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Occurrence of Multiple Steady States in the Biphasic Alkaline Hydrolysis of C-4 to C-8 Ethyl Alkanoates

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The autocatalytic biphasic alkaline hydrolysis of C-4 to C-8 ethyl alkanoates was studied in a CSTR. In our experimental conditions, the two shorter esters (C-4 and C-5) showed monostable behavior while the longer ones (C-6 to C-8) showed bistability. Both the occurrence of bistability and the amplitude of the bistable domain in the CSTR can be related to the strength of the autocatalysis in batch conditions. For C-4 and C-5, the mild autocatalysis stems from a slight increase of their solubilization rate due to the salting-in and solvent effects of the alcohol and alkanoate ions formed. As the critical micellar concentration (cmc) decreases with increasing chain length, for the longer esters this critical concentration was reached during the course of the reaction. The formation of micelles (that are able to solubilize the ester in their core) in the reactive medium considerably accelerates the solubilization process, leading to stronger autocatalysis and a wider bistability domain.

Introduction

Biphasic liquid−liquid reactions are of interest in various fields of chemistry.[1] The first example of alkaline hydrolysis conducted under two-phase conditions was reported by Bachmann et al.[2] The experiment described involved the sparingly water-soluble ethyl octanoate and an aqueous solution of sodium hydroxide under slow stirring so that the two phases remained clearly separated. In these conditions, the kinetics of the reaction start with a long induction period followed by a very steep acceleration typical of a highly autocatalytic reaction. To clarify the importance of the solubilization processes on the nonlinear kinetics, we extended the experimental observations to emulsified systems[3] of weakly soluble esters with shorter chain lengths. The whole set of experiments involving butanoate (C-4) to octanoate (C-8) ethyl esters[4] showed autocatalytic behavior. The longer the aliphatic chain, the more pronounced the autocatalysis.

The reaction is as follows:

$$C_{n-1}H_{2n-1}COOEt + OH^- = C_{n-1}H_{2n-1}COO^- + EtOH \; (n = 4-8)$$

with surfactant alkanoate anions and ethanol being the products of the reaction. These products have been shown to enhance the solubility of the hydrophobic ester in the aqueous phase, and hence to be at the origin of the autocatalysis.

For C-4 and C-5 the mild autocatalysis observed was attributed to enhanced dissolution of ester caused by solvent and salting-in effects,[5] due respectively to the formation of ethanol and alkanoate ions. For the three other compounds (C-6, C-7, and C-8) aggregation occurred during the course of the reaction when the cmc of the amphiphile alkanoate ions was reached. These aggregates allow extensive additional solubilization of ester in the water bulk, leading to a stronger acceleration.

We also studied the highly autocatalytic hydrolysis of C-8 in a continuously stirred tank reactor (CSTR)[6] and bistable behavior was observed. For specific values of the residence time, two different steady states (high or low conversion) were reached depending on the initial conditions of the reactor. The kinetics of the shorter chain length esters remained to be studied in CSTR conditions. Here, we underline the influence of the solubilization processes involved during the reaction on mono- or bistability. We present the experimental results obtained in a CSTR for the biphasic hydrolysis of C-4 to C-8 ethyl alkanoates.

Experimental Section

Materials. All chemicals were purchased from Fluka at the highest grade available. They were used without further purification.

Esters: C-8, ethyl octanoate (MW = 172.27); C-7, ethyl heptanoate (MW = 158.24), C-6: ethyl hexanoate (MW = 144.22); C-5, ethyl pentanoate (MW = 130.19); C-4, ethyl butanoate (MW = 116.16).

Surfactants: sodium hexanoate (MW = 138.14). Sodium pentanoate (MW = 124.14) was obtained by exact neutralization of pentanoic acid (MW = 102.14) with sodium hydroxide.

Reactor. The CSTR,[7,8] a Pyrex round-bottom baffled flask (V_r = 5.9 mL), was stirred magnetically at 800 rpm for emulsification by a 0.5 cm × 1.5 cm PTFE rod. Two input stainless steel injectors (0.12 mm internal diameter) were fitted into a plastic stopper with a small inverted cone at the bottom to trap bubbles and a PTFE output tube (internal diameter 1 mm). Ester was injected into the bottom, and the NaOH aqueous phase into the upper part. The device was totally immersed in a thermostatic bath. The two phases were pumped using two independent pumps: the maximum flow rate was of 5 mL/min per pump with a minimum increment of 0.01 mL/min.

