Richter et al.(2) Rayleigh fractionation technique for determining isotopic fractionation by diffusion in solvents other than water. Methanol is a strong polar solvent with properties such as dipole moment and dielectric constant close, when compared to other solvents, to water, and so provides an interesting comparison and a good starting point for exploring the phenomenon of isotopic fractionation in other classes of solvents.

Experimental Setup

The set of ten bulbs (Rayleigh fractionators) we used in our experiments were fashioned of quartz glass, with interior volumes ranging from 0.59 to 0.75 cm^3 (average of all 10 is 0.66 cm^3) with a 1 mm inner-diameter tube providing communication with the outside environment (Figure 1). The experimental design produces precise values for the ratios of diffusivities; however absolute values of diffusivities are not as well constrained because of size variations among the different bulbs.(2)
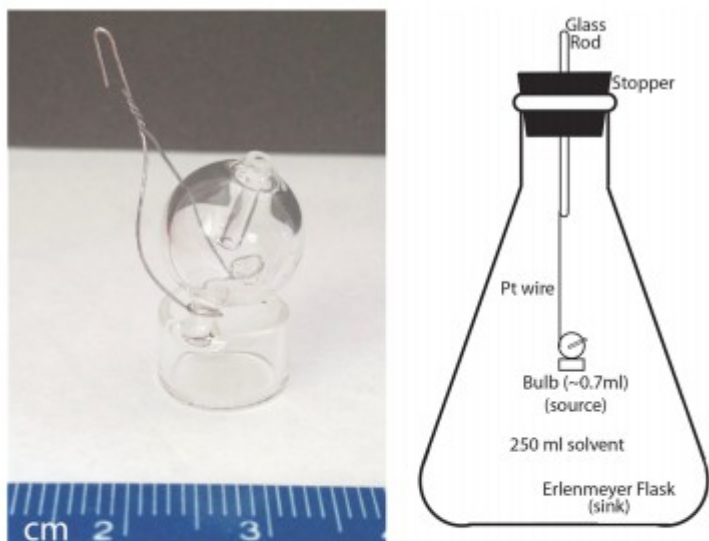
Figure 1. Photograph (left) of the Rayleigh fractionation bulb used in experiments to determine the isotopic fractionation of K by diffusion in methanol. The bulb consists of a quartz glass sphere that is filled with a solute—solvent mixture and acts as a source for diffusion via a tube to a much larger volume of the solvent that acts as an effective infinite sink for the solute. The glass cylinder attached to the sphere provides a base for standing the bulb during filling and sampling. A platinum wire is used to hang the bulb within the volume of solvent contained in a 300 mL Erlenmeyer flask (right).

A starting solution was made with KCl (Sigma-Aldrich, ACS reagent grade, dried for 12 h in an oven at 115 °C and cooled in a desiccator prior to weighing) and methanol (Aldrich Honeywell PURANAL, semiconductor grade, max. 0.05% H_2O by wt) to a K concentration of 9.0 mM, which is ~16% of the solubility at 25 °C.(16,17) Each bulb was filled with this starting solution using a syringe fitted with a quartz-glass needle to draw in the solution, and then hung within an Erlenmeyer flask by platinum wire from a glass rod wand and submerged ~2–3 cm in ~250 mL of pure methanol. The glass rod was passed through a silicone stopper fitted to the Erlenmeyer flask and sealed with silicone sealant to avoid evaporative loss of the methanol (Figure 1). The bulbs were allowed to diffusively exchange with the flask volumes for periods ranging from 1 day to 35 days (Table1) while held in a constant temperature bath at 25 °C (298 K). At the end of their individual experimental periods, the bulbs were removed from their flasks and the methanol KCl solution in the bulbs quantitatively removed. An aliquot of this solution was dried down and brought up in 3 M HNO_3 for K concentration analysis by Q-ICPMS. The remaining portion of the methanol was analyzed for water content by Karl-Fischer titration using a Mettler Toledo DL39 coulometric KF Titrator and EMD Millipore Aquastar CombiCoulomat fritless reagent, all located inside an Ar-purged glovebox. The postexperiment concentrations of H_2O in the methanol solutions from the bulbs were 0.10–0.17% by weight.

