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ORIGINAL ARTICLE

Synthesis and Surface Properties of a Novel Sodium 3-(3-Alkyloxy-3-oxopropoxy)-3-oxopropane-1-sulfonate at the Air–Water Interface

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Abstract The present paper describes the synthesis and evaluation of surface properties of a novel series of anionic surfactant, namely sodium 3-(3-alkyloxy-3-oxopropoxy)-3-oxopropane-1-sulfonate with varying alkyl chain length (C8–C16). Synthesis involves initial formation of the 3-alkyloxy-3-oxopropyl acrylate along with fatty acrylate during the direct esterification of fatty alcohol with acrylic acid in the presence of 0.5 % $NaHSO_4$ at 110 °C followed by sulfonation of the terminal double bond of the 3-alkyloxy-3-oxopropyl acrylate. Synthesized compounds were evaluated for surface and thermodynamic properties such as critical micelle concentration (CMC), surface tension at CMC (γ_{cmc}), efficiency of surface adsorption (pC_{20}), surface excess (Γ_{max}), minimum area per molecule at the air–water interface (A_{min}), free energy of adsorption ($\Delta G°_{ads}$), free energy of micellization ($\Delta G°_{mic}$), wetting time, emulsifying properties, foaming power and calcium tolerance. Effect of chain length on CMC follows the classic trend, i.e. decrease in CMC with the increase in alkyl chain length. High pC_{20} (>3) value indicates higher hydrophobic character of the surfactant. These surfactants showed very poor wetting time and calcium tolerance, but exhibited good emulsion stability and excellent foamability. Foaming power and foam stability of C14-sulfonate were found to be the best among the studied compounds. Foam stability of C14-sulfonate was also studied at different concentrations over time and excellent foam stability was obtained at a concentration of 0.075 %. Thus this novel class of surfactant may find applications as foam boosters in combination with other suitable surfactants.

Keywords Acrylic acid · Fatty alcohol · Surface tension · Emulsifying properties · Foaming power · Calcium tolerance

Introduction

Fatty acid-derived acrylic esters are versatile monomers having wide industrial applications [1]. There are several methods reported in the literature for acrylation of fatty acid moieties, e.g. through alcoholysis of methyl methacrylate, acylation with acrylyl chloride, dehalogenation of alkyl α,β-dibromopropionate, dehydrohalogenation of β-halopropionic ester etc. [2]. Commercially, *n*-alkyl acrylates are prepared by direct esterification of fatty alcohol with acrylic acid in the presence of an esterification catalyst such as sulfuric acid, hydrofluoric acid, *p*-toluene sulfonic acid etc. [2–4]. These acid catalysts are toxic, corrosive and difficult to remove from the product. These acidic catalysts can be replaced with various solid acid catalysts such as acidic cation exchange resin, solid oxides, heteropolyacids supported onto suitable supports etc. [5–9].

Direct esterification of fatty alcohol with acrylic acid catalysed by all the reported acid catalysts in general results in about 90 % selectivity for fatty acrylate, but suffers from very poor conversion [7]. This is primarily due to the subsequent reactions of products occurring under the same reaction conditions. The literature also reports the formation of a range of by-products along with fatty acrylate

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during the direct esterification reaction; the extent of their formation was found to be dependent on the type of catalyst, chain length of fatty alcohol and the reaction conditions [7]. The major by-product is the 3-(alkyloxy)-3-oxopropyl acrylate, formed by the Michael addition of oxygen functionality of unreacted acrylic acid with the terminal double bond of alkyl acrylate; however, there is no report in which more than 12 % formation of this by-product was formed. In the present study, direct esterification of *n*-octanol with acrylic acid at 2:1 molar ratio was carried out in the presence of 0.5 % w/w of $NaHSO_4$ at 110 °C for 2 h. Column chromatographic purification followed by spectral characterization using several spectral techniques indicated near equal formation of the expected octyl acrylate along with 3-(octyloxy)-3-oxopropyl acrylate as a major side product.

Synthesis of structurally novel surfactants has attracted organic and physical chemists to study their surface properties. The present reaction has given us an opportunity to concentrate more on interesting functionalities of 3-(alkyloxy)-3-oxopropyl acrylate rather than alkyl acrylate to synthesize a new range of products either by functionalization of the active terminal olefin or by polymerization. In the present work, sulfonation of the double bond was carried out to synthesize five new sulfonates of varying alkyl chain length. All the sulfonates were evaluated for surface and thermodynamic properties such as critical micelle concentration (CMC), surface tension at cmc (γ_{cmc}), efficiency of surface adsorption (pC_{20}), surface excess i.e. the amount of surfactant adsorbed per unit are at the air–water interface (Γ_{max}), minimum area per molecule at the air–water interface (A_{min}), free energy of adsorption (ΔG°_{ads}), free energy of micellization (ΔG°_{mic}), wetting time, foaming, emulsion stability and calcium tolerance were evaluated.

