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Origin of Autocatalysis in the Biphasic Alkaline Hydrolysis of C-4 to C-8 Ethyl Alkanoates

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The alkaline hydrolysis of C-4 to C-8 (butanoate to octanoate) ethyl esters shows autocatalytic kinetics when performed under two-phase conditions without any mixing solvent. Alkanoate anions and ethanol are the products of the reaction. A dynamic model is proposed that describes quantitatively this kinetic behavior. The model includes the main processes occurring in the biphasic medium and the corresponding thermodynamic calculations of the average size and stoichiometry of the molecular aggregates. Modeling indicates that salting-in and solvent effects caused by the alkanoate anions and ethanol determine the autocatalytic kinetics in the hydrolysis of C-4 ethyl ester where no aggregation occurs. In the C-5 to C-8 experiments, ester-containing micelles (ECM) are mainly formed by cooperative aggregation of alkanoate anions with ester molecules. ECM is formed only after a threshold concentration of the alkanoate anion has been reached. In a phase-transfer-like process, ECM carries ester molecules into the aqueous phase, where hydrolysis takes place yielding alkanoate anions. Additionally, in C-6 and C-7 ethyl ester hydrolysis, autocatalysis appears to be delayed, since acceleration only starts after the extent of hydrolysis has reached a certain level. A transient storage of alkanoate anions in a reservoir has been assumed to explain this delay. Collective adsorption of alkanoate anions at the oil−water interface, which occurs without any threshold concentration, could play the role of such a transient storage. The model also shows that empty micelles are without any kinetic importance, since they are formed at the end of reaction after the ester is completely depleted.

I. Introduction

Biphasic liquid−liquid reactions are of particular interest in many fields of chemistry such as industrial and chemical engineering,[1] organic synthesis,[2] phase-transfer catalysis,[3] molecular and chiral recognition,[4] membrane chemistry,[5] and prebiotic chemistry.[6] Despite this broad interest, extensive kinetic studies are scarce.

However, owing to its highly autocatalytic behavior, the biphasic alkaline hydrolysis of ethyl octanoate (Luisi experiment)[7] became a prominent example for the kinetics of two-phase reaction systems. This reaction shows a pronounced induction period in which the medium remains biphasic and almost at its initial composition. This induction period is then followed by a rapid clarification, yielding a transparent single-phase aqueous solution of ethanol and micellized sodium octanoate as the final hydrolysis products. The highly nonlinear kinetics of this reaction system has been attributed by the previous authors to so-called "micellar autocatalysis".

In a recent study,[8] we revisited the Luisi experiment. The analysis of new kinetic data, obtained in a well-stirred reactor, enabled us to propose and to confirm quantitatively a mechanism involving a micelle-mediated phase transfer at the origin of the autocatalytic behavior.

From our previous conclusions, one can expect that the biphasic alkaline hydrolysis of ethyl alkanoates with short aliphatic chain lengths would not display such an autocatalytic behavior. In these cases and under our experimental conditions the corresponding sodium alkanoates hardly form molecular aggregates, and consequently, they cannot build host aggregates for a micelle-mediated phase transfer.

Surprisingly, the experimental results reported in this publication show that the kinetic behavior of the biphasic alkaline hydrolysis of C-4 to C-8 ethyl alkanoates is always autocatalytic whatever the chain length, i.e., even if micellization does not occur within the experimental concentration range.

To understand this unexpected kinetic behavior, we present an improved kinetic model for this specific type of two-phase reaction. The model takes into account the results of thermodynamic calculations that have been performed to estimate the average size and stoichiometry of sodium alkanoate ester containing aggregates. The respective values were used as fixed parameters in the kinetic model. By application of the method of inverse treatment, a curve fitting of experimental kinetic data was realized.

II. Experiments

1. Biphasic Alkaline Hydrolysis of C-4 to C-8 Ethyl Alkanoates. Ethyl esters of C-4 to C-8 (i.e., ethyl butanoate to ethyl octanoate) have been chosen on the basis of thermodynamic and physicochemical properties that show significant variations vs the chain length.

The kinetics of the alkaline hydrolysis of ethyl alkanoates has been monitored by measuring the volume of the residual oil phase vs time (see Experimental Section). Whatever the aliphatic chain length, the kinetics at 80 °C shows an acceleration effect. The maximum of the reaction rate is situated near the clarification point where the medium becomes monophasic. For ethyl octanoate (C-8), an induction period is observed during which hydrolysis is very slow. However, after this induction period, rapid hydrolysis occurs. For intermediate chain lengths

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TABLE 1: Effect of Initial Addition of Reaction Products on the Kinetics of the Biphasic Alkaline Hydrolysis of C-4 (60 °C), C-6 (80 °C), and C-8 (80 °C) Ethyl Alkanoates (EtOH is Ethanol, and S is Sodium Butanoate in C-4, and Sodium Octanoate in C-8)[a]

chain	additive	concentration ($\mathrm{mol\ L^{-1}}$) of the additive	observed clarification time (min)	calcd clarification time (min)
C-4 (60 °C)	none	0	25	25
C-4 (60 °C)	S	0.02	29	24
C-4 (60 °C)	S	0.8	17	15
C-4 (60 °C)	EtOH	0.8	11	15
C-6	none	0	60	60
C-6	EtOH	1.36	15	20
C-8	none	0	95	95
C-8	EtOH	0.05	87	90
C-8	EtOH	1	40	45
C-8	S	0.01	55	40
C-8	S	0.02	42	22.5
C-8	S	0.035	18	17
C-8	S	0.05	18	16.5
C-8	S	0.075	14	14
C-8	S	0.1	10	12.5
C-8	C-8 final solution	1.55 mL	32	23

[a] Observed times of clarification are known with an accuracy of ±5 min. Calculated times of clarification are from kinetic modeling.

