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NOTATION

$B(L)$	birth function
$D(L)$	death function
G	growth rate
K	coagulation rate constant
L, L_o, L_M	particle size; subscript o—defined by eq. (6), subscript M—maximum size—defined by eq. (10)

Greek letters

$\eta(L), \eta^o$	population of size L; superscript o—nuclei population
γ	aggregation parameter defined by eq. (7).
τ	mean residence time

REFERENCE

Lamey, M. and Ring, T. A., 1986, *Chem. Engng Sci.* **41**, 1213–1219.

A model of autooscillations in association reactions

INTRODUCTION

The association phenomenon is the generation of complexes A_2 (dimers), A_3 (trimers), etc. from substance A, in a simple case. The generation of these complexes is characteristic of liquids and adsorbed substances on a solid surface. It is also possible for a gas phase (Vukalovich and Novikov, 1948).

The aim of this paper is to show that association reactions can result in the appearance of autooscillations in nonlinear systems. The nonlinearity can be understood in two ways: (a) as substance exchange with the exteriority which is not in the thermodynamic equilibrium state; (b) as the existence of reactions in a system which tend comparably slowly to their equilibrium. In case (a), autooscillations and other phenomena (e.g. dissipative structures) can be observed for an indefinitely long period of time (if they exist). In case (b), the "rate constants" of the simple reaction mechanisms considered below are the effective constants depending on the concentrations of other substances. These effective constants vary in time. Therefore, some time after the beginning of the reaction all the exotic effects (autooscillations, dissipative structures, etc.) disappear; they are possible only on the way to equilibrium.

As in our previous work devoted to bifurcations (Bykov *et al.*, 1976, 1981; Bykov and Yablonskii, 1981a; Yablonskii *et al.*, 1983, 1984), autooscillations (Bykov *et al.*, 1978, 1979a, b; Bykov and Yablonskii, 1981b), slow relaxations (Gorban' and Cheresiz, 1981; Bykov *et al.*, 1982; Gorban', 1984; Yablonskii *et al.*, 1984) and dissipative structures (Gorban' *et al.*, 1980; Bykov *et al.*, 1983), we will seek the simplest reaction scheme presenting the effect of interest to us.

SCHEME AND MODEL

Let us consider the following simple association reaction scheme:

$$\begin{align}
(1) \quad & A \rightleftharpoons A^* \\
(2) \quad & A + 2A^* \rightarrow 3A^* \\
(3) \quad & A_2 + A^* \rightleftharpoons A_3
\end{align} \tag{1}$$

where A, A_2 and A_3 are the monomer, dimer and trimer, respectively. A^* is an excited (or active) monomer form. Mechanism (1) is similar to the reaction scheme of the simplest autocatalytic oscillator proposed in Bykov and Yablonskii (1981a, b). The main distinction consists in the nature of the third stage. It should be noted that stage (3) of mechanism (1) may be interpreted as a "buffer" reaction.

Scheme (1) is related to two linear conservation laws:

$$A_2 + A_3 = \text{const}_1 \tag{2}$$

$$A^* + A + 2A_2 + 3A_3 = \text{const}_2. \tag{3}$$

We take $\text{const}_2 = 1$, $\text{const}_1 = \alpha (\alpha < 1)$. The nonstationary kinetic model of scheme (1) is of the form

$$\dot{A} = -k_1 A + k_{-1} A^* + k_2 A A^{*2} = P(A, A_3) \tag{4}$$

$$\dot{A}_3 = k_3 A_2 A^* - k_{-3} A_3 = Q(A, A_3) \tag{5}$$

where A and A_3 are the concentrations of substances A and A_3, respectively, and the values of A^* and A_2 are determined from eqs (2) and (3), i.e.

$$A^* = 1 - 2\alpha - A - A_3 \tag{6}$$

$$A_2 = \alpha - A_3. \tag{7}$$

It should be noted that scheme (1) may be considered as a part of certain detailed association reaction mechanism. It does not contain the separate stage of a dimer generation looking like $A + A^* \rightleftharpoons A_2$. Henceforth, even this simple scheme allows us to describe the autooscillations. Hence, if one needs to consider a more realistic transformation scheme, mechanism (1) should be used as a basic one.

