J. Phys. Chem. A **1997,** *101,* 5215−5217

Experimental Evidence of Kinetic Bistability in a Biphasic Surfactant System

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Received: April 11, 1997; In Final Form: June 3, 1997[⊗]

The biphasic alkaline hydrolysis of ethyl caprylate, which has attracted attention as a prototype reaction for the so-called self-reproduction of micelles (Bachmann, P. A.; et al. *Nature* **1992,** *357,* 57), was shown to give rise to kinetic bistability in a continuous flow stirred tank reactor. At higher flow rates, the stationary state composition was characterized by a turbid two-phase oil/water mixture, while at lower flow rates a single transparent aqueous phase was obtained. For intermediate residence times, either situation may be attained depending on the initial conditions in the reactor. Near the hysteresis limits, the characteristic increase in relaxation times was observed. A macroscopic model, which accounts for the nonlinear behavior in terms of micelle-mediated phase transfer, predicts the bistability, and the observed transient kinetics are in good agreement with the experimental results.

Introduction

Since the first experimental example of kinetic bistability in an isothermal system in the late sixties[1] and the adoption of the continuous flow stirred tank reactor (CSTR) technique[2] for studies of systems under "far from equilibrium" conditions, many autocatalytic reactions have been shown to exhibit multiple stationary states.[3] However, kinetic bistability has been described almost exclusively in redox reactions involving inorganic compounds.

This Letter reports on what is believed to be the first experimental example of kinetic bistability in an organic two-phase oil/water reacting system. It involved the alkaline hydrolysis of neat ethyl caprylate, which is placed in contact with a 3 M aqueous solution of NaOH. The reaction yields amphiphilic sodium caprylate, which can form anionic micelles in aqueous media. The highly autocatalytic kinetics of this reaction was first described by Bachmann *et al.*,[4] who suggested a reaction mechanism governed by a micellar catalytic process. In a previous study,[5] we have reinvestigated this system in new batch experiments. We proposed a kinetic model, which describes the main dynamics of the reaction by a micelle-mediated phase-transfer mechanism rather than a classical micellar catalytic process. This model provides an excellent fit to the kinetics of sodium caprylate and ethyl caprylate observed under batch conditions.

Experimental Results

In the present study, we used a thermostated CSTR of an approximate volume of 3.5 mL equipped with a magnetic stirrer operating at about 800 revolution per minute. Under the usual reaction conditions,[4,5] i.e., using the initial amounts of 78% (vol) aqueous 3 M NaOH and 22% (vol) neat ethyl caprylate at a temperature of 90 °C, we observed a total time for the hydrolysis reaction of ~13.5 min when the reaction was carried out in batch mode.[6] Under CSTR conditions and at residence times of $\tau \geq 4.9$ min, the composition of the reaction mixture approached that of the batch reaction at thermodynamic equilibrium. In this case, ethyl caprylate was completely depleted, and a single transparent aqueous phase was observed. Otherwise, at $\tau \leq 2.9$ min, the stationary state composition corresponded to that of the two combined reactant streams pumped into the reactor. In this case, the reactor contained approximately the initial amount of ethyl caprylate and aqueous 3 M NaOH; i.e., the system was biphasic and turbid under our stirring conditions.

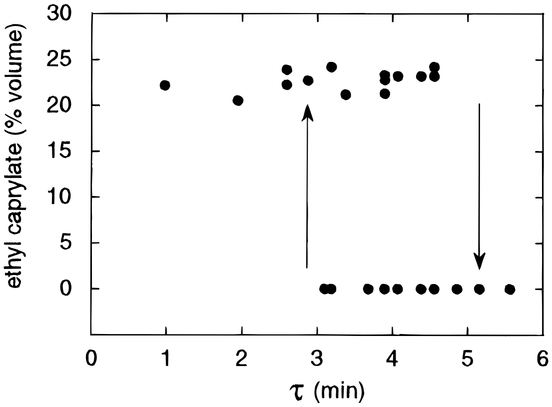

Figure 1. Stationary state amount (% vol) of ethyl caprylate in the reaction mixture of the biphasic alkaline hydrolysis of ethyl caprylate as a function of the residence time (τ) in a CSTR at $T = 90 \pm 2$ °C. The arrows represent the positions at which transitions between the two stationary branches were measured (see Figure 2). Experimental points were obtained by altering the flow rates from the two high-precision HPLC pumps. The combined reaction streams were adjusted to a ratio of 78% (vol) aqueous 3 M NaOH and 22% (vol) neat ethyl caprylate. A thermostated cylindrical glass reactor of ∅ ~ 19 mm and 16 mm height, fitted with an ellipsoidal magnetic bar of 17 × 10 mm, two feed-stream Teflon tubes (∅ ~ 0.6 mm), an overflow tube (∅ ~ 3 mm), and with a high-density polyethylene top, was used. Stationary state compositions were determined by measuring the volume of unreacted ethyl caprylate and of the aqueous phase at the reactor outlet after phase separation. True stationary states were judged by the lack of change in ethyl caprylate after waiting for at least 20 residence times at each experimental point.

