

# Synthesis of Sodium (+)-(12*S*,13*R*)-Epoxy-*cis*-9-octadecenyl Sulfonate from Vernonia Oil

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**Abstract** A water-soluble, foaming epoxyalkene sulfonate, sodium (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenyl sulfonate, was synthesized from vernonia oil (VO) by a series of simple reactions that include transesterification, metal hydride reduction, tosylation, and S<sub>N</sub>2 reactions. Conversion of VO into vernonia oil methyl esters (VOME) using sodium methoxide was quantitative. Subsequent reduction of VOME with lithium aluminum hydride yielded (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenol (94%), along with minor amounts of hexadecenol, octadecenol, *cis*-9-octadecenol, and *cis*-9,12-octadecandienol. The (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenol, was tosylated with *p*-toluenesulfonyl chloride to give (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenyl tosylate at 96% yield. Iodination of the tosylate with sodium iodide and subsequent S<sub>N</sub>2 reaction with sodium sulfite afforded (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenyl sulfonate (63% yield). This study demonstrates the ability to produce an epoxyalkenyl sulfonate, belonging to a class of anionic surfactants, from VO without destroying the epoxy functionality in the (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenyl moiety of VO. The critical micelle concentration of the synthesized sulfonate was also determined.

**Keywords** Fatty acids · MALDI-TOF MS · Seed oil · Sulfonate · Surfactant · Triacylglycerol · Vernonia oil

## Introduction

Vernonia oil (VO) is extracted from the seed of the *Vernonia galamensis* plant [1]. This plant has been cultivated on a semi-commercial scale in Kenya, Zimbabwe, and parts of Central and South America [1, 2]. The fatty acid composition of vernonia oil triacylglycerols include palmitic, stearic, oleic, linoleic, and (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenoic acids [2]. The naturally epoxidized VO contains about 80% of (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenoic acid [2] upon hydrolysis, thus potentially providing unique oleochemicals that could find applications in the production of new surfactants.

In previous work in our laboratory, we demonstrated the ability to control the lithium aluminum hydride (LAH) reduction of the epoxy functionality in VO or vernonia oil methyl esters (VOME) with the choice of polar or nonpolar solvents [3]. The use of polar solvents resulted in the formation of 12(13)-hydroxy-*cis*-9-octadecenol, while nonpolar solvent afforded (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenol.

Fatty alcohols have been studied extensively for their use as raw materials for the production of surfactants [4, 5]. Ricinoleic acid (12-hydroxy-9-octadecanoic acid), is the only naturally occurring functionalized, hydroxylated fatty acid presently used in the oleochemistry industry [6, 7], and it is the major component of castor bean oil, comprising approximately 85–90% of the fatty acids present [6, 8]. Ricinoleyl alcohol is a precursor of anionic surfactants, [5, 9–12] used in commercial formulations such as cosmetics, lubricants, de-icers, and in the industrial processing for paper, plastics and biopolymers [13–15]. Both ricinoleic acid and vernolic acid are C-18 molecules with unsaturation at the 9, 10, and oxygen at the 12 positions of their aliphatic chain. Studies of a ricinoleic acid-based

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anionic surfactants show good wetting ability, detergent power, emulsifying power, and surface tension lowering ability, but poor to average foaming characteristics and detergent efficiency [9, 12]. The uniqueness of vernolic acid is derived from the presence of the epoxy functionality at the 12, 13, positions, and thus vernolic acid-based surfactants would be expected to display some unique surfactancy characteristics similar to those from castor-based surfactants.

As part of an ongoing research effort aimed at demonstrating the potentials of using VO to generate industrial chemicals [3], this paper reports on the laboratory conversion of VO to (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenyl sulfonate and the measurement of its critical micelle concentration.

