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Micelles into Glycerol Solvent: Overcoming Side Reactions of Glycerol

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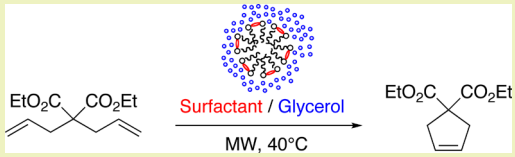
Supporting Information

ABSTRACT: The ring-closing metathesis (RCM) of diethyl diallylmalonate in glycerol micellar conditions was studied using microwave irradiation. The micellization of different cationic surfactants in glycerol was first investigated. The results show the superiority of micellar catalysis in glycerol for a RCM reaction compared to glycerol alone, limiting byproduct formation. In comparison with the classical solution syntheses, the method here described allows safer reaction conditions, less hazardous chemical syntheses, and use of renewable feedstocks. The practical workup, separation, and purification operations minimize the use of materials.



KEYWORDS: *Glycerol, Micellar catalysis, Ring-closing metathesis, Microwaves, Critical micellar concentration, Gemini surfactants*

INTRODUCTION

One of the major challenges in academia and industry is the development of environmentally friendly synthetic processes through a chemistry "*benign by design*".[1,2] In this context, the replacement of classical volatile organic solvents[3] by new sustainable media[4] coupled with energy-saving[5,6] and selective protocols for catalytic and organic processes is an economical and societal concern. This is enabling wider use of glycerol, switching its status as a waste in biodiesel fuel production[7] to an economical and eco-friendly solvent in organic[8−11] and inorganic material synthesis,[12−15] as a substrate for the production of value-added chemicals,[16−18] or as a hydrogen donor for transfer hydrogenation (TH) reactions.[16,19−22] It is readily available from renewable sources after triglyceride saponification of natural fats and oils.[23] It isalso a cheap and a large volume market product that is biodegradable and nontoxic. Due to its strong hydrogen network,[24] glycerol displays solvent properties similar to those of water[25] and a polarity similar to that of other organic solvents such as DMSO or DMF, allowing its use as a solvent for microwave irradiation.[26] Due to its importance for many industrial and pharmaceutical preparations and despite its high potential application as an environmentally friendly solvent to perform green synthesis, glycerol use is still limited in organic transformations, mainly for two reasons: (i) the intrinsic reactivity of the polyol backbone leading to the formation of side products and (ii) the very poor solubility of the vast majority of organic compounds. In order to overcome the drawbacks described, micellar catalysis in glycerol is a valid and unexplored alternative. The presence of some hydrophobic environments inside the micelle allows for better diffusion of organic substrates into the glycerol phase and also inhibits its reactivity as reported for base-catalyzed transformations (ring-opening of epoxydes, Michael addition, Henry and Knoevenagel reactions).[25] The study of the micellization process in "pure glycerol" is limited, both in the field of biology and in organic synthesis. Many studies related to the use of glycerol micellar conditions for biological applications (e.g., protein crystallization or cellular cryoprotectors) were reported only in aqueous binary solvent mixtures, ranging from a few percent to 40% of glycerol.[27−29] Very few studies report a higher concentration of glycerol in the range from 50% to 80%,[30,31] and only a few papers deal with the surfactant in pure glycerol, where the investigated concentrations were extremely high in order to obtain lyotropic mesophases[32] and liquid crystals[33] inappropriate for organic synthesis. Moreover, the critical micellar concentration (cmc) of commercially available surfactants was never reported, and micellar systems in pure glycerol still remain an underdeveloped field of research, especially in organic synthesis. The study of the surfactant aggregation and of the micellization process in polar organic nonaqueous solvents such as glycerol is limited in regards to the importance of these applications in green chemistry, pharmaceutical

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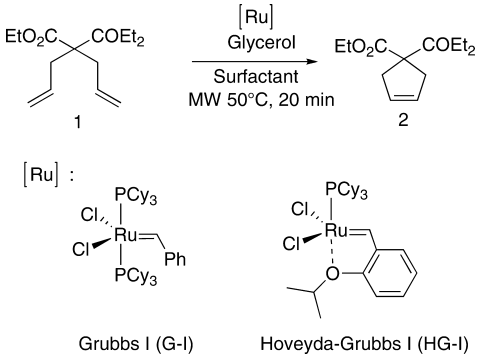
sciences, and cosmetics, in which glycerol and surfactants are simultaneously present in many different products.