Experimental Procedures

Chemicals

Acrylic acid and calcium acetate were purchased from SD Fine Chemicals Pvt. Ltd., Mumbai (India). Different long chain fatty alcohols (1-octanol, 1-decanol, 1-dodecanol, 1-tetradecanol and 1-hexadecanol) and the fluorescence probe *N*-phenyl-1-naphthylamine (NPN) were purchased from Sigma Aldrich. All other solvents, anhydrous $NaHSO_4$ and paraffin liquid (light) were purchased from SD Fine (Mumbai, India).

Synthesis

Synthesis of sodium 3-(3-alkyloxy-3-oxopropoxy)-3-oxopropane-1-sulfonate involves direct esterification of acrylic acid with fatty alcohol to get a mixture of alkyl acrylate and 3-(alkyloxy)-3-oxopropyl acrylate. Column chromatographic purification of 3-(alkyloxy)-3-oxopropyl acrylate and its subsequent sulfonation at the terminal olefin produced the desired compound (Fig. 1).

General Procedure for the Synthesis of 3-(Alkyloxy)-3-oxopropyl Acrylate

In a round-bottom flask, acrylic acid and fatty alcohol were taken in a 1:2 molar ratio followed by the addition of 0.5 % w/v of $NaHSO_4$ (with respect to acrylic acid). The reaction mixture was stirred at 110 °C and the progress of the reaction was monitored by TLC as well as GC. Both fatty acrylate and 3-(alkyloxy)-3-oxopropyl acrylate were found to be formed nearly in equal proportion within 2 h, as indicated by GC analysis. After 2 h, the reaction mixture was solubilized in hexane and washed with water to

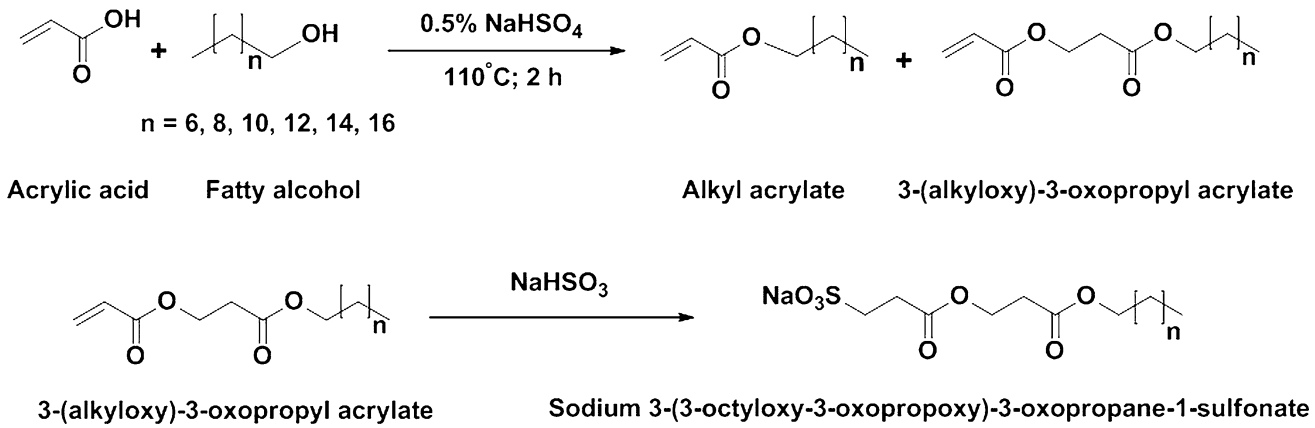

Fig. 1 Direct esterification of fatty alcohol with acrylic acid in the presence of 0.5 % $NaHSO_4$ followed by sulfonation of 3-(alkyloxy)-3-oxopropyl acrylate

remove unreacted acrylic acid and $NaHSO_4$, dried over anhydrous Na_2SO_4 and concentrated using rotary evaporator to get the crude product. Finally, the reaction mixture was purified by column chromatography using hexane and ethyl acetate as eluent. The fatty acrylate was eluted with 0.3 % ethyl acetate in hexane and 3-(alkyloxy)-3-oxopropyl acrylate was eluted with 0.5 % ethyl acetate in hexane.

