J Surfact Deterg (2012) 15:207–215
DOI 10.1007/s11743-011-1294-z

ORIGINAL ARTICLE

Synthesis and Micellization Properties of New Anionic Reactive Surfactants Based on Hydrogenated Cardanol

**Suresh Kattimuttathu I · Gesche Foerst ·
Rolf Schubert · Eckhard Bartsch**

Received: 23 May 2011 / Accepted: 30 July 2011 / Published online: 22 November 2011

Abstract We report the synthesis, characterization and micellization properties of two anionic reactive surfactants based on 3-pentadecyl phenol obtainable from a renewable resource, cardanol. The synthesis is achieved through simple chemical transformations, first converting the phenol to the acrylate that is sulfonated in a second step. The products were characterized by elemental analysis and spectroscopic techniques. The surfactant properties of the sulfonated acrylates were measured and compared with the standard non-reactive anionic surfactant sodium dodecyl sulfonate. The micellization behavior of aqueous solutions was studied using conductivity, surface tension measurements, and the fluorescence probe technique based on diphenyl hexatriene. Characterization by surface tension measurements facilitated the determination of basic surfactant properties like the critical micelle concentration (CMC), the surface tension at the CMC, surface excess and area per surfactant molecule. The Gibbs free energy of micellization showed a negative value suggesting spontaneous micellization in aqueous solution. The micellization of the surfmer with an ethylene spacer between the phenyl ring and the acrylate group seems to be enhanced as indicated by the lower surface excess and lower free energy. Its CMC was also lower.

Keywords Cardanol · Reactive surfactant · Critical micelle concentration · Fluorimetry · Conductance

Introduction

Cashew Nut Shell Liquid (CNSL), a byproduct of the cashew processing industry, has received the attention of researchers worldwide as a sustainable raw material for the development of fine chemicals. Cardanol and anacardic acid (10 and 63%, respectively) are the major phenolic constituents present in natural cashew nut shell oil (*Anacardium occidentale* sp.-natural CNSL) [1, 2]. The main constituent of technical grade cashew nut shell liquid obtained by distillation of natural CNSL is cardanol [2, 3]. It has served as a valuable raw material in the synthesis of many fine chemicals and monomers for polymer synthesis [4, 5]. The alkyl chain in the *m*-position of cardanol makes it a valuable starting material for the synthesis of surfactants and plasticizers for the polymer industry. The side chain also carries unsaturation that can be derivatized to make thermal or photo curable resins [6]. It comprises 41% of the triene (2-hydroxy-6-pentadeca-8,11,14-trienyl benzoic acid) and 3-pentadeca-8,11,14-trienyl phenol), while 22% are the diene, 34% monoene and the remaining saturated. Cardanol has been used in many industrial applications such as paints and varnishes [7], phenol–formaldehyde resins [8, 9], surface active polymers [10] and others [11, 12]. Because of their renewable nature and structural characteristics, anacardic acid and cardanol are likely candidates for preparing "green" surfactant species like sulfonates, ethoxylates and cardanol-formaldehyde

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S. Kattimuttathu I · E. Bartsch
Institute for Macromolecular Chemistry,
Stefan-Meier-Straße 31, 79104 Freiburg, Germany

S. Kattimuttathu I (✉)
Organic Coatings and Polymers Division,
Indian Institute of Chemical Technology,
Uppal Road, Tarnaka, Hyderabad 500 007, India
e-mail: kisuresh@iict.res.in

G. Foerst · R. Schubert
Department of Pharmaceutical Technology,
University of Freiburg, Hermann-Herder-Straße 9,
79104 Freiburg, Germany

ethoxylate polymers [13, 14] to replace the petroleum based nonyl phenol surfactants. They have also been used in semi-synthetic processes to prepare derivatives with biological and pharmaceutical applications [15].

Cardanol and its saturated analogue, 3-pentadecyl phenol has been earlier studied for its surface activity and biodegradability characteristics by Tymann and Bruce [13]. They found that cardanol and cardol polyethoxylates derived from technical cashew nut shell liquid are potential replacement for synthetic nonyl phenol based surfactants. Scorzza et al. [16] carboxylated the main phenolic components of cashew nut shell oil, cardanol and anacardic acids, and tested them as anionic surfactants. It was observed that these derivatives lower the surface tension, exhibit a critical micelle concentration, and useful in the preparation of microemulsions in mixtures with conventional dodecyl sulfate surfactant. In another work, Dantas et al. [17] reported the synthesis of 2,4-sodium disulfonate-5-*n*-pentadecylphenol) and studied the effect of temperature and electrolyte concentration on micellization of aqueous solutions. The CMC decreased with increasing electrolyte concentration and temperature. In terms of biodegradability it was found that the saturated analogue of cardanol polyethoxylate degraded to the maximum in comparison to the unsaturated component. The synthetic *t*-nonylphenyl polyethoxylate remained substantially undegraded (77%), whereas glucose was almost completely degraded (5%) [14].

