

A gemini amphiphilic phase transfer catalyst for dark singlet oxygenation

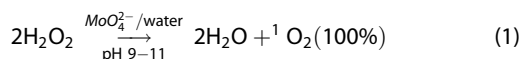
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A new gemini surfactant phase transfer catalyst, namely diethyl-ether- α,ω -bis-(dimethyldodecylammonium molybdate) codified as 12-EO-12-Mo, was prepared by anion exchange from the analogous gemini dichloride (12-EO-12-Cl₂). The physico-chemical properties of these compounds such as Krafft temperature, critical micelle concentration, surface activity and binary water-surfactant behavior were compared and the influence of the molybdate counterion was examined. Though both compounds are highly hydrophilic, the cmc of 12-EO-12-Mo (0.4 mmol L⁻¹) is about five times lower than of its dichloride analogue (2.2 mmol L⁻¹). Moreover, 12-EO-12-Mo exhibits an additional cubic liquid crystal phase between 53 and 64 wt%. The usefulness of 12-EO-12-Mo as an amphiphilic phase transfer catalyst for the dark singlet oxygenation was demonstrated with the peroxidation of two typical organic substrates: α -terpinene which reacts with ¹O₂ according to a [4 + 2] cycloaddition and the less reactive β -citronellol, which provides two hydroperoxides according to the ene-reaction. 12-EO-12-Mo provides a simple reaction medium with only three components for the preparative peroxidation of hydrophobic substrates by chemically generated singlet oxygen. Copyright © 2008 John Wiley & Sons, Ltd.

Keywords: singlet oxygen; oxidation; catalytic amphiphile; gemini surfactant; phase transfer catalyst; lyotropic liquidcrystal

INTRODUCTION

In organic synthesis, hydrophobic molecules often have to react with hydrophilic species. Despite the incompatibility between antagonist reactants, interactions and reactions can be favored by several ways using: (i) monophasic media based on dipolar aprotic solvents (DMSO, DMF, NMP...) or homogenous mixtures of water and a miscible organic solvent (alcohols, THF...), (ii) biphasic media of two immiscible solvents, generally associated with a phase transfer catalyst (PTC) typically quaternary ammonium compounds, and (iii) submicronic and thermodynamically stable dispersions of two immiscible solvents stabilized by an appropriate amphiphile, that is, microemulsions.^[1–4] Among these strategies, phase transfer catalysis is probably the most widely used in industry. This process is applicable to a large number of reactions involving (in)organic anions and organic reactants.^[5–8] Therefore, it has known a remarkable development during these last decades, owing to its numerous advantages. Besides its simplicity, reaction rates can considerably be increased compared to a simple biphasic system.^[9,10] Still, as most PTC do not exhibit amphiphilic properties, the unstable emulsions formed under stirring are coarse. Moreover, at the end of the reaction, the PTC is partitioned between the two phases, thus complicating the recovery of the products. Furthermore, phase transfer catalysis is unsuitable when short lifetime species have to react with hydrophobic substrates. In particular, it cannot be simply applied to the use of singlet molecular oxygen, ¹O₂ (¹Δ_g). This reagent is efficiently chemically generated in aqueous phase by disproportionation of hydrogen peroxide catalyzed by molybdates anions (Eqn 1):^[11–15]



In contrast to ground state molecular oxygen, singlet oxygen is a selective and powerful oxidizing species that has found considerable synthetic utility since it can undergo reactions with a wide variety of electron-rich molecules such as olefins, conjugated dienes, polycyclic aromatic hydrocarbons, phenols, sulfides, and heterocycles.^[16–18] However, some drawbacks, inherent to its transitory nature and to its mode of formation, have to be taken into account: (i) owing to its short lifetime (about a few microseconds in water), ¹O₂ must be generated close to the organic substrate, (ii) the disproportionation of the intermediate triperoxomolybdate, MoO(O₂)₃²⁻, which is the main precursor of ¹O₂, is efficient solely in an aqueous or highly polar environment, and (iii) poorly reactive substrates require important amounts of hydrogen peroxide that induces an important dilution of the reaction medium resulting in a significant competition between the chemical reaction of ¹O₂ with the substrate S (rate constant *k_r*) and the physical deactivation by the solvent molecules (rate

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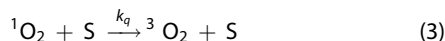
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constants k_d) (Eqns 2–4).^[19]



The cumulative amount of $^1\text{O}_2$ generated in the medium ($[^1\text{O}_2]_\infty$) is thus related to the final concentration of the substrate $[\text{S}]_\infty$ by the following relation:^[19]

$$\frac{k_r}{k_r + k_q} [^1\text{O}_2]_\infty = \frac{k_d}{k_r + k_q} \ln \frac{[\text{S}]_0}{[\text{S}]_\infty} + [\text{S}]_0 - [\text{S}]_\infty \quad (5)$$

The ratio $\gamma = k_r/(k_r + k_q)$ expresses the contribution of the chemical quenching in the overall quenching whereas $\beta = k_d/(k_r + k_q)$ is the Foote reactivity index that corresponds to the minimum concentration of substrate required so that the interaction of $^1\text{O}_2$ with S (Eqns 3 and 4) becomes predominant over the deactivation of $^1\text{O}_2$ by the solvent (Eqn 2).

