Model for selection of O-water isotopomers by primary amines in a magnetic field - Effects on $\Delta^{17}O$

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Abstract

Applying a external magnetic field (B) during the hydration of primary amines $(R-NH_2)$ with water O-isotopomers $(H_2^{16}O; H_2^{17}O; H_2^{18}O)$ should show correlation with ¹⁷O-selection. This effect is due to the mass-independent partition of nuclear properties (i.e. spin and quadrupole) in the ¹⁶O, ¹⁷O, ¹⁸O series, the nuclear-spin and nuclear-quadrupole properties of ¹⁴N, and the involvement of B in the interaction between nuclear spin isomers (spinomers) of ¹H¹HX type (e.g. NH_2 and H_2O). We show results of a numerical analysis of the relationship between amine-hydration, B and $\Delta^{17}O$. At 300K the MIF(mass independent fractionation) of the water from the hydration sphere of ¹⁴NH₂ increased from $\Delta^{17}O \sim 6.8 \cdot 10^{-5}$ ‰ at B = 0.5 Gauss (the B at earth's surface), to $\Delta^{17}O \sim 0.63$ ‰ at B = 0.46T (~ the B on the surface of magnetite crystals). When the concentration of $R-NH_2$ was very small ($\leq 1\mu M$) isotopic changes in the bulk solution were small and did not require corrections for diffusion. In nature this effect can create $\Delta^{17}O = \sim 0 - 0.7$ ‰ heterogeneity on magnetite surfaces coated with primary amines.

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1 Introduction

We propose that spin-chemical interactions between $H_2^{17}O$ and AAs (e.g. 3s-spinomer/3sspinomer $(H_2^{17}O/-NH_2)$ interactions, and spinomer/enantiocenter $(H_2^{17}O/*C)$ interactions) connect isotopic and chiral anomalies on a scale found in meteorites. The $H_2^{17}O$ is relatively abundant in nature (20 mM in water), simple AAs are common in prebiotic syntheses, and B_o reaches 0.5T within 1 μm from the surface of magnetite (a mineral present in most basalt rocks, the dominant type of rock on the early Earth and Mars). So far, we made NMR measurements on ribose, glucose, Asn, Ala and mandelic acid, and found differences between enantiomers correlated with $[H_2^{17}O]$, and that in AAs these differences are also controlled by pH (Figures 1-5; [1]; [3] and [2]). The mechanism and implications of this asymmetry are unclear. We propose that ${}^{17}O/{}^{16}O$ fractionation occurs in nature at the micro-scale level through interactions of the $H_2^{17}O$ 3s-spinomer with other complex spinomers such as $-NH_2$ from *C of AAs in a large B_o . Though

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little studied, chemical interactions 3s-involving spinomers may open new research avenues in spin-chemistry, mass-independent isotopic fractionation, magnetochirality and cosmochemistry [15], [14], [17]. We put forward a mechanism explaining this connection and posit that evaporative crystallization could have amplified the e.e. of some AAs at the origin of life ([2]). The asymmetric effects seen by $TD^{-1} HNMR$ consist of differences in K_a in $H_2^{17}O$ /solute complexes relative to $H_2^{16}O$ /solute complexes, as well as differences in proton exchange properties between enantiomers. In AAs, both the pH and $[H_2^{17}O]$ control these chiral chemical effects ([2]). These results were confirmed using As nenantiomers purified by re-crystallization from microbes-free racemic solutions. By comparisons with other chiral chemicals, such as mandelic acid and sugars, we showed the role of the amino group from the chiral center $(*C - NH_2)$ of AAs in this asymmetry ([2]). During experiments of Asn crystallization from racemic solutions we also found differences in solubility between D- and L-Asn, and that the amplitude and variance of chiral amplification is also controlled by the concentration of $H_2^{17}O([H_2^{17}O])$ and by external magnetic fields B_o . The role of $H_2^{17}O$ in revealing this asymmetry indicated the participation of nuclear spin chemistry in the hydration with $H_2^{17}O$, and interactions between molecular structures carrying three adjacent nuclear spins (i.e. 3s-spinomers) and carrying nuclear quadrupoles. Examples of such spinomers are ${}^{14}NH_2$ and $H_2^{17}O$. We propose that during the origin of life combined abiotic effects (i.e. L:D electromagnetic asymmetry in chiral centers, interactions between 3s-spinomers, external B_o and evaporative crystallization) led to biochemistry-independent chiral amplification [2].