3-(Octyloxy)-3-oxopropyl Acrylate

Acrylic acid (16.5 g, 0.23 M) was reacted with 1-octanol (60 g, 0.46 M) in the presence of sodium bisulfate (82.5 mg) at 110 °C. After 2 h, the reaction mixture was worked up and purified by column chromatography to get 20.3 g of pure octyl acrylated (isolated yield 48.2 %) and 28.0 g of 3-(octyloxy)-3-oxopropyl acrylate (isolated yield 47.7 %). The desired compound was characterized by NMR (^{1}H and ^{13}C), IR and mass spectroscopy. IR (cm^{-1}): 2928, 2958 (aliphatic C–H stretching), 1734 (carbonyl stretching), 1466 (C–H scissoring), 1177 (O–C–O stretching), 721 (C–H rocking); ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.4 (d, 1H; CH_2=CH–; *cis* to carbonyl), 6.1 (dd, 1H; CH_2=C*H*–), 5.8 (d, 1H; CH_2=CH–; *trans* to carbonyl), 4.45 (t, 2H; CH_2=CH–CO–O–CH_2–), 4.1 (t, 2H; –CH_2–CO–O–CH_2–), 2.7 (t, 2H; CO–O–CH_2–CH_2–CO–O), 1.65 (t, 2H; –O–CH_2–CH_2–), 1.3 [m, 10H; –$(CH_2)_5$–CH_3], 0.9 (t, 3H; –CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 170 (–CH_2–CO–O–CH_2–), 165 (CH_2=CH–CO–O–CH_2–), 131 (CH_2=CH–), 127.5 (CH_2=CH–), 64.5 (CH_2=CH–CO–O–CH_2–), 59.5 (–CH_2–CO–O–CH_2–), 22.5–33.8 [–O–CH_2–$(CH_2)_6$–CH_3], 14 (CH_3); ESI MS: *m/z* 279 (M + Na), 295 (M + K), 127 [M − O$(CH_2)_7$–CH_3].

3-(Decyloxy)-3-oxopropyl Acrylate

Acrylic acid (5.0 g, 0.07 M) was reacted with 1-decanol (22.0 g, 0.14 M) in the presence of sodium bisulfate (25.0 mg) at 110 °C. After 2 h, the reaction mixture was worked up and purified by column chromatography to get 5.2 g of pure decyl acrylate (isolated yield 35 %) and 7.7 g of 3-(decyloxy)-3-oxopropyl acrylate (isolated yield 39 %). The desired compound was characterized by NMR (^{1}H and ^{13}C), IR and mass spectroscopy. IR (cm^{-1}): 2928, 2958 (aliphatic C–H stretching), 1734 (carbonyl stretching), 1466 (C–H scissoring), 1177 (O–C–O stretching), 721 (C–H rocking); ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.4 (d, 1H; CH_2=CH–; *cis* to carbonyl), 6.1 (dd, 1H; CH_2=CH–), 5.8 (d, 1H; CH_2=CH–; *trans* to carbonyl), 4.4 (t, 2H; CH_2=CH–CO–O–CH_2–), 4.1 (t, 2H; –CH_2–CO–O–CH_2–), 2.65 (t, 2H; CO–O–CH_2–CH_2–CO–O), 1.6 (t, 2H; –O–CH_2–CH_2–), 1.3 [m, 14H; –$(CH_2)_7$–CH_3], 0.9 (t, 3H; –CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 170 (–CH_2–CO–O–CH_2–), 165 (CH_2=CH–CO–O–CH_2–), 131 (CH_2=CH–), 127 (CH_2=CH–), 64.5 (CH_2=CH–CO–O–CH_2–), 59.5 (–CH_2–CO–O–CH_2–), 22.5–33.8 [–O–CH_2–$(CH_2)_8$–CH_3], 14 (–CH_3); ESI MS: *m/z* 307 (M + Na), 323 (M + K), 127 [M − O$(CH_2)_9$–CH_3].