Several solutions have been brought up in order to apply the chemical source of $^1\text{O}_2$ to organic synthesis involving the use of dipolar aprotic solvents such as DMF,^[20] of polar protic solvents such as methanol,^[20,21] and of w/o microemulsions.^[22–29] These latter systems are particularly well suited to the peroxidation of hydrophobic substrates because the size of the aqueous microdomains (10–100 nm) is smaller than the mean travel distance of $^1\text{O}_2$ in water (≈ 200 nm). However, several drawbacks such as the use of high amounts of surfactants and cosurfactants to obtain a microemulsion, the difficulty to recover the catalyst and the oxidation products from the complex final reaction medium, and the instability of the system toward dilution generated by the addition of hydrogen peroxide have limited the industrial applications of these media.

In the present work, we developed a new PTC exhibiting interfacial properties, which enables efficient dark singlet oxygenation of organic substrates by chemically generated $^1\text{O}_2$. Because of the divalent nature of the molybdate anion, we have chosen a gemini amphiphilic PTC based on two quaternary ammonium functions to which one molybdate anion has been associated as a counterion (Fig. 1).

The behavior of 12-EO-12-Mo in aqueous solution was investigated and compared with one of the known dichloride analogue 12-EO-12-Cl₂, and its usefulness for dark singlet oxygenation in biphasic media was demonstrated.

EXPERIMENTAL

Chemicals

α -terpinene (**1**) (85%) was purchased from Acros. β -citronellol (**2**) (95%), molybdenum trioxide (95%) and Amberlite Ira-400(Cl) resin were from Aldrich. Ethyl acetate (Puro) was used as received

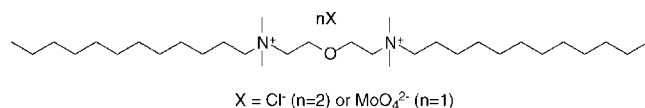


Figure 1. Chemical structure of gemini surfactants diethyl-ether- α,ω -bis(dimethyldodecylammonium) salts (12-EO-12- X_n). For $\text{X} = \text{Cl}^-$, Br^- , salicylate: $n = 2$; for $\text{X} = \text{MoO}_4^{2-}$: $n = 1$

from Carlo Erba. Hydrogen peroxide 50% (17.5 M) was from Prolabo. Milli-Q water (18.2 M Ω cm) was used.

Methods

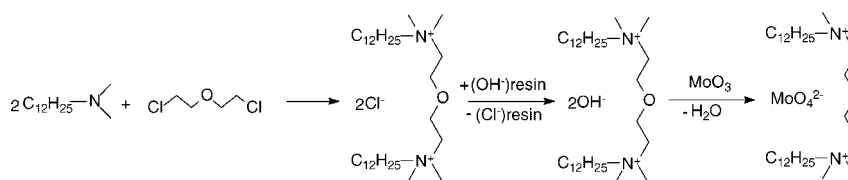
Elemental analysis was performed by the University College of London. NMR spectra were taken with an Avance 300 apparatus (Bruker). Thermogravimetric experiments were performed under nitrogen with a TGA/SDTA851 apparatus (Mettler Toledo), heating rate 10 °C/min. Surface tensions were measured at 25 °C for different concentrations of geminis using a Tracker Tensiometer supplied by IT Concept. These measurements have been performed by analysis of the profile of an air bubble formed in the surfactant solutions. All measurements were made as a function of time until stabilization of the surface tension.

Krafft temperatures were estimated by observing the dissolution of a small crystal of the gemini compounds in water by a microscope equipped with a hot stage. The binary phase diagrams were built by preparing 12-EO-12- X_n /water samples by weight in glass tubes, which were homogenized by repeated heating and centrifugation back and forth. No results are presented for concentrations higher than 85 wt%, because the solubility temperature increases rapidly with concentration, while excessive heating induces a decomposition of 12-EO-12- X_n . Polarized optical microscopy (POM) was used to characterize the mesophases formed in 12-EO-12- X_n -water mixtures. POM texture was observed with an Olympus BX60 ($\times 100$ magnification) equipped with a LTS120 Analysa Peltier temperature controlling stage (Linkam). In penetration experiments, pieces of broken lamella were placed between the microscopic slide and coverslip to form a gradient of thickness. The compounds were deposited on the thinner corner and a drop of water was carefully placed on the thicker side, and allowed to diffuse toward the solid compound, creating a concentration gradient throughout the slide. High-performance liquid chromatography (HPLC) analyses were carried out with a Waters 600 chromatograph equipped with Novapak C18 (4 μm) column. A mixture of Milli-Q water and HPLC grade CH_3CN was used as eluent, and UV detection was performed with a variable-wavelength monitor Waters 490E multi-wavelengths. UV/visible spectrophotometry analyses were carried out with a Varian Cary 50 spectrometer.

Synthesis of diethyl-ether- α,ω -bis(dimethyldodecylammonium molybdate) (12-EO-12-Mo)

The dimeric surfactant 12-EO-12-Mo was prepared by exchanging the chloride counterions (Cl^-) of diethyl-ether- α,ω -bis(dimethyldodecylammonium chloride (12-EO-12-Cl₂) against hydroxide counterions and making the latter species react with molybdenum trioxide to form the molybdate (MoO_4^{2-}). The parent dimeric surfactant dichloride was synthesized by alkylating an excess of *N,N*-dimethyldodecylamine by 2,2'-dichloro-diethylether^[30] as shown in Scheme 1.