The synthesis of reactive surfactants (surfmers) based on 3-pentadecyl phenol (hydrogenated cardanol) has not been reported, to the best of our knowledge. The reactive surfactants (surfmers), unlike conventional non-reactive surfactants, take part in the polymerization with the main monomer and forms part of the polymer chain. Today, the reactive surfactants are important additives for emulsion polymers useful in protective coatings and adhesives, because they improve the product properties [18, 19]. In this paper the synthesis and basic surfactant properties of two anionic surfmers based on 3-pentadecyl phenol are reported. Apart from structural characterization of the synthesized surfmers techniques like surface tension measurement, conductivity and fluorescence probe method were used to measure the aqueous solution characteristics and CMC behavior of the synthesized surfactants. The probable micellization mechanism was inferred from the fluorescence probe method.

Experimental

Materials and Methods

3-pentadecyl phenol, acrylic acid, chlorosulfonic acid, sodium carbonate, chloroethanol and 1,6-diphenyl-1,3,5-hexatriene were purchased from Aldrich and used without further purification. The solvents diethyl ether, chloroethanol, toluene, ethyl acetate, dichloromethane, triethyl amine were commercial grade (S.D. Fine Chem, Mumbai) and distilled before use. The product obtained after each step was characterized by IR, ^{1}H, ^{13}C-NMR and elemental analysis. The NMR analysis was carried out on a Bruker 400 MHz machine and an EL Vario instrument was used for elemental analysis. Two surfmers synthesized were designated as S1 and S2. The synthesis of the surfmer was carried out using a two step procedure as outlined below.

Synthesis of the Acrylate Surfmer (S1)

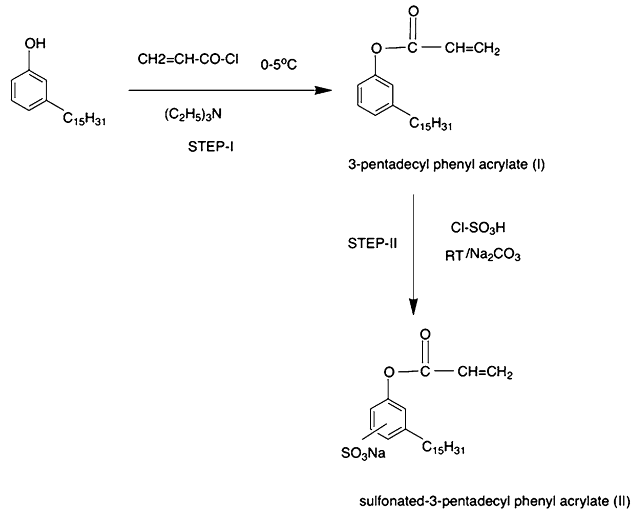
Step I. Synthesis of 3-pentadecyl phenyl acrylate: The reaction steps used are summarized in Scheme 1. In the first step the acrylate was prepared from pentadecyl phenol [5, 6], followed by its sulfonation and neutralization. In a typical experiment, a two-necked round-bottom flask fitted with a mechanical stirrer and dropping funnel was charged with 15 g (0.05 mol) of 3-pentadecyl phenol, dissolved in 25 mL of toluene along with an equimolar concentration of triethyl amine (7 mL). The flask was kept in an ice bath, and the temperature maintained at 0–5 °C. The contents of the flask were kept stirring and 5 mL (0.05 mol) of acryloyl chloride was added through dropping funnel. The reaction was run for 12 h and the product washed with excess water till the washings were neutral to litmus. Finally, the product was extracted into diethyl ether, dried over anhydrous sodium sulfate and the solvent evaporated. The isolated product was further purified by passing through a basic alumina column, to remove traces of phenol using toluene as the eluent. Yield 87%.

Step II. Synthesis of sulfonated 3-pentadecyl phenyl acrylate: The acrylate prepared in the first step was reacted with chlorosulfonic acid in a 1:1 mol ratio. Typically, 8 g (0.022 mol) of 3-pentadecyl phenyl acrylate dissolved in 10 mL of dichloromethane was put into a round-bottom flask and stirred for 15 min to obtain a well mixed solution. To this solution 2.6 g (0.022 mol) of chlorosulfonic acid, dissolved in 5 mL of dichloromethane was added drop wise. The reaction continued for 4 h at room temperature. The product obtained was neutralized with 10% Na_2CO_3 solution. The final product, sulfonated pentadecyl phenyl acrylate (II), was recovered by freeze-drying process. Yield 65%. Composition: $C_{21}H_{39}SO_4$; C: obs. 64.9%, calc. 65.1%; H: obs. 10.0%, calc. 10.07%; S: obs. 8.3%, calc. 8.2%.

