Stirring Effect on Bistability in a CSTR. 2. Theoretical Analysis of the Coalescence−Redispersion Model for One-Variable Systems

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A theoretical analysis is given of the dynamic consequences of reactor inhomogeneity arising from the incomplete mixing of a single premixed feedstream into a CSTR, in nonlinear reactive systems with a single dynamical variable. The coalescence−redispersion (CR) model is used to describe the interaction of feeding, mixing, and chemical reaction, and the corresponding Langevin equation is derived in which the fluctuating term due to feeding and mixing is a multiplicative colored noise process. From the stationary solution of the corresponding Fokker−Planck equation, we obtain an analytical expression for the stochastic steady states, using the white-noise approximation. This leads to an expression for the degree of reactor inhomogeneity (defined as the variance of concentration in a single representative volume element) as a function of flow rate, stirring rate, and the difference between the inflow and bulk concentrations. Finally, we derive a linear scaling law that relates the shift of the stochastic steady state from its deterministic limit to the reactor inhomogeneity. Analysis of the numerical and experimental results for the arsenous acid−iodate reaction obtained in part 1 of this series [preceding paper] confirms the appropriateness of this approach and validates the CR model for describing the stirring effects in one-variable nonlinear reactions.

1. Introduction

This paper continues the investigations in the preceding part 1[1] of the kinetic and dynamic effects of reactor inhomogeneities that arise from the incomplete mixing of reactant feedstreams in flow reactors (e.g., CSTR) with nonlinear reactions. The long-term goal of these ongoing studies is to understand quantitatively and qualitatively the roles of different types of inhomogeneities on the dynamic responses of different classes of nonlinear reactions. The dependence of reaction rates and hence of steady-state concentrations, bifurcation points, and oscillation attributes on stirring rate is usually called "*stirring effect*". Their dependence on the mixing mode, i.e., the way in which the reactant streams are injected into the reactor (as a single, premixed feedstream or as several, non-premixed feedstreams), we refer to as "*mixing effect*".

The type of inhomogeneity may be manipulated through the mixing mode. When reactants enter as separate, *non-premixed feedstreams* (NPM), they cannot react until they have mixed with each other. This process, called *stream mixing*, initially enhances the reaction rate as the stirring rate is raised. All subvolumes have different elementary compositions−a fact that complicates the modeling of the reactor with NPM feeds. When the reactants enter in a single, *premixed feedstream* (PM), the entering parcels all have the same composition and are at their highest concentration. Hence, the reaction rate is maximal in the unstirred reactor if the rate law is a simple power law in reactant concentrations, and the rate decreases as the stirring rate is raised and as the feedstream is mixed into the already aged and partly reacted reactor bulk.

While the various mixing models described in the literature[2] allow one to simulate stirring and mixing effects with varying degrees of success, not much is known about the causal links between the mechanism of a reaction and the stirring and mixing effects it exhibits. For instance, we do not generally know whether a given reaction responds to decreased stirring with decreased or increased rate or conversion, as the surprisingly opposite stirring responses of the bistability hystereses in the minimal bromate system[3,4] and in the Belousov−Zhabotinsky reaction[5] show.

A key issue in studying stirring and mixing effects is to quantify the reactor inhomogeneity and to relate it to chemical conversion. As a first step in this direction, we analyzed recently[5] the generic case of bistable systems with a single dynamical variable, which requires a single, premixed reactant feedstream. We showed that in this class of system decreased stirring always causes the hysteresis loop to contract inside the high-stirring loop. To distinguish it from other possible and observed[3,4,6] responses, we called this the "stirring effect of the first kind". In the preceding paper (part 1[1]), we studied the stirring effect of the bistable arsenite−iodate system, which shows a stirring effect of the first kind when the reactant streams are premixed, by experiment and by numerical simulation. We used the coalescence−redispersion (CR) model[7] and chose reaction conditions where the system can be described by a single variable. The CR mixing model was chosen because it describes in a simple but physically realistic manner the interaction of feeding, mixing, and chemical reaction and because it provides directly the probability distribution function[1,8] that characterizes the reactor inhomogeneity on a more fundamental level than macroscopic averages do.

The objectives of the present paper are to describe theoretically the stirring effect of the first kind and to use the results to analyze the experimental and numerical data obtained in part

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1. In section 2, the one-dimensional Langevin equation that corresponds to the CR model is derived. Its corresponding Fokker−Planck equation is then solved in section 3, and an analytical expression for the stochastic steady states is obtained. The main results of the analysis are an expression (eq 31) that relates the fluctuation amplitude (reactor inhomogeneity) σ to the forcing of the reactor by the rates of inflow and stirring and a scaling relation (eq 33) between the stirring effect—the shift Δ of the stochastic steady state from its deterministic limit—and the amplitude σ of fluctuations. Finally, the analysis of the numerical and experimental results of part I[1] confirms the validity of the assumptions of the CR model and of the analytical reduction of the model.

2. The Langevin Equation for the CR Model

The CR model regards the CSTR as a collection of N fluid elements or cells that are randomly replaced by fresh reactant and which collide randomly with each other at the respective replacement and mixing rates. The numerical algorithm is described in part 1.[1] At any time t the reactor is characterized by the concentration vector $\{x_1(t), ..., x_i(t), ..., x_N(t)\}$, where $x_i(t)$ is the concentration in the ith cell. Our goal is to obtain closed-form expressions for the average stationary concentration in a CSTR and for the intensity of the reactor inhomogeneity, i.e., for the first and second moments of the stochastic variable x_i, the concentration in the ith cell. In the limit of sufficiently high stirring, one obtains a stochastic representation of the CR model[9] in terms of a one-variable Langevin equation for x_i. To further analyze this Langevin equation, we follow standard procedures described elsewhere.[10,11] The CR model has previously been formulated in terms of integrodifferential equations for the stationary probability distribution of concentrations.[7] These equations, however, have no known analytical solutions; hence, Evangelista *et al.*[13] and Horsthemke and Hannon[14] performed perturbation expansions of the probability distribution with respect to the small parameter $\tau_{\mathrm{mix}}/\tau_{\mathrm{flow}}$ to obtain approximate solutions. To avoid complications related to the analysis of the integrodifferential equation, we present here an alternative, heuristic analysis of the CR model. It leads to a closed-form solution for the stochastic steady states that agrees with the results of Hannon and Horsthemke.[15]

Between feeding and mixing events, each cell evolves according to its batch kinetics

$$\mathrm{d}x_i/\mathrm{d}t = f(x_i) \tag{1}$$

In the well-stirred, deterministic limit, the CSTR is governed by

$$\mathrm{d}x_i/\mathrm{d}t = g(x) = f(x) + k_{\mathrm{flow}}(x_0 - x) \tag{2}$$

where $g(x)$ is given explicitly by eq 6 of part 1 for the arsenite−iodate reaction. Schematically this function is shown in Figure 1 by the solid line.

