

On the Klemm model for bistability of mixtures of interacting enantiomers

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The solution of the Klemm model for spontaneous chiral stereoselection has been obtained. It is shown that a system whose time-evolution is described by the Klemm model, independently of the initial value of the enantiomeric excess, always reaches a racemic terminal state. In a system described by the Klemm model bistability never occurs.

Keywords: chirality, homochirality, bistability, Klemm model, Frank model.

INTRODUCTION

The physico-chemical conditions under which a system that is initially racemic (or without chiral constituents) can spontaneously evolve into a homochiral or almost homochiral terminal state is a topic that has been investigated for a long time.^{1,2} It is directly related to the puzzle of how homochirality of the biomolecules in modern terrestrial life forms could have evolved from the racemic “primordial soup”. The problem gained a great deal in importance after such phenomena were experimentally observed, first in the crystallization of sodium chlorate^{3–5} and other compounds,⁶ and, independently, within certain autocatalytic chemical reactions.^{7,8} Long before these experiments were performed, Frank had already demonstrated⁹ that a very simple kinetic scheme may lead to spontaneous chiral stereoselection. Eventually, numerous modifications and amendments of the Frank model were put forward.^{10–23}

Some time ago Klemm considered^{12,23} a general expression for the time-evolution of a system containing $n x$ moles of one enantiomer (say, R) and $n(1-x)$ moles of the other enantiomer (say, S):

$$\frac{d[nx]}{dt} = e + n [f_1 x + f_2 (1-x)] + n^2 [g_1 x^2 + g_2 x (1-x) + g_3 (1-x)^2] \quad (1)$$

where $e, f_1, f_2, g_1, g_2, g_3$ are the respective rate constants. Consequently, in Eq. (1) all possible zeroth, first and second order terms are included, whereas higher than second

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order reactions are assumed to be absent. Because of symmetry, Eqs. (1) and (2):

$$\frac{d[n(1-x)]}{dt} = e + n [f_1 (1-x) + f_2 x] + n^2 [g_1 (1-x)^2 + g_2 x (1-x) + g_3 x^2] \quad (2)$$

have to be simultaneously satisfied.

In the notation just introduced, the enantiomeric excess (expressed as the relative excess of the enantiomer R over the enantiomer S) is equal to $ee = 2x - 1$. Therefore, by determining the time-dependence of x , the time-evolution of ee is also established. If for $t \rightarrow \infty$, $ee \rightarrow 0$, it can be said that the system reaches a racemic terminal state. If, however, for $t \rightarrow \infty$ there are two equally plausible limit values: $ee \rightarrow +\eta$ and $ee \rightarrow -\eta$, then the system evolves into a bistable terminal state. If, in addition, $\eta = 1$, then the terminal states of the system are homochiral.

The various kinetic models⁹⁻²³ proposed for spontaneous chiral stereoselection can be viewed as special cases of Eqs. (1) and (2). In particular, the original Frank model is obtained by choosing $e = f_2 = g_1 = g_3 = 0$, $f_1 > 0$ and $g_2 < 0$. Recall that in the Frank model the parameter n is not time-independent, but is an exponentially increasing function of t . This drawback of the Frank model was eventually overcome by an open-flow-reactor modification.^{16,19} Both in the original Frank model and in its open-flow-reactor variant, $ee \rightarrow +1$ or $ee \rightarrow -1$, depending on the initial conditions.

THE KLEMM MODEL

The model put forward by Klemm¹² is based on Eqs. (1) and (2), but, in addition (and in contrast to the Frank model), it is required that n , the total amount of the two enantiomers, be constant, *i.e.*, time-independent. If so, then by adding Eqs. (1) and (2) one obtains

$$2e + n (f_1 + f_2) + n^2 [g_1 + g_3 - 2 (g_1 - g_2 + g_3) x (1-x)] = 0 \quad (3)$$

In a previous publication,¹² by means of Eq. (3), the rate constant f_1 was expressed as

$$f_1 = -2e/n - f_2 - n [g_1 + g_3 - 2 (g_1 - g_2 + g_3) x (1-x)] \quad (4)$$

and substituted back into Eqs. (1) and (2). From a physico-chemical point of view such an algebraic manipulation is not legitimate. First, according to Eq. (4), the rate constant f_1 would now be dependent on the concentrations of R and S . Second, by substituting relation (4) into (1), a third-order term would appear in the model, contrary to the initial assumption.

It will now be shown how the Klemm model can be solved without having to rely on Eq. (4).

SOLUTION OF THE KLEMM MODEL

Assuming that $dn/dt = 0$ and that $n \neq 0$, Eqs. (1) and (2) are immediately transformed into

$$\frac{dx}{dt} = e/n + f_2 + n g_3 + [f_1 - f_2 + n(g_2 - 2g_3)]x + n(g_1 - g_2 + g_3) x^2 \quad (5)$$

$$-\frac{dx}{dt} = e/n + f_1 + n g_1 + [f_2 - f_1 + n(g_2 - 2g_1)]x + n(g_1 - g_2 + g_3) x^2 \quad (6)$$

which must hold simultaneously.