## Experimental Procedures

### Reagents

Crude VO was obtained from IXTT Corporation (Culver, IN). Sodium methoxide, methanol, lithium aluminum hydride, *p*-toluenesulfonyl chloride, chloroform, acetone, isopropyl alcohol, sodium sulfite, sodium sulfate, pyridine, diethyl ether, hydrochloric acid, sodium iodide, sodium bicarbonate, sodium chloride, and sodium hydroxide were purchased from Aldrich Chemicals Co. (Milwaukee, WI).

### Instrumentation

Reactions and products were monitored with an Agilent 6890 N gas chromatograph interfaced with an Agilent 5973 inert mass spectrometer. The interface oven was maintained at 250 °C, the ionizer temperature setting was at 230 °C, using electron ionization (EI) with electron energy at 70 eV. High resolution capillary gas chromatography was conducted with a Supelco fused-silica SPB-1 (30 m, 0.32 mm ID, 0.25 μm film) column (Bellefonte, PA), oven temperature was programmed from 50 to 300 °C (20 °C/min), and helium was used as the carrier gas with head pressure 9.8 psi. The <sup>13</sup>C nuclear magnetic resonance (<sup>13</sup>C NMR) and proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were recorded on a Bruker Avance 400 MHz spectrometer with chloroform-*d* (CDCl<sub>3</sub>) as solvent and source of internal standard. The molecular mass of the sulfonate was determined by matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) using an Applied Biosystems Voyager-DE STR BioSpectrometry Workstation equipped with a two-stage acceleration ion source. Positive ion MALDI spectra (200 summed acquisitions) were acquired in delayed-extraction (150 ns) and reflector modes. The

acceleration voltage was 20 kV, the grid voltage at 75%, nitrogen laser (337 nm, 3 ns pulse width), and low mass gate at *m/z* 50. The matrix, *meso*-tetrakis (pentafluorophenyl) porphyrin (F20TPP), was purchased from Aldrich Chemical Co. (Milwaukee, WI, USA). Matrix solution (10 mg/mL CHCl<sub>3</sub>) and analyte solution [2 mg/mL methanol/H<sub>2</sub>O (4:1)] were mixed (80 μL/20 μL) in 2-mL Eppendorf microcentrifuge tubes. After vortexing for 10 s, 1 μL of the sample solution was deposited on the sample plate and then allowed to evaporate at room temperature to enable co-crystallization of matrix and analyte.

Conversions of VO to VOME (1) and (+)-(12*S*,13*R*)-Epoxy-*cis*-9-octadecenol (2)

Previously reported procedures were used without modification [3].

Tosylation of (+)-(12*S*,13*R*)-Epoxy-*cis*-9-octadecenol (2)

In a 100-mL round-bottom flask equipped with a stirring bar, was transferred (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenol (2) (2.4 g, 8.5 mmol), followed by 10 mL of chloroform and dried pyridine (1.3 g, 17 mmol). The solution was cooled in an ice bath (5 °C) for 15 min. To this solution *p*-TsCl was added (2.4 g, 13 mmol) at a rate of approximately 0.2 g every 10 min while stirring. After 3 h of stirring at 5 °C, 10 mL of water was added, followed by 40 mL of diethyl ether. The ethereal solution was washed with HCl (10 wt.%, 3 × 40 mL, 5 °C) followed by sodium bicarbonate, and brine. The resulting solution was stripped with a rotary evaporator to yield, 3.6 g of a colorless liquid (96%), consisting of (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenyl tosylate (3) and trace amount of starting alcohol. MS (EI) analysis showed the molecular ion for (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenyl tosylate (3) was at *m/z* 436, and diagnostic ion at *m/z* 281 (M-SO<sub>2</sub>C<sub>7</sub>H<sub>7</sub>). A small amount of the crude 3 was purified for characterization purposes. About 0.5 g of 3 was column chromatographed on silica gel column (5% ethyl acetate/*n*-hexane, 45 g silica gel, 70–230 mesh, 60 Å pore size) to yield pure 3 (0.4 g, 80% based on amount chromatographed). <sup>1</sup>H NMR (CDCl<sub>3</sub>) δ 0.95 (t, 3H, CH<sub>3</sub>), 1.05–2.00 (m, 22H, 11CH<sub>2</sub>), 2.10 (q, 2H, CH<sub>2</sub>CH=CH), 2.50 (s, 3H, Ar CH<sub>3</sub>), 2.95 (broad, 2H, epoxide CHCH), 4.05 (t, 2H, CH<sub>2</sub>O), 5.40–5.70 (m, 2H, CH=CH), 7.35–7.80 (AA'BB', 4H, Ar H); <sup>13</sup>C NMR (CDCl<sub>3</sub>) δ 14.2 (1C, CH<sub>3</sub>), 21.1 (1C, Ar CH<sub>3</sub>), 22.2 (1C, CH<sub>3</sub>CH<sub>2</sub>), 26.0–33.0 (11C, CH<sub>2</sub>), 57.5 and 58.0 (2C, epoxy CHCH), 71.0 (1C, CH<sub>2</sub>O), 123.0 and 132.0 (2C, CH=CH), 128.0, 130.0, 133.0 and 145.0 (5C, Ar carbons); MALDI-TOF MS, showed molecular ion *m/z* 459.9 ([ROTs + Na]<sup>+</sup>).

