CHIRALITY OF ELECTRONS FROM BETA-DECAY AND THE LEFT-HANDED ASYMMETRY OF PROTEINS

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Abstract. A simplified mathematical model of the origin of the left-handed asymmetry of proteins in living matter is presented. The model is based on the hypothesis of Vester and Ulbricht that the chirality of (left-handed) electrons from naturally beta-active elements, e.g., ^{14}C, ^{40}K, etc., was the specific source of the asymmetry; it requires for its application data on the interaction of electrons having non-zero chirality with racemic mixtures of amino acids. This interaction is here treated theoretically in an order-of-magnitude calculation. Our analysis yields a very approximate value of the induced steady-state asymmetry in the amino acids at the beginning of protein synthesis and indicates that this asymmetry, though small, may have been suffcient to account for the dominant left-handedness of proteins now observed.

1. The Hypothesis

The left-handed (laevo-) asymmetry of the polymeric molecules that form the basis of living matter, i.e. proteins, is most obviously manifested in their optical activity. The origin of the asymmetry has been the subject of serious enquiry since the beginning of this century. One widely held supposition is that the present asymmetry is due to a chance fluctuation in the original racemic mixture of the simpler molecules – amino acids – from which the more complicated proteins were synthesized. On the other hand, several specific mechanisms have also been suggested as possible sources of a small asymmetry in the prebiotic era [1]. In either alternative, it is assumed that an initial small asymmetry in the amino acids was subsequently greatly amplified by protein synthesis.

As first proposed by Vester and Ulbricht [2], a possible source of the asymmetry induced in the original racemic mixture of amino acids was the action of beta-rays from radioactive elements. This is an especially attractive suggestion for two reasons: (i) almost all known beta-active elements found in nature are electron and not positron emitters because of considerations of nuclear energetics, and (ii) an electron from a beta-emitter is polarized with a negative (left-handed) helicity (chirality) equal numerically to the ratio of the electron velocity to the velocity of light. Unit negative helicity indicates unit probability for antiparallel alignment of the electron spin relative to its momentum, while zero helicity corresponds to equal probability for antiparallel and parallel alignment.

2. Mathematical Model

In this paper we examine further the Vester-Ulbricht hypothesis; specifically, we consider, in part for simplicity, the suggestion of Noyes *et al.* [3] that the radioactive

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element in question was ^{14}C, although other elements, e.g., ^{40}K and ^{90}Sr, would also be expected to contribute, possibly even more importantly than ^{14}C. We assume that the specific mechanism for the production of the asymmetry is the difference between the probability ε_L for the decomposition of an (laevo) L-molecule by a ^{14}C electron and the probability ε_D for the decomposition of a (dextro) D-molecule by a ^{14}C electron, where ε_L and ε_D are reckoned per incident ^{14}C electron; a brief discussion of the physical basis of this mechanism is given below. We assume further that the ^{14}C, produced by cosmic ray neutrons in n–p reactions on ^{14}N, was present in the gases (mostly NH_3, N_2, CH_4, H_2O, and H_2) that constituted the early atmosphere of the Earth, and that the ^{14}C electrons fell upon racemic mixtures of target amino acid molecules which may have been condensed as films on various solid or liquid surfaces or possibly dissolved in water or dispersed in the atmosphere. Our results are to a large extent independent of the chemical and physical forms in which the target molecules existed; hence the assumption that the target molecules were amino acids is not essential.

The rate equations for the numbers of laevo- and dextro-molecules n_L and n_D present at any time t after their creation are then

$$\frac{dn_L}{dt} = \alpha + (\beta + \gamma S)\, n_D - (\beta + \gamma S + \varepsilon_L S + \delta)\, n_L \tag{1}$$

$$\frac{dn_D}{dt} = \alpha + (\beta + \gamma S)\, n_L - (\beta + \gamma S + \varepsilon_D S + \delta)\, n_D. \tag{2}$$

