ACS Sustainable Chemistry & Engineering
Research Article
pubs.acs.org/journal/ascecg

Vegetable-Derived Long-Chain Surfactants Synthesized via a “Green” Route

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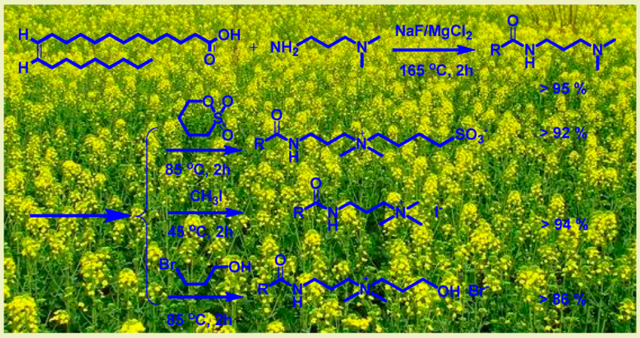
Supporting Information

ABSTRACT: There is no doubt that the surfactant and detergent industry is facing increasing severe environmental impact, and environmentally benign pathways are preferred to prepare these materials. We report herein a green route toward the preparation of vegetable-derived long-chain surfactants. The synthesis process possesses the following characteristics: bioresource-derived erucic acid (leftovers of rapeseed oil) was used as a starting material; no solvent was used and no chemical waste was produced; and high-yield products could be obtained in short reaction time. Compared with traditional surfactants bearing a saturated hydrophobic tail shorter than C18, the erucic acid-derived surfactants are more environmentally friendly because of their lower dosages in practical applications and the presence of the chemical degradable unsaturated bond and amido group in their molecular architecture.



KEYWORDS: *Biomass, Green chemistry, Vegetable-derived surfactants, No-solvent synthesis, Modified amidation reaction*

INTRODUCTION

Surfactants are amphiphilic compounds bearing both hydrophobic tail and hydrophilic head in the same molecule. They are widely used as not only detergents in daily applications but also templates for constructing nanoparticles,[1] carrier vehicles for drug delivery,[2] catalysts in organic synthesis,[3] and even the models for fundamental understanding of self-assembly mechanism due to their polymorphism ordered topologies in aqueous solution.[4] To date, most of the surfactants available in the market are derived from the crude oil-based products,[5] and a huge volume of these petrochemical-based surfactants are discharged into the environment from instant to instant, the majority of which are not readily degradable, bringing potential influence to microbial, plant, and animal life.[6]

As sustainability is mandated for the chemical industry,[7] the detergent industry has turned its attention to greener routes to create environmentally benign surfactants over the past decade.[8] Accordingly, three directions may be the possible ways to address the current challenges: (i) the utility of degradable or renewable raw materials, such as vegetable oil that is universal in the seeds, nuts, and fruits of the plants, for the synthesis;[8−10] (ii) the introduction of degradable functionality, for instance, amido or ester group, to the products;[10,11] (iii) and the decrease of the dosage by using long-chain surfactants with high surface activity[12] and low critical micelle concentration (cmc).