### Iodination of Epoxy Tosylate

In a 100-mL round-bottom flask equipped with a stirring bar, was added crude (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenyl tosylate (**3**) (1.0 g, 2.3 mmol), followed by 60 mL of acetone. To the resulting solution was added sodium iodide (0.72 g, 4.8 mmol) with stirring. The flask was then fitted with a condenser, and the mixture was refluxed with stirring for 4 h. The resulting brownish solution was allowed to cool to room temperature, after which 40 mL of water was added to the flask. Acetone was then evaporated on a steam bath. The aqueous solution was transferred to a 125-mL separatory funnel. The aqueous solution was extracted with diethyl ether (3 × 50 mL). The ethereal solution was washed with water and brine, dried with sodium sulfate, and stripped with a rotary evaporator to give 0.78 g of a light-yellow product (87% yield). GC-MS analysis indicated (+)-(12*S*,13*R*)-epoxy-1-iodo-*cis*-9-octadecene (**4**) with trace amount of the starting tosylate. MS (EI) data showed the molecular ion for (+)-(12*S*,13*R*)-epoxy-1-iodo-*cis*-9-octadecene (**4**) at  $m/z$  392, and a diagnostic ion at  $m/z$  265 (M-I). A small amount of the crude **4** was purified for characterization purposes. About 0.50 g of **4** was column chromatographed on silica gel column (1.0% ethyl acetate/*n*-hexane, 45.0 g silica gel, 70–230 mesh, 60-Å pore size) to give purified **4** (0.33 g, or 63% recovery).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  0.95 (t, 3H,  $\text{CH}_3$ ), 1.05–2.00 (m, 22H, 11 $\text{CH}_2$ ), 2.10 (q, 2H,  $\text{CH}_2\text{CH}=\text{CH}$ ), 2.95 (broad, 2H, epoxide  $\text{CHCH}$ ), 3.20 (t, 2H,  $\text{CH}_2\text{I}$ ), 5.40–5.70 (m, 2H,  $\text{CH}=\text{CH}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  8.0 (1C,  $\text{CH}_2\text{I}$ ), 14.2 (1C,  $\text{CH}_3$ ), 22.2 (1C,  $\text{CH}_3\text{CH}_2$ ), 26.0–33.0 (11C,  $\text{CH}_2$ ), 57.5 and 58.0 (2C, epoxy  $\text{CHCH}$ ), 123.0 and 132.0 (2C,  $\text{CH}=\text{CH}$ ).

