

# Convenient singlet oxygenation in multiphase microemulsion systems

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## Abstract

Two and three-phase microemulsion systems have been investigated as new potential reaction media for the "dark" i.e. non photochemical, singlet oxygenation of organic substrates by the molybdate-catalyzed disproportionation of hydrogen peroxide. Examination of the phase behaviour of various oil/water/alcohol/surfactant/sodium molybdate systems has been carried out to reveal the boundaries separating the different Winsor systems. Comparative peroxidations of a model substrate in the multiphase systems showed surprising results with regard to the influence of the microemulsion microstructure and of the water excess phase. The latter dramatically favors the <sup>1</sup>O<sub>2</sub> quenching by the solvent. The influence of hydrogen peroxide addition on the substrate conversion has also been investigated, showing decreasing performances as the reaction medium is diluted. Successful oxidations of α-terpinene and β-citronellol have been carried out in a two-phase system (Winsor I) with similar efficiency but with much simpler work-up of the reaction media than in monophasic microemulsions.

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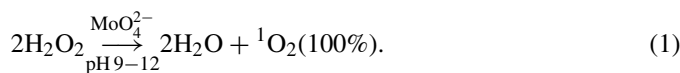
**Keywords:** Microemulsion; Multiphase; Singlet oxygen; Peroxidation; Winsor

## 1. Introduction

Four-component systems consisting of oil, water, surfactant and cosurfactant may form isotropic and thermodynamically stable mixtures, namely microemulsions (μems) [1,2]. A wide range of reactions have been performed in such microheterogeneous media on a laboratory scale [3,4], showing their great potential as new and atypical solvents but they only received little attention as reaction media for industrial applications [5–8]. Actually, considerable amounts of surfactant/cosurfactant are often required to prepare them, which is not desirable from an industrial point of view and makes recovery of the reaction products from these complex media somewhat tricky.

Nevertheless, μems offer several benefits: (i) cosolubilization of great amounts of hydrophilic and hydrophobic compounds, (ii) compartmentalization of hydrophilic and hydrophobic species avoiding side reactions, (iii) huge water/oil interface (≈ 10<sup>5</sup> m<sup>2</sup> l<sup>-1</sup>). Additional advantages come from the nanometric size (10–100 nm) of the droplets found in such systems. These nanoreactors are particularly suitable for organic reactions involving short live species generated in aqueous nan-

droplets. In particular, water-in-oil μems, typically made of CH<sub>2</sub>Cl<sub>2</sub>/sodium dodecyl sulfate/BuOH/H<sub>2</sub>O, have been developed for the chemical peroxidation of hydrophobic compounds by singlet oxygen <sup>1</sup>O<sub>2</sub> (<sup>1</sup>Δ<sub>g</sub>) [9]. This excited species, which may be chemically generated by the molybdate-catalyzed disproportionation of hydrogen peroxide (1), has a relatively long lifetime [10] (3 μs in water up to 60 ms in CCl<sub>4</sub>) compared to usual excited molecules. Thus, given the adequacy between the mean travel distance of <sup>1</sup>O<sub>2</sub> (about 200 nm in water) and the average droplet size in such systems, μems constitute a reaction medium of choice for the reaction between hydrophobic substrates, localized in the oily phase, and <sup>1</sup>O<sub>2</sub> generated in the aqueous nanodomains:



To overcome the problems of work-up and product recovery inherent to μems, two or three-phase systems may be prepared by decreasing the amount of surfactant required to obtain monophasic μems [11,12]. In these polyphasic systems, namely Winsor I, II and III systems according to the eponymous classification, the μem phase coexists respectively with oil, water or both, depending on the surfactant hydrophilicity [13]. These three types of μems may be microscopically very different

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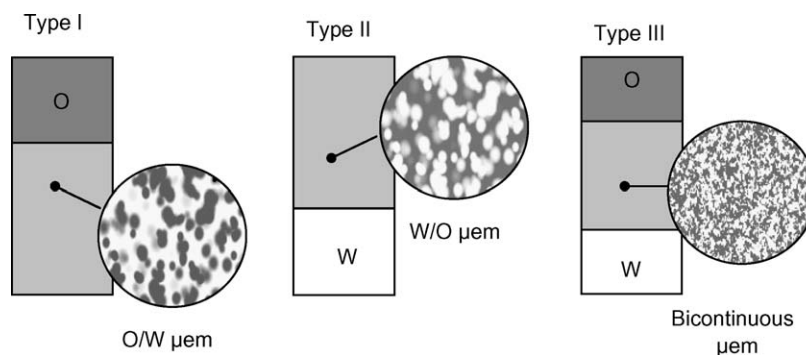


Fig. 1. Schematic representation of the three types of polyphasic  $\mu\text{em}$  systems.