The stochasticity arises from the random, independent choice of cells because of mixing and feeding. Mixing is described by the stochastic process

$$\chi_{ij}(t) = \begin{cases} 1 & \text{if the } i\text{th and } j\text{th cells are mixed at time } t \\ 0 & \text{otherwise} \end{cases} \tag{3}$$

The probability per unit time that $\chi_{ij}(t) = 1$ is $k_{\mathrm{mix}} = 1/\tau_{\mathrm{mix}}$, and the cumulative probability for the interval Δt is $\Delta t k_{\mathrm{mix}}$. The mixing process is characterized by

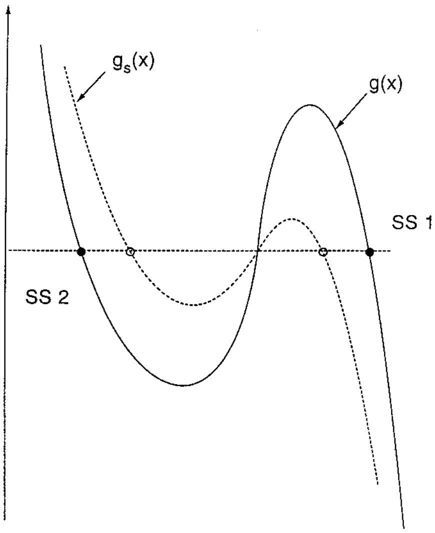

Figure 1. Schematic representation of the deterministic and stochastic rate functions $g(x)$ and $g_s(x)$ defined by eqs 2 and 28, respectively, to illustrate the bistability of the steady-state solutions of $g(x_d) = 0$ and $g_s(x_s) = 0$ and the origins of the shifts $\Delta = x_s - x_d$ of the stochastic steady states x_s (open circles) from their deterministic limits x_d (closed circles).

$$\chi_{ij}\delta x_{ij} = -\chi_{ji}\delta x_{ji} \tag{4}$$

$$\langle\chi_{ij}\rangle = \frac{1}{N^2}\sum_{i,j}^{N}\chi_{ij} = \Delta t k_{\mathrm{mix}} \tag{5}$$

where $\delta x_{ji} = 1/2(x_j(t) - x_i(t))$ is the half the concentration difference prior to mixing the cells.

Feeding is described by the stochastic process

$$\phi_i(t) = \begin{cases} 1 & \text{if the } i\text{th cell is replaced by a new cell} \\ & \qquad \text{with concentration } x_0 \text{ at time } t \\ 0 & \text{otherwise} \end{cases} \tag{6}$$

The probability per unit time that $\phi_i = 1$ is $k_{\mathrm{flow}} = 1/\tau_{\mathrm{flow}}$, and the cumulative probability for the interval Δt is $\Delta t k_{\mathrm{flow}}$.

We derive now an equation for the concentration change $\Delta x_i = x_i(t+\Delta t) - x_i(t)$ in the ith cell due to feeding, mixing, and chemical reaction during the interval Δt. In this representation, mixing and feeding events take place only at discrete times t, $t + \Delta t$, $t + 2\Delta t$, ..., while during the interval Δt, x_i evolves according to the batch kinetics equation (1). Because a cell i cannot undergo feeding and mixing events at the same time, we allow for mixing only at the beginning and for feeding at the end of the interval, but the opposite choice is equally valid and leads to the same result. If the ith cell is mixed with cell j at time t (i.e., $\chi_{ij}(t) = 1$), then the concentration in the ith cell at time $t + \Delta t$ is given by

$$\begin{aligned} x_i(t + \Delta t) &= \frac{x_i(t) + x_j(t)}{2} + \Delta t f\left(\frac{x_i(t) + x_j(t)}{2}\right) \\ &= x_i(t) + \delta x_{ji} + \Delta t f(x_i + \delta x_{ji}) \end{aligned} \tag{7}$$

If no mixing event takes place at t (i.e., if $\chi_{ij}(t) = 0$),

$$x_i(t+\Delta t) = x_i(t) + \Delta t f(x_i(t)) \tag{8}$$

Hence, when mixing takes place with probability $\chi_{ij}(t)$

$$x_i(t+\Delta t) = [1 - \chi_{ij}(t)][x_i(t) + \Delta t f(x_i(t)] + \chi_{ij}(t)[x_i(t) + \delta x_{ji} + \Delta t f(x_i(t)+\delta x_{ji})] \quad (9)$$

If the ith cell is replaced by a new cell at $t + \Delta t$ (i.e., $\phi_i(t+\Delta t) = 1$)

$$x_i(t + \Delta t) = x_0 \quad (10)$$

When both random processes occur concurrently, the concentration in the ith cell is given by

$$x_i(t + \Delta t) = \phi_i(t+\Delta t)x_0 + [1 - \phi_i(t+\Delta t)]\{[1 - \chi_{ij}(t)] \times [x_i(t) + \Delta t f(x_i(t)] + \chi_{ij}(t)[x_i(t) + \delta x_{ji} + \Delta t f(x_i(t)+\delta x_{ji})]\} \quad (11)$$

and its change in the interval by

$$\begin{aligned}\Delta x_i &\equiv x_i(t+\Delta t) - x_i(t)\\ &= \Delta t f(x_i(t)) + \Delta t\chi_{ij}(t)f(x_i(t)+\delta x_{ji} - \Delta t f(x_i(t))\chi_{ij}(t) + \phi_i(t+\Delta t)\{x_0 - x_i(t) + \Delta t\chi_{ij}(t)f(x_i(t)) - \chi_{ij}(t)\delta x_{ji} +\\ &\quad \chi ij(t)f(x_i(t) + \delta x_{ji}) - \Delta t f(x_i(t))\} + \chi_{ij}(t)\delta x_{ji}\end{aligned} \quad (12)$$