(C-7 and especially C-6), the shape of the induction period is somewhat different. In these cases, hydrolysis occurs at a slow constant rate until around 13% and 35%, respectively, of the initial ester has been consumed. After that, acceleration and clarification take place. For short-chain esters (C-5 and especially C-4), no significant induction period can be detected under our experimental conditions. However, also in these cases the kinetic curves show a characteristic convex shape, indicating autocatalytic dynamics.

In all cases, the reaction yields an equimolar mixture of ethanol and sodium alkanoate. Total depletion of the ester at the end of reaction has been confirmed by IR spectroscopic analysis to correspond exactly to the formation of an equivalent amount of sodium alkanoate in the aqueous phase.

2. Effect of Reaction Products. A series of complementary experiments have been performed to study the kinetic effect of the initial addition of reaction products, i.e., of ethanol, sodium alkanoate, and the final reaction solution itself, which was obtained from a previous experiment. These studies allow us to confirm the autocatalytic nature of the reaction and to characterize the specific autocatalytic species. Indeed, results listed in Table 1 show that the initial addition of sodium alkanoates and aliquots of final reaction solutions exhibit significant catalytic effects. In the C-8 case, ethanol displays only poor catalytic activity (for instance, addition of 1 $\mathrm{mol\ L^{-1}}$ ethanol has less effect than the addition of 3.5×10^{-2} $\mathrm{mol\ L^{-1}}$ sodium octanoate). However, in the case of C-4, both butanoate and ethanol account for the rate acceleration.

III. Kinetic Model

We considered for the proposed kinetic model the main reactive species and macroscopic physicochemical processes expected to be involved in an oil−water biphasic hydrolysis reaction of long-chain ethyl esters.

The liquid−liquid reaction system has been regarded to consist of three phases. One phase is the *organic phase* (org), which is considered to contain solely neat ester. Tests using sodium alkanoates or water have shown that their dissolution in the ester phase is negligible. Moreover, 200 MHz NMR measurements using $CDCl_3$ as solvent have shown that during the C-6 reaction the volumic ratio of ethanol within this phase remained always less than 8%.

The second phase is the *interfacial phase* (int), which corresponds to a small volume in which the density profiles of ester and water are functions of the distance from their respective bulk phases. This is supported by molecular dynamics simulations of a water−oil interface in the presence of micelles performed by Karaborni et al.[9] The authors show that the interface is rough, that there are surfactant molecules adsorbed at the oil surface, and that the thickness of the interface layer is of about one micellar diameter.

The third phase is the *aqueous phase* (aq) that initially contains hydroxide and sodium ions. During the reaction, several other species accumulates in this phase: dissolved ester (E_{aq}), free surfactant molecules (S), ester-containing micelles that consist of g' surfactants and p ester molecules (ECM), empty micelles (M), and ethanol (EtOH).

For the purpose of modeling the following variables and parameters have been considered.

1. Variables. The number of moles of compound X in phase j is written as X_j.

E_{org}: ester in the bulk organic phase

E_{int}: ester in the interfacial phase

E_{aq}: ester dissolved in the aqueous phase

S_{aq}: surfactant monomers dissolved in the aqueous phase

EtOH: ethanol dissolved in the aqueous phase

OH^-: hydroxide ions in the aqueous phase

ECM: ester-containing micelles in the aqueous phase

AS: adsorbed surfactant in the interfacial phase

M: empty micelles in the aqueous phase

V_{org}: volume of the bulk organic phase

V_{int}: interfacial volume

V_{aq}: volume of the aqueous phase

$[X]_j$: molar concentration of X in phase j, $[X]_j = X_j/V_j$

r_i: rate of process i, written in $\mathrm{mol\ min^{-1}}$ according to the mass balance equations

2. Parameters

k_i: rate constant of process i with usual units

g': weight average aggregation number of sodium alkanoate in ECM

p: average number of solubilized ester molecules in ECM

g: weight average aggregation number of empty micelles M

TABLE 2: Estimated Parameter Values from Thermodynamic Calculations at $T = 80\,^{\circ}\mathrm{C}$ and in the Presence of 3 mol L^{-1} Salt (See Appendix 2 for Details)[a]

	C-4 (60 °C)	C-4 (80 °C)	C-5	C-6	C-7	C-8
s (mol L^{-1})	4.1×10^{-3}	5.5×10^{-3}	1.7×10^{-3}	5.3×10^{-4}	1.6×10^{-4}	5.1×10^{-5}
v (L)	0.132	0.132	0.149	0.166	0.182	0.199
α (L mol^{-1})	0.56	0.56	0.64	0.71	0.78	0.85
g'			4	5	14	29
p			1.4	1.5	2.2	4.5
g			12	24	36	47
cmc (mol L^{-1})			1	0.3	8.3×10^{-2}	2.5×10^{-2}
K_m mol^{1-g} L^{g-1}			3.5×10^{-3}	$9.2 \times 10^{+8}$	$2.6 \times 10^{+34}$	$1.1 \times 10^{+70}$

[a] The micellization equilibrium constant[24] is $K_\mathrm{m} = k_8/k_{-8} = \mathrm{cmc}^{1-g}/(2g^2)$. C-4 does not aggregate under our experimental conditions. Values of cmc for C-6 and C-8 have been checked experimentally to be ≅0.46 and ≅2.5 10^{-2} mol L^{-1}, respectively, at room temperature and in the presence 3 mol L^{-1} salt.

