Aggregation and electrochemical properties of 1-(4-chlorophenyl)-3-dodecanoylthiourea: A novel thiourea-based non-ionic surfactant

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Abstract. A novel thiourea-based non-ionic surfactant 1-(4-chlorophenyl)-3-dodecanoylthiourea (4CPDT) was synthesized from decanoyl chloride, potassium thiocyanate and 4-chloroanline in high yield. The structural chemistry of the compound was done by multiple nuclear NMR (^{1}H, ^{13}C) and FT-IR. UV-Visible spectrophotometry and pendant drop methods were used to evaluate their critical micelle concentration in ethanol and hexane. This surfactant showed very low solubility in water, and interestingly low but well-defined, sub-millimolar critical micelle concentration (CMC) in ethanol and hexane, demonstrating that this is moderately amphiphobic. Its low value of critical micelle concentration indicates economical use for cleaning purposes and environment-friendly applications. It was also characterized by cyclic and square wave voltammetry and found to be electrochemically active giving sharp signal in different pH media.

Keywords. Synthesis; critical micelle concentration; non-ionic surfactant; spectroscopy; electrochemistry.

1. Introduction

Surfactants are organic substances which decrease the interfacial tension of liquids. They have long chains of hydrophobic hydrocarbons and hydrophilic polar heads. In the past, surfactants were limited to use for cleaning purposes but nowadays; they are the backbone of modern industrial uses.[1–6] Non-ionic surfactants is second in the industrial production of surfactants and they are not ionizable in aqueous solution due to their hydrophilic group which is non-dissociable by nature. These groups may be amide, thio, alcohol, phenol, ether, etc. The non-ionic surfactants are neutral and can be applied to many different chemical research areas such as electrochemistry, where neutral surfactants are needed for positive responses in direct potentiometric measurements of various ionic species in clinical, environmental and industrial processes.[7–10] They are used in ion-selective electrodes and their association results in increased washing capability and decreased the entrapment of air bubbles in flow channels. New surfactants are being explored to uncover their potential as replacement of known harmful surfactants excessive use of which have affected the flora and fauna.[11–13]

This article discusses the chemistry of a new surfactant with a thiourea-based group that is known to possess environmentally friendly properties. The problem with this surfactant is its partial solubility in water and further study is in progress to enhance this property.

2. Experimental

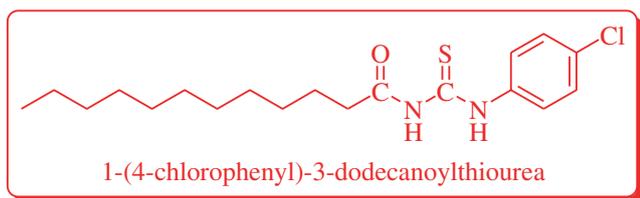### 2.1 *Chemicals, Instruments and Methods*

Lauryl chloride (99.9%), potassium thiocyanate (99.9%), different aliphatic and aromatic primary and secondary amines (99.9%) were purchased from Sigma Aldrich (USA). Fresh analytical grade dry acetone was used as the solvent and dried before experiments. The product was purified by thin layer chromatography. NMR spectra were recorded on Bruker AC Spectrometers at 300.13 MHz for ^{1}H and 75.47 MHz for ^{13}C. Thermo Nicolet-6700 FTIR spectrophotometer was also used for IR characterization. A double beam Shimadzu UV-1800 scan UV-Visible spectrophotometer and pendant drop methods were used for CMC determination and investigation of pH effect in acidic to basic media.

2.2 *1-(4-chlorophenyl)-3-dodecanoylthiourea*

For the synthesis of 1-(4-chlorophenyl)-3-dodecanoy-lthiourea, long chain hydrocarbon dodecanoyl chlorides was treated with potassium thiocynate in 1:1 mole ratio in 50 mL dry acetone as solvent and reflux for about 40 minutes at temperature 70°C to form the respective isothiocyanate. Long chain dodecanoyl isothiocyanate solution (in dry acetone) was separated using cannula filtration, leaving behind KCl precipitate, and the density was compared to the isothiocyanate gravimetrically. Subsequently, dodecanol isothiocyanate was coupled with 4-chloroanaline in dry distilled acetone under an N_2 atmosphere, and stirred for 12 h. The progress of the reaction was monitored by TLC at regular intervals. Finally, the product collected on condensing in iced water was washed with doubly distilled water for the removal of impurities. The pure product with more than 84% yield was obtained as white solid powder. The structure of the compound can be seen in scheme 1 and the stepwise preparation protocol is given in scheme 2. The purity of the compound was ascertained by ^1H NMR, ^{13}C NMR and FTIR spectroscopy and the spectral details are given below:

^1H NMR (300 MHz, CDCl$_3$, δ-ppm): 0.87–0.91(3H, t, CH$_3$, $^3J[^1H\text{-}^1H] = 7$ Hz), 1.28–1.34 (18H, m, 9CH$_2$), 2.37–2.42 (2H, t, CH$_2$, $^3J[^1H\text{-}^1H] = 7$ Hz), 7.28–7.39 (2H, d, 2CH, $^3J[^1H\text{-}^1H] = 7$ Hz), 7.61–7.765(2H, d, 2CH, $^3J[^1H\text{-}^1H] = 7$ Hz), 8.89 (1H, s, ^{1}NH), 12.48 (1H, s, ^{2}NH). ^{13}C NMR (75.5 MHz CDCl$_3$, δ-ppm): 14.1(C$_{17}$), 22.7–37.4 (C$_{7-17}$), 125.4–135.9 (C$_{1,2,2,3,3,4}$) 174.4 (C$_6$), 178.4 (C$_5$). IR (υ cm^{-1}): 3240.3, 3193.5 (N-H), 3037.5 (Ar-H, sp^2), 2916.9 2849.0 (sp^3, C-H), 1686.3 (CO), 1567.3, 1489.2 (sp^2, C=C).
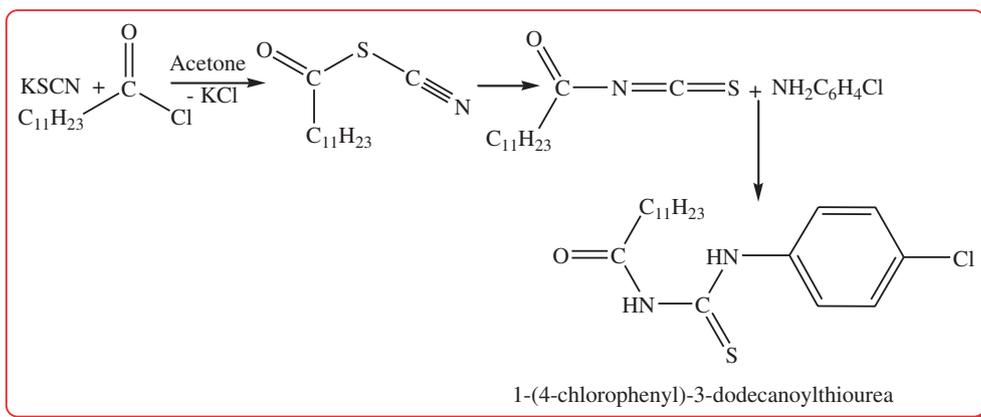
3. Results and Discussion

3.1 *Surface and aggregation properties*

The tendency of surfactants to adsorb at interfaces and aggregate in bulk systems is responsible for the rational and key performances in the modification of liquid properties. The adsorption and aggregation phenomena of the surfactants are vital and can be studied by a variety of physicochemical methods such surface tension, conductance, light scattering, viscosity, etc. The selection of a technique to evaluate their properties is concerned with the structural and chemical formulation of the surfactant. Due to the induction of thiourea group into the new surfactant solubility of the compound in aqueous medium was reduced. To overcome this and to determine the critical micelle concentration, both UV-visible spectroscopy and interfacial tension are demonstrated as effective tools and these are used to explore aggregation.

3.2 *UV/Vis method*

The CMC of 4CPDT in ethanol was determined by UV-visible spectroscopy. A double beam UV–Visible spectrophotometer was used to record the absorbance spectra of surfactant solutions as a function of concentration over a wavelength range of 200 to 800 nm.
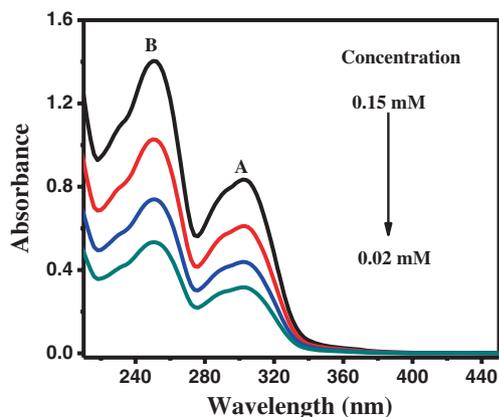

1-(4-chlorophenyl)-3-dodecanoylthiourea

Scheme 1. Chemical structures and names of non-ionic thiourea-based surfactants.

