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RESEARCH

Sequential Amplification of Amino Acid Enantiomeric Excess by Conglomerate and Racemic Compound: Plausible Prebiotic Route Towards Homochirality

A. Sharma[1]

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Abstract
Some amino acids can crystallize from aqueous solution both as conglomerates and racemic compounds: under high supersaturation following rapid evaporation, dissolved amino acids draining over porous sand-bars behave like conglomerates whereas in the resulting deeper pool of water, amino acid solution switches to the more common racemic-compound system. We show how the two forms might have sequentially combined under prebiotic conditions to form the basis of homochirality. The paper is a quantitative analysis of enantiomeric excess (EE) this dual behavior of amino acids is capable of producing in tandem: Initial amplification by preferential crystallization (PC) in conglomerate system (CS) followed by further amplification in the racemic compound system (RCS). Using aspartic acid as a model system, ternary phase diagram shows that a minimum supersaturation of 1.65 is required in the CS for the solution-EE to reach its maximum value of 50% at the RCS eutectic point. A relationship is derived for the dependence of this threshold supersaturation on the eutectic solubilities of CS and RCS. For given supersaturation in CS, a relation is also derived for minimum solution-EE that must be produced by PC before CS switches to RCS. Required PC-induced threshold solution-EE of 0.194, 0.070, 0.033 is calculated for supersaturation of 2, 5, 10 respectively in aspartic acid. Switching from CS to RCS further amplifies solution-EE, resulting in an overall growth of aspartic acid solution EE from near-zero in CS to around 50% in RCS.

Keywords Homochirality · Enantiomeric excess · Amino acids · Preferential crystallization · Conglomerates · Racemic compounds

Introduction

Homochirality of biological molecules remains a mystery (Blackmond 2011; Perez-Garcia and Amabilino 2007; Buhse et al. 2021; Sallembien et al. 2022). Thus, chiral proteinogenic amino acids are primarily left-handed (laevo-L) and nucleic acids are

✉ A. Sharma
anup.sharma@aamu.edu

[1] Department of Physics, Alabama A&M University, Huntsville, AL 35762, USA

primarily right-handed (dextro-D). There is consensus that homochirality was accomplished in two steps: production of a seed enantiomeric excess followed by amplification of this seed EE to full homochirality (Blackmond 2011; Breslow and Cheng 2009). It is believed that homochirality is a requirement for life although it has also been proposed that homochirality could be a consequence of life itself (Wu et al. 2012).

Several sources for creating the initial seed EE have been discussed in the literature, among them the possibility that seed EE of L-amino acids and D-sugars was transported to earth on meteorites from distant reaches of our galaxy. Indeed, a class of meteorites does show an excess of L-amino acids and D-sugars although for a large majority of meteorites, population of organic molecules is racemic (Elsila et al. 2016). Several other concerns have also been raised for the EE on meteorites, among them a possibility of contamination (Burton et al. 2014) with biomolecules from earth's biosphere and questions about the stability of organic molecules under high temperatures encountered as the meteorites travelled through earth's atmosphere (Glavin and Bada 2001). Concerns about racemization of amino acids over their lifetime on meteorites have also been raised (Cohen and Chyba 2000). Magneto-chiral effect was shown to produce EE among some molecules although its applicability for life-molecules remains to be demonstrated (Hattori et al. 2017). An EE of 10^{-18} by parity violating energy difference (PVED) has been calculated for amino acids (Bada 1995). Recently, we showed that although Archean earth's surface atmosphere was anoxic, there was enough oxygen in stratosphere that could have produced magnetic circular dichroism (MCD) in paramagnetic O_2 molecules (Sharma 2023). MCD in stratospheric O_2 resulted in relative differential circular polarization of 10^{-10} for UVC light in 200–250 nm region and an asymmetric photolysis of amino acid molecules produced in volcanic plumes, to give an EE of 10^{-12}. This EE is several orders of magnitude higher than PVED and, at the same time does not require the extra-terrestrial source for seed EE.