In the limit of high stirring $\delta x_{ji}(t) \ll x_i(t)$, the last term may be neglected. Performing a Taylor expansion of f near $x_i(t)$ and keeping only terms that are linear in δx_{ji}, one obtains

$$\Delta x_i = \Delta t f(x_i(t)) + \Delta t\chi_{ij}(t)\delta x_{ji}f'(x_i(t)) + \phi_i(t+\Delta t)\{x_0 - x_i(t) - \chi_{ij}(t)\delta x_{ji} - \Delta t\chi_{ij}(t)\delta x_{ji}f'(x_i(t)) - \Delta t f(x_i(t))\} \quad (13)$$

The stochastic feeding process is now replaced by a constant process[16] whose value is equal to its time average: $\phi_i(t+\Delta t) \to k_{\text{flow}}\Delta t$. Thus,

$$\begin{aligned}\Delta x_i &= \Delta t\{f(x_i(t)) + k_{\text{flow}}(x_0 - x_i(t)) + (f'(x_i(t)) - k_{\text{flow}})\chi_{ij}(t)[\delta x_{ij}]\} + O^2\\ &= \Delta t\{g(x_i(t)) + g'(x_i(t))\chi_{ij}(t)[\delta x_{ij}]\} + O^2\end{aligned} \quad (14)$$

where $[\delta x_{ij}]$ is the average value of δx_{ij} when the flow occurs as just described, and $O(2)$ denotes terms containing $(\Delta t)^2$.

In the limit $\Delta t \to 0$, eq 14 reduces to the Langevin equation for the evolution of the concentration in a representative cell i (i.e., a "local" variable)

$$dx/dt = g(x) + g'(x)\xi(t) \quad (15)$$

where the index i has been dropped and $\xi(t)$ is a random process defined by

$$\xi(t) = \chi_{ij}[\delta x_{ji}] \quad (16)$$

To analyze the Langevin equation (15), we first characterize the properties of process $\xi(t)$. When this is done, it is sufficient to obtain the expression for the mean value of the process and its correlation function $\langle\xi(t)\xi(t')\rangle$, where $\langle\ \rangle$ symbolizes averaging over an ensemble of systems. It follows from the antisymmetry of $\chi_{ij}(t)$, given by eq 4, that

$$\langle\xi(t)\rangle = 0 \quad (17)$$

An estimate of the autocorrelation function follows from analyzing eq 16. For this purpose one should rewrite it at times t and $t + \Delta t$, multiply the results, and perform the averaging. This is done explicitly in Appendix 1. Finally, we obtain

$$d\langle\xi(t)\xi(t')\rangle/dt = -k_{\text{mix}}\langle\xi(t)\xi(t')\rangle \quad (18)$$

which implies that the process $\xi(t)$ is characterized by an exponentially decaying correlation function:

$$\langle\xi(t)\xi(t')\rangle = Ae^{-k_{\text{mix}}|t-t'|} \quad (19)$$

The value of the initial amplitude A is given by the initial condition of eq 18. It may be estimated as follows. The main source of fluctuations in the CSTR is its forcing by the feeding process. This is characterized by the frequency k_{flow} of replacing a cell by a new one with concentration x_0. Therefore, the change of concentration due to this perturbation is approximately $x_s - x_0$, where x_s is the steady-state concentration. The fraction of these cells is proportional to k_{flow}. Using the assumption that the concentration of all other cells lies near the steady state x_s (i.e., $\delta x_{ij} \ll x_s$), the fraction of the rest of the cells is proportional to the chemical relaxation time, given by $-g'(x_s)$. In Appendix 2 we show that the initial perturbation may be estimated as

$$A = -\frac{k_{\text{flow}}}{g'(x_s)}(x_s - x_0)^2 \quad (20)$$

The simplest way of analyzing eq 15 is to go to the limit of white noise—a good approximation for weakly colored noise.[17] This is achieved by formally substituting $\exp(-k_{\text{mix}}t) \to 1/k_{\text{mix}}\delta(t)$, giving the correlation function

$$\langle\xi(t)\xi(t')\rangle = D\delta(t - t') \quad (21)$$

where

$$D = \tau_{\text{mix}}A = -\frac{\tau_{\text{mix}}}{\tau_{\text{flow}}}\frac{(x_s - x_0)^2}{g'(x_s)} \quad (22)$$

In the well-stirred limit τ_{mix}, $D \to 0$, one recovers the deterministic rate law (eq 2). As expected, fluctuations diverge as the bifurcation $g'(x_s) \to 0$ is approached. Our analysis treats only steady states sufficiently far from the bifurcation points. However, this restriction is of little practical importance because *noise-induced transitions* occur long before the bifurcation points are reached.

2.1. Analysis of the Langevin Equation. We further analyze eq 15 by introducing the density distribution $P(x,t|x_0,t_0) \equiv P(x,t)$ for the conditional probability of finding the system at a point x at time t, provided that it was at x_0 at time t_0. The evolution of this probability density is governed by a Fokker−Planck equation that can be obtained from eq 15 by the standard techniques[10,11]

$$\partial_t P(x,t) = -\partial_x(g(x)P(x,t)) + D(x_s)\partial_{xx}(g'(x)^2P(x,t)) \quad (23)$$

where the Stratonovich interpretation[10] of the white-noise approximation of eq 15 is used. The stationary solution of eq 23 is[12]

$$P_s(x) = \frac{N}{g'(x)}e^{U(x)/D} \quad (24)$$

where N is a normalizing factor and $U(x)$ is given by

$$U(x) = \int^{x} \frac{g(x)\,\mathrm{d}x}{g'(x)g'(x)} \tag{25}$$

For a bistable system, the probability distribution has two maxima which correspond to the stochastic steady states. They are obtained from the stationary condition $\mathrm{d}P(x)/\mathrm{d}x = 0$:

$$g(x_{\rm s}) - D(x_{\rm s})g'(x_{\rm s})g''(x_{\rm s}) = 0 \tag{26}$$

or, using eq 22

$$g(x_{\rm s}) + \frac{\tau_{\rm mix}}{\tau_{\rm flow}}(x_{\rm s} - x_0)^2 g''(x_{\rm s}) = 0 \tag{27}$$

