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Ultrasound to Enhance a Liquid–Liquid Reaction

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Liquid–liquid mass transfer with ultrasound was investigated experimentally during the hydrolysis of *n*-amyl acetate. Power ultrasound is supposed to improve the yield and kinetics of such "multiphase chemical reactions thanks to the mechanical effects of cavitation. Indeed, implosion of micro-bubbles at the vicinity of the liquid–liquid interface generates disruption of this surface, and enhances mixing in the liquid around the inclusion, thus improving mass transfer between the two phases. This effect has been demonstrated here on the hydrolysis of *n*-amyl acetate by sodium hydroxide, a rather slow reaction but influenced by mass transfer; the reaction is carried out in a glass jacketed reactor, 500 mL of volume, equipped with a Rushton turbine and a 20 kHz sonotrode dipping in the solution. The ester is initially pure in the organic dispersed phase, and sodium hydroxide has an initial concentration of 300 mol/m³; one of the products, pentanol partitions between the two phases and the sodium salt stays in the aqueous phase. The initial apparent reaction rate is measured from the record of the conductivity giving the concentration of alkali versus time. The reaction rate was always found to increase when ultrasound is superimposed to mechanical stirring (at 600 rpm), with a positive influence of input power (20 and 50 W). When varying initial concentration (300 and 600 mol/m³), temperature (36 and 45°C) and ultrasound emitter (sonotrode or cuphorn), the benefit of ultrasound over mechanical agitation was systematic. The only case of a weak influence of ultrasound was the sonication of a dense medium, containing 23% of organic phase and impeding the propagation of ultrasound.

Introduction

Power ultrasound is known to improve the yield and kinetics of some multiphase physical processes and chemical reactions thanks to mechanical effects of cavitation. Acoustic cavitation involves nucleation, growth, oscillation and collapse of gas and vapour micro-bubbles. The violent implosion of these bubbles at the vicinity of a solid–liquid or liquid–liquid interface generates disruption of this surface, enhances mixing in the liquid around the inclusion, and thus improves interfacial area and mass transfer coefficient between the two phases.

In emulsification process, ultrasound has been mainly used in order to increase the stability of emulsions thanks to the decrease of the size and to the narrowing of the size distribution of the droplets (Abismail *et al.*, 1999, 2000). In the case of liquid–liquid extraction, ultrasound improves mass transfer thanks to the increase of k_L and a . Some liquid–liquid reactions have been successfully carried out with ultrasound, like phase transfer catalytic reactions (Naik and Doraiswamy, 1998). But no detailed investigation of mass transfer has

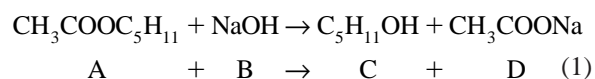
been carried out in such systems.

In the present work, the apparent kinetics of a liquid–liquid reaction is investigated in presence of ultrasound, and the enhancement of the mass transfer volumetric coefficient $k_L a$ is evaluated for different values of operating parameters. The ultrasound frequency of 20 kHz has been chosen because it is known to result in high mechanical effects.

1. The Reaction

1.1 System of phases

The model liquid–liquid reaction chosen is the hydrolysis of *n*-amyl acetate by sodium hydroxide, producing pentanol and sodium acetate:



Initially, *n*-amyl acetate is pure in the organic phase, and diffuses to the aqueous phase where it reacts with sodium hydroxide. Then, the formed pentanol partitions between the two phases and sodium acetate stays in the aqueous phase.

This reaction has been studied previously (Alwan *et al.*, 1983; Hiraoka *et al.*, 1990; Issanchou *et al.*, 2003;

Table 1 Values of pre-exponential factors and activation energies for k , m_A and m_C (Issanchou *et al.*, 2003)

	Pre-exponential factor	Activation energy = E/R [K]
Kinetic constant k [$\text{m}^3 \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$]	22532	5790
Part. coef. m_A [—]	13418	957
Part. coef. m_C [—]	34711	2225

Viallard, 1959) and it is known as a rather slow reaction, but influenced by mass transfer. Consequently, its kinetics law (orders: 1 and 1, and kinetic constant $k(T)$) and the partition coefficients, m_i , of A and C are tabulated (Eqs. (2) and (3), **Table 1**).

$$r = k(T) \cdot C_A^c C_B \quad \text{with: } k = k_0 \cdot \exp(-E/RT) \quad (2)$$

$$m_i = m_{i0} \cdot \exp(-E_{mi}/RT) \quad \text{for } i = A, C \quad (3)$$

where C_A^c is the concentration in ester in the continuous aqueous phase.