s: solubility of the ester in the aqueous phase (mol L^{-1})

α: correction factor related to solvent and salting-in effects (L mol^{-1})

cmc: critical micellar concentration

CAC: critical aggregation concentration

v: molar volume of neat ester

a: molar area of neat ester

D: mean oil droplet diameter

3. Reaction Scheme. The sequence network for the biphasic alkaline hydrolysis of C-4 to C-8 ethyl alkanoates can be summarized by the following steps: (1) formation of a free organic aqueous interface by macromixing, (2) dissolution of ester in the aqueous phase, (3) hydrolysis of the ester, (4) formation of ester-containing micelles by cooperative aggregation, (5) adsorption of surfactant monomers at the interface, (6) formation of ester-containing micelles through collective desorption, (7) dissociation of ester-containing micelles and phase transfer, and (8) formation of empty micelles. The eight steps are

$$\mathrm{E_{org}} \rightleftarrows \mathrm{E_{int}} \tag{1}$$

$$\mathrm{E_{int}} \rightleftarrows \mathrm{E_{aq}} \tag{2}$$

$$\mathrm{E_{aq}} + \mathrm{OH^-} \rightarrow \mathrm{S_{aq}} + \mathrm{EtOH} \tag{3}$$

$$g'\mathrm{S_{aq}} + p\mathrm{E_{int}} \rightleftarrows \mathrm{ECM} \tag{4}$$

$$(g')\mathrm{S_{aq}} + (p)\mathrm{E_{int}} \rightleftarrows \mathrm{AS} \tag{5}$$

$$\mathrm{AS} \rightarrow \mathrm{ECM} \tag{6}$$

$$\mathrm{ECM} \rightleftarrows g'\mathrm{S_{aq}} + p\mathrm{E_{aq}} \tag{7}$$

$$g\mathrm{S_{aq}} \rightleftarrows \mathrm{M} \tag{8}$$

Step 1: Formation of a Free Organic/Aqueous Interface. This process corresponds to the dispersion of ester in water. It has been studied by Polat and Chander[10] using an experimental setup quite similar to ours. Kinetic data show that the dispersion proceeds rapidly. In the early stage of stirring, the change in the median oil droplet size as a function of time follows approximately first-order behavior. On this basis, first-order reversible steps between the organic phase ($\mathrm{E_{org}}$) and the interface ($\mathrm{E_{int}}$) were chosen to represent the dispersion of the ester in the aqueous phase.

Step 2: Dissolution of the Ester in the Aqueous Phase. This is regarded as an equilibrium between the ester located at the interface ($\mathrm{E_{int}}$) and the ester dissolved in the aqueous phase ($\mathrm{E_{aq}}$). Since the solubility of a solute in a solvent is independent of the available quantity of the solute (here, the bulk organic phase), the process of dissolution has been simply described by zero-order kinetics. However, we also considered that the solubility of long-chain alkyl esters in water varies with the presence of dissolved additives. In our case these are ethanol and sodium alkanoate formed during the reaction process. Ethanol displays a solvent effect and sodium alkanoate a so-called salting-in effect,[11] both increasing the solubility of the ester in the aqueous phase. The reversal process (phase separation) has been considered to be of first order with a rate ensuring that at equilibrium the actual saturation concentration of ethyl alkanoates is reached. Solubility values and the salting-in and solvent-correcting factor (α) have been estimated by thermodynamic calculations at an ionic strength of 3 mol kg^{-1} (see Table 2 and section 2 of Appendix).

Step 3: Hydrolysis of Ethyl Alkanoates. This reaction has been studied by Evans et al.[12] under monophasic conditions. Second-order rate constants and activation energies have been determined in binary mixtures of 85% ethanol/15% water (v/v) and 70% acetone/30% water (v/v). From these studies, it appears that the values of the rate constants increase with the water content in the reaction medium and that they are almost independent of the chain lengths of the esters. Activation energies were found to be of 63 kJ mol^{-1} in aqueous ethanol. From these reported values, the second-order rate constant k_3 for the alkaline hydrolysis in pure water has been estimated to be about 60 L mol^{-1} min^{-1} for the C-4 to C-8 esters at 80 °C and 17 L mol^{-1} min^{-1} at 60 °C. Hydrolysis occurring inside the interfacial volume has been neglected because of the expected lack of hydroxide ions in this pseudophase.

Steps 4−6: Stepwise Cooperative Aggregation, One-Step Adsorption, and Collective Desorption. Karaborni et al.[9] identified by molecular dynamics calculations the formation of ester-containing micelles (ECM) in oil−water−surfactant systems. Both take place in the interfacial volume. The first one (step 4) involves the direct formation of ECM aggregates at the oil−water interface by a cooperative aggregation, while the second one (step 6) corresponds to a collective desorption of adsorbed surfactant molecules (AS) at the oil−water interface.