These equations are rather general in that they take into account the production and decomposition of molecules by the following mechanisms: (i) a time averaged (and hence constant) total rate of synthesis α of a racemic mixture of the molecules by, e.g., the passage of lightning through the atmospheric gases; (ii) a rate of racemization (or conversion) β of laevo to dextro and dextro to laevo which, when multiplied by the number of opposite-handed molecules present at any time, yields the total conversion rate induced by chemical, e.g., photochemical, reactions; (iii) a rate of racemization γS induced by the ^{14}C source of strength S; (iv) a rate of decomposition δ of both laevo- and dextro-molecules which, when multiplied by the number of same-handed molecules present at any instant, yields the total decomposition rate due to thermal dissociation, solar radiation, etc.; and finally, (v) the handedness-dependent rates of decomposition by the ^{14}C source, $\varepsilon_L S$ and $\varepsilon_D S$, described above, with $\varepsilon_D > \varepsilon_L$ since (with very few exceptions) only laevo forms are found now.

3. Steady State Solution

We have little definite knowledge of the magnitudes of α, β, γ, δ, ε_L and ε_D in Equations (1) and (2). The steady state ($dn_{L,D}/dt = 0$) solutions of the coupled equations are useful despite this limitation. These solutions are

$$n_L = \frac{\alpha\,(\varepsilon_D S + 2\gamma S + 2\beta + \delta)}{(\gamma S + \varepsilon_D S + \beta + \delta)\,(\gamma S + \varepsilon_L S + \beta + \delta) - (\beta + \gamma S)^2} \tag{3}$$

$$n_D = \frac{\alpha\,(\varepsilon_L S + 2\gamma S + 2\beta + \delta)}{(\gamma S + \varepsilon_D S + \beta + \delta)\,(\gamma S + \varepsilon_L S + \beta + \delta) - (\beta + \gamma S)^2} \tag{4}$$

and yield a steady state laevo-dextro asymmetry A, which is independent of α,

$$A = \frac{n_L - n_D}{n_L + n_D} = \frac{(\varepsilon_D - \varepsilon_L)S}{(\varepsilon_D + \varepsilon_L + 4\gamma)\,S + 2\,(2\beta + \delta)} \tag{5}$$

with limiting cases

$$A \approx \frac{(\varepsilon_D - \varepsilon_L)\,S}{2\,(2\beta + \delta)} \quad \text{when} \quad S \ll \frac{2\,(2\beta + \delta)}{\varepsilon_D + \varepsilon_L + 4\gamma} \tag{6}$$

and

$$A \approx \frac{\varepsilon_D - \varepsilon_L}{\varepsilon_D + \varepsilon_L + 4\gamma} \quad \text{when} \quad S \gg \frac{2\,(2\beta + \delta)}{\varepsilon_D + \varepsilon_L + 4\gamma}. \tag{7}$$

Equation (7) obtains when the rates of the processes (represented by β and δ) that are independent of the strength of the ^{14}C source are much smaller than the rates of the processes that are ^{14}C-induced. Otherwise, Equation (6) holds.

In general, the asymmetry A of Equation (5) will be different from zero if $\varepsilon_D \neq \varepsilon_L$, and A will achieve its maximum value when $\beta = \delta = \gamma = 0$. Further, it is likely that in the prebiotic era the value of $2\,(2\beta + \delta)/(\varepsilon_L + \varepsilon_D + 4\gamma)\,S$ was large (Equation (6)); indeed, we estimate this quantity as $> 10^3$ (see below where $\beta \lesssim \delta$, $3 \times 10^{-13}/\text{s} > \delta > 3 \times 10^{-17}/\text{s}$, $\varepsilon_L + \varepsilon_D \approx 1.0 \times 10^{-16}$, $\gamma \approx 1.0 \times 10^{-18}$, $S \approx 3 \times 10^{-4}$ electrons/s).

4. Time-Dependent Solution

We may also employ the time-dependent solution of Equations (1) and (2) together with the definition of the asymmetry A to cast further light on the Vester-Ulbricht hypothesis. To do this we consider the results that might be obtained in an experiment where (longitudinally) polarized electrons from an accelerator fall upon a racemic mixture of target amino acid molecules [4]. The time-dependent solution of Equations (1) and (2) with initial conditions appropriate to such an experiment, viz: $n_L(0) = n_D(0)$, and with $\alpha = 0$, $\gamma S \gg \beta$, $\varepsilon_L S \approx \varepsilon_D S \gg \delta$, yields