Synthesis of Acrylate Surfmer (S2)

The acrylate surfmer S2 was prepared through the following steps:

Step I. Preparation of 3-Pentadecyl (ω-hydroxyethoxy) benzene: The synthetic steps are summarized in Scheme 2.



Scheme 1 Schematic of the reactions used for the synthesis of surfmers S1 starting from 3-pentadecyl phenol

In the first step a three-neck round-bottom flask fitted with a mechanical stirrer and water condenser was charged with 15 g of hydrogenated cardanol dissolved in 10 mL of ethanol. The flask was kept in an oil bath and the temperature maintained at 70 °C. To this equimolar amount of NaOH dissolved in water was added slowly along with 50 mg of sodium iodide through a dropping funnel. Finally, equimolar amount of 2-chloroethanol was added, maintaining the reaction temperature. The reaction was continued for 24 h to achieve maximum conversion.

The reaction product was washed with water to remove water soluble impurities and then extracted into tetrahydrofuran. The product was dried over anhydrous sodium sulfate and the solvent evaporated on a rotoevaporator. The residue was further purified by preparative column chromatography on a basic alumina column using toluene as the eluent. The product (I) yield was 86%.

Step II. Preparation of 3-pentadecyl (ω-hydroxyalkoxy) benzene acrylate: In this reaction 3-pentadecyl (ω-hydroxyalkoxy) benzene and acrylic acid were reacted in a 1:1 mol ratio. A two-neck round-bottom flask fitted with Dean–Stark trap and stirrer, containing 7.5 g of 3-pentadecyl (ω-hydroxy ethoxy) benzene dissolved in 10 mL of toluene was charged with 50 mg of hydroquinone, 1 g of *p*-toluene sulfonic acid (PTSA). The flask was kept in an oil bath under reflux conditions. To this solution 1:1 ratio of acrylic acid was added using an addition funnel, and the water that evolved during the reaction was removed from the Dean–Stark trap. The reaction was continued for about 6 h. The reaction product was washed with water and extracted in tetrahydrofuran.

The product was further purified on a 60–120 mesh silica gel column using toluene and ethyl acetate. The different fractions were collected and concentrated on a rotoevaporator. The purified product was used in the second step to prepare the sulfonated acrylate. For sulfonation, 3 g of pentadecyl (ω-hydroxy ethoxy) benzene acrylate was taken in a round-bottom flask and dissolved in 10 mL of toluene. The solution was stirred for 15 min to obtain a well mixed solution. Then, an equimolar amount of (0.8 g) chloro-sulfonic acid, diluted with 5 mL toluene was added drop-wise. The reaction was continued for 4 h at room temperature under stirring. The product was neutralized with 10% sodium carbonate solution. The neutralized compound (III, c.f. Scheme 2) was concentrated by using the freeze-drying process. Product (S2, Scheme 2) yield was 65%. Composition: $C_{26}H_{41}SO_6Na$; C: obs. 61.85%, calc. 61.88%; H: obs. 8.08%, calc. 8.11%; S: obs. 6.30%, calc. 6.35%.

Critical Micelle Concentration (CMC) Measurements

To assess the surfactant properties and CMC of the synthesized surfmers different method were used as outlined below.

Fluorescence Method

The fluorescence measurements were performed at 25 °C using a Perkin Elmer LS 5B luminescence spectrometer in the single read mode. A stock solution of the fluorescent probe DPH was prepared in THF at a concentration 0.005 mM. To exclude solvent effects 20 μL of this stock solution is pipetted with a Hamilton syringe into a spike test tube and solvent was evaporated. Then 1 mL of Millipore water is added and the sample is dispersed with a spike and again diluted with de-ionized water so as to achieve a concentration of 16.7 μM. From this solution a constant volume of DPH was added to all the sample tubes containing the surfmer and filled up to a fixed volume of 3.0 mL.