Step 4 corresponds to the stepwise cooperative aggregation of g' surfactant monomers incorporating p ester molecules coming from the interface. The process can be described by a Becker−Döring-like model similar to that of Anianson and Wall[13] or Wattis and Coveney.[14] It results in a size distribution where g' and p are average values. As already described in our previous paper, it is reasonable for kinetic modeling purposes

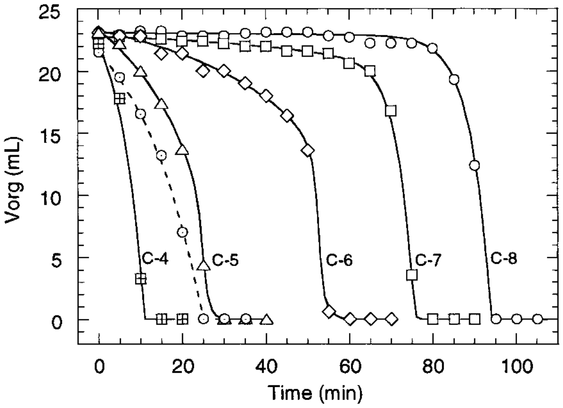

Figure 1. Kinetics of the biphasic alkaline hydrolysis of C-4 to C-8 ethyl alkanoates (dots): (continuous line) model fitting at 80 °C; (dashed line) model fitting of the C-4 experiment at 60 °C.

to reduce this multistep description into a high order ($g' + p$) one-step aggregation with a reversal first-order dissociation. The high-order rate law gives rise to a threshold value in the surfactant concentration that corresponds to a critical aggregation concentration (CAC) above which ECMs are formed.

Step 5 is the adsorption of surfactant monomers at the free interface. Second-order kinetics were used to describe the adsorption that is assumed to occur without any threshold concentration. Since the adsorbed surfactant is a precursor of ECM and to ensure mass balance, the same stoichiometry (g' and p) has been used for the description of AS as for ECM.

In step 6, ECM is the result of the detachment of a bud of AS, i.e., a collective desorption of surfactant and ester molecules from the adsorbed surfactant layer. This process has been described by a first-order reaction.

The difference between step 4 and steps 5 and 6 is mainly due to their kinetic rate law rather than to their net chemical results.

Step 7: Phase Transfer. Coming either from the cooperative or collective pathway, ester-containing micelles (ECM) are dispersed in the bulk aqueous phase where they dissociate, releasing g' surfactant and p ester molecules. The dissociation rate of ester-containing micelles has been taken to be first order.

*Step 8: Formation of Empty Micelles***.** This process has been described by a one-step high-order aggregation and a reversal first-order dissociation process. The numerical values of g and cmc used for the kinetic modeling were obtained from thermodynamic calculations (see section 2 of Appendix, Figure 3, and Table 2).

The skeleton mechanism in Figure 2 shows the reaction pathways and the reactive species in their respective phases (organic, interfacial, and aqueous).

IV. Results and Discussion

1. Equilibrium Thermodynamics Calculations. Equilibrium parameters that were used in the model were predicted by thermodynamic calculations. Figure 3 shows the dependency of g', p, and g on the total surfactant concentration. Although these values depend on the concentration of the surfactant, we considered an approximate final concentration of sodium alkanoates in our experiments to be around $[S_{tot}] = 1$ mol L^{-1}, which corresponds to the concentration that has been reached when the reaction rate is at its maximum. The values that are gathered in Table 2 were used throughout the fitting procedure.

2. Kinetic Curve-Fitting Calculations. Each experiment has been fitted separately. Some parameters that appeared to be sensitive have been adjusted to the best fit. These parameters values are given in Table 3 (see section 1 of Appendix for a complete survey of parameters values used for modeling).

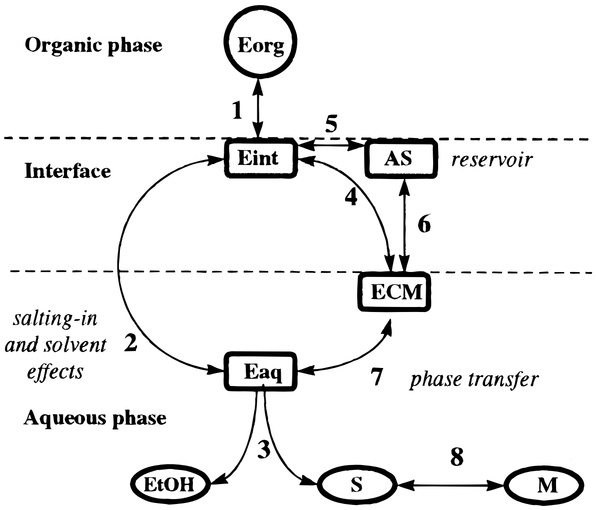

Figure 2. Skeleton mechanism of the autocatalytic biphasic hydrolysis of ethyl alkanoates showing the main reaction pathways and the various reacting species located in the three phases or pseudophases.

Values of k_{-2} obtained by numerical fitting show that under our experimental conditions, solubilization times are about 0.1 min, which is in agreement with literature data.[15] They are also in accordance with the expected tendency that solubility decreases and time of dissolution increases with increasing aliphatic chain length of the ester. Another strong trend is expressed by the value of k_4. This parameter corresponds to the equilibrium constant for the formation of ester-containing micelles (ECM). As expected, aggregation equilibrium constants increase with increasing chain length.

3. Analysis of Time Profiles. *a. C-4 Experiments*. Satisfactory curve fitting of kinetic data at 60 and 80 °C was obtained. It strongly indicates that only solvent and salting-in effects (leading to an increase of the solubility of ethyl butanoate in the aqueous phase) are at the origin for the weak autocatalytic behavior of this system.

b. C-5 Experiments. The interpretation of the kinetics requires the consideration of both salting-in and solvent effects and cooperative phase transfer by ECM.