The total flow rate was F = ester flow rate + NaOH flow rate. The residence time was $\tau = V_r/F = 5.9/F$. The input ester volumetric ratio Y_0 = (ester flow rate)/F was maintained at 0.23

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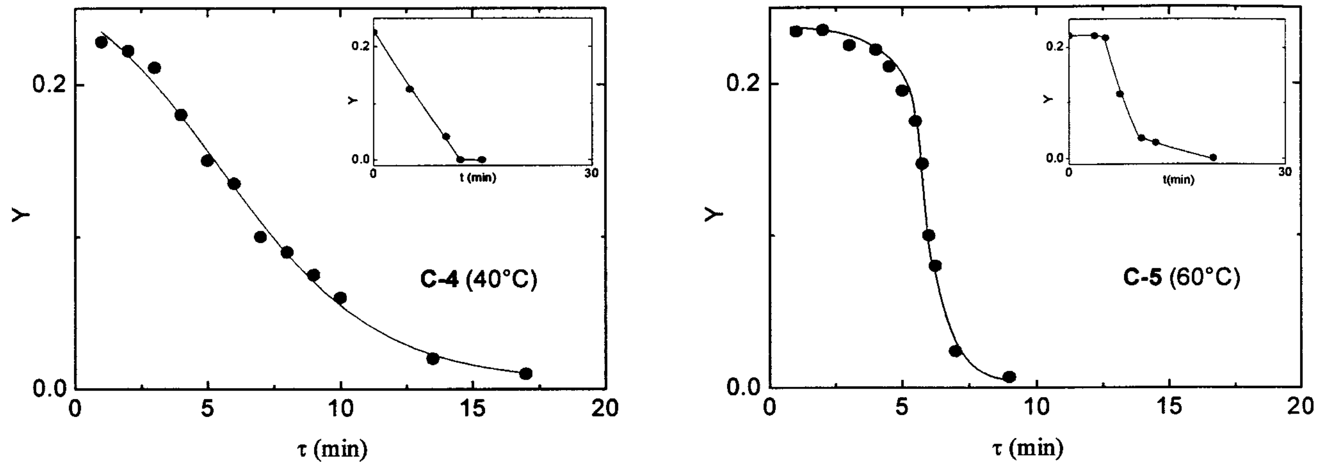
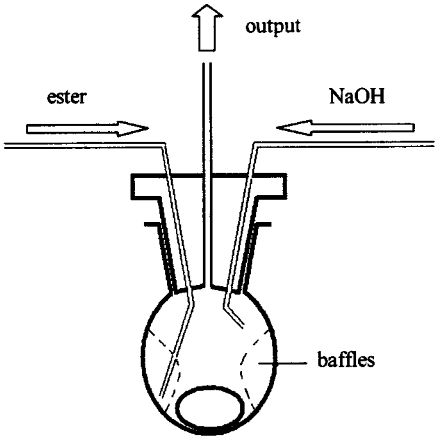


Figure 1. Stable stationary state locus of the volumetric ratio *Y* vs residence time τ during the biphasic liquid−liquid alkaline hydrolysis of ethyl alkanoates in the CSTR: C-4, ethyl butanoate at 40 °C; C-5, ethyl pentanoate at 60 °C. Insets*:* Corresponding batch kinetics (*Y* vs time) recorded under the same conditions.

SCHEME 1



± 0.01 in all experiments. When feeding the reactor at the maximum flow rate, we checked that the volumetric ratio in the output was the same that in the input of the reactor. Aliquots of the reactor output were collected at regular intervals and decanted into a measuring cylinder; the ratio

$$Y = \text{(volume of collected ester)/(total collected volume)}$$

was noted.When the system was far from the hysteresis limits, five (or less) residence times were sufficient to obtain a stationary state. However, near the hysteresis limit, full stabilization was observed for around 30 residence times due to critical slowing down.[9−11]

For C-4, the reaction was carried out at 40 °C, as the hydrolysis was too rapid at higher temperatures. For longer chain lengths the hydrolysis was slower. The temperature was set at 60 °C for C-5 and C-6 and 80 °C for C-6, C-7, and C-8.

Batch kinetics were recorded at the same temperature and stirring conditions as for the CSTR experiments. The aqueous phase pump was set at its maximum flow rate (5 mL·min^{-1}), while ester was pumped in at 1.46 mL·min^{-1} ($Y_0 = 0.23$). Under these conditions, the residence time was 0.9 min and reaction had not started. Both pumps were then stopped simultaneously, and after a fixed period of time the two-phase mixture was rapidly poured out into a measuring cylinder for determination of the ratio *Y*. Each point of the kinetics was obtained from a new experiment.