The roots of eq 27 give the position of the stochastic steady states $x_{\rm s}$. By analogy with the definition of deterministic steady states $g(x) = 0$, we introduce the *stochastic rate function*

$$g_{\rm s}(x) = g(x) - D(x)g'(x)g''(x) \tag{28}$$

which is schematically drawn in Figure 1 together with $g(x)$. Both functions intercept the abscissa at different points, reflecting the effect of stirring on the steady states.

The variance of x is given by[10]

$$\begin{aligned}\langle \delta x^2 \rangle &= \frac{-2D(x_{\rm s})}{U''(x_{\rm s})} \\ &= \frac{-2Dg'}{1 - 2D(g''^2/g')} \qquad \text{using eqs 20 and 26} \\ &= 2\frac{\tau_{\rm mix}}{\tau_{\rm flow}}(x_{\rm s} - x_0)^2 \frac{1}{1 + \frac{\tau_{\rm mix}}{\tau_{\rm flow}}(x_{\rm s} - x_0)^2 (g''/g')^2}\end{aligned} \tag{29}$$

At sufficiently high stirring, $(\tau_{\rm mix}/\tau_{\rm flow})(x_{\rm s} - x_0)^2(g''/g')^2 \ll 1$ and eq 29 reduces to

$$\langle \delta x^2 \rangle = 2\frac{\tau_{\rm mix}}{\tau_{\rm flow}}(x_{\rm s} - x_0)^2 \tag{30}$$

Because this is the variance of the concentration in a single representative cell, we refer to it also as the *local variance* $\sigma_{\rm l}^2$ to distinguish it from the *global variance* $\sigma_{\rm g}^2$ of the concentration, averaged over the whole reactor. The relation of these two quantities and their measurement is discussed elsewhere.[9,18]

The *degree of spatial inhomogeneity* of the reactor

$$\sigma_{\rm l}^2 = 2\frac{\tau_{\rm mix}}{\tau_{\rm flow}}(x_{\rm s} - x_0)^2 \tag{31}$$

is a consequence of the stochastic process $\xi(t)$, specified by eqs 19 and 20; i.e., it results from the forcing of the reactor by the inflow. We will show that this equation correctly reproduces both the CR model and the experiments.

Finally, the stirring effect on the steady states is defined as the shift $\Delta = x_{\rm s} - x_{\rm d}$ of the stochastic steady state $x_{\rm s}$ from its deterministic, high stirring limit $x_{\rm d}$. The latter are the roots of $g(x_{\rm d}) = 0$, and the stochastic steady states $x_{\rm s}$ are the roots of eq 26, as illustrated by Figure 1. Substituting and performing a Taylor expansion to first order in Δ leads to

$$\Delta = \frac{1}{4}\left[\frac{g''(x_{\rm d})}{g'(x_{\rm d}) - \frac{1}{4}\sigma_{\rm l}^2 g'''(x_{\rm d})}\right]\sigma_{\rm l}^2 \tag{32}$$

Sufficiently far from the transition points, this expression for the *shift of the steady state* reduces to

$$\Delta = \frac{1}{4}\frac{g''(x_{\rm d})}{g'(x_{\rm d})}\sigma_{\rm l}^2 \tag{33}$$

In the range of validity of this key result (i.e., at sufficiently high stirring and far from the transition), the observed shift Δ of the stochastic steady state is proportional to the reactor inhomogeneity $\sigma_{\rm l}^2$. For fixed control parameters (varying only the stirring rate), the relationship is linear and the direction of the shift is determined by the sign of $g''(x_{\rm d})$, because $g'(x_{\rm d})$ is always negative as $x_{\rm d}$ is a stable state. We show below that eq 33 allows one to make general conclusions regarding the stirring effect on bistability hystereses in one-variable systems.

3. Data Analysis

The purpose of part 1[1] was to test the agreement between the experimentally measured stirring effect in the bistable arsenous acid–iodate reaction and the numerical simulations based on the coalescence redispersion model. That comparison involved the average signals $x_{\rm s}(S)$ (stochastic steady states or first moment of the fluctuating signal), as well as the noise intensity (or second moment of the fluctuating signal) and the probability distribution functions (pdf's), all as functions of stirring or mixing rate. In the present section the analytical results of the previous section are compared with experimental and numerical results, obtained in part 1.

To verify eq 31, the dependences of the experimental and calculated noise intensities $\sigma_{\rm l}^2$ were tested for both steady states as functions of all arguments in the equation. Figures 2 and 3 show $\sigma_{\rm l}^2$ as functions of the inverse stirring rate $1/S$ for the experiments and of the mixing time $\tau_{\rm mix}$ for the simulated data, respectively. Best straight lines through the origin connect the data points. Unconstrained least-squares fits miss the origin by amounts that are insignificant, given the scatter of data points. There appears to be a slight deviation from linearity near the origin, i.e., in the limit of high stirring. Its origin is unclear because there are no limitations on the theory in this limit.

The dependence of $\sigma_{\rm l}^2$ on the feed concentration x_0 was also studied at constant mixing and feeding rates. Only the simulation data are given in Figure 4, because the experimental data are very similar. The straight line fits the data points extremely well over the full range. The slopes of the fitted lines are sufficiently close to the theoretical value to confirm the validity of eq 31. The linear dependence of the stirring effect $\Delta(\sigma^2)$ (eq 32) was tested, and the results are summarized in Figures 5 and 6 by plotting the measured (Figure 5) and calculated shifts (in Figure 6) as functions of the fluctuation intensity, where stirring rate S and $\tau_{\rm mix}$, respectively, were the independent variables. The straight lines through the data points and the origin agree well with the predictions of eqs 31 and 32 over the full range of stability of the competing steady states.