c. C-6 and C-7 Experiments. In this case, the beginning of the acceleration period takes place only after a relatively large amount of ester has been already hydrolyzed. Satisfactory data fitting failed when only α and cooperative phase-transfer effects were considered. Adsorption of the surfactant at the oil−water interface has to be taken into account as well. The adsorbed surfactant AS acts as a transient reservoir for a part of surfactant molecules that are trapped at the interface. These trapped surfactant molecules are consequently not available for the subsequent phase-transfer process. For the C-7 experiments, critical aggregation concentration or CAC is readily reached, the cooperative formation of ester-containing micelles (ECM) is the predominant process, and AS accumulates moderately. The behavior of the C-6 experiments is more difficult to interpret because modeling shows a high transient value of AS. This high value could be understood either by considering that the roughness of the interface could provide a sufficiently large interfacial volume or by assuming that “AS” would not be really adsorbed at the interface but is rather located in the bulk aqueous phase as nontransporting ester-containing micelles.

d. C-8 Experiments. In this case, cooperative aggregation is the only source of ester-containing micelles (ECM) and phase

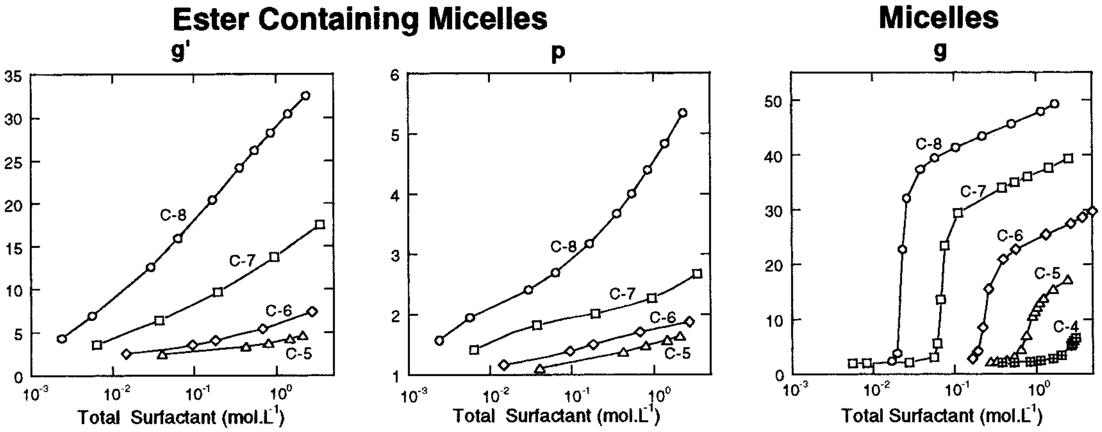

Figure 3. Weight average aggregation number vs the total concentration of surfactant for ester-containing micelles (g' and p) and micelles (g).

TABLE 3: Values of the Parameters Obtained from Fitting of Kinetic Experimental Data[a]

	C-4 (60 °C)	C-4 (80 °C)	C-5	C-6	C-7	C-8
k_{-2}	13.05	18.7	16	14.1	5.35	4.76
k_4	–	–	$1.87 \times 10^{+1}$	$1.61 \times 10^{+6}$	$2.06 \times 10^{+19}$	$1.11 \times 10^{+49}$
k_5	–	–	–	150	23.1	–
k_6	–	–	–	0.10	0.53	–
k_7	–	–	1.59	1.50	1.65	1.42

[a] k_{-2}, k_6, and k_7 are first order, k_5 is second order, and k_4 is $(g' + p)$th order. The sign (–) indicates that it has not been necessary to activate the corresponding process.

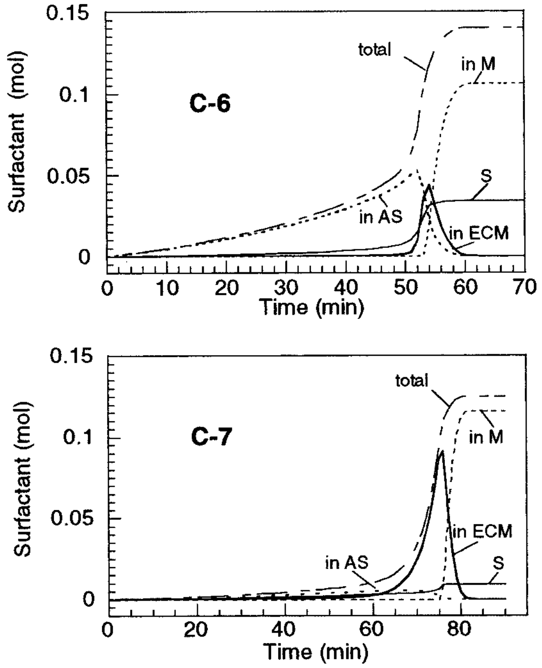

Figure 4. Calculated time profiles of surfactant-containing species during the biphasic alkaline hydrolysis of C-6 and C-7 ethyl alkanoates using the fitted model parameters.

transfer is the main process. Formation of ECM occurs at a critical aggregation concentration (CAC) that is smaller than the cmc of the empty micelles. Model calculations show that the phase-transfer equilibria of steps 4 and 7 are strongly displaced toward the transportation of the ester from the organic to the aqueous phase. This phenomenon is likely due to the ester gradient concentration between the two phases. Considering collective adsorption–desorption at the interfacial volume is not necessary for a satisfactory curve fitting. The salting-in effect due to the accumulation of sodium octanoate monomers in the aqueous phase is not important because the corresponding CAC and cmc are small. This reasoning is supported by the experimental results (Table 1) showing the weak catalytic activity of ethanol and the strong catalytic effect of a small quantity of sodium octanoate.

