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Inhomogeneities of CSTR on a Macroscale Due to Spatial Dependence of Micromixing Time: The BZ Reaction

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Macroscopic concentration gradients are measured through spatial microelectrode scans in the most turbulently stirred zone of a CSTR on both steady states of the bistable Belousov−Zhabotinsky reaction. The concentration distribution that exists on the macroscale is shown to arise indirectly from the spatial dependence of the micromixing time through the coupling of chemical reaction with micromixing.

1. Introduction

Stirring effects on nonlinear reactions in continuous flow stirred tank reactors (CSTR) demonstrate that the notion of the "well-stirred reactor" is an idealization and that the rate and dynamics of nonlinear systems may depend sensitively on reactor inhomogeneities.[1,2] The nature, origin, and dynamical consequences of reactor inhomogeneities are important for the correct interpretation of CSTR and rapid flow kinetics experiments[3] and for practical applications, since stirring and mixing are crucial and nontrivial steps in industrial processes.

Inhomogeneities in CSTRs are thought to arise passively through the incomplete, hydrodynamic mixing of the feedstream(s) into the reactor bulk, and they cover a wide range of length scales: large-scale mixing or macromixing entrains the feedstream(s), blends them into the reactor bulk, and reduces concentration gradients on the macroscale of the reactor. Concurrently, the feedstream packets undergo a turbulent stretching-and-folding process known as micromixing that reduces them to successively smaller, fractal eddies down to the Kolmogorov-length scale. The final dissipation of these eddies occurs by molecular diffusion.[4]

The purpose of the present work is to show that there exists also an indirect, reactive mode by which macroscopic concentration gradients arise in reactive flows through the coupling of chemical reaction with the inhomogeneous hydrodynamic flow field that always exists in a CSTR.[5] In a recent CSTR experiment[6,7] a microelectrode was scanned across the reactor just below the stirrer, using the bistable chlorite−iodide system. Surprisingly large,[1] stationary concentration gradients were observed on the macroscopic scale of the reactor in the most intensely stirred, turbulent zone of the CSTR, where the circulation and macromixing rates are sufficiently high to let one expect a much higher degree of homogeneity than what is actually observed. At a stirring rate of 880 rpm the concentration monitored by a Pt-electrode changed by 800% between the axis and the tip of the propeller stirrer.

To rationalize this finding,[6] two facts have to be taken into account: first, the turbulent flow field is highly inhomogeneous and anisotropic,[2] as expressed for instance by the scalar field of energy dissipation density $\epsilon(r)$. Its highest values are near the tip and edge of the stirrer blade, and the lowest values are found in stagnant dead zones in the far corners of the reactor. Second, the potential of a spatially fixed Pt-microelectrode $E(S)$, which monitors the logarithm of the concentration of a readily oxidized species, shows a marked dependence on stirring rate S, the usual macroscopic stirring effect. Consequently, the inhomogeneous turbulence makes the local micromixing time $\tau_{\mathrm{mix}}(r)$ dependent on spatial position and gives rise to a spatial dependence of the stirring effect.

We possess now a quantitative description of stirring effects in bistable systems with one variable.[9−11] In such systems the hysteresis contracts, in response to reduced stirring, inside the high-S loop, and the steady states approach each other. This "stirring effect of the first kind" is also observed in some multivariable systems which may be termed "effectively one-dimensional", among them the Belousov−Zhabotinsky (BZ) reaction,[9] the chlorite/iodide reaction,[12,13] and the arsenite/iodate system.[10,11] To show the connection between the stirring dependence of the steady states and concentration gradients in nonlinear chemical systems, we chose here the bistable Belousov−Zhabotinsky reaction, using a single, premixed feedstream, to be able to analyze the results by the one-dimensional theory.[9,11]

2. Experiments

The experiments were conducted in a cylindrical plexiglass CSTR described elsewhere[9,10] at $T = 36$ °C. To maximize turbulence, the reactor was fitted with four vertical, 5 mm wide baffles and with a rectangular impeller (8 × 15 mm, stainless steel coated with Teflon), positioned 30 mm above the bottom of the reactor. The spatial dependence of the system state in the CSTR was monitored by a Pt-microelectrode (20 μm diameter Pt-wire fused in glass and trimmed to ~30 μm length) which was mounted radially, 25 mm above the bottom of the reactor on a micrometer for spatial scans, relative to a $Hg/HgSO_4$ reference electrode. The microelectrode could be moved 20 mm in a radial direction. In addition, the state of the system was monitored by a space-fixed Pt electrode (0.1 mm Pt-wire fused in glass) relative to a $Hg/HgSO_4$ reference electrode. The impedance-matched electrode signals were fed via an A/D converter into a personal computer.