We developed a theoretical model to explain this source of asymmetry and request support to verify hypotheses of this model. Understanding this mechanism will shed light on chemical consequences of the electromagnetic asymmetry of chiral centers, and the potential role of this asymmetry in prebiotic evolution and the origin of e.e. in earlier stages of terrestrial and extraterrestrial environments.

Hypotheses: Hypothesis 1. ${}^{1}H^{1}H$ nuclear spin coupling in $H_{2}^{17}O$ and ${}^{14}NH_{2}$. Nuclear spins with quadrupoles (e.g. ${}^{17}O$ and ${}^{14}N$) impair the nuclear ${}^{1}H^{1}H$ spin:spin coupling in 3s-spinomers such as $H_{2}^{17}O$ and ${}^{-14}NH_{2}$. Information about this coupling is hard to obtain by conventional High Resolution Nuclear Magnetic Resonance (HR - NMR), because of the broad spectral shift caused by the ${}^{17}O$ and ${}^{14}N$ quadrupoles. Experimental approaches for such studies include Nuclear Quadrupole Resonance (NQR) which only applies to solids, and $TD - {}^{1}HNMR$ which is generally used for liquids. In $TD - {}^{1}HNMR$ the signal amplitude is correlated with the sum of the uncoupled plus ortho-coupled ${}^{1}H^{1}H$ spin pairs, and thus changes in $TD - {}^{1}HNMR$ amplitude can help determine changes in the abundance of ${}^{1}H^{1}H$ para couplings. We found that in $H_{2}^{17}O$ the ${}^{1}H^{1}H$ para couplings are lower than in $H_{2}^{16}O$. The likeliest explanation for this result is the ortho coupling of ${}^{1}H^{1}H$ spin pairs or uncoupling caused by the dynamics of the ${}^{17}O$ quadrupole. This can be studied by comparing $H_{2}^{17}O$, $H_{2}^{16}O$, $H_{2}^{18}O$, and the variation of $TD - {}^{1}HNMR$ signal amplitude with temperature. A drop in ${}^{1}H^{1}H$ para couplings is also predicted in ${}^{14}NH_{2}$, different from $H_{2}^{16}O$.

Hypothesis 2. The effect of near nuclear spins and m on the organization of ${}^{14}NH_2$ spinomers. ${}^{14}NH_2$ spinomers are more sensitive to organization by neigh B_o ring magnetic moments (e.g. m- ${}^{14}NH_2$) and nuclear spins (e.g. ${}^{13}C-{}^{14}NH_2$) because of large quadrupole moments.

Also, due to $D\mu \downarrow \neq L\mu \uparrow$ from AAs dissimilar ${}^{1}H{}^{1}H$ nuclear spin coupling abundance may be seen between L- and $D - *C - {}^{14}NH_2$. Decrease in the $TD - {}^{1}HNMR$ signal amplitude (i.e. additional ${}^{1}H{}^{1}H$ para couplings) is predicted when nuclear spins or μ are adjacent to ${}^{14}NH_2$ spinomers. $D\mu \downarrow \text{vs } L\mu \uparrow$ will also produce L vs. D asymmetry in the orientation of nuclear spins of ${}^{14}NH_2$ and in the electromagnetic organization of ${}^{14}NH_2$ relative to the molecule. These interactions involve the effect of $D\mu \downarrow$ and $L\mu \uparrow (\mu \sim 10^{-1} - 10^{-2}\mu_B)$ on the spin of ${}^{14}N$ (I = 1; and $\mu_{(1^4N)} \sim 10^{-3}\mu_B$) and on the quadrupole of ${}^{14}N$ (nuclear quadrupole moment Q = 20.4mbarn). The nuclear spin of ${}^{14}N$ spin responds to the direction and magnitude of μ (energy of interaction of $2.4 \cdot 10^{-33}J$ or $0.65 \cdot 10^{-12}kT$ at 300K at 0.13nm distance), while nuclear quadrupoles (such as ${}^{14}N$) interact with the electric field gradient associated with μ . The sources of this asymmetry are the opposite orientation of $D\mu \downarrow$ vs $L\mu \uparrow$, and the mirror asymmetric direction of μ relative to the plane of NH_2 . With regard to the effect of adjacent nuclear spins and m on ${}^{1}H{}^{1}H$ spin couplings; the $TD - {}^{1}HNMR$ comparisons should reveal differences in signal amplitude in Gly relative to $H_2^{16}O$. We do not seek measuring electromagnetic effects of μ on ${}^{14}NH_2$.