Herein, the micellization process in pure glycerol in the presence of various surfactants was investigated first. Then, the micellar approach was applied to the study of the ring-closing metathesis (RCM) reaction of diethyl diallyl malonate **1** (Scheme 1).

Scheme 1. RCM in Glycerol Micellar Conditions



RESULTS AND DISCUSSION

We previously reported[10] the ruthenium-catalyzed ring-closing metathesis (RCM) of diethyl diallylmalonate **1** in glycerol under microwave activation. The conversion of the starting material was always quantitative; however, the yield of the cyclic product **2** was compromised by the formation of various glycerol ester byproducts through transesterification between glycerol and the substrate or the product. The micellar catalysis approach in glycerol could be an effective alternative to overcome the problem of side reactions between glycerol and ester substrates (Scheme 1).

Following the above, it is expected that the solubilized substrate inside the micellar core is protected from glycerol.

To date, no data have been reported on pure glycerol for conventional cationic surfactants such as dodecyltrimethylammonium bromide (DTAB), tetradecyltrimethylammonium bromide (TTAB, and hexadecyltrimethylammonium bromide (CTAB), or for cationic gemini (dimeric) surfactants such as alkanediyl-α,ω-bis(dodecyldimethylammonium bromide), referred to as 12-*s*-12,[34] for which *s* is the spacer length and represents the number of methylene groups (2 or 10) (Figure 1). Due to the high viscosity of polyol liquids and polyol/water

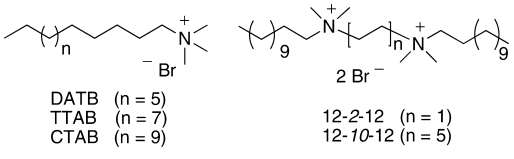


Figure 1. Chemical structure of the investigated surfactants.

mixtures, difficulties were encountered in measurements of the critical micelle concentration (cmc) using methods such as tensiometry, conductimetry, or calorimetry. An alternative method, based on pyrene fluorescence spectroscopy, was used in the present study. The ratio I_1/I_3 (called the 1:3 ratio) of the intensities of the first and third vibronic peaks in the fluorescence emission spectrum of solubilized pyrene give a measure of the polarity of the pyrene microenvironment[35,36] and is therefore a convenient method to determine the cmc of surfactant in glycerol. Figure 2 shows the pyrene 1:3 ratio plots for DTAB, TTAB, CTAB, 12-2-12 and 12-10-12 in glycerol. The pyrene 1:3 ratio data points were fitted using a Boltzmann sigmoidal function. The 1:3 ratio decreased as the concentration of surfactant increased, and an inflection point could be identified when the surfactant concentration reached the micellar concentration.[36] The second derivative of the Boltzmann sigmoidal fit shown in Figure 2 permitted determination of the center of the sigmoid associated with the critical micellar concentration using the method previously reported.[36] A summary of the values of cmc in glycerol compared with those obtained in water is shown in Table 1. It was observed that the cmc value decreased with an increase in carbon chain length. Dimeric surfactants exhibited a cmc noticeably lower than monomeric surfactants with the same alkyl chain length. Moreover, the cmc values in pure glycerol increased considerably compared to those in water. Previous studies concerning the micellization in polyol aqueous mixtures reported an increase in the cmc with polyol content.[27,28,37,38]

The micellization process in polar nonaqueous solvents was described with an important entropic contribution called solvophobic interaction, which is responsible for micellization.[39,40] This interaction results from the presence of one or more potential hydrogen bonding centers.[40] It was suggested that the ability of a solvent to form hydrogen bonds was a necessary condition for surfactant aggregation and that the micellization[41,42] in polar nonaqueous solvent occurred when the surfactant concentration was sufficient to allow effective dispersive interactions between alkyl chains. Consequently, a certain amount of the solvent molecules surrounding the hydrophobic groups were released, resulting in a positive change of entropy. Hence, the micellization in polar nonaqueous solvent is a thermodynamically favored process. Nevertheless, the reported values for critical micellar concentrations were much higher than in water because the hydrogen bond network was weaker. As the glycerol dielectric constant (ε_r = 42.5) is lower than that of water (ε_r = 78.5), an enhancement of repulsion was also expected among the cationic head groups, along with an increase in their surface area in the micelle, leading to a lower aggregation number.[27,31,35,36,43−45]

The data reported in Table 1 are important in determining which surfactant was most suitable for micellar catalysis in glycerol as the cmc value reflects the surfactant efficiency to form a nonpolar solvophobic domain in which the solubilized substrate was protected from the reactive medium. Furthermore, the cmc value indicates the amount of free monomers in the solution; thus, nonmicellized surfactant molecules DTAB and TTAB with cmc values of 130 and 50 mM were inappropriate for micellar catalysis. CTAB displayed a lower value of cmc. However, it can only be used at temperatures above 323 K because of its poor solubility at room temperature, which could complicate the micellar solubilization of the reactive substrates. In contrast, the dimeric surfactant 12-2-12 is well suited for micellar catalysis with the lowest cmc value (9.6 mM, Table 1) in glycerol at room temperature, and it was thus selected to study the RCM of diethyl diallylmalonate **1**.