### Sulfonation of Epoxy Iodide

To a 100-mL round-bottom flask equipped with a stirring bar was added crude (+)-(12*S*,13*R*)-epoxy-1-iodo-*cis*-9-octadecene (1.9 g, 4.8 mmol), followed by 30 mL of isopropyl alcohol (IPA) and 30 mL of deionized water. To the resulting solution, while stirring, was added sodium sulfite (0.93 g, 7.4 mmol). The flask was fitted with a condenser and the mixture was refluxed with stirring for 12 h. The IPA was then evaporated on a steam bath, and the resulting aqueous solution was allowed to cool to room temperature. The aqueous solution was washed with diethyl ether (3 × 45 mL), followed by hexane (3 × 45 mL) and then allowed to dry overnight. To the dried product was added 3 mL water with gentle swirling and then cooled (−5 °C). The supernatant was pulled off with a pipet to remove unreacted sodium sulfite and sodium iodide by-product, and the solid was air-dried. The dried product was further washed with 25 mL of acetone and then vacuum filtered. The precipitate was then allowed to dry under the hood

overnight to yield 1.4 g of sodium (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenyl sulfonate (**5**) (63% yield).  $^1\text{H}$  NMR ( $\text{CD}_3\text{OD}$ )  $\delta$  0.95 (t, 3H,  $\text{CH}_3$ ), 1.05–2.00 (m, 22H, 11 $\text{CH}_2$ ), 2.10 (q, 2H,  $\text{CH}_2\text{CH}=\text{CH}$ ), 2.80 (t, 2H,  $\text{CH}_2\text{SO}_3\text{Na}$ ), 2.95 (broad, 2H, epoxide  $\text{CHCH}$ ), 5.40–5.70 (m, 2H,  $\text{CH}=\text{CH}$ );  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$  14.2 (1C,  $\text{CH}_3$ ), 24.2 (1C,  $\text{CH}_3\text{CH}_2$ ), 26.0–33.0 (11C,  $\text{CH}_2$ ), 57.5 and 58.0 (2C, epoxy  $\text{CHCH}$ ), 53.0 (1C,  $\text{CH}_2\text{SO}_3$ ), 123.0 and 132.0 (2C,  $\text{CH}=\text{CH}$ ); MALDI-TOF MS, showed sodiated molecular ion at  $m/z$  391.3 ( $[\text{RSO}_3\text{Na} + \text{Na}]^+$ ).

### Critical Micelle Concentration (CMC) Measurement

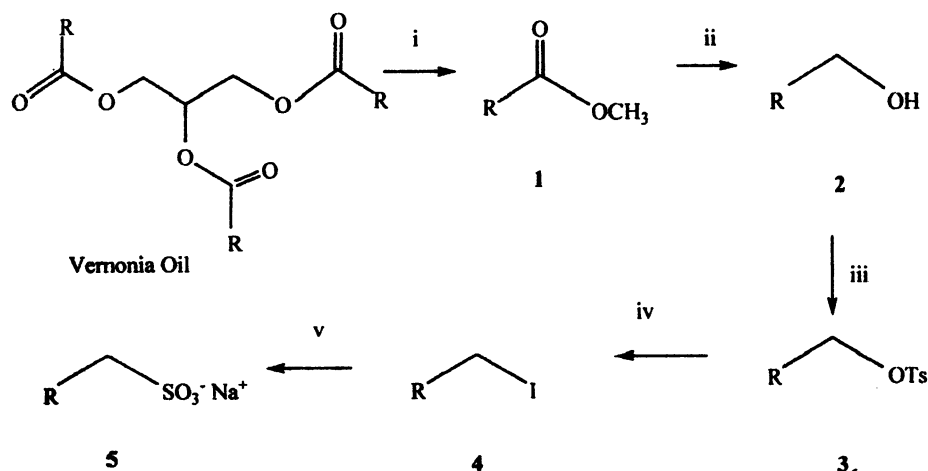
Determination of the CMC was performed using a Kruss Processor Tensiometer K12 by the Wilhelmy Plate method at room temperature. A 1% by weight solution of the epoxyalkene sulfonate was prepared and added to deionized water in a glass vessel equipped with a magnetic stirrer of which automated serial dilutions were prepared ranging from  $6.11 \times 10^{-5}$ –0.016 mol/L for run 1 and  $3.06 \times 10^{-5}$ –0.008 mol/L for run 2.