The first step of the study was to evaluate Ha number and the regime of reaction:

$$Ha = \frac{\sqrt{k \cdot C_B \cdot D_A}}{k_L} \quad (4)$$

D_A was estimated thanks to Wilke and Chang correlation, and k_L in the mechanically stirred system was calculated with the correlation by Alwan *et al.* (1983). The experimental conditions (temperature and concentrations in reactants) have been chosen for the reaction to be influenced by mass transfer ($0.02 \ll Ha$).

At 36 and 45°C, $C_{B0} = 300$ and $1500 \text{ mol} \cdot \text{m}^{-3}$, $N = 600 \text{ rpm}$, the calculated Ha numbers ranged between 0.08 and 0.2 (**Table 2**), meaning that the reaction is in regime II (rather slow, but influenced by mass transfer, (Sharma and Nanda, 1968)).

1.2 Experimental conditions

A jacketed glass reactor (60 mm in diameter) is equipped with a mechanical stirrer (Rushton turbine, 30 mm in diameter) and an ultrasound probe (20 kHz), 13 mm in diameter (**Figure 1**). The ultrasound generator and emitter are from Sonics and Materials. Water is circulated through the double jacket in order to keep a constant temperature; and in fact, the temperature measured during the reaction was constant within $\pm 1^\circ\text{C}$.

Another reactor has also been used for comparison, a cuphorn: a stainless steel mechanically stirred autoclave with the ultrasound emitting surface located at the bottom of the reactor (see Laugier *et al.*, 2008 for more details).

In standard conditions (glass reactor, $300 \text{ mol} \cdot \text{m}^{-3}$), 11.11 g (12.5 mL) of ester are poured in the reactor con-

taining 200 mL water, stirring and ultrasound are switched on; when the temperature is stable, 50 mL of concentrated sodium hydroxide ($1500 \text{ mol} \cdot \text{m}^{-3}$) is added to the system ($t = 0$). For runs in the cuphorn, all quantities have been multiplied by 3. During reaction, the sodium hydroxide concentration C_B is followed by measurement of the solution conductivity $\gamma(t)$ as suggested by Hiraoka *et al.* (1990), and Issanchou *et al.* (2003). From the conductivities at time t , γ , at time zero, γ^0 , and at the end of reaction, γ^∞ , (when all the sodium hydroxide has reacted), C_B can be calculated:

$$C_B = C_{B0} \frac{\gamma - \gamma^\infty}{\gamma^0 - \gamma^\infty} \quad (5)$$

The influences of temperature ($T = 35$ and 45°C) and of alkali initial concentration ($C_{B0} = 300, 600$ and $1500 \text{ mol} \cdot \text{m}^{-3}$) have been investigated. To obtain $C_{B0} = 600 \text{ mol} \cdot \text{m}^{-3}$, only the concentration of sodium hydroxide was increased to $3000 \text{ mol} \cdot \text{m}^{-3}$. To obtain $C_{B0} = 1500 \text{ mol} \cdot \text{m}^{-3}$ and an organic volume fraction of 23%, the quantities were: 52.2 g ester, 122 mL water, 80 mL sodium hydroxide solution ($4475 \text{ mol} \cdot \text{m}^{-3}$). For each set of experimental conditions, ultrasound power has been varied between 0 and 65 W.

1.3 Modelling

The reaction was modeled by a simple double-film model with the following assumptions:

- the reaction is first-order with respect to the ester and the alkali. k value is given by Eq. (2) and Table 1,
- in the dispersed organic phase, mass transfer resistance is neglected, and the concentrations are uniform,
- as the reaction is slow, it is assumed to take place in the bulk of the continuous aqueous phase,
- mass transfer volumetric coefficients $k_L a$ are supposed to be constant during the reaction, and equal for A and C.