The single feedstream was peristaltically pumped into the high-turbulence zone of the reactor through a single tube located just below the impeller blade, at a rate of 5.97 mL/min,

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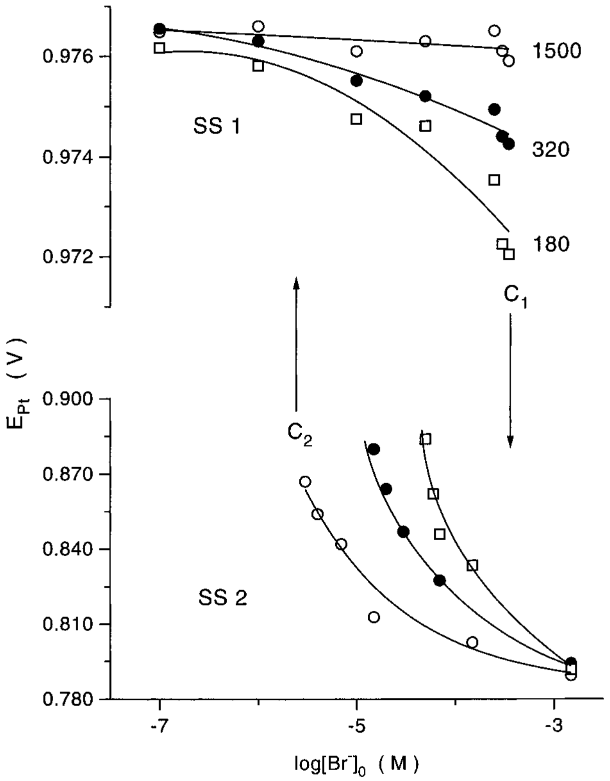

Figure 1. Dependence of the system response (first moment of the Pt-electrode signal) on the control parameter at different stirring rates (rpm).

corresponding to a residence time of $\tau_0 = 282$ s. Reactants, prepared from analytical grade chemicals, were stored in three solutions: (1) 8.1×10^{-3} M $NaBrO_3$; 4.35×10^{-3} M $Ce_2(SO_4)_3$ and (2) 0.03 M malonic acid; (3) the third solution contained NaBr, whose concentration ($[Br^-]_0$) was used as a control parameter to map a hysteresis. In addition, each solution contained 1.5 M H_2SO_4. Feedstreams 2 and 3 were premixed and subsequently combined with feedstream 1 in two T-shaped capillary tubes just prior to entering the reactor. To find the spatial gradients in an oscillatory regime we also changed the malonic acid concentration.

3. Results and Discussion

Figure 1 shows the hysteresis at three different values of the stirring rate (*S*). Decreasing *S* shifts the upper branch (SS 1) down and shifts the lower branch (SS 2) up; that is, the system exhibits a stirring effect of the first kind. This stirring dependence of the position of steady states indicates a possibility for the existence of concentration gradients in a CSTR. Figure 2 gives the spatial dependence of the time-averaged microelectrode potential *E*(*r*) at three stirring rates for SS 1 and SS 2. The error bars represent the amplitude of fluctuations. The parameter values, given in the caption, correspond to a bistable state near the transition from SS 1 to SS 2. Additional experiments at lower values of the control parameter $[Br^-]_0$ or at higher values of the malonic acid concentration give qualitatively similar results.

This description of spatial gradients in a CSTR is based on the analysis of the stirring dependence of the steady states, taking into account the spatial dependence of the hydrodynamic parameters. Recently we showed[10] that a stirring effect of the first kind occurs in bistable systems with one dynamical variable.

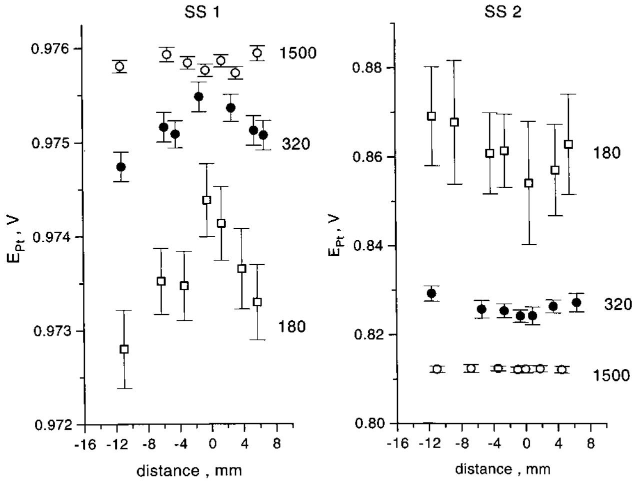

Figure 2. Spatial dependence of the Pt-microelectrode potential in bistable regime ($[Br^-]_0 = 1.5 \times 10^{-4}$ M).

