



Synergy between bis(dimethyldioctylammonium) molybdate and tetraethylene glycol monoethyl ether: A winning combination for interfacial catalysis in thermo-controlled and switchable microemulsions

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ABSTRACT

A simple thermo-responsive one-phase microemulsion (μem) is designed to enable the dark singlet oxidation of organic substrates while allowing a straightforward separation of the catalytic surfactant and products in two distinct phases by cooling down the reaction medium. This latter is prepared by combining a small amount (1%) of the catalytic surfactant bis(dimethyldioctylammonium) molybdate, $[\text{DiC}_8]_2[\text{MoO}_4]$, with the nonionic amphiphile tetraethylene glycol monoethyl ether, C_8E_4 . Tensiometry and dynamic light scattering are used to rationalize the synergy between the two surfactants which strongly interact. The oxidation takes place in the effective one-phase Winsor IV system which separates into two phases (μem + oil, i.e. Winsor I) just by temperature change thanks to the presence of the thermo-sensitive C_8E_4 . The thermal-controlled nanostructured reaction medium is applied to the ene reaction, [4+2] cycloaddition and sulfide oxidation.

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1. Introduction

Microemulsions (μems) are thermodynamically stable liquid mixtures of oil (O), water (W) and surfactant (S). In contrast to ordinary emulsions, which are traditionally prepared by high shear mixing of components, μems form spontaneously upon mixing of O, W and suitable surfactants. There are four “types” of μems , called Winsor systems: (i) type I with a O/W μem in equilibrium with an excess oil phase, (ii) type II with a W/O phase floating on an aqueous phase, (iii) type III referring to a three-phase system in which an intermediate μem lies between excess W and O phases, and (iv) type IV corresponding to a one-phase system [1,2]. Microemulsions are efficient and smart reaction media since they allow the co-solubilization of hydrophilic reactants and hydrophobic substrates at the nanoscale [3,4]. In Winsor IV systems, the W/O interfacial area is multiplied by $\approx 10^5$ compared to a simple W/O biphasic system while keeping a compartmentalization. This feature induces beneficial effects on the kinetics and selectivity of the

reactions. However, one-phase μems suffer from two main drawbacks: (1) they require high amounts of surfactants ($\approx 15\text{--}20\%$) plus generally some co-surfactants and (2) the product and catalyst recovery is tedious due to the complexity of the system [5,6]. The WIII system allows overcoming these issues [6]. Indeed, one strategy to fulfill the challenges of selective oxyfunctionalization of highly hydrophobic compounds combined with full recovery of catalysts and products under eco-friendly conditions consists in resorting to Winsor III μems elaborated with “balanced catalytic surfactants” (BCS) [6,7]. It has recently been reported that bis(dimethyldioctylammonium) molybdate, $[\text{DiC}_8]_2[\text{MoO}_4]$ and bis(didecyldimethylammonium) tungstate $[\text{DiC}_{10}]_2[\text{WO}_4]$ behave as BCSs providing, at room temperature, WIII systems just in the presence of water and an appropriate solvent [6,7]. However, transitions between the Winsor systems induced by the formation of amphiphilic products during the reaction can take place by changing the W/O interfacial film curvature. As an example, epoxycitronellol which completely hydrolyzes into a hydrophilic and amphiphilic triol induces a WIII \rightarrow WI transition [7]. In contrast, epoxystearic acid, which can be considered as a hydrophobic amphiphile, leads to a WIII \rightarrow WII transition [7]. Hence, to avoid undesired Winsor changes during or at the end of the reaction, it can

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be interesting to have a tuning controllable and reversible parameter such as the temperature. This can be achieved with strongly thermo-sensitive surfactants such as the nonionic polyethoxylated alcohols, C_nE_j . Since a relevant catalytic μem reaction medium must be elaborated with a minimal amount of surfactants, the strategy developed in the present work consists in taking advantage of synergies that operate in nonionic and ionic surfactant mixtures. Indeed, it is known for a long time that aqueous mixtures of ionic and nonionic surfactants can lead to beneficial synergistic effects [8,9]. Several applications take advantage of mixing surfactants to improve their detergent [10], foaming [11], emulsifying [12], solubilizing [13] or biocidal [14] properties. As far as microemulsions are concerned, a dramatic enhancement of the efficiency of the non-ionic surfactant, reflected by the minimal amount required to reach the monophasic μem , can be obtained by addition of very small amounts (<1%) of an ionic surfactant [15–18]

In this paper, the well-defined nonionic tetraethylene glycol monoethyl ether surfactant, abbreviated as C_8E_4 , was used to elaborate a thermo-responsive catalytic μem . The synergistic effect between $[\text{DiC}_8]_2[\text{MoO}_4]$ and C_8E_4 is discussed in terms of cloud point, surface tension and self-aggregation. The mixed micelle size in the binary system is studied by dynamic light scattering (DLS). The $\text{H}_2\text{O}/C_8E_4-[\text{DiC}_8]_2[\text{MoO}_4]/\text{cyclohexane}$ system is successfully applied to the dark singlet oxygenation (i.e. [4+2] cycloaddition, ene reaction and sulfide oxidation) of organic substrates. The reaction is thus conducted in the effective one-phase Winsor IV μem while cooling down the final reaction medium triggers a phase transition from the monophasic Winsor IV μem to a biphasic Winsor I μem , allowing the recovery of product and catalyst in two different phases.