Determination of Ester Solubility vs Surfactant Concentration. Aqueous solutions of sodium alkanoate (C-5 and C-6) surfactant and NaCl were prepared to keep the total [Na$^+$] concentration constant (3 mol·L^{-1}). Ten milliliters of these solutions was hand shaken at room temperature with 1 mL of the corresponding ethyl alkanoate. An aliquot of the aqueous phase was then pipetted off using a capillary needle and extracted by an aliquot of cyclohexane with *n*-octane as the internal standard. This organic sample was then analyzed by GC. In the text, s_0 is the saturation concentration of ester in water with no surfactant and s_f corresponds to the saturation concentration obtained when the surfactant is at its final concentration at the end of the hydrolysis reaction. The cmc was estimated at the break point of the solubilization curve.

Results

Biphasic alkaline hydrolysis of C-4 to C-8 ethyl alkanoates was carried out in the CSTR for various residence times. The output mixture was then collected periodically, and the volumetric ratio *Y* was measured after decantation. The stationary values were then plotted vs the residence times, producing the steady-state locus of the system. Each CSTR experiment was complemented by a series of batch measurements performed under the same conditions designed to relate the overall shape of the batch kinetics with the dynamics in the CSTR.[12]

As presented in Figure 1, for C-4 at 40 °C, a smooth variation of stationary state composition over the whole range of residence times was obtained. For C-5 at 60 °C, the steady-state locus was more abrupt but remained smooth.

Comparison of the batch reaction time with the corresponding CSTR residence time revealed two different behavior patterns. For ethyl butanoate (C-4) at 40 °C, the monostable stationary state locus shows that 100% hydrolysis was obtained at $\tau > 17$ min, while under batch conditions (see inset), the same extent of reaction only took 12 min. The greater overall time observed in the CSTR stemmed from the dilution afforded by the flow of fresh reactants. Both CSTR and batch curves exhibit a smooth variation related to a mild autocatalytic effect. C-5 at 60 °C, is also monostable but a 100% reaction was obtained at $\tau > 10$ min in the CSTR, while in batch conditions it took longer ($t \approx 20$ min). In comparison to C-4, the order was reversed. Dilution by the fresh inflow was compensated by a stronger autocatalytic effect. This effect is related to the more abrupt variation in both CSTR and batch curves.