3-(Dodecyloxy)-3-oxopropyl Acrylate

Acrylic acid (5.5 g, 0.076 M) was reacted with 1-dodecanol (28.5 g, 0.153 M) in the presence of sodium bisulfate (28.0 mg) at 110 °C. After 2 h, the reaction mixture was worked up and purified by column chromatography to get 6.6 g of pure dodecyl acrylate (isolated yield 36 %) and 7.7 g of 3-(dodecyloxy)-3-oxopropyl acrylate (isolated yield 40.5 %). The desired compound was characterized by NMR (^{1}H and ^{13}C), IR and mass spectroscopy. IR (cm^{-1}): 2928, 2958 (aliphatic C–H stretching), 1734 (carbonyl stretching), 1466 (C–H scissoring), 1177 (O–C–O stretching), 721 (C–H rocking); ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.4 (d, 1H; CH_2=CH–; *cis* to carbonyl), 6.1 (dd, 1H; CH_2=CH–), 5.8 (d, 1H; CH_2=CH–; *trans* to carbonyl), 4.4 (t, 2H; CH_2=CH–CO–O–CH_2–), 4.1 (t, 2H; –CH_2–CO–O–CH_2–), 2.65 (t, 2H; CO–O–CH_2–CH_2–CO–O), 1.6 (t, 2H; –O–CH_2–CH_2–), 1.3 [m, 18H; –$(CH_2)_9$–CH_3], 0.9 (t, 3H; –CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 170 (–CH_2–CO–O–CH_2–), 165 (CH_2=CH–CO–O–CH_2–), 131 (CH_2=CH–), 127 (CH_2=CH–), 64.5 (CH_2=CH–CO–O–CH_2–), 59.5 (–CH_2–CO–O–CH_2–), 22.5–33.8 [–$(CH_2)_{10}$–CH_3], 14 (–CH_3). ESI MS: *m/z* 313 (M + 1), 335 (M + Na), 351(M + K), 127 [M − O$(CH_2)_{11}$–CH_3].

3-(Tetradecyloxy)-3-oxopropyl Acrylate

Acrylic acid (3.1 g, 0.043 M) was reacted with 1-tetradecanol (18.5 g, 0.086 M) in the presence of sodium bisulfate (16.0 mg) at 110 °C. After 2 h, the reaction mixture was worked up and purified by column chromatography to get 4.4 g of tetradecyl acrylate (isolated yield 39 %) and 6.2 g of 3-(tetradecyloxy)-3-oxopropyl acrylate (isolated yield 42.0 %). The desired compound was characterized by NMR (^{1}H and ^{13}C), IR and mass spectroscopy. IR (cm^{-1}): 2928, 2958 (aliphatic C–H stretching), 1734 (carbonyl stretching), 1466 (C–H scissoring), 1177 (O–C–O stretching), 721 (C–H rocking); ^{1}H NMR: (300 MHz, $CDCl_3$, ppm): δ 6.4 (d, 1H; CH_2=CH–; *cis* to carbonyl), 6.1 (dd, 1H; CH_2=CH–), 5.8 (d, 1H; CH_2=CH–; *trans* to carbonyl), 4.4 (t, 2H; CH_2=CH–CO–O–CH_2–), 4.1 (t, 2H;–CH_2–CO–O–CH_2–), 2.65 (t, 2H; CO–O–CH_2–CH_2–CO–O), 1.6 (t, 2H; –O–CH_2–CH_2–), 1.3 [m, 22H; –$(CH_2)_{11}$–CH_3], 0.9 (t, 3H; –CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 170 (–CH_2–CO–O–CH_2–), 165 (CH_2=CH–CO–O–CH_2–), 131 (CH_2=CH–), 127 (CH_2=CH–), 64.5 (CH_2=CH–CO–O–CH_2–), 59.5 (–CH_2–CO–O–CH_2–), 22.5–33.8 [–$(CH_2)_{12}$–

CH_3], 14 (–O–CH_2–$(CH_2)_{12}$–CH_3); ESI MS: *m/z* 363 (M + Na), 379 (M + K), 127 [M − O$(CH_2)_{13}$–CH_3].

3-(Hexadecyloxy)-3-oxopropyl Acrylate

Acrylic acid (2.55 g, 0.0354 M) was reacted with 1-hexadecanol (17.15 g, 0.0708 M) in the presence of sodium bisulfate (13.0 mg) at 110 °C. After 2 h, the reaction mixture was worked up and purified by column chromatography to get 3.66 g of hexadecyl acrylate (isolated yield 35.0 %) and 5.3 g of 3-(hexadecyloxy)-3-oxopropyl acrylate (isolated yield 41.0 %). The desired compound was characterized by NMR (^{1}H and ^{13}C), IR and mass spectroscopy. IR (cm^{-1}): 2928, 2958 (aliphatic C–H stretching), 1734 (carbonyl stretching), 1466 (C–H scissoring), 1177 (O–C–O stretching), 721 (C–H rocking); ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 6.4 (d, 1H; CH_2=CH–; *cis* to carbonyl), 6.1 (dd, 1H; CH_2=CH–), 5.8 (d, 1H; CH_2=CH–; *trans* to carbonyl), 4.4 (t, 2H; CH_2=CH–CO–O–CH_2–), 4.1 (t, 2H; –CH_2–CO–O–CH_2–), 2.65 (t, 2H; CO–O–CH_2–CH_2–CO–O), 1.6 (t, 2H; –O–CH_2–CH_2–), 1.3 [m, 26H; –$(CH_2)_{13}$–CH_3], 0.9 (t, 3H; –CH_3); ^{13}C NMR (75 MHz, $CDCl_3$, ppm): δ 170 (–CH_2–CO–O–CH_2–), 165 (CH_2=CH–CO–O–CH_2–), 131 (CH_2=CH–), 127 (CH_2=CH–), 64.5 (CH_2=CH–CO–O–CH_2–), 59.5 (–CH_2–CO–O–CH_2–), 22.5–33.8 [–O–CH_2–$(CH_2)_{14}$–CH_3], 14 (–CH_3); ESI MS: *m/z* 391 (M + Na), 407 (M + K), 127 [M − O$(CH_2)_{15}$–CH_3).