Figure 1 shows that kinetic bistability is observed in the domain between $\tau = 3.1$ min and $\tau = 4.6$ min. When the reactor residence time is increased stepwise, say, from $\tau = 2$ min, where the system is well-situated at the upper flow branch, the stationary state is characterized by the approximate initial reactant composition until $\tau = 4.6$ min. Above this value, the

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[⊗] Abstract published in *Advance ACS Abstracts,* July 1, 1997.

S1089-5639(97)01258-9 CCC: $14.00

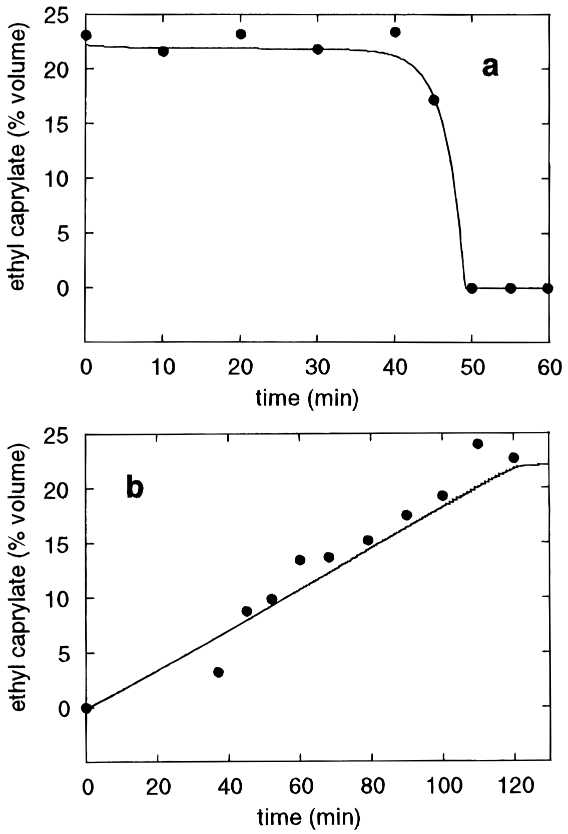

Figure 2. Typical transient kinetics of ethyl caprylate near limits of the bistable domain: (a) transition from the flow to the thermodynamic branch at the residence time of $\tau = 5.2$ min (down arrow in Figure 1); (b) transition from the thermodynamic to the flow branch at $\tau = 2.9$ min (up arrow in Figure 1). Points, experimental data; solid line, simulation by the phase-transfer model, see eqs 1−6. Simulations were performed at (a) $\tau = 4.49$ min (down arrow in Figure 3) and (b) $\tau = 1.62$ min (up arrow in Figure 3) by using the kinetic parameters noted in the caption of Figure 3. Note that the bistable domain is between $\tau = 3.1$ and 4.6 min (experiment) and $\tau = 1.64$ and 4.25 min (simulation).

system displays a transition down to the lower thermodynamic branch corresponding to the single-phase equilibrium composition where the volume of ethyl caprylate becomes zero. If the residence time is now reduced, the system remains at the lower thermodynamic branch until $\tau = 3.1$ min. Over this range, the reaction mixture remained transparent and no ethyl caprylate was detected at any point. The hysteresis loop is completed by the transition to the flow branch at $\tau = 2.9$ min, where the reaction mixture again becomes turbid.

The time required to establish a new stationary state, e.g., after a change in the flow rate, has been shown to depend on the distance from limits of the bistable domain.[7] In our experiments, the characteristic increase in the relaxation time near the hysteresis limit was clearly observed, albeit in two quite different patterns (see Figure 2).

Figure 2a represents a typical experiment showing the transition from the flow branch down to the thermodynamic branch at $\tau = 5.2$ min (down arrow in Figure 1). In this condition, the transient behavior *versus* time is characterized by an induction period during which the reactant composition remains close to initial values. This period, which occupies about 10 reactor residence times, is followed by a rapid depletion of ethyl caprylate, finally resulting in a stationary state established at the thermodynamic branch.