By summing (5) and (6) one arrives at Eq. (3). The left-hand side of relation (3) can be viewed as a polynomial in the variable x . This polynomial will be *identically equal to zero* if all its coefficients are equal to zero, *i.e.*, if

$$2e + n(f_1 + f_2) + n^2(g_1 + g_3) = 0 \quad (7)$$

$$-2n^2(g_1 - g_2 + g_3) = 0 \quad (8)$$

Because of (8), the differential equations (5) or (6) can now be simplified as

$$\frac{dx}{dt} = A - Bx \quad (9)$$

where

$$A = e/n + f_2 + ng_3$$

$$B = f_2 - f_1 - n(g_2 - 2g_3).$$

Note that from (8),

$$\begin{aligned} 2A - B &= 2e/n + f_1 + f_2 + ng_2 \\ &= 2e/n + f_1 + f_2 + n(g_1 + g_3) \end{aligned}$$

and thus because of (7).

$$2A - B = 0. \quad (10)$$

Denote by x_0 the initial value of the variable x .

From the identity (10) it can be seen that $B=0$ if and only if $A=0$. If $A=B=0$ then Eq. (9) reduces to $dx/dt=0$ which implies $x=x_0$ for all values of t , *i.e.*, no change occurs in the system considered. Therefore, in what follows it is assumed that A and B differ from zero.

The differential equation (9) is easy to integrate because both A and B are independent of x and t . One immediately obtains

$$|A + Bx| = |A + Bx_0| e^{-Bt}$$

which in view of relation (10) becomes

$$|2x - 1| = |2x_0 - 1| e^{-Bt} \quad (11)$$

or

$$|ee| = |ee_0| e^{-Bt} \quad (12)$$

Eqs. (11) and (12) represent the solution of the Klemm kinetic model.¹²

DISCUSSION

Because of $0 \leq x \leq 1$ or because of $-1 \leq ee \leq +1$, the left-hand sides of (11) and (12) cannot be greater than 1. If B were negative-valued then the right-hand sides of (11) and (12) would exceed 1 for large values of t . Therefore B must be positive-valued.

Now three cases:

Case 1° : $x_0 > 0.5$

Case 2° : $x_0 = 0.5$

Case 3° : $x_0 < 0.5$

have to be distinguished.

Case 1°. The right-hand side of (11) is now equal to $(2x_0 - 1) \exp(-Bt)$ and is positive-valued for all $t > 0$. Therefore the right-hand side of (11) will never be equal to zero.

For near-zero values of t also $2x - 1$ must be positive-valued and therefore $|2x - 1| = 2x - 1$. Because $2x - 1$ will never be equal to zero it must be concluded that it must remain positive-valued for all $t > 0$. Therefore Eqs. (11) and (12) become:

$$2x - 1 = (2x_0 - 1) e^{-Bt} \text{ i.e. } x = \frac{1}{2} [1 + (2x_0 - 1) e^{-Bt}] \quad (13)$$

$$ee = ee_0 e^{-Bt} \quad (14)$$

From (13) and (14) is now evident that with increasing t , $x \rightarrow 0.5$ and $ee \rightarrow 0$. In other words: if $x_0 > 0.5$, no matter what the initial value of the enantiomeric excess is, the system evolves towards a racemic terminal state.

Case 2°. If $x_0 = 0.5$ then the right-hand sides of (11) and (12) are equal to zero for all values of t and hence are independent of t . Then for all values of t , $x = 0.5$ and $ee = 0$. In other words: if the system is racemic in the initial moment, it remains racemic all the time.

Case 3° is analyzed analogously as Case 1°. Eqs (13) and (14) remain valid implying again that no matter what the initial value of the enantiomeric excess is, the system evolves towards a racemic terminal state.

The conclusion of this analysis is that a system in which the total amount of the enantiomers R and S is constant, and in which only chemical reactions of the zeroth, first and second order may occur (= the Klemm model) will become racemic irrespective of the chirality of its initial state. In such a system no bistability will occur.

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ИЗВОД

О КЛЕМОВОМ МОДЕЛУ ЗА БИСТАБИЛНОСТ СМЕШЕ ИНТЕРАГУЈУЋИХ ЕНАНТИОМЕРА

ИВАН ГУТМАН

Природно-математички факултет у Крагујевцу

Нађено је решење Клемовог модела за спонтану хиралну стереоселекцију. Показано је да систем чија временска еволуција је описана Клемовим моделом, независно од почетне вредности енантиомерног вишка, увек достиже рацемско коначно стање. У систему описаном Клемовим моделом бистабилност се никада не јавља.

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