General Procedure for the Synthesis of Sodium 3-(3-Alkyloxy-3-oxopropoxy)-3-oxopropane-1-sulfonate

Sulfonation of 3-(alkyloxy)-3-oxopropyl acrylate was carried out according to the method reported in the literature [10]. Briefly, a solution of 3-(alkyloxy)-3-oxopropyl acrylate in isopropanol was added to an aqueous solution of $NaHSO_3$ (1.5 mole equivalent) and the resultant reaction mixture was stirred at 50 °C for 28 h. After completion, the organic solvent was evaporated using a rotary evaporator and the dried mass was solubilized in 100 mL of methanol and filtered through Whatman filter paper to remove unreacted $NaHSO_3$. The filtrate was concentrated to obtain a white powder, which was washed extensively with dry ether to remove unreacted 3-(alkyloxy)-3-oxopropyl acrylate. The residue was dried under vacuum to get sodium 3-(3-alkyloxy-3-oxopropoxy)-3-oxopropane-1-sulfonate as a white amorphous powder.

Isolated yields of all the analogues are in the range of 75–78 %. The structures of final compounds were confirmed by high resolution mass spec (HRMS) data and are given below along with melting points.

Sodium 3-(3-octyloxy-3-oxopropoxy)-3-oxopropane-1-sulfonate (C8-sulfonate): melting point 119 °C; HRMS (*m/z*) calculated for $C_{14}H_{25}O_7S$ is 337.13155, found 337.13187; *sodium 3-(3-decyloxy-3-oxopropoxy)-3-oxopropane-1-sulfonate* (C10-sulfonate): melting point 131 °C; HRMS (*m/z*) calculated for $C_{16}H_{29}O_7S$ is 365.16285, found 365.16298; *sodium 3-(3-dodecyloxy-3-oxopropoxy)-3-oxopropane-1-sulfonate* (C12-sulfonate): melting point 152 °C; HRMS (*m/z*) calculated for $C_{18}H_{33}O_7S$ is 393.19415, found 393.19443; *sodium 3-(3-tetradecyloxy-3-oxopropoxy)-3-oxopropane-1-sulfonate* (C14-sulfonate): melting point 177 °C; HRMS (*m/z*) calculated for $C_{20}H_{37}O_7S$ is 421.22545, found 421.22621; *sodium 3-(3-hexadecyloxy-3-oxopropoxy)-3-oxopropane-1-sulfonate* (C16-sulfonate): melting point 182 °C; HRMS (*m/z*) calculated for $C_{22}H_{41}O_7S$ is 449.25675, found 449.25691.

Analytical Methods

All ^{1}H and ^{13}C NMR spectra were recorded on 300 and 75 MHz (Varian, Palo Alto, USA) spectrometers, respectively. HRMS data was recorded on a Thermo Scientific Exactive Orbitrap Mass spectrometer (Germany) and are given in mass units (*m/z*). ESI MS spectra were also recorded on a Waters LC–MS mass spectrometer (Palo Alto, USA) in the EI mode and are given in mass units (*m/z*). Melting points were determined using a Branstead Electro Thermal melting point apparatus. Synthesized compounds were crystallized from ethanol before evaluating their surface properties using surface tension. The surface tension was measured using a Kruss K100 tensiometer (Krüss GmbH, Hamburg, Germany) equipped with a platinum ring having a mean circumference of 6 cm. The surface tension (γ) was measured at different concentrations by adding a subsequent volume of stock surfactant solution with a 765 Dosimat (Metrohm), connected to the system. All surface tension measurements were performed at 27 °C. Foaming properties were evaluated at ambient temperature using a Ross-Miles pour foam apparatus [11], which consists of a jacketed cylindrical column of 90 cm height and 5 cm internal diameter. The studied surfactant solution (0.025 %) was taken in a 200-mL pipette with an orifice of 3 mm and fixed at the top of the column containing the same test solution (50 mL). The surfactant solution in the pipette was allowed to drop onto the solution in the column. Foam height obtained initially and after a regular interval of time was recorded on the scale attached to the column. Emulsification properties of the studied surfactant solutions (0.025 %) were determined according to the method described in the literature [12]. Equal volumes (40 mL) of surfactant solution and paraffin liquid (light) were taken in a 500-mL Erlenmeyer flask and the mixture was given 10 downward strokes and transferred immediately to a 100-mL measuring cylinder. The times taken for the separation of 10 mL and 20 mL of the