140 mL of an Amberlite Ira-400(Cl) resin were allowed to swell in 300 mL Milli-Q water for 10 min. The resin was then introduced in a glass column over a height of ca 30 cm. Precautions were taken to keep the resin wet and to obtain a homogenous repartition of the resin beads within the column. The resin was rinsed in the column with 300 mL Milli-Q water. Subsequently, it was activated by a slow passage of 400 mL of a 10 wt% solution of sodium hydroxide through the column. It was then washed with



Scheme 1. Synthetic route to 12-EO-12-Cl₂ and the ion-exchanging route toward 12-EO-12-Mo

Milli-Q water until a pH value of 7 was obtained. After that, a solution of 12-EO-12-Cl₂ (5 g, 8.8 mmol, 100 mL H₂O) was progressively passed through the resin and the resulting solution was collected in a double-necked flask under a stream of argon. Two fractions of 100 mL of Milli-Q water were finally added to recover a maximum amount of ion-exchanged product. Then, the collected solution was reacted at room temperature with a stoichiometric amount (1.26 g, 8.8 mmol) of molybdenum trioxide MoO₃ under stirring over 12 h in an argon atmosphere. After reaction, the possible excess of MoO₃ was filtered off on a Buchner funnel with a small pore size. The filtrate was finally freeze dried to recover a white hygroscopic powder corresponding to 12-EO-12-Mo.

Elemental analysis

(C₃₂H₇₀MoN₂O₅, Mw = 658.85). Calculated for dihydrate (%): C 55.31; H 10.73; N 4.03; Mo 13.81. Found (%): C 55.24; H 10.49; N 4.08; Mo 13.00; Cl 0.70.

¹H-NMR (300 MHz, CDCl₃, δ in ppm): 0.88 (t, 6H, CH₃—); 1.20–1.40 (m, 36H, —(CH₂)₉—); 1.70 (m, 4H, —CH₂—C—N⁺); 3.37 (s, 12H, CH₃—N⁺); 3.49 (m, 4H, —CH₂—N⁺); 3.93 (m, 4H, —O—C—CH₂—N⁺); 4.25 (m, 4H, —CH₂—O—).

¹³C NMR (50 MHz, CDCl₃, δ in ppm): 14.1 (CH₃—); 22.7, 23.0 (CH₃—CH₂—; —CH₂—C—N⁺); 26.6 (—CH₂—C—C—N⁺); 29.4, 29.6, 29.8, 29.8 (—(CH₂)₆—); 32.0 (CH₃—C—CH₂—); 51.4 (CH₃—N⁺); 63.7, 64.8 (—CH₂—N⁺—CH₂—); 65.5 (—CH₂—O—).

The ion exchange was effective beyond 97% according to the amount of molybdate in the product determined by elemental analysis and by UV spectroscopy (the molybdate anion shows a UV-band at 208 nm with a molar extinction coefficient ε = 10430 L cm^{−1} mol^{−1} as determined from aqueous solution of sodium molybdate), in agreement with the small residual amount of chloride found.

Elaboration of the biphasic reaction medium

The biphasic system was prepared at room temperature by adding 1 mL of ethyl acetate to a magnetically stirred aqueous solution of 12-EO-12-Mo (93 mg in 1 mL, 7.10^{−2} mol L^{−1}). A biphasic system was obtained with a lower aqueous phase, containing the catalytic amphiphile and some ethyl acetate. The upper phase was ethyl acetate free of 12-EO-12-Mo.

Oxidation of α-terpinene (1)

160 mg of α-terpinene (85%) (**1**) (1.0 mmol, 0.5 mol L^{−1}) were added to the biphasic system and were treated with 30 μL (0.5 mmol) of H₂O₂ 50%. The dark orange solution was stirred at room temperature for 30 min until the color faded to pale yellow. Four other fractions of 30 μL of H₂O₂ 50% were allowed to react in the same way, and the reaction was monitored by HPLC. An internal standard, that is p-xylene 0.4 mol L^{−1}, was introduced

in the reaction medium and detected at 210 nm. Thus, after 3 h, 98% of (**1**) was oxidized. The organic phase was separated from the aqueous phase and evaporated under vacuum. Ascaridole was recovered as a pure oxidation product in a quantitative yield. The cumulated amounts of H₂O₂ consumed, the reaction times, and the yields are reported in Table 2.

Oxidation of β-citronellol (2)

155 mg of β-citronellol (95%) (**2**) (0.95 mmol, 0.47 mol L^{−1}) in the biphasic system were treated with 30 μL (0.5 mmol) of H₂O₂ 50%. The dark orange solution was stirred at room temperature for 30 min until the color faded to pale yellow. Ten other fractions of 30 μL of H₂O₂ 50% were allowed to react in the same way, and the reaction was monitored by HPLC. An internal standard, that is p-xylene 0.4 mol L^{−1}, was introduced in the reaction medium and detected at 210 nm. Thus, after 5 h, 95% of (**2**) was oxidized. The organic phase was separated from the aqueous phase and evaporated under vacuum. The two expected hydroperoxides were recovered as pure oxidation products with a yield of 80%. The cumulated amounts of H₂O₂ consumed, the reaction times, and the yields are reported in Table 2.

RESULTS AND DISCUSSION

Physico-chemical properties of the catalytic gemini amphiphile

Gemini amphiphiles have two hydrophobic tails and two hydrophilic heads linked by a spacer. They are known to exhibit enhanced surface-active properties.^[31–35] The greater efficiency and effectiveness of geminis over comparable conventional surfactants make them more cost-effective as well as environmentally desirable. The first studied gemini surfactants were the bis(quaternary ammonium halides) which exhibit superior performances, compared to their monomeric counterpart, as catalysts in organic reactions.^[36] This class of cationic surfactants has been studied for over two decades^[37] and detailed structure-performance relationship has been published by Zana *et al.*^[38–48] and more recently by Laschewsky *et al.*^[49–52] and Devi *et al.*^[53]

12-EO-12-Cl₂ decomposes according to the thermogravimetric analysis at about 220 °C.^[30] The thermogravimetric analysis of 12-EO-12-Mo shows an amount of 5 wt% water contained in the sample which is consistent with the dihydrate form found by elemental analysis. The thermal decomposition starts above 160 °C. Both dimeric surfactants are soluble in water at room temperature, as their Krafft temperatures are below 0 °C.