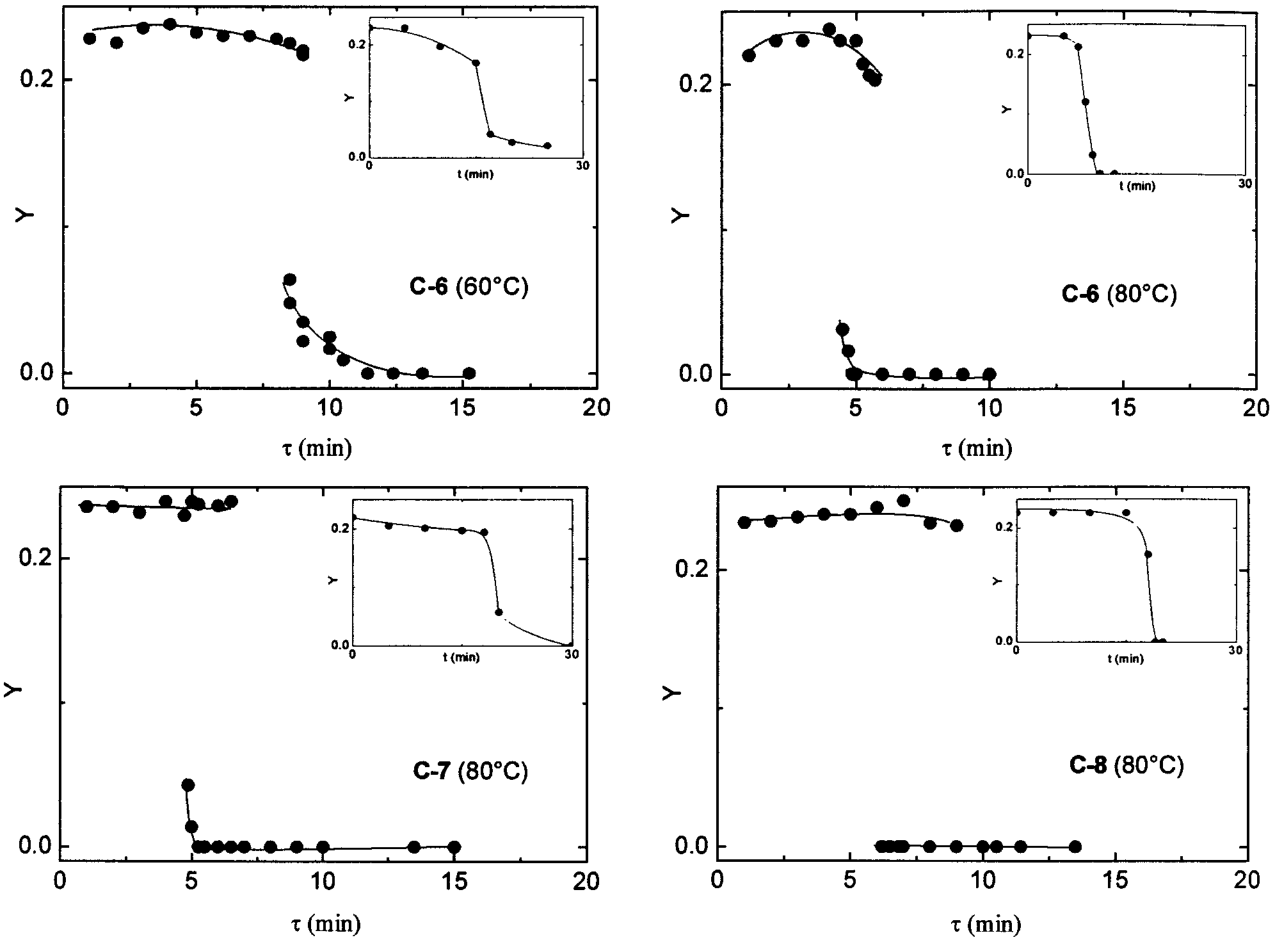


Figure 2. Stable stationary state locus of the volumetric ratio Y vs residence time τ during the biphasic liquid−liquid alkaline hydrolysis of ethyl alkanoates in the CSTR: C-6, ethyl hexanoate at 60 and 80 °C; C-7, ethyl heptanoate at 80 °C; C-8, ethyl octanoate at 80 °C. Insets: Corresponding batch kinetics (Y vs time) recorded under the same conditions.

In contrast, for C-6 at 60 °C and C-6, C-7, and C-8 at 80 °C, the stationary-state locus was bistable: between two limiting residence times, the system exhibited two possible stationary compositions depending on the initial conditions. For shorter residence times, the molecules do not, on average, spend long in the reactor, so little reaction is possible. The composition of the reacting medium is close to that of the input flow ($Y \approx Y_0$; flow branch). On the other hand, for longer residence times, there are very few exchanges with the external medium, the CSTR behaves as a closed system, and its composition approaches thermodynamic equilibrium ($Y \approx 0$; thermodynamic branch).

If we first compare the batch reaction time (insets) to the residence time corresponding to 100% hydrolysis in the CSTR, the behavior for the C-6 to C-8 experiments was equivalent to that of C-5 revealing strong autocatalysis, i.e., faster in CSTR than in batch conditions. This is clearly seen in the batch kinetics, as the extent of reaction was almost zero during the induction period followed by an abrupt acceleration.

According to the dynamics of autocatalytic reactions in a CSTR, the occurrence of mono- vs bistability is expected to be related to the overall shape of the batch kinetics:[13] the stronger the autocatalysis, the wider the bistability domain. Such a qualitative[14] correlation was verified in our experiments. The results concerning the bistable domains and the strength of autocatalysis in batch conditions (related to the ratio between maximum and initial rate: (r_{max}/r_0)) are displayed in Table 1.

The kinetics of C-6 at 60 and 80 °C show that an increase in temperature results in a higher nonlinear effect. The same dependence is observed as a function of the hydrophobicity of the ester: as the carbon chain length was increased, the bistable domain became larger and the two branches of the steady-state locus flatter. For C-8 the two branches were horizontal and an "all or nothing" type behavior was observed.

Table 1[a]

ester	T (°C)	τ_1	τ_2	$\Delta\tau$	(r_{max}/r_0) batch
C-6	60	8.5	9	0.5	44.7
C-6	80	4.5	5.7	1.2	60.8
C-7	80	4.7	6.8	1.9	228
C-8	80	6.2	9	2.8	2050

[a] τ_1 and τ_2 are the limits of bistability, $\Delta\tau$ is the width of the bistability domain, and (r_{max}/r_0) characterizes the strength of the acceleration in batch experiments.

Discussion

These results showed that the strength of the autocatalytic effect increased from C-4 to C-8. The borderline between monostable and bistable behavior in the CSTR occurred between C-5 and C-6 in our experimental conditions.

