CHIRAL SYMMETRY BREAKING IN NONLINEAR AUTOCATALYTIC REACTIONS AND THE EFFECT OF EXTERNAL NOISE

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Abstract. A mathematical model based on difference equations is presented to show that minute chiral perturbations are sufficient for spontaneous breaking of L, D symmetry in nonlinear autocatalytic reactions. The effect of noise on rate constants is analysed and it was noted that, below a critical noise level, the influence of the chiral perturbation results selection of the biased isomer with certainty.

1. Introduction

The mechanism of chiral symmetry breaking in biochemical evolution continues to remain unresolved. However, several investigations strongly suggest that chiral symmetry breaking in nonlinear kinetics based on a minute chiral influence could be the cause of stereoselection. (Frank, 1953, Decker, 1974; Kondepudi and Nelson, 1983; Morozov, Kuzmin and Goldanskii, 1983; Avetisov, Goldanskii and Kuzmin, 1991; Tennakone, 1984, 1991). As a result of weak neutral currents or presence of β-radiation from radio active sources, the rates of parallel chemical reactions involving L and D isomers could differ by a small amount (Garay, 1968; Letokhov, 1975; Kondepudi and Nelson, 1983; Mason, 1984; Hegstrom, 1985). If the dynamical system, spontaneously break the symmetry under the parity operator P $(L, D) = (D, L)$, a small global chiral perturbation is expected to select the favoured isomer. Investigations by Kondepudi and Nelson (1983) have suggested that selection could occur even in the presence of thermal fluctuations in the rate constants. The model of the above authors is based on two coupled non-linear differential equations. The same effect (i.e., spontaneous breaking of the symmetry under the parity operator) is manifested in coupled difference equations. Multiplication of molecules by autocatalysis is a discrete process, in that sense difference equations are more appropriate. Furthermore conclusions arrived at from differential equations is not necessarily same as those from the analogues differences equations. Consequently problems in population growth are studied from both points of view. Again difference equations are much more amenable to computer experimentation and the associated computational errors are minimal. In this paper we present a simple model based on coupled difference equations, which clearly illustrate the chiral symmetry breaking and the effect to external noise on bifurcation.

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2. Model and Discussion

The rate of production of L and D isomers could be expected to follow kinetic equations of the form,

$$\frac{dL}{dt} = C + L\,F(L, D) \tag{1}$$

$$\frac{dD}{dt} = C + D\,F(D, L) \tag{2}$$

where the symbols L and D are also used to denote the concentrations of the two species. The constant term C is the non-catalytic (i.e., direct radiation induced) production of the two isomers. The second autocatalytic term is nonlinear and the rate constant (i.e., the function F) depends on the concentrations of the L and D isomers in the reactive medium. In asymmetric organic synthesis, the parameter that favours the formation of L isomer (D isomer) is $L/L + D$ ($D/D + L$). (i.e., L (D) biasing is measured by the fraction of $L(D)$ molecules). Consequently we assume that $F(L,D)$ is a function of $L/L + D$ and $D/D + L$, i. e.,

$$F(L, D) = G(L/L + D, D/D + L)\,. \tag{3}$$

To the first order in the variables $L/L + D$ and $D/D + L$, Equations (1) and (2) approximate to,

$$\frac{dL}{dt} = C + bL + \frac{kL^2}{L + D} - a\,\frac{LD}{L + D} \tag{4}$$

$$\frac{dD}{dt} = C + bD + \frac{kD^2}{D + L} - a\,\frac{DL}{D + L} \tag{5}$$

where b, k and a are positive constants. The sign of the last two terms of (4) and (5) are chosen as above, because the development of an isomer of one type, hinders the development of the isomer of other type. One arrives at a conclusion similar to (4) and (5), if the assumption is made, that F is a function of the assymmetry parameter (L-$D/L + D$), i.e.,

$$F(L, D) = H\left(\frac{L - D}{L + D}\right). \tag{6}$$

The condition (6) makes $a = k$ in (4) and (5). In order to make the rate equations more general, we have adopted the assumption (3). The difference equivalent of the equations (4) and (5) are,

$$L_{t+1} = C + hL_t + \frac{kL_t^2}{L_t + D_t} - a\,\frac{L_t D_t}{L_t + D_t} \tag{7}$$