The response diagram (Figure 7) illustrates again[1] the pronounced stirring effect on SS1 and the relative insensitivity of SS2. Its purpose is to compare the stochastic steady states $x_{\rm s}$ calculated from eq 26, given here by the dashed curves, with

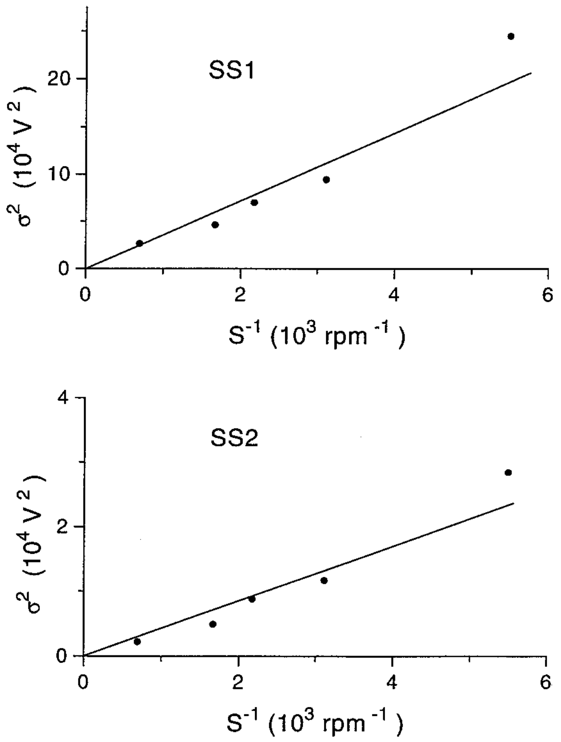

Figure 2. Dependence of the experimentally measured noise intensity (second moment of the fluctuating electrode potential) σ^2 on the inverse stirring rate. $[I^-]_0 = 1 \times 10^{-5}$ M for SS1. $[I^-]_0 = 1.5 \times 10^{-5}$ M for SS2. The remaining experimental parameters are the same as those in part 1.

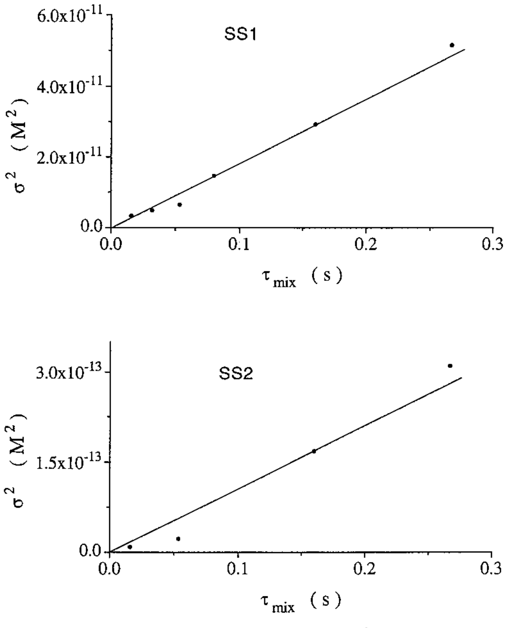

Figure 3. Dependence of the noise intensity σ^2 on mixing time. Data points were simulated by the CR model. The line was constrained to go through the origin to demonstrate the validity of eq 31. $\tau_{\text{flow}} = 1.6$ s; $[I^-]_0 = 4 \times 10^{-5}$ M for both steady states.

the numerical results obtained from simulations of the CR model, as described in ref 1. The latter are given by the data points.

4. Discussion

The reduction of the CR model to the Langevin equation (15) is based on the assumption that the intensity of noise is sufficiently small. Further assumptions were made to obtain eq 26 for the stochastic steady state. The inflow is taken to represent a constant perturbation, leading to the colored noise with correlation function equation 19. This perturbation is small enough that only a small fraction of cells ($\tau_{\text{mix}}/\tau_{\text{flow}} \ll 1$) is replaced by reagents. Both conditions are well met in typical CSTR experiments. The forcing of the reactor is balanced by chemical reaction which tends to increase the concentration in each cell. As a result, the system finds itself in a stochastic steady state at any finite value of the mixing rate. Near the critical points, the transitions are in reality noise-induced transitions between stochastic steady states.

The noise intensity (eq 20) is determined by forcing through the inflow and by imperfect mixing. The perturbation caused by the inflow decays with a finite relaxation time. According to eq 32, the reactor inhomogeneity σ_I^2 is thus the "cause" of the stirring effect $\Delta(k_{\text{mix}})$, and both are linearly related.

In summary, the conditions of validity of the present considerations are (1) the system behaves effectively as one-dimensional, (2) experiments involve a single, premixed reactant flow, and (3) the stirring rate is sufficiently high. In the reactor described in ref 1, deviations from the linear predictions become appreciable below $S < 30-50$ rpm.

When these conditions are fulfilled, the system can exhibit only a stirring effect of the first kind. It arises as the system responds chemically to the perturbations due to feeding and incomplete mixing. This response is governed by the sign of the curvature $g''(x)$. Figure 1 illustrates that the curvature of the rate function is always negative at SS1 and positive at SS2. Consequently, the upper branch shifts down and the lower branch shifts up as the noise intensity increases (Figures 6 and 7).

Analysis of Figure 1 and of eq 32 also gives the correct direction of shift of the critical points. The stochastic steady states correspond to the intersections of the stochastic rate function $g(x_s)$, defined by eq 26 with the x axis. Assume that decreasing the control parameter shifts the function $g(x)$ down. This is equivalent to moving the x axis up and keeping $g(x)$ fixed. Below a critical value C_1 of the control parameter, SS1 disappears and the x axis intersects $g(x)$ only once. The corresponding stochastic critical value C_1^s where the x axis is tangent to the stochastic rate function $g_s(x)$ lies at a higher value of the control parameter. Hence, in the presence of noise, the left critical point shifts to the right, and by the same argument the right critical point moves to the left. This agrees with Figure 7, even if the magnitude of the shift of the right critical value is too small to be resolved by our experiment. So, eq 32 gives qualitatively correctly the direction of the shifts of the steady states and of the critical points: as the reactor inhomogeneity is made to grow, the hysteresis shrinks along both coordinates of the response diagram.