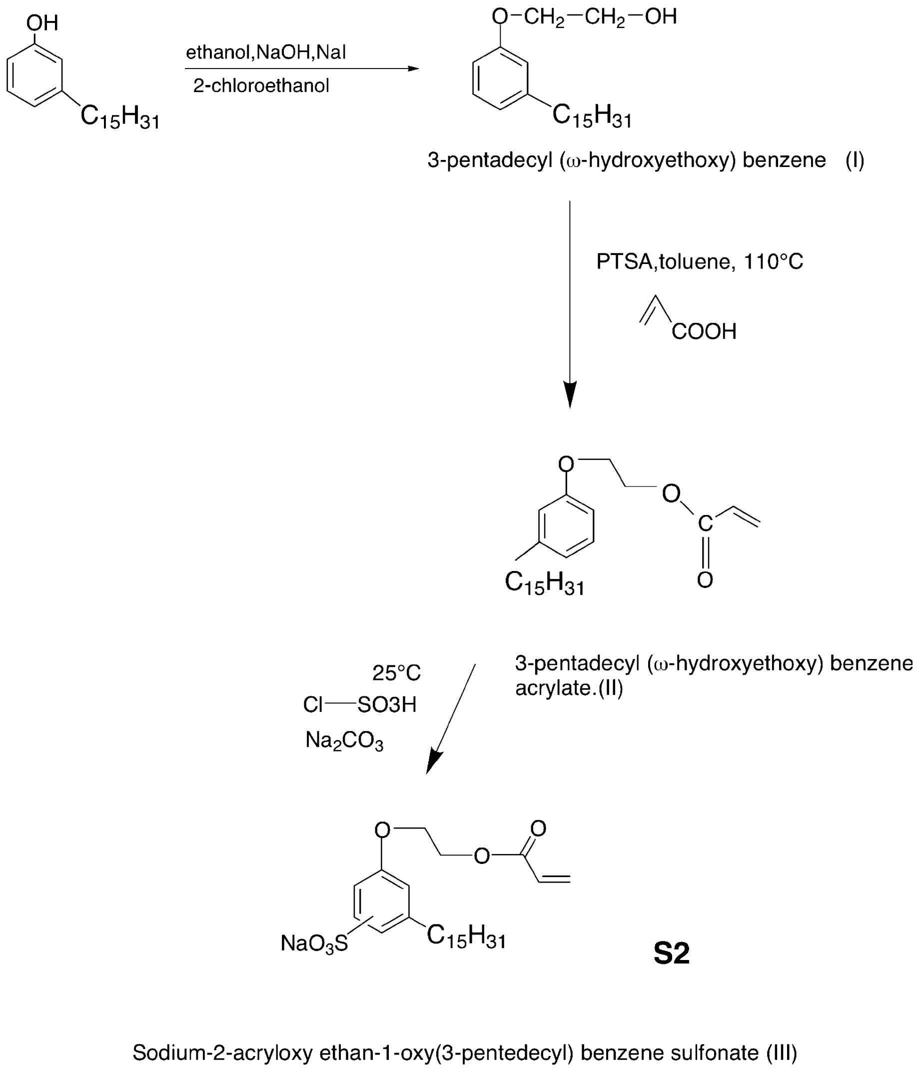
The solutions, while protected from light, were allowed to stand overnight and equilibrated in a water bath at 25 °C for 1 h before measurements. A plot of measured intensity versus conc. of solute was made. From the intersection points, the CMC was calculated.

Tensiometry

The surface tension measurements were carried out on a Krüss K-100 Tensiometer in plate mode according to ASTM D-1331 56. An aqueous solution of the surfmer was prepared at a concentration of 0.5 wt%.

Conductivity Measurements

For conductivity measurements aqueous solutions were prepared at different dilutions and the conductivity was



Scheme 2 Schematic of the Reactions used for the synthesis of surfmers S2 starting from 3-pentadecyl phenol

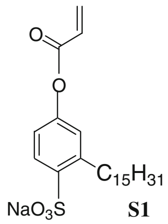
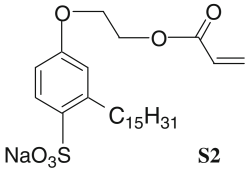
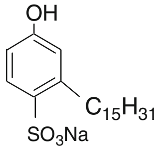
measured after successive dilution of the samples starting with a concentration of 0.5 mg/mL. The electrolytic conductivity of the solutions was directly measured using a WTW conductometer. To control the temperature within 0.1 °C, a water thermostated Haake NK22 water bath was used.

Results and Discussion

Surfmer Synthesis and Characterization

In this work, we report the synthesis of two novel anionic reactive surfactants starting from 3-pentadecyl phenol (hydrogenated cardanol). The synthesized surfmers were labelled as S1 and S2 (cf. Schemes 1, 2). The structural characterization of the synthesized surfmer was carried out using spectroscopic techniques. Important spectral characteristics along with the structure of the synthesized surfmers are given in Table 1. The characteristic peaks in IR, ^{1}H- and ^{13}C-NMR of hydrogenated cardanol and the final products S1 and S2 are tabulated in Table 1. The formation of S1 is confirmed by characteristic bands due to the acrylate group at 1,745 cm^{-1} of the ester carbonyl and at 1,194 and 1,160 cm^{-1} due to SO$_3$ stretch. The corresponding peaks due to acrylate protons appear at 5.94–6.62 ppm in ^{1}H-NMR and in ^{13}C-NMR spectra and the additional peak due to the carbonyl carbon appears at 162.98 ppm. Similarly, for S2 the IR spectrum shows bands at 1,728 cm^{-1} and S=O stretch at 1,150–1,200 cm^{-1}. The spectral data in combination with the elemental analysis results support the assigned structure of S1 and S2. However, it must be noted that some ortho isomer will be formed in this type of reaction and no attempt was made to separate the different isomers in the present work. The presence of the different isomers may also influence the micellization of the surfmers. For simplicity of analysis and interpretation the structure of the para isomer is shown in Table 1. As seen