STEADY STATES

We will seek the single and nonstable steady state of system (4)–(7), as we have done in Bykov and Yablonskii (1981a, b). This steady state will guarantee the existence of autooscillations. The (4)–(7) steady states are determined as the

solutions of the system of two algebraic equations

$$P(A, A_3) = 0 \tag{8}$$

$$Q(A, A_3) = 0. \tag{9}$$

It is convenient to rewrite eqs (8) and (9) in the form

$$A_3 = 1 - 2\alpha - A^* - K_{-1}A^*/(K_1 + A^{*2}) = f(A^*) \tag{10}$$

$$A_3 = A^*/(K_{-3} + A^*) = g(A^*) \tag{11}$$

where $K_{-1} = k_{-1}/k_2$, $K_1 = k_1/k_2$, $K_{-3} = k_{-3}/k_3$. One can take $k_2 = 1$ without any generalization limit. The steady states are the intersection points of the curves $f(A^*)$ and $g(A^*)$ (see Fig. 1). We will seek the conditions of uniqueness of the intersection. For example, let us take the inflexion point $\tilde{A}^*$ of the function $f(A^*)$ to be the steady state and the inequality $f' < g'$ to hold true, i.e.

$$f''(\tilde{A}^*) = 0 \tag{12}$$

$$f(\tilde{A}^*) = g(\tilde{A}^*) \tag{13}$$

$$f'(\tilde{A}^*) < g'(\tilde{A}^*). \tag{14}$$

$A^* = \sqrt{3K_1}$ according to eq. (12). Equality (13) means that

$$\sqrt{3K_1} = \frac{3}{4}\left(1 + \frac{1}{4}K_{-1}/K_1\right)^{-1} \tag{15}$$

if one takes for simplicity

$$K_{-3} = \sqrt{3K_1}. \tag{16}$$

Inequality (14) can be reduced to the form $K_{-1}/K_1 < 8.8$ at $\alpha = 0.1$. Conditions (12)–(14) guarantee the steady state A^* uniqueness. In addition, we take $f'(\tilde{A}^*) > 0$, so that the situation shown in Fig. 1 should exist.

The last inequality means that $K_{-1}/K_1 > 8$. Finally,

$$8 < K_{-1}/K_1 < 8.8. \tag{17}$$

AUTOOSCILLATIONS

The stability of the steady state is determined by the roots of the characteristic equation

$$\lambda^2 - \sigma\lambda + \Delta = 0 \tag{18}$$

where $\Delta = a_{11}a_{22} - a_{12}a_{21}$, $\sigma = a_{11} + a_{22}$, a_{ij} are Jacobi matrix elements of the system (8), (9) calculated in the related steady state. If $\Delta < 0$, then the steady state is an unstable one. If $\Delta > 0$, then the type of steady state is determined by a σ sign;
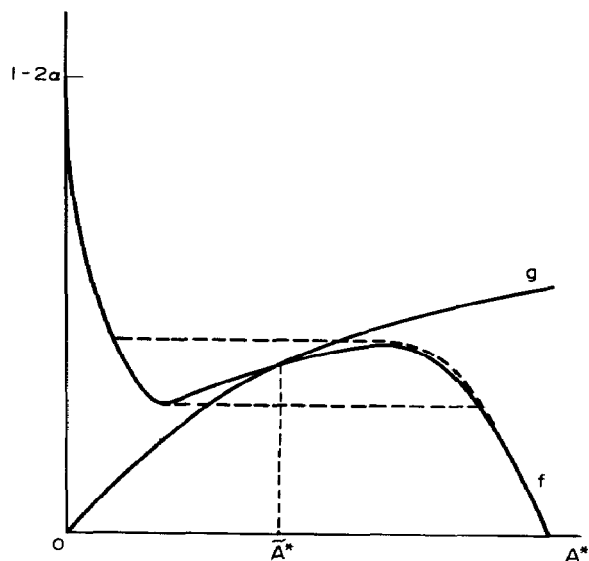
namely, the steady state is stable for $\sigma < 0$, but this former is unstable for $\sigma > 0$. σ may be presented as

$$\sigma = a_{11} - k_3 A^* - k_{-3}.$$

where a_{11} does not depend on k_3 and k_{-3}. Consequently, the steady state is unstable for $\Delta > 0$ and sufficiently small k_3, k_{-3}. Furthermore, one can easily see that sign $\Delta = \text{sign}(g' - f')$ for the steady state, i.e. the steady state is a single one if $f' < g'$ and its stability is determined by the σ sign.