Equilibrium surface tension γ versus surfactant concentration is plotted in Fig. 2. The inflection on the curves defines the critical micelle concentration (cmc). Both dimeric surfactants form micelles at room temperature, with values for the cmc of 2.2 mmol L^{−1}

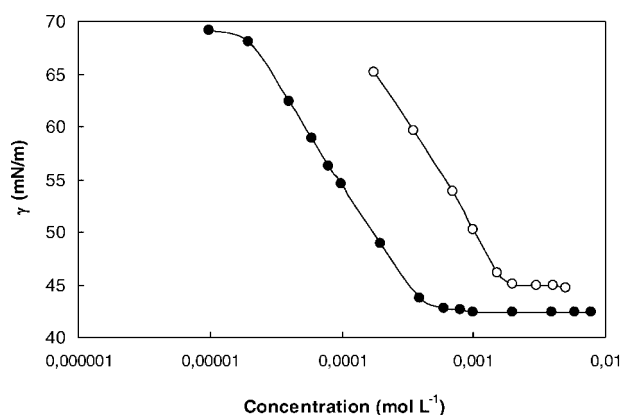


Figure 2. Surface tension curves of cationic dimers 12-EO-12-Cl₂ (○) and 12-EO-12-Mo (●). This figure is available in color online at www.interscience.wiley.com/journal/poc

and 0.4 mmol L⁻¹ for 12-EO-12-Cl₂ and for 12-EO-12-Mo, respectively. Also, the surface tension is somewhat reduced by ca 3 mN m⁻¹.

The evolution of the amphiphilic properties according to the nature of the counterion is well known for classical, that is, monomeric surfactants.^[54–56] This is also true for the gemini surfactants. For instance, the bromide analogue 12-EO-12-Br₂ exhibits a cmc of ca 0.5 mmol L⁻¹ and gives a surface tension at the cmc of ca 40 mN m⁻¹, that is notably reduced compared to 12-EO-12-Cl₂.^[30,57] Thus, the surface active behavior of 12-EO-12-Mo with a divalent molybdate counterion compares well to its bromide analogue. Although the MoO₄²⁻ lowers the hydrophilicity of the gemini surfactant, it must be still considered as a relatively hydrophilic counterion, taken the much more pronounced effect of organic counterions such as salicylate into account (Table 1).^[51]

Penetration scans provide a glimpse of all possible mesophases formed in a full concentration range. The samples were prepared at room temperature. Phase sequences of both gemini surfactants are presented in Fig. 3. The 12-EO-12-Cl₂ penetration scan indicates the existence of only one type of liquid crystal phase. With regards to 12-EO-12-Mo, the penetration scan reveals the existence of two different isotropic phases at low concentration, the frontier of which being specified on Fig. 3 by a white dotted line, and at upper concentration a birefringent region. For both gemini compounds, the birefringent region are hexagonal phase H₁. On progressive heating until 95 °C, the birefringent region does not vanish.

Table 1. Values of the cmc, γ_{cmc} for the gemini amphiphiles for the 12-EO-12-X_n series

Surfactant	cmc (mM)	γ_{cmc} (mN m ⁻¹)	References
12-EO-12-Mo	0.4	42	This work
12-EO-12-Cl ₂	2.2	45	[30]
12-EO-12-Br ₂	0.52	40	[57]
12-EO-12-(salicylate) ₂	0.08	32.0	[51]

Partial phase diagrams of the water-12-EO-12-X_n binary systems drawn as a function of temperature and gemini concentration are shown in Fig. 4. 12-EO-12-Mo shows successively, as its concentration is increased, a micellar phase L₁ (until 53 wt%), a cubic phase I₁ (from 53 to 64 wt%), and a hexagonal phase H₁ (from 64 to 85 wt%). All these phases are still observed at 80 °C. The phase behavior of 12-EO-12-Cl₂ is different since only L₁ and H₁ phases are observed until 85 wt%. The H₁ hexagonal phase is observed between 53 and 85 wt%. However, at high concentration (>80 wt%) of 12-EO-12-Cl₂ and above 45 °C, a new isotropic viscous phase appears.

The cubic phase of 12-EO-12-Mo could be determined precisely by simple visual observation since the samples obtained in the range of concentrations of 53–64 wt% are very viscous gels with no birefringent behavior under crossed polarizers. The presence of a cubic phase is often found for surfactant systems with bulky head groups, which disfavors the formation of rod-shaped aggregates on account of the large area needed per polar headgroup. It is the case in particular for dodecyl-1,3-propylene-bis(ammonium chloride)^[58] and its monovalent homologue.^[59] On the contrary, 12-EO-12-Cl₂ does not form any cubic phase in this region. This can be explained by the fact that 12-EO-12-X_n is much more dissociated when X = MoO₄²⁻ than when X = Cl⁻ as explained by Gordon and co.^[60]