$$A(t) = \frac{n_L(t) - n_D(t)}{n_L(t) + n_D(t)} = -\frac{\chi_+\chi_-\,[1 - e^{-(\lambda_+ - \lambda_-)St}]}{\chi_+\,(2 + \chi_-) + \chi_-\,(2 + \chi_+)\,e^{-(\lambda_+ - \lambda_-)St}}, \tag{8}$$

where

$$\chi_{\pm} \equiv -1 \pm \frac{1}{2\gamma}[(\varepsilon_D - \varepsilon_L) - \sqrt{(\varepsilon_D - \varepsilon_L)^2 + 4\gamma^2}],$$
$$\lambda_{\pm} \equiv \frac{1}{2}[(2\gamma + \varepsilon_D + \varepsilon_L) \pm \sqrt{(\varepsilon_D - \varepsilon_L)^2 + 4\gamma^2}]. \tag{9}$$

Assuming $4\gamma^2 \gg (\varepsilon_D - \varepsilon_L)^2$, we obtain

$$A(t) \simeq \frac{(\varepsilon_D - \varepsilon_L)}{4\gamma}(1 - e^{-2\gamma St}), \tag{10}$$

which, for $2\gamma St \ll 1$ (see [5]), becomes

$$A(t) \simeq \frac{(\varepsilon_D - \varepsilon_L)}{2} St. \tag{11}$$

This last equation shows that the asymmetry obtained in an accelerator experiment, under the conditions most likely to hold in such an experiment, i.e.,

$$\frac{\beta}{\gamma}, \frac{\beta + \delta}{\varepsilon_L}, \frac{\beta + \delta}{\varepsilon_D} \ll S \ll \frac{1}{2\gamma t}$$

(see the numerical values at the end of the previous section and the end of the next section), depends, to a good approximation, only on $\varepsilon_D - \varepsilon_L$.

5. Central Result

We now recall that, for the exposure of a racemic amino acid mixture to the electrons of ^{14}C in the early atmosphere, the weak source, steady state limit of Equation (6) is valid, viz

$$A(^{14}C) = \frac{(\varepsilon_D - \varepsilon_L) S(^{14}C)}{2(2\beta + \delta)}, \tag{12}$$

where $A(^{14}C)$ is the asymmetry due to, and $S(^{14}C)$ is the source strength of, the ^{14}C. Comparison of Equation (12) with Equation (11) yields

$$A(^{14}C) = A(t) \frac{S(^{14}C)}{S} \frac{T}{t}, \tag{13}$$

where we have written $T = (2\beta + \delta)^{-1}$ since, on the basis of Equations (1) and (2), $(2\beta + \delta)^{-1}$ is approximately equal to the time to reach steady state values of n_L and n_D [6]. Equation (13) is the central result of our analysis; it gives the asymmetry at the beginning of protein synthesis in terms of the asymmetry obtained in an accelerator

experiment multiplied by the ratios of prebiotic to accelerator source strengths and exposure times.

To evaluate S (^{14}C), we avoid the question of the constancy of the relative abundance of ^{14}C and take $^{14}C/^{12}C \approx 10^{-12}$, as it is at present. We assume that the electrons from the $^{14}CH_4$ in the atmosphere acted on the target amino acid molecules in a film of small area. If the $^{14}CH_4$ gas were at normal pressure and temperature, the range of the ^{14}C electrons would be roughly 1 cm and there would be 5×10^{19} molecules in a hemispherical volume of radius 1 cm surrounding each π (1 cm)^2 of the film. Thus, with a half life of ^{14}C of 5.7×10^3 yr, we obtain S (^{14}C) $\approx 3 \times 10^{-4}$ electrons/s, while in accelerator experiments performed so far (4) one had $S = S_a \simeq 1.5 \times 10^{11}$ electrons/s and $t = t_a \simeq 1.0 \times 10^5$ s. These numbers, together with Equation (13), give

$$A\,(^{14}\mathrm{C}) \approx A\,(t_a)\,(2 \times 10^{-20}\ \mathrm{s}^{-1})\,T. \tag{14}$$

It remains then only to insert values of T and A (t_a).