A typical transition from the thermodynamic branch up to the flow branch at $\tau = 2.9$ (up arrow in Figure 1) is shown in Figure 2b. The transient kinetics in this case exhibit a significantly different pattern: ethyl caprylate increases almost linearly until its stationary volume of approximatively 22% is reached after ~2 h, corresponding to about 40 reactor residence times.

Within the experimental uncertainties, at all residence times studied, an "all or nothing" behavior was observed for the stationary state composition; i.e., no stable states other than those characterized by a volume amount of ethyl caprylate of ~22% (flow branch) or 0% (thermodynamic branch) were detected.

Simulations

A phase-transfer model for the dynamics of this reaction, which we have recently proposed on the basis of batch experiments,[5] reproduces the experimentally observed effect of kinetic bistability on simulation of CSTR conditions. It can also account for the characteristic differences in relaxation kinetics observed on either side of the hysteresis limits. This model consists of the following six kinetic steps, where the reaction rates (r) are represented in mol min^{-1}, the total quantities of each species are expressed in number of moles, the rate constants are expressed by the usual units, and V corresponds to the volume of the aqueous phase:[8]

$$\mathrm{EC_{org}} \rightleftarrows \mathrm{EC_{int}}$$

$$r_1 = k_1\mathrm{EC_{org}},\ r_{-1} = k_{-1}\mathrm{EC_{int}} \tag{1}$$

$$\mathrm{EC_{int}} + \mathrm{OH^-} \rightarrow \mathrm{C} + \mathrm{EtOH}$$

$$r_2 = k_2V^{-1}(\mathrm{EC_{int}})(\mathrm{OH^-}) \tag{2}$$

$$g\mathrm{C} \rightleftarrows \mathrm{M}$$

$$r_3 = k_3V^{1-g}\mathrm{C}^g,\ r_{-3} = k_{-3}\mathrm{M} \tag{3}$$

$$\mathrm{M} + p\mathrm{EC_{int}} \rightleftarrows \mathrm{MEC}$$

$$r_4 = k_4V^{-1}\mathrm{M}(\mathrm{EC_{int}}),\ r_{-4} = k_{-4}\mathrm{MEC} \tag{4}$$

$$\mathrm{MEC} \rightleftarrows \mathrm{M} + p\mathrm{EC_{aq}}$$

$$r_5 = k_5\mathrm{MEC},\ r_{-5} = k_{-5}V^{-1}\mathrm{M}(\mathrm{EC_{aq}}) \tag{5}$$

$$\mathrm{EC_{aq}} + \mathrm{OH^-} \rightarrow \mathrm{C} + \mathrm{EtOH}$$

$$r_6 = k_6V^{-1}(\mathrm{EC_{aq}})(\mathrm{OH^-}) \tag{6}$$

Step 1 describes the formation of a macroscopic organic/aqueous interface ($\mathrm{EC_{int}}$) from dispersion of bulk ethyl caprylate ($\mathrm{EC_{org}}$). Process 2 accounts for the spontaneous hydrolysis of ethyl caprylate at the organic/aqueous interface yielding caprylate monomers (C) and ethanol (EtOH). Step 3 formally summarizes a step-by-step micellization process by an overall single-stage aggregation[9] of $g = 40$ caprylate monomers, where g denotes the average aggregation number of caprylate micelles as predicted by thermodynamic theory.[5] This theory suggests that micelles are very narrowly dispersed and justifies the simplification of a single population of micelles. Steps 4 and 5 denote the micelle-mediated phase-transfer process, i.e., the dissolution of an average of $p = 5$ molecules of $\mathrm{EC_{int}}$ per micelle, yielding a micelle−ethyl caprylate complex (MEC), and their transport into the aqueous phase by MEC. The value of $p = 5$ was obtained experimentally, as described in ref 5. Process 6 represents the fast hydrolysis of ethyl caprylate ($\mathrm{EC_{aq}}$), which has been transported into the aqueous phase.

Autocatalysis stems from the formation of the micelle−ethyl caprylate complex (MEC), which catalyzes the production of caprylate monomers *via* a phase-transfer process followed by rapid hydrolysis of ethyl caprylate. In turn, caprylate monomers

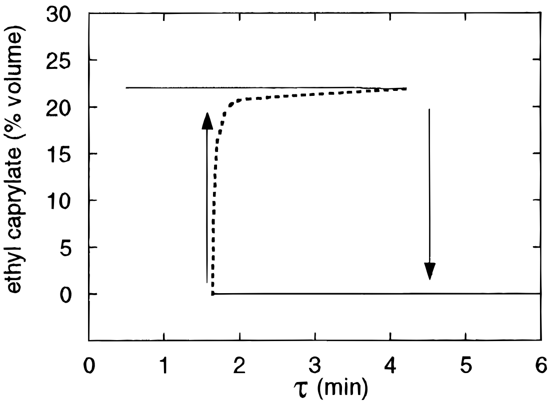

Figure 3. Numerical simulation of kinetic bistability in the biphasic hydrolysis of ethyl caprylate by the phase-transfer model under CSTR conditions, see eqs 1−6. The straight line represents the stable stationary state solutions, while the dotted line represents the unstable stationary branch. The arrows represent the positions at which transitions between the two stationary branches have been simulated (see Figure 2). Parameters used for simulations are: $k_1 = 1.2 \times 10^5$ min^{-1}, $k_{-1} = 1.7 \times 10^5$ min^{-1}, $k_2 = 2.6 \times 10^{-3}$ mol^{-1} L min^{-1}, $k_3 = 10^{64}$ mol^{-39} L^{39} min^{-1}, $k_{-3} = 1$ min^{-1}, $k_4 = 6.9 \times 10^{19}$ mol^{-1} L min^{-1}, $k_{-4} = 7.5 \times 10^7$ min^{-1}, $k_5 = 5.0$ min^{-1}, $k_{-5} = 2.4 \times 10^5$ mol^{-1} L min^{-1}, $k_6 = 2.1 \times 10^7$ mol^{-1} L min^{-1}.

are the building blocks of MEC. This gives rise to a positive feedback loop in which more and more sodium caprylate is formed. Total caprylate and the consumption of ethyl caprylate thus exhibit autocatalytic kinetics.

The model also shows that the critical aggregate concentration of MEC is smaller than that of the pure caprylate micelles (M). This is consistent with the phenomenon of solubilization in micellar systems.[10] As a consequence, as long as any ethyl caprylate is available, only MEC is produced, and the formation of pure micelles occurs only when ethyl caprylate is completely depleted.

Numerical fitting of the experimentally observed kinetics of ethyl caprylate and total sodium caprylate, as described in our previous publication,[5] was based on experiments in which the stirring conditions led to a total hydrolysis time of ∼80 min.[6] For simulations in the present study, the fitting parameters were readjusted to represent a total hydrolysis time of 13.5 min, corresponding to that observed in the CSTR at infinite residence times.

After adding flow terms to the kinetic equations of the readjusted model, stationary state compositions as a function of the flow rate were calculated from computer simulations. As shown in Figure 3, the kinetic model enabled us to simulate bistability and hysteresis over a domain close to that observed experimentally. The simulations also predicted the experimentally observed "all or nothing" behavior of ethyl caprylate in the stationary state composition, i.e., two stable stationary branches running almost horizontally.

The computed unstable stationary branch, situated at the bistable domain between $\tau \approx 1.6$ min and $\tau \approx 4.2$ min, is folded close to the upper stable flow branch until it drops down, striking the lower stable thermodynamic branch almost at a right angle. Although this unstable branch was undetectable under our experimental conditions, the transient kinetics close to the limits of the bistable domain were well simulated by the model (see Figure 2a,b). In particular, the simulations reproduced with good agreement the experimentally observed increase in the relaxation time as well as the two different transient patterns, i.e. the depletion of ethyl caprylate exhibiting an induction period in the course of the transition from the flow to the thermodynamic branch (down arrow in Figure 3) and the almost linear increase of ethyl caprylate during the transition from the thermodynamic to the flow branch (up arrow in Figure 3).

Conclusion

To our knowledge, this is the first experimental evidence of kinetic bistability in a biphasic surfactant system. CSTR behavior of this system was characterized by two stationary state compositions, in which the volume amount of ethyl caprylate was either close to its initial injection stream value or zero. The observed transient kinetics near the limits of the bistable domain exhibited the characteristic increase in relaxation times as well as the two different kinetic behaviors of ethyl caprylate on either side of the hysteresis limit. Our model also reproduced these main dynamic properties of the system under CSTR conditions. Previous models accounting for kinetics of this system under batch conditions[11] may also exhibit bistablity under CSTR conditions, as we have verified by computations. However, these models do not reproduce the experimentally observed "all or nothing" behavior of ethyl caprylate in the reaction mixture, i.e., two stable stationary branches running almost horizontally. All these models are based on catalysis by the pure caprylate micelles. In contrast, our model was based on a phase-transfer mechanism, in which molecular aggregates act as the carrier. Both the fitting of experimental data of batch experiments, as shown in our previous study,[5] as well as the semiquantitative prediction of kinetic bistablity, reported here, support the idea of a transport process playing the main role in the dynamics of this reaction mechanism.

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