## Results and Discussion

### Synthesis of Epoxidized Linear Alkenyl Sulfonate (**5**)

The most important property of the synthetic approach was preservation of the epoxy functionality, which is expected to have a positive impact on the surfactant properties of the desired product. Synthesis of the epoxidized alkenyl sulfonate **5** from VO required five reaction steps (Scheme 1) with an overall yield of 48%. Conversion of VO to VOME (**1**) was achieved with a base-catalyzed methanolysis (transesterification) of VO, a method previously published [3]. The yield of this reaction was 98% (crude product). Similarly, reduction of VOME (**1**) to epoxy alcohol **2** was achieved with a previously published method in a 94% yield [3].

Conversion of the primary alcohol to a tosylate (**3**) was undertaken in order to create a good leaving group for the subsequent  $\text{S}_{\text{N}}2$ -type reaction. However, tosylation of the epoxy alcohol (**2**) was not as straightforward as expected owing to the presence of a reactive epoxy functional group, whose preservation was key in the synthetic strategy. A number of published synthetic methods were attempted, including reacting **2** with *p*-TsCl dissolved in dry pyridine with the mixture kept at 0 °C [16], treating **2** with sodium hydride to form an alkoxide and adding *p*-TsCl to the resulting solution; and treating **2** with sodium hydroxide and *p*-TsCl in pyridine with the mixture at 0 °C [17]. In the first case, the yield was extremely low, under 20%. Furthermore, the epoxy ring opened to give the hydroxy group.



**Scheme 1** Synthetic scheme of sodium (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenyl sulfonate (**5**) from vernonia oil. **1** is a mixture with R=CH<sub>3</sub>(CH<sub>2</sub>)<sub>13</sub>CH<sub>2</sub>–, CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>CH<sub>2</sub>–, *cis*-9-C<sub>8</sub>H<sub>17</sub>CH=CHC<sub>7</sub>H<sub>14</sub>–, *cis,cis*-9,12-C<sub>5</sub>H<sub>11</sub>CH=CHCH<sub>2</sub>CH=CHC<sub>7</sub>H<sub>14</sub>–, and *cis*-9-*cis*-12,13-

C<sub>5</sub>H<sub>11</sub>CH(O)CHCH<sub>2</sub>CH=CHC<sub>7</sub>H<sub>14</sub>– as major components. Reagents and reaction conditions: (1) NaOCH<sub>3</sub>/MeOH, hexane, rt, 80 min; (2) LiAlH<sub>4</sub>, hexane, rt, 2 h; (3) *p*-TsCl, CHCl<sub>3</sub>, pyr., 0 °C, 3 h; (4) NaI, acetone, reflux, 4 h; (5) Na<sub>2</sub>SO<sub>3</sub>, IPA, H<sub>2</sub>O, reflux, 12 h

For the second and third cases, tosylation was not achieved and the epoxy ring opened forming a hydroxy group, the evidence of which was obtained with both FT-IR and <sup>1</sup>H NMR: the IR spectrum revealed the presence of a hydroxy group at 3,350 cm<sup>-1</sup> and <sup>1</sup>H NMR revealed the disappearance of the epoxy group at 2.9 ppm and the presence of the hydroxy group at 3.6 ppm.