Moreover, 12-2-12 also exhibited a large solubility at 298 K, suitable for practical application in the field of organic synthesis.

In previous findings,[46] it was demonstrated that diethyl diallylmalonate **1** was completely solubilized in the hydrophobic core of the micelles formed by 12-2-12 in water. The

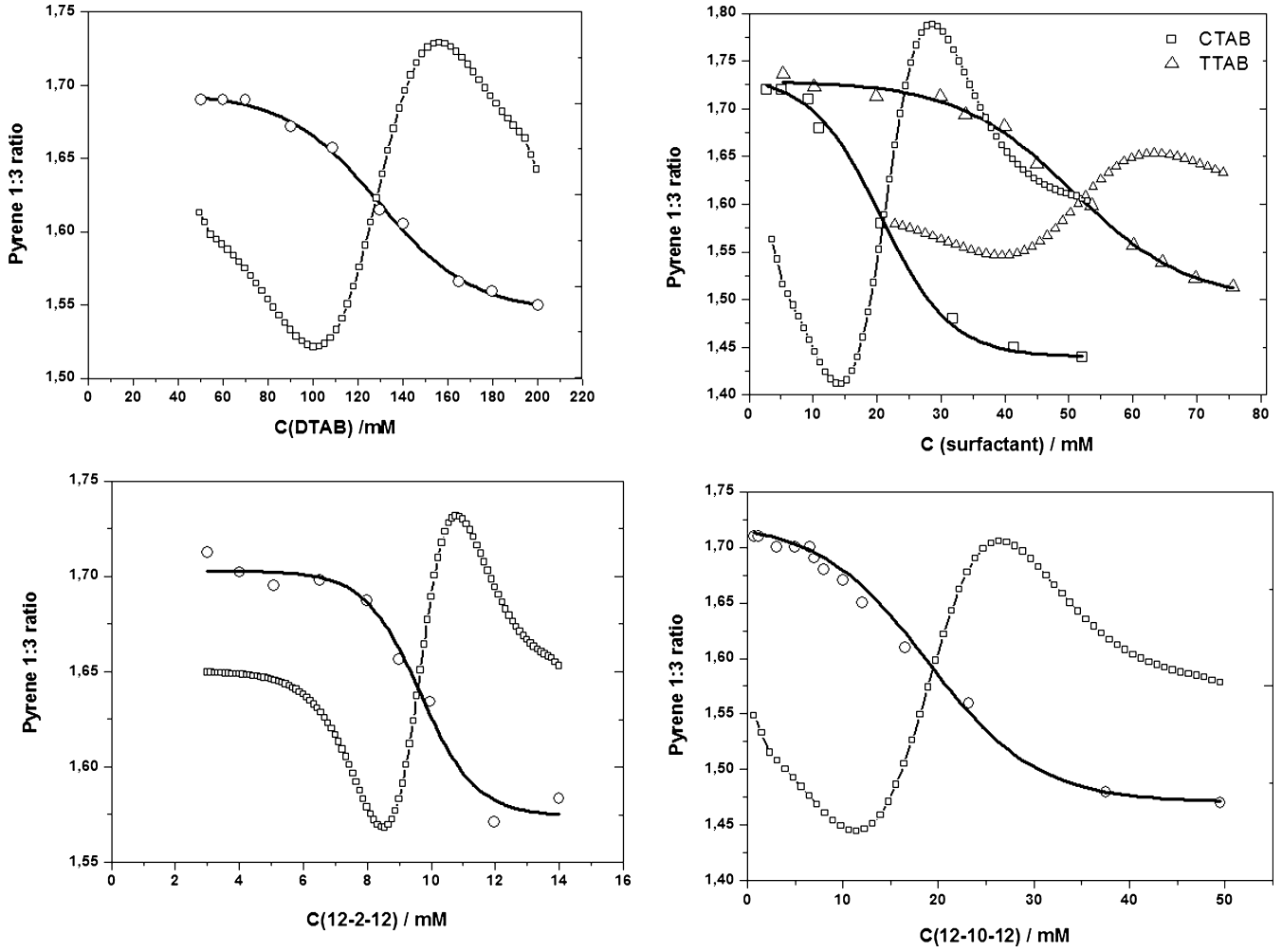


Figure 2. Plots of pyrene 1:3 ratio versus concentration of surfactants. The bold lines are the Boltzmann sigmoidal fit to the data, and the dashed lines are the second derivative of the fit curve to determine the sigmoid center associated with the surfactant cmc.