This assumption is very simplistic since it is known that the organic phase volume decreases with time; but the model is only aimed at giving the trends of the variations.

The mass balances on the three components A, B, C, can be written as follows:

(^c: continuous, ^d: dispersed; _i: interface, _e: bulk)

$$\begin{aligned} k_{LA} a \cdot (C_{Ai}^c - C_{Ae}^c) \cdot V &= -\frac{dn_A^d}{dt} = \frac{dn_A^c}{dt} + k \cdot C_B \cdot C_{Ae}^c \cdot V^c \\ \frac{dn_B}{dt} &= -k \cdot C_B \cdot C_{Ae}^c \cdot V^c \\ k_{LC} a \cdot (C_{Ce}^c - C_{Ci}^c) \cdot V &= \frac{dn_C^d}{dt} = -\frac{dn_C^c}{dt} + k \cdot C_B \cdot C_{Ae}^c \cdot V^c \end{aligned} \quad (6)$$

where: $n_i^d = C_i^d \cdot V^d$ $n_i^c = C_i^c \cdot V^c$ with $i = A, C$

At the interface, A and C are supposed to partition be-

Table 2 Values of the physico-chemical parameters and Hatta numbers for the three sets of operating conditions (part 1–4)

	Part 1	Part 2	Part 3	Part 4
C_{B0} [mol · m ⁻³]	300	600	300	1500
T [°C]	36	36	45	36
m_A	606	606	662	606
C_{A0}^d [mol · m ⁻³]	6682	6682	6682	6682
C_{A0}^c [mol/m ⁻³]	11.01	11.01	10.03	11.01
D_A [m ² · s ⁻¹]	1.07×10^{-9}	1.07×10^{-9}	1.30×10^{-9}	1.07×10^{-9}
k_L [m · s ⁻¹]	8.55×10^{-5}	8.55×10^{-5}	$1.02 \cdot 10^{-4}$	8.55×10^{-5}
k [m ³ · mol ⁻¹ · s ⁻¹]	1.66×10^{-4}	1.66×10^{-4}	2.81×10^{-4}	$1.66 \cdot 10^{-4}$
Ha	0.085	0.120	0.102	0.206

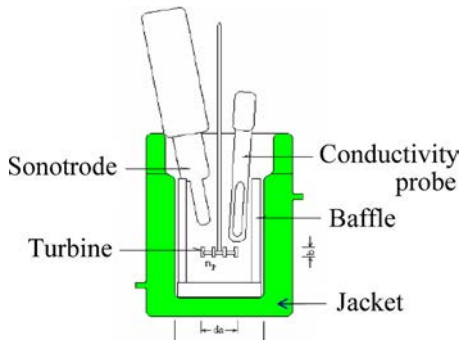


Fig. 1 Experimental setup with glass reactor and dipping sonotrode

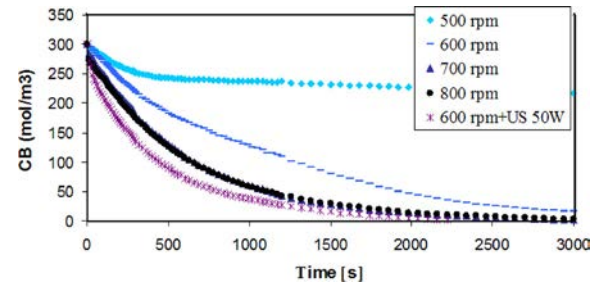


Fig. 2 Alkali concentration versus time for different rotation speeds and one ultrasound power: $T = 36^\circ\text{C}$, $C_{B0} = 300 \text{ mol} \cdot \text{m}^{-3}$

tween the two phases according to equilibrium laws:

$$C_A^d = m_A \cdot C_{Ai}^c \quad C_C^d = m_C \cdot C_{Ci}^c \quad (7)$$

The continuous phase volume, V^c , is assumed to stay constant, whereas the dispersed phase volume, V^d , depends on time through its composition in A and C:

$$V = V^c + V^d \quad V^d = v_A \cdot n_A^d + v_C \cdot n_C^d \quad (8)$$

(where v_i are the molar volumes of A and C).