aqueous phase solution were determined. For estimating the wetting time, the Draves–Clarkson method was employed [13]. Briefly, skeins of 34 cm circumference weighing 5.0 ± 0.05 g were prepared from unbleached grey carded Indian yarn of single 20s. A hook weighing 4.5 g carrying a lead anchor weighing 27.1 g was attached to the skeins and sinking times were determined on surfactant solution (0.025 %) taken in a 500-mL measuring cylinder. Calcium tolerance of a surfactant solution is defined as the amount of Ca^{2+} ion required to make 1 mL of surfactant solution turbid and was determined by a modified Hart's method [14]. Surfactant solution (0.025 %, 50 mL) was taken in a conical flask and titrated against 1 % calcium acetate solution in water, taken in a 50-mL burette. Titration was carried out till the turbidity of the solution just obscured a strip of printed paper fastened to one side of the beaker.

Results and Discussion

Synthesis and Characterization

Direct esterification of 1-octanol with acrylic acid catalysed by 0.5 % $NaHSO_4$ at 110 °C results not only in the formation of the expected octyl acrylate but also a major side product. Column chromatographic purification and thorough characterization of the side product using NMR (^1H and ^{13}C), IR and mass spectroscopy indicated the compound to be 3-(octyloxy)-3-oxopropyl acrylate. Such a side reaction during the esterification of acrylic acid is well documented in the literature [7, 15]. The mechanism for the generation of this side product is by Michael-type addition through hydroxyl functionality of one acrylic acid to the terminal double bond of the formed fatty acrylate. In the present work, direct esterification of 1-octanol and acrylic acid under the studied reaction conditions resulted in very high conversion (>95 %) and near equal specificity towards the formation of octyl acrylate (48.2 %) and 3-octyloxy-3-oxopropyl acrylate (47.7 %). This indicates that both esterification and Michael-type addition of esterified product happened simultaneously. There is no literature wherein such a large formation of Michael adduct was reported during direct esterification of fatty alcohol and acrylic acid. Further variations in reaction conditions did not improve much the specificity towards the formation of 3-(octyloxy)-3-oxopropyl acrylate. Accordingly, a series of fatty alcohols (1-decanol, 1-dodecanol, 1-tetradecanol and 1-hexadecanol) were similarly esterified with acrylic acid to get their corresponding Michael adducts. The structures of all the esterified products were established by NMR (^1H and ^{13}C), IR and mass spectral data. Finally, the sulfonation of 3-alkyloxy-3-oxopropyl acrylate was carried out efficiently at the active terminal olefin according to the method reported in the literature [10]. The structures of the sodium 3-(3-alkyloxy-3-oxopropoxy)-3-oxopropane-1-sulfonates were confirmed by HRMS data.

Surface Activity

Aqueous solutions of the studied surfactants were prepared by dissolving appropriate amounts in Milli-Q water, and surface tension and CMC were measured using a Kruss K100 tensiometer. Variation of surface tension as a function of logarithm of surfactant concentration is shown in Fig. 2. The CMC was determined from this plot of surface tension vs log C, from the intersection of two lines after fitting linearly. Three measurements were taken in total for all the studied analogues and were averaged. The surface properties of the synthesized surfactants measured by the surface tension method are given in Table 1. The CMC of the synthesized sulfonates decreases with the increase in chain length. This is expected as the increase in chain length is associated with increased hydrophobicity, favouring aggregation in the aqueous environment. The surface tensions at CMC of the synthesized surfactants are in the range of 30–47 mN/m. The efficiency of a surfactant can be assessed by the value of pC_{20}, estimated as the negative logarithm of concentration of surfactant required to reduce the surface tension of water by 20 units. Higher values of pC_{20} (>3) indicate higher hydrophobic character of the surfactant, resulting in higher efficiency of reduction of surface tension [16].