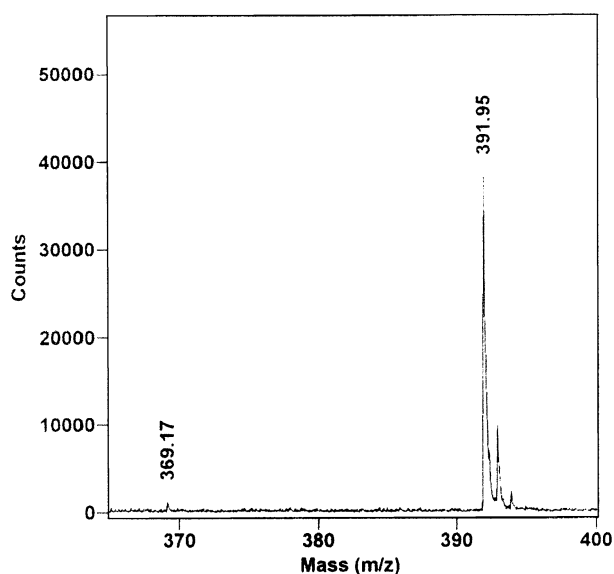
However, when **2** was dissolved in chloroform and pyridine, cooled to 0 °C, and *p*-TsCl added over a period of time with stirring, tosylation was achieved with a 96% yield. Furthermore, the epoxy ring remained intact. Care had to be exercised during workup, particularly when extracting pyridine in the form of the water-soluble pyridinium chloride. Addition of very concentrated hydrochloric acid opened the epoxy ring. However, extraction of pyridine with 10% aqueous hydrochloric acid (5 °C) was found to be mild enough to prevent epoxy ring opening.

After obtaining the epoxy tosylate (**3**), attempts were made to obtain the epoxy alkenyl sulfonate (**5**), by treating **3** with sodium sulfite: a more direct way of obtaining a sulfonate in contrast to substituting the tosylate with a halogen—bromine or iodine—followed by nucleophilic substitution of halogen with the sulfonate group. Contrary to the published methods' assertion that such a transformation was achievable [18, 19], when attempted, the transformation was not achieved. Consequently, we transformed **3** to (+)-(12*S*,13*R*)-epoxy-1-iodo-*cis*-9-octadecene (**4**). The choice of iodination over bromination was dictated by the fact that alkyl iodides give a characteristic peak of the  $\alpha$ -methylene carbon (alpha to iodo) in the <sup>13</sup>C NMR spectrum. Even more direct would have been the conversion **2** to 1-bromo-(+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecene with phosphorous tribromide. However, one by-product of

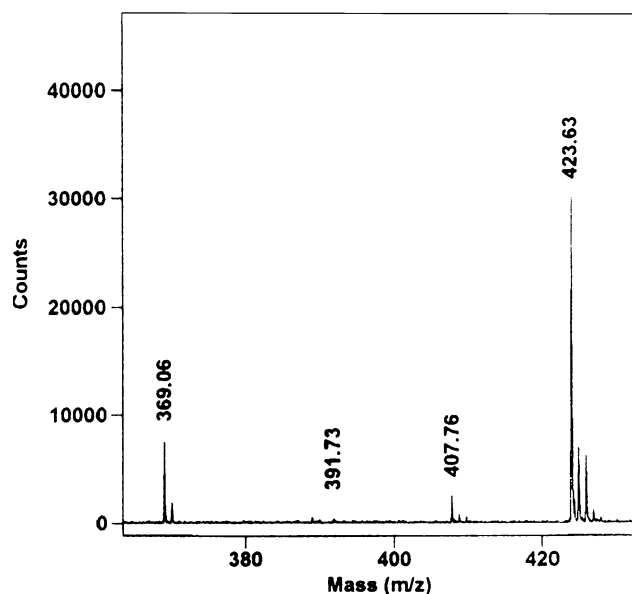
the phosphorous tribromide reaction, phosphoric acid, would have potentially opened the epoxy ring: our previous studies of the reactivity of the epoxide ring of VO have indicated that it was susceptible to ring opening under strong acidic conditions.