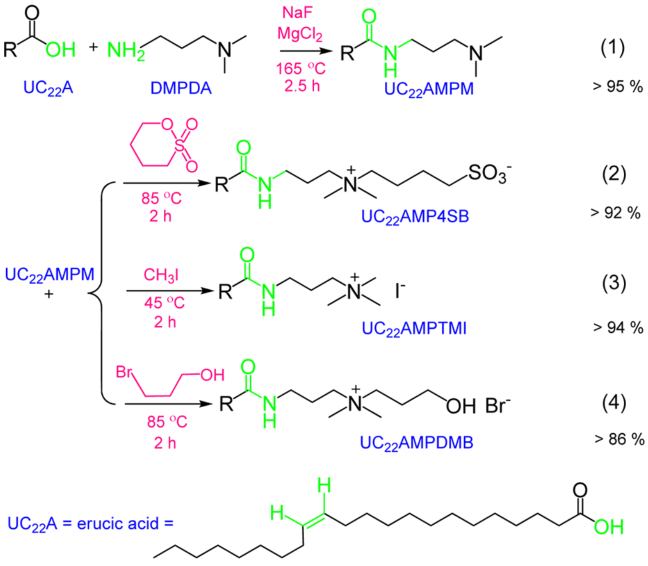
Although the surfactant industry has looked to the oleochemical value chain as the counterbalance to a crude oil-based system since the oil embargoes of the early 1970s and the accelerated adoption of palm- and coconut-derived oleochemicals as “the answer” to a depleting and nonrenewable resource since the early 1990s,[13] the use of palm and soybean is still debated as they can be used as both food and biodiesel. In recent years, the vegetable oil market has started to behave increasingly like the crude market, which leaves surfactant producers looking for a viable alternative feedstock source that is renewable and less tightly correlated with the petrol and oleo oils now supporting the industry. China has a long history of planting rapeseed, and rapeseed oil is one of the most popular edible oils in China. It is estimated that more than 4 000 000 tons of rapeseed oil are consumed every year in China,[14] and there are also a large number of rapeseed oil consumers in India, Canada, and other countries. However, rapeseed oil has certain negative characteristics because an unneglectable amount of erucic acid is accompanied. The content of the erucic acid in rapeseed oil depends highly on the origin of the plants and sometimes exceeds 50%. An erucic acid level of below 5% was considered to be less harmful to human health, and the standard level in edible oil should be less than 2%.[15] Health problems could arise from rapeseed oil consumption because erucic acid was proved to cause heart lesions in rats fed on a rapeseed diet.[15] Thus, excessive erucic acid was separated from higher-erucic-acid rapeseed oil to meet the safety level of edible oil and became leftovers. Therefore, a heavy volume of

Received: July 8, 2012
Revised: October 5, 2012
Published: October 8, 2012

erucic acid is produced every year worldwide, and it can be a great potential replacement of petro-based chemicals for surfactant feedstocks.

On the basis of the above facts, three high-performance, environmentally benign amido-surfactants (Scheme 1) bearing an unsaturated C22 hydrophobic chain were prepared via no-solvent reactions, ultlizing erucic acid as the starting material. Surface activity of their dilute aqueous solutions and rheological properties of their semidilute solutions were also examined.

Scheme 1. Green Route Toward the Preparation of Environmentally Friendly Surfactants



METHODS

Materials. Erucic acid (>99%, GC, Fluka), *N,N*-dimethyl-1,3-propanediamine (99%, GC, Alfa Aesar), 1,4-butanesultone (99%, GC, Sinopharm Chemical Reagent Co. Ltd.), iodomethane (98%, GC, Sinopharm Chemical Reagent Co. Ltd.), and 3-bromopropanol (97%, GC, Sinopharm Chemical Reagent Co. Ltd.) were used without further purification. All other chemicals were of analytical grade.

Characterizations. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker Avance 300 spectrometer (300 MHz) in CD_3OD at room temperature. Electrospray ionization high-resolution mass spectrometry (ESI HRMS) spectra were taken on a Bruker Daltonics Data Analysis 3.2 system. High-performance liquid chromatography (HPLC) analysis was performed on a Waters HPLC system equipped with Alltech 2000 ELSD detector with a reverse phase (C18) column.

Surface Tension. Surface tension measurements were done on a Krüss K100 tensiometer by the automatic model of the du Nöuy Ring technique at 30 ± 0.01 °C.

Rheology. Long-chain surfactants have been proven to show better thickening ability since the formation of entangled wormlike micelles in aqueous solution.[16] Therefore, rheological properties of semidilute solutions of the synthesized surfactants were also investigated. Rheological measurements were made on a Physica MCR 301 (Anton Paar, Austria) rotational rheometer equipped with concentric cylinder geometry CC27 (ISO3219) at 30 ± 0.1 °C, which was set by a Peltier temperature-control device.