(Fig. 1). Indeed, in the case of Winsor I systems, the  $\mu\text{em}$  consists of oil droplets dispersed into water whereas in Winsor II systems, aqueous droplets are dispersed in oil. Winsor III systems exhibit a bicontinuous sponge-like structure, which contains comparable amounts of oil and water and corresponds to the highest cosolubilization of hydrophilic and hydrophobic species for a given amount of surfactant [14]. In addition, extremely low interfacial tensions (typically  $10^{-4}$ – $10^{-2}$   $\text{mN m}^{-1}$ ) may be achieved in such systems, which is of great practical importance since it allows a fast phase separation after stirring.

The aim of the present work was to investigate these multiphase  $\mu\text{em}$  systems as new potential reaction media for the chemical peroxidation of hydrophobic substrates by  $^1\text{O}_2$ , generated from the system  $\text{H}_2\text{O}_2/\text{MoO}_4^{2-}$ . Firstly, optimization diagrams were elaborated in order to identify the different Winsor types based on a mixture of SDS with various solvents and alcohols. Formulation scans were thus carried out by varying the amount of sodium molybdate in the aqueous phase. Secondly, comparative peroxidations of  $\alpha$ -terpinene in the different types of  $\mu\text{ems}$  were performed and reaction conditions were optimized.

## 2. Materials and methods

### 2.1. Chemicals

Sodium molybdate dihydrate (99%), *n*-propanol (99%), sodium hydroxide (98%),  $\alpha$ -terpinene **1** (85%),  $\beta$ -citronellol **2** (95%) and  $\beta$ -pinene **3** (90%) were purchased from Aldrich and used without further purification. Sodium dodecyl sulfate (SDS) (98%), toluene (99%), ethyl acetate (99%), dichloromethane (99%), *n*-butanol (98.5%) and hydrogen peroxide (50%) were obtained from Prolabo. Milli-Q water ( $18.2 \text{ M}\Omega \text{ cm}$ ) was used.

### 2.2. Procedures

Salinity scans: samples (5 ml) were prepared in SVL tubes by mixing appropriate amounts of oil, cosurfactant, water, catalyst and surfactant. Mixtures were gently stirred and maintained at a constant temperature ( $25 \pm 0.1^\circ\text{C}$ ) for a sufficient time in order to get thermodynamically stable systems. To further identify each phase according to Winsor label, water was coloured in blue and oil in yellow so that the microemulsion phase was

green. Comparative oxidations: 40 g of  $\mu\text{em}$  were prepared by predissolving SDS and sodium molybdate in water + *n*-PrOH and by adding toluene to the mixture. After shaking, the systems were allowed to stabilize overnight at  $25 \pm 0.1^\circ\text{C}$ . For modified Winsor II and III systems, greater volumes were prepared. After sufficient time to reach thermodynamic stability, the phases were separated and mixed again in the desired proportions. Finally,  $\alpha$ -terpinene was added to the mixtures ( $0.1 \text{ mol kg}^{-1}$ ). Oxidations were performed at  $25^\circ\text{C}$  under vigorous stirring, by adding hydrogen peroxide in two batches ( $1$  and  $0.5 \text{ mol kg}^{-1}$  after 30 min). The substrate conversion was followed by gas chromatography and the peroxidation products were characterized by  $^1\text{H NMR}$ .