The surface excess, Γ_{max} (mol/cm^2), i.e. the amount of surfactant adsorbed per unit area at the air–water interface after complete monolayer formation, and minimum surface area occupied by each surfactant molecule (A_{min}) were calculated using Eqs. 1 and 2 from the slope of the linear

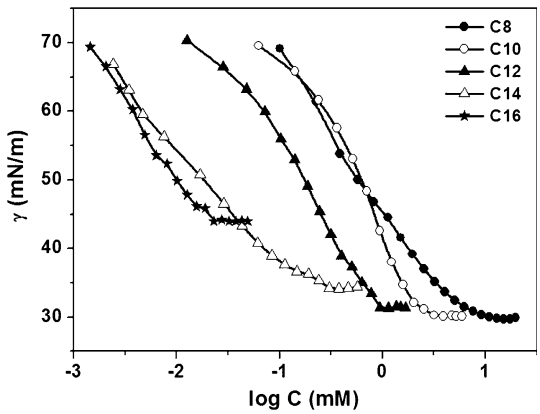

Fig. 2 Plot of surface tension (γ) versus log C of 3-(alkyloxy-3-oxopropyl)-3-oxopropane-1-sulfonates having varying chain lengths (C8–C16)

Table 1 Surface properties of sodium 3-(3-alkyloxy-3-oxopropoxy)-3-oxopropane-1-sulfonate of varying alkyl chain length (C8–C16)

Surfactant	CMC (mM)	γ_{cmc} (mN/m)	$\Gamma_{max} \times 10^{10}$ (mol/cm^2)	pC_{20}	A_{min} (nm^2/mol)	ΔG_{mic} (kJ/mol)	ΔG_{ads} (kJ/mol)
C8-sulfonate	5.3 ± 0.4	30.3 ± 0.3	1.69 ± 0.3	3.24 ± 0.16	0.98 ± 0.18	−26.14 ± 0.12	−50.46 ± 1.6
C10-sulfonate	1.6 ± 0.12	31.5 ± 0.9	3.11 ± 0.2	3.35 ± 0.07	0.53 ± 0.1	−32.11 ± 0.41	−44.57 ± 0.41
C12-sulfonate	0.88 ± 0.04	30.7 ± 0.7	2.38 ± 0.1	3.78 ± 0.12	0.7 ± 0.05	−35.09 ± 0.74	−52.07 ± 0.75
C14-sulfonate	0.17 ± 0.04	35.4 ± 1.0	1.36 ± 0.3	4.64 ± 0.21	1.22 ± 0.13	−43.30 ± 0.58	−68.01 ± 1.90
C16-sulfonate	0.01 ± 0.002	47.1 ± 1.6	1.79 ± 0.3	5.37 ± 0.06	0.93 ± 0.07	−57.43 ± 0.10	−70.98 ± 0.89

CMC critical micelle concentration measured by surface tensiometer, γ_{cmc} surface tension at CMC, pC_{20} efficiency of surface adsorption, Γ_{max} surface excess at the air–water interface, A_{min} minimum area per molecule at the air–water interface, ΔG_{ads} free energy of adsorption, ΔG_{mic} free energy of micellization

part of the surface tension plot using the Gibbs adsorption isotherm [17].

$$\Gamma_{max} = -(1/nRT)(d\gamma/d\ln C) \quad (1)$$

$$A_{min} = 1/N.\Gamma_{max} \quad (2)$$

where R is the gas constant (8.314 J mol^{-1} K^{-1}), T is absolute temperature, γ is surface tension, C is surfactant concentration, $n = 2$ for 1:1 type anionic surfactant and N is Avogadro's number. Γ_{max} and A_{min} predict the packing pattern and orientation of the surfactant molecule at the air–water interface. Both parameters are found to be dependent on alkyl chain length or hydrophobicity of the surfactant. However, in this studied class of surfactant, no specific trend was observed in the values of Γ_{max} and A_{min}, indicating their independence on alkyl chain length.

The adsorption of a surfactant at the air–water interface and its micellization in the bulk aqueous solution occur simultaneously. The free energy of adsorption ($\Delta G°_{ads}$) and free energy of micellization ($\Delta G°_{mic}$) of the synthesized surfactants at the air–water interface were calculated using Eqs. 3 and 4 [18, 19].

$$\Delta G°_{mic} = nRT \ln CMC \quad (3)$$

where R is gas constant 8.314 J mol^{-1} K^{-1}, $n = 2$ for 1:1 type anionic surfactant and T is absolute temperature.

$$\Delta G°_{ads} = \Delta G°_{mic} - (\Pi_{cmc}/\Gamma_{max}) \quad (4)$$

The negative values of $\Delta G°_{ads}$ and $\Delta G°_{mic}$ shown in Table 1 indicate that both adsorption and micellization occur spontaneously at 27 °C. Generally, a surfactant with high $\Delta G°_{ads}$ and low $\Delta G°_{mic}$ will be more favourable for adsorption rather than micellization and hence will exhibit higher CMC and vice versa. This is exactly what is observed in the case of sodium 3-(3-octyloxy-3-oxopropoxy)-3-oxopropane-1-sulfonate having a CMC in the millimolar range (5.3 mM), whereas that for sodium 3-(3-hexadecyloxy-3-oxopropoxy)-3-oxopropane-1-sulfonate is in the micromolar range (0.01 mM). Thus, with the increase in chain length, micellization is more favourable over adsorption.