Table 1 Reaction yield and spectroscopic data of the products

Compound	Yield (%)	Chemical shifts ^{1}H, ^{13}C (δ, ppm)	IR (cm^{-1})
 **S1**	65	^{1}H = 0.8 (t, **CH**$_3$), 1.25 (m, **CH**$_2$), 1.61 (–C**H**$_2$–CH$_2$–Ar), 2.60 (–C**H**$_2$–Ar), 5.94–6.62 (m, –C**H**$_2$, m, –C**H** of acrylate), 6.91–7.24 (m, arom). 7.94–8.17 ppm ^{13}C: 162.98, 153.63 (phenolic, carbonyl) 139–127.33 (alkene, aroma) 14–36 (aliphatic)	1,745 cm^{-1} carbonyl stretch 2,925; 2,853 cm^{-1}. Aliphatic C–H stretch, 1,226 cm^{-1}, 1,194 cm^{-1} and 1,160 cm^{-1} SO$_3$ stretch
 **S2**	82	0.927, t, C**H**$_3$; 1.292, m, C**H**$_2$; 1.614, m, C**H**$_2$CH$_2$Ar; 2.55, m, C**H**$_2$–Ar; 4.21, m–C**H**$_2$–OCOR; 5.8–6.3, m, acrylate; 6.40–7.30, m, aroma ^{13}C: 162.98, 153.63 (phenolic, carbonyl); 139–127.33 (alkene, aromatic); 62,69 –**C**H$_2$**C**H$_2$–; 14–36 (aliphatic)	3,000–3,100 cm^{-1} arom-C–H 2,800–3,000 cm^{-1} aliph. C–H stretch 1,728 cm^{-1} ester C=O stretch 1,590 cm^{-1}, 1,459–1,485 cm^{-1} C=C ring 1,370 cm^{-1} C–H bend, 1,150–1,200 cm^{-1}, S=O stretch
[a] 	–	0.8 (t, **CH**$_3$), 1.25 (m, **CH**$_2$), 1.61(–C**H**$_2$–CH$_2$–Ar), 2.60 (–C**H**$_2$–Ar) *6.91–7.24 (m, arom)* ^{13}C: 14–36, m, aliphatic C; 112–145, m, aromatic; 155, s, phenolic carbon	O—H stretch, 3350; C—H stretch, arom, 3010; C—H stretch, meth 2930, 2830; C==C ring stretch, arom 1590, 1450. C–O; stretch, 1150 C–H bend, methylene, 780, 700

[a] Values taken from Ref. [20]

from Table 1, the main difference between these surfmers is that in S2, there is an ethylene spacer between the polymerizable acrylate group and the phenolic ring. This is expected to influence the reactivity of the acrylate group and hence its incorporation efficiency during emulsion polymerization [18]. It is anticipated that S1 reactivity will be higher than that of S2, because the acrylate group is conjugated to the electron withdrawing effect of the sulfonate group and phenolic nuclei [20]. The reactivity of S2 may be comparable to that of ordinary acrylates, as the acrylate group is isolated from the electron withdrawing effect of phenolic ring and sulfonate group.

Critical Micelle Concentration (CMC) Measurements

The surfactant properties may be assessed in various ways. The CMC determination is generally based on localization of the position of a break in concentration dependence of a selected physical or chemical property of the surfactant solution. The reduction in surface tension of water by dilute solution of the reactive surfmer was used in this study to determine the optimal efficiency. The study of surfactant properties of aqueous solutions are important because the performance of the surfactant in many industrial processes like enhanced oil recovery as corrosion inhibitors depend on its concentration and orientation at the interface.

In analogy to the micellization phenomena of conventional surfactants it may be assumed that very dilute surfactant solutions contain only monomeric surfactant molecules [17]. As the concentration is increased, a point reached at which the individual surfactant molecules start to aggregate and form micelle structures called CMC. The CMC of the developed surfactant was obtained in water as 0.5% w/v solutions using the Wilhelmy plate method. Here, the relative surface tension of water is measured continuously as the surfactant solution is added in small increments. The reduction in surface tension as a function of surfmer S1 concentration is presented in Fig. 1.