Oxidation of substrates **1,2,3** in a Winsor I system: 10 ml of two-phase mixture were prepared as previously described by mixing 9 ml of oily phase and 1 ml of microemulsion phase. Substrates were added to the reaction media (1.36 g of **1** or 1.56 g of **2** or 1.36 g of **3**) under stirring. The solutions were treated at  $25^\circ\text{C}$  with  $125 \mu\text{l}$  of 50%  $\text{H}_2\text{O}_2$  giving a red-brown colour. After about 13–15 min, the colour faded to yellow which was the signal for another addition of  $\text{H}_2\text{O}_2$ . The reaction was monitored by GC and  $\text{H}_2\text{O}_2$  was added until at least 95% of the substrate was peroxidized. For substrate **3** a plateau was reached at 25% conversion. After demixing, the oily phase was rotary evaporated and the microemulsion phase was extracted with fresh oil phase.

### 2.3. Instrumentation

Gas chromatography (GC) analyses were performed on an Agilent 6890 N chromatograph equipped with an apolar HP-1 ( $60 \text{ m} \times 0.32 \text{ mm} - 0.25 \mu\text{m}$ ) column.  $^1\text{H NMR}$  of the peroxidation products was carried out on an AC 200 Bruker spectrometer. Molybdate concentrations were determined by UV spectrometry on a Varian Cary50 Probe spectrometer at 208 nm ( $\epsilon = 10430 \text{ L mol}^{-1} \text{ cm}^{-1}$ ).

## 3. Results and discussion

### 3.1. Salinity scans and optimization diagrams

Most of the microemulsions of interest contain more than three constituents. Representing the whole phase behaviour for these systems would require a prohibitive number of

experiments. “Pseudo-ternary” phase diagrams are usually preferred, using pseudo-components to reduce the domain of study. Similarly, binary diagrams, known as “optimization” or “fish-like diagrams”, are of interest to investigate the influence of one parameter on the phase behaviour of  $\mu\text{ems}$  without exploring the whole phase diagram. Classical formulation scans may be achieved at fixed alcohol-to-surfactant and water-to-oil ratios by changing temperature or the electrolyte concentration, the nature of the oil or that of the alcohol [11]. Temperature changes may promote phase transitions provided that appropriate surfactants are chosen. Olsson and co. illustrated the influence of temperature on monophasic  $\mu\text{ems}$  for enzymatic catalysis: by shifting these systems to two-phase regions, the desired products could be recovered in an oil-rich phase whereas surfactant remained in the water-rich phase, which could be reused [15]. Holmberg proceeded in a similar way by performing enzymatic ester hydrolysis in a Winsor I type  $\mu\text{em}$  and inducing a phase transition to a Winsor III system to separate the desired products from the  $\mu\text{em}$  phase [16]. Bayer also developed a process for the *O*-alkylation of phenols in  $\mu\text{em}$  based on temperature changes to separate surfactants from target molecules [17].

Temperature is actually a judicious way to promote phase transitions when nonionic surfactants are used as it is reversible and does not require extra substances. However, we preferred to achieve salinity scans by gradually increasing the amount of electrolyte, i.e. sodium molybdate, as most peroxidation products (hydroperoxides or dioxetanes for instance) are temperature-sensitive and because the hydrophilicity of ionic surfactants is more sensitive to salinity than to temperature [11]. In addition, as molybdate acts as a catalyst in the formation of  $^1\text{O}_2$ , higher rates of hydrogen peroxide decomposition and  $^1\text{O}_2$  formation may be achieved by increasing concentration. Addition of electrolytes to ionic  $\mu\text{ems}$  efficiently induces  $\text{I} \leftrightarrow \text{III} \leftrightarrow \text{II}$  transitions since they decrease the repulsion between the surfactant polar heads, leading to a curvature inversion [18]. In order to prepare catalyst-rich polyphasic  $\mu\text{ems}$ , we investigated the influence of sodium molybdate on the phase behaviour of several oil/water/alcohol/surfactant systems. Toluene, dichloromethane and ethyl acetate were chosen as candidate oils for the present study to cover the solvent polarity scale, in association with classical short chain alcohols (*n*-propanol and *n*-butanol) and a typical anionic surfactant (sodium dodecyl sulfate). The conditions for the preparation of attractive reaction media are (i) low amounts of surfactant, (ii) high amounts of catalyst, (iii) environmentally friendly constituents and (iv) industrially acceptable solvents.