In a previous paper,[15] dedicated to the two-phase hydrolysis of C-6, we showed that the solubilization rate determines the reaction rate and that the solubilization rate is roughly proportional to solubility. The autocatalysis stems from the increase of solubility of the ester along the reaction as products are formed. To model the reaction kinetics, we took into account:

—the spontaneous solubilization of the ester in the aqueous phase (the saturation value is s_0),

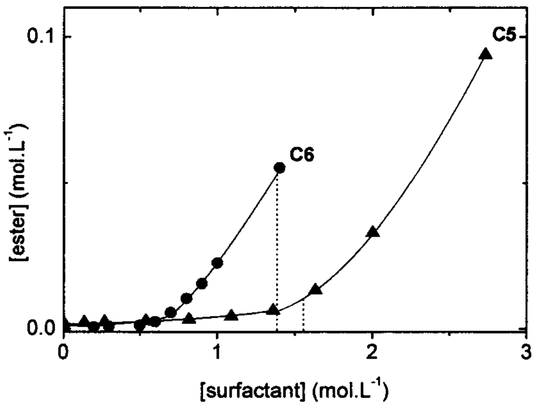


Figure 3. Plot of the saturation concentration of solubilized ethyl alkanoate (ester) vs the concentration of surfactant alkanoate ions in the aqueous phase at room temperature. [Na$^+$] was maintained at 3 mol·L^{-1}. Dotted lines correspond to the final surfactant concentration in the reaction mixture: 1.54 mol·L^{-1} for C-5 and 1.39 mol·L^{-1} for C-6.

TABLE 2: Characteristic Parameters of the Reaction[a]

	s_0 (mol·L^{-1})	cmc (mol·L^{-1})	% reacn at cmc	$10^2 s_f$ (mol·L^{-1})	s_f/s_0
C-5	2.1×10^{-3}	1.5	97	1.07	5.1
C-6	4.8×10^{-4}	0.46	33	4.4	92

[a] s_0: spontaneous ester solubility. s_f : solubility of the ester at the end of the hydrolysis reaction. (s_f /s_0): solubility ratio.

—the solvent effect due to the formation of alcohol,

—the salting-in effect of the anionic alkanoates,

—and the solubilization in micelles.

The first two effects act from the very beginning but lead to a relatively low increase of solubility. The strong effect, which results in the very sharp acceleration, appears after a certain quantity of alkanoate is formed, corresponding to the cmc.

To compare the last two effects on the kinetics of C-5 and C-6, the saturation solubilization curves were plotted vs the alkanoate ion concentration.

The effect of the surfactant concentration on solubility is directly visualized in Figure 3. The maximum alkanoate concentrations obtained at the end of the hydrolysis reaction are indicated with a dotted line in the graph. These values clearly show that for C-6, the cmc is largely exceeded during the course of the reaction (Table 2), leading to a greatly enhanced solubility (s_f / s_0 = 92). For C-5, the reaction ends just at the cmc and the increase in solubility s_f / s_0 is only about 5-fold. This low increase corresponds to the salting-in effect which, in cooperation with the solvent effect due to ethanol, are at the origin of the mild autocatalysis. In these conditions, a strong acceleration effect is not expected and consequently the system cannot give rise to kinetic bistability.

Table 2 lists several characteristic parameters of the reaction obtained from Figure 3.

The monostability of the alkaline hydrolysis of C-4 can be understood from the C-5 scenario. The hydrophobicity is low, and as a consequence, the spontaneous solubility s_0 is high. As there is no micellization in our concentration range, the slight increase in solubility due to salting-in and solvent effects is not sufficient to lead to a high s_f /s_0 ratio and consequently to a strong acceleration.

For C-7 and C-8, the behavior is similar to C-6. However, as the cmc is lower, it is attained at the onset of the reaction, i.e., when most of the ester remains to be hydrolyzed. Because s_0 is lower, the initial rate is also lower; and as C-7 and C-8 micelles are stronger solubilizing agents, the solubility is expected to be much higher, giving rise to a much more pronounced acceleration and a larger bistable domain.

Conclusion

Kinetic bistability or monostability was observed experimentally during the biphasic hydrolysis of C-4 to C-8 alkanoates in a CSTR. Under our experimental conditions, the borderline between monostable and bistable behavior was found to be between C-5 and C-6. C-4 and C-5 remained monostable, while C-6, C-7, and C-8 were bistable. The width of the bistability domain increased from C-6 to C-8; it was related to the carbon chain length. A strong link was observed between the shape of the batch kinetics and the occurrence of bistability in the CSTR. Moreover, the strength of the autocatalytic effect was related to the variation in hydrophobic ester solubility during the course of the reaction. As a consequence of the lower spontaneous solubility of the ester and lower cmc of the surfactant, longer carbon chain esters are characterized by a higher solubility ratio s_0 / s_f, by a stronger autocatalytic effect and thus by a larger domain of bistability.

References and Notes

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