As shown in Fig. 1 the surface tension starts to decrease and once the CMC is reached the value levels off. From the plot of surface tension versus concentration of added surfactant, the CMC is calculated as the intercept of the two straight lines (c.f. Fig. 1). This plot shows that the acrylate surfmer based on hydrogenated cardanol exhibit a reduction in surface tension with a low CMC value reported in the literature [20] for other derivatives. For example, 0.5% w/v solution of cardanol sulfonate was reported to possess a surface tension of 32.25 mN/m with a CMC value of 0.372 mol/L. In the present work we obtained surface tension value of 35.52 mN/m for S1 with a corresponding CMC value of 40.11 mg/L (8.7 × 10^{-5} mol/L). The surfmer S2 showed a lower value of 31.61 mN/m for the surface tension and a CMC value of 8.8 mg/L (1.7 × 10^{-5} mol/L) and a surface area per molecule 25.13°A^2. All other parameters obtained for S1 & S2 are tabulated in Table 2.

The surfmer samples exhibit, a constant high surface tension region at low concentrations followed by a decreasing surface tension with increasing concentration.

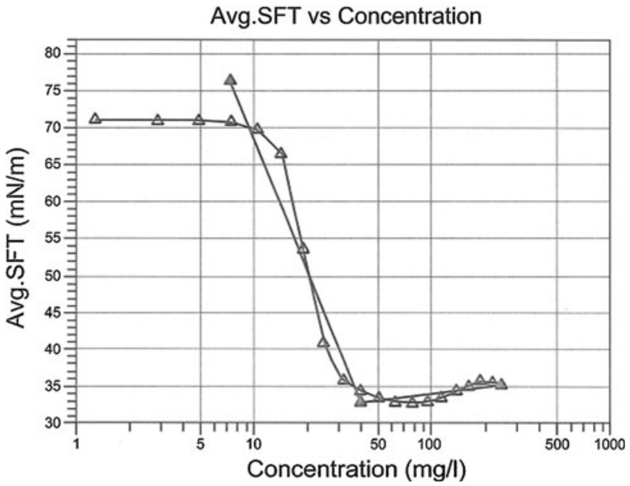


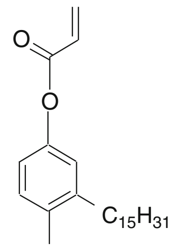
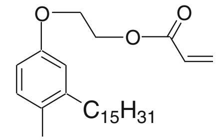
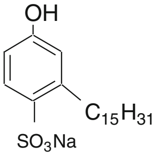
Fig. 1 Typical plot showing the variation in surface tension of surfmer S1 measured using the Wilhelmy plate method (For actual values refer to Table 2)

Ionic surfactants in general show a decrease in CMC value with any factor, like addition of salt or increase of temperature by which the interactions between the charged hydrophilic groups are weakened, and micelle formation is favoured [20]. A surfactant with sulfonate groups in the *ortho* position with respect to the alkyl chain exhibit higher surface tension and solubility in water.

The Gibbs free energy of micelle formation is another parameter that can be calculated from the CMC value. The appropriate relation depends upon the nature of the surfactant. Ionic surfactants are represented as dissociated molecules in solution but not completely and necessarily at the surface or in the form of micelles. The observed surface tension is low and CMC lower when compared with commercial surfactant like SDS (2.8 g/L). As shown by earlier researchers this may be attributed to the fact that a surfactant with the sulfonate group in the *ortho* position with respect to the alkyl chain had lower optimal salinity, higher surface tension and lower solubility in water than surfactants with the sulfonate group in the *para* or *meta* position [21, 22].

Analyzing the free energy of micellization of S1 and S2 (cf. Table 2), based on CMC data it may be concluded that the micellization process was spontaneous as indicated by the negative value of $\Delta_{mic}G$ ($\Delta_{mic}G < 0$) for both surfmers.

Table 2 Physico-chemical properties of the prepared reactive surfactants (surfmers)

Compound	Surface tension at CMC (mN/m)	CMC (mol L^{-1}), method			Surface area per molecule a_m (°A^2)	ΔG_{max} kJ/mol
		Tensiometry	Conductivity	Fluorescence		
 NaO$_3$S **S1**	35.52	8.7×10^{-5} (40.11 mg/L)	7.2×10^{-6} (3.32 mg/L)	9.76×10^{-5} (44.9 mg/L)	16.39	−33.4
 NaO$_3$S **S2**	31.61	1.7×10^{-5} (8.8 mg/L)	2.89×10^{-5} (14.3 mg/L)	3.81×10^{-7} (0.188 mg/L)	25.13	−37.11
[a] 	32.25	0.37	–	–	–	–

SDS-area per surfactant molecule = 5.4×10^{-19} m^2 (5.4°A^2)

[a] Values taken from Ref. [20]

The fact that the value is larger for S1 indicates that here the sulfonate group is preferably in the *o*-position of the alkyl group.