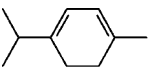
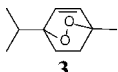
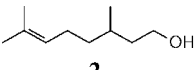
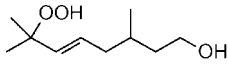
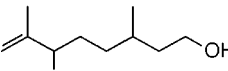
Dark singlet oxygenation in biphasic system based on 12-EO-12-Mo

Because of the very short lifetime of ¹O₂ in water (≈4 μs), water-organic solvent biphasic systems are totally inefficient for the peroxidation of hydrophobic substrates by this excited species chemically generated by disproportionation of hydrogen peroxide catalyzed by molybdate ions. Actually, H₂O₂ and MoO₄²⁻ are localized in the aqueous phase where they react to form several peroxomolybdates MoO_{4-n}(O₂)_n²⁻ among which the triperoxo, and to a lesser extent the diperoxo, decompose into ¹O₂ (Scheme 2).^[15]

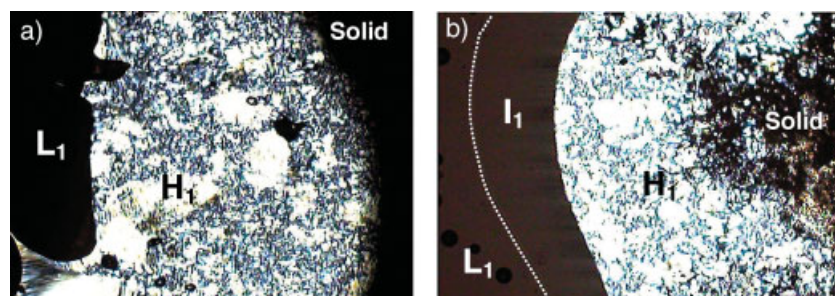
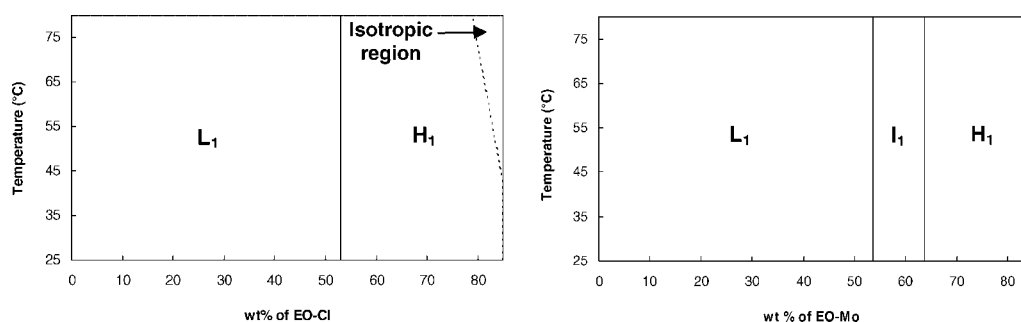
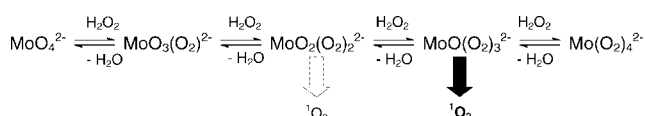
However, ¹O₂ cannot diffuse into the organic phase to reach the organic substrate because it is deactivated into ³O₂ in the aqueous phase by transfer of its energy to the vibrational levels to the water molecules. Addition of typical PTCs such as alkylammonium chlorides does not improve the process significantly. To solve the problem, a first alternative is to resort to microemulsions, particularly efficient for the dark singlet oxygenation of highly hydrophobic substrates but these media are intricate and unstable through water addition (arising from H₂O₂ decomposition). The second alternative, described in the present work, consists in using an amphiphilic PTC based on molybdate, the diethyl-ether- α,ω -bis(dimethyldodecylammonium molybdate (12-EO-12-Mo)) that allows the generation of ¹O₂ near the substrate in order to favor the chemical reaction instead of the deactivation by water molecules.

In the presence of the same volume of water and an immiscible organic solvent, 12-EO-12-Mo, as well as 12-EO-12-Cl₂, are preferentially localized into the aqueous phase whatever the polarity of the solvent is, what attests of their hydrophilic nature. However, the amphiphilic character of both these compounds allows the cosolubilization of a small amount of organic solvent into the aqueous phase because of the formation of swollen micelles of 12-EO-12-X_n. Such systems are similar to the two-phase microemulsion systems, called Winsor I, but the low proportion of cosolubilized solvent into the aqueous phase

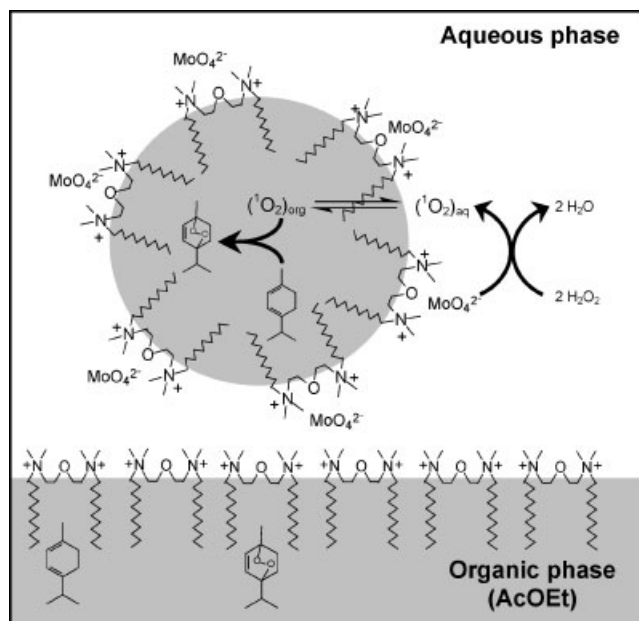
Table 2. Oxidation of 0.5 M of organic substrates in the oxidizing biphasic water/ethyl acetate (1/1 v/v) system in the presence of 12-EO-12-Mo at 25 °C