Classical Winsor  $\text{I} \leftrightarrow \text{III} \leftrightarrow \text{II}$  phase transitions were obtained for the investigated systems (Fig. 2). For the sake of clarity, boundaries of systems (1), (2) and (4) were truncated and only the critical point areas were reported. Given its hydrophilicity, sodium dodecyl sulfate exhibits a positive curvature (Winsor I) without electrolyte for all the investigated oils. Adding sodium molybdate to the Winsor I  $\mu\text{ems}$  decreases the surfactant affinity for water, which leads to Winsor III and II systems. The influence of the organic solvent can also be explained in terms of surfactant affinity. Increasing the surfactant affinity for the organic solvent decreases the amount of electrolyte required to

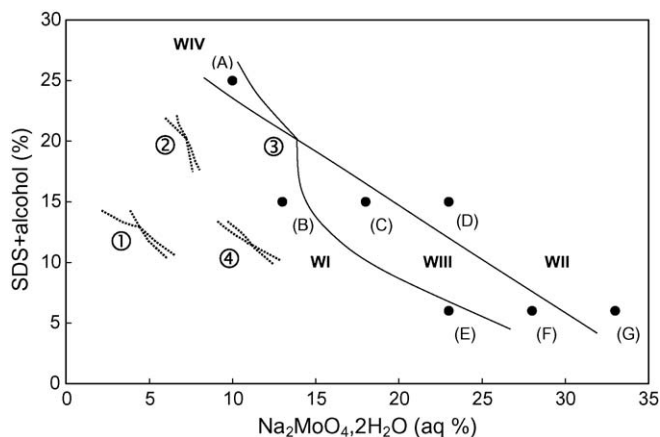


Fig. 2. Optimization diagrams for various oil/water/SDS/alcohol/ $\text{Na}_2\text{MoO}_4$  systems at 25 °C (SDS/alcohol = 1/1 (w/w); oil/(water + catalyst) = 1/1 (w/w); abscissa = catalyst/(water + catalyst) (w/w)). (1) AcOEt/*n*-PrOH (2)  $\text{CH}_2\text{Cl}_2$ /*n*-PrOH (3) Toluene/*n*-PrOH (4) Toluene/*n*-BuOH. (For dots A–G, see Table 1).

observe  $\text{I} \leftrightarrow \text{III} \leftrightarrow \text{II}$  phase transitions. Thus, gamma boundaries are shifted to high catalyst concentration as the polarity of the oil decreases. However, apolar organics are quite poor solvents and a compromise had to be found between catalyst concentration and solvent abilities. Thus toluene was selected to prepare rich catalyst Winsor I, II and III  $\mu\text{ems}$  with an industrially acceptable solvent.

Moreover, *n*-propanol (3) was preferred as a cosurfactant to *n*-butanol (4). This latter increases the surfactant affinity for the oil and thus decreases the amount of catalyst before phase transitions, which is not in favour of high reaction rates.

### 3.2. Comparative peroxidations

In order to decrease the amount of amphiphilic molecules which are responsible for work-up problems and high cost of  $\mu\text{ems}$ , two- or three-phase  $\mu\text{ems}$  may be prepared with low amounts of surfactant and cosurfactant, as indicated on Fig. 1. In addition, the presence of an oil excess phase as in the case of Winsor I or Winsor III systems allows an easier recovery of the oxidation products as they partition between the organic and  $\mu\text{em}$  phases.

To investigate the influence of the  $\mu\text{em}$  type on the peroxidation yield, i.e. to determine if globular (w/o or o/w) or bicontinuous microstructures are preferable for the reaction of  $^1\text{O}_2$  and organic substrates,  $\alpha$ -terpinene was chosen as a model substrate and was peroxidized in a wide variety of reaction media (Table 1).

The three types of microemulsion were prepared at two different percentages of amphiphilic species (surfactant + cosurfactant), namely 15 and 6%. In addition, aqueous excess phases were removed after equilibrium for Winsor II and Winsor III systems (giving the “modified” Winsor II and III) to investigate their influence on the oxidation yield.