The most promising mechanism for amplification of seed EE to full homochirality is believed to involve preferential crystallization (PC) of a conglomerate enantiomer from solution (Elsner et al. 2005; Rougeot and Hein 2015), or one of the several variations of this mechanism like Viedma ripening (VR) (Viedma et al. 2008; Sogutoglu et al. 2015; Belletti et al. 2022). However, EE produced by PC is transient and it invariably goes to the equilibrium value of zero in both solution and solid form. VR does produce large EE in crystalline form but requires an essential mechanism of racemization in solution. No such racemization mechanism is known for amino acids that would be viable under prebiotic conditions. These restrictions of PC and the requirements of VR are absent in the conglomerate racemic compound system described here and has the potential for amplifying seed EE of some amino acids to large permanent EE in solution. Mechanism for generating large solution-EE (50–99%) at the eutectic point of racemic compound amino acids has also been discussed and demonstrated (Morowitz 1969; Klussmann et al. 2006a, b; Klussmann et al. 2006a, b; Breslow and Levine 2006) but it requires a small starting EE of around 1% or greater. No such requirement is there with the system discussed here, and seed solution-EE can be amplified sequentially from near-zero value in conglomerate to 50% or greater at the eutectic point of the racemic compound. Such prebiotic scenarios might be commonly around as is explained by a simple model of water with dissolved amino acids seeping over porous bed (CS) and collecting into a deeper pool (RCS). The requirements for such a sequentially-coupled system and possible end result of large permanent EE (~ 50%) in solution are explained with the help of ternary phase diagrams.

Theory

Most proteinogenic amino acids crystallize from solution as racemic compounds (Klussmann et al. 2006a, b) whereas chiral resolution by PC or VR requires crystallization as conglomerates (Rougeot and Hein 2015; Viedma et al. 2008). The mode of crystallization depends on thermodynamic as well as kinetic considerations and it has been proposed that compared to their normal RC behavior in bulk solutions, amino acids could crystallize differently for high degrees of supersaturation due to rapid evaporation in porous media (Viedma 2001). Indeed, two very common amino acids, aspartic and glutamic acids normally crystallize as racemic compounds, but results in crystallization as conglomerates under rapid evaporation of aqueous solutions and high supersaturation (Viedma 2001). Both, glutamic and aspartic acids are present in Ferredoxin (Eck 1966), known to be one of the first proteins involved in the origin of life. As shown here, this dual behavior of some amino acids as conglomerates and racemic compounds might have been exploited under widely prevalent prebiotic circumstances for amplification of their solution enantiomeric excess.

Sequentially linked CS-RCS system is shown in a schematic diagram (Fig. 1a) where aqueous solution of amino acid switches from CS to RCS as the ambient condition changes from one of rapid evaporation and high supersaturation in a porous medium to normal evaporation in a bulk medium. Physical realization of such a schematic (Fig. 1b) shows aqueous solution of amino acid slowly seeping over a porous bed (CS) (Viedma 2001) and collecting in a deeper pool of water (RCS).

Figures 2 shows the ternary phase diagrams for the same amino acid behaving as CS and RCS under different ambient conditions. Phase diagrams in Fig. 2 are based on data for aspartic acid (Cao et al. 2022) which shows unusual behavior even in bulk aqueous solutions. Thus, aqueous solution with equal proportion of L and D aspartic acid results in a conglomerate upon crystallization. This lasts for several hours before aspartic acid reverts to its normal crystallization as a racemic compound (Lee and Lin 2010). Bulk solution of racemic compound aspartic acid always results in a racemic compound upon crystallization (Viedma 2001). This unusual behavior of aspartic acid makes it possible to measure its solubility both as a conglomerate and a racemic compound (Lee and Lin 2010).