This system of equations is solved in Excel, and $C_B(t)$ curves are plotted and compared to experimental ones.

2. Results and Discussions

2.1 Influence of the different operating parameters on $C_B(t)$

Sodium hydroxide concentrations, C_B , have been plotted versus time and can be compared for different conditions.

Ultrasound has always been used together with mechanical agitation, since it is very effective in reducing drops size (formed thanks to mechanical stirring) but not in forming drops out of a flat interface (Abismail *et al.*, 1999, 2000).

2.1.1 Mechanical agitation First, the influence of rotation speed has been investigated in the case of mechanical stirring alone.

It can be observed (**Figure 2**) that 500 rpm is not enough to give a homogeneous emulsion: after 5 min of reaction, the reaction rate stays almost constant and very low, suggesting a low value of interfacial area, which is confirmed by the direct visualization of the medium containing large and irregular drops. Then, from 600 rpm, the reaction medium is well emulsified and the reaction rate increases with an increase of N . It can be noticed that 700 and 800 rpm give the same reaction rate, which suggests that mass transfer is no more limiting, and that the chemical regime is reached. Finally, the addition of ultrasound to mechanical stirring (600 rpm) yields a further increase of the reaction rate. In order to see clearly the benefit of ultrasound, it was decided to choose a rotation speed of 600 rpm when investigating the influence of ultrasound.

It can be also noticed that some curves exhibit a change of slope, which is not systematic and reproducible, and more frequent at low mixing level: it can be attributed to problems of conductivity measurements in this heterogeneous system (adhesion of organic drops on the probe).

2.1.2 Ultrasound power **Figure 3** shows the effect of the ultrasound power for two temperatures (36 and 45°C). Increasing ultrasound power results in an in-

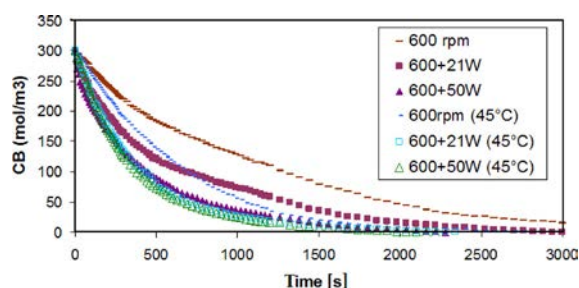


Fig. 3 Alkali concentration versus time for different ultrasound input powers and a rotation speed of 600 rpm: $T = 36$ or 45°C ; $C_{B0} = 300 \text{ mol} \cdot \text{m}^{-3}$

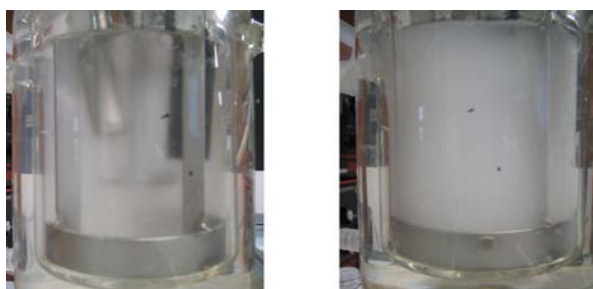


Fig. 4 Aspect of the reacting medium with ultrasound ($P = 16$ and 67 W)

crease of the reaction rate. But here again, this increase is limited by reaching the chemical regime: at high ultrasound power, mass transfer is no longer limiting and the reaction rate tends to the chemical kinetic rate.

Photographs of the reacting medium (**Figure 4**) were taken for two values of power: 16 and 67 W, and showed that the increase in power induced a decrease of the dispersed phase drop size (observable by the 'milky' appearance of the medium at high power).

Of course, with a temperature increase, the reaction rates increase and the effect of ultrasound is weaker, but always present.

2.1.3 Ultrasound emitter Two emitting systems have been compared: the glass reactor with the dipping sonotrode and the cuphorn autoclave (**Figure 5**). In both systems, ultrasound has a positive effect related to input power, but in the autoclave the effect of ultrasound is not as important as in the small glass reactor. Indeed, the autoclave has standard shape and dimensions and the mechanical mixing is more 'efficient'; curves corresponding to high powers (50 W glass reactor—21 and 50 W autoclave) are very near, tending to the chemical regime.