1-(4-chlorophenyl)-3-dodecanoylthiourea

Scheme 2. Synthetic method for the preparation of non-ionic thiourea-based surfactants.
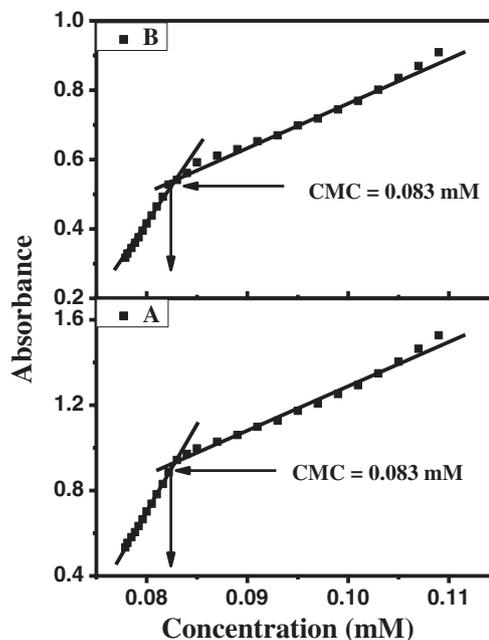
It has been previously shown[14,15] that a discontinuity is seen in the plot of absorbance versus concentration due to micellisation, thus providing an effective method for locating the CMC. The UV-visible spectrum of the compound in ethanol at room temperature is presented in figure 1. The CMC was determined by plotting absorbance versus concentration of both peaks of the spectrum. In both cases, the plots presented two linear parts with different slopes and the CMC was evaluated from their intersection point. This process along with the CMC values were obtained is shown in figure 2. The obtained value for the CMC is surprisingly low, given the high solubility in ethanol (>50 mg/mL), possibly indicating a significant level of solvophobicity of the surfactant. By comparing the solubility of decane and thiourea in ethanol and water however, the behavior is readily rationalized. Decane is effectively insoluble in water, but highly soluble/miscible in ethanol. Thiourea however is only moderately soluble in water (mole fraction ∼0.04 at 25°C), and even less so in ethanol (mole fraction ∼0.02 at 25°C).[16] This indicates that inverse micelles of the thiourea surfactant form in ethanol, where the well-solvated decane tails would be exposed to the solvent and the insoluble thiourea heads would be shielded inside the aggregate.

3.3 *Pendant drop tensiometry*

Besides bulk aggregation of the surfactant, the surface adsorption properties are also of great interest. Measurement of surface and interfacial tension is invaluable for determining the suitability of a surfactant for a given system, in terms of effectiveness and efficiency of adsorption. We explored the properties of 4CPDT at the hexane-water interface in order to investigate its usefulness as an oil-water emulsifier.
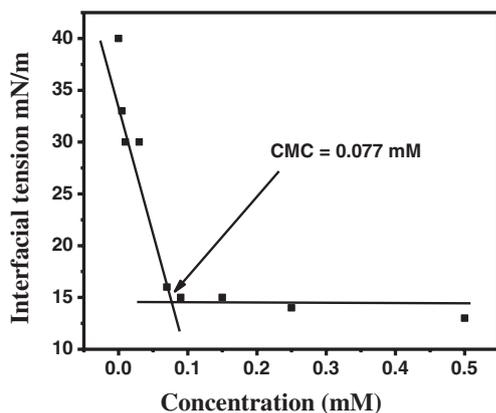
Figure 2. Absorbance vs concentration plots of 4CPDT at 250 and 302nm in ethanol.