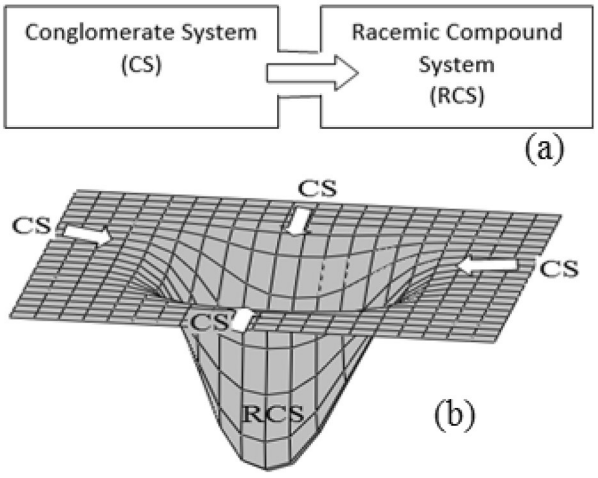

Fig. 1 **a**: Schematic for dual behavior where amino acid solution produces conglomerate system (CS) under high evaporation and racemic compound system (RCS) otherwise. **b**: Physical realization of schematic. Amino acid solution seeping through porous bed results in high evaporation (CS) and collects in a deeper pool (RCS)

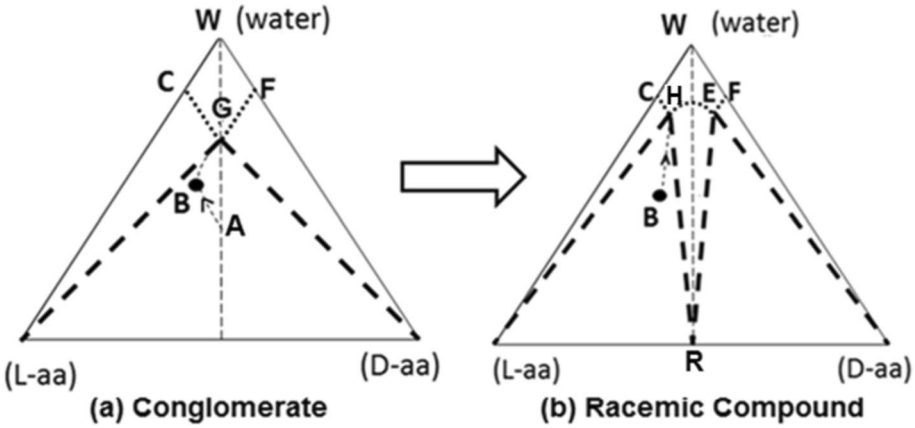

Fig. 2 Ternary phase diagrams of **a** CS (1a) and RCS (1b) of the same compound (example, aspartic acid). Trajectory from supersaturated solution A → B is due to PC in CS. CS switches to RCS at point B (**b**)

Phase diagram switches from 2(a) to 2(b) as the amino acid behavior changes from conglomerate to racemic compound. In above phase diagrams, vertices W, L, D correspond to pure water, L-amino acid and D-amino acid respectively. Points C and F give solubility of pure L and D enantiomer respectively. G is the eutectic point (EE = 0) for conglomerate amino acid and points H, E are eutectic points (EE ≠ 0) for racemic compound amino acid. Plausible path ABG (Fig. 2a) is shown for preferential crystallization of D-amino acid as a conglomerate and also the path shift from BG to BH (Fig. 2b) following a transition of amino acid from conglomerate to racemic compound at point B.

Mass fraction units are used here. Lower case letters **l, d** and **w** (**l** + **d** + **w** = 1) will be used throughout for mass-fraction of L-amino acid, D-amino acid and water respectively. As an example for aspartic acid (Cao et al. 2022; Lee and Lin 2010; Dalton and Schmidt 1933), for point C on the ternary diagram, $\mathbf{l}_C = 0.004$, $\mathbf{d}_C = 0$, $\mathbf{w}_C = 0.996$; and for point F, $\mathbf{l}_F = 0$, $\mathbf{d}_F = 0.004$, $\mathbf{w}_F = 0.996$. For some other points (aspartic acid, 25 °C):