Adsorption Behavior

The relationship between surface adsorption and surfactant concentration in solution for an anionic surfactant is expressed on the basis of the Frumkin adsorption equation [17, 23].

$$\Phi = \frac{\Gamma}{\Gamma_{\max,}F} = \frac{K_F C \exp(-A\theta)}{1 + K_F C \exp(-A\theta)},$$

where Γ is the surface excess and θ is the surface layer coverage, K_F is the adsorption equilibrium constant and A is the parameter accounting for lateral interaction. The Frumkin equation is reduced to the Langmuir equation for $A = 0$. If $A > 0$, a decrease in the effective adsorption constant occurs that is caused by the repulsive interactions between the adsorbed surfactant monolayer and the molecules into the bulk solution. When $A < 0$, there is high compatibility between the bulk solution and the adsorbed monolayer. The affinity for micelle formation of these surfmers is also indicated by the negative surface excess values.

The difference in surface excess of S1 and S2 is further indicative of a change in micellar structure [17]. For S2 surface excess was 6.61 $\times$ 10^{-12} mol/mm^2 as compared to 1.01 $\times$ 10^{-11} mol/mm^2 for S1, i.e. a reduction in surface excess on going from S1 to S2. This also suggests a change in micelle formation. Dantas et al. [17] while studying micellization of 2,4-sodium disulfonate-5-*n*-pentadecylphenol have observed a similar effect on the addition of electrolyte. The micellar structure of aqueous solutions of phenolic lipids has been widely studied [24] and it was suggested that they can form spherical, cylindrical or lamellar shaped micelles, the fact directly dependent on the geometry of the monomeric units and their molecular environment. According to Rosen and Dhanayake [25] the cross sectional area occupied by the hydrophilic group at the interface often varies with the molecular environment like pH, ionic strength, temperature, concentration of surfactant, temperature etc. For example, in ionic surfactants, the cross sectional area decreases with increasing surfactant concentration or temp or ionic strength allowing formation of more complex structures.

In the light of earlier studies on cardanol based surfactants and the reduced surface excess of S2 when compared with S1 in water we assume lateral interaction between –CH_2 groups present in the side chain of the molecules is operating. Such interactions, when compared with repulsive interaction caused by the polar hydrophilic group, are greatly relevant for micelle formation because the extended long chain (15 C atoms) makes the formation of monolayer difficult [16].

Fluorimetry

To supplement the micellization behavior of the studied surfmer and to determine the critical micelle concentration another commonly used fluorescence probe method employing 1,6-diphenyl-3,5,6-hexatriene (DPH) as probe molecule was used. It has already been shown to be useful to investigate the micellization of Pluronics [26] and various other surfactants [27]. The hydrophobic DPH exhibits negligible fluorescence in hydrophilic environment, whereas it is highly fluorescent in hydrophobic compartments. A rise in fluorescence intensity upon increasing the surfmer concentration indicates solubilization of the probe in the formed micelles. Since fluorescence intensity of DPH is known to be temperature sensitive [23], all measurements were carried out at 25 °C. The CMC was determined as the point of intersection of two extrapolated straight lines when plotting the fluorescence intensity against the log concentration of the surfactant. A typical plot obtained for surfmer S1 using the fluorescence probe method is shown in Fig. 2.

It can be seen from Table 2 that the values obtained are comparable to that of phenolic lipids reported in the literature. The phenolic lipids are reported to have very low CMC values about 0.5–5 µM [15], quite comparable to the value obtained in the present work. Another feature of the studied system, seen from Fig. 2, is that the fluorescence intensity decreases with decreasing concentration but never becomes a constant or zero as reported earlier for other systems [26]. This could be because very diluted surfactant solutions contain only monomeric surfactant molecules and

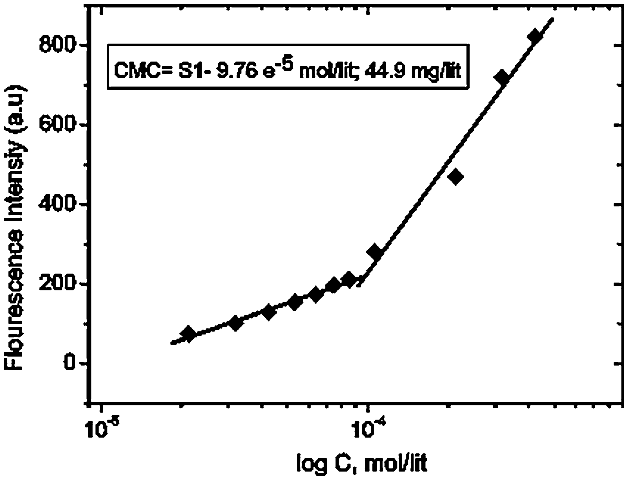


Fig. 2 Fluorescence data for the 3-pentadecyl phenol based polymerizable surfactant S1 determined in distilled water with DPH at 25 °C