The pendant drop technique also provides an effective method for determination of CMC in the oil phase (hexane), as this surfactant is only minimally soluble in water. A concentration range of 0.02–0.15 mM was assessed, with the surfactant dissolved in the hexane phase, kept in a standard 1 cm path-length quartz cuvette. A pendant droplet of pure water was then dispensed from a glass syringe equipped with a stainless steel blunt cannula (0.72 mm outer diameter). With increasing surfactant concentration, the hexane-water interfacial tension rapidly dropped from its equilibrium value to ∼16 mN/m (figure 3). When compared to conventional surfactants such as AOT and its analogues,[17] the decrease in interfacial tension is modest, indicating that these surfactants are not particularly effective at the hexane-water interface and would thus not make good single-component emulsifiers. For the same solubility arguments as with ethanol, we can assume that inverse micelles are formed in hexane after the CMC.
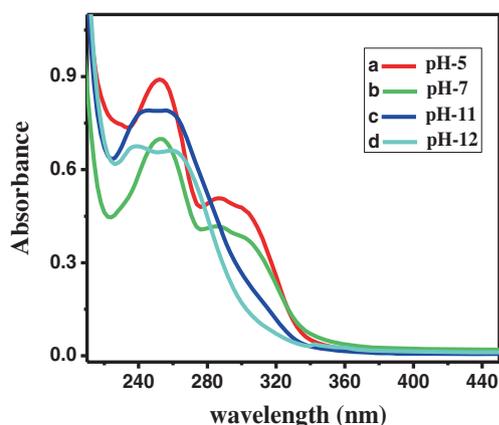
Of note is that the CMC of 4CPDT in hexane and ethanol is surprisingly similar – particularly unusual for surfactants, given the different polarities and chemical characteristics of ethanol and hexane. This indicates that the thiourea moiety is controlling aggregation by its poor solubility in the solvents of interest here (water, ethanol and hexane), despite their widely ranging polarity. Interestingly, this highlights the thiourea group as a potential design feature in future surfactants, acting as an amphiphobic moiety.

Figure 1. UV-Vis spectrum of 4CPDT in ethanol.

3.4 *pH effect*

1-(4-chlorophenyl)-3-dodecanoylthiourea (4CPDT) was also studied in different pH media to visualize their electronic absorption behavior in acidic, neutral and basic media. The compound absorbs at 250, 302 nm and effect of pH on the spectrum is shown in figure 4. The results indicate that absorbance of surfactant gets lowered with change in pH from 4 to 9 and the two peaks merge into a single peak (at pH 11) and absorbance increases with further rise in pH up to 12. In strongly alkaline conditions of pH 11-12, the narrowness and increase in peak intensity of surfactant is attributed to the deprotonation of –NH group and consequent increase in conjugation as shown in scheme 3. Further pH study is in progress for getting useful insights about the indefinite aspects of thiourea-based non-ionic surfactants.

Figure 3. Interfacial tension vs concentration plots of 4CPDT in hexane.

3.5 *Electrochemistry*

Electrochemical characterization of the synthesized surfactant was carried out using the following techniques to investigate its activity in different pH media.

3.5a *Cyclic voltammetry*: Cyclic voltammogram of 1 mM 1-(4-chlorophenyl)-3-dodecanoylthiourea was first witnessed in the potential range of $0 - +1.4$ V at a scan rate of 100 mV s^{-1} using supporting electrolyte of pH 10.0 as the signal at the mentioned pH was more prominent.[18–20] An irreversible anodic peak at $+1.029$ V related to the oxidation of the compound was observed as portrayed in figure 5.
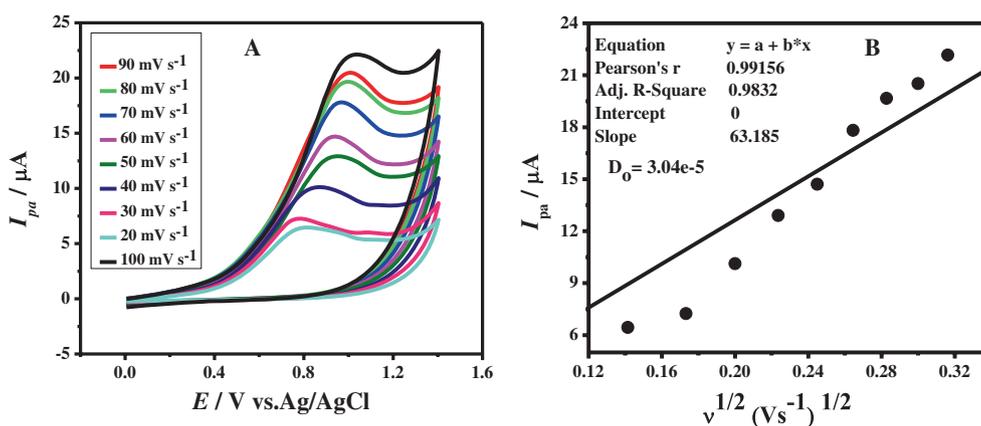
Cyclic voltammograms were recorded at different scan rates figure 6A. The voltammograms revealed that the anodic peak shifts to more positive potentials with the increase in scan rate. By plotting anodic peak current vs. square root of scan rate using Randles-Sevcik equation, diffusion coefficient for the compound was