6. Prebiotic Exposure Time

There is, to our knowledge, no directly determined value of T, but T was at most of the order of magnitude of the time interval between establishment of the early atmosphere of the Earth and the beginning of protein synthesis. It is therefore very unlikely that T exceeded $\approx 10^9$ yr because the earliest appearance of life so far detected is in rocks that are about 3.3×10^9 yr old [7], and the age of the Earth is about 4.6×10^9 yr. The lower limit on T is harder to specify, but a value $\approx 10^5$ yr is not inconsistent with available evidence on the lifetimes of amino acids ($\approx \delta^{-1} \approx T$) derived from fossilized material and ancient human artefacts [8]. Racemization and decay rates of amino acids determined from such studies depend sensitively, however, on the origin and history of the samples employed. For example, the dependence on temperature is exponential, and in some cases bacterial activity must have extensively modified the composition of the sample. Nevertheless, lifetimes of at least 10^5 yr appear not unreasonable for amino acids hidden in fissures of the Earth or otherwise isolated and protected from sunlight and high temperatures. With these limits for T, Equation (14) yields

$$6 \times 10^{-8}\,A\,(t_a) \lesssim A\,(^{14}\mathrm{C}) \lesssim 6 \times 10^{-4}\,A\,(t_a) \tag{15}$$

for the bounds on the *time-independent*, average laevo-dextro asymmetry which would have been present when protein synthesis began.

7. Laboratory Produced Asymmetry

As regards the determination of the value of A (t_a), two experiments have been carried out using polarized electrons from an accelerator incident on a thin racemized amino

acid (DL-leucine) target [4]. In the first of these (by Bonner *et al.*), the electrons had kinetic energy of 120 keV and average helicity $\simeq -0.2$; the measured value of $A\,(t_a)$ was $(9.0 \pm 0.9) \times 10^{-3}$. Furthermore, $A\,(t_a)$ was observed to remain at about the same magnitude but to change sign when the helicity of the electrons was reversed. The second, more recent experiment (by Hodge *et al.*), sought to confirm the earlier result; it used electrons of the same kinetic energy but of average helicity $\simeq -0.4$ incident on a similar target; target thickness, exposure time, and fractional decomposition of the target by the electron beam were also similar in the two experiments. The second experiment observed only an upper limit on $A\,(t_a)$, 0.6×10^{-3} with 90% confidence when normalized to the same electron helicity as in the first experiment, and no change of sign of $A\,(t_a)$ when the helicity of the incident electrons was reversed.

We remark that on theoretical grounds there is a wide, but not enormous, latitude in the value of $A\,(t_a)$ to be expected in such an experiment. It has been correctly argued that the dominant handedness-dependent interaction between an incident electron and a target electron in, say, DL-leucine is unlikely to be due to the exchange of polarized bremsstrahling radiation between them [9], because the fraction of the bremsstrahlung radiation spectrum emitted by the incident electron with appreciable circular polarization is very small. The most likely interactions that might account for a significant value of $A\,(t_a)$ are (i) that between the spin of the incident polarized electron and the orbital angular momenta of the bound electrons in the target chiral (L or D) molecule, viz., a spin-other orbit interaction, and (ii) that between the spin of the incident electron and the spins of the target electrons which are partly aligned by the spin-same orbit interaction within the target chiral molecule. These interactions have been well studied in experiments on atomic and molecular spectra, but not in scattering experiments; they are difficult to calculate precisely because their effective values depend sensitively on the details of the orbital configuration of the electrons in the target molecule.

We have, however, made an order-of-magnitude estimate of $A\,(t_a)$ from a comparison of the approximate relative strengths of the spin-other orbit i.e., magnetostatic, interaction with the Coulomb i.e., electrostatic, interaction between the incident and target electrons – inclusion of the spin-spin interaction between these electrons, as mentioned in (ii) above, is not likely to modify the result in any essential way. To make the estimate, we rewrite Equation (11), on the basis of Equations (1) and (2), and [5], as

$$A\,(t_a) = \left(\frac{\varepsilon_D - \varepsilon_L}{\varepsilon_D + \varepsilon_L}\right)\left[\frac{1}{2}\,(\varepsilon_D + \varepsilon_L)\,S_a t_a\right] = 0.7\left(\frac{\varepsilon_D - \varepsilon_L}{\varepsilon_D + \varepsilon_L}\right)$$