2. Experimental

2.1. Specific notation

To specify the amount of $[\text{DiC}_8]_2[\text{MoO}_4]$ (surfactant 1), C_8E_4 (surfactant 2), H_2O (W) and oil (O) in the phase diagrams, the total mass fraction of surfactant 1 and surfactant 2, γ , was defined as:

$$\gamma = \frac{m_1 + m_2}{m_O + m_W + m_1 + m_2}$$

The mole fraction of the ionic surfactant $[\text{DiC}_8]_2[\text{MoO}_4]$ in the surfactant mixture, α , was defined as:

$$\alpha = \frac{\alpha_1}{\alpha_1 + \alpha_2}$$

2.2. Surface tension measurements

The CMCs of the surfactants were obtained by the surface tension measurements with the tensiometer K11 (Krüss) using the Wilhelmy plate method with the precision of the force transducer to 0.1 mN m^{-1} . For each surfactant mixture of specified α , the surface tensions of different concentrations were recorded after equilibration. The average quantity of at least three measurements was adopted for all equilibrium surface tension values. Before each experiment, the platinum plate was cleaned in red/orange color flame. The temperature was stabilized at $25 \pm 0.05^\circ\text{C}$ with a thermo-regulated bath Lauda RC6.

2.3. Dynamic light scattering (DLS)

DLS measurements were performed on a ALV/CGS-3 Super Compact Goniometer System at 25°C (thermo regulated bath $\pm 0.1^\circ\text{C}$). Pseudo cross correlation mode is used with two APD to improve

the detection of small size micelle (<5 nm). Each sample was centrifuged directly in the glass cell to avoid dust signal (30 min, 4500 rpm) during the DLS analysis. 13 angles from 30 to 150° were record to determine the diffusion coefficient ($R_h \pm 0.1 \text{ nm}$). Cumulant method was applied as data treatment of the correlogram for each angle and polydispersity index was in all cases lower than 0.2 indicating that only monodisperse micelles were observed.

2.4. Binary diagrams

The water/surfactant mixture pseudo-binary diagram as a function of temperature was determined by visual inspection. At each constant α , the solutions of different concentrations were prepared and kept in the thermostatic bath. The temperature was increased slowly ($1.0^\circ\text{C}/\text{min}$) from 15 to 80°C and then decreased to 15°C , the temperature resulted in the turbid and phase separation for each sample was recorded and this process was repeated for three times to affirm the deviation under 0.1°C .

2.5. Fish diagrams.

The Winsor types in the $\text{H}_2\text{O}/\text{surfactant}/\text{cyclohexane}$ fish diagram were also determined by visual inspection with the same volume of water and cyclohexane. For each constant α , several microemulsions with increased γ were prepared. From 10 to 45°C with 1.0°C increment for each time, all microemulsion tubes were kept in the thermostatic bath for 6 h for each temperature and the Winsor types were recorded. The Fish diagrams were constructed by investigating the phase behavior of the $C_8E_4-[\text{DiC}_8]_2\text{MoO}_4/\text{cyclohexane}/\text{water}$ systems at a constant water-to-oil weight ratio as a function of temperature (ordinate) and surfactant mass percentage (abscissa). The “Fish-tail” point located at the intersection of the four Winsor (Winsor I, II, III and IV) regions, corresponds to the minimal surfactant concentration required to obtain a one-phase microemulsion (Winsor IV). Water, oil and surfactant were introduced in a thin glass tube ($\varnothing = 2 \text{ mm}$), the headspace of which was filled with Argon and then frozen at -78°C with a dry ice/acetone mixture. The tubes were sealed by flame to avoid any loss of oil or water during the experiment. Samples were gently shaken and placed in a water bath, maintained at a constant temperature $T \pm 0.1^\circ\text{C}$, until the equilibrium was reached. The fish diagrams were constructed by visual inspection of the Winsor phases. The “fish-tail” temperature T^* values were obtained with an accuracy better than 1°C .

2.6. Typical catalytic experiments

$[\text{DiC}_8]_2[\text{MoO}_4]$ (11.1 mg, $15.8 \mu\text{mol}$), C_8E_4 (211.1 mg, 0.689 mmol), H_2O (1.0 g), cyclohexane (1.0 g) were added consecutively to prepare the microemulsion in a reaction tube. Then α -terpinene (50 mg, 0.367 mmol) was added into the mixture and kept at 30°C (Winsor IV), the H_2O_2 (50 wt.%, 17 M) was added stepwise ($10 \mu\text{L}$, each 20 min). The conversion was complete after the addition of $6 \times 10 \mu\text{L}$ (1.02 mmol). Then the reaction tube was kept still at 5°C for 3 h, the oil phase was separated and the microemulsion phase was washed with cyclohexane (1 mL) at 5°C , the organic phases were combined and cyclohexane was removed by evaporation, the crude product was purified by a small chromatography on silica gel (cyclohexane/AcOEt = 5:1) and pure colorless oil was obtained (56.6 mg, 92%). $^1\text{H NMR}$ (300 MHz, CDCl_3 , 20°C , TMS): δ (ppm) = 1.01 (d, $J = 2.25$, 3H; CH3), 1.03 (d, $J = 2.25$, 3H; CH3), 1.39 (s, 3H; CH3), 1.19–1.57 (m, 2H, $-\text{CH}_2-\text{CH}_2-$), 1.87–2.03 (m, 1H; isopropyl), 2.03–2.14 (m, 2H; $-\text{CH}_2-\text{CH}_2-$), 6.47 (dd, $J = 25.77$, 8.55 Hz; $\text{CH}=\text{CH}$). $^{13}\text{C NMR}$ (75 MHz, CDCl_3 , 20°C): δ (ppm) = 17.2, 17.3, 21.4, 25.6, 29.5, 32.1, 133.0, 136.4.

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