2.1.4 Volume fraction The volume fraction of dispersed phase was increased from 4 to 23%. The influence of ultrasound is different from the previous results (**Figure 6**): it eliminates the delay present with mechanical stirring, due to the time necessary to yield a good emulsion. With ultrasound, the emulsion is immediate so that the reaction begins instantaneously. But the rate dur-

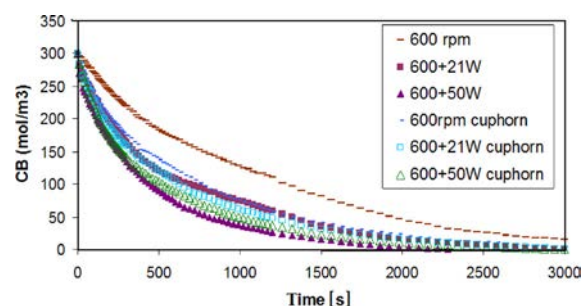


Fig. 5 Alkali concentration versus time for different ultrasound input powers for glass reactor and cuphorn: $T = 36^\circ\text{C}$, $C_{B0} = 300 \text{ mol} \cdot \text{m}^{-3}$

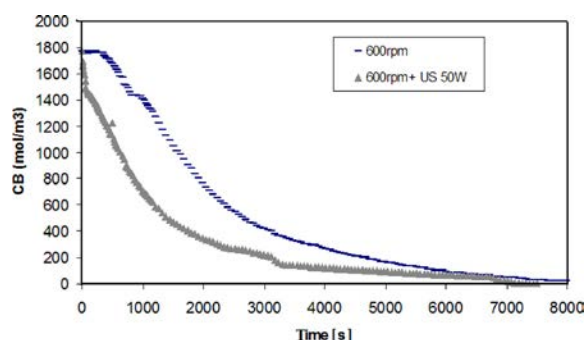


Fig. 6 Alkali concentration versus time at high ester holdup: $C_{B0} = 1500 \text{ mol} \cdot \text{m}^{-3}$, $T = 36^\circ\text{C}$

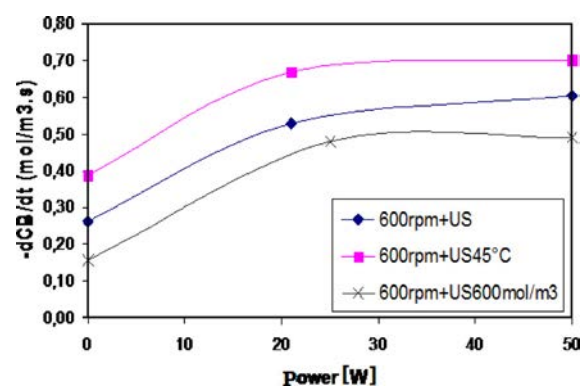


Fig. 7 Initial apparent reaction rate versus ultrasound power for different operating conditions

ing the reaction is not very much faster with ultrasound than in silent conditions. The higher volume fraction of dispersed phase may cause absorption of the ultrasound wave and reduce the efficiency of acoustic cavitation.

2.2 Interpretation

From the plots of $C_B(t)$, the quasi initial apparent reaction rates were calculated (initial slope). These values of $(-dC_B/dt)_0$ have been plotted (**Figure 7**) versus ultrasound power input, for the two values of temperature and the two alkali concentrations. All these curves show the benefic influence of ultrasound power: in all cases, the apparent reaction rate increases when ultra-

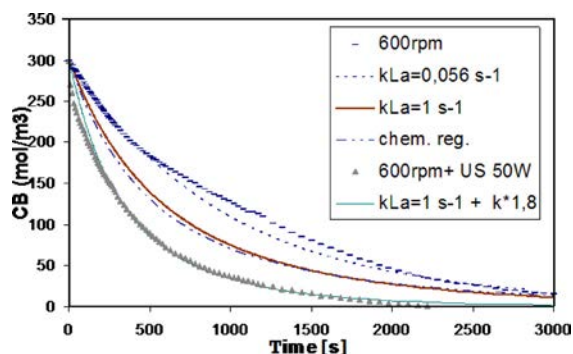


Fig. 8 Alkali concentration: comparison of experimental and model.

sound is added to mechanical stirring. The influence of input power is positive, but the difference is not large between 20 and 50 W. Therefore, it can be concluded that ultrasound is very effective in improving the reaction rate, but that high powers are not necessary for that reaction; in fact, when ultrasound power is increased above 20 W, cavitation increases but its effect on mass transfer cannot be observed anymore because the reaction rate is no more limited by mass transfer.