The nucleophilic substitution of the iodide with a sulfite was fairly straightforward. It entailed dissolving sodium sulfite in aqueous isopropyl alcohol and adding **4** while refluxing. The reaction was monitored by the disappearance of epoxy iodide using GC-MS, which also revealed the formation of minor by-products that were attributed to dehydrohalogenation. After 12 h of refluxing, the isopropyl alcohol was evaporated, and the resulting aqueous solution was washed with diethyl ether, hexane, and then air-dried under the hood to yield **5** as a white powder-like solid in order to remove any unreacted iodide and alkene by-products. The acetone wash was used to remove any sodium iodide by-product. MALDI-TOF MS was used to determine the molecular mass of the sulfonate as shown in Fig. 1 with a sodiated molecular ion at *m/z* 391.0 (RSO<sub>3</sub>Na + Na). To further confirm the molecular mass of the (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenyl sulfonate, the MALDI sample was spiked with 1  $\mu$ L of a 5-mg KOH/mL methanol solution. The resulting MALDI-TOF MS (Fig. 2) revealed the disappearance of the sodiated ion at *m/z* 391.0 (RSO<sub>3</sub>Na + Na) in Fig. 1, and the appearance of an ion at *m/z* 423.0, corresponding to the formation of potassium (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenyl sulfonate, (RSO<sub>3</sub>K + K), in the MALDI ion source.

To establish the surfactancy of the synthesized epoxy sulfonate, a preliminary study of the CMC was carried out using the Wilhelmy Plate method. A plot of Log C[M] as a function of surface tension was constructed, Fig. 3, and the

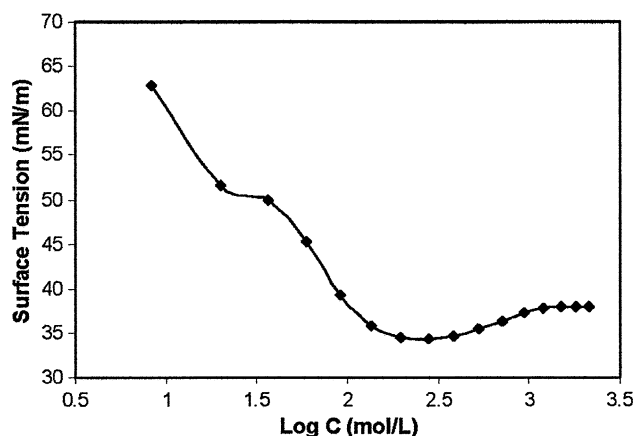


**Fig. 1** MALDI-TOF MS of sodiated (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenyl sulfonate represented by the molecular ion at  $m/z$  391 ( $\text{RSO}_3\text{Na} + \text{Na}$ ) and the molecular ion at  $m/z$  369 is due to charge transfer



**Fig. 2** MALDI-TOF MS of potassiated (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenyl sulfonate represented by the molecular ion at  $m/z$  423 ( $\text{RSO}_3\text{K} + \text{K}$ ) along with an isotopic cluster of peaks. The molecular ions at  $m/z$  407, 391, and 369 are representative of ( $\text{RSO}_3\text{K} + \text{K}$ ), ( $\text{RSO}_3\text{Na} + \text{Na}$ ), and ( $\text{RSO}_3\text{Na} + \text{H}$ ), respectively

CMC was determined to be 0.0010 M. Compared to the CMC (0.0018 M) of the industry standard, sodium lauryl sulfate (SLS), the epoxy sulfonate has a slightly lower CMC, suggesting that the epoxy functionality could have some impact on its water solubility and subsequent micelle formation.



**Fig. 3** Plot of  $\text{Log } C[M]$  as a function of surface tension for (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenyl sulfonate in which the CMC was determined to be 0.0010 M

In summary, this study demonstrates the ability to produce an epoxyalkenyl sulfonate, belonging to a class of anionic surfactants, from VO without destroying the epoxy functionality in the (+)-(12*S*,13*R*)-epoxy-*cis*-9-octadecenyl moiety of VO. The low critical micelle concentration of the epoxy sulfonate could lead to unique applications.

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