Rate Equation Approaches to Amplification of Enantiomeric Excess and Chiral Symmetry Breaking

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Abstract Theoretical models and rate equations relevant to the Soai reaction are reviewed. It is found that in production of chiral molecules from an achiral substrate autocatalytic processes can induce either enantiomeric excess (ee) amplification or chiral symmetry breaking. The former means that the final ee value is larger than the initial value but is dependent upon it, whereas the latter means the selection of a unique value of the final ee, independent of the initial value. The ee amplification takes place in an irreversible reaction such that all the substrate molecules are converted to chiral products and the reaction comes to a halt. Chiral symmetry breaking is possible when recycling processes are incorporated. Reactions become reversible and the system relaxes slowly to a unique final state. The difference between the two behaviors is apparent in the flow diagram in the phase space of chiral molecule concentrations. The ee amplification takes place when the flow terminates on a line of fixed points (or a fixed line), whereas symmetry breaking corresponds to the dissolution of the fixed line accompanied by the appearance of fixed points. The relevance of the Soai reaction to the homochirality in life is also discussed.

Keywords Flow trajectory · Homochirality · Nonlinear autocatalysis · Recycling · Soai reaction
1 Introduction

In the Human Genome Project (from the year 1990 to 2003) sequences of chemical base pairs that make up human DNA were intensively analyzed and determined, as they carry important genetic information. DNA is a polymer made up of a large number of deoxyribo nucleotides, each of which is composed of a nitrogenous base, a sugar, and one or more phosphate groups [1]. Similar ribonucleotides polymerize to form RNA, which is also an important substance for producing a template for protein synthesis. RNA sometimes carries genetic information but rarely shows enzymatic functions [1].

One big issue of the post-Genome Project era is proteomics since proteins play crucial roles in virtually all biological processes such as enzymatic catalysis, coordinated motion, mechanical support, etc. [1]. A protein is a long polymer of amino acids, and folds into a regular structure for its biological function.

Sugars and amino acids in these biological polymers contain carbon atoms, each of which is connected to four different groups, and consequently are able to take two kinds of stereoisomers. The two stereoisomers are mirror images or enantiomers of each other, and are called the D- and L-isomers. The two isomers should have the same physical properties except for their optical response to polarized light. Therefore, a simple symmetry argument leads to the conclusion that there are equal amounts of D- and L-amino acids or sugars in life. But the standard biochemical textbook [1] tells us that “only L-amino acids are constituents of proteins” [1] (p 17) and that “nearly all naturally occurring sugars belong to the D-series” [1] (p 346). There is no explanation why chiral symmetry is broken in life and how the homochirality has been brought about on earth.

It was Pasteur, in the middle of the 19th century, who first recognized the breaking of chiral symmetry in life. By crystallizing optically inactive sodium ammonium racemates, he separated two enantiomers of sodium ammonium tartrates, with opposite optical activities, by means of their asymmetric crystalline shapes [2]. Since the activity was observed even in solution, it was concluded that optical activity is due to the molecular asymmetry or chirality, not due to the crystalline symmetry. Because two enantiomers with different chiralities are identical in every chemical and physical property except for optical activity, in 1860 Pasteur stated that “artificial products have no molecular asymmetry” and continued that “the molecular asymmetry of natural organic products” establishes “the only well-marked line of demarcation that can at present be drawn between the chemistry of dead matter and the chemistry