The four  $\mu\text{em}$  types (entries A–D) are rather different as far as the substrate conversion is concerned. Similar trends are observed for polyphasic  $\mu\text{ems}$  with 15% of surfactant/cosurfactant and with 6%, namely a performance decrease

Table 1

Dependence of the substrate conversion on the  $\mu\text{em}$  type and composition (toluene/(water + catalyst) = 1/1 (w/w); SDS/*n*-PrOH = 1/1 (w/w);  $\alpha$ -terpinene = 0.1 mol kg<sup>-1</sup>; H<sub>2</sub>O<sub>2</sub> = 0.15 mol kg<sup>-1</sup>)

Entry	Winsor type	Composition		$\alpha$ -Terpinene conversion (%)	
		Na <sub>2</sub> MoO <sub>4</sub> ·2H <sub>2</sub> O (mol kg <sup>-1</sup> )	SDS + <i>n</i> -PrOH (% w/w)	a	b
A	IV	0.15	25	78	
B	I	0.23	15	77	
C	III	0.32		45	79 (C*)
D	II	0.40		22	81 (D*)
E	I	0.45	6	65	
F	III	0.54		36	75 (F*)
G	II	0.64		20	74 (G*)

<sup>a</sup> Without modification.

<sup>b</sup> Without water excess phase (entry).

in the order WI > WIII > WII. Comparison of entries A and B indicates that the presence of an oil excess phase does not affect the performances of the reaction medium. The dramatic decrease of substrate conversion observed for Winsor III and II  $\mu\text{ems}$  can be imputed to the presence of an aqueous excess phase. Indeed, as the catalyst and hydrogen peroxide equally partition between the aqueous micro-domains and the aqueous excess phase, <sup>1</sup>O<sub>2</sub> is largely wasted through physical deactivation by the water molecules. Homogenization of the Winsor type  $\mu\text{ems}$  by stirring leads to emulsions which are generally of the same type than the original  $\mu\text{ems}$ ; e.g. homogenization of a Winsor II (w/o)  $\mu\text{em}$  gives most of the time a w/o emulsion, the continuous phase of which is itself a w/o  $\mu\text{em}$  [19]. Thus, Winsor II systems can be seen as mixtures of huge macrodroplets and small microdroplets of water dispersed into oil. <sup>1</sup>O<sub>2</sub> is only efficiently trapped by the substrate when it is generated in the small aqueous nanoreactors. Its production in water macrodroplets is inefficient as it is deactivated by water molecules before it reaches the organic phase and the substrate (Fig. 3).

The elimination of the water excess phase in Winsor III and II systems (entries C\*, D\*, F\*, G\*) induces an increase

in the substrate conversion, noticed for the 15% and 6% series, which is consistent with our previous explanation. In addition, lower substrate conversions are recorded for the 6% series. This may be imputed to cosurfactant partitioning: as the amount of (surfactant + cosurfactant) decreases, the  $\mu\text{em}$  phase composition evolves leading to more opaque systems. The effect of alcohol addition on  $\mu\text{em}$  system is well known and has been widely investigated in literature [11]: the systems turn to stable emulsions as less alcohol is available at the water/oil interface. Changes in the size and dynamics of droplets lead to a performance decrease. In addition, lower rates of phase separation have been recorded as the (surfactant + cosurfactant) amount decreases, which is in favour of the cosurfactant partitioning and emulsion stabilization.

### 3.3. Dilution effect

Previous results show that multi-phase  $\mu\text{ems}$  may be used for the chemical oxidation of hydrophobic substrates provided <sup>1</sup>O<sub>2</sub> is exclusively generated in aqueous microdomains, which implies that no water excess phase exists or is formed as hydrogen peroxide is added [20]. Attractive reaction media can be prepared by varying the proportions of oil and  $\mu\text{em}$  phases. To investigate the influence of addition of H<sub>2</sub>O<sub>2</sub> (adding 1 mole of 50% H<sub>2</sub>O<sub>2</sub> leads to the dilution of the reaction medium by almost 3 moles of water), comparative oxidations were performed in Winsor I type  $\mu\text{ems}$  made of 10% of  $\mu\text{em}$  and 90% of oil excess phase (Fig. 4).