Synthesis. *Synthesis of N-Erucamidopropyl-N,N-dimethylamine.* As exhibited in Scheme 1, the first step for the preparation of the surfactants is synthesis of the intermediate, *N*-erucamidopropyl-*N,N*-dimethylamine ($UC_{22}AMPM$). A typical procedure is listed as follows: 33.86 g (100 mmol) of erucic acid, 12.26 g (120 mmol) of *N,N*-dimethyl-1,3-propanediamine (DMPDA), and 0.14 g of NaF were added to a three-necked flask. The reaction mixture was refluxed at ~165 °C under N_2 atmosphere, during which the byproduct H_2O was absorbed continuously by anhydrous $MgCl_2$ (3.22 g) placed in a solvent head above the reactor. The excess of DMPDA was recycled by distillation. The mixture during the reaction was monitored by HPLC at a certain interval (HPLC, Figure S2, Supporting Information). After 12 h of reaction, the purity of the resulting compound $UC_{22}AMPM$ without any further purification reached 99.19% (HPLC, Figure S2–12, Supporting Information). ^{1}H NMR (300 MHz, CD_3OD), δ/ppm: 0.87 (t, J = 6.73 Hz, 3H), 1.26 (m, 28H), 1.59 (m, 2H), 1.72 (m, 2H), 2.00 (m, 4H), 2.15 (t, J = 7.48 Hz, 2H), 2.33 (s, 6H), 2.49 (t, J = 6.49 Hz, 2H), 3.33 (m, 2H), 5.34 (m, 2H).

Synthesis of 3-(N-Erucamidopropyl-N,N-dimethyl Ammonium) Butane Sulfonate ($UC_{22}AMP4SB$). Untreated $UC_{22}AMPM$ (42.30 g (100 mmol)) was directly added to a flask and heated to 85 °C; then 13.62 g (100 mmol) of 1,4-butanesultone was dropped into the reactor in no more than 0.5 h accompanied with vigorous mechanical stirring. The final product $UC_{22}AMP4SB$ was obtained after another 2 h of reaction at 85 °C. The purity was analyzed without any further purification, given 92.01% $UC_{22}AMP4SB$ and 6.17% $UC_{22}AMPM$ (Figure S6, Supporting Information). The minor part of the product was purified by repeated washing with acetone to further characterize the chemical structure of the product via ^{1}H NMR, ^{13}C NMR, and ESI HRMS. ^{1}H NMR (300 MHz, CD_3OD), δ/ppm: 0.90 (t, J = 6.59 Hz, 3H), 1.30 (m, 28H), 1.59 (m, 2H), 1.75–2.04 (m, 10H), 2.20 (t, J = 7.82 Hz, 2H), 2.89 (t, J = 6.65 Hz, 2H), 3.08 (s, 6H), 3.30–3.35 (m, 6H), 5.34 (m, 2H). ^{13}C NMR (75 MHz, CD_3OD), δ/ppm: 14.43, 22.02, 23.94, 26.93, 28.13, 30.33–30.85, 33.05, 37.11, 51.23, 63.24, 64.91, 75.62, 130.83, 131.49, 176.57. ESI HRMS: Calcd: 581.4323 ($C_{31}H_{62}N_2N_aO_4S$, $UC_{22}AMP4SB + Na^+$); Found: m/z = 581.4309.