$$= 0.7\left(\frac{\sigma_D - \sigma_L}{\sigma_D + \sigma_L}\right), \tag{16}$$

where σ_D (σ_L) is the cross-section for decomposition of the target D (L) molecule by the incident polarized electron from ^{14}C. Further

$$\sigma_D \mp \sigma_L = |\,\Psi_e + \Psi_m|^2 \mp |\,\Psi_e - \Psi_m|^2, \tag{17}$$

where Ψ_e and Ψ_m are the amplitudes for molecular decomposition by the electrostatic (e) and magnetostatic (m) interactions between the incident and target electrons. Thus

$$A\,(t_a) \cong 1.4\,|\,\Psi_m|/|\,\Psi_e| \tag{18}$$

with the ratio $|\,\Psi_m|/|\,\Psi_e|$ given roughly by

$$|\,\Psi_m|/|\,\Psi_e| \approx (e^2/\hbar c)^2 = (1/137)^2. \tag{19}$$

Equation (19) follows from the form of the magnetostatic and electrostatic interactions [10], i.e., from

$$\left(\frac{e\hbar}{mc}\right)\left(\frac{e\hbar}{2mc}\right)\left\{\frac{8\pi}{3}\,\mathbf{s}\cdot\mathbf{l}\,\delta\,(\mathbf{r}) + \frac{1}{r^3}\,(3\,\mathbf{s}\cdot\hat{r}\,\mathbf{l}\cdot\hat{r} - \mathbf{s}\cdot\mathbf{l})\right\} \tag{20a}$$

and

$$e^2/r \tag{20b}$$

and from that fact that, with $\langle\ldots\rangle$ indicating appropriate averages over all spin and orbital angular momentum orientations and incident electron – target electron distances

$$\langle\delta\,(\mathbf{r})\rangle\Big/\left\langle\frac{1}{r}\right\rangle \approx \left\langle\frac{1}{r^3}\right\rangle\Big/\left\langle\frac{1}{r}\right\rangle \approx \left[\left(\frac{\hbar c}{e^2}\right)\left(\frac{\hbar}{mc}\right)\right]^{-2} \tag{21a}$$

and

$$\langle\mathbf{s}\cdot\mathbf{l}\rangle \approx 1, \tag{21b}$$

where $(\hbar c/e^2)\,(\hbar/mc)$ is the electron Bohr radius, and where the numerical value of the helicity of the incident electron is always less than 1 while the numerical value of $\langle|\mathbf{l}|\rangle$ may be appreciably greater than 1. Equations (18) and (19) yield $A\,(t_a) \approx 10^{-4}$ but in view of the approximate nature of our estimate it is more realistic to take

$$10^{-5} \lesssim A\,(t_a) \lesssim 10^{-3}. \tag{22}$$

The upper bound on $A\,(t_a)$ in Equation (22) is about at the limit of present measurement sensitivity [4]. To detect smaller values of $A\,(t_a)$, which according to our estimate are more likely, will require a significant improvement in the technique for determining very small left-right asymmetries induced in racemic mixtures by bombardment with polarized electrons.

It is worth adding that oversimplified but physically reasonable wavefunctions for the bound electrons of the target chiral molecule yield the correct sign correlation of $A\,(t_a)$ with the helicity of the incident electron i.e., $\sigma_D > \sigma_L$ for incident electrons with negative helicity; we have however not demonstrated this result for any specific chiral molecule. Furthermore, it should be recalled that the effective chirality of the bound

electrons of the target chiral molecule is independent of the spatial orientation of the molecule so that an incident polarized electron interacts with target electrons of a given effective chirality in a manner that does not depend on reflection of the symmetry axes of the molecule with respect to an arbitrary axis in space. Hence, no cancellation of the $\sigma_D > \sigma_L$ effect should occur because of the random alignment of the target chiral molecules; this is similar to the case of circularly polarized light incident on the randomly oriented chiral molecules of an optically active solution.