Table 1. Results of K Diffusion in Methanol Experiments

bulb	duration, days	K, mM[a]	F[b]	$\delta^{41}K$, ‰[c]	±2sd
D	2.01	5.48	0.608	0.270	0.091
A	1.01	7.39	0.822	0.093	0.082
E	3.01	5.59	0.621	0.136	0.074
B	29.90	2.97	0.330	0.428	0.094
F	1.00	4.80	0.534	0.226	0.082
J	34.89	1.54	0.171	0.799	0.077
G	4.02	4.43	0.492	0.219	0.080
K	25.84	3.92	0.436	0.330	0.084
L	21.84	4.14	0.460	0.214	0.077
H	11.82	3.76	0.418	0.412	0.088
A	9.91	4.69	0.521	0.176	0.082
F	13.82	2.97	0.330	0.539	0.075
start		9.00	1.00		

[a]Uncertainty is ~10% of value. [b]Relative to starting solution. [c]Relative to in-house K isotopic standard.

K Isotopic Analysis

The K isotopic compositions (reported as $\delta^{41}K$, see below) of experimental samples were measured using an IsoProbe (VG Instruments, Ltd) multicollector magnetic sector inductively coupled plasma source mass spectrometer. The IsoProbe is equipped with a RF hexapole ion-guide that allows the introduction of gasses to provide both energy focusing, as well the removal of isobaric interferences arising from Ar ions. In the case of the K isotopic measurements reported here, He and H_2 were introduced to the hexapole region at rates of 10 and 1 mL/min, respectively, to suppress mass interferences from Ar isotopes. Aliquots of the K bearing methanol solutions were taken to provide 500 ng of K and dried down. The dried samples were then taken up in 0.3 M HNO_3 to a concentration of 500 ppb to match the K concentration of a bracketing in-house K isotopic reference.(18) Sample solutions were introduced to the mass spectrometer using an Aridus II (CETAC Technologies) desolvation system with a Teflon nebulizer with a measured uptake of 60 μL/min. For further details of the K isotopic analysis see refs.(3,18) The potassium isotopic composition is reported as

$$\delta^{41}K, ‰ = 1000 \times \{[(^{41}K/^{39}K)_{sample}/(^{41}K/^{39}K)_{reference}] - 1\} \quad (2)$$

where $(^{41}K/^{39}K)_{reference}$ is the average of the two bracketing analyses of the K reference solution prior to and after the analysis of the sample. The uncertainties in $\delta^{41}K$ provided in Table1 are based on the combined uncertainties in the analyses of the bracketing reference and the sample.

Molecular Dynamics Simulations

To place our experimental results for K diffusion in methanol into a molecular-scale context and relate them to previous results for K diffusion in water, we conducted molecular dynamics simulations at 298 K in

the *NVT* ensemble using version 4 of LAMMPS,(19) with the Jorgensen OPLS force field(20) and Lennard-Jones potential parameters for K^+ taken from Jensen and Jorgensen.(21) Long-range K^+-methanol interactions were calculated via Ewald summation, and time integrations were calculated using a standard velocity-Verlet integrator,(22) while short-range interactions were calculated using a combination of Lennard Jones and Coulombic potentials with a global cutoff of 12 Å. Simulations consisted of a single K^+ cation and 398 methanol molecules in a periodically replicated, cubic simulation cell with sides 30 Å in length, thereby approximating infinite dilution conditions with a simulation cell density of approximately 0.78647 g cm^{-3}—the density of pure methanol at 298 K. In order to investigate *D* as a function of isotopic mass, K^+ diffusion was simulated for a range of hypothetical isotopic masses, from *m* = ~10 to 156 Da.

Simulations were run in 100 ps slices (with a 1 fs timestep), and the results from each slice were compiled to create a dataset for 1 ns worth of simulation time. Each successive 100 ps simulation began where the previous simulation ended in order to maintain continuity. A total of nine 1 ns datasets created in this way resulted in 9 ns of total simulation time. Prior to the "start" of the 9 ns simulation, the entire system was subjected to 1 ns of equilibration at 298 K.