Substrate	$\log(k_r + k_q)^a$	$\frac{k_r}{k_r + k_q}^a$	$[\text{H}_2\text{O}_2]^b$ (M)	Δt (h)	Product	Yield (%) ^c
 1	8.0	1 ^a	1.3	2.8	 3	98
 2	6.0	0.87 ^a	3.2	4.8	 4a  4b	37 43

^a According to Reference^[24].
^b Cumulative amount of H₂O₂ for a 95% substrate conversion.
^c Yield in isolated and pure products directly from the organic phase by evaporation of the solvent.

**Figure 3.** Liquid crystal texture by POM in the penetration scan experiment at 25 °C for (a) 12-EO-12-Cl₂-water and (b) 12-EO-12-Mo-water. L₁ denotes an isotropic liquid phase, I₁ is an isotropic cubic phase, and H₁ is an anisotropic hexagonal phase**Figure 4.** Partial phase diagrams of the binary (left) 12-EO-12-Cl₂-water and (right) 12-EO-12-Mo-water systems. The types of phases were determined by POM and visual observation**Scheme 2.** Mechanism of singlet oxygen formation from the system hydrogen peroxide/molybdate ions^[15]

does not allow us to talk about microemulsions in the present case. The hydrophobic substrate partitions between the organic phase in excess and the proportion of this phase contained in the swollen micelles. Thus, during the reaction, 12-EO-12-Mo, which is localized at the interface, reacts with hydrogen peroxide and ¹O₂ is produced close to the substrate so that it can react with it before being deactivated by water molecules (Scheme 3).



Scheme 3. Schematic representation of the peroxidation of α -terpinene **1** by $^1\text{O}_2$ generated from $\text{H}_2\text{O}_2/\text{MoO}_4^{2-}$ in a biphasic system based on the 12-EO-12-Mo amphiphilic PTC

It is noteworthy that, as soon as hydrogen peroxide is added to the biphasic system, a third middle-phase rich in the red-brown tetraperoxomolybdate $\text{MoO}(\text{O}_2)_4^{2-}$ appears suggesting that the highest peroxidized derivative of 12-EO-12-Mo catalyst is much less hydrophilic, loosing its affinity both for water and for the organic solvent. Some phase transfer catalytic systems with a third liquid phase have already been described previously in the literature.^[61] This third 'catalytic phase' allows a local concentration of the reactants improving the activity of the reaction during the catalytic process and constitutes a simple mean to recover the catalyst at the end of the reaction contrary to usual biphasic systems based on PTC.

The two substrates, namely α -terpinene (**1**) and β -citronellol (**2**), were oxidized on the preparative scale (ca 0.5 M) in a water/ethyl acetate mixture (50/50) to show the scope of the oxidizing biphasic system based on the amphiphilic 12-EO-12-Mo PTC. These substrates represent two standard types of the $^1\text{O}_2$ reactions, namely, the ene reaction for β -citronellol and the [4 + 2] cycloaddition for α -terpinene. The overall rate constants ($k_r + k_q$) of β -citronellol and α -terpinene are respectively equal to 10^6 and $10^8 \text{ M}^{-1} \text{ s}^{-1}$ in dichloromethane (Table 2).^[24] Although these values have been measured in CH_2Cl_2 , a similar reactivity is expected in ethyl acetate since both these solvents are non hydrogenated and of comparable polarity.^[19,62] α -Terpinene reacts with $^1\text{O}_2$ very efficiently according to a pure chemical process whereas β -citronellol has a fair reactivity with significant physical quenching (k_q). The respective oxidation products were isolated in high yields as indicated in Table 2. During the process, hydrogen peroxide must be added in batches to favor the formation of the triperoxomolybdate $\text{MoO}(\text{O}_2)_3^{2-}$, the main precursor of $^1\text{O}_2$, leading to a characteristic red-brown coloration. Each fraction of H_2O_2 corresponds to about 3.5 equivalents with respect to MoO_4^{2-} in order to maximize the reaction rate. When the medium fades, an additional batch of H_2O_2 can be added.

With such a biphasic system, the recovery of the oxidation products is straightforward. First, when stirring is stopped, the phase separation is very rapid (only a few seconds). Then, as only a small amount of oil is located in the water phase, almost all the oxidation products are extracted into the organic phase. Thus, more than 95% of ascaridole resulting from the oxidation of **1** and about 80% of the two hydroperoxides of **2** are present in the organic phase. In that latter case, a significant proportion of the oxidation products are also partitioned in the aqueous phase due to their amphiphilic nature providing them a cosurfactant behavior. Evaporation of the oil phase without any other post treatment allows a very good recovery of the oxidation products, as shown in Table 2. When some oxidation products are present in the aqueous phase, they can easily be recovered and separated from the catalyst by addition of an excess of H_2O_2 which leads to a third middle-phase concentrated in peroxidized catalyst.