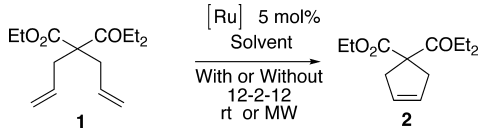
Table 1. Comparative Values for cmc of Surfactants in Glycerol and in Water

	cmc (mM)	
surfactant	in glycerol	in water
DTAB	129.3	15.6[43]
TTAB	50.6	3.71[43]
CTAB[a]	20.57	0.91[43,44]
12-2-12	9.65	0.84[45]
12-10-12	18.38	0.63[45]

[a]Measurements were carried out above the Krafft temperature of CTAB at 323 K in glycerol and 308 K in aqueous solution.

ring-closing metathesis was studied by replacing water with glycerol and using 12-2-12 as the micellization agent using microwave activation (Scheme 1). The reactivity of glycerol was inhibited by the presence of hydrophobic surroundings protecting the substrate from the formation of glycerol ester byproducts as observed for RCM in glycerol alone.[10] The results using two different ruthenium catalysts (G-I and HG-I, Scheme 1 and Table 2) were also compared to those previously reported in eco-friendly solvents such as PEG-3400[47] and glycerol alone,[10] in water micellar conditions at room temperature,[46] or under microwave activation.

Table 2. Comparative Studies for Ring-Closing Metathesis[a] in Green Solvents at Room Temperature or Using Microwave Activation (MW)



		without surfactant[b]		micellar catalysis with 12-2-12		
entry		glycerol (%)	PEG-3400 (%)	water (%)		glycerol (%)
1	G-I	49[10,c]	30[47,c]	62[46,d]	0[e]	75[f]
2	HG-I	57[c]	quantitative[c]	traces[d]	0[e]	82[f]

[a]Yields were determined by ^{1}H NMR using CH_2Br_2 as internal standard. [b]Concentration of the substrate was 0.30 mM. [c]Reaction performed at 50 °C, using microwave irradiation for 1 h. [d]Reactions performed at room temperature for 4 h; substrate concentration was 0.30 mM. [e]Reaction conditions: **1** (0.04 mmol, substrate concentration was 0.016 mM), catalyst (5 mol %), 12-2-12 (2.43 mg, 0.004 mmol), water (2.63 mL), and 20 min at 50 °C using microwave irradiation. [f]Reaction conditions: **1** (0.159 mmol, substrate concentration was 0.16 mM), catalyst (5 mol %), glycerol/12-2-12 mixture (1.2 g), 12-2-12 (15 mg), and 20 min at 50 °C using microwave irradiation.

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In the first set of experiments, the reactivity of substrate **1** in aqueous micellar conditions was studied using microwave activation and compared with the data of previous results at room temperature in water[46] (Table 2).

In these cases, the reaction was investigated at the same substrate concentration (0.30 mM). In water, using microwaves, the conversion of diethyl diallylmalonate **1** was quantitative after only 20 min with both G-I and HG-1 catalysts, but the cyclized product **2** was not detected in the raw by LC/MS analyses. The heating characteristics of the solvents play a crucial role when using microwave irradiation.[26] High microwave absorption due to the high dielectric constant of water proved to be detrimental on the outcome of the cyclization process in aqueous micellar conditions, promoting a fast polymerization even at a far more diluted substrate concentration (0.16 mM).

This hypothesis was confirmed during the workup. A suspension formed in the aqueous phase during the extraction with diethyl ether. Suspecting this was due to the formation of insoluble polymers, the aqueous phase was analyzed by a dynamic light scattering (DLS) technique to measure their size (Supporting Information). Consistent with the better efficiency of the HG-I catalyst in the cross-metathesis polymerization reaction, particles of 345 and 585 nm in size were obtained in reactions catalyzed by G-1 and HG-1, respectively. For RCM in aqueous media,[46] it was reasoned that micelles acted carriers of the insoluble substrate from the solution to the catalyst surface and improved the diffusion to reactive centers. Cyclized product **2** was then expelled from the micelles as its solubility was decreased. Likewise, catalyst, allylic substrate **1**, and cyclized product **2** were not soluble in pure glycerol.