8. Suggested Experiments

It appears therefore that, while there is some theoretical support for the hypothesis of Vester and Ulbricht, unequivocal experimental support is lacking. Thus it is necessary that additional experiments with accelerator electrons be carried out to determine the magnitude of the induced asymmetry $A(t_a)$, and, if this magnitude is measurable with present or extended techniques, to delineate the nature of the specific interaction that gives rise to it. In this connection we wish to suggest an experiment that would simulate the conditions hypothesized in our calculation, and thereby provide an independent determination of the magnitude of the asymmetry, subject to different possible systematic errors than in an accelerator experiment. Consider a racemic target (which might be an amino acid) laid down as a thin film on a thin substrate over which is placed an atmosphere of methane enriched in ^{14}C. Present isotope enrichment technique would allow a volume of a few cm^3 to be filled at normal temperature and pressure with methane containing $>98\%$ ^{14}C. This would make up a factor of roughly 10^{12} relative to the source strength in the prebiotic era, i.e., yield an $S(^{14}C) \approx (3 \times 10^{-4})(10^{12})\ s^{-1}$, and according to Equation (11) should lead, in an exposure of one year, to an asymmetry $A(^{14}C) \approx 4.5 \times 10^{15}(\varepsilon_D - \varepsilon_L)$. From the $A(t_a)$ of Bonner *et al.* [4], $\varepsilon_D - \varepsilon_L \simeq 2 \times 10^{-18}$, after correction for different average helicities, giving $A(^{14}C) \approx 9 \times 10^{-3}$; the $A(t_a)$ of Hodge *et al.* [4] or our estimate of $A(t_a)$ in Equation (22) would, of course, predict a value of $A(^{14}C)$ at least an order of magnitude smaller. We suggest using as the initial racemic target stereoisomers that have the asymmetric C atom surrounded by four groups which are as different from one another as possible, since such configurations are likely to maximize $(\varepsilon_D - \varepsilon_L)$.

It would be more difficult to carry out the corresponding experiment using an emitter of positrons (with positive helicity) as the source of radioactivity because of the generally short lifetimes of positron emitters. Possible sources for such an experiment are, however, ^{22}Na and ^{26}Al. These might require greater initial strength and a different form than the ^{14}C source, and involve also molecular decomposition by annihilation gamma rays, but the additional test of the hypothesis provided by an experiment with positrons (where $A(t)$ is expected to be negative) is attractive despite its difficulty.

9. Efficacy of Prebiotic Asymmetry

It should furthermore be emphasized that the efficacy of a given, small asymmetry A

(^{14}C) in the prebiotic era is not immediately apparent. It can be argued, as one does in population statistics [11], that two configurations such as the L- and D-amino acids under discussion here, with relative 'adaptive values' of $(1 + A)$:1 for eventual polymeric synthesis into L- and D-proteins, will be 'neutral' if and only if

$$|NA| \ll 1. \tag{23}$$

Here N is a number which depends on two quantities: (i) a number specifying the sequence of chemical steps involved in protein synthesis in a single amino acid film, and (ii) a number characterizing the population of favorably disposed amino acid films. Neutrality implies that the 'differential adaptivity', A, does not determine the relative abundances of the synthesized L- and D-proteins; rather, these would change in a random way governed by comparatively high frequency statistical fluctuations. For $|NA| \gtrsim 1$, however, a difference in the populations of the L- and D-proteins would be determined by the selective influence of A. In this case the effect of A might be superimposed on a (zero time-averaged) fluctuating asymmetry. However, even when the absolute value of the amplitude of the fluctuating asymmetry exceeds A, the ultimate effect of A is not negated.

It is clear that N was a very large number, because (a) the two quantities on which it depended entered multiplicatively, as can be shown directly [12], and (b) the number of chemical steps involved in protein synthesis in a single favorably disposed amino acid film was at least as large as the ratio of the mass of a typical protein to the mass of a typical amino acid. It is perhaps possible to make a more quantitative estimate of the number of chemical steps by detailed study of the chemical kinetics that led to protein evolution [13]. However, even a value as small as 10^3 steps, i.e., the rough ratio of protein mass to amino acid mass, would have contributed to a very large value of N, because the amount of organic material accumulated during the prebiotic formation of amino acids has been estimated to have been very large [14], and therefore the number of favorably disposed amino acid sites probably also was very large.