**Figure 4.** UV–Vis spectra of 4CPDT in different pH media.
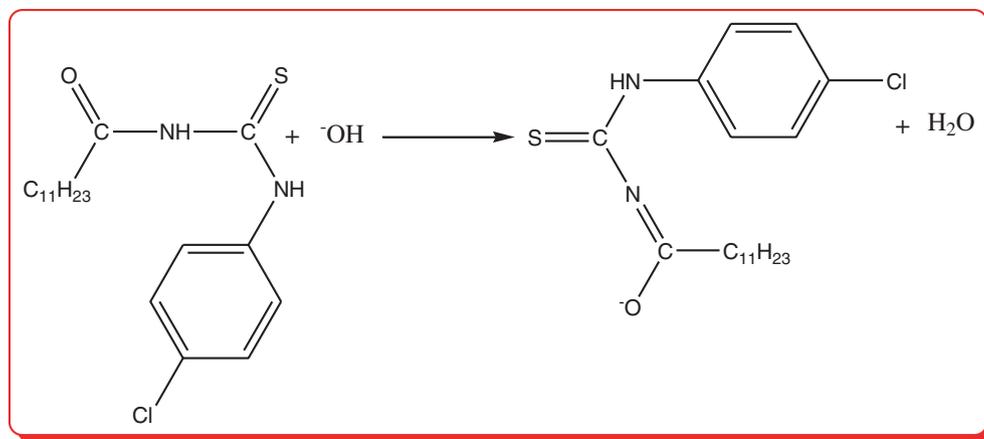
Scheme 3. Demonstration of the increase in volume of chromophore of 4CPDT under alkaline conditions leading to more intense peak in UV-Vis spectra.
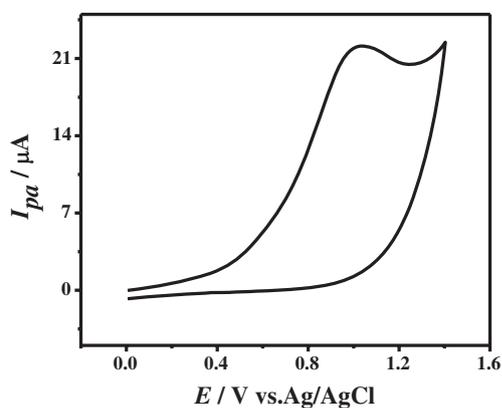
Figure 5. CV of 1 mM compound **(c)** in oxidation region recorded in pH=10 at a scan rate of 100 mVs^{-1}.

evaluated aand presented in figure 6B. The value of diffusion coefficient found is 3.04×10^{-5} cm^2 s^{-1}.

In order to investigate electro-reduction of the compound, cyclic voltammograms were recorded in the potential range 0 to -1.5 V using 1 mM solution of the compound buffered in a medium of pH 4, 7 and 10 as shown in figure S1 (A-C). It was observed that there is no reduction peak in the medium at pH 4; a reduction peak appeared at pH 7 at -0.859 V, but after thorough purging with nitrogen gas the peak intensity dramatically got decreased accompanied with a shift in peak potential to -0.815 V. Such a behavior might be due to involvement of oxygen in the redox reaction which is forcing the peak current to decrease so much