To determine if the use of glycerol micellar catalysis using a microwave could lead to a more successful outcome, the efficiency of the RCM of diethyl diallylmalonate **1** (in a glycerol/12-2-2 micellar mixture) with the G-1 catalyst was initially tested at a concentration of 0.30 mM and compared with previous experiments in glycerol alone,[10] in PEG-3400,[47] and in an aqueous micellar catalysis[46] (Table 2, entry 1). Here too, the reaction proved to be sensitive to the substrate concentration, and only traces of the RCM product **2** were obtained. Despite the full conversion of the starting material, the positive outcome was hampered by a fast polymerization reaction due to the "high concentration" of diethyl diallylmalonate **1** around the catalyst.

It was reported that the internal viscosity of the micelle was increased with addition of glycerol in the aqueous surfactant mixture.[31] Accordingly, it was expected that the residence time of diethyl diallylmalonate **1** was prolonged, and the amount increased in the immediate vicinity of the reactive center on the catalyst surface. Due to the high viscosity of the micellar core and the slowed diffusion of the reactive species, the polymerization reactivity was strongly increased. The substrate dilution in the reaction mixture was thus key to limiting the polymerization reaction and in promoting the cyclization reaction leading to product **2**.

The RCM in glycerol micellar conditions was also explored at more diluted concentrations (using microwaves). Good yields were obtained with both catalysts at 0.16 mM (Table 2), and at 0.08 mM, the reaction was equally effective but was not further investigated for practical reasons (handling of very small quantities). Cyclized product **2** was obtained in shorter times (20 min) compared to PEG-3400[47] or glycerol alone[10] (1 h) (Table 2), and glycerol esters or isomerization byproducts were not formed. Lowering the catalytic loading (2.5 mol %) proved to be ineffective in terms of substrate conversion or yield of cyclized product **2**. As shown in Table 2, when using the G-I catalyst, micellar catalysis was possible both in aqueous media at room temperature and in glycerol using microwaves (Table 2, entry 1), whereas with the HG-I catalyst the glycerol micellar system using microwaves remained the only suitable approach for RCM (Table 2, entry 2).

At the end of the reaction and as previously demonstrated,[46] cyclized RCM product **2** was insoluble in the micellar media, and it was expelled from the nanoreactor leading to the formation of two immiscible phases. Consequently, the recovery of final product **2** could be achieved by decantation, without assistance of any organic solvent. In order to obtain full recovery of the product and especially for small-scale preparations, a glycerol-immiscible and renewable solvent such as 2-methyl-tetrahydrofuran (2-Me-THF) in which the surfactant was also insoluble could be used. The environmental benefit of using glycerol as a solvent was mantained by using the biomass derivative solvent 2-Me-THF and avoiding the use of any other toxic organic solvents.

CONCLUSIONS

In conclusion, solvents play a key role in controlling the process of micellization of surfactants. Glycerol is similar to water in that it is polar in nature and forms intra- and inter-hydrogen bonds though less strong than those in water. As the cmc is the most important parameter in investigations concerning the micellization of surfactants, the behavior of monocationic DTAB, TTAB, and CTAB (commercially available) and dicationic 12-2-12 and 12-10-12 (laboratory manufactured and now commercially available) were studied, and their cmc values were measured for the first time in pure glycerol. It was observed that the surfactant cmc in glycerol was higher compared to those in water. This was mainly due to the fact that the cohesive energy density and dielectric constant of glycerol were lower than those of water. The results obtained using microwave activation for RCM in aqueous or glycerol micellar media need to be analyzed with consideration to the relative solubility of the substrate and catalysts in the glycerol or water phase, the different viscosity of the media, and the diffusion properties of the compounds but also the difference in microwave absorption of each media, including the surfactant. Although glycerol alone can be a valid alternative for environmentally friendly organic transformation,[16] the micellar catalysis approach could be an alternative to improve the solubility of organic substrates enhancing their diffusion in this particular medium and to inhibit the reactivity of its polyol system. Finally, another advantage of the catalytic system described here is the use of commercially available catalysts, under nonconventional conditions, without the need to synthesize specific catalysts[48] or expensive "catsurf"[49,50] (*cat*alysts behaving as *surf*actants, explored in aqueous micellar conditions) that require additional production steps and are not always commercially available. The possibility to realize organic syntheses and catalysis in glycerol micellar conditions will open new perspectives and approaches for expanding the scope of glycerol use.