Synthesis of N-Erucamidopropyl-N,N,N-trimethylammonium Idiom ($UC_{22}AMPTMI$). Untreated UC_{22}-AMPM (42.30 g (100 mmol)) was added to a flask and heated to 45 °C, and 14.19 g (100 mmol) of iodomethane was dropped into the reactor in no more than 0.5 h accompanied with vigorous mechanical stirring. The final product $UC_{22}AMPTMI$ was obtained after another 2 h of reaction at 45 °C. The purity was analyzed without any further purification, given 94.80% $UC_{22}AMPTMI$ and 0.50% $UC_{22}AMPM$ (Figure S10, Supporting Information). The minor part of the product was purified by repeated washing with acetone so as to run the ^{1}H NMR, ^{13}C NMR, and ESI HRMS. ^{1}H NMR (300 MHz, CD_3OD), δ/ppm: 0.91 (t, J = 6.49 Hz, 3H), 1.31 (m, 28H), 1.62 (m, 2H), 1.98–2.05 (m, 6H), 2.24 (t, J = 7.59 Hz, 2H), 3.19 (s, 9H), 3.30 (m, 2H), 3.44 (m, 2H), 5.35 (m, 2H). ^{13}C NMR (75 MHz, CD_3OD), δ/ppm: 14.43, 23.88, 24.44, 26.91, 28.12, 30.33–30.82, 33.04, 37.19, 53.80, 53.85, 53.90, 65.79, 130.82, 130.48, 176.62. ESI HRMS: Calcd: 437.4465 ($C_{28}H_{57}N_2O$, $UC_{22}AMPTMI - I^-$); Found: m/z = 437.4454.

Synthesis of N-Erucamidopropyl-N,N-dimethyl-N-(3-hydroxypropyl)ammonium Bromide ($U_{22}AMPDMB$). Untreated UC_{22}-AMPM (42.30 g (100 mmol)) was added directly to a flask and heated to 85 °C, and 13.90 g (100 mmol) of 3-bromopropanol was dropped into the reactor in no more than 0.5 h accompanied with vigorous mechanical stirring. The final product was obtained after another 2 h of reaction at 45 °C. The purity was analyzed without any further purification, given 86.91% $UC_{22}AMPDMB$ and 11.62% $UC_{22}AMPM$ (Figure S14, Supporting Information). The minor part of the product was purified by repeated washing with acetone so as to perform the ^{1}H NMR, ^{13}C NMR, and ESI HRMS. ^{1}H NMR (300 MHz, CD_3OD), δ/ppm: 0.91 (t, J = 6.66 Hz, 3H), 1.31 (m, 28H), 1.59 (m, 2H), 1.98–2.06 (m, 8H), 2.24 (t, J = 7.59 Hz, 2H), 3.14 (s, 6H), 3.31 (m, 2H), 3.44 (m, 4H), 3.67 (m, 2H), 5.36 (m, 2H). ^{13}C NMR (75 MHz, CD_3OD), δ/ppm: 14.43, 18.85, 23.98, 26.93, 28.13, 30.33–30.84, 33.05, 37.14, 51.60, 59.68, 63.35, 75.62, 130.81, 131.47, 176.57. ESI HRMS: Calcd: 481.4728 ($C_{30}H_{61}N_2O_2$, $UC_{22}AMPDMB - Br^-$); Found: m/z = 481.4717.

RESULTS AND DISCUSSION

Since the development of chemical products without or with a reduced amount of solvents is a great challenge,[7] green routes with no solvent and no chemical waste produced using renewable natural erucic acid as the starting material are preferred for the synthesis of the long-chain amido-based surfactants (Scheme 1). The preparation of the tertiary amine intermediate is a key step for such amphiphilies; however, the synthesis of amides under neutral conditions without the generation of waste is a challenging goal.[17] Nevertheless, we previously[18] succeeded in shortening the amidation reaction from around 65 h to about 12 h by replacing the traditional inefficient catalysts such as bleaching earth, silica gel, zeolite, sulfuric acid, etc.[19] with a NaF/Al_2O_3 (or NaF/4 Å molecular sieves) system. In that report,[18] a high-yield and high-purity amido intermediate was obtained after washing with a large amount of organic solvents. The intermediate was then quaternized by 1,3-propanesultone to obtain crude product. To get the final high-purity surfactants, the purification process again with a large volume of solvents is inevitable. Such a two-step process could not be easily accomplished in scale-up manufacturing the surfactants in the detergent industry because of the following reasons: both Al_2O_3 and 4 Å molecular sieves were of poor efficiency, and they just fit to the removal of small amount of water; the overuse of organic solvents is harmful to the environment; and the quaternization agent 1,3-propanesultone is a highly hazardous chemical agent that has been proven to be carcinogenic to mammals, and industrial use of such a compound was abandoned.[11] Thus, the synthesis procedure was further modified here to meet the demand of sustainable chemistry and industrial applications. The weak water capture, Al_2O_3 or 4 Å molecular sieves, was replaced by a more powerful alternative desiccant, $MgCl_2$, instead, and the industrially abandoned 1,3-propanesultone was also replaced by other mild quaternization agents such as 1,4-butanesultone, iodomethane, and 3-bromopropanol. Most importantly, high-purity target compounds could be readily obtained in just several hours of reaction without producing any side-products and solvent waste.