The position and velocity output data from LAMMPS were recorded every 5 fs; these data were used to calculate the velocity autocorrelation function (VACF) using an in-house program based on the Fortran VACF code internal to MOLDY 3.6.(23) Briefly, the VACF was calculated by applying a 5 ps moving average window to each 100 ps simulation slice; 90 of these "windowed" VACFs (i.e., 10 VACFs for each ns of simulation time) were produced for each hypothetical K isotope. A representative normalized VACF for $^{39}K^+$ (the most abundant naturally occurring stable isotope of K) at 298 K is given in Figure 2a; the value decays to approximately zero within about 3 ps.
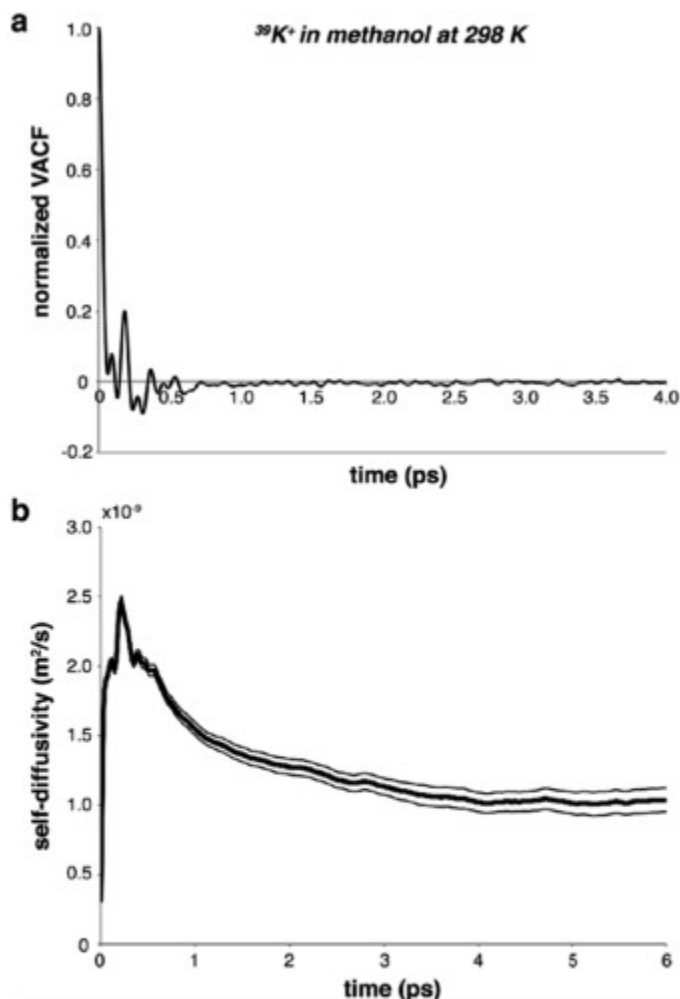
Figure 2. (a) Normalized VACF of $^{39}K^+$ in methanol at 298 K. (b) Value of the self-diffusion coefficient (D) prior to correcting for system-size effects is given in the thick black line as calculated via eq 3 as a function of time (i.e., the integral upper limit). The thin black lines outline the 95% confidence error envelope.

Each 20 ps-long "windowed" VACF was in turn individually integrated using the following Green–Kubo relation (eq 3; e.g., ref (22)) to determine the corresponding self-diffusion coefficient, D_i, where i refers to an individual 20 ps "windowed" VACF

$$D_i = 1/3 \lim_{\tau \to \infty} \int_0^\tau \langle v(0) \cdot v(t) \rangle_i \, dt \quad (3)$$

The plot of D averaged over all data for $^{39}K^+$ at 298 K is given in Figure 2b, which shows that the self-diffusion profile plateaus at around 4 ps, indicating that the upper limit of the integral must be calculated with $\tau > 4$ ps. The infinite-time limit in eq 3 was therefore approximated by calculating the value of D_i for $\tau = 4.5$–5.5 ps. As noted by Bourg et al.,(3) self-diffusion coefficients calculated in this way can differ by up to 24% between two consecutive 2 ns-long blocks; therefore, the overall self-diffusion coefficient for a given K isotope (D) was calculated by averaging over all D_i values for

that isotope, and precision was quantified in terms of standard errors. Calculating D at larger values of τ gave comparable results, albeit with lower precision.

Translational diffusion coefficients are known to have system-size dependence in MDS performed with periodic boundary conditions (cf., refs(24,25)). We therefore corrected our average D values for each isotope using eq 12 in Yeh & Hummer:(25)$D_0 = D_{PBC} + 2.837297k_BT/(6\pi\eta L)$, where D_{PBC} is our average D (PBC = "periodic boundary condition"); k_B is the Boltzmann constant; T is the absolute temperature of our simulation (298 K); η is the viscosity of methanol at T (0.544 mPa s at 298 K(26)); and L is the length of our cubic periodic box (30 Å). We note that this is described by Yeh & Hummer(24,25) as an "ideal" correction: as detailed in Yeh & Hummer, (24) charged particles in polar solvents require the correction factor to be scaled by a value less than one (e.g., 0.88 for K^+ in H_2O) in order to accurately account for the observed system-size dependencies. As such, our correction may be a slight overestimate, but it accounts for the size of the simulation box nonetheless.