EXPERIMENTAL SECTION

General Experimental Procedure. 12-2-12 (15 mg, 0.024 mmol) was added to a solution of 12-2-12 in glycerol (1.2 g, prepared using 5 mg of surfactant/g of glycerol). The mixture was heated gently under

vigorous stirring at 60 °C for 10 min. The solution was left to reach room temperature under stirring and then diethyl diallylmalonate **1** (38.3 mg, 0.159 mmol) was added. The mixture was sonicated for 5 min to allow dispersion of the substrate in the medium. The ruthenium catalyst (5 mol %) was added, and the suspension was irradiated using microwaves at 50 °C for 20 min. The cyclized product **2** could be recovered after a simple workup; 2-methyl-tetrahydrofuran (2 mL, Me-THF) and aqueous $NaCl_{sat.}$ (1 mL) were added directly into the reaction vessel. The mixture was vigorously stirred for 5 min. The surfactant was not soluble in Me-THF, while the cyclized product **2** was in the upper organic layer. The organic layer was recovered by simple decantation, dried over $MgSO_4$, filtered, and evaporated under reduced pressure. Yields are reported in Table 2. Spectral data of RCM product **2** are identical to those in the literature.[46,51]

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and methods. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Anastas, P. T.; Kirchhoff, M. M. Origins, current status, and future challenges of green chemistry. *Acc. Chem. Res.* **2002**, *35*, 686−694.

(2) Anastas, P. T.; Warner, J. *Green Chemistry: Theory and Practice*; Oxford University Press, Oxford, 1998.

(3) Clark, J. H.; Tavener, S. J. Alternative solvents: Shades of green. *Org. Proc. Res. Dev.* **2006**, *11*, 149−155.

(4) Kerton, F. M. In *Alternative Solvents for Green Chemistry*; Clarck, J., Ed.; RSC Green Chemistry Series; Royal Society of Chemistry (RSC): Cambridge, U.K., 2009.

(5) Baig, R. B. N.; Varma, R. S. Alternative energy input: Mechanochemical, microwave and ultrasound-assisted organic synthesis. *Chem. Soc. Rev.* **2012**, *41*, 1559−1584.

(6) Kappe, C. O. Microwave dielectric heating in synthetic organic chemistry. *Chem. Soc. Rev.* **2008**, *37*, 1127−1139.

(7) Zakaria, Z. Y.; Amin, N. A. S.; Linnekoski, J. A perspective on catalytic conversion of glycerol to olefins. *Biomass Bioenergy* **2013**, *55*, 370−385.

(8) Azua, A.; Mata, J. A.; Heymes, P.; Peris, E.; Lamaty, F.; Martinez, J.; Colacino, E. Palladium N-heterocyclic carbene catalysts for the ultrasound-promoted Suzuki−Miyaura reaction in glycerol. *Adv. Synth. Catal.* **2013**, *355*, 1107−1116.

(9) Azua, A.; Mata, J. A.; Heymes, P.; Peris, E.; Lamaty, F.; Martinez, J.; Colacino, E. Alternative energy input for transfer hydrogenation using iridium NHC-based catalysts in glycerol as hydrogen donor and solvent. *Organometallics* **2012**, *31*, 3911−3919.

(10) Bakhrou, N.; Lamaty, F.; Martinez, J.; Colacino, E. Ring-closing metathesis in glycerol under microwave activation. *Tetrahedron Lett.* **2010**, *51*, 3935−3937.

(11) Gu, Y. L.; Jérôme, F. Glycerol as a sustainable solvent for green chemistry. *Green Chem.* **2010**, *12*, 1127−1138.

(12) Guo, P.; Cui, L.; Wang, Y.; Wang, M.; Lv, B.; Zhao, X. S. Facile synthesis of $ZnFe_2O_4$ nanoparticles with tunable magnetic and sensing properties. *Langmuir* **2013**, *29*, 8997−9003.

(13) Zavyalova, U.; Girgsdies, F.; Korup, O.; Horn, R.; Schlögl, R. Microwave-assisted self-propagating combustion synthesis for uniform deposit of metal nanoparticles on ceramics monoliths. *J. Phys. Chem. C* **2009**, *113*, 17493−17501.

(14) Liu, Z.; Peng, S.; Xie, Q.; Hu, Z.; Yang, Y.; Zhang, S.; Qian, Y. Large-scale synthesis of ultralong Bi_2S_3 nanoribbons via a solvothermal process. *Adv. Mater.* **2003**, *15*, 936−940.