If we speculate, not altogether unjustifiably, that the prebiotic steady state asymmetry A (^{14}C) had an order-of-magnitude value of 10^{-8} [see Equations (15) and (22)], and use the fact that N was given by the product of the number of chemical steps per site times the number of favorable sites, we see that the number-of-sites factor need not have been unreasonably large (of order $10^8/10^3 = 10^5$) to satisfy the condition $|NA| \approx 1$. Hence, despite our lack of detailed knowledge of either N or $A(^{14}\text{C})$, rough conjectures of possible values of these quantities suggest that their product may indeed have been of the order of unity or greater, and that, as a consequence, a very small induced steady state asymmetry A (^{14}C) in the prebiotic era may have been responsible for the present left-handed asymmetry of proteins. Such a small value of A (^{14}C) would, according to our analysis, correspond to a value of an asymmetry induced in laboratory experiments of $A(t_a) \approx 10^{-4}$, which is not verifiable in present experiments without a significant improvement in measurement sensitivity.

10. Summary

The contents of this paper may be summarized as follows. We have considered a simplified mathematical model of the origin of the left-handed asymmetry of molecular subunits of proteins, based on an extension of a hypothesis of Vester and Ulbricht, which assumes that the non-zero chirality of (left-handed) electrons from beta-active elements, e.g., ^{14}C, was the specific source of the asymmetry. The essential result of the model is an equation relating the steady-state asymmetry A (^{14}C) in the prebiotic era to the time-dependent asymmetry A (t) that may possibly be observed in laboratory experiments. As yet, there is not experimental agreement on even the order of magnitude of A (t). Nor is there clear experimental identification of a specific interaction between the incident electron and the target molecule that might give rise to A (t). In addition, the prebiotic exposure time T, a necessary parameter in our model, is known only within wide bounds. Nevertheless, the model provides a basis on which to order and interpret various data and conjectures concerning the Vester-Ulbricht hypothesis. The model and the lack of experimental agreement also motivated an order-of-magnitude calculation of the left-right asymmetry to be expected from the magnetic interaction between an incident polarized electron and the bound electrons of a target chiral molecule in present laboratory experiments. Further, new, and potentially useful, laboratory experiments are suggested by the model.

The rough estimates made here indicate that the magnitude of the steady-state left-right asymmetry A (^{14}C) that would have been induced in the prebiotic era by polarized electrons from beta-active elements may have been sufficient to account for the observed left-handedness of the proteins in living matter. This conclusion may be valid despite the relatively small value of A (^{14}C) estimated here since the condition for the asymmetry to have been effective involves a large amplification factor associated with the synthesis of proteins from amino acids. The relatively small value of A (^{14}C) would in turn explain the failure to observe a significant induced asymmetry A (t_a) in present laboratory experiments.

Finally, we wish to emphasize the general importance of verifying or rejecting the Vester-Ulbricht hypothesis, if it is at all possible to do so, because the left-handed electrons from natural beta-active emitters constitute the sole, intrinsically parity violating, i.e., left-right symmetry breaking, mechanism in nature that is known to us. It is, therefore, of significance to know with certainty whether or not the magnitude of the resultant effect produced by this mechanism would have been sufficient to explain the protein asymmetry that is such an important property of life on Earth [15].

Notes

[1] See, for example, W. A. Bonner in *Exobiology*, p. 170, edited by C. Ponnamperuma (North-Holland, Amsterdam), 1972; L. Keszthelyi, *Origins of Life* **8**, 299–340 (1977).

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[5] Note that:

$$\frac{n_L(t) + n_D(t)}{n_L(0) + n_D(0)} \approx e^{-1/2(\varepsilon_D + \varepsilon_L)St} = e^{-1/2\left(\frac{\varepsilon_D + \varepsilon_L}{2\gamma}\right)2\gamma St}$$

This ratio is determined by the decomposition of the target at the end of the exposures in the laboratory experiments. If the ratio is $\approx \frac{1}{2}$ (for $t = t_a$; $S = S_a$: note 4), and with $2\gamma \ll \frac{1}{2}(\varepsilon_D + \varepsilon_L)$, then $2\gamma S_a t_a \ll 1$. The assumption $2\gamma \ll \frac{1}{2}(\varepsilon_D + \varepsilon_L)$ is supported by the recent experiments of Bonner and Lemmon (*J. Mol. Evol.* **11**, 95 (1978); *Biog. Chem.* **7**, 175 (1978)) on the amounts of amino acid racemization induced by gamma rays which, when analyzed on the basis of Equations (1) and (2), yield $2\gamma/\frac{1}{2}(\varepsilon_D + \varepsilon_L) \approx 0.05$. We also note that with $e^{-1/2(\varepsilon_D + \varepsilon_L)S_a t_a} = \frac{1}{2}$ and $S_a t_a = 1.5 \times 10^{16}$ (note 4), $\varepsilon_D + \varepsilon_L = 1.0 \times 10^{-16}$.