The amidation reaction was monitored by HPLC, and the experimental results surprised us due to the fact that the reaction efficiency is beyond our expectations. If the conversion P is defined as $P = A_S/(A_S + A_P)$, where A_S and A_P stand for the peak area of starting erucic acid and $UC_{22}AMPM$ in HPLC spectrum, respectively, one will find that P can reach to more than 95% in just 2.5 h of reaction, and is more than 98% if extending the reaction time to 6 h (Figure 1, and see Figure S2−9 in the Supporting Information for original HPLC spectra), implying almost pure intermediate could be obtained without any further purification. This result was far superior to that prepared using the previously mentioned inefficient catalysts.[19] The minor residue DMPDA and the $MgCl_2 \cdot xH_2O$ of the reaction could be recycled by distillation and torrefaction, respectively, which again meet one of important criteria of green chemistry. If one does not like to recycle the residue $MgCl_2 \cdot xH_2O$ from the amidation reaction, it can serve as an additive to improve the solubility of the long-chain surfactants.[20] In a word, the amidation reaction that produces no chemical waste was totally an environmentally benign process.

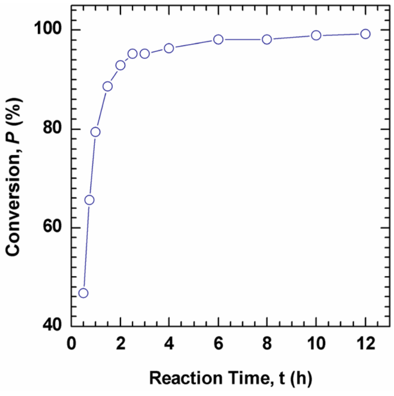


Figure 1. Conversion plotted as a function of reaction time for the amidation reaction.

It is worth noting that $CaCl_2$ was also a good water capture for this reaction, and the conversion could reach 98.5% after 12 h of reaction (Figure S4, Supporting Information). Nevertheless, the water capture $MgCl_2$ or $CaCl_2$ must be placed in the solvent head rather than directly added to the reactor. For instance, when $MgCl_2$ was directly added to the reactor, only 71.4% conversion was obtained after the same time of reaction (Figure S3, Supporting Information).

The intermediate, $UC_{22}AMPM$, is an organic compound with low melting point (mp ≈ 35−40 °C) and can act as a reaction solvent above 40 °C. When equivalent molar liquid quaternization reagents, for example, 1,4-butanesultone or iodomethane or 3-bromopropanol, were dropped into the reactor in no more than 0.5 h accompanied with strongly mechanical stirring, the liquid reaction mixture became solid-like after another 2 h of reaction, and then the reaction was stopped. The conversions, calculated from HPLC, for the reaction **2**, **3**, and **4**, are 92.01% (Figure S6), 94.80% (Figure S10), and 86.91% (Figure S14, Supporting Information), respectively. Such high conversions not only mean high purity of the products but also suggest high yield of the reactions. As there was no side-products produced from these three reactions, the atom economy of such reactions was 100%.