The effect was described by the coalescence-redispersion (CR) model, which takes into account only the micromixing process as random collisions of turbulent eddies. The CR model is adequately represented by the following Langevin equation for the concentration *x* which fluctuates due to the stochastic mixing and feeding:[11]

$$\frac{dx}{dt} = g(x) + g'(x)\,\xi(t) \tag{1}$$

where the function $g(x) = f(x) + k_0(x_0 - x)$ is the rate law for the deterministic case, i.e., for well-stirred conditions, $f(x)$ represents the chemical relaxation, k_0 is the inverse residence time ($k_0 = 1/\tau_{flow}$), and x_0 is the inflow concentration. The fluctuations are accounted for by the stochastic process $\xi(t)$, whose correlation function, in the white-noise approximation, is given by

$$\langle \xi(t)\,\xi(t')\rangle = 2D(x_s)\,\delta(t - t') \tag{2}$$

with constant intensity of fluctuations $D(x_s)$ that depends on the value of the stochastic steady state $x_s = \langle x \rangle$.

$$D(x_s) = \frac{1}{2}\frac{\tau_{mix}}{\tau_{flow}}\frac{(xs - x_0)^2}{g'(x_s)} \tag{3}$$

The stirring effect is conveniently represented as the shift Δ of a given stochastic steady state x_s from the deterministic state x_d.

$$x_s = x_d + \Delta \tag{4}$$

where x_d is a solution of the equation $g(x) = 0$. Assuming that the shift Δ is sufficiently small, a straightforward analysis of eq 1 gives the following estimate for the position of the steady states:[11]

$$\Delta = \alpha(x_d)\tau_{mix} \tag{5}$$

where

$$\alpha(x_d) = \frac{1}{2\tau_{flow}}\frac{g''(x_d)}{g'(x_d)}(x_d - x_0)^2 \tag{6}$$

Equation 5 gives the linear scaling between the shift Δ and mixing time which is in good agreement with the experimental

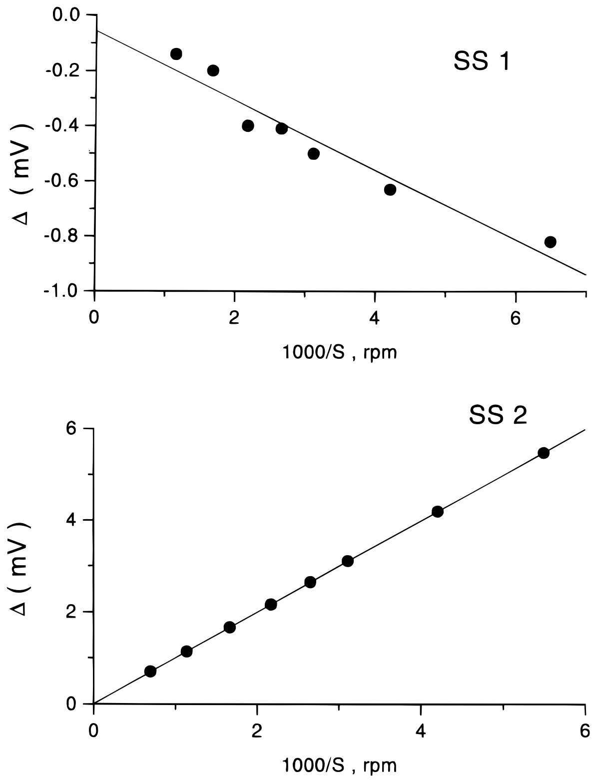

Figure 3. Dependence of the shift Δ on the inverse stirring rate (SS 1: $[\mathrm{Br}^-]_0 = 1 \times 10^{-6}$ M; SS 2: $[\mathrm{Br}^-]_0 = 1.5 \times 10^{-4}$ M).

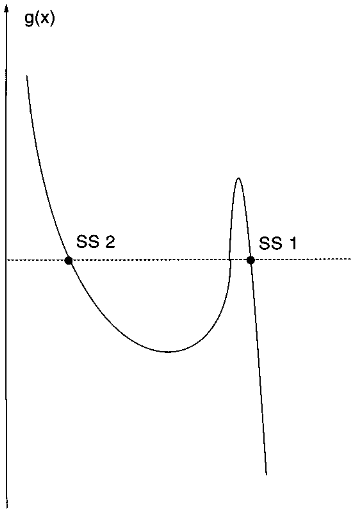

Figure 4. Schematic presentation of rate function *f*(*x*) which gives bistability.

data presented in Figure 3. To apply this scaling to the experimental data, we assumed that $\tau_{\mathrm{mix}} \approx 1/S$.

The linear scaling between the shift and mixing time provides a description of concentration gradients in a CSTR because the parameter $\alpha(x_{\mathrm{d}})$ does not depend on the stochastic processes of mixing and inflow. The mixing time τ_{mix} is the only parameter that corresponds to the mixing process. Taking into account a realistic hydrodynamic picture in the CSTR[2] allows one to introduce the spatial dependence of the mixing time $\tau_{\mathrm{mix}}(r)$. This gives the following expressions for the spatial dependence of the concentration ($x_{\mathrm{s}}(r)$) and for the spatial gradient ($\nabla x_{\mathrm{s}}(r)$).

$$x_{\mathrm{s}}(r) = x_{\mathrm{d}} + \Delta(r) = x_{\mathrm{d}} + \alpha(x_{\mathrm{d}})\, \tau_{\mathrm{mix}}(r) \tag{7}$$

$$\nabla x_{\mathrm{s}}(r) = \frac{\partial \Delta(r)}{\partial r} = \alpha(x_{\mathrm{d}}) \nabla \tau_{\mathrm{mix}}(r) \tag{8}$$

For a given CSTR at a given flow and stirring rate, the function $\tau_{\mathrm{mix}}(r)$ is independent of chemical relaxation given by *f*(*x*). Therefore, the opposite concentration gradients for SS 1 and SS 2 are explained by $\alpha(x_{\mathrm{d}})$ alone. This constant has the same sign as the second derivative of the deterministic rate function $g''(x_{\mathrm{d}})$ because both steady states are stable and $g'(x_{\mathrm{d}}) < 0$. In the generic case the rate function $g(x)$ has a plot as shown in Figure 4. Its outermost intersections with the *x*-axis define the deterministic steady states SS 1 and SS 2. The second derivative $g''(x)$ is the curvature of the rate function $g(x)$ at these two points. This curvature is always negative for SS 1 and positive for SS 2. Therefore, the spatial dependence of the concentration in a CSTR is qualitatively different for SS 1 and SS 2. Namely, the region with the highest concentration for SS 1 corresponds to that of the lowest concentration for SS 2. Figure 2 gives exactly this picture for the concentration gradients for SS 1 and SS 2. Moreover, eq 5 indicates that Figure 2 depicts the spatial dependence of the micro-mixing time τ_{mix}, which is related to the energy dissipation as[14]

$$\tau_{\mathrm{mix}}(r) = C\left(\frac{L^2}{\epsilon(r)}\right)^{1/3} \tag{9}$$

where *L* is a characteristic length of the reactor and the constant *C* takes values in the range $C = 2-5$.

Typically, the local energy dissipation is higher in the vicinity of the impeller and much lower in most of the liquid volume.[5,15] Therefore, the micromixing time is smaller for $r = 0$ and larger near the walls of the reactor, in agreement with the experimental data presented in Figure 2.

Equation 5 shows that larger stirring dependence of the position of the steady state leads to larger spatial gradients. Figure 1 shows that the stirring effect is more pronounced for SS 2. As a result, the spatial gradients are larger for SS 2, as shown by Figure 2. The correspondence between the analysis of eq 5 and experimental results (Figure 2) indicates that our approach gives the correct description for the spatial gradients in a CSTR. The spatial gradients are more pronounced for the most sensitive branch where the constant $\alpha(x_{\mathrm{d}})$ is larger.

Equation 5 indicates the generic property of the spatial gradients in the reactor: spatial gradients are oppositely directed for SS 1 and SS 2, while the spatial profile shown in Figure 2 is not generic because $\epsilon(r)$ may have different spatial profiles depending on the vertical position in the reactor.[5,16] Particularly, in previous chlorite/iodide experiments,[6,7] the concentration gradients were oppositely directed and they were substantially more pronounced than in the present BZ study. As reasons for this difference we consider the greatly enhanced turbulence achieved in the present work through the use of baffles and a rectangular impeller (the previous study employed a two-blade propeller), the use of premixed feedstreams, which reduces both stirring effects and concentration gradients, and last but not least the intrinsically smaller stirring effect (through $\alpha(x_{\mathrm{d}})$), traceable to the derivatives $g''(x_{\mathrm{d}})$ and $g'(x_{\mathrm{d}})$, of the BZ system, compared to the chlorite/iodide reaction.

The existence of spatial gradients for both steady states in the bistable regime indicates that gradients may exist even in the oscillatory regime. The oscillating signals recorded at 100 rpm at the center of the reactor ($r = 0$) and in the region beyond the tip of the impeller ($r = 12$ mm) were smoothed to eliminate rapid noise and are shown in Figure 5a. At higher stirring rates

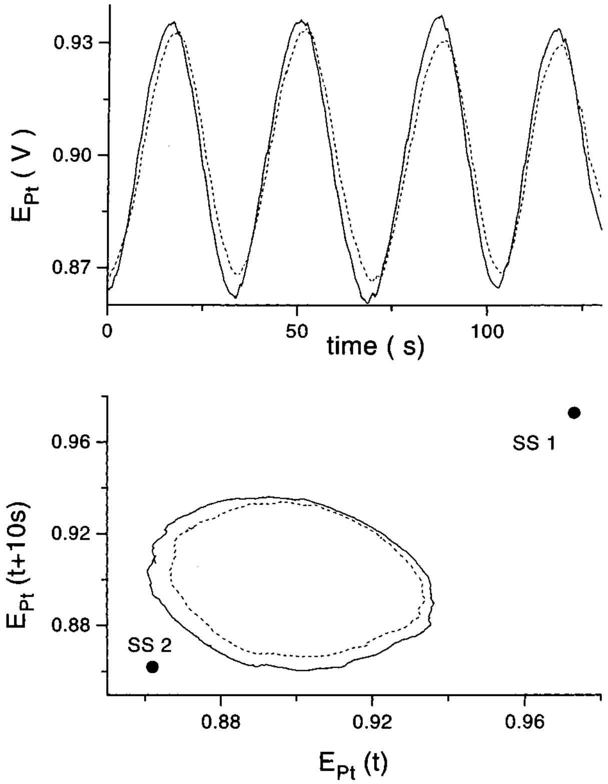

Figure 5. Oscillations of the Pt microelectrodes potentials recorded simultaneously in a vicinity of the stirrer ($r = 0$, a, solid line) and in a vicinity of the wall of the reactor ($r = 12$ mm, a, dashed line) at $S = 100$ rpm ($[\mathrm{Br}^-]_0 = 1.0 \times 10^{-6}$ M, $[\mathrm{MA}]_0 = 0.09$ M. To eliminate noise, curves were obtained by adjacent averaging using 50 points from the initial signals collected with the frequency 10 Hz. The bottom panel (b) gives the reconstructed phase portraits and the position of steady states for conditions in Figure 2.

we did not observe any significant difference between these two signals. The oscillation amplitude is larger near the stirrer ($r = 0$), i.e., in the strongly mixed region of the CSTR. Therefore, the limit cycle shrinks along the radial direction in the reactor and it becomes smaller near the walls, i.e., in the less mixed region. This is in qualitative accord with the spatial gradients in the bistable regime because oscillations may be represented as a switch between two pseudosteady states and reduced stirring moves these steady states toward each other. This representation is in accord with the prevalent observation that reduced micromixing time increases oscillation amplitude. According to the analogy between oscillations and bistability, the effect should be more pronounced in the oscillation phase where the system evolves near the image of SS 2, i.e., near the oscillation minimum. Figure 5b, the 2-D phase portraits reconstructed from the time series using the time-delay technique, confirms this expectation.

In conclusion, we showed that concentration gradients appear in a CSTR due to the spatial dependence of the characteristic micromixing time. Equation 5 satisfactorily describes the concentration gradients and provides means for obtaining the spatial dependence of the micromixing time from the kind of concentration measurements reported here. The concentration gradients are governed by two factors: chemical relaxation and micromixing. The effect of the chemical relaxation is described by the value of $\alpha(x_d)$, which does not depend on the position r in the reactor. Therefore, the rate of chemical process defines only the intensity of the concentration gradients and their direction for a given hydrodynamic state. In turbulent flows, mixing is usually viewed[2,4] as proceeding from the macroscale through the turbulent cascade down to the microscale. Here we have shown that rapid chemical reaction, coupled with the spatial dependence of the mixing time, provides an additional mechanism by which macroscopic gradients may arise indirectly via micromixing.

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