In comparison with polyphasic microemulsions of Winsor I type (i.e., a microemulsion in equilibrium with an oil phase in excess) based on aqueous $\text{Na}_2\text{MoO}_4/\text{SDS}/\text{PrOH}/\text{toluene}$,^[28] this biphasic system presents two advantages: (1) it allows the addition of important amounts of hydrogen peroxide without the loss of efficiency and (2) it can be used with any hydrophobic organic solvent (e.g., dichloromethane, benzene, cyclohexane...) provided that the substrate is soluble whereas the formation of a Winsor I based on sodium molybdate is conditioned both by the nature of the solvent and the concentration of Na_2MoO_4 otherwise an inefficient Winsor II system, that is, a microemulsion in equilibrium with a water excess phase, is formed. Under the same conditions, the system based on sodium molybdate and SDS requires a cosurfactant such as PrOH to form a microemulsion. Otherwise the resulting biphasic system is completely inefficient since all the catalyst lies in the water phase.

CONCLUSION

A new diammonium gemini surfactant phase-transfer catalyst with molybdate anion as the counterion was prepared from the chlorinated analogue by anion exchange. The replacement of the chloride ion by the molybdate ion notably modifies the amphiphilic properties of the gemini compound leading to a lower cmc, reduced surface tension at the cmc, and the formation of a cubic liquid crystalline phase. By virtue of its interfacial properties, this compound provides biphasic systems in the presence of water and an organic solvent, whatever its polarity is, in which the aqueous phase contains swollen direct micelles. Hence, formation of singlet oxygen by addition of hydrogen peroxide occurs at the interface, thus enabling the interaction with the organic substrate contrary to biphasic systems based on typical PTCs such as alkylammonium chloride, used in combination with sodium molybdate, which are much less inefficient since $^1\text{O}_2$ is produced far from the organic droplets and most of it is deactivated by the water molecules. Furthermore, with 12-EO-12-Mo, the resulting system constitutes a very simple reaction medium with only three components in comparison to known Winsor I microemulsions based on sodium molybdate which requires addition of surfactant (e.g., SDS) and cosurfactant (e.g., PrOH). The new compound provides very simple and efficient biphasic reaction media for the preparative peroxidation of electron-rich substrates from which the recovery of the oxidation products and the catalyst is easy.