Eutectic point G of conglomerate: $\mathbf{l}_G = 0.004$, $\mathbf{d}_G = 0.004$, $\mathbf{w}_G = 0.992$.
Eutectic point H of racemic compound: $\mathbf{l}_H = 0.004$, $\mathbf{d}_H = 0.0014$, $\mathbf{w}_H = 0.9946$.
Eutectic point E of racemic compound: $\mathbf{l}_E = 0.0014$, $\mathbf{d}_E = 0.004$, $\mathbf{w}_E = 0.9946$.
Vertex L: $\mathbf{l}_L = 1$, $\mathbf{d}_L = 0$, $\mathbf{w}_L = 0$; Vertex D: $\mathbf{l}_D = 0$, $\mathbf{d}_D = 1$, $\mathbf{w}_D = 0$; Vertex W: $\mathbf{l}_W = 0$, $\mathbf{d}_W = 0$, $\mathbf{w}_W = 1$.
Racemic point R on the L-D base: $\mathbf{l}_R = 0.5$, $\mathbf{d}_R = 0.5$, $\mathbf{w}_R = 0$.

To understand the transition from conglomerate form of aspartic acid to its racemic compound form, an overlap of Fig. 2(a) and (b) is shown in Fig. 3. Some additional lines are also drawn in Fig. 3. These include straight lines (DTP, DAM) for constant concentrations of L-amino acid.

The behavior of amino acid as a conglomerate is described by the ternary phase diagram and solubility isotherm CGF in Fig. 2(a). For such supersaturated, almost racemic solution of an amino acid described by point A (EE ≈ 0, $\mathbf{d}_A > \mathbf{l}_A$) in Figs. 2(a) and 3, seeds of D-enantiomer are more likely to form spontaneously, triggering preferential crystallization of D-enantiomer of amino acid with the solution acquiring a greater