In short, the synthesis procedure described above is environmentally friendly in the following aspects: (i) Compared with long alkyl halides and long acyl halides, bioresource-derived erucic acid is much safer and cheaper and will become a promising renewable resource for the synthesis of surfactant.[8−10] (ii) Compared with 1,3-propanesultone, of which the industrial use was abandoned because of its high carcinogenicity,[11] the quaternization agents 1,4-butanesultone, iodomethane, and 3-bromopropanol were less toxic and frequently used in organic synthesis. (iii) The tertiary amine intermediate could be directly used without any further purification for the next step quaternization. (iv) High conversion could be achieved in a short reaction time for all four reactions. (v) No solvent was used, and no chemical waste was produced in the whole synthesis process.

It is worth noting that the green synthesis route reported here can also be applied to other plant substrates such as caprylic acid, myristic acid, oleic acid, nervonic acid, and any other acid as long as the corresponding tertiary amine intermediate has a low melting point and can serve as a solvent for the quaternization reaction.

The cost for the large-scale production of the long-chain surfactants following the above procedure was a little bit more expensive than the traditional shorter-chain counterparts available in the market; however, the dosage amount of the long-chain surfactants in industrial applications can be much lower, which will be discussed later.

The introduction of unsaturated bond in the hydrophobic tail and amido group in the head part is crucial to the long-chain surfactants because it improves both the water solubility[16] and degradability.[11] Normally, long-chain surfactants have high Krafft temperature (T_K), which restricts their applications due to the limited hydrosolubility. However, the incorporation of an unsaturated bond to the hydrophobic tail depresses T_K drastically and improves the water solubility significantly, owing to the kink in the erucyl tail.[16] The other advantage of the introduction of unsaturated bond and amido group is that they can obviously improve the degradability of the surfactants.[8−10] The unsaturated "C═C" double-bond is a chemical active bond and easier to be decomposed when comparing with its "C−C" single-bond associate.[8,9] Because it tends to be more easily hydrolyzed,[8−10] the amido group also makes the surfactants $UC_{22}AMP4SB$, $UC_{22}AMPTMI$, and $UC_{22}AMPDMB$ prepared in this work readily decomposed when compared with nonamido surfactants. For instance, succinamidosulfobetaines hydrolyze to the extent of 10% in just 1 h when 0.5 M of such betaine solution in the presence 0.05 M NaOH is heated to 85 °C.[21] Therefore, $UC_{22}AMP4SB$, $UC_{22}AMPTMI$, and $UC_{22}AMPDMB$ are friendly to the environment, and in particular the sulfobetaine inner salt $UC_{22}AMP4SB$ may be the most attractive among them because betaine is very gentle to human skin and the environment.[11]

The improvement of the efficiency and effectiveness of surfactants lowers the dosage and thus favors the protection of the environment.[12] Most surfactants available in the market bear a hydrophobic tail no longer than C_{16},[11] show a large dosage in practical applications, and thereby deteriorate the environment because of their release. However, long-chain surfactants are supposed to be more versatile, showing fairly good surface activities and extremely low cmc.[16] Exhibited in Figure 2 is the surface tension of the ultralong C_{22}-chain surfactants plotted as a function of their concentration in 0.5 M NaCl at 30 °C. One of the most important surface-active parameters, cmc, which is obtained by extrapolation of the two linear parts in the curve, is as low as 2, 4, and 6 mg/L for $UC_{22}AMP4SB$, $UC_{22}AMPTMI$, and $UC_{22}AMPDMB$, respectively, and these values are much lower than those of their shorter-chain counterparts.[11] This implies that the surfactants are high-performance—they are still effective even at extremely low dosage, say, less than 10 ppm. In other words, the use of these high-performance surfactants has the potentiality to reduce the total amount of surfactants in daily applications.

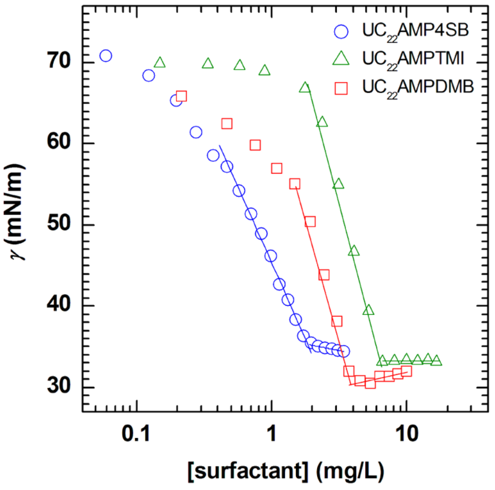


Figure 2. Surface tension plotted as a function of surfactant concentration in 0.5 M NaCl at 30 °C.