The quantitative expression for this generic behavior is given by eq 26, the expression for the stochastic steady states. It gives the stochastic steady states as the roots of a polynomial in the same way as the solutions of $g(x) = 0$ represent the deterministic steady states. In the limit of ideal mixing ($\tau_{\text{mix}} \rightarrow 0$), the second term in eq 26 vanishes and the equation reduces to the deterministic limit. Therefore, the second term in eq 26 represents the stochastic effects. From the expression for this stochastic term, it follows that the stirring effect increases as the stirring rate decreases, the flow rate increases, and the difference between the inflow and bulk concentration grows. The stirring effect is most pronounced when $g''(x)/g'(x)$ is large. This rate reflects the influence of chemical relaxation.

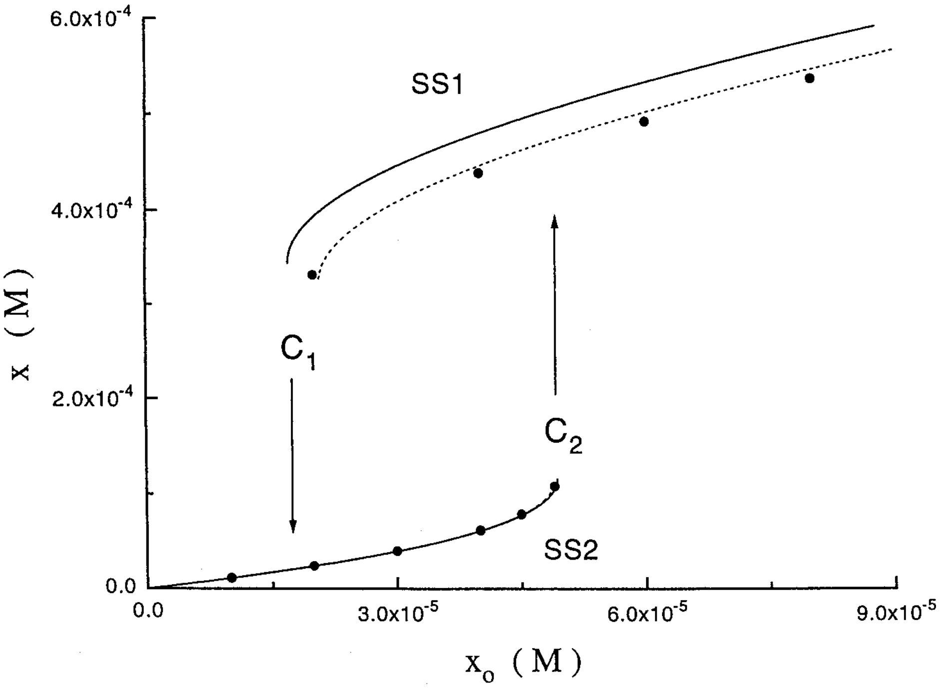

Figure 4. Linear relation between σ^2 and $(\tau_{mix}/\tau_{flow})(x_s - x_0)^2$ calculated for both steady states, where x_0 was the independent variable, at fixed $\tau_{mix} = 0.0533$ s and $\tau_{flow} = 1.6$ s.

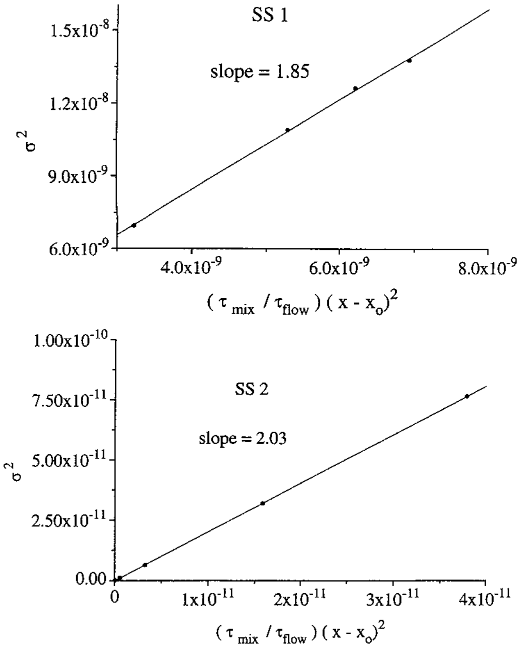

Figure 5. Experimental relation between the shifts $\Delta(S) = x_s(S) - x_s(S_{max})$ of the steady states at stirring rate S from the "high stirring limit" at $S_{max} = 2000$ rpm and $(x - x_0)$. For SS1, $[I^-]_0 = 1 \times 10^{-5}$ M, and for SS2, $[I^-]_0 = 1.5 \times 10^{-5}$ M. All other parameters are the same as those in part 1.

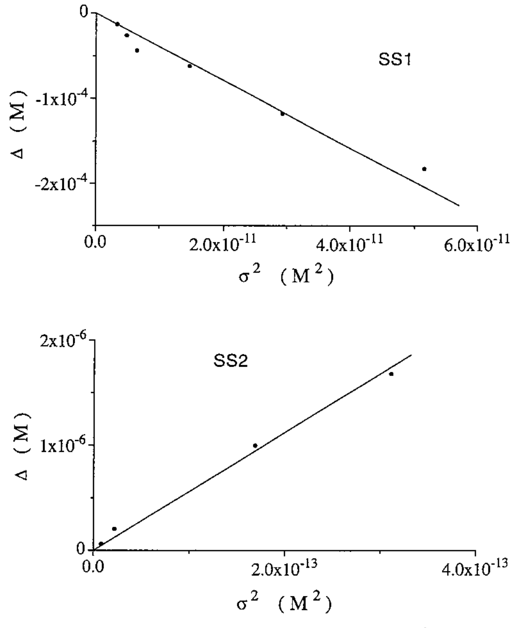

Figure 6. Linear relationship between Δ and σ^2 obtained from simulations, where τ_{mix} is the independent variable. Parameters are $\tau_{flow} = 1.6$ s and $[I^-]_0 = 4 \times 10^{-5}$ M.