Thus,  $\mu\text{ems}$  were prepared from Fig. 1 (point E) and were enabled to stabilize. After sufficient time to achieve thermodynamical separation, the different phases were isolated and mixed in the desired proportions. Increasing amounts of water were added to simulate the dilution induced by additions of H<sub>2</sub>O<sub>2</sub>. Identical amounts of  $\alpha$ -terpinene (1 mol kg<sup>-1</sup>) were introduced in the series and substrate conversions were measured after addition and decomposition of H<sub>2</sub>O<sub>2</sub> (2 mol kg<sup>-1</sup>). The dilution limitation of the reaction medium may be easily calculated from Fig. 2. From 3 mol kg<sup>-1</sup> of <sup>1</sup>O<sub>2</sub>, additions of H<sub>2</sub>O<sub>2</sub> induce a

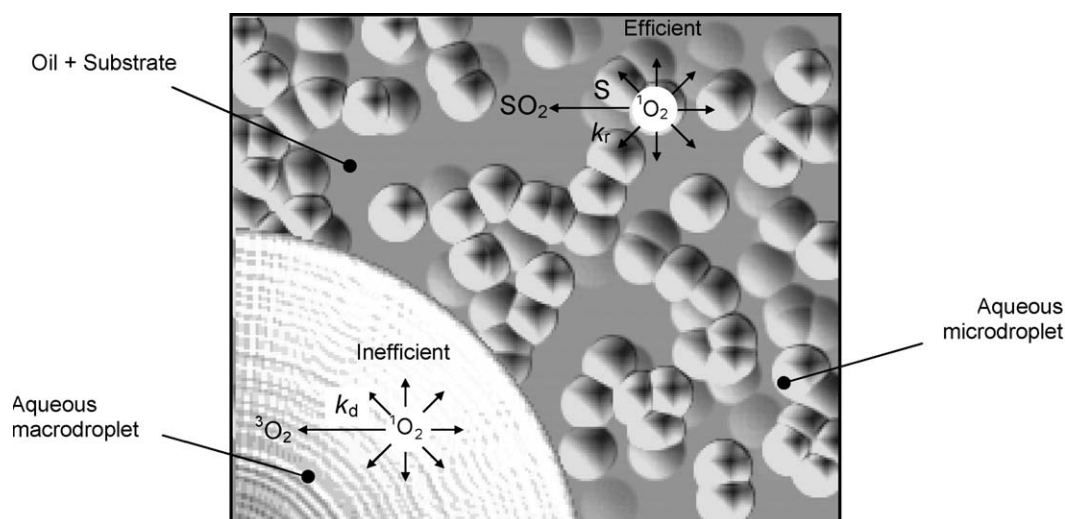
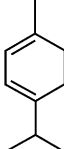
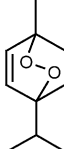
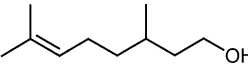
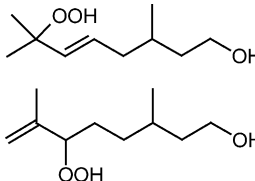
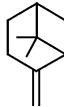
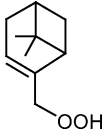


Fig. 3. Schematic representation of a Winsor II system under stirring.



Table 2  
Oxidation of terpene derivatives (1 mol kg<sup>-1</sup>) in Winsor I microemulsion systems by the system H<sub>2</sub>O<sub>2</sub>/MoO<sub>4</sub><sup>2-</sup> (T = 25 °C).

Substrate	log (k <sub>r</sub> +k <sub>q</sub> )	k <sub>r</sub> /(k <sub>r</sub> +k <sub>q</sub> )	[H <sub>2</sub> O <sub>2</sub> ] (mol L <sup>-1</sup> )	Yield (%)	Product (s)
<b>1</b> 	8.0	1.0	3	>95	
<b>2</b> 	5.9	0.87	15	>95	
<b>3</b> 	4.7	1.0	48	25	

decreasing performance and a stabilization of emulsions. From about 10 mol kg<sup>-1</sup> (extrapolated value), the reaction medium becomes inefficient. The theoretical amount of <sup>1</sup>O<sub>2</sub> required to peroxidize a substrate *S* may be calculated from (2), where rate constants *k<sub>d</sub>*, *k<sub>r</sub>* and *k<sub>q</sub>* are related respectively to the solvent, chemical and physical quenching [21]:

$$[{}^1\text{O}_2]_{\infty} = \frac{k_d}{k_r} \ln \frac{[S]_0}{[S]_{\infty}} + \frac{k_r + k_q}{k_r} ([S]_0 - [S]_{\infty}). \quad (2)$$