The synthesized surfactants were also evaluated for their surface active properties such as wetting time, calcium tolerance, emulsion stability and foaming characteristics. As a result of the poor solubility of the higher homologue (C16-sulfonate), all these properties were evaluated by preparing 0.025 % aqueous solutions of these surfactants. The studied surfactants exhibited poor wetting time and moderate calcium tolerance but exhibited excellent foamability and emulsion stability. Except C8-sulfonate, all other studied surfactants exhibited superior emulsion stability (35–94 s for 10 mL separation and 78–200 s for 20 mL separation) compared to sodium lauryl sulfate (SLS; 18 s for 10 mL separation and 46 s for 20 mL separation). The emulsion stabilities of the studied surfactants were found to be dependent on the hydrophobicity, showing an increasing trend (C8-sulfonate, 10 s for 10 mL separation and 25 s for 20 mL separation; C16-sulfonate, 94 s for 10 mL separation and 200 s for 20 mL separation) with the increase in alkyl chain length.

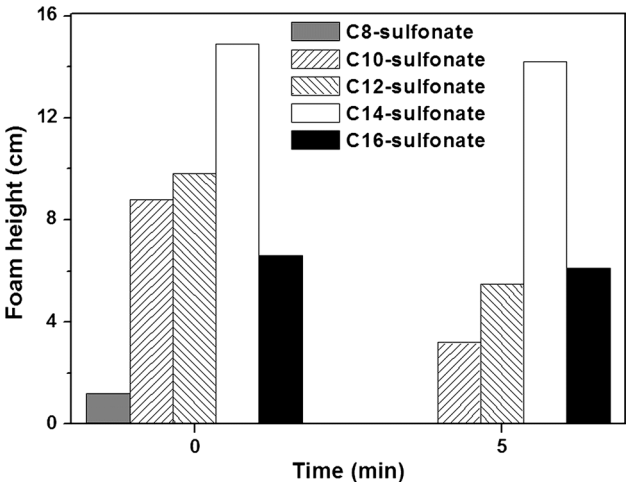

Fig. 3 Foaming properties of 0.025 % of 3-(alkyloxy-3-oxopropyl)-3-oxopropane-1-sulfonates having varying chain lengths (C8–C16) at 0 min and after 5 min

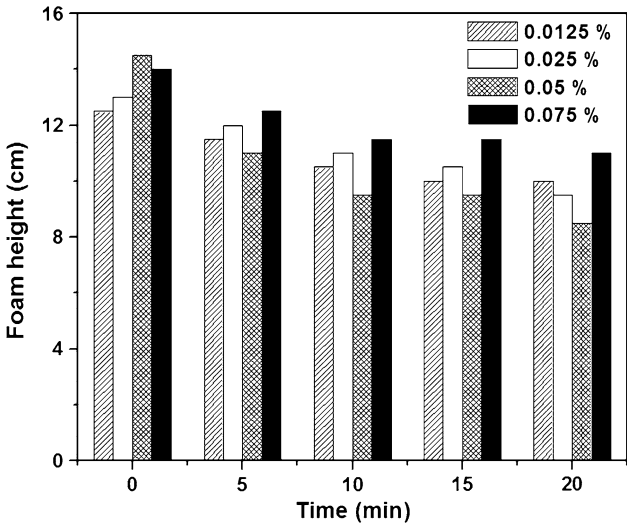

Fig. 4 Foam stability of 3-(tetradecyloxy-3-oxopropyl)-3-oxopropane-1-sulfonate at different weight percentage (0.0125–0.075 %) as a function of time

The foamability and foam stability of all the synthesized sulfonates were evaluated by a simple foaming test. The foamability is simply the ability to produce foam immediately after agitation and the foam stability is estimated by studying the foam volume after some time. Figure 3 shows the foaming power of the studied sulfonates at 0 min and also after 5 min. An increase in foamability of the surfactant was observed with the increase in alkyl chain length, reaching maxima at C14-sulfonate and thereafter decreasing. Thus among the studied surfactants, sodium 3-(3-tetradecyloxy-3-oxopropoxy)-3-oxopropane-1-sulfonate exhibited maximum foamability. This prompted us to pick C14-sulfonate and study the dependence of foam stability as a function of concentration. Figure 4 shows such dependence of foam stability over 20 min at four different concentrations of C14-sulfonate (0.0125, 0.025, 0.05 and 0.075 %). Although the influence of surfactant concentration on foam stability is not pronounced at the studied concentration range, an increasing trend was observed.

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