V. Conclusion

Although we are aware that drastic simplifications have been made in our model, we think that the main reacting species, paths, couplings, and features of the kinetics have been correctly identified. As a general property, the rate of oil–water biphasic reaction is independent of the remaining amount of supernatant organic phase. As a consequence, biphasic reactions display intrinsically zero-order kinetics. However, if the reaction products are able to change the physicochemical properties of the interface, for instance, by increasing the saturation concentration of the organic solute in the aqueous phase, autocatalytic behavior is expected. During the biphasic alkaline hydrolysis of C-4 to C-8 ethyl alkanoates, several phenomena alter the interfacial properties and increase the solubility of the ester in the aqueous phase. For ethyl butanoate (short chain length), only the salting-in and solvent effect by the reaction products accounts for the autocatalytic kinetics. For longer chain lengths (C-5 to C-8) cooperative stepwise formation of ester-containing micelles (ECM) (occurring with a threshold concentration) and subsequent phase transfer have to be taken into account. However, for intermediate chain lengths (C-6 and C-7), kinetic modeling shows that there is also a transient capture of surfactant molecules that proceeds without any threshold concentration. Those surfactant molecules are temporarily withdrawn from the cooperative phase. Empty micelles have to be considered as an inactive end product. They can be omitted during kinetic modeling without any effect on curve fitting.

Liquid–liquid biphasic reactions in which products have an influence on the interfacial properties appear to be a new class of nonlinear chemical systems; kinetic studies are at the beginning. Highly nonlinear behavior giving rise to kinetic bistability in a CSTR has been recently studied in the biphasic alkaline hydrolysis of ethyl octanoate.[16] Further examples of such systems could be found in "classic" organic chemistry like the sulfonation of aromatic compounds, N-oxidation of amines, nucleophilic substitution of alkyl halides, or acetalization of sugars when performed under biphasic conditions.

VI. Experimental Section

Reagents. Reagents of highest purity commercially available (Fluka) were used without further purification. Alkyl chains are C-4 butanoate, C-5 pentanoate, C-6 hexanoate, C-7 heptanoate, and C-8 octanoate. Sodium hydroxide (pro analysi) was purchased from Prolabo, and water was doubly distilled.

Biphasic Hydrolysis of Ethyl Alkanoates. The reactions were performed in a thermostated ($T = 80$ or 60 °C) round-bottom two-neck 250 mL flask under reflux. Macromixing of the two phases (70 mL of aqueous 3 M NaOH and 23 mL of ester) was achieved by magnetic stirring at 800 ± 5 rpm with an ellipsoidal magnetic bar of about 25 mm × 6 mm size. Initial amounts were the following: OH^- at 0.21 mol and E_{org} at 0.163, 0.168, 0.156, 0.140, 0.125, and 0.116 mol for, respectively, C-4 (60°), C-4 (80°), C-5, C-6, C-7, and C-8 experiments.

Kinetic Measurements. At fixed time intervals the reaction mixture was poured into a graduated volumetric cylinder, and after phase separation (within a few seconds) the volume of the residual organic phase was measured. Time elapsed during the measurements was taken off.

Model Calculations. Model calculations and fitting of the experimental kinetic curves have been performed on a workstation HP 9000-710. The general algorithm used combines a semiimplicit Runge–Kutta method[17] for the numerical integration of the differential equations and a nonlinear minimization procedure.[18] Fitting calculations have been started using estimations of the unknown parameters.

VII. Appendix

1. Modeling Techniques. *(a) Rate Laws*. The following rates laws and rate constants have been used for the model:

r	k	comments
$r_1 = k_1 E_{org}$	$k_1 = 7.75$	a
$r_{-1} = k_{-1} E_{int}$	$k_{-1} = 1.66 \times 10^3$	b
$r_2 = k_{-2} V_{aq} s \exp(\alpha([EtOH] + [S])$	$k_2 = k_{-2} s$	c
$r_{-2} = k_{-2} E_{aq}$	k_{-2}	d
$r_3 = k_3 E_{aq}\, OH^- V_{aq}{}^{-1}$	$k_3 = 60$ (80 °C); 17 (60 °C)	
$r_4 = k_4 [S_{aq}]^{g'} [E_{int}]^p V_{int}$	k_4	de
$r_{-4} = k_{-4}$ ECM	1	b
$r_5 = k_5 E_{int} [S_{aq}]$	k_5	d
$r_{-5} = k_{-5} AS$	1	b
$r_6 = k_6 AS$	k_6	d
$r_7 = k_7 ECM$	k_7	d
$r_{-7} = k_4 [S_{aq}]^{g'} [E_{aq}]^p V_{aq}$	k_4	f
$r_8 = k_8 [S_{aq}]^g V_{aq}$	$k_8 = K_m$	
$r_{-8} = k_{-8} M$	1	b

The table comments refer to the following.

(a) Assuming spherical and smooth ester droplets, the ratio $E_{int}/E_{org} = k_1/k_{-1} = (6/D)(\upsilon/a) \cong 7 \times 10^{-9}/D = 4.67 \times 10^{-3}$ for a spherical droplet diameter of 1.5 μm.[19]

(b) For the sake of simplicity, k_{-4}, k_{-5}, and k_{-8} have been taken arbitrarily at unity and $k_{-1} = 1.66 \times 10^3$ assuming that the corresponding equilibria are rapid.

(c) The same value of α has been taken for EtOH and the surfactant.

(d) Adjusted parameters values are from Table 3.

(e) Surfactant concentration at the interface is assumed to be equal to those in the aqueous phase.

(f) The back reaction of step 7 denotes a cooperative stepwise aggregation of g' surfactant molecules with p ester molecules such as in step 4. For this reason, its reaction order ($g' + p$) and rate constant have been taken to be the same ($k_{-7} = k_4$).