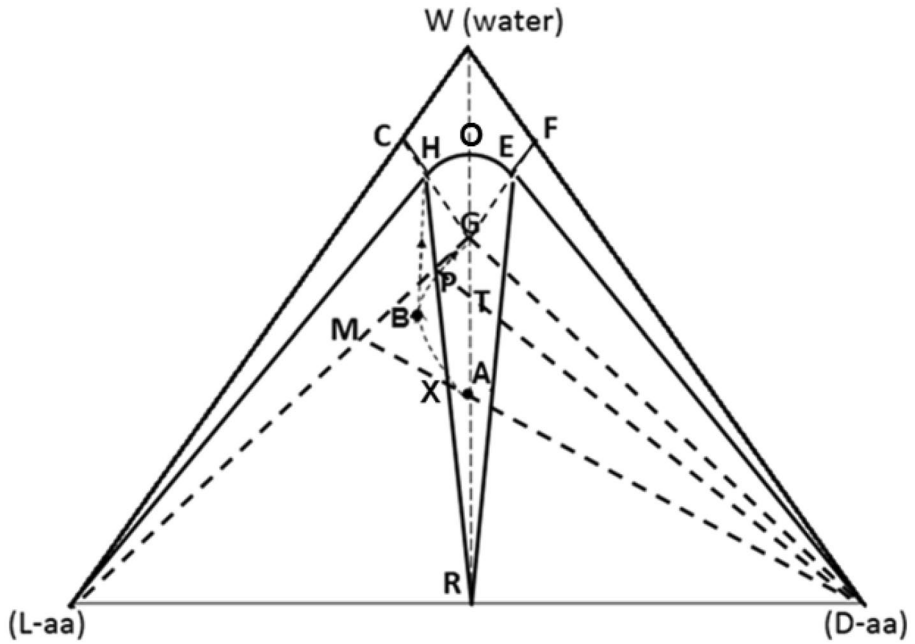

Fig. 3 Combined ternary phase diagram for CS and RCS

L-concentration than D (solution $EE_L > 0$). Eventually, seeds of L-enantiomer form and trigger crystallization of L-enantiomer with EE_L going to zero for both the crystallized solid and in solution. Path ABG (Figs. 2a and 3) is one of many along which the solution can evolve, beginning with the onset of preferential crystallization at A and terminating at the eutectic point (G) of the conglomerate solubility isotherm. If however, the conglomerate system switches (at point B) to racemic compound before point G is reached, it is possible that the solution will terminate at point H, the eutectic point of the racemic compound solubility isotherm. For this to happen, the path ABG must intersect the tie line HR of the racemic compound system. For given initial supersaturation (point A), preferential crystallization of D-enantiomer triggers the evolution of the conglomerate system along any path within the triangular region AMG; AM representing path of constant L-concentration for crystallization of D-enantiomer and MG is the path of constant D-concentration for eventual crystallization of L-enantiomer. Clearly, point T represents the minimum initial supersaturation ($S_{min} \equiv S_T$) necessary for the system to evolve to eutectic point H following a switch from conglomerate to the racemic compound, i.e. for $S < S_T$, the path of preferential crystallization will be confined to triangular region TPG and will not intersect the tie line HR. It can be shown (supplementary information) that S_{min} depends on the enantiomeric mass fraction at eutectic points for conglomerate (G) and racemic compound (H). Thus,

$$S_{min} \cong \frac{l_H + l_G - d_H}{l_G} \tag{1a}$$

For several amino acids (Klussmann et al. 2006a, b), $l_H, l_G = l_C$ (Figs. 2a and 3), giving,

$$S_{min} \cong 2 - \frac{d_H}{l_H} \tag{1b}$$

For aspartic acid solution at 25 °C, $\mathbf{l}_H = 0.004$, $\mathbf{d}_H = 0.0014$, $\mathbf{l}_G = 0.004$, giving $S_{min} = 1.65$. Higher initial supersaturation ($S > S_{min}$) shown by point A, results in increasing triangular phase space area PMX (left of the tie line HR, in the tri-phasic space of racemic compound) within which transition from conglomerate → racemic compound will take the solution from point B to the eutectic point H of the racemic compound ($EE_L \approx 0.48$ at H, for aspartic acid). If conglomerate → racemic compound switch takes place right of the tie line HR, resultant equilibrium solubility and solution EE_L is described by a point on segment HO of the racemic compound isotherm. This is explained later in more detail. Ratio of phase space areas of triangle PMX to triangle GMA (Fig. 4) increases with ($S—S_{min}$) (supplementary information) and is given by,

$$\frac{Area(PMX)}{Area(GMA)} \cong \left[\frac{S - S_{min}}{S - 1}\right]^2 \tag{2}$$

This ratio of areas can be looked upon as a measure of the likelihood that conglomerate → racemic compound transition will amplify the solution EE_L from near zero at point A of conglomerate to its equilibrium value, $EE_L = (\mathbf{l}_H — \mathbf{d}_H)/(\mathbf{l}_H + \mathbf{d}_H)$ at eutectic point H of the racemic compound, which is 0.48 for aspartic acid. This is illustrated in Fig. 4. Viability of supersaturation as large as 10 or even greater, is discussed later (Section 3).

If conglomerate → racemic compound transition point B is to the right of tie line HR, the resultant equilibrium solubility of the racemic compound is given by the point of intersection between lines BR and section HO of the solubility isotherm, with excess solute crystallizing out as a racemic compound at point R. In this case, the solution EE_L will have a value between 0 and $EE_{L,max}$ of 0.48 for aspartic acid. In the biphasic domain (HOR) of the racemic compound, the difference of enantiomeric concentration **(l-d)/w** remains constant along line BR and can be correlated to the resultant equilibrium solution-EE_L on isotherm HO (supplementary information). To the left of tie line HR, the concentration-difference

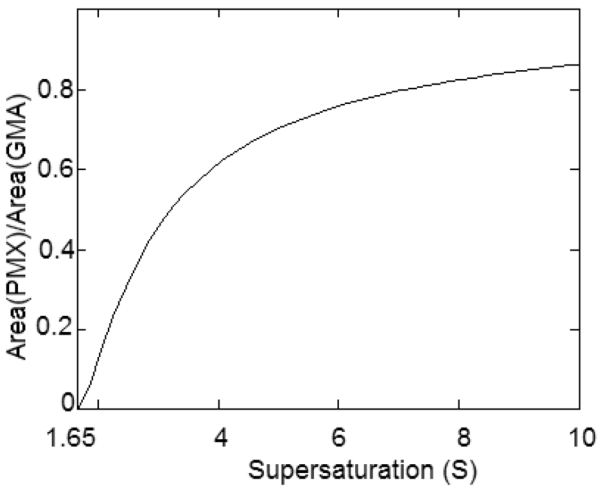

Fig. 4 Ratio of triangular areas PMX/GMA in ternary diagram is a measure of likelihood that CS → RCS transition will result in the solution EE at the eutectic point of RCS

in the tri-phasic domain HLR is in general greater than in the biphasic domain HOR (supplementary information) and conglomerate → racemic compound transition in this region results in solution EE_L at point H (Fig. 5).