Results and Discussion

The results of the diffusion experiments are presented in Table1. From the starting concentration of 9 mM, the postexperiment K concentrations in the bulbs ranges from 1.5 to 7.4 mM, while the isotopic composition ($\delta^{41}K$, see eq 2) of the K remaining in the bulbs ranges from 0.09 to 0.8‰. The highest $\delta^{41}K$ is associated with the lowest remaining concentration (1.5 mM), while the lowest $\delta^{41}K$ is associated with the highest concentration (7.4 mM), indicating that an isotopic fractionation of K occurred with the diffusion of K from the bulbs into the surrounding methanol contained by the Erlenmeyer flasks. In Figure 3a, the data are presented as a plot of F (the fraction of K remaining in the flasks relative to the starting concentration, see Table1) against the $\delta^{41}K$ of the remaining K in the methanol contained in the bulbs. As expected from the experimental set-up, the data follow the form of a Rayleigh fractionation model given by eq 4 $R/R_0 = F^{(\alpha-1)}$(4)where R/R_0 represents the fractional change of the K isotopic composition relative to the starting composition, F is the fraction of K remaining in the bulb relative to the starting concentration, and α (see eq 1) is the isotopic fractionation factor. For a derivation of eq 4 in the context of the diffusion bulbs see Richter et al. (2) Taking the log of both sides of eq 4 yields the linear relationship $\log(R) = (\alpha - 1)\log(F) + \log(R_0)$(5)where $\log(R) = \log((\delta^{41}K/1000) + 1)$, and $\log(R_0) = \log(((\delta^{41}K)_0/1000) + 1)$. Using eq 5 to plot the experimental data (Table1) results in Figure 3b.
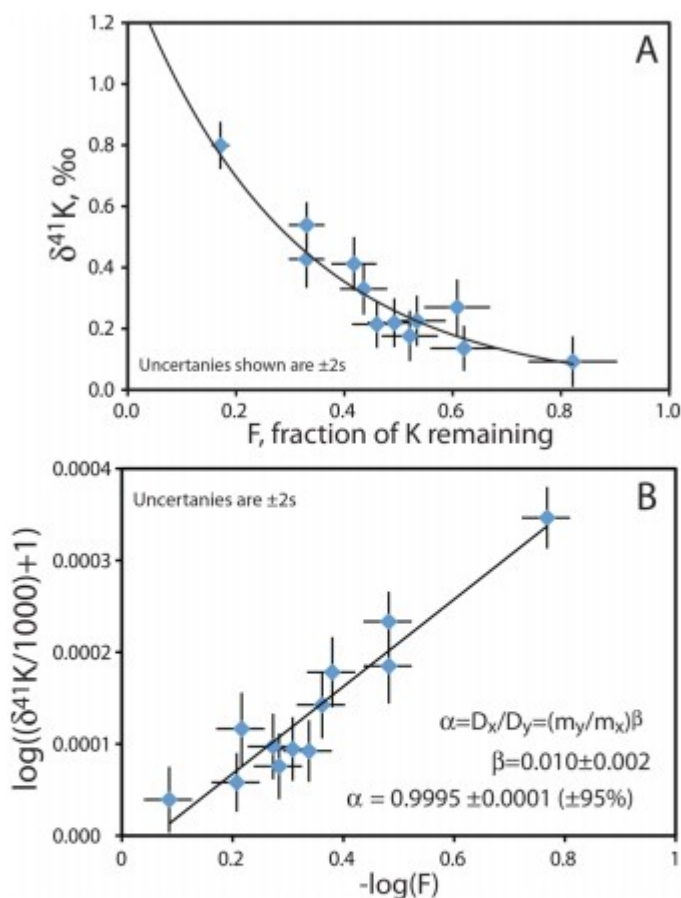
Figure 3. Panel (A) shows the relationship between the K isotopic composition of bulb contents and the fraction of K remaining in those bulbs (i.e., that which had not diffused into the "infinite" reservoir). Data are from Table 1. The same data were input into eq 5 (see text) to produce panel (B), from which the fractionation factor α is derived from the slope, $(1-\alpha)$, of the best fit line to $\log((\delta^{41}K/1000) + 1)$ plotted against the negative of $\log(F)$ (see eq 5). Errors shown in each panel are 2 times the standard deviation.