Equation 32, the linear approximation of eq 26, is useful for analyzing experimental data, specifically the proportionality between the observed shift Δ, or the first moment of the signal, and the fluctuation intensity, or second moment σ_I^2. For both branches independently, the coefficient of proportionality $g''(x)/g'(x)$ increases slightly as the critical points are approached on either branch. Hence, the shifts Δ of the steady states increase as the critical points are approached. Figures 5 and 6 illustrate this kind of behavior for experiment and simulations, respectively. It is important to note that this growth of the shift with decreasing stirring rate follows from the condition that $g''(x)/g'(x)$ estimated at the deterministic steady state is affected only by the control parameter x_0, whereas the intensity of fluctuations is affected only by the stirring rate. Therefore, the flow rate is not an appropriate bifurcation parameter for studying stirring effects. Indeed, the mixing time in eq 26 appears only as a ratio τ_{mix}/τ_{flow}. Under certain conditions, the effect of a decreasing flow rate is the same as that of an increasing mixing rate. Moreover, varying the flow rate changes the entire hydrodynamic picture of inflow and mixing in a CSTR. This may lead to complications in applying the results of our theoretical consideration. Hence, the inflow concentration x_0 is the most suitable bifurcation parameter for studying stirring effects in nonlinear chemical systems.

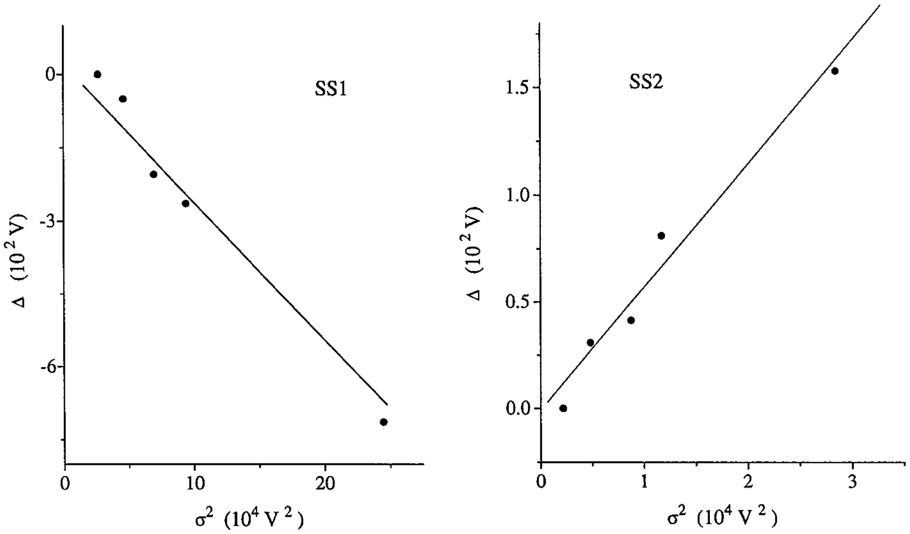

Figure 7. Response diagram $x_s(x_0)$, calculated from the CR model. Dots represent the results of the simulations, at $\tau_{\mathrm{mix}} = 0.0533$ s, $\tau_{\mathrm{flow}} = 1.6$ s and $[I^-]_0 = 8 \times 10^{-5}$ M. Dashed lines represent the stochastic steady states x_s calculated from eq 26. The solid line represents the deterministic hysteresis.

The linear relation (32) illustrates the fluctuation−dissipation theorem according to which the linear system response is given by the autocorrelation function of the fluctuations.[19] In particular, eq 32 is similar to an expression obtained by Hannon and Horsthemke[15] for the model of the arsenate−iodate reaction. Their analysis is based on the integrodifferential equation of the Fokker−Planck type for the pdf from which one can deduce the expression for the shift of the deterministic steady state under incomplete mixing. Our analysis gives the explicit eq 26 for the stochastic steady states. It is based on the representations of the CR model by a Langevin equation at high stirring rate and of incomplete mixing as a multiplicative colored noise process. The validity of this approach is confirmed by the good correspondence between experiments, simulations, and theoretical results.

The only known exceptions from the stirring effect of the first type are the minimal bromate system oscillator[3,4] and the Briggs−Rauscher reaction,[6] both in a CSTR. In the minimal bromate system the fluctuations were controlled through the stirring rate, as described above, while in the light-sensitive Briggs−Rauscher reaction a fluctuating light source was used for that purpose. In both systems the *hysteresis loop was found to broaden and to shift outside the low-noise hysteresis, as the external noise intensity (due to mixing or to light) grows*. This type of “stirring effect of the second kind” might be explained along the lines developed in this paper by taking into account the essential multidimensionality of the reacting systems. Indeed, if a system is effectively one-dimensional, a stirring effect of the first type is necessarily observed. Equation 32 indicates that in the one-dimensional case the direction of the shift is governed by the curvature of the rate function. As a possible extension of this result, we may assume that in the multidimensional case the direction of the shift is also governed by the generalized curvature of the rate function, which becomes a vector which may have positive and negative components. As a result, the hysteresis may shift in a complex manner and a priori in any direction, depending on the components of this vector, when projected into the 1D response diagram.

Finally, the analysis performed in this paper suggests a new way of utilizing the stirring effect on chemical bistability as a taxonomic tool. If the hysteresis shrinks in response to decreased stirring and both branches are stabilized (stirring effect of the first type), the system may be considered as *effectively* one-dimensional. Otherwise, the appropriate kinetic model must be at least two-dimensional.