Discussion

One theory (Klussmann et al. 2006a, b) for prebiotic chiral resolution rests on the observation that most proteinogenic amino acids are racemic compounds and for any supersaturated state (for example, point B in Figs. 2b and 3) in the triphasic domain HLR, the equilibrium solution EE_L will be given by the solubility of enantiomers at the eutectic point (H). This is independent of the overall EE_L for the amino acid or EE_L(B) at point B. As an example, for solubility in water at 25 °C, the solution EE_L(H) for alanine and serine at eutectic point H is 0.59 and 0.99 respectively, independent of EE_L(B) which could be just 1%. This is relevant since it is understood that most prebiotic biochemical reactions must have taken place in aqueous medium. However, starting from an almost racemic, supersaturated state A ($EE_L(A) > 0$, Fig. 3), the racemic compound amino acid solution cannot evolve on its own to state B within the triphasic domain HLR. If the amino acid is a conglomerate, PC can result in evolution of solution from A to B with solution EE_L(B) of few percent. But PC trajectory eventually terminates at the equilibrium eutectic point G of the conglomerate, with $EE_L(G) = 0$. An ideal situation would require an amino acid that is initially a conglomerate and PC increases the solution EE_L from $EE_L(A) \approx 0$ to $EE_L(B) \approx$ few percent. It then switches to racemic compound, resulting in the final amplified EE_L(H) at the eutectic point H. This is exactly the case described here. Aqueous solution of amino acid seeping over a porous bed is subject to high evaporation rate and large supersaturation. Aspartic acid and glutamic acids are known to behave like conglomerates in this situation. Amino acid solution collecting in a deeper pool and subject to lower evaporation rates then switches to a racemic compound in a time of few hours.

It is understood that in an almost-racemic sample of molecules, minimum seed-EE that can be amplified must exceed the mean amplitude ($\delta|EE|$) of its statistical fluctuation (Lente 2012), i.e. $\delta|EE| \approx 1/\sqrt{N} < EE_{seed}$. Here N is the total number of enantiomers in

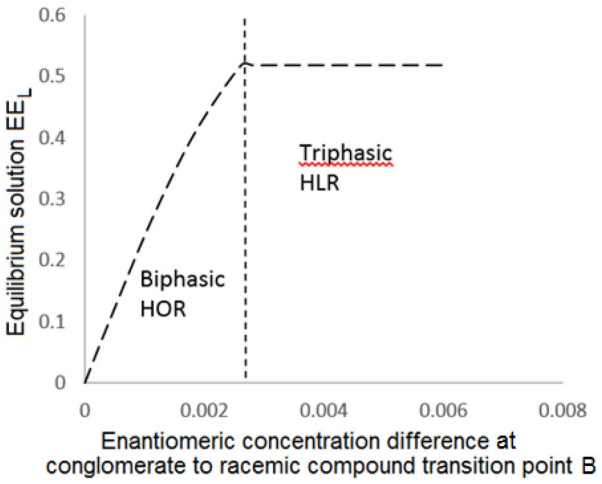

Fig. 5 Solution-EE of the RCS as a function of the enantiomeric concentration difference at the CS → RCS transition point B

the given sample. This is seen experimentally in Soai reaction (Soai 2022) where seed EE $\approx 5\times10^{-7}$ can force the reaction in the direction of predetermined chirality (Soai et al. 2014). For a racemic solution of an amino acid like aspartic acid, solubility is around 10 mg/g H_2O (Cao et al. 2022). For a small pool of volume Vm^3, number of amino acid molecules in a saturated solution is $N=(10^4\ V/M)N_A$, where M is the molecular weight of amino acid (M = 133 g/mol for aspartic acid) and N_A is the Avogadro number. For the pool volume $V=1m^3$, $\delta\left|EE\right| \approx 1/\sqrt{N}=1.5\times10^{-13}$ for aspartic acid. Similar reasoning has been used to propose (Kondepudi and Nelson 1985) that even seed EE of 10^{-18} due to PVED can be amplified by autocatalytic reactions (Blackmond 2020) to homochirality.