From these values of $(-dC_B/dt)_0$ and the equation of apparent reaction rate derived by Sharma and Nanda (1968).

$$-\frac{dC_B}{dt} = \frac{1}{\frac{1}{k_L a} + \frac{1}{k C_B}} \cdot C_{Ai}^c \quad (9)$$

for the intermediate regime (between I and II, that is for a moderate influence of mass transfer), $k_L a$ could be calculated. ($k_L a = k_{LA} a = k_{LC} a$)

In some cases (high temperature: 40°C or high alkali concentration: 600 mol · m⁻³), $k_L a$ could be estimated and proved to be enhanced by ultrasound: at 35°C, $k_L a$ values ranged from 0.014 s⁻¹ without ultrasound, to 0.045 s⁻¹ at 25 W and for $C_{B0} = 600$ mol · m⁻³; at 45°C, $k_L a$ value increased from 0.086 s⁻¹ without ultrasound, to 1.3 s⁻¹ at 25 W and for $C_{B0} = 300$ mol · m⁻³. In these cases, the values of $k_L a$ given by this equation gave model curves in agreement with the experimental ones. But for higher values of power, the estimation becomes no more accurate, due to the very low influence of mass transfer. As mass transfer ($k_L a$) has been increased by ultrasound, the system becomes limited by the reaction rate (shift from regime II to regime I).

This phenomenon is still enhanced at low temperature and initial concentration ($T = 35^\circ\text{C}$ and $C_{B0} = 300$ mol · m⁻³), where the calculation of $k_L a$ was even not possible by this equation (= it yielded negative values of $k_L a$). The calculation of $C_B(t)$ curves and the comparison to experimental curves showed that, in these cases, the apparent reaction rate is higher than the intrinsic chemi-

cal reaction rate (Figure 8). Three possible explanations can be proposed: the kinetic law found in literature was not adequate here; the reaction is chemically improved by ultrasound; the equilibrium partition of A and C is modified by ultrasound. As an example, a factor of 1.8 was applied to the reaction kinetics, which allowed a good fitting of the experiments with ultrasound (Figure 8). Some complementary experiments and modeling will be necessary to understand the origin of the effect of ultrasound.

Conclusions

The hydrolysis of *n*-amyl acetate proved to be influenced by ultrasound: its apparent reaction rate was improved by cavitation, by an increase of the mixing around the droplets or the reduction of droplets size. This improvement does not require a high ultrasound power. But the estimation of $k_L a$ was not very accurate since the reaction is rather slow and the effect of mass transfer not very limiting, which suggested to use a faster reaction. This positive effect could be confirmed in all investigated cases.

Nomenclature

a	= interfacial specific area	[m ² /m ³]
C_i	= concentration in i	[mol/m ³]
D_A	= diffusion coefficient of ester in aqueous phase	[m ² /s]
E, E_{mi}	= activation energies	[J/mol]
Ha	= Hatta number	[—]
k	= kinetic constant	[m ³ /(mol · s)]
k_0	= pre-exponential factor for k	[m ³ /(mol · s)]
k_L, k_{LA}, k_{LC}	= mass transfer coefficients	[m/s]
m_i	= partition coefficient of i	[—]
m_{i0}	= pre-exponential factor for m_i	[—]
n	= moles number	[mol]
N	= rotation speed	[s]
r	= reaction rate	[mol/(m ³ · s)]
T	= temperature	[°C]
V	= volume	[m ³]
γ	= conductivity	[μS]

<Superscript>

c	= in continuous phase
d	= in dispersed phase

<Subscript>

e	= in the bulk
i	= at interface
0	= initial

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