Appendix 1

Our aim is to derive the autocorrelation function $C(t,t') = \langle \xi(t)\xi(t')\rangle$, defined by eq 16 for the random process $\xi(t)$. Consider first the change of the autocorrelation function in the time interval $\Delta t'$:

$$\begin{aligned}\Delta C(t,t',\Delta t') &= C(t,t'+\Delta t') - C(t,t') \\ &= \langle \xi(t)\xi(t'+\Delta t') - \xi(t)\xi(t')\rangle \\ &= \langle \chi_{ij}(t)[\delta x_{ji}(t)]\chi_{ij}(t'+\Delta t')[\delta x_{ji}(t'+\Delta t')] - \\ &\qquad \chi_{ij}(t)[\delta x_{ji}(t)]\chi_{ij}(t')[\delta x_{ji}(t')]\rangle \quad (34)\end{aligned}$$

By introducing changes of $\chi(t')$ and $\delta x_{ji}(t')$ during the same time interval

$$\Delta\chi_{ij}(t',\Delta t') = \chi_{ij}(t'+\Delta t') - \chi_{ij}(t')$$

$$\Delta\delta x_{ji}(t',\Delta t') = \delta x_{ji}(t' + \Delta t') - \delta x_{ji}(t')$$

Equation 34 may be rewritten in the following form:

$$\begin{aligned}\Delta C(t,t',\Delta t') &= \langle \chi_{ij}(t)[\delta x_{ji}(t)]\Delta\chi_{ij}(t',\Delta t')[\delta x_{ji}(t')]\rangle + \\ &\quad \langle \chi_{ij}(t)[\delta x_{ji}(t)](\chi_{ij}(t') + \Delta\chi_{ij}(t',\Delta t'))[\Delta\delta x_{ji}(t',\Delta t')]\rangle \quad (35)\end{aligned}$$

The second term in this expression may be omitted because on average its leading term contains $\Delta t'^2$. To simplify the analysis, we assume that $t = t'$. This allows us to rewrite eq 35 as

$$\Delta C(t,t,\Delta t) = \langle \chi_{ij}(t)[\delta x_{ji}(t)]\chi_{ij}(t)[\delta x_{ji}(t)]\Delta\chi_{ij}(t,\Delta t)\rangle \quad (36)$$

The last term in this expression $\chi_{ij}(t,\Delta t)$ depends on $\chi_{ij}(t)$. Namely, if $\chi_{ij}(t) = 1$, then $\chi_{ij}(t,\Delta t) = -1$ with probability $1 - k_{\mathrm{mix}}\Delta t$. Otherwise, the product in brackets equals zero. Therefore, the right side of this equation is always negative. Moreover, the conditional probability that it is not zero is defined by the condition that $\chi_{ij}(t) = 1$, given by $k_{\mathrm{mix}}\Delta t$. Finally we arrive at

$$\Delta C(t,t,\Delta t) = -k_{\mathrm{mix}}\Delta t\langle \chi_{ij}(t)[\delta x_{ji}(t)]\chi_{ij}(t)[\delta x_{ij}(t)]\rangle \quad (37)$$

which gives eq 18.

Appendix 2

Here we derive eq 20 for the amplitude A of the inflow perturbation. Assuming that the initial concentration of the ith cell lies near its steady state, the corresponding concentration change may be estimated as

$$\Delta x_i = x_0 - x_i \approx x_0 - x_s \tag{38}$$

Therefore, the initial condition for the autocorrelation function is given by

$$A = \frac{N_f}{N}(x_0 - x_s)^2 \tag{39}$$

where N_f is the number of cells perturbed by the inflow and N is the total number of cells. The number of cells unperturbed by the inflow is $N_s = N - N_f$.

At every moment the following condition must hold:

$$\langle \delta x_i(t)\rangle = \frac{1}{N}\sum_{i=1}^{N}\delta x_i(t) = 0 \tag{40}$$

Denoting by δx_f the average perturbation of a single cell by the inflow and by δx_s the average perturbation of a single cell among the remaining cells, one may rewrite this condition as

$$N_s\delta x_s + N_f\delta x_f = 0 \tag{41}$$

This gives the following relation between δx_s and δx_f:

$$\delta x_s = -\frac{N_f}{N_s}\delta x_s \tag{42}$$

The ratio N_f/N may be estimated, based on the correspondence between stochastic and deterministic description of dynamics in a CSTR in the limit of perfect mixing. For this purpose, we rewrite eq 13

$$\Delta x_i = (1 - \phi_i(t+\Delta t))\Delta t f(x_i(t)) + \phi_i(t+\Delta t)(x_0 - x_i(t)) \tag{43}$$

Averaging both sides of this equation gives

$$\langle \Delta x_i\rangle = \Delta x = \langle \Delta t f(x_i(t))\rangle - \langle \phi_i(t+\Delta t)\Delta t f(x_i(t)\rangle + \langle \phi_i(t+\Delta t)x_0\rangle - \langle \phi_i(t+\Delta t)x_i(t))\rangle \tag{44}$$

where the second term may be neglected because its first nonzero term contains Δt^2. Performing the Taylor expansion near steady state results in

$$\Delta x = \Delta t\langle f(x_s)\rangle + \Delta t\langle f'(x_s(t)\delta x_i(t)\rangle + \langle \phi_i(t+\Delta t)x_0\rangle - \langle \phi_i(t+\Delta t)x_s\rangle - \langle \phi_i(t+\Delta t)\delta x_i(t)\rangle \tag{45}$$

Using the property $\langle \phi_i(t)\rangle = k_{flow}\Delta t$ of the stochastic feeding process, we arrive at

$$\Delta x = \Delta t f(x_s) + k_{flow}(x_0 - x(t)) + \langle \Delta t f'(x_s)\delta x_i(t) - \phi_i(t+\Delta t)\delta x_i(t)\rangle \tag{46}$$

where the first two terms give explicitly the deterministic equation. Therefore, in the perfect mixing limit the last term vanishes:

$$\begin{aligned} 0 &= \langle \Delta t f'(x_s)\delta x_i(t) - \phi_i(t+\Delta t)\delta x_i(t)\rangle \\ &= \Delta t f'(x_s)\delta x_s - k_{flow}\Delta t\delta x_f \end{aligned} \tag{47}$$

Substituting δx_s from eq 42 gives

$$0 = \Delta t\delta x_f(N_s f'(x_s) + N_f k_{flow}) \tag{48}$$

The last expression holds for any value of δx_f if

$$\frac{N_f}{N} = -\frac{k_{flow}}{g'(x_s)} \tag{49}$$

Substituting this into eq 39 gives the final result of eq 20.

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