(15) Chen, Y.; Tian, G.; Ren, Z.; Tian, C.; Pan, K.; Zhou, W.; Fu, H. Solvothermal synthesis, characterization, and formation mechanism of a single-layer anatase TiO_2 nanosheet with a porous structure. *Eur. J. Inorg. Chem.* **2011**, *5*, 754−760.

(16) Diaz-Alvarez, A. E.; Francos, J.; Lastra-Barreira, B.; Crochet, P.; Cadierno, V. Glycerol and derived solvents: new sustainable reaction media for organic synthesis. *Chem. Commun.* **2011**, *47*, 6208−6227.

(17) Pagliaro, M.; Ciriminna, R.; Kimura, H.; Rossi, M.; Della Pina, C. From glycerol to value-added products. *Angew. Chem., Int. Ed.* **2007**, *46*, 4434−4440.

(18) Pagliaro, M. Rossi, M. *The Future of Glycerol*, 2nd ed.; RSC Publishing: Cambridge, U.K., 2010; p 170.

(19) Azua, A.; Mata, J. A.; Peris, E. Iridium NHC-based catalysts for transfer hydrogenation processes using glycerol as solvent and hydrogen donor. *Organometallics* **2011**, *30*, 5532−5536.

(20) Farnetti, E.; Kaspar, J.; Crotti, C. A novel glycerol valorization route: Chemoselective dehydrogenation catalyzed by iridium derivatives. *Green Chem.* **2009**, *11*, 704−709.

(21) Tavor, D.; Sheviev, O.; Dlugy, C.; Wolfson, A. Transfer hydrogenations of benzaldehyde using glycerol as solvent and hydrogen source. *Can. J. Chem.* **2010**, *88*, 305−308.

(22) Wolfson, A.; Dlugy, C.; Shotland, Y.; Tavor, D. Glycerol as solvent and hydrogen donor in transfer hydrogenation−dehydrogenation reactions. *Tetrahedron Lett.* **2009**, *50*, 5951−5953.

(23) Chiu, C.-W.; Schumacher, L. G.; Suppes, G. J. Impact of cold flow improvers on soybean biodiesel blend. *Biomass and Bioenergy* **2004**, *27*, 485−491.

(24) Chen, Y.; Ozaki, Y.; Czarnecki, M. A. Molecular structure and hydrogen bonding in pure liquid ethylene glycol and ethylene glycol-water mixtures studied using NIR spectroscopy. *Phys. Chem. Chem. Phys.* **2013**, *15*, 18694−18701.

(25) Karam, A.; Villandier, N.; Delample, M.; Koerkamp, C. K.; Douliez, J.-P.; Granet, R.; Krausz, P.; Barrault, J.; Jérôme, F. Rational design of sugar-based-surfactant combined catalysts for promoting glycerol as a solvent. *Chem.—Eur. J.* **2008**, *14*, 10196−10200.

(26) Kappe, C. O. Controlled microwave heating in modern organic synthesis. *Angew. Chem., Int. Ed.* **2004**, *43*, 6250−6284.

(27) Carnero-Ruiz, C.; Díaz-López, L.; Aguiar, J. Self-assembly of tetradecyltrimethylamonium bromide in glycerol aqueous mixtures: a thermodynamic and structural study. *J. Colloid Interface Sci.* **2007**, *305*, 293−300.

(28) D'Errico, G.; Ciccarelli, D.; Ortona, O. Effect of glycerol on micelle formation by ionic and nonionic surfactants at 25 °C. *J. Colloid Interface Sci.* **2005**, *286*, 747−754.

(29) Rodríguez, A.; Graziani Mdel, M.; Angulo, M.; Moyá, M. L. Effects of organic solvent addition on the aggregation and micellar growth of cationic dimeric surfactant [12-3-12],2Br-. *Langmuir* **2007**, *23*, 11496−11505.

(30) Kolay, S.; Ghosh, K. K.; Quagliotto, P. Micellization behavior of [C_{16}-12-C_{16}], 2Br- Gemini surfactant in binary aqueous-solvent mixtures. *Colloids Surf., A* **2009**, *348*, 234−239.

(31) Fletcher, P. D. I.; Gilbert, P. J. Structure and dynamic properties of decylamonium chloride micelles in water and in glycerol. *J. Chem. Soc., Faraday Trans 1* **1989**, *85*, 147−156.