Thus the amount of <sup>1</sup>O<sub>2</sub> required to peroxidize 95% of [S] = 1 mol kg<sup>-1</sup> is given by (3):

$$[{}^1\text{O}_2]_{95\%} \cong 3 \frac{k_d}{k_r} + 0.95 \frac{k_r + k_q}{k_r}. \quad (3)$$

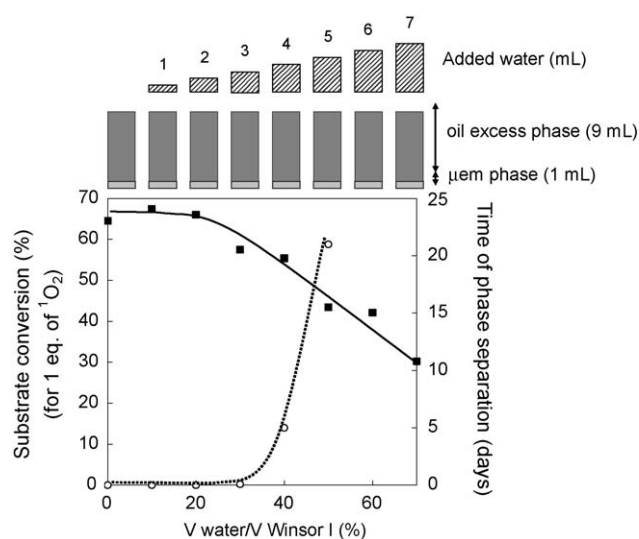


Fig. 4. Influence of the dilution of the Winsor I type μem on the substrate conversion of α-terpinene 1 mol kg<sup>-1</sup> (full line) and on the time of phase separation (dotted line).

For highly reactive substrates (*k<sub>r</sub>* ≫ *k<sub>d</sub>*), [<sup>1</sup>O<sub>2</sub>]<sub>95%</sub> only depends on the ratio *k<sub>q</sub>/k<sub>r</sub>*, whereas when *k<sub>r</sub>* ≪ *k<sub>d</sub>*, [<sup>1</sup>O<sub>2</sub>]<sub>95%</sub> depends on the <sup>1</sup>O<sub>2</sub> lifetime in the given environment. Poorly reactive substrates (for instance β-pinene **3**) induce great wastes of <sup>1</sup>O<sub>2</sub> and severe dilution of the reaction medium, which increases *k<sub>d</sub>* and thus decreases the lifetime of <sup>1</sup>O<sub>2</sub>. To check the suitability of the process, β-citronellol **2** (1 mol l<sup>-1</sup>) was thoroughly peroxidized in the Winsor I system composed of 90% oil–10% μem described previously, whereas under the same conditions, only 25% of β-pinene (1 mol l<sup>-1</sup>) could be oxidized and a milky emulsion was obtained. The oily excess phase enabled the direct recovery of 40% of the peroxidation products after evaporation whereas the remaining hydroperoxides (60%) were recovered by extractions of the microemulsion phase with fresh oily excess phase followed by gentle evaporation. This simple treatment provides a straightforward way of separating the desired products from the catalyst/surfactant mixture (Table 2).

#### 4. Conclusion

Winsor I type μems may be conveniently applied to the chemical oxidation of hydrophobic substrates by <sup>1</sup>O<sub>2</sub> generated from molybdate-catalyzed hydrogen peroxide disproportionation. The amount of surfactant can be considerably decreased in these systems in comparison with one-phase μems. In addition, the presence of an organic excess phase enables the recovery of the peroxidation products by common techniques (decantation, evaporation, extraction) as the surfactant and the catalyst are mainly located in the μem phase.