(b) Differential and Algebraic Equations. Corresponding differential and algebraic equations are shown below.

$$d[E_{org}]/dt = -r_1 + r_{-1}$$

$$d[E_{int}]/dt = r_1 - r_{-1} - r_2 + r_{-2} - p(r_4 - r_{-4} + r_5 - r_{-5})$$

$$d[E_{aq}]/dt = r_2 - r_{-2} - r_3 + p(r_7 - r_{-7})$$

$$d[S]/dt = r_3 - g'(r_4 - r_{-4} + r_5 - r_{-5} - r_7 + r_{-7}) - g(r_8 - r_{-8})$$

$$d[EtOH]/dt = r_3$$

$$d[OH^-]/dt = -r_3$$

$$d[ECM]/dt = r_4 - r_{-4} + r_6 - r_7 + r_{-7}$$

$$d[M]/dt = r_8 - r_{-8}$$

$$d[AS]/dt = r_5 - r_{-5} - r_6$$

$$V_{int} = (E_{int} + (g' + p)AS)\upsilon$$

$$V_{aq} = V_{tot} - E_{org}\upsilon - V_{int}$$

$$V_{exp} = (E_{org} + E_{int} + pAS)\upsilon$$

where the total reacting volume (V_{tot}) is assumed to be constant. The experimentally measured volume (V_{exp}) of the organic phase after decanting and phase separation corresponds to the ester in the bulk phase (E_{org}), in the interface (E_{int}), and in the adsorbed layer (ester part in AS). The molar volume υ has been taken to be equal for the ester and the corresponding sodium alkanoate.

2. Solution Thermodynamic Properties of Sodium Alkanoates and Ethyl Alkanoates. *a. Solubility of Ethyl Alkanoates in Water*. The correlation of experimental solubility data of ethyl alkanoates in water[20] at 298 K yields $\Delta G_s^\circ = 1.317 + 0.688N$ expressed in units of kcal mol^{-1} K^{-1}, and N denotes the number of carbon atoms in the alkanoate ($N = 8$ for octanoate). Here, ΔG_s° is the free energy change associated with dissolution and is equal to $RT \ln X$ where X is the mole fraction solubility. Experimental data on the dependence of solubility on temperature and salt concentration for ethyl alkanoates are not available. Therefore, the corrections for temperature and salt effects have been made using information available for alkanes. The corrections are made using group contribution procedure and account for all the CH_2 and CH_3 groups in the ethyl alkanoate but ignore any correction for the COO group. In the presence of NaCl, the free energy $\Delta G_s^\circ/RT$ changes by $0.384C$ for the CH_3 group and by $0.064C$ for the CH_2 group, where C is the molar concentration of the added salt.[21] We do not have information about this correction term at other temperatures, and therefore, this correction is taken as temperature-independent. From solubility data for alkanes,[20] we know that $\Delta G_s^\circ/RT$ for the CH_2 group is 1.496 at 298 K and 1.311 at 353 K. For the CH_3 group, $\Delta G_s^\circ/RT$ is 3.536 at 298 K and 3.548 at 353 K. Therefore, the change in temperature from 298 to 353 K will cause a change in solubility given by

$\Delta G_s^o/RT$ of −0.185 for CH_2 and 0.012 for CH_3. Taking into account the salt and temperature effects on solubility, we can calculate the solubility at 353 K and 3 M NaOH using the solubility information at 298 K and 0 M NaOH as follows:

$$\ln X(T{=}353\mathrm{K},C{=}3\mathrm{M}) = \ln X(T{=}298\mathrm{K},C{=}0\mathrm{M}) + [0.185n_{\mathrm{CH_2}} - 0.012n_{\mathrm{CH_3}}] - C[0.064n_{\mathrm{CH_2}} + 0.384n_{\mathrm{CH_3}}]$$

The first correction term is for the temperature dependence, and the second is for the salt dependence. The number of methylene and methyl groups in ethyl alkanoate are denoted by $n_{\mathrm{CH_2}}$ and $n_{\mathrm{CH_3}}$, respectively. The mole fraction solubility data are converted to molar concentration by multiplying by 55.55.

b. Estimation of Parameter α *Representing Solubility Enhancement Caused by ethancol and Sodium Alkanoate*. The solubility of ethyl alkanoate in water is affected by the presence of ethanol and sodium alkanoate. Both contribute to an increase in the aqueous solubility of ethyl alkanoates by modifying the structure of water. To describe the influence of ethanol, we view the problem as that of the solubility of ethyl alkanoate in a mixed solvent consisting of ethanol and water. The solubility in the mixed solvent (X_{mix}) can be related to the solubility in the pure solvents of water and ethanol (X_W and X_E) by applying the framework of any suitable solution theory. The Flory−Huggins solution model[22] yields

$$\ln X_{\mathrm{mix}} = \phi_w \ln X_W + \phi_E \ln X_E + \chi_{WE}\phi_E\phi_W$$

where ϕ_W and ϕ_E denote the volume fractions of water and ethanol in the mixed solvent and χ_{WE} is the interaction parameter between water and ethanol. Since the interaction term in the above equation is less important compared to the other terms, the above expression reduces to

$$X_{\mathrm{mix}} = X_W \exp\left[\phi_E \ln \frac{X_E}{X_W}\right] = X_W \exp\left[0.0585 \ln \frac{X_E}{X_W} C_E\right] = X_W \exp[\alpha C_E]$$

The volume fraction ϕ_E and the molar concentration C_E of ethanol are related by $\phi_E = 0.0585C_E$, and α denotes the factor 0.0585 $\ln(X_E/X_W)$. To calculate α, the known group contributions at 25 °C to $\ln X_E$ and $\ln X_W$, namely, $-0.178kT$ and $-0.935kT$ for CH_2 and CH_3 groups when ethanol is the solvent and $-1.425kT$ and $-3.875kT$ when water is the solvent, are used. Since the contribution of the polar COO group would be comparable in both solvents, the ratio $\ln(X_W/X_E)$ is not significantly affected by it. Further, the temperature dependencies of X_E and X_W would approximately cancel each other, and thus, to a first approximation, α is temperature-independent. The values of α calculated in this manner are listed in Table 2.