2 MODEL

In earlier paper ([4]), The probability of formation of a specific spinomer: spinomer pair is proportional to:

$$p[A_i W_j] \sim \frac{(E_H)_{A_i W_j}}{kT} \cdot [A_i][W_j].$$

$$\tag{1}$$

where: $[A_iW_j]$ = the concentration of the A_iW_j spinomer:spinomer pair; i = ortho or para spinomers of the primary amine; j = ortho or para spinomers of water; $[A_i]$ = the concentration of the A_i spinomer; $[W_j]$ = the concentration of the W_j spinomer; $(E_H)_{A_iW_j}$ = the energy of interaction during the hydration of A_i with W_j . k = Boltzmann constant; T = temperature. Both the exchange kinetics and the equilibrium of spinomer:spinomer interactions are controlled by E_H/kT . Yet, if diffusion effects are ignored the ratio between the abundance of any two spinomer:spinomer pairs is kT-independent.

For example:

$$\frac{p[A_o W_o]}{p[A_p W_p]} = \frac{(E_H)_{A_o W_o}}{(E_H)_{A_p W_p}} \cdot \frac{[A_o][Wo]}{[A_p][W_p]}$$
(2)

The energy of interaction between two spinomers during hydration (E_H) includes a very small magnetic component (E_M) which is due to the direct interaction of magnetic moments.

$$E_H = E_X + E_M \tag{3}$$

Because (E_X) is the same for all A_iW_j spinomer pairs and E_M = the energy of the magnetic interaction between two spinomers; E_X = the part of the energy of interaction between two spinomers that is not due to direct magnetic interaction between nuclear spins. If $E_M < E_X$ then $E_X \simeq E_H = 750$ J/mol (~ $1.25 \cdot 10^{-21}J$ for each spinomer:spinomer pair). In a solution containing the spinomers A_0 ; A_p ; W_0 and W_p the four populations of different spinomer: spinomer pairs are represented by the relative abundance terms, the general formula for solutions with two N-amino isotopomers and three O-water isotopomers and after normalizing to 1 is:

$$p[A_i W_{j,k}] = \frac{\left[(E_X)_{A_i W_{j,k}} + (E_M)_{A_i W_{j,k}} \right] \cdot p[A_i] p[W_{j,k}]}{\sum_{i=o,pj=o,pk=16} \sum_{k=1}^{18} \left[\left[(E_X)_{A_i W_{j,k}} + (E_M)_{A_i W_{j,k}} \right] \cdot p[A_i] p[W_{j,k}] \right]}$$
(4)

where: i, j = o, p for ortho and para respectively; and k = the different oxygen isotopes. The calculation above did not account for the fact that in the hydration sphere of primary amines more than one water molecules are present and only very few are directly affected by E_M . Henceforth, Eq. 4 will lead to an overestimate of the $\Delta^{17}O$. The total population of water molecules hydrating the primary amines is:

$$\left(\left(\left[Ao\right] + \left[Ap\right]\right) \cdot V \cdot n = \left[A\right] \cdot V \cdot n$$

$$\tag{5}$$

where: V = volume; n = the average number of water molecules in the hydration sphere of A. This overall population is composed of:

$$[A] \cdot V \cdot n = [A] \cdot V \cdot (n-1) + [A] \cdot V$$

where: $[A] \cdot V \cdot (n-1)$ is the population of water molecules from the hydration sphere of A not engaged in the magnetic interaction analyzed here. $[A] \cdot V =$ the population of molecules from the hydration sphere of A engaged in the magnetic spinomer:spinomer interaction analyzed here.

Next we calculate E_M for different spinomer:spinomer pairs and the effect of the external B_o on each $(E_M)_{A_i W_{i,k}}$.

The energy of magnetic interaction between two spinomers is derived from:

$$E = \frac{\mu_0}{4\pi} \left[\frac{\overrightarrow{\mu_1} \overrightarrow{\mu_2}}{r^3} - 3 \frac{(\overrightarrow{\mu_1} \overrightarrow{r}) (\overrightarrow{\mu_2} \overrightarrow{r})}{r^5} \right]$$
(6)

In this case the magnetic moment of the spinomers are derived from the magnetic moments (μ) of the individual atoms: $\mu = 2.7928 \ \mu_N$ for ¹*H*; $\mu = 0.4037 \ \mu_N$ for ¹⁴*N*; $\mu = 1.8937 \ \mu_N$ for ¹⁷*O* [9].