(32) Auvray, X.; Petipas, C.; Anthore, R.; Rico, I.; Lattes, A. X-ray diffraction study of mesophases of cetyltrimethylammonium bromide in water, formamide, and glycerol. *J. Phys. Chem.* **1989**, *93*, 7458−7464.
(33) Lin, Z.; Davis, H. T.; Scriven, L. E. Cryogenic electron microscopy of micelles and lyotropic liquid crystals in some polar solvents. *Langmuir* **1996**, *12*, 5489−5493.
(34) Zana, R. Dimeric (Gemini) surfactants: Effect of the spacer group on the association behavior in aqueous solution. *J. Colloid Interface Sci.* **2002**, *248*, 203−220.
(35) Kalyanasundaram, K.; Thomas, J. K. Environmental effects on vibronic band intensities in pyrene monomer fluorescence and their application in studies of micellar systems. *J. Am. Chem. Soc.* **1977**, *99*, 2039−2044.
(36) Aguiar, J.; Carpena, P.; Molina-Bolívar, J. A.; Ruiz, C. C. On the determination of the critical micelle concentration by the pyrene 1:3 ratio method. *J. Colloid Interface Sci.* **2003**, *258*, 116−122.
(37) Teiborlang, M.; Kochi, I. Aggregation, counter ion binding and adsorption behaviors of cetylpyridinium chloride in water/glycerol media at 25 °C. *J. Surfact. Detergents* **2012**, *15*, 47−51.
(38) Sarkar, B.; Lam, S.; Alexandridis, P. Surfactants in water−polar organic solvent mixtures. *Langmuir* **2010**, *26*, 10532−10540.
(39) Ionescu, L. G.; Fung, D. S. Formation of micelles of acylcarnitines in glycerol. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2503−2506.
(40) Akhter, M. S. Studies on solvophobic interactions and micelle formation in non aqueous solvents. *Colloids Surf., A* **1999**, *150*, 25−30.
(41) Beesley, A. H.; Evans, D. F.; Laughlin, R. G. Evidence for the essential role of hydrogen bonding in promoting amphiphilic self-assembly: measurements in 3-methylsydnone. *J. Phys. Chem.* **1988**, *92*, 791−793.
(42) Seguin, C.; Eastoe, J.; Clapperton, R.; Heenan, R. K.; Grillo, I. Alternative non-aqueous water-miscible solvents for surfactants. *Colloids Surf., A* **2006**, *282−283*, 134−142.
(43) Carpena, P.; Aguiar, J.; Bernaola-Galvan, P.; Carnero Ruiz, C. Problems associated with the treatment of conductivity-concentration data in surfactant solutions: Simulations and experiments. *Langmuir* **2002**, *18*, 6054−6058.
(44) Chaghi, R.; de Ménorval, L.-C.; Charnay, C.; Derrien, G.; Zajac, J. Competitive solubilization of phenol by cationic surfactant micelles in the range of low addtive and surfactant concentrations. *Langmuir* **2009**, *25*, 4868−4874.
(45) Bendjeriou, A.; Derrien, G.; Hartmann, P.; Charnay, C.; Partyka, S. Microcalorimetric studies of cationic gemini surfactant with a hydrophilic spacer group. *Thermochim. Acta* **2005**, *434*, 165−170.
(46) Laville, L.; Charnay, C.; Lamaty, F.; Martinez, J.; Colacino, E. Ring-closing metathesis in aqueous micellar medium. *Chem.—Eur. J.* **2012**, *18*, 760−764.
(47) Bantreil, X.; Sidi-Ykhlef, M.; Aringhieri, L.; Colacino, E.; Martinez, J.; Lamaty, F. Comprehensive study on olefin metathesis in PEG as an alternative solvent under microwave irradiation. *J. Catal.* **2012**, *294*, 113−118.
(48) Jordan, J. P.; Grubbs, R. H. Small-molecule N-heterocyclic carbene-containing olefin-metathesis catalysts for use in water. *Angew. Chem., Int. Ed.* **2007**, *46*, 5152−5155.
(49) Gawin, R.; Czarnecka, P.; Grela, K. Ruthenium catalysts bearing chelating carboxylate ligands: application to metathesis reactions in water. *Tetrahedron.* **2010**, *66*, 1051−1056.
(50) Lipshutz, B. H.; Ghorai, S. PQS: A new platform for micellar catalysis. RCM reactions in water with catalyst recycling. *Org. Lett.* **2009**, *11*, 705−709.
(51) Mwangi, M. T.; Runge, M. B.; Bowden, N. B. Occlusion of Grubbs' catalysts in active membranes of polydimethylsiloxane: Catalysis in water and new functional group selectivities. *J. Am. Chem. Soc.* **2006**, *128*, 14434−14435.