A linear best-fit to the data in Figure 3b using Isoplot(27) yields a value for α of 0.9995 ± 0.0001 (±95% confid.) from the slope (a fractionation of 0.5‰), and from the y-intercept an initial $\delta^{41}K$ for the starting solution of −0.081 ± 0.099‰ (±95% confid.), which is indistinguishable from our in-house K isotopic reference. Using this value of α in eq 1 with the masses of ^{39}K and ^{41}K, β is calculated to be 0.010 ± 0.002 (±95% confid.). The MDS we conducted (Figure 4 and Table2) results in a β of 0.011 ± 0.024 (±95% confid.) (or an α of 0.9995 ± 0.0011 (±95% confid.)). Though the MDS results have relatively large uncertainties (about 10 times greater than the results from the diffusion experiments), the MDS results are similar to our experimental values. Our MDS also yields a value (using ^{39}K to stand for K) for the diffusivity of K in methanol of 1.393 ± 0.006 × 10^{-5} cm^2/s, which is within the uncertainties of the experimental value 1.396 ± 0.001 × 10^{-5} cm^2/

s for 25 °C (using the Nernst–Einstein equation with limiting conductance data(28)), lending support to the validity of the simulation.

Table 2. Results of MD Simulations

modeled K mass, Da	MDS ave.d D, m^2/s	system size corr.d D, m^2/s	±1SE
9.74	1.0541×10^{-9}	1.4336×10^{-9}	3.1×10^{-12}
19.48	1.0439×10^{-9}	1.4234×10^{-9}	3.1×10^{-12}
38.96	1.0132×10^{-9}	1.3927×10^{-9}	3.0×10^{-12}
40.96	9.8723×10^{-10}	1.3667×10^{-9}	2.5×10^{-12}
77.92	9.9481×10^{-10}	1.3743×10^{-9}	2.4×10^{-12}
155.85	1.0271×10^{-9}	1.4066×10^{-9}	2.8×10^{-12}
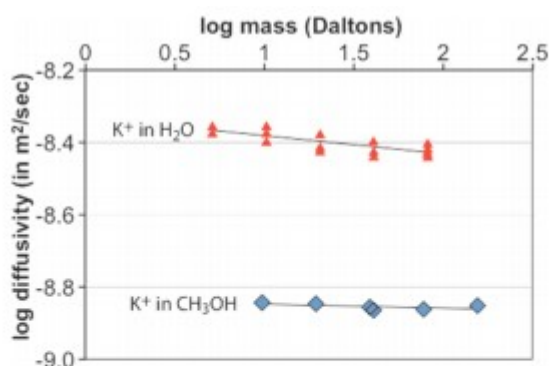
Figure 4. Comparison of the MDS results for diffusion of K^+ in water[3] and the MDS result for diffusion K^+ in methanol over a range of hypothetical isotopic masses. The slope of the best-fit lines gives β values of 0.049 ± 17 for K^+ diffusion in water[3] and 0.011 ± 0.017 for diffusion in methanol.

Our experimental results for the isotopic fractionation of K by diffusion in methanol can be directly compared to published experimental results by Bourg et al.(3) using the same technique for the isotopic fractionation of K by diffusion in water. They report a value for β of 0.042 ± 0.002, which corresponds through eq 1 to an α of 0.9979 ± 0.0001 (a fractionation of 2.1‰) representing an approximately four times larger isotopic effect. From molecular dynamics modeling of the effect of isotopic mass on the diffusion of K^+ and other monovalent ions (Li^+, Na^+, and Cs^+) as well as divalent (Mg^{2+} and Ca^{2+}) and neutral (He, Ne, Ar, and Xe) species, Bourg et al. (3) observed an inverse relationship between tau (residence time of water in the first solvation shell of the solute) and β. From this inverse relationship, Bourg et al.(3) infer that solute species that are less hydrodynamically coupled to solvent molecules (reflected by solvent molecules having short mean residence times around the solute) experience greater isotopic fractionation attending diffusion (i.e., β's increasing toward the limiting value of 0.5, cf. ref (6)). Comparing then the isotopic fractionation of K^+ by diffusion in water to that by diffusion in methanol suggests that the hydrodynamic

coupling between K^+ and methanol molecules is stronger than between K^+ and water. This is consistent with MD simulations comparing diffusion of ionic and uncharged solutes (including K^+ and K) in water and methanol that found a lower Stokes friction but a higher dielectric friction for solutes in methanol indicating greater hydrodynamic solute–solvent coupling in methanol.(29)

Conclusions

We have demonstrated that a simple set of experiments using a Rayleigh fractionator bulb developed by Richter et al.(2) to determine isotopic fractionation of dissolved species by diffusion in water can also be used with a different solvent, methanol. Presumably isotopic fractionation by diffusion in other nonaqueous solvents could also be determined in this manner. Our experiments regarding isotopic fractionation of K^+ in methanol yields a fractionation factor, α, of 0.9995 ± 0.0001 ($\pm 95\%$ confid.), about 25% of the isotopic fractionation factor for K^+ diffusion in water. This result is consistent with greater hydrodynamic coupling between K^+ and solvating methanol molecules compared to K^+ and solvating water molecules.

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