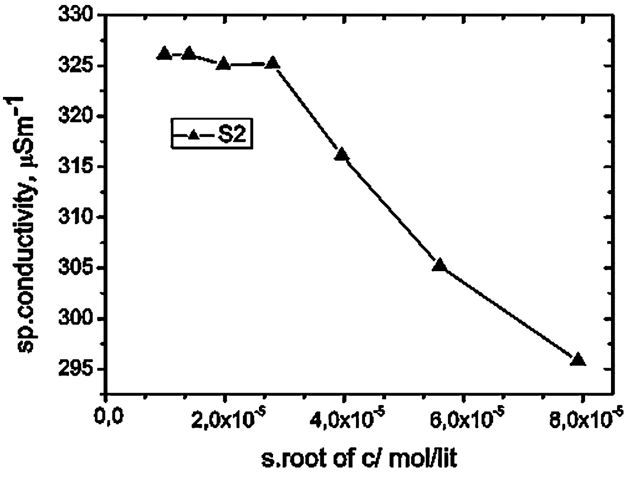


Fig. 3 Conductance of surfmer S2 in water at successive dilutions (c.f. Refer Table 2 for CMC values)

the pentadecyl phenyl segment adopts a structure in solution with a straightened hydrophobic alkyl chain where the DPH could adsorb and show fluorescence.

Conductivity Measurements

In the case of ionic surfactants, the utilization of electrochemical measurements is much more convenient, especially measurement of the electrical conductivity of the aqueous solution at varying concentrations [28, 29]. The method is based on the finding of a breaking point on the curves, which describe the concentration dependence of the conductivity. The conductivity of any solution is directly proportional to the concentration of its ions. The point where the micelle formation starts is indicated by the concentration dependence of specific conductivity (κ) as a breaking point. Typical plot showing the CMC value of S2 is shown as Fig. 3. The CMC values obtained from all the methods are further summarized in Table 2 and agreed more or less within limits.

Conclusions

The development of two anionic reactive surfactants based on 3-pentadecyl phenol (hydrogenated cardanol) is reported. The micellization behavior of the reactive surfactants based on 3-pentadecyl phenol in water is found to be spontaneous for both the synthesized surfactants as indicated by the negative free energy of mixing. The CMC of the surfactants decreased with increasing concentration and comparable to the other alkyl phenol derivatives but much lower than the conventional SDS surfactant. The fluorescence probe method and surface tension measurements gave low but comparable CMC values for S1 & S2. The conductivity method gave slightly higher values of the CMC for S2 than S1. The discrepancy may be because the conductivity method depends on ion concentration in the bulk of the solution compared with surface tension measurement. The change of observed surface excess from surface tension measurements further indicates a change in micelle aggregation. The surface area per molecule of the surfmers is larger than that of SDS due to increased molecular size. The evaluation of the synthesized surfmer in the emulsion polymerization and its influence on the film formation and film properties will be reported in forthcoming publications.

Acknowledgments This research was supported by a Marie Curie International Incoming Fellowship to Dr. K. I. Suresh within the 7th European Community Framework Programme (FP-7).

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Author Biographies

Suresh Kattimuttathu I received his M.Sc. (1990) in Polymer Chemistry from Mahatma Gandhi University Kottayam, and M.Tech. (1993) (Polymer Technology) from the Cochin University of Science & Technology, India. He completed his Ph.D. (2005) in Applied Chemistry under CSIR (India)–DAAD (Germany) Sandwich model fellowship. He is currently principal scientist at the Organic Coatings & Polymers Division of the Indian Institute of Chemical Technology, Hyderabad, India. His research interests focus on emulsion polymerization, morphology control during emulsion polymerization, polymers and monomers from renewable resources, atom transfer radical polymerization and structure property correlation studies, as well as adhesives and coatings.

Gesche Foerst received her diploma of pharmaceutical sciences in 2008 from the University of Freiburg. She is currently a Ph.D. student in the group of Prof. Schubert at the Department of Pharmaceutical Technology and Biopharmacy at the University of Freiburg Germany, working on model membranes.

Rolf Schubert is a professor and head of the Department of Pharmaceutical Technology and Biopharmacy at the University of Freiburg. He received his Ph.D. in biochemistry from the University of Tübingen in 1981. The main fields of his research are model systems for biological membranes and nanocarriers as drug delivery systems, especially liposomes.

Eckhard Bartsch is a professor at the Institute of Macromolecular Chemistry at the Faculty of Chemistry, Pharmacy and Earth Sciences at the University of Freiburg, Germany. He received his Ph.D. (1987) from the Julius-Maximilians-University at Würzburg. He then joined the group of Prof. Hans Sillescu at the Institute of Physical Chemistry, University of Mainz, as a researcher and a lecturer. Since 2004 he has been an associate professor in physical and macromolecular chemistry at the University of Freiburg. His research focuses on fundamental and applied characteristics of concentrated colloidal dispersions, colloid synthesis and characterization, latex film formation and scattering techniques for microstructural characterization of colloidal systems.