In a recent work (Sharma 2023) we showed that in terrestrial magnetic field, magnetic circular dichroism by stratospheric oxygen creates a net circular polarization of 10^{-10} in UVC light from sun. This in turn results in asymmetric photodissociation of amino acid enantiomers produced in volcanic eruptions to give seed EE of 10^{-12} and with a sign that remains constant over a large area of earth. This seed EE could potentially be amplified by the mechanism described in this report. Other possible sources include seed EE delivered on meteorites (Elsila et al. 2016). As mentioned earlier, while a small class of meteorites have shown an excess of L-amino acids, majority of them show a racemic population. Several questions remain unanswered including lack of knowledge of an estimate for average seed EE delivered on meteorites over large area of earth.

Figure 1 illustrates a realistic scenario on primitive earth for amplification of seed EE of some amino acids like aspartic and glutamic acids which behave like conglomerates under condition of rapid evaporation and high supersaturation in porous medium but are racemic compounds otherwise in conventional bulk solution form. Both of these amino acids are present on Ferrodoxin, one of the oldest known proteins.

Supersaturation values around 2.5 are seen in some experiments involving bulk solution of DL-aspartic acid (racemic compound). Rapid evaporation of such solution in porous medium (Fig. 1) results in higher supersaturation before onset of precipitation of conglomerate crystals. In general, supersaturation that can be achieved (before nucleation) increases with evaporation rates. For low initial concentrations, supersaturation as high as 10 has been observed for glycine following rapid evaporation in solution (He et al. 2006). Assuming there is a slight excess of D-enantiomer in the almost-racemic seed-EE, the scenario of Fig. 1 can result in preferential crystallization of D-enantiomer initially and a slight excess of L-enantiomer in the conglomerate solution of amino acid, seeping over the porous substrate and collecting in the deeper pool. The conventional body of bulk solution in the pool, with relatively low evaporation rates and lower supersaturation, favors amino acids in the racemic compound form. As seen experimentally, for aspartic acid already present in the pool in conglomerate form, it can take between 16 h (at 25 C) and 6 h (at 45C) for conversion to racemic compound solution (Lee and Lin 2010).

As mentioned earlier, for eutectic point G of aspartic acid conglomerate, $\mathbf{l}_G=0.004$, $\mathbf{d}_G=0.004$, $\mathbf{w}_G=0.992$ with racemate solubility in water of 8.06 mg/g. As an example, for large supersaturation induced by rapid evaporation, S = 10 and metastable solubility at point A (Figs. 2a and 3) is $\frac{l_A+d_A}{w_A}=80.6mg/g$, giving $\mathbf{l}_A=0.039$, $\mathbf{d}_A=0.039$, $\mathbf{w}_A=0.922$. With PC of only the D enantiomer in the beginning, solution EE_L increases along path AX. PC can evolve along various paths ABG within the triangular phase space AMG. Trajectory ABG must intersect section PX of tie line to reach solution EE_L of eutectic point H. Starting from $EE_L(A)=0$ at point A with $S>S_{min}$ ($S_{min}=1.65$ for aspartic acid) intersection with PX at point X results in minimum increase of solution $EE_{L,min}(X)$ due to PC. As shown in the supplementary section,