The influence of sodium alkanoates on the solubility of ethyl alkanoates can be described by the concept of salting-in/salting-out applied to solutions containing salts. The solubility of an organic nonelectrolyte solute in the presence of a salt can be represented as

$$\ln \frac{X(C)}{X(C{=}0)} = kC$$

where k is the salting-in/salting-out equilibrium constant and C is the molar concentration of the salt. For inorganic salts, k is a negative constant and the solute is salted-out. For an organic salt (sodium alkanoate, in the present case), depending upon the importance of the organic part, the constant k can be positive and the solute is salted-in.

Quantitative methods for a priori estimation of the salting-in constant k are not sufficiently well-developed, and hence, experimental estimates based on measured solubility data are more commonly used. The magnitude of k will depend on both the organic salt (sodium alkanoate) and the solute molecule (ethyl alkanoate). k has been found to increase linearly with the alkyl chain length of large organic salts. The influence of long-chain quaternary ammonium salts (carbon numbers between 4 and 12) on the aqueous solubility of benzoic acid is accounted for by values of k in the range 0.35−0.91 M^{-1}, with k having a methylene group contribution of 0.07 M^{-1}. We note that the incremental variation in the parameter α, which accounts for the influence of ethanol on the solubility of ethyl alkanoates, is also 0.07 per methylene group (see Table 2). Since no direct measurement of k relevant to our system is presently available and since the incremental variation in α is comparable to that in k for an analogous system, k is equated to α for simplifying our kinetic calculations. In summary, the solubility X of ethyl alkanoates in the presence of ethanol and sodium alkanoate has been calculated using the relation

$$X = X(\mathrm{EtOH}{=}0,\mathrm{S}{=}0) \exp \alpha([\mathrm{EtOH}]+[\mathrm{S}])$$

where [EtOH] and [S] are the molar concentrations of ethanol and sodium alkanoate in the aqueous solution and values of α are those listed in Table 2.

c. Calculation of Micellization Variables g, cmc, and K_m for Sodium Alkanoates. The aggregation characteristics of sodium alkanoates ($C_{n-1}H_{2n-1}COONa$) such as the cmc, the average aggregation number of micelles, the variance of the micelle size distribution, and the micellization equilibrium constant (step 8 in the reaction scheme of section III.3) can all be predicted a priori using the molecular thermodynamic theory formulated by Nagarajan and Ruckenstein.[23] For a surfactant solution containing micelles of various aggregation numbers g, the equilibrium condition of a minimum in the Gibbs free energy stipulates

$$\mu_g^\circ + kT \ln X_g = g(\mu_1^\circ + kT \ln X_1)$$

where X_1 and X_g are the mole fractions of the singly dispersed molecules and aggregates of size g, respectively, and are their respective standard chemical potentials, defined as those corresponding to infinitely dilute solution conditions. Expressions for the standard chemical potentials have been developed in ref 23, and the methods of calculating the equilibrium micellization properties have been described in ref 23 and also in our previous paper, ref 8.

The predicted results summarized in Table 2 and Figure 3 correspond to the experimental conditions of 80 °C and the presence of 3 M NaCl in the surfactant solution. The weight-average aggregation number g as a function of the total concentration X_{tot} ($=X_1 + \sum gX_g$) of sodium alkanoate in solution is plotted in Figure 3. The mole fractions X are converted to molar concentrations C by multiplying by 55.5. One may notice that for the C_4 alkanoate, no aggregate formation occurs up to a concentration of 2 M. For other tail lengths, one can observe that the aggregation number is increasing with increasing surfactant concentration. This is a typical behavior anticipated when the aggregation numbers are small. Indeed, this behavior corresponds to a somewhat polydispersed distribution of aggregates in solution. The aggregation numbers listed in Table 2 are the values predicted corresponding to a concentration of 1 M sodium alkanoate but have been used as constants in the kinetic model calculations. A sharp transition in the plot of X_1

against the total concentration $X_{tot} = X_1 + \sum gX_g$ is used to predict the cmc values listed in Table 2. The micellization equilibrium constant K_m is calculated from the predicted cmc and g.

d. Calculation of Solubilization Variables g′ and p. When sodium alkanoates and ethyl alkanoates are both present, solubilizate (ethyl alkanoate) containing aggregates (designated as ECM in the kinetic model) form at surfactant concentrations that are lower than the cmc calculated for surfactant solutions. To predict the aggregation number g' and the number of solubilizate molecules p present in an ECM aggregate, one can adopt exactly the same approach as that used for micelle formation. Such a theory has been developed and described in detail in ref 23. The calculated results for g' and p are plotted in Figure 3 as functions of the total concentration of sodium alkanoate in solution. One can notice that both g' and p are dependent on the total concentration of the surfactant and increase with increasing surfactant concentration. This is a feature characteristic of systems where the aggregation numbers are small. The values of g' and p listed in Table 2 are those predicted at a total surfactant concentration of 1 M but have been used as constants for performing the kinetic model calculations.

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