[6] If, for example, $\delta \gg \beta + (\varepsilon_{L,D} + \gamma)S$, Equations (1) and (2) give $n_{L,D}(t) = (\alpha/\delta) + [n_{L,D}(0) - (\alpha/\delta)]e^{-\delta t}$.

[7] J. W. Schopf, *Biol. Rev.* **45**, 319–352 (1970); *Evol. Biol.* **7**, 1–43 (1974); *Endeavour* **122**, 51–58 (1975).

[8] The literature here is extensive. Some recent references are: G. Eglinton and M. Calvin, *Sci. Am.* **216**, 32–43 (1967); G. Eglinton and Sister M. T. J. Murphy (eds.), *Organic Geochemistry – Methods and Results* (Springer-Verlag, Berlin), 1970; F. M. Swain, *Non-Marine Organic Geochemistry*, (Cambridge Univ. Press. London), 1970; W. Ferdinand *et al.*, *Comp. Biochem. Physiol.* **44B**, 889–913 (1973); P. E. Hare, *MASCA Newsletter* **10**, No. 1, July 1974; K. Wehlte, *The Materials and Techniques of Painting*, p. 209ff, (Van Nostrand Reinhold Co., New York), 1975.

[9] L. Keszthelyi, *Nature* **264**, 197 (1976); W. A. Bonner, M. A. Van Dort, and M. B. Yearian, *Nature* **264**, 197–198 (1976).

[10] The symbols used have the following significance: r = distance between the incident and target electrons, δ = Dirac delta function, e and m = electron charge and mass, $2\pi\hbar$ = Planck's constant, c = speed of light, $\hbar\mathbf{s}$ and $\hbar\mathbf{l}$ are, respectively, the spin angular momentum of the incident ^{14}C electron and orbital angular momentum of the target bound electron while $(e/mc)(\hbar\mathbf{s})$ and $(e/2mc)(\hbar\mathbf{l})$ are the corresponding magnetic dipole moments.

[11] See, for example, T. Dobzhansky, F. J. Ayala, C. L. Stebbins, and J. W. Valentine, *Evolution*, p. 305ff. (W. H. Freeman, San Francisco), 1977.

[12] It can be shown directly that the number N which appears in Equation (23) is just the product of the number of chemical steps involved in protein synthesis at a typical amino acid site and the number of such sites. Let n_i be the number of chemical steps that occur in the evolution of a protein at site i. If, at each site, there exists a steady state L–R asymmetry A, then the corresponding total differential advantage when J sites are present is given by

$$\sum_{i=1}^{J}[(1 + A)^{n_i} - 1^{n_i}] \cong \sum_{i=1}^{J}(e^{n_i A} - 1^{n_i}) \cong AJ\left(\sum_{i=1}^{J} n_i/J\right) \equiv AJ <n>,$$

where $<n>$ is the number of chemical steps at a typical or average site and where we have made use of the approximation $n_i A \ll 1$. We thus see that the total differential advantage is indeed given by AN where $N = J<n>$. Our derivation is also seen to account for the inequality in Equation (23) since, if $NA \ll 1$, the total differential advantage $\cong Je^{\langle n \rangle A} - J$, is, in turn $\cong e^{NA} - 1$ which is close to zero when $|NA| \ll 1$.

[13] W. Langenbeck and G. Triem, *Z. Physik Chem.* **A177**, 401 (1936); R. Böhm and G. Losse, *Zeitschr. Chem.* **7** (11), 409 (1967).

[14] L. E. Orgel, *The Origins of Life: Molecular and Natural Selection*, (Wiley, N.Y.), 1973.

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