The steady state $\tilde{A}^*$ is unique, if eqs (15) and (16) hold true. This steady state will be unstable for sufficiently small k_3, k_{-3} (for the situation presented in Fig. 1). Particularly, the model (4)–(7) calculations performed for the parameter values $\alpha = 0.1$, $k_1 = 0.02048$, $k_{-1} = 8.1\ k_1$, $k_2 = 1$, $k_3 = 10^{-4}$, $k_{-3} = 0.2479\ k_3$ show that the steady state corresponding to eqs (10) and (11) is the unstable one and all the solutions $A(t)$, $A_3(t)$ on the phase plane (A, A_3) tend to some limit cycle. The oscillation amplitude can be evaluated *a priori* from analysis of the graph in Fig. 1. The autooscillations are organized in such a manner that they exist in the dotted line neighbourhood shown in Fig. 1. The behaviour of solutions $A(t)$ and $A_3(t)$ looks like the relaxation oscillations for sufficiently small k_3, k_{-3}. Two types of motion are distinguished during the period: a fast one and a slow one. The former corresponds to the transition from one monotonic branch of $f(A^*)$ to the other; the latter corresponds to the slow variation of the solution along these branches.

CONCLUSION

Scheme (1) presented above can serve as the simplest autooscillation model in the complex-generation reaction. More detailed reaction schemes allowing the autooscillation percolation regimes are able to contain scheme (1) as a constituent part, or to approximate separate stages of (1). For example, the autocatalytic stage (2) may be approximated by two stages, $2A^* \rightleftarrows A_2^*$, $A + A_2^* \rightarrow 3A^*$, without any autocatalysis. In the future, we hope to provide a more detailed analysis of the autooscillation model separately.

We note one more simple but, we believe, very interesting effect which may appear in the association reactions. Let the system be closed and be in a thermodynamic equilibrium state. Then there are no autooscillations, on the average, over the macroscopic volume, although local autooscillations are possible. Their phase φ may be considered as a random function of a point. Generally speaking, the correlation radius of φ is a microscopic value. However, it may be large enough for the autooscillations to be detected by local measurements.

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NOTATION

A_i	symbols of substances or its concentrations
$\dot{A}$	$= dA/dt$
a_{ij}	Jacobi matrix elements of system (8), (9)
f'	$= df/dA^*$
f''	$= df'/dA^*$
$f(A^*)$	function, defined in eq. (8)
$g(A^*)$	function, defined in eq. (9)
k_i	reaction rate constants
$P(A, A_3)$	function, defined in eq. (4)
$Q(A, A_3)$	function, defined in eq. (5)
t	time

Fig. 1.

Greek letters

α	positive constant
φ	phase of local oscillations
λ	root of eq. (18)
σ, Δ	coefficients of eq. (18)

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Accuracy of chromatographic moments—effect of peak treatment and approximations

INTRODUCTION

The chromatographic technique is extensively used for obtaining parameters describing processes taking place in columns packed with solid adsorbents or liquids supported on solids. Quite popular is the evaluation of adsorption characteristics (e.g. adsorption equilibrium constants in gas–solid chromatography) or effective diffusivities in pores of the solid packing.

The evaluation of these parameters from the shape of chromatographic curves (CC) usually follows one of two routes: (1) with minimum number of CC's the parameters are obtained by fitting theoretical expressions to complete CC in the time-domain or (2) with larger number of CC's (which are easily obtained) corresponding to varying carrier-gas velocities or packing size, the moments of experimental CC's are fitted to theoretical expressions. Because of signal noise which affects heavily the CC tail only the first ordinary, μ'_1, and second central, μ_2, moments are usually employed.

When this moment approach is used it is important to know the precision with which the peak moments can be obtained via different approximate procedures. Also, because the raw response signal is never ideal it is always necessary to treat the CC's in some way (e.g. by shortening the CC tail and/or by taking into account the signal base-line instability and noise).

The aim of this contribution is to generate theoretical CC's and compare moments obtained from them in two approximate ways with theoretical values and to compare theoretical CC moments with values calculated according to the definitions

$$\mu'_i = \int_0^\infty t^n c(L, t)\, dt \Big/ \int_0^\infty c(L, t)\, dt \quad n = 1, 2, \dots \quad (1)$$

$$\mu_n = \int_0^\infty (t - \mu'_1)^n c(L, t)\, dt \Big/ \int_0^\infty c(L, t)\, dt \quad n = 2, 3, \dots \quad (2)$$

from CC's obtained by defining an uncertainty band of different width around the base-line. This uncertainty band takes into account the base-line noise as well as shortening of the CC tail. The main attention is concentrated on second