The two other polyphasic μem types, namely Winsor II and III, are considerably less efficient as <sup>1</sup>O<sub>2</sub> is partially wasted in the aqueous excess phase, due to the presence of catalyst. By removing the water excess phase, these systems appear to behave similarly to the Winsor I and IV systems. This result clearly demonstrates that <sup>1</sup>O<sub>2</sub> can be generated either in w/o,

o/w or bicontinuous  $\mu\text{ems}$ , provided that the distance between the dispersed domains is of the same order of magnitude as the mean travel distance of  $^1\text{O}_2$ , which is not the case when the systems are over diluted.

The process may be applied to the peroxidation of fairly reactive substrates at preparative concentrations. It is limited by the substrate reactivity as the reaction medium cannot be infinitely diluted without a loss of efficiency. Poorly reactive substrates require prohibitive amounts of  $\text{H}_2\text{O}_2$  and the reaction medium becomes inefficient as the  $\mu\text{em}$  phase is diluted. To prevent the reaction medium from dilution, water can be removed by membrane processes [20].

## References

- [1] J. Sjöblom, R. Lindberg, S.E. Friberg, *Adv. Colloid Interface Sci.* 65 (1996) 125–287.
- [2] B.K. Paul, S.P. Moulik, *J. Disper. Sci. Technol.* 18 (1997) 301–367.
- [3] M.A. Lopez-Quintela, C. Tojo, M.C. Blanco, L. Garcia Rio, J.R. Leis, *Curr. Opin. Colloid Interface Sci.* 9 (2004) 264–278.
- [4] P.Y. Chow, L.N. Gan, *Adv. Polym. Sci.* 175 (2005) 257–298.
- [5] C. Solans, H. Kunieda, *Industrial Applications of Microemulsions—Surfactant Science Series*, 66, Dekker, New York, 1999.
- [6] B. Gupta, H. Singh, *Polym. Plast. Technol. Eng.* 31 (1992) 635–658.
- [7] K. Holmberg, *Adv. Colloid Interface Sci.* 51 (1994) 137–174.
- [8] J. Klier, C.J. Tucker, T.H. Kalantar, D.P. Green, *Adv. Mater.* 12 (2000) 1751–1757.
- [9] J.-M. Aubry, S. Bouttemy, *J. Am. Chem. Soc.* 119 (1997) 5286–5294.
- [10] M.A.J. Rodgers, P.T. Snowden, *J. Am. Chem. Soc.* 104 (1982) 5541–5543.
- [11] M. Bourrel, R.S. Schechter, *Microemulsions and Related Systems—Surfactant Science Series*, 30, Dekker, New York, 1988.
- [12] M. Kalhweit, R. Strey, D. Haase, H. Kunieda, T. Schmeling, B. Faulhaber, M. Borkovec, H.F. Eicke, G. Busse, F. Eggers, T. Funck, H. Richmann, L. Magid, O. Soderman, P. Stilbs, J. Winkler, A. Dittrich, W. Jahn, *J. Colloid Interface Sci.* 118 (1987) 436–453.
- [13] M. Bourrel, R.S. Schechter, *The R ratio Microemulsions and Related Systems—Surfactant Science Series*, 30, Dekker, New York, 1988, 1–30.
- [14] J.L. Salager, R.E. Anton, D.A. Sabatini, J.H. Harwell, E.J. Acosta, L.I. Tolosa, *J. Surfact. Deterg.* 8 (1) (2005) 3–21.
- [15] K.M. Larsson, P. Adlercreutz, B. Mattiasson, U. Olsson, *Biotechnol. Bioeng.* 36 (1990) 135–141.
- [16] K. Holmberg, A. Lif, *Colloids Surf. A* 129–130 (1997) 273–277.
- [17] O. Wagner, R. Shomaecker, US Patent Application 5912390, 1999.
- [18] R.H. Healy, R.L. Reed, D.G. Stenmark, *Soc. Petr. Eng. J.* 16 (3) (1976) 147–160.
- [19] B.P. Binks, W.-G. Cho, P.D.I. Fletcher, D.N. Petsev, *Langmuir* 16 (2000) 1025–1034.
- [20] L. Caron, V. Nardello, J. Mugge, E. Hoving, P.L. Alsters, J.-M. Aubry, *J. Colloid Interface Sci.* 282 (2005) 478–485.
- [21] F. Wilkinson, W.P. Helman, A.B. Ross, *J. Phys. Chem. Ref. Data* 24 (1995) 663–1021.