Besides the environmental concern, the excellent rheological response of long-chain surfactants due to the formation of wormlike micellar aggregates[16,22] represents the other motivation of this work. Unlike traditional shorter-chain surfactants that mainly form simple spheric micelles, the C_{22}-tailed surfactants can self-assemble into entangled wormlike micelles at low surfactant concentration, imparting unique viscoelastic properties to the solution.[16,22] Thus, the thickening ability of the three synthesized surfactants was also studied preliminarily. As shown in Figure 3, 10 g/L $UC_{22}AMP4SB$ in 0.5 M NaCl solution at 30 °C shows slightly shear-thinning behavior with plateau viscosity (zero-shear viscosity, η_0) 15 mPa·s, and $UC_{22}AMPTMI$ and $UC_{22}AMPDMB$ solutions with the same concentration are typical pseudoplastic fluids with shear-thinning response occurring at a shear rate of ∼0.02 s^{-1}. Such a shear-thinning behavior can be taken as evidence of the presence of wormlike micelles that undergo structural changes.[23] η_0 of both solutions are 4 orders of magnitude higher than that of water (∼1 mPa·s). The high viscosity of the solution could be attributed to the entanglement of long worms to form transient networks.[16,22,23]

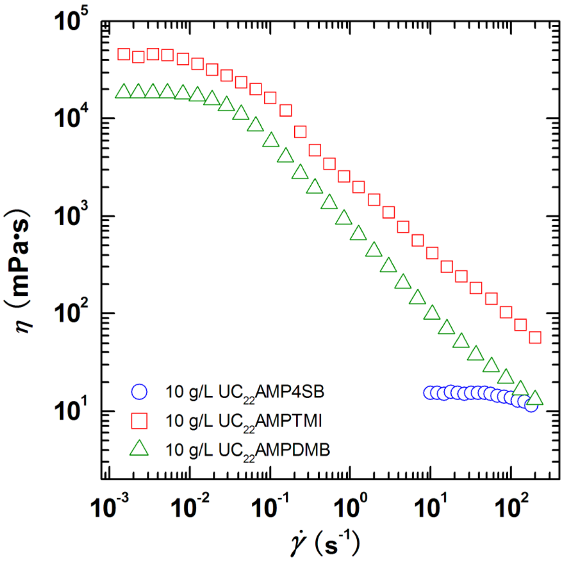


Figure 3. Shear viscosity plotted as a function of shear rate for the 10 g/L long-chain surfactant in 0.5 M NaCl at 30 °C.

■ CONCLUSIONS

In summary, a green route was successfully employed to prepare three degradable long-chain surfactants, utilizing bioresource-derived erucic acid (leftovers of rapeseed oil) as the main starting material. The synthesis procedures possess characteristics of no solvent and no waste, short reaction time, high purity, and high yield. Extremely low cmc imparts these amphiphilies high-performance, favoring a lower the dosage in practical applications. In particular, the sulfobetaine inner salt $UC_{22}AMP4SB$ is the most promising among the three surfactants obtained in this work because betaine is very gentle to human skin and the environment. The long C_{22}-chain further furnishes their solutions with interesting rheological responses. We take the view that the modified green synthesis procedure has great potential to be carried out in scaled-up industrial surfactant manufacturing and will gain increasing interest from environmental protection, green chemistry, and detergent industry.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The characterization of the compounds. 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.

■ ACKNOWLEDGMENTS

This work was financially supported by the National Nature Science Foundation of China (21173207, 21273223) and Science and Technology Department of Sichuan Province (2012NZ0006, 2010JQ0029).

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