External B will organize the direction of magnetization of spins and spinomers according to the well known Langevin theory of classical paramagnetism (Levitt, 2008):

$$E_B = -\overrightarrow{M} \cdot \overrightarrow{H} = MH\cos(\theta) \tag{7}$$

where: E_B = energy of interaction between a spin isomer and the external B; μ = magnetic moment vector of the spin isomer; B = magnetic field vector. θ = angle between the direction of μ moment and the magnetic field's direction. The organization of magnetic moments in space changes the orientation of μ . The degree of orientation is equivalent with the thermal average of $\cos(\theta)$, which is a Langevin function of $\mu B/kT$:

$$\langle \cos(\theta) \rangle = L\left(\frac{\mu B}{kT}\right) = \coth\left(\frac{\mu B}{kT}\right) - \left(\frac{\mu B}{kT}\right)^{-1}$$
(8)

This relation shows dependence of energy of interaction on the relative orientation of individual spinomers. In the absence of any order in the spinomers population the total energy of spinomers population is very low because of random orientation of spinomers.

When sistems of spins is perfectly organized by external magnetic field, we can calculate, for examples, the E_M for all different spinomer pairs in a primary amine solution in Table 1.

Also we can calculate energy of interaction between spinomers and external magnetic field. For example, in presence of external B, relative to spinomer $oH_2^{16}O$, we obtain $1.41 \cdot 10^{-27}J$. In absence of external B, the magnetic field of $oH_2^{16}O$ at distance of $1\mathring{A}$ is about $2.81 \cdot 10^{-3}T$, and we can conclude that interaction spinomer-spinomer is at lest 10^{-2} smaller than in strong magnetic field.

Spinomer	$oH_{2}^{16}O$	$pH_{2}^{16}O$	$oH_{2}^{17}O$	$pH_{2}^{17}O$	$oH_{2}^{18}O$	$pH_{2}^{18}O$
$o^{14}NH_2$	$8.53 \cdot 10^{-29}$	0	$1.14 \cdot 10^{-28}$	$2.89 \cdot 10^{-29}$	$8.53 \cdot 10^{-29}$	0
$p^{14}NH_2$	$5.75 \cdot 10^{-30}$	0	$7.70 \cdot 10^{-30}$	$1.95 \cdot 10^{-30}$	$5.75 \cdot 10^{-30}$	0

Table 1: The energy of magnetic interaction between pairs of ${}^{1}H^{1}HX$ -type spinomers (E_{M}) at a distance of $1\mathring{A}$ (in Joules per pair).

At B = 0.46T the E_B value is ~ 100 times larger than the direct magnetic interaction between individual nuclear spins with B = 0. Still, even at 0.46T, E_B is petite, only about $10^{-5} kT$ for ortho- $H_2^{17}O$, and $\Delta E_B = (E_{H_2^{17}O/B_o} - E_{H_2^{16}O/B_o}) = 2.87 \cdot 10^{-29} J$.

Next we present a way for calculating population of spins in solutions with primary amine groups containing ¹⁴N. In this model we used: $1mM - {}^{14}NH_2$ ($OPR_{N14} = 3.445$) ([5];[6];[7]) in 55.54M water composed of 99.7525 % $H_2^{16}O$ (OPR16 = 3), 0.0375 % $H_2^{17}O$ ($OPR_{O17} = 4.58$) and 0.21 % $H_2^{18}O$ ($OPR_{O18} = 3$) ([10] [8], [3]). The energy of the amine hydration bond $E_H \sim 750 J/mol$ [16] we can use this values as an estimate average for E_X .

After calculating the abundance of different spinomer:spinomer pairs we derive the abundance of the different water isotopomers in the hydration sphere of ${}^{14}NH_2$. The mass independent isotopic fractionation of oxygen in this population is:

$$\Delta^{17}O = 10^6 \left\{ \left[1 + \left(\frac{\delta^{17}O}{10^3}\right) \right] - \left[1 + \left(\frac{\delta^{18}O}{10^3}\right) \right]^{5/2} \right\}$$

[13], [11], [12], where: $\Delta^{17}O$ is expressed in per meg units and,

$$\delta^{17}O = \left[\left(\frac{{}^{17}O}{{}^{16}O} \right)_{spl} / \left(\frac{{}^{17}O}{{}^{16}O} \right)_{std} \right] \cdot 1000,$$

in $\%_0$ units, spl = sample; and std = standard (abundance of different O-isotopomers in the source bulk water) [18].

After calculus, we obtain $\Delta^{17}O \sim 0.63 \%$ in magnetic field of 0.46*T*, relative to $\Delta^{17}O \sim 6.8 \cdot 10^{-5} \%$ at B = 0.5 Gauss (~ the *B* at earth's surface).

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