REFERENCES

- [1] K. Holmberg, *Eur. J. Org. Chem.* **2007**, 5, 731–742.
- [2] K. Holmberg, M. Haeger, *Surf. Sci. Ser.* **2003**, 190, 327–342.
- [3] K. Holmberg, *Curr. Opin. Colloid Interface Sci.* **2003**, 8(2), 187–196.
- [4] F. M. Menger, A. R. Erlington, *J. Am. Chem. Soc.* **1991**, 113(25), 9621–9624.
- [5] D. Albanese, *Mini-Rev. Org. Chem.* **2006**, 3(3), 195–217.
- [6] E. V. Dehmloew, *Aqueous-Phase Organometallic Catalysis* (2nd edn) (Eds.: B. Cornils, W. A. Hermann), Wiley-Vch, Weinheim, **2004**, 272–287.
- [7] M. Makosza, M. Fedorynski, *Interfacial Catalysis* (Ed.: A. G. Volkov), Marcel Dekker, New York, **2003**, 159–201.
- [8] R. Alan Jones, *Quaternary Ammonium Salts: their Use in Phase-Transfer Catalysed Reactions*, London, UK, Academic Press, **2001**.
- [9] B. Bayer, A. Hambardzoumian, J. P. Roque, N. Beylerian, *Tetrahedron* **2000**, 56, 303–307.
- [10] C. M. Starks, *Tetrahedron* **1999**, 55(14), 6261–6274.
- [11] J.-M. Aubry, *J. Am. Chem. Soc.* **1985**, 107, 5844–5849.
- [12] J.-M. Aubry, B. Cazin, *Inorg. Chem.* **1988**, 27, 2013–2014.
- [13] K. Boehme, H. D. Brauer, *Inorg. Chem.* **1992**, 31, 3468–3471.
- [14] Q. J. Niu, C. S. Foote, *Inorg. Chem.* **1992**, 31, 3472–3476.
- [15] V. Nardello, J. Marko, G. Vermeersch, J.-M. Aubry, *Inorg. Chem.* **1995**, 34, 4950–4957.
- [16] M. Prein, W. Adam, *Angew. Chem. Int. Ed.* **1996**, 35, 477–494.
- [17] E. L. Clennan, *Tetrahedron* **2000**, 56, 9151–9179.
- [18] J. Wahlen, D. E. De Vos, P. A. Jacobs, P. L. Alsters, *Adv. Synth. Catal.* **2004**, 346, 152–164.
- [19] F. Wilkinson, W. P. Helman, A. B. Ross, *J. Phys. Chem. Ref. Data* **24** **1995**, 663.
- [20] V. Nardello, S. Bogaert, P. L. Alsters, J.-M. Aubry, *Tetrahedron Lett.* **2002**, 43, 8731–8734.
- [21] J.-M. Aubry, B. Cazin, F. Duprat, *J. Org. Chem.* **1989**, 54, 726–728.
- [22] M. Bourrel, R. S. Schechter, **1988**, *Microemulsions and Related Systems—Surfactant Science Series*, Vol. 30, Dekker, New York.
- [23] J. Sjöblom, R. Lindberg, S. E. Friberg, *Adv. Colloid Interface Sci.* **1996**, 65, 125–287.
- [24] J.-M. Aubry, S. Bouttemy, *J. Am. Chem. Soc.* **1997**, 119, 5286–5294.
- [25] V. Nardello, M. Herve, P. L. Alsters, J.-M. Aubry, *Adv. Synth. Catal.* **2002**, 344, 184–191.
- [26] V. Nardello, L. Caron, J.-M. Aubry, S. Bouttemy, T. Wirth, R. S.-M. Chantou, W. Adam, *J. Am. Chem. Soc.* **2004**, 126, 10692–10700.
- [27] L. Caron, V. Nardello, J. Mugge, E. Hoving, P. L. Alsters, J.-M. Aubry, *J. Colloid Interface Sci.* **2005**, 282, 478–485.
- [28] L. Caron, V. Nardello, P. L. Alsters, J.-M. Aubry, *J. Mol. Catal. A: Chem.* **2006**, 251, 194–199.
- [29] J.-M. Aubry, W. Adam, P. L. Alsters, C. Borde, S. Queste, J. Marko, V. Nardello, *Tetrahedron* **2006**, 62, 10753–10761.
- [30] A. Laschewsky, K. Lunkenheimer, R. H. Rakotoaly, L. Wattebled, *Colloid Polym. Sci.* **2005**, 283, 469–479.
- [31] Y. P. Zhu, A. Masuyama, M. Okahara, *J. Am. Oil Chem. Soc.* **1990**, 67, 459–463.
- [32] M. J. Rosen, *Chem. Tech.* **1993**, 23, 30–33.
- [33] Y. P. Zhu, A. Masuyama, Y. Kobata, Y. Nakatsuji, M. Okahara, M. J. Rosen, *J. Colloid Interface Sci.* **1993**, 158, 40–45.
- [34] S. Karaborni, K. Esselink, P. A. J. Hilbers, B. Smit, J. Karthaus, N. M. Van Os, R. Zana, *Science* **1994**, 266, 254–256.
- [35] F. M. Menger, J. S. Keiper, *Angew. Chem. Int. Ed. Engl.* **2000**, 39, **1907**.
- [36] C. A. Bunton, L. B. Robinson, J. Schaak, M. F. Stam, *J. Org. Chem.* **1971**, 36, 2346–2350.
- [37] H. C. Parreira, E. R. Lukenbach, M. K. O. Lindemann, *J. Am. Oil Chem. Soc.* **1979**, 56, 1015–1021.
- [38] R. Zana, M. Benraou, R. Rueff, *Langmuir* **1991**, 7, 1072–1075.
- [39] E. Alami, G. Beinert, P. Marie, R. Zana, *Langmuir* **1993**, 9, 1465–1467.
- [40] E. Alami, H. Levy, R. Zana, A. Skoulios, *Langmuir* **1993**, 9, 940–944.
- [41] D. Danino, Y. Talmon, R. Zana, *Langmuir* **1995**, 11, 1448–1456.
- [42] R. Zana, H. Levy, *Colloids Surf. A: Physicochem. Eng. Asp.* **1997**, 127, 229–232.
- [43] R. Zana, M. In, H. Levy, G. Duportail, *Langmuir* **1997**, 13, 5552–5557.
- [44] W. Ulbricht, R. Zana, *Colloids Surf. A: Physicochem. Eng. Asp.* **2001**, 183–185, 487–494.
- [45] L. Grosmaire, M. Chorro, C. Chorro, S. Partyka, R. Zana, *J. Colloid Interface Sci.* **2002**, 246, 175–181.
- [46] R. Zana, *J. Colloid Interface Sci.* **2002**, 246, 182–190.
- [47] L. Grosmaire, M. Chorro, C. Chorro, S. Partyka, R. Zana, *J. Colloid Interface Sci.* **2002**, 246, 175–181.
- [48] R. Zana, *J. Colloid Interface Sci.* **2002**, 246, 182–190.
- [49] A. Laschewsky, L. Wattebled, M. Arotçarèna, J.-L. Habib-Jiwan, R. H. Rakotoaly, *Langmuir* **2005**, 21, 7170–7179.
- [50] L. Wattebled, A. Laschewsky, A. Moussa, J.-L. Habib-Jiwan, *Langmuir* **2006**, 22, 2551–2557.
- [51] L. Wattebled, A. Laschewsky, *Langmuir* **2007**, 23, 10044–10052.
- [52] L. Wattebled, C. Note, A. Laschewsky, *Tenside, Surfactants, Detergents* **2007**, 44, 25–33.
- [53] S. Borse Mahendra, S. Devi, *Adv Colloid Interface Sci.* **2006**, 123–126, 387–399.
- [54] G. Para, E. Jarek, P. Warszynski, *Adv Colloid Interface Sci.* **2006**, 122, 39–55.
- [55] J. Mata, D. Varade, P. Bahadur, *Thermochimica Acta* **2005**, 428, 147–155.
- [56] S. Berr, R. M. R. Jones, J. S. Johnson, *J. Phys. Chem.* **1992**, 96, 5611–5614.
- [57] M. J. Rosen, J. H. Mathias, L. Davenport, *Langmuir* **1999**, 15, 7340–7346.
- [58] H. Hagslaett, O. Soederman, B. Joensson, L. B. A. Johansson, *J. Phys. Chem.* **1991**, 95, 1703–1710.
- [59] L. B. A. Johansson, O. Soederman, *J. Phys. Chem.* **1987**, 91, 5275–5278.
- [60] S. Hassan, W. Rowe, J. Gordon, *Handb. Appl. Surf. Colloid Chem.* **2002**.
- [61] S. Goto, *Catal. Surv. Asia* **2004**, 8(4), 241–247.
- [62] J.-M. Aubry, B. Mandard-Cazin, M. Rougee, R. V. Bensasson, *J. Am. Chem. Soc.* **1995**, 117, 9159–9164.