Figure 6. CVs of 1 mM compound **(c)** recorded in pH=10 at (A) different scan rates, (B) plot of anodic peak currents *vs.* square root of scan rate using CV data of compound **(c)** obtained in pH 10.
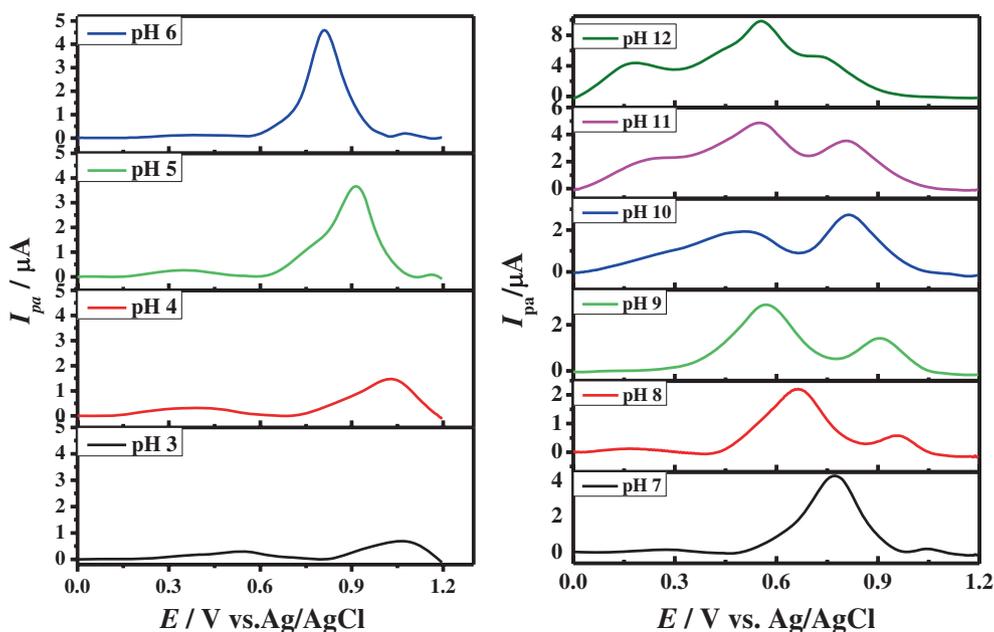
Figure 7. Square wave voltammograms showing oxidation of compound **(c)** at 100 mV s^{-1} in (A) pH=3-6, **(B)** pH 7-12.

and also a shift in peak potential.[21,22] At pH 10, without purging with nitrogen gas a broad reduction peak appeared at −1.15 V and, after thoroughly purging the solution with nitrogen gas, this broad peak disappeared and a reduction peak was observed at −0.628 V. In figure S1 (D), CV scans of purged solution are shown at pH 7 and 10 and shift in peak potential was found to be 62.33 mV/pH, which was in close agreement to the theoretical value 59 mV/pH. This indicates the participation of equal number of electrons and protons in the redox process. On the basis of these experimental evidences, it was inferred that the compound under investigation undergoes electro-reduction in the given potential range with strong involvement of oxygen in the redox reactions.[23]

3.5b *Square wave voltammetry (SWV)-Electro oxidation of compound*: SWVs of the compound were recorded in a wide pH range to identify the mechanism for the electro-oxidation. The peak potentials of the anodic peaks were found to depend strongly on the pH of the medium. In the pH range 3–6, a single anodic peak was witnessed which shifts to more negative potentials accompanied with an increase in peak intensity in the mentioned pH range as shown in figure 7 (A, B). However, the anodic signal started splitting into two peaks from pH 7 which got prominent as the pH of the medium increases.[24–28] Under highly basic medium of pH 11 and 12 more splitting was observed giving rise to three peaks.

In order to check the reversibility of the anodic peaks, forward and backward current components of SWVs at pH 6, 8 and 12 were plotted along with total current and shown in figure S2 (A-C). It was noted that the anodic peaks are irreversible at all the mentioned pH values.

4. Conclusion

A novel non-ionic thiourea-based surfactant was successfully synthesized by a new method from simple raw materials. The synthesized surfactant was characterized by UV-Visible, FTIR, ^{1}H and ^{13}C-NMR spectroscopy. Electronic absorption spectroscopy and pendant drop methods were successfully employed for the evaluation of the critical micelle concentration of the synthesized surfactant. As introduction of thiourea group in the structure of a surfactant lowers its solubility in water. Further study is in progress to incorporate such moieties in thiourea-based non-ionic surfactant to improve water solubility, cleaning action and biodegradability.

Supplementary Information

All additional information pertaining to characterization and electrochemical behaviour of the surfactant (4CPDT) using NMR technique (figures S3 and S4), cyclic voltammograms (figures S1(A-D), S2(A-C)) are given in the supporting information which is available at www.ias.ac.in/chemsci.

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