$$EE_{L,min}(X) \cong \frac{l_H - d_H}{2.S.l_G - l_H + d_H} \tag{3}$$

This gives $EE_{L,min}(X) = 0.194, 0.070, 0.049, 0.033$ for S = 2, 5, 7, 10 respectively. This is the smallest EE_L which must be produced by PC for trajectory ABG to cross over into the triphasic domain at point X before transition to racemic compound. For increasing supersaturation (S), $EE_{L,min}(X)$ is inversely proportional to S and the sequential mechanism in the CS-RCS described here for amplification of solution EE_L becomes increasingly viable. In reality, nucleation of the other (D) enantiomer as well as heterogeneous nucleation will drive PC along trajectory ABG, intersecting tie line PX at a point above X. Thus, the smallest EE_L which must be produced by PC will be greater than $EE_{L,min}(X)$. For aspartic acid, conglomerate → racemic compound transition in the pool will result in the equilibrium $EE_L(H)$ of 0.48 at the racemic compound's eutectic point H, provided the transition point B is in the triphasic domain PMX. For such aspartic solution in the pool, conglomerate → racemic compound phase transition thus results in maximum amplification of $EE_L(X) \rightarrow EE_L(H)$ by a factor of 2.5, 6.9, 9.8 and 14.5 for S = 2, 5, 7, 10 respectively. For an initial supersaturation of just 1.06, solution EE_L of 0.04 has been demonstrated in PC experiments with conglomerate amino acid threonine (Elsner et al. 2005). Clearly, higher supersaturation increases the likelihood that PC trajectory will cross over into the triphasic domain PMX. Likelihood that PC will result in a state within the triphasic domain PMX is also measured by the ratio of area of phase space PMX to the total available phase space GMA (Eq. 2) available under PC. As seen from Fig. 4, this ratio increases with supersaturation and is 0.12, 0.70, 0.80, 0.86 for S = 2, 5, 7, 10 respectively.

To summarize, starting from an almost racemic ($EE_L < 0$), highly supersaturated conglomerate solution represented by point A on ternary phase diagram (Fig. 3), equilibrium enantiomeric excess (EE_L) of the racemic compound solution will depend on the position of point B (Fig. 3) up to which preferential crystallization occurs in conglomerate solution flowing over shallow porous bed, followed by conglomerate → racemic compound transition in the pool. As given in Fig. 5, if point B is in the tri-phasic area of racemic compound (triangle PMX of Fig. 3), the equilibrium solution EE_L of the pool will be given by its maximum value at the eutectic point, $EE_{L,max}(H) = (\mathbf{l}_H — \mathbf{d}_H)/(\mathbf{l}_H + \mathbf{d}_H)$. For aspartic acid, $EE_{L,max}(H)$ is 0.48. If point B is in the bi-phasic area of racemic compound (quadrilateral AXPG of Fig. 3), the equilibrium solution EE_L of the pool is given by a value between 0 and $EE_{L,max}(H)$ (Fig. 5).

Conclusion

While it is known that some amino acids can behave either as conglomerates or as racemic compounds depending on the prevailing ambient, we have shown how this dual behavior could have combined sequentially under viable prebiotic conditions to produce near homochirality in solution. Starting with CS in near racemic condition, PC produces a solution-EE of ~ 1%. With change of ambient conditions, the CS switches to RCS, resulting in solution-EE at the eutectic point of RCS. For aspartic acid as a model system, this solution eutectic-EE is ~ 50%. For sequential amplification to be effective, we have derived an equation that can be used to calculate the required threshold supersaturation of CS and is 1.65 for aspartic acid at 25 C. For given supersaturation, we also derive an equation to calculate the minimum required solution-EE in CS before switching to RCS can be effective

for further sequential amplification to its eutectic EE value. While the analysis is based on available data for aspartic and glutamic acids which show such dual behavior, unusual crystallization behavior under rapid evaporation is not uncommon in other materials (Hilden et al. 2003). In such conditions of rapid evaporation and highly saturated metastable solubility, crystallization is dominated by kinetic (Ostwald's step rule) rather than thermodynamic considerations (van Santen 1984). Such dual behavior might be common in hitherto unexplored crystallization of other amino acids as well.

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Data Availability Not Applicable.

Declarations

Ethics Approval Not applicable.

Consent to publish All material is owned by the author and no permission is required to publish.

Conflict